THE UNIVERSITY OF
SYDNEY

THE CHEMISTRY OF VINYLLEAD TRIACETATES

A Thesis submitted in partial fulfilment

of the requirements for the admission to the

DEGREE OF

DOCTOR OF PHILOSOPHY

by

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University of Sydney

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" 'I don't know!' the poor little scientist stressed yet again. Durf was being like the usual idiots, the people who acted as if science was a series of definite facts and scientists benign, all-seeing, all-knowing teachers. The truth was that every door that science opened revealed a corridor full of them, all barred and bolted."

Ben Elton, "STARK", 1989.

CONTENTS

PREFACE

This thesis concerns the study of a variety of vinyllead tricarboxylates, and their reactions both intramolecularly, and with soft carbon nucleophiles. The work was carried out under the supervision of Dr. J.T. Pinhey in the Department of Organic Chemistry, University of Sydney between March 1986 and June 1990.

Unless otherwise stated, all results recorded in this thesis are those of the author. Parts of this work have appeared elsewhere:

1) "Vinyl Cation Formation by Decomposition of Vinyl-lead Triacetates. The Reactions of Vinylmercury and Vinyltin Compounds with Lead Tetraacetate."

Moloney, M.G., Pinhey, J.T. and Stoermer, M.J., *J. Chem. Soc. Perkin Trans. 1*. In Press.

2) "Generation of Vinyl Cations from Vinyllead Triacetates."

Mark G. Moloney, John T. Pinhey and Martin J. Stoermer, Royal Australian Chemical Institute, Division of Organic Chemistry. 9th National Conference, The University of Adelaide and The Flinders University of South Australia, May 11-15, 1986.

3) "Vinyllead Triacetates: A source of Vinyl Cations or Alkylidene Carbenes?"

Mark G. Moloney, John T. Pinhey and Martin J. Stoermer, Royal Australian Chemical Institute, Division of Organic Chemistry. 11th National Conference, James Cook University of North Queensland, Townsville, July 3-7, 1989.

ACKNOWLEDGEMENTS

I would like to thank Dr. J.T. Pinhey for his guidance, encouragement and patience throughout the course of these last four and a bit years.

I would also like to thank all members of the Department of Organic Chemistry, particularly my fellow Tutors, who have been a constant help in making the time pass both more profitably and enjoyably. Thanks are also due to Dr. Jacques Nemorin, Dr. Bruce Rowe and Sue Boyd, for their help with n.m.r. spectroscopy; and Jacqui Morgan and Chris Parkinson, for helpful discussions.

The author gratefully acknowledges the receipt of a position as a Tutor in the Department of Organic Chemistry for the term of this work.

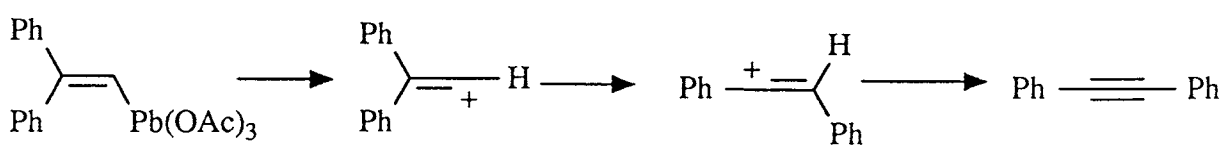
ABSTRACT

This thesis is concerned with the investigations of the reactions of vinyllead tricarboxylates, derived from vinylstannanes and divinylmercury compounds, and their applications to organic synthesis.

The work is discussed in three sections:

Section 1: VINYLLEAD TRICARBOXYLATES AS A SOURCE OF VINYL CATIONS

The reaction of a vinylstannane or divinylmercury compound with lead tetraacetate (or other tetracarboxylates), generally performed in chloroform solution, gives rise to a vinyllead triacetate. These species are usually unstable compounds that decompose via either a vinyl cation mechanism, or a β-elimination (Reactions A and B). Compelling evidence for vinyl cation formation was obtained in a number of cases, in which rearrangement across the double bond occurred (e.g. Reaction A).



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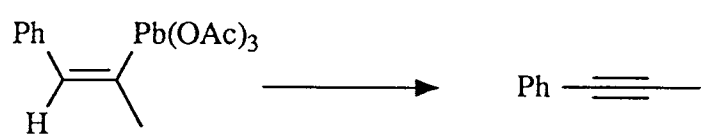
Reaction A



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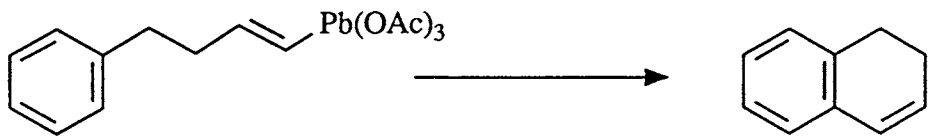
Reaction B

By using suitably substituted vinylstannanes, it was possible to generate primary vinyl cations, species which are thought not to be formed in solvolysis reactions. In two cases, the vinyl cations formed underwent intramolecular aromatic electrophilic substitution (e.g. Reaction C).



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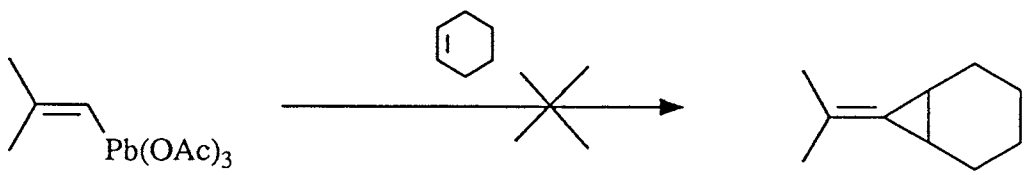
Reaction C

It was shown in a series of experiments that the mechanism was not of a carbene nature, as species arising from carbene insertion into carbon-carbon double bonds were not observed (e.g. Reaction D). Capture of the cationic intermediate by neighbouring methoxyl groups was also observed (Reaction E).



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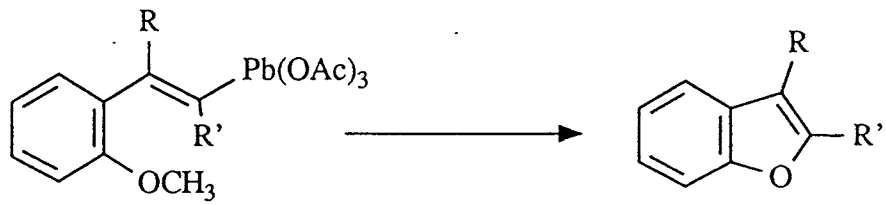
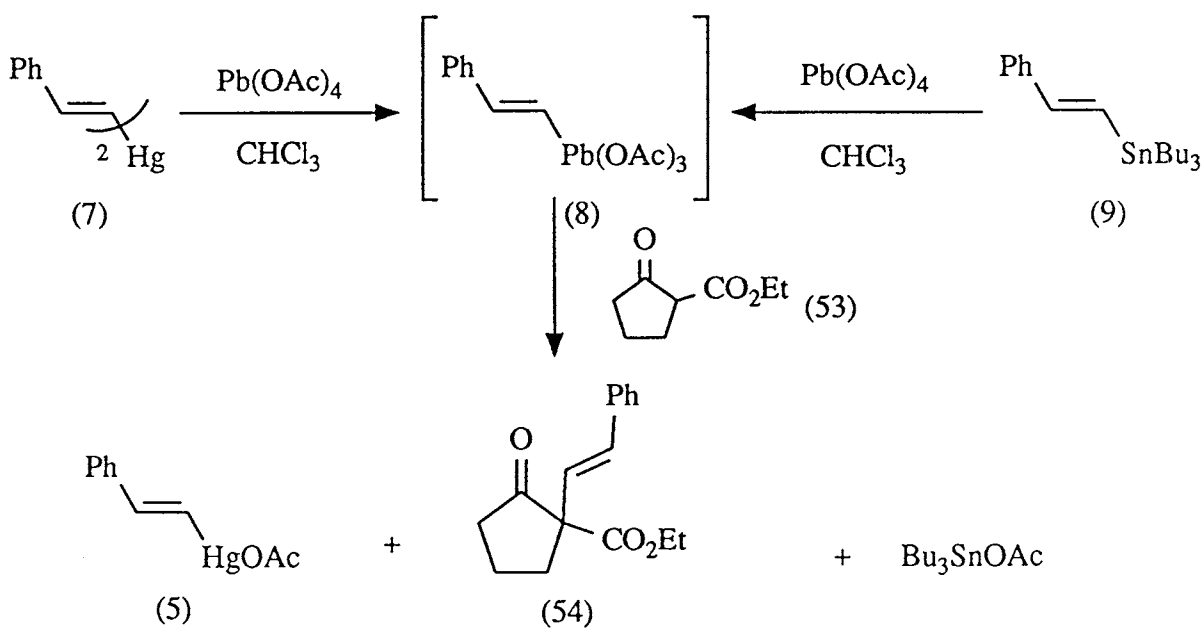
Reaction D



Reaction E

SECTION 2: IMPROVEMENTS IN THE α-VINYLATION REACTION OF β-DICARBONYL COMPOUNDS

The vinyllead tricarboxylates mentioned above, have been used in the past* as vinylating reagents for β-dicarbonyl compounds (Reaction F). The use of tributylvinylstannanes and divinylmercury compounds as the precursors of the lead reagent, had serious limitations, both in the ease of purification of the products and in the production of "wasted" vinylic residues. The use of trimethylvinylstannanes has now been shown to produce not only easier workup procedures, but also in general higher yields of the vinylated products than was previously attainable.



Reaction F

It was also found that lead tetrabenzoate was a superior reagent in this reaction, producing faster exchange times and better yields. Lead tetrapivalate was found to be better than lead teraacetate in some cases, but inferior to lead tetrabenzoate.

* Moloney, M.G., and Pinhey, J.T., *J. Chem. Soc. Perkin Trans. 1*, 1988, 10, 2847.

SECTION 3: ^{1}H AND ^{13}C NMR STUDIES OF VINYLLEAD TRICARBOXYLATES

By the use of high resolution n.m.r. spectroscopy, it was possible to characterise a large number of vinyl-lead tricarboxylates by means of the ^{207}Pb satellites about the vinylic protons in the ^{1}H n.m.r. spectra of these compounds. These ^{207}Pb-H coupling costants were very large (690-1660 Hz) and found to decrease in the series:

$$J_{207Pb,Htrans} > J_{207Pb,Hgem} > J_{207Pb,Hcis}$$

In a few cases it was also possible to observe ^{207}Pb-C coupling constants in the ^{13}C n.m.r. spectra of these compounds.

It was also found that the lead compounds were identical, whether derived from the tributylstannanes or trimethylstannanes, or from the mercury compounds.

INTRODUCTION

The use of organolead(IV) tricarboxylates* as reagents in organic synthesis has expanded rapidly in the last 20 years, as methods for their preparation have improved. Panov and Kocheshkov[1] were the first to prepare phenyllead triacetate in 1952, and since then, interest has still mainly centred on the aryllead triacetate series, as they are the most readily prepared, being usually solids which are readily stored. They are, however, somewhat susceptible to polymerisation in the presence of moisture.[2,3]

The aryllead triacetates are conveniently prepared by a number of routes, incuding direct plumbation of activated aryl systems such as anisole[4], and metal-lead exchange reactions. The metals which have been found to be useful in the exchange with lead tetraacetate are lead[1], mercury,[5,6] silicon,[7,8] thallium,[9,10] tin,[11,12,13] and boron.[14,15]

The original route used by Panov and Kocheshkov[1] to prepare phenyllead triacetate and *p*-tolyllead triacetate utilised the reaction of a diaryllead diacetate with mercury(II) acetate in acetic acid (Scheme 1). Alternatively, the aryllead triacetate may be prepared directly from the diarylmercury compound with lead tetraacetate (Scheme 2).

$$Ar_4Pb + 2AcOH \longrightarrow Ar_2Pb(OAc)_2 + 2\ ArH$$

$$Ar_2Pb(OAc)_2 + Hg(OAc)_2 \longrightarrow ArPb(OAc)_3 + ArHgOAc$$

Scheme 1

---

* Any further reference to the oxidation state of the lead species will be omitted, as is usually implied in the name or structure.

$$Ar_2Hg + Pb(OAc)_4 \longrightarrow ArPb(OAc)_3 + ArHgOAc$$

Scheme 2

However, both of these approaches suffer from the significant problem that the product, aryllead triacetate, must be separated from the by-product, arylmercury acetate. This is usually performed by fractional crystallization, or alternately, by conversion of the arylmercury acetate to an arylmercury chloride, followed by fractional crystallization.

The reaction of an aryltrimethylsilane with lead tetraacetate in the presence of trifluoroacetic acid has been shown to yield the corresponding aryllead tristrifluoroacetate (Scheme 3).

$$ArSiMe_3 + Pb(OAc)_4 \xrightarrow{TFA} ArPb(OCOCF_3)_3 + Me_3SiOCOCF_3$$

Scheme 3

Arylthallium bistrifluoroacetates[9] have also been shown to react with lead tetrakistrifluoroacetate to yield aryllead tristrifluoroacetates by n.m.r. spectroscopy[10] (Scheme 4); however, the lead compounds produced by this route and from the silanes are highly susceptible to cleavage by trifluoroacetic acid to yield the aryl trifluoroacetates, hence these reactions are limited to the less reactive aryllead compounds.

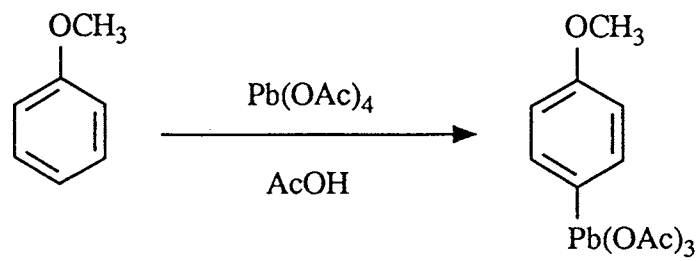
$$ArTl(OCOCF_3)_2 + Pb(OCOCF_3)_4 \longrightarrow ArPb(OCOCF_3)_3 + Tl(OCOCF_3)_3$$

$$ArPb(OCOCF_3)_3 \xrightarrow{TFA} ArOCOCF_3 + Pb(OCOCF3)_2$$

$$ArOCOCF_3 \xrightarrow{Hydrolysis} ArOH$$

Scheme 4

The direct plumbation of activated aromatic systems is a simple method, which has been used to prepare a number of aryllead triacetates (Scheme 5). The reaction is often slow, but can be accelerated by the use of haloacids as solvent[2], or by mercury(II) acetate catalysis.[16] The reaction proceeds by an electrophilic substitution mechanism, and hence the haloacid produces a more electrophilic lead species; however, only aromatic systems with activating substituents can be used.



Scheme 5

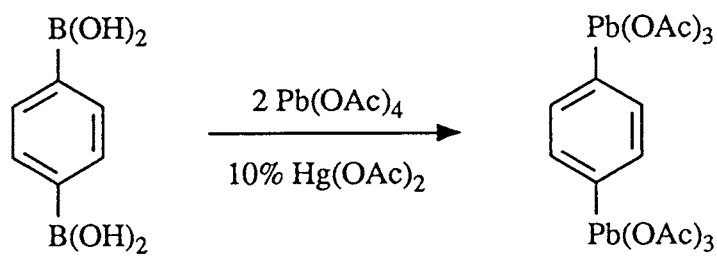
The reaction of aryltributylstannanes with lead tetraacetate in the exchange reactions was found to be the best method for the preparation of aryllead triacetates, as the metal-metal exchange can be performed on aromatics with a wide range of substituents attached. Both electron-withdrawing and electron-donating substituents can be tolerated. In addition, the by-product of this exchange, tributyltin acetate, is readily removed from the reaction mixtures by simply washing the lead compound with dry light petroleum.

$$ArSnBu_3 + Pb(OAc)_4 \longrightarrow ArPb(OAc)_3 + Bu_3SnOAc$$

Scheme 6

Another advantage of this technique was that the lead reagents formed could be used *in situ* without the need for any isolation, if the compounds were at all unstable, since they were prepared in the absence of acidic reagents.

Arylboronic acids have also been used to prepare aryllead triacetates in a very rapid boron-lead exchange.[14,15] The method is very useful for the *in situ* generation of aryllead triacetates, due to this rapid exchange. *p*-Phenylenediboronic acid (1) has been converted to the corresponding dilead compound (2) in the presence of mercury salts (Scheme 7) by this method.[14,15] The bis(tributyl)stannane (3) was found to exchange too slowly for this work, and the major product obtained was the *p*-tributylstannylphenyllead triacetate (4).

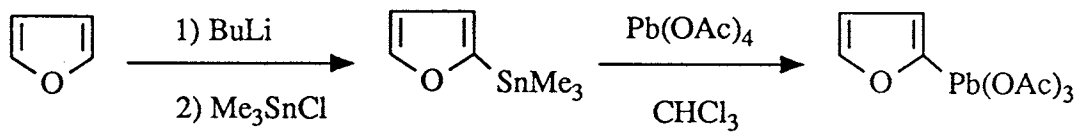


(1) (2)

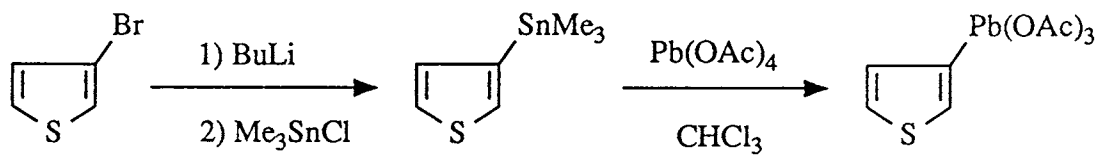
Scheme 7

(3) (4)

More recently, these methods have been extended to the preparation of several heteroaryllead triacetates[17,18] (Schemes 8 and 9), which although being somewhat less stable than the benzenoid series, are still very useful reagents for organic synthesis. In these cases it was possible to use the trimethylstannanes instead of the tributylstannanes, and these were found to react faster with lead tetraacetate. The trimethylstannanes had not been used in the benzenoid aryllead work as it had been found that methyl-tin cleavage competes with the desired aryl-tin cleavage.

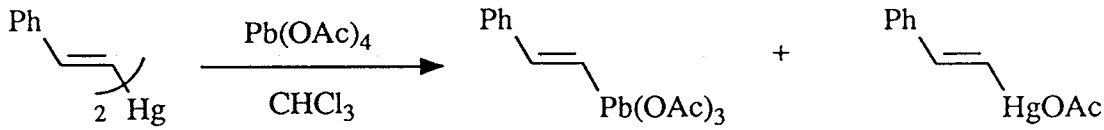


Scheme 8

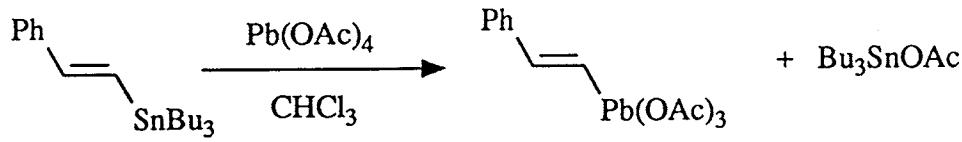


Scheme 9

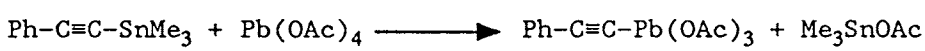
The logical extension of this work to include alkenyllead triacetates[19,20,21,22] and alkynyllead triacetates[17,19,23,24] has only recently been achieved as these compounds are, with a few significant exceptions, very unstable compounds. In general, they are prepared *in situ* by mercury-lead or tin-lead exchange reactions and used immediately for subsequent reactions (Schemes 10, 11, and 12).



Scheme 10



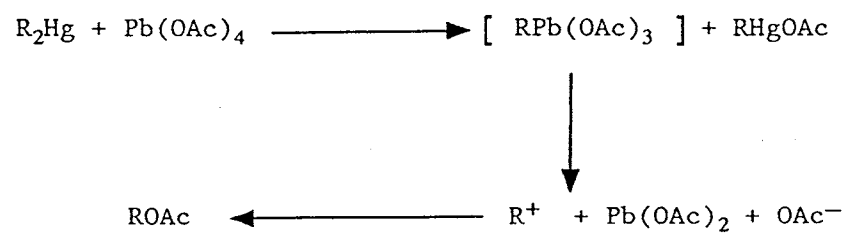
Scheme 11



Scheme 12

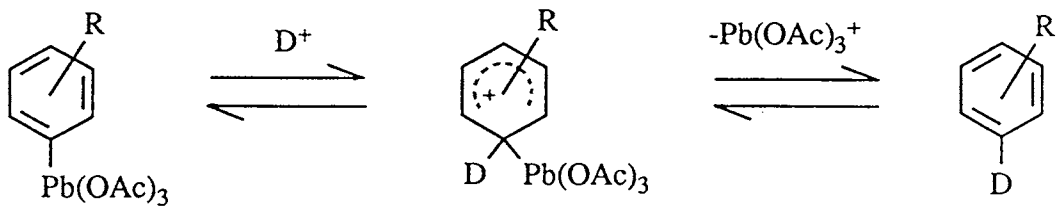
1) REACTIONS OF ORGANOLEAD(IV) TRICARBOXYLATES

Criegee[5] found that bis(alkyl)mercury compounds reacted with lead tetraacetate to give alkyl acetates as the main products. The alkyllead triacetate produced from the exchange decomposed rapidly to give an alkyl cation, which traps acetate ion to yield the product (Scheme 13).

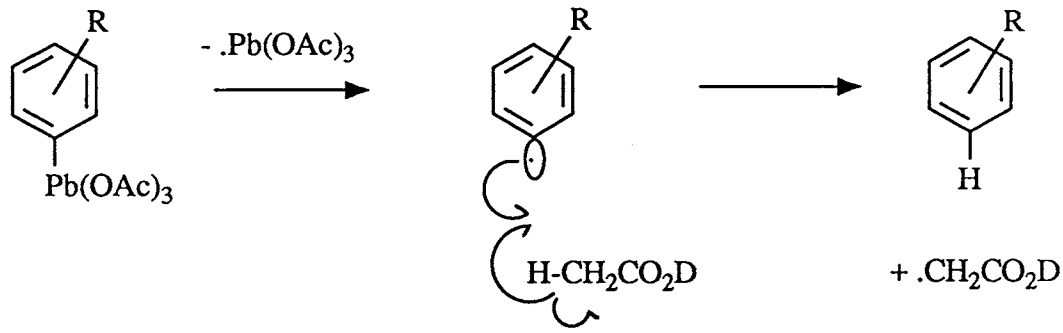


Scheme 13

The aryllead triacetates are more stable and require forcing conditions to effect the decompositions. Norman and Thomas[25] found that activated aryllead triacetates under acidic conditions protodemetallate readily by two competing mechanisms. Both an S_E2 mechanism (Scheme 14) and a homolytic mechanism (Scheme 15) were found to be operating. Studies with d_1-acetic acid showed that there was initially a large incorporation of deuterium in the anisole formed (via the S_E2 mechanism), but that with time there appeared a proportionately higher concentration of non-deuterated anisole (via the homolytic mechanism, and abstraction of the methyl hydrogens of d_1-acetic acid). Also, it was found that the addition of radical promoters increased the amount of non-deuterated anisole formed.

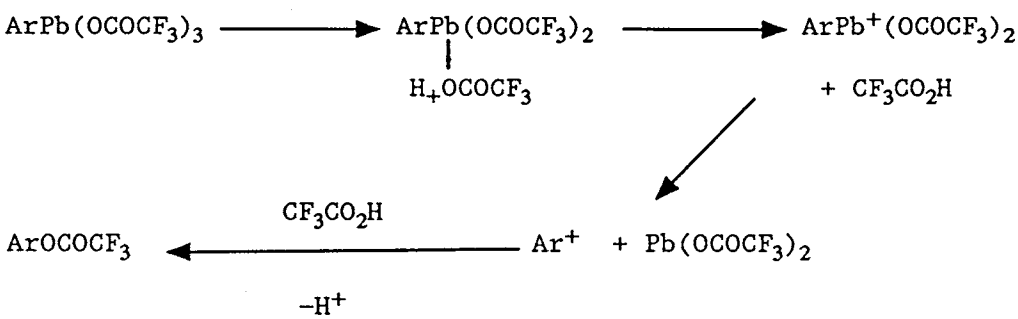


Scheme 14



Scheme 15

Arylead tristrifluoroacetates in trifluoroacetic acid react rapidly at room temperature to give the respective aryl trifluoroacetates (Scheme 16). There is strong evidence that these reactions proceed via an aryl cation intermediate.[8]

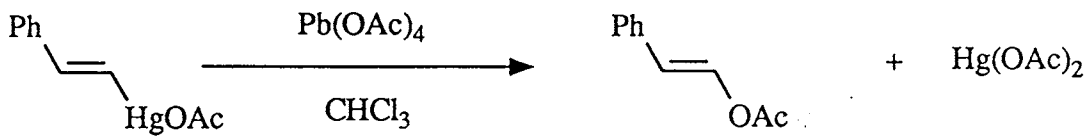


Scheme 16

Alkynyllead triacetates decompose by a different pathway, and generally give the tetraalkynyllead compounds upon standing in a chloroform solution[17,23,24] (Scheme 17).

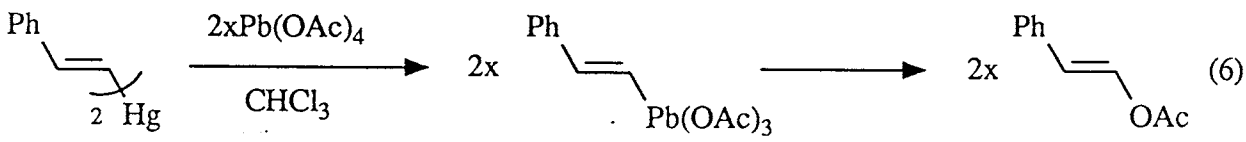
Scheme 17

Moloney[19] found that alkenyllead triacetates could be readily generated by mercury-lead and tin-lead exchange reactions in chloroform solution; he showed that if the exchanges were carried out on an n.m.r. scale in deuterochloroform, the existence of these previously speculative intermediates, could be confirmed by n.m.r. spectroscopy. It was found that new vinylic resonances appeared downfield of the vinylic proton resonances of the starting materials, and that these intermediates decomposed with time at the same rate as the appearance of the products ultimately observed. It was also found that the products formed in these reactions were heavily dependent on the substitution at the double bond. Larock *et al.*[26] found that (*E*)-2-phenylethenylmercury acetate (5) reacted with lead tetraacetate to give the corresponding enol acetate, (*E*)-2-phenylethenyl acetate (6) (Scheme 18). Other alkenylmercury salts and divinylmercury compounds studied by Moloney[19] exhibited the same behaviour, with enol acetates being the major products (Scheme 19).



(5) (6)

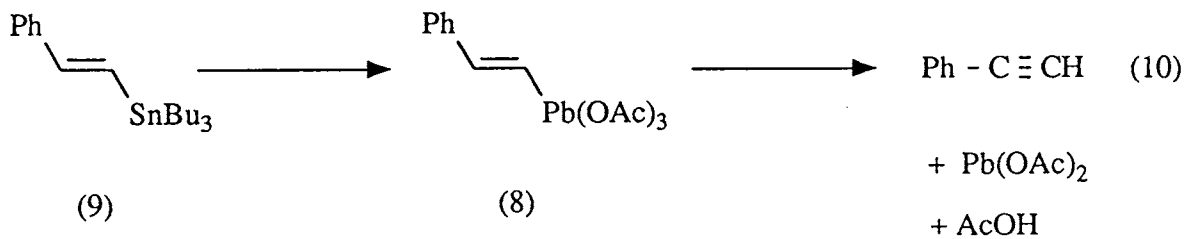
Scheme 18



(7) (8)

Scheme 19

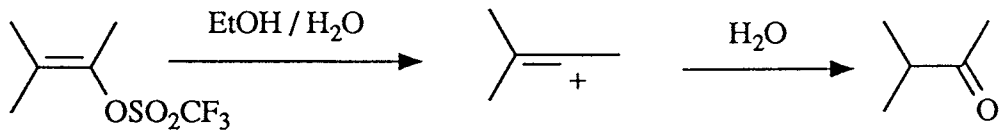
When alkenyltributylstannanes are used in place of the mercury compounds, significantly different results are often obtained.[19,20] For example, tributyl[(*E*)-2-phenylethenyl]stannane (9) reacts with lead tetraacetate in chloroform solution to yield phenylacetylene (10) as the major product (Scheme 20). Mercury(II) was found to be intimately involved in the course of these reactions,[19] since the addition of mercury(II) compounds to the exchange reaction of the stannane (9) resulted in the formation of enol acetate (6), whilst the addition of tributyltin acetate to the exchange reaction of the mercurial (7) had no effect on the reaction.



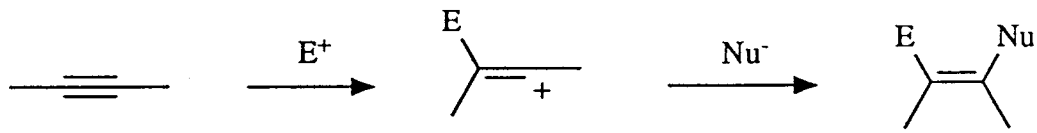
Scheme 20

It was found[19] that, in general, stannanes gave rise to acetylenes, unless the substitution at the double bond made elimination impossible. Moloney[19] suggested that the enol acetates arose from a collapse of the intermediate alkenyllead triacetate to lead(II) acetate, acetate ion and a vinyl cation.

Previous extensive investigations have shown that vinyl cations may be generated in solvolyses, using super-leaving groups such as triflates[27a] (Scheme 21), or by the addition of electrophiles to acetylenes and allenes[27b] (Scheme 22).



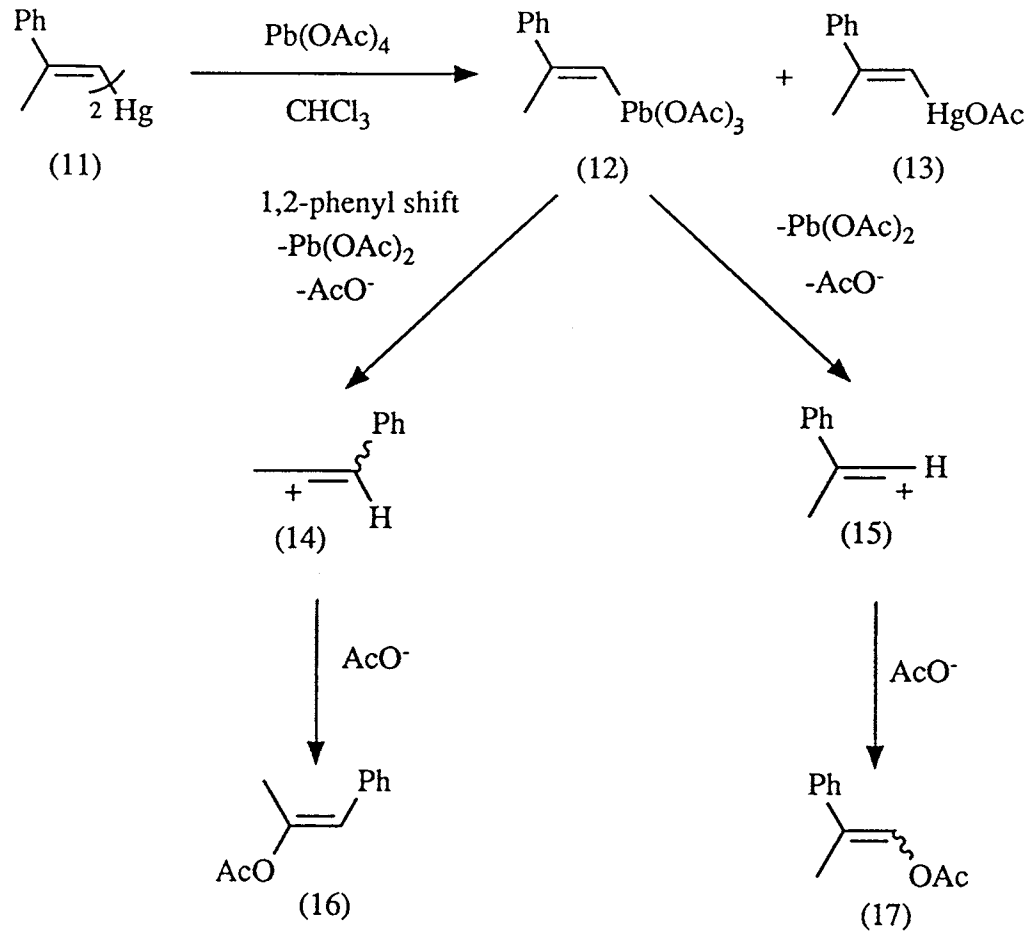
Scheme 21



Scheme 22

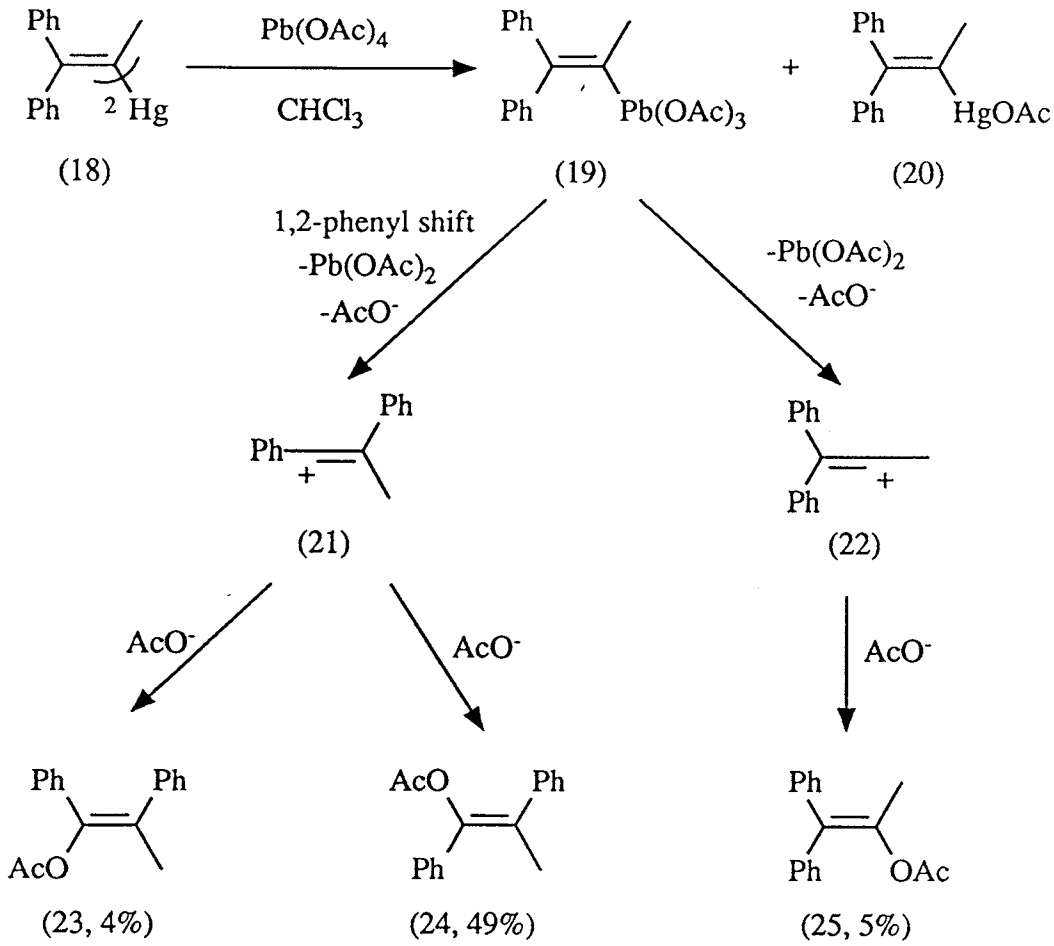
Moloney[19] also found other evidence for the intermediacy of vinyl cations in a number of other reactions.

Bis[(*E*)-2-phenyl-1-propen-1-yl]mercury (11) was shown to react with lead tetraacetate to give the enol acetate (16) (Scheme 23). He[19] suggested that the initially-formed alkenyllead triacetate (12) rearranges via a concerted loss of lead(II) and a 1,2-phenyl migration to give the vinyl cation (14), which then traps acetate ion to give the observed enol acetate (16). Simple collapse of the alkenyllead triacetate (12) to the cation (15) was ruled out, as the cation formed would be primary, hence very unstable, and indeed, neither of the two enol acetates (17) which could result from attack of acetate on the cation (15) was produced.



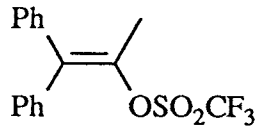
Scheme 23

The divinylmercury compound (18) was found to react via an analogous pathway, involving a 1,2-phenyl migration. The products ultimately observed were the enol acetates (23), (24), and (25), in yields of (4%), (49%), and (5%) respectively (Scheme 24).



Scheme 24

The difference in this case is that the vinyl cation (22) arising from simple loss of lead(II) is not primary, and is therefore significantly more stable. Hence some of the enol acetate (25) arising out of this cation is observed. However, the major products are the enol acetates obtained from the rearranged cation (21), which is more stable than the initially formed secondary cation (22). Moloney suggests[19] that the conversion of cation (22) to (21) is a stepwise process; however it is possible that the 1,2-phenyl migration and loss of lead(II) are concerted, and that both cations are forming from competing reactions, directly from the vinyllead triacetate (19). This reaction parallels the solvolysis of the triflate (26), which gives the ketone (27) in almost quantitative yield.[28]



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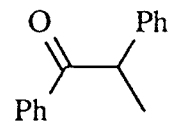
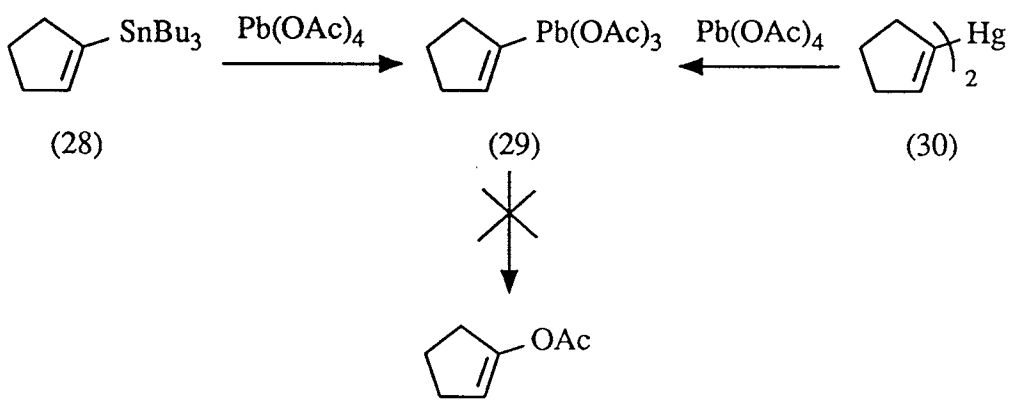


(27)

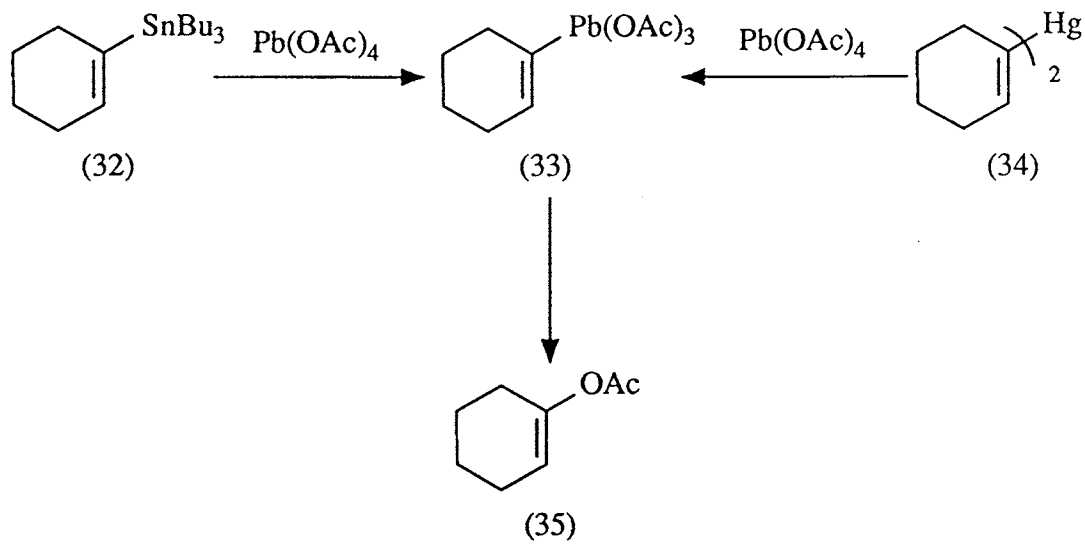
Further evidence obtained by Moloney[19] for the existence of vinyl cations as intermediates in mercury and tin-lead exchange reactions involved the observation that tributyl(cyclopenten-1-yl)stannane (28) and bis(cyclopenten-1-yl)mercury (30) both produce a stable alkenyllead triacetate (29) upon treatment with lead tetraacetate (Scheme 25), whereas the six-membered analogues, tributyl(cyclohexen-1-yl)stannane (32) and bis(cyclohexen-1-yl)mercury (34) react normally with lead tetraacetate to give cyclohexen-1-yl acetate (35) in high yield (Scheme 26). Cyclopenten-1-yllead triacetate (29) could be isolated from the exchange reaction, and could be used successfully in the α-alkenylation of β-keto esters (see Introduction, Part 2).



(28) (29) (30)

(31).

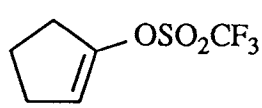
Scheme 25



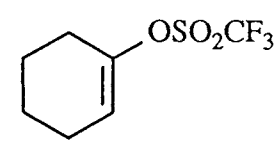
(32) (33) (34) (35)

Scheme 26

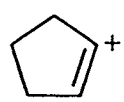
The different behaviour of the cyclopenten-1-yllead and cyclohexen-1-yllead compounds is exactly analogous to that of the cyclopenten-1-yl and cycohexen-1-yl triflates (36) and (37); the latter compound readily undergoes solvolysis in ethanol, whereas the former does not, reacting preferentially by sulfur-oxygen cleavage.[28] This has been rationalised in terms of the stabilities of the cyclopenten-1-yl cation (38) and the cyclohexen-1-yl cation (39), the former being of particularly high energy.[27c]



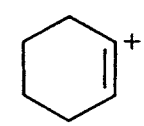
(36)



(37)



(38)

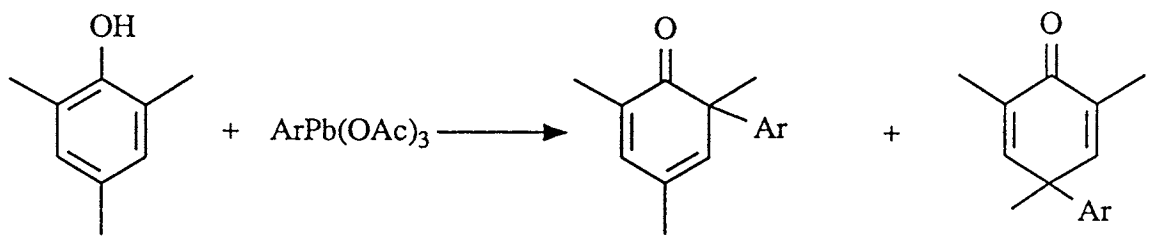


(39)

2) SYNTHETIC APPLICATIONS OF ORGANOLEAD TRIACETATES.

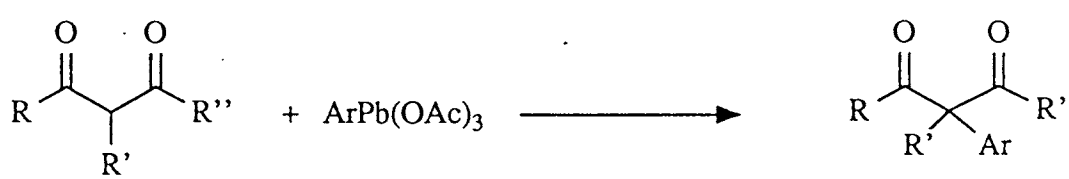
Aryllead triacetates, vinyllead triacetates and alkynyllead triacetates have been put to a number of synthetic uses in this Department over the last 18 years. The bulk of this work has involved their reactions with a range of soft carbon nucleophiles.

Aryllead triacetates react readily with appropriately substituted phenols in chloroform solution in the presence of between 3 and 5 equivalents of pyridine to yield mixtures of the 2- and 4-arylated cyclohexadienones (Scheme 27).[29,30]



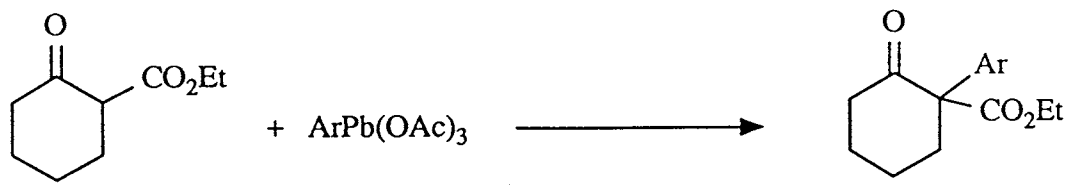
Scheme 27

Both acyclic and cyclic β-diketones react with aryllead triacetates under the same conditions to give α-aryl-β-diketones readily[31,32] (Scheme 28). If there are two enolisable protons available then diarylation takes place, since the second arylation is faster than the first.[31,32]



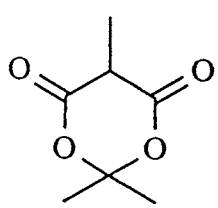
Scheme 28

When β-keto esters are used in place of diketones, α-aryl-β-keto esters are formed in good to excellent yield[32,33] (Scheme 29).

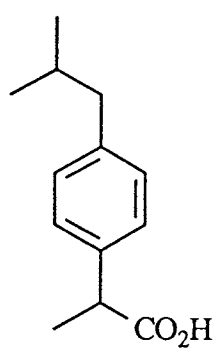


Scheme 29

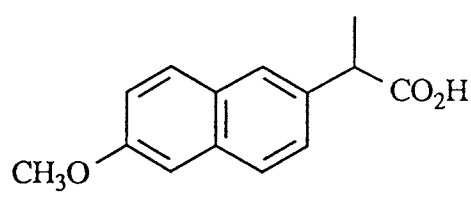
Whereas α-substituted malonic esters were found to react very slowly under the standard reaction conditions,[32] the derivative, methyl Meldrums acid (40) was found to be very reactive, and could be readily arylated in high yield.[34,35] This route was found to be remarkably useful, and has lead to simple syntheses of the anti-inflammatory drugs, Ibuprofen (41)[34] and Naproxen (42).[36]



(40)

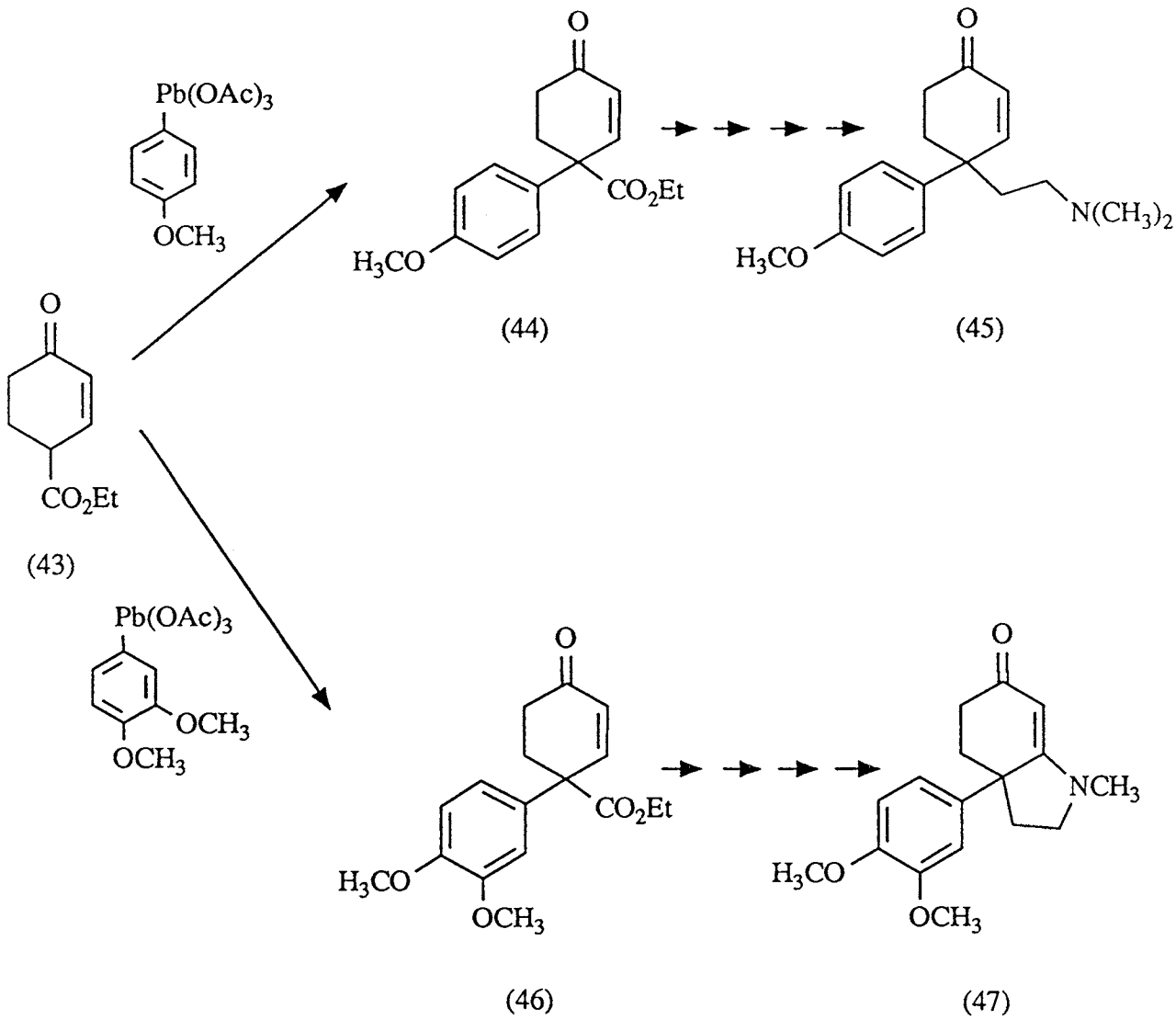


(41)



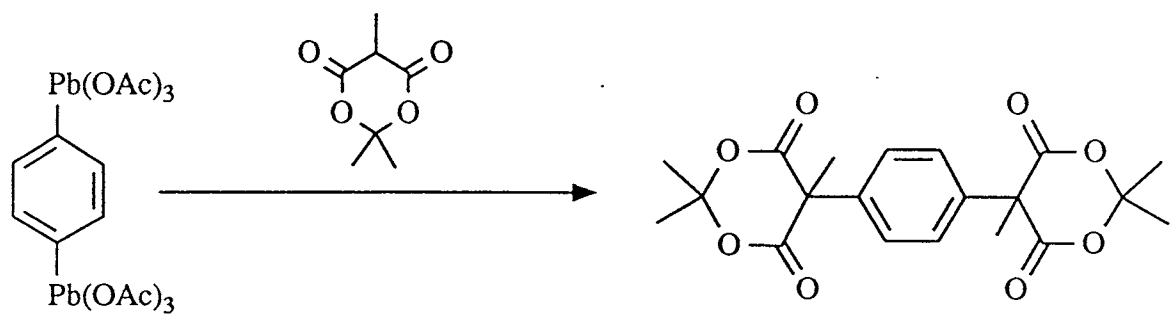
(42)

Vinylogous β-keto esters have also been successfully arylated under these standard conditions.[37,38,39,40,41] The vinylogous β-ketoester (43) has been arylated with *p*-methoxyphenyllead triacetate and 3,4-dimethoxyphenyllead triacetate to give the compounds (44) and (46), which are key intermediates in the synthesis of the Sceletium alkaloids (±)-O-methyl joubertiamine (45) and (±)-mesembrine (47) respectively (Scheme 30).



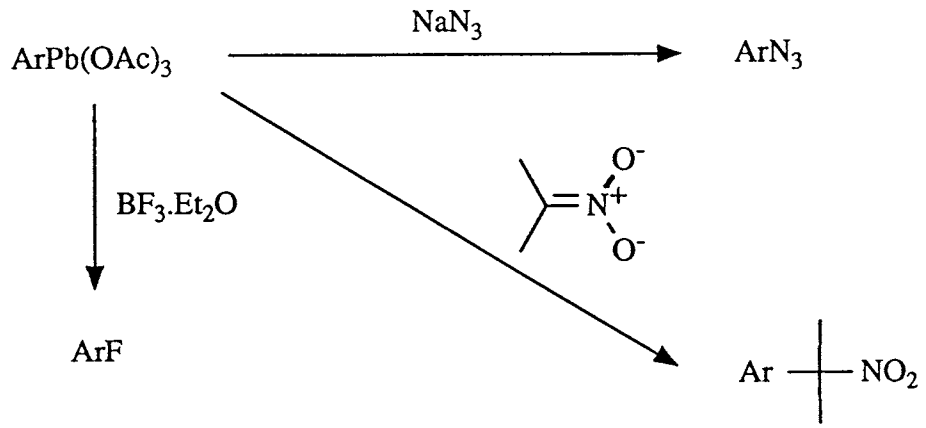
Scheme 30

The aryl dilead reagents described earlier have also been shown to react with two equivalents of a β-dicarbonyl compound[14,15] as exemplified in Scheme 31.



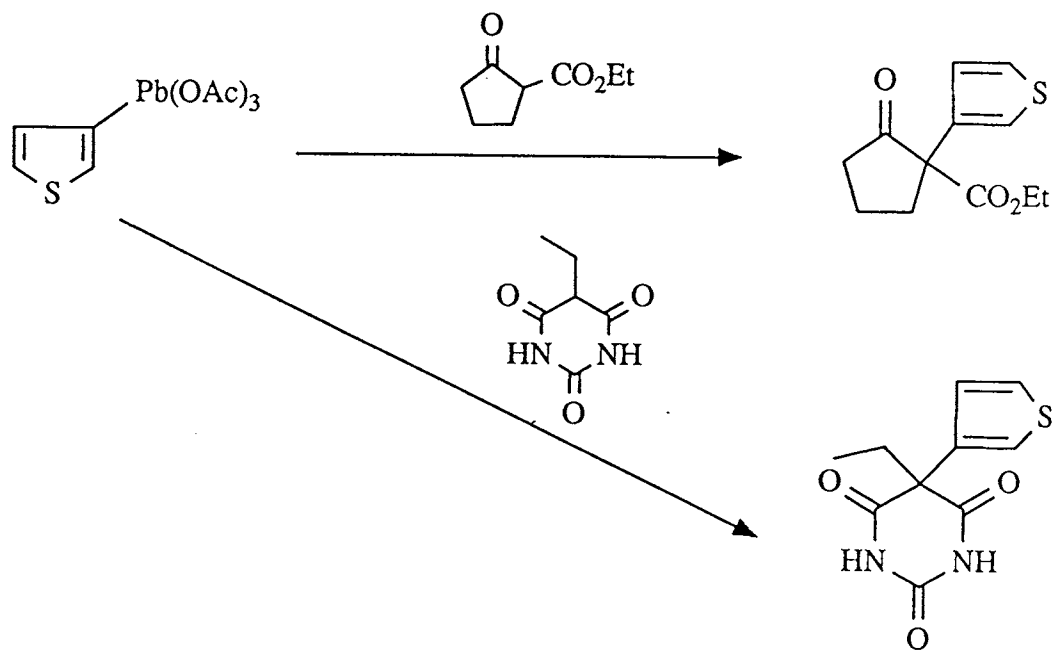
Scheme 31

The reactions of aryllead triacetates with nuceophiles other than β-dicarbonyls have also been studied. They have been found to react with sodium azide to give aryl azides,[42,43] nitronate salts[11,44,45] to yield α-aryl nitroalkanes, and boron trifluoride to afford aryl fluorides[46] (Scheme 32).

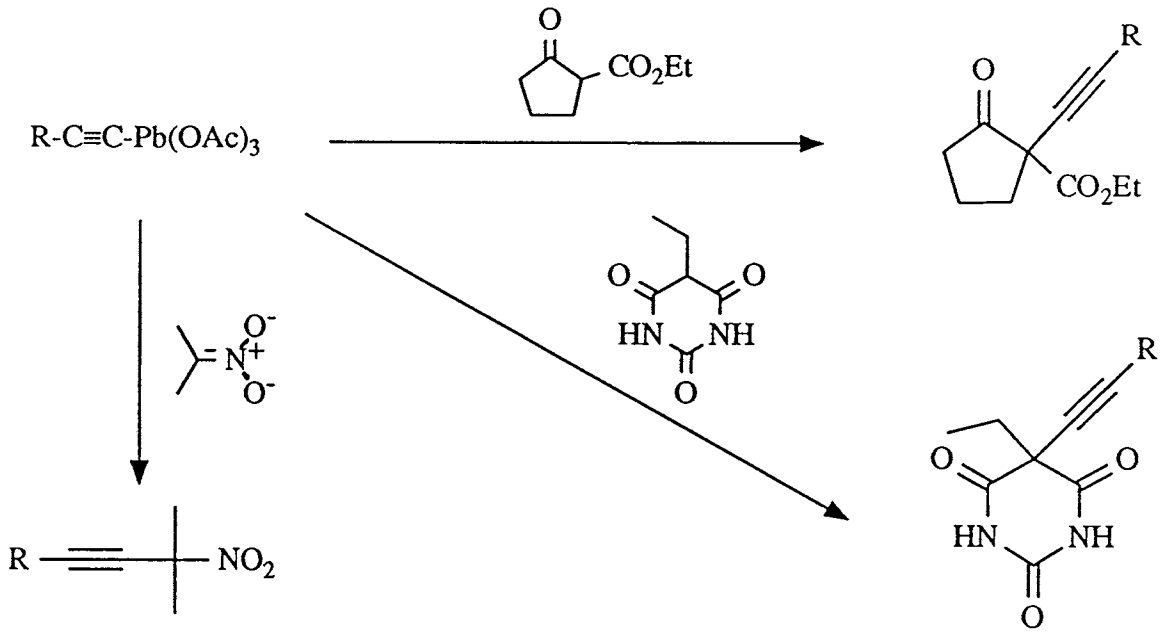


Scheme 32

Heteroaryllead triacetates (Scheme 33)[17,18] and alkynyllead triacetates (Scheme 34)[17,19,23,24] have been shown to react with a similarly diverse array of β-dicarbonyl compounds and nitronate salts.

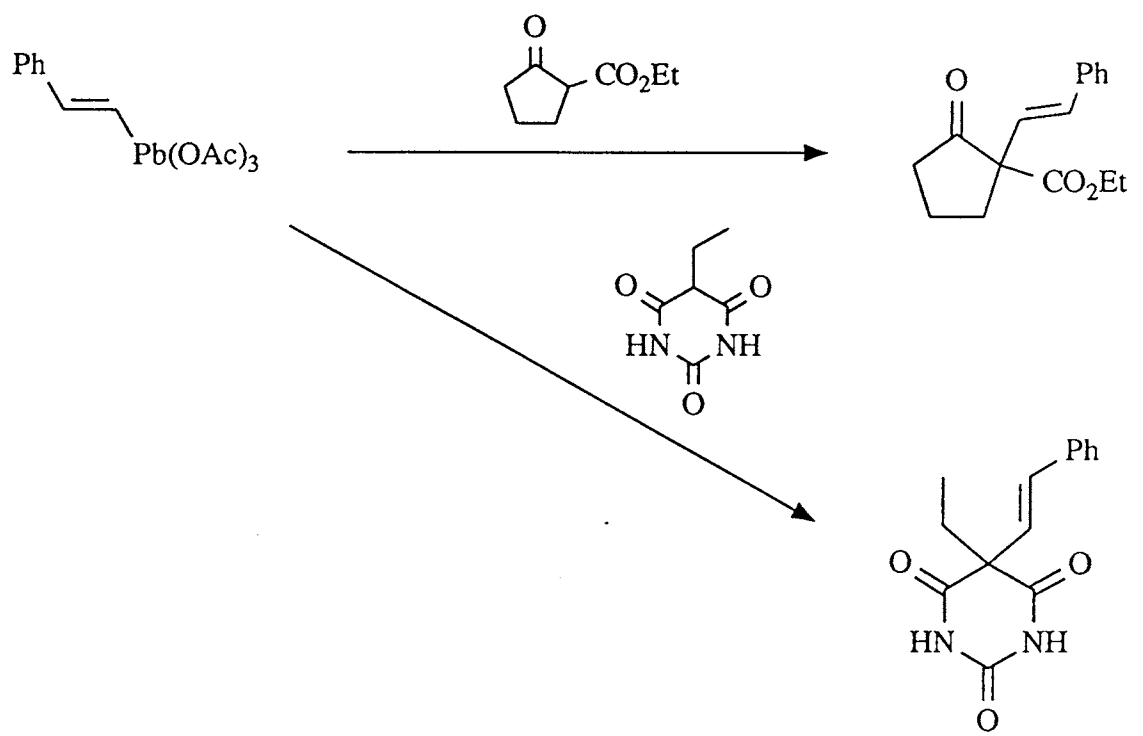


Scheme 33

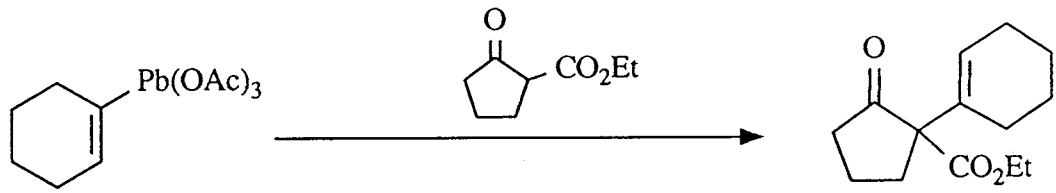


Scheme 34

The reactions of β-dicarbonyl compounds with a variety of vinyllead triacetates were extensively studied by Moloney[19,21,22] (Schemes 35,36).



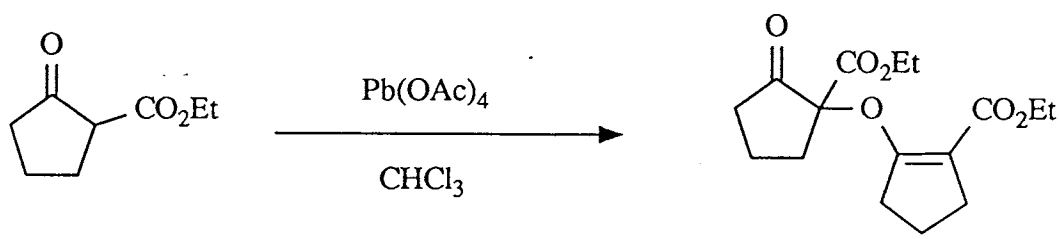
Scheme 35



Scheme 36

It was found that the best yields of α-vinylated products were obtained by use of solutions of vinyllead triacetates generated from reactions of divinylmercury compounds with one equivalent of lead tetraacetate in chloroform/pyridine solution; the amount of pyridine used was about 3-5 equivalents, mirroring the ideal conditions observed for aryllead triacetates. The reactions of vinylmercury bromides and acetates with lead tetraacetate were found to be quite slow, and this resulted in lowered yields of vinylated products.

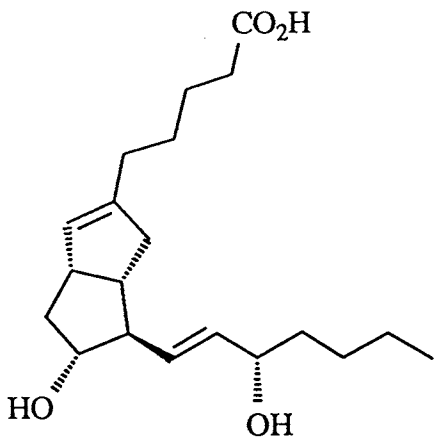
The main problem with the use of divinylmercury compounds was that the by-product of the initial exchange, a vinylmercury acetate, played no further part in the vinylation sequence, and hence, one vinyl residue was not employed in the reaction. Attempts to utilise this by-product by using two equivalents of lead tetraacetate were unsuccessful, since the second exchange was slow, and unreacted lead tetraacetate rapidly oxidised the substrate[19] as indicated for one case in Scheme 37.



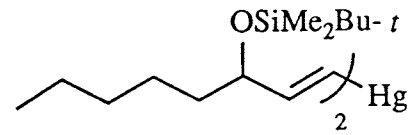
Scheme 37

In an effort to circumvent this problem, Moloney went on to study the use of tributylvinylstannanes as the precursors of the vinyllead compounds. He found that the exchange reactions were in many cases slow, but that useful yields of vinylation products could be obtained. The major drawback in this procedure came again from the initial metal-metal exchange. The by-product of this reaction is tributyltin acetate, a highly covalent compound, which is extremely difficult to remove from these vinylation mixtures.

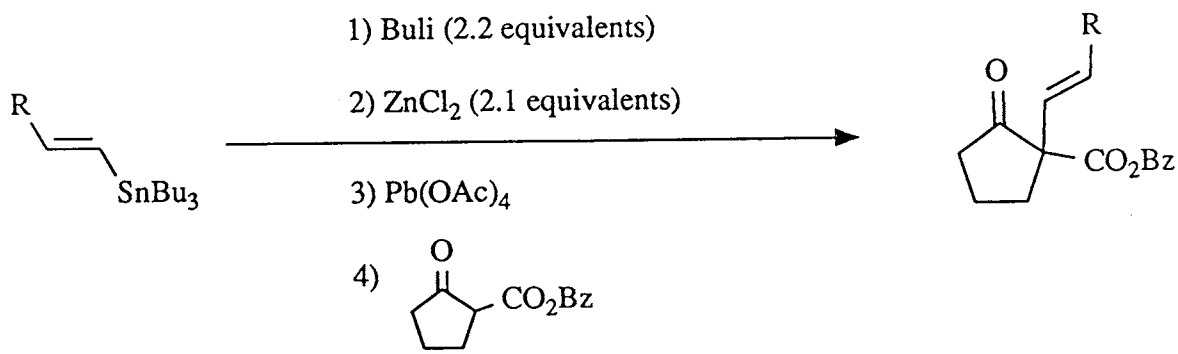
The vinylation reaction has recently been used by Japanese workers[47] to prepare the carbocyclic analogue of prostacyclin, isocarbacyclin (48). The key step in their synthesis is the introduction of the ω-side chain, which was achieved using the divinylmercury compound (49). Quite obviously, if the route to the divinylmercury compound is long, wastage of one vinylic residue in the exchange reaction is a significant problem in the synthetic sequence. More recently, in a preliminary communication,[48] these workers have described a method of preparing the lead reagent from a vinylzinc chloride, which is prepared by reacting the corresponding tributylstannane with butyllithium, then zinc chloride (Scheme 38). This technique, however, still suffers the problem of removal of tin residues, and the best yields are only obtained when two equivalents of the vinylating reagent are used, thus defeating the purpose of using a monovinyl metallic starting material.



(48)

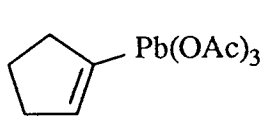


(49)

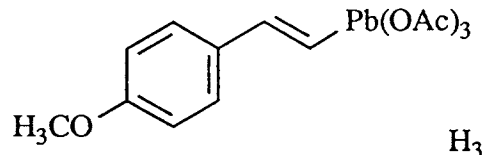


Scheme 38

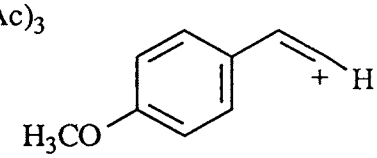
Two methods have been explored[19,22] to circumvent the problems of product purification, and vinyl residue wastage. The first method involved isolation of the intermediate lead compound. This was only found to be practical in two cases, cyclopentenyllead triacetate (29), and [(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]lead triacetate (50).



(29)



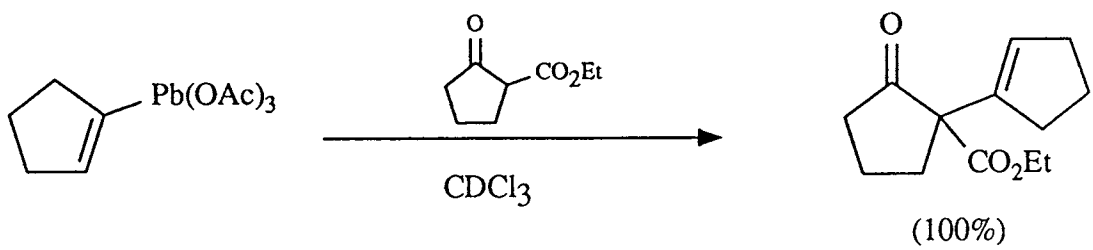
(50)



(51)

The reason for the relative stability of (29) has been discussed earlier; however, the stability of (50) is puzzling, as the electron-rich anisyl group would be expected to stabilize the vinyl cation (51) arising from the decomposition of (50).

In these cases, the tin-lead exchange mixtures were treated with cold dry light petroleum, and the lead compounds (29) and (50) were collected by filtration under nitrogen or argon. They could then be used in vinylation reactions with the only by-products being lead(II) acetate and acetic acid (Scheme 39).



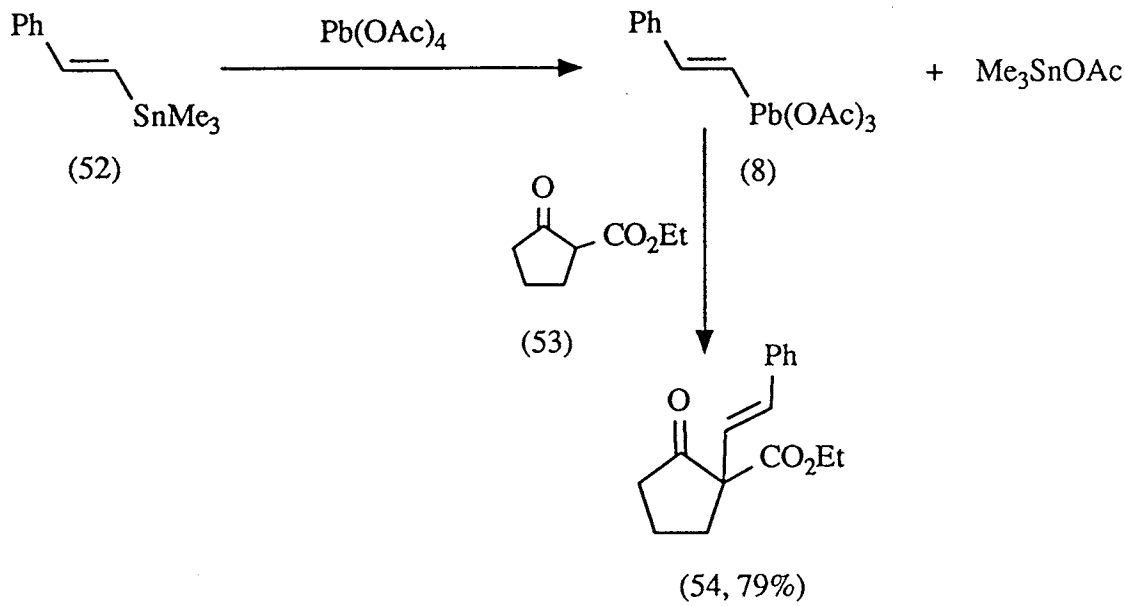
(100%)

Scheme 39

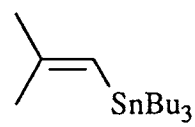
The other method of circumventing the problems of tin-lead exchange involved the use of trimethylvinylstannane (52) instead of the tributyl compound (9).[19] The exchange reaction produced the same lead compound (8), with trimethyltin acetate as the by-product. Trimethyltin acetate was found to be much less soluble than tributyltin acetate and could be readily removed from the vinylation mixutures. The other major advantage of this method was that the exchange reaction was found to be much faster, and this led to cleaner reaction mixtures, and less oxidation of the

substrate by unreacted lead tetraacetate.

Moloney[19] only studied the reaction of the stannane (52) with lead tetraacetate, and the vinylation of one substrate, the β-keto ester (53); however, the yield of the α-vinyl-β-keto ester (54) was the highest which had been obtained for that product (Scheme 40). In the present work, the reactions of a number of trimethylstannanes with a range of lead reagents and substrates have been examined.



Scheme 40



(55)

Moloney[19] also observed that tributyl(2-methyl-1-propen-1-yl)stannane (55) exchanged rapidly with lead tetrabenzoate at a rate that was "much more rapid than when lead tetraacetate was used". This reaction was not studied further by Moloney, but it now appears that the yields of vinylation reactions can be greatly improved if the exchange is rapid, since the lead reagent can no longer oxidise the substrate. In the

current work therefore, the use of other lead reagents, in particular lead tetrabenzoate, was examined in more detail, since it was anticipated that faster metal-metal exchange rates would lead to better yields of α-vinylated products.

3) N.M.R. STUDIES OF VINYLLEAD TRIACETATES

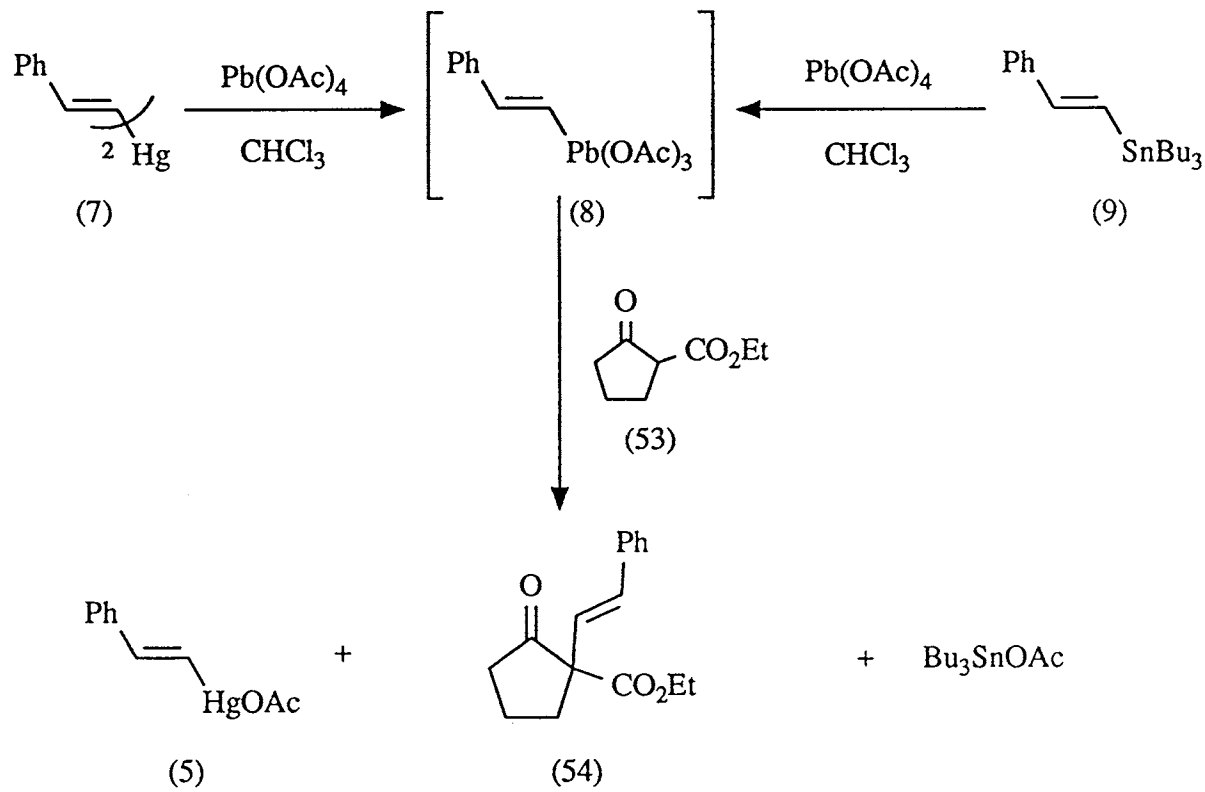
In the previous sections and in much of the earlier work,[19,21,22] it has been assumed that mercury-lead and tin-lead exchange reactions occur to give vinyllead triacetates with retention of their double bond stereochemistry. In many cases the existence of these intermediate species has been inferred from ^{1}H n.m.r. studies, where the exchange reactions have been carried out in deuterochloroform solution. The appearance of vinylic signals in the n.m.r. spectra downfield from the starting materials was attributed to these intermediates, as they reduced in intensity with time, as the signals corresponding to the final products increased in intensity. By using these results as a gauge of the longevity of the intermediates, it was possible to maximise the yields of vinylation reactions[19,21,22,23] by introducing the β-dicarbonyl substrates at a time when concentrations of these intermediates were known to be at a maximum. The fact that such techniques worked, showed that the intermediates observed were most likely those responsible for the vinylation reactions. Also, since two of these intermediates were isolable (see Introduction, part 2, page 23) lead species, it seemed likely that the intermediates in all cases were vinyllead triacetates. In this current work, it was envisaged that by the use of high resolution (400 and 200 MHz) ^{1}H and ^{13}C n.m.r. spectroscopy it would be possible to observe such species more effectively, and determine via their H-H couplings and their ^{207}Pb-H couplings whether they were formed with retention of configuration.

RESULTS AND DISCUSSION

Section 1

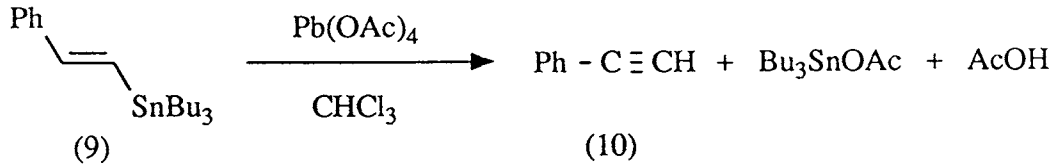
FORMATION OF VINYL CATIONS FROM VINYLLEAD TRIACETATES

Vinyllead triacetates, derived from trialkylvinylstannanes, and divinylmercury compounds, have been shown[19,21,22] to be the active species involved in the vinylation of β-dicarbonyls and β-keto esters (e.g. Scheme 41).



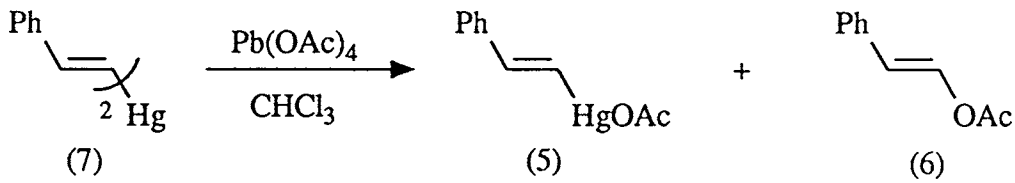
Scheme 41

Preliminary work by Moloney[19] indicated that in the absence of such soft carbon nucleophiles, the vinyllead triacetates decompose rapidly, with a few significant exceptions. In general, they yielded acetylenes if the lead species was derived from a stannane (e.g. Scheme 42), and enol acetates if the lead species was derived from a mercury compound (e.g. Scheme 43).



(9) (10)

Scheme 42



(7) (5) (6)

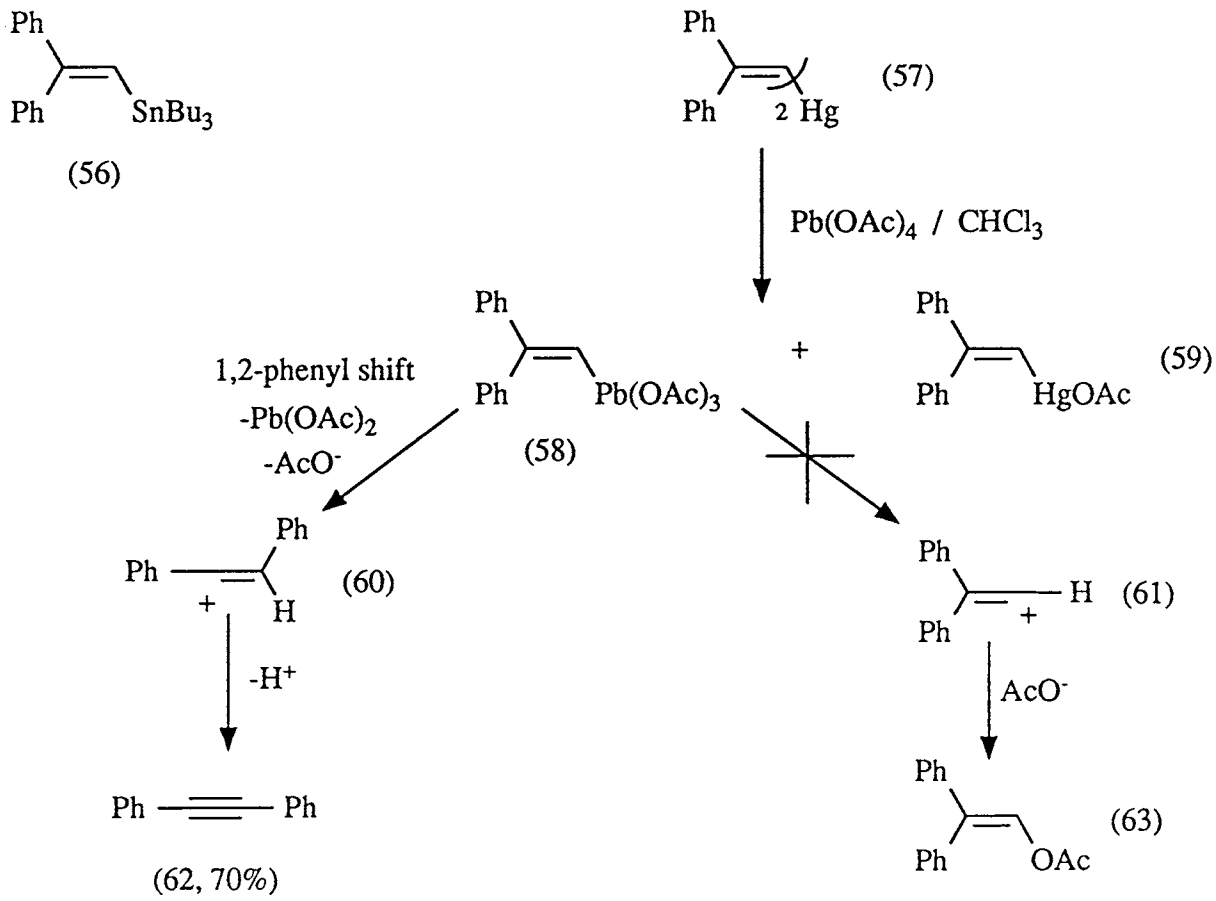
Scheme 43

It was noted that in many cases, the products of these decompositions implicated the intermediacy of vinyl cations, as a rearrangement of the carbon skeleton had occurred, consistent with the formation of the most stable vinyl cations, followed by enol acetate formation or elimination to give an acetylene. In this current work, several vinylstannanes were prepared which, it was hoped, would lead to vinyl cations, which would either rearrange or be trapped intramolecularly, to yield easily recognisable products, as proof of the intermediacy of the vinyl cations.

REARRANGEMENTS

The first compound examined was tributyl-(2,2-diphenylethenyl)stannane (56). Both this compound, and its divinylmercury analogue (57) had been studied by Moloney.[19] The divinylmercury compound was found to react readily with lead tetraacetate to yield the acetylene, tolan (62), as the major product (Scheme 44). It was proposed that the product of the metal-metal exchange, 2,2-diphenylethenyllead triacetate (58), decomposed via a 1,2-phenyl shift, concommitant with a loss of lead(II) acetate and

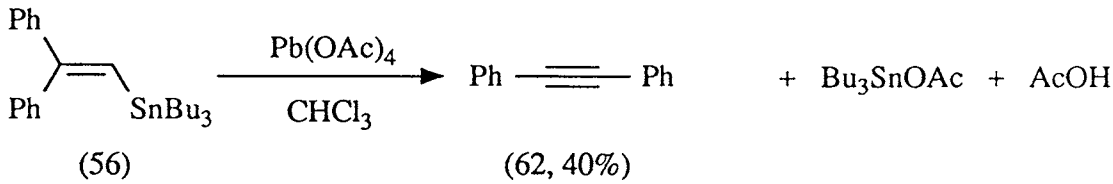
acetate ion to yield the vinyl cation (60), which loses a proton to yield the acetylene. The stannane (56) was found by Moloney to give tolan in only 13% yield, whereas the divinylmercury compound (57) reacted with lead tetraacetate to give tolan in 70% yield.



Scheme 44

In the current work, it was found, after exhaustive manipulation of the reaction conditions that the yield of tolan from the stannane (56) could only be increased to 40% (Scheme 45). It is proposed that the acetylene was formed via the same pathway as in the case of the divinylmercury compound, and that the yield was lower due to a comparatively slow tin-lead exchange. In the n.m.r. spectroscopic studies described later in Section 3, it was not possible to detect the vinyllead triacetate (58) when it was prepared from the tributylstannane, as the exchange was indeed slow. The lead species was however, detectable when the divinylmercury

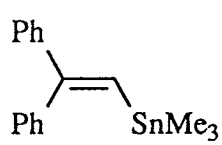
compound (57) was the precursor.



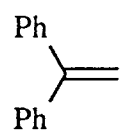
(56) (62, 40%)

Scheme 45

It was known that trimethylvinylstannnanes underwent a faster tin-lead exchange than the corresponding tributylvinylstannanes[17,19], and therefore the trimethyl analogue of (56), trimethyl(2,2-diphenylethenyl)stannane (64), was prepared. It was found to exchange rapidly with lead tetraacetate, and after 16 hours the mixture was found to contain tolan (62) in 90% yield, as well as 1,1-diphenylethylene (65) in 4% yield. When the tin-lead exchange reaction was carried out on an n.m.r. scale, it was possible to observe the rapid disappearance of the starting stannane (64). The proposed intermediate vinyllead triacetate (58) however, could not be detected, and was assumed to be too unstable (see Results and Discussion, Section 2). As in the case of the tributyltin compound above, it is proposed that the vinyllead triacetate decomposes via the same vinyl cation pathway as the divinylmercury compound (57). The alkene (65) is most likely formed by proto-demetallation of either the vinyllead triacetate (58), or the starting stannane (64) by the acetic acid formed in the elimination. A study of the proto-demetallation of the stannane (64) with acetic acid by ^1H n.m.r. spectroscopy showed that the reaction was 90% complete after 16 hours.

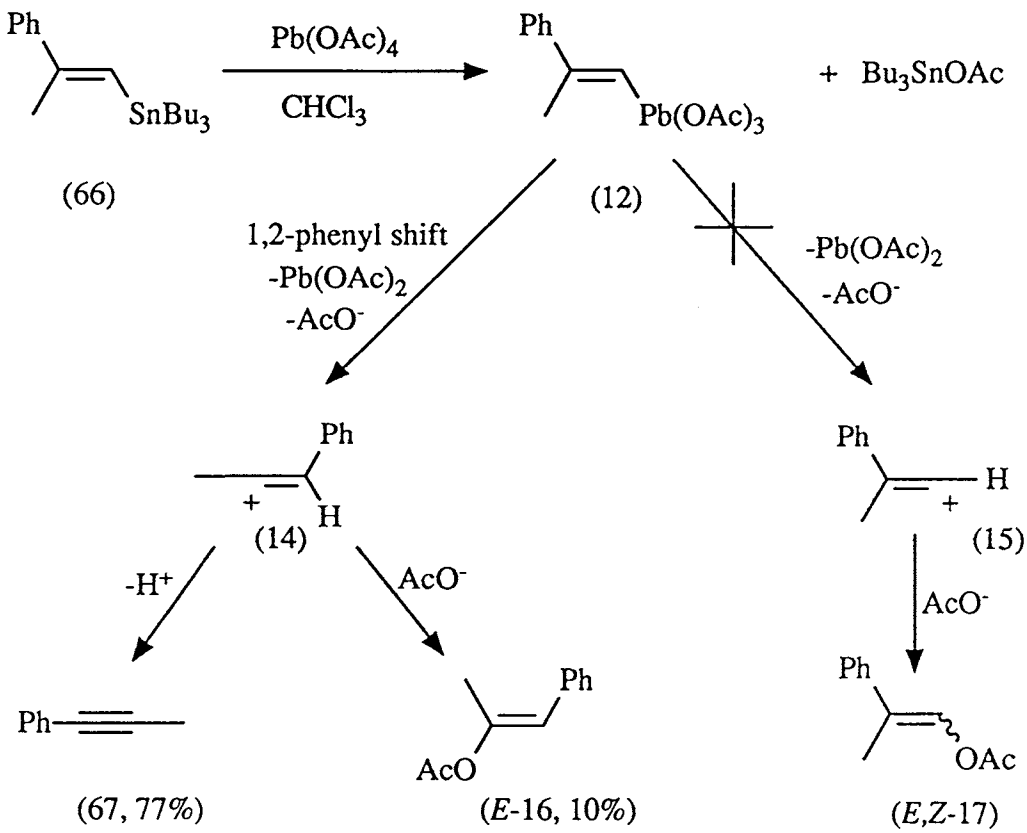


(64)



(65)

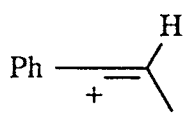
The next compound studied was the stannane (66), where one phenyl group was replaced by a methyl group. Moloney[19] had studied the reaction of the divinylmercury analogue (11), (see Introduction, Part 1, page 12), and found it to proceed via a 1,2-phenyl shift, as in the case of stannanes (56) and (64) above, giving rise to the enol acetate (*E*-16), with rearrangement of the carbon skeleton. When the stannane (66) was treated with lead tetraacetate, the major product observed was 1-phenylpropyne (67), which was formed in 77% yield (Scheme 46).



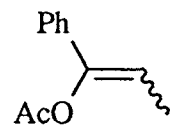
Scheme 46

It is proposed that the reaction takes place by an exactly analogous reaction, with the 1,2-phenyl shift occurring with concommitant loss of lead(II) acetate. In contrast to the result obtained by Moloney however, this reaction gives only 10% of the rearranged enol acetate (*E*-16). It is proposed that this is due to the "mercury effect" noted by Moloney[19]; that

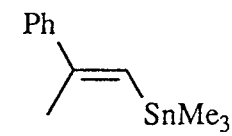
is, that mercury compounds tend to give enol acetates, whereas stannanes tend to give acetylenes, if the substitution at the double bond allows it. Worthy of special note is the fact that it is the phenyl group which migrates in this case, and not the methyl group. If the methyl group had migrated, then the resultant vinyl cation (68) would have been formed. Thus even though this cation, being benzylic in nature, is the most stable vinyl cation possible in this case, it is not being formed, as a different set of enol acetates (*E*,*Z*-69) would be expected. This result reflects the higher migratory aptitude of the phenyl group in such systems. In addition, the fact that the phenyl group and lead are in a *trans* arrangement no doubt aids the migration process.



(68)



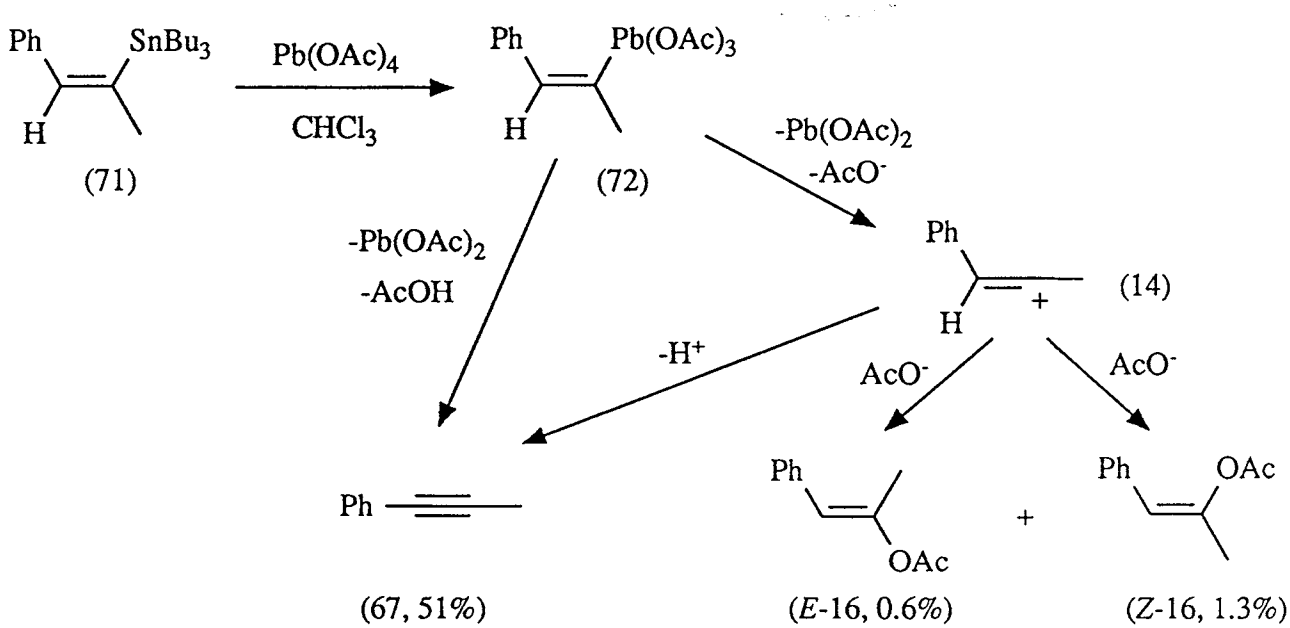
(*E*,*Z*-69)



(70)

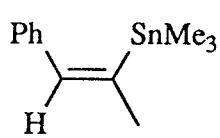
Replacing the tributylstannane (66) with the trimethylstannane (70) produced, in contrast to the result obtained above for (56) and (64), only a marginal increase in the yield (83%) of acetylene (67). The reason for this became apparent in the n.m.r. spectroscopic studies described later. When this reaction was carried out on an n.m.r. scale it was found that the stannane (66) reacted rapidly with lead tetraacetate, and hence, little side reaction occurred. It was possible to observe signals due to the intermediate vinyllead triacetate (12) at δ 6.89, with a ^{207}Pb-H coupling constant of 864.8 Hz. Thus, as the exchange of stannane (66) is already fast, little is gained by using the more reactive stannane (70). The stannane (70) may react marginally faster, but any increase in the yield of the acetylene formed was offset by this being an isolated yield, with some of the quite volatile acetylene (67) being lost in the workup and purification.

The stannane (71) when treated with lead tetraacetate, produced the acetylene (67) in 56% yield (by gas chromatography) (Scheme 47). Also formed were the enol acetates (*E*-16) and (*Z*-16), in yields of 0.6% and 1.3% respectively. The reaction can be thought of as proceeding either through a stepwise generation of the vinyl cation (14), followed by loss of the β-proton, or *via* a concerted β-elimination.

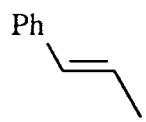


Scheme 47

The reason for the low yield of (67) is thought to be due to the very slow exchange reaction of (71) with lead tetraacetate, and indeed, in the n.m.r. spectroscopic studies, no vinyllead triacetate was observed. The main effect of a slow tin-lead exchange is to allow competing side reactions to occur. In these cases, the major side reaction is generally oxidation of the acetylene product.

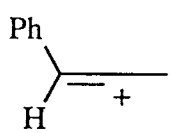


(73)

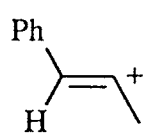


(74)

In this case, replacement of the tributylstannane (71) by the trimethylstannane (73) in the exchange reaction, produced no significant increase in yield of the acetylene (67) (51%); however, the product of protodemetallation, the alkene (74), was formed in 12% yield. This is consistent with the higher acid-sensitivity of trimethylvinylstannanes. If the tin-lead exchange reaction is slow, then the competing proto-demetallation of the starting material by the acetic acid produced will be a significant side reaction. The enol acetates (*E*-16) and (*Z*-16) were formed in 1% and 5% yields respectively. The stannane (73) was found to exchange slightly faster than (71), as shown by the disappearance of the vinylic signal in the ^1H n.m.r. spectrum, but the exchange was not sufficiently rapid to give an observable vinyllead triacetate. The lead compound may now undergo one of the two fates discussed above, and this result would appear to imply that the vinyl cation route is operating, as the enol acetates are best explained by this mechanism. In the case of the mercury compound (11) studied by Moloney[19], and the stannane (66), only the (*E*)-enol acetate (*E*-16) is formed, whilst in this case , both (*E*-16) and (*Z*-16) are formed.



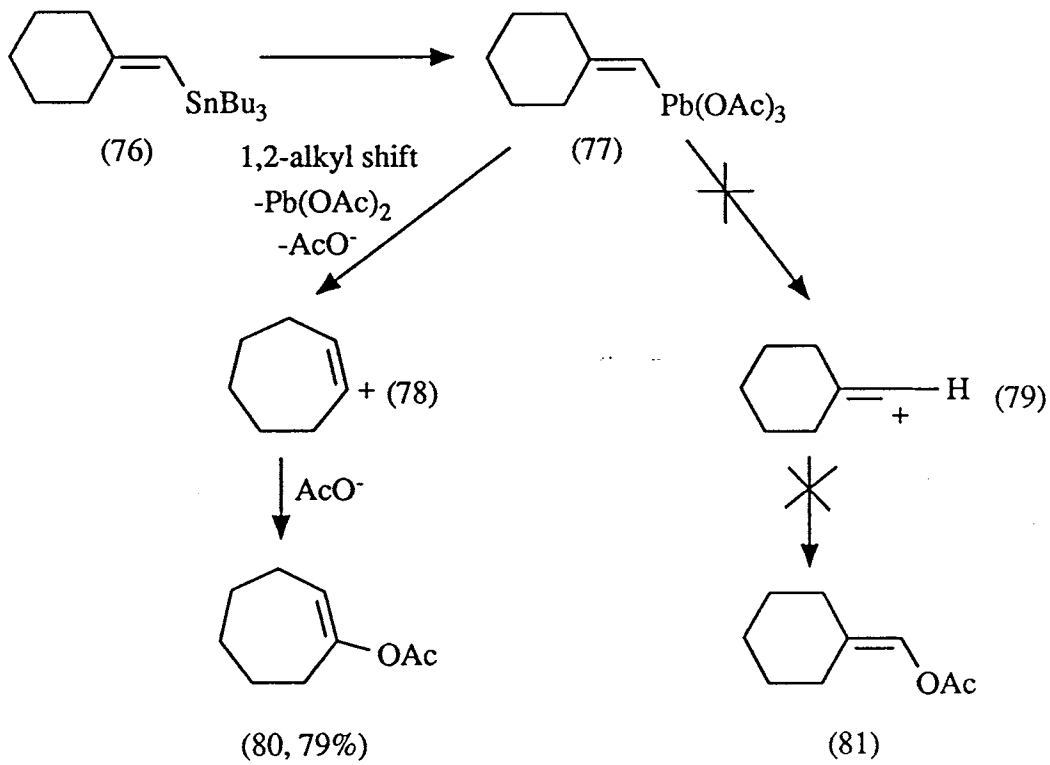
(14)



(75)

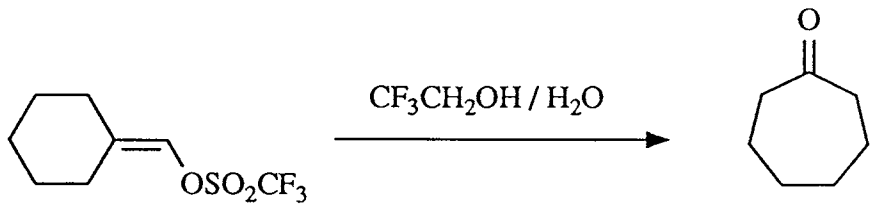
This result may explain the structure of the vinyl cations formed. In the case of mercury compound (11) and stannane (66), the rearranged cation is most likely linear (14), and traps the acetate ion on its least hindered side, to give the (*E*)-enol acetate (*E*-16). In the case of stannanes (71) and (73) the cation (75) may not have sufficient time to become linear before it traps the acetate, hence the major enol acetate formed would be the (*Z*)-isomer (*Z*-16).

The next reaction studied was that of tributyl(cyclohexylidenemethyl)stannane (76) with lead tetraacetate (Scheme 48). This stannane was found to react slowly by ^1H n.m.r. spectroscopy, and after 16 hours the reaction mixture was found to contain cyclohepten-1-yl acetate (80) in 79% yield.



Scheme 48

It is proposed therefore, that the product of the exchange, cyclohexylidenemethyllead triacetate (77), decomposes via a 1,2-alkyl shift, concommitant with loss of lead (II). The vinyl cation (78) which is formed, then captures acetate to yield the observed enol acetate (80). This reaction mirrors almost exactly the solvolysis of the triflate (82), which affords cycloheptanone (83) as the major product (Scheme 49).[49]



(82) (83)

Scheme 49

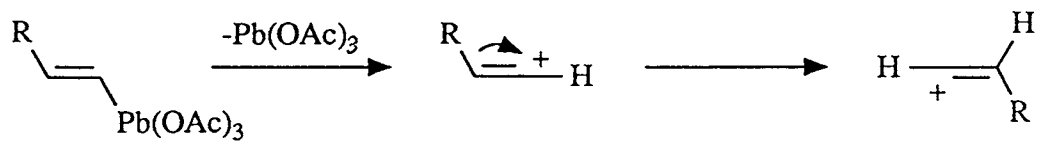
This would appear to be the only case in which an alkyl group migration across the double bond of a vinyl cation has been observed. The vinyl cation formed from simple decomposition of the vinyllead triacetate (79) would be of exceptionally high energy, and is thought not to develop fully, as none of the enol acetate (81) arising from it is found in the reaction mixture.

PRIMARY VINYL CATIONS

In all of the experiments discussed above, the reactions generally occur with rearrangement to give the most stable vinyl cation, before either trapping acetate to give an enol acetate, or losing a proton to give the acetylene. In none of the above cases are any products arising from primary vinyl cations observed.

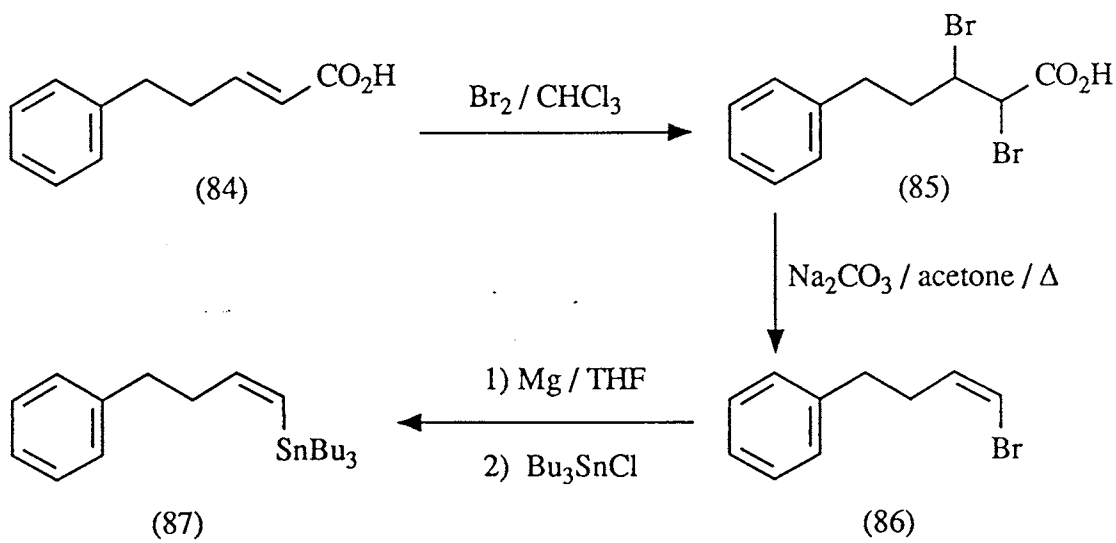
It has been argued that of all the vinyl cations studied to date, primary vinyl cations, that is, vinyl cations bearing only a hydrogen at C1 are the most unstable and highest in energy. Indeed, these species are almost never observed in the plethora of solvolysis reactions that have been performed, and are usually only found in the gas-phase (specifically mass spectroscopy).[50,51,52]

It seemed from the above and earlier[19] work that the triacetoxyplumbyl group was an exceptionally good leaving group, and the reductive elimination of such groups was at least as good a source of vinyl cations as solvolysis reactions. Hence the preparation of a number of compounds which bore only hydrogens at the α-position, and thus would yield primary vinyl cations, was undertaken. The simplest method of preparing such compounds appeared to be the use of only one alkyl or aryl substituent at the β-position, as any migrations that the compound may undergo would be degenerate (Scheme 50).



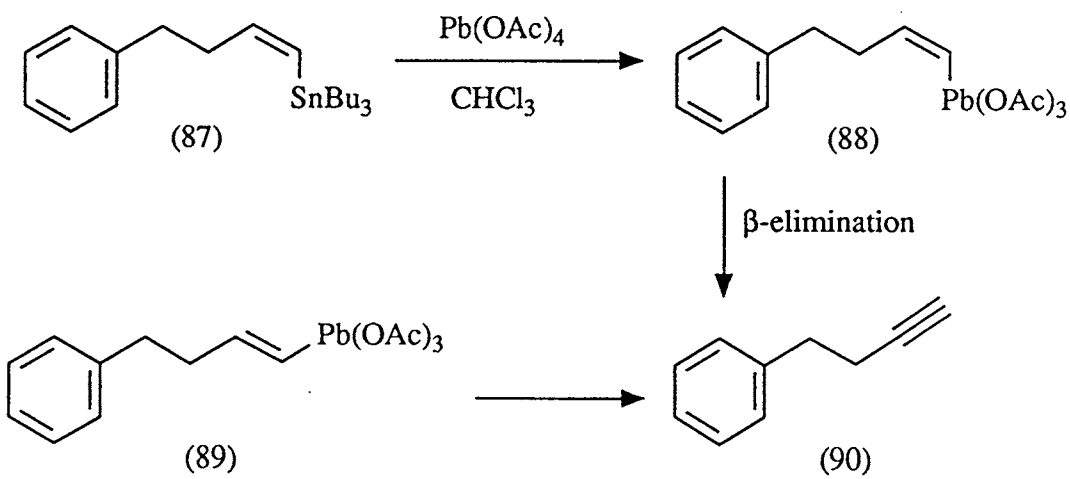
Scheme 50

The first compound examined in this area was tributyl[(*Z*)-4-phenyl-1-buten-1-yl)]stannane (87). This compound was prepared from the Grignard reaction of the vinyl bromide (86). The vinyl bromide itself was prepared from the corresponding α,β-unsaturated carboxylic acid (84), *via* bromination followed by decarboxylative debromination (Scheme 51).



Scheme 51

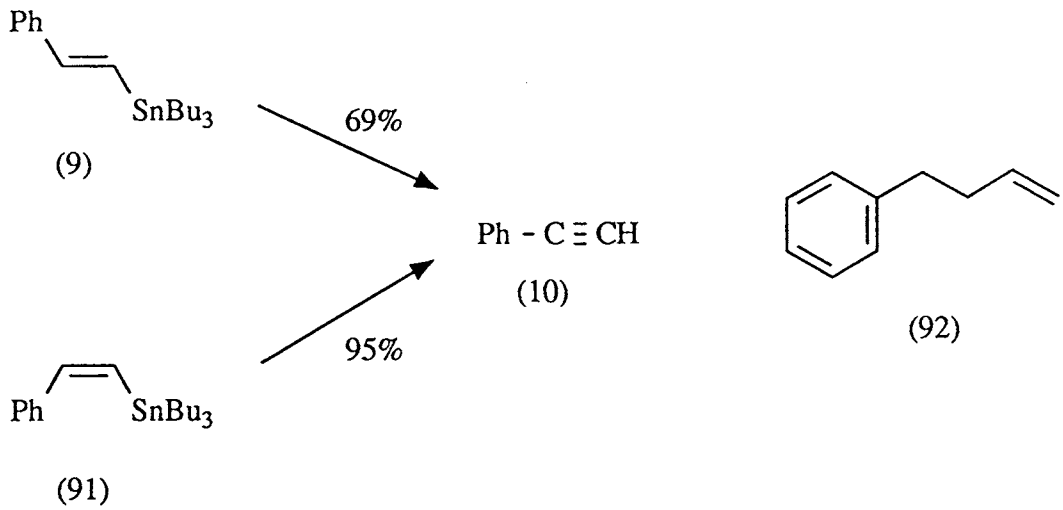
This sequence almost invariably yields the (*Z*)-vinyl bromide, unless the substituent β to the carboxylic acid is an aromatic system with one or more electron-donating substituents attached.[53] The vinyl bromide (86) was found to contain approximately 18% of the (*E*)-isomer by ^{1}H n.m.r. spectroscopy, but the Grignard reaction produced a stannane with an (*E*)-isomer content of only 10%. This stannane was found to be inert under the normal exchange conditions with lead tetraacetate, and prolonged or harsher exchange reactions lead to decomposition to butyl acetate, rather than the desired exchange. The only recognisable product obtained was a small amount (<5%, GLC) of the acetylene (90), which may have arisen from a normal β-elimination of the (*Z*)-vinylead triacetate (88) (Scheme 52), or from the (*E*)-contaminant (89) via either a vinyl cation or a *cis*-β-elimination.



Scheme 52

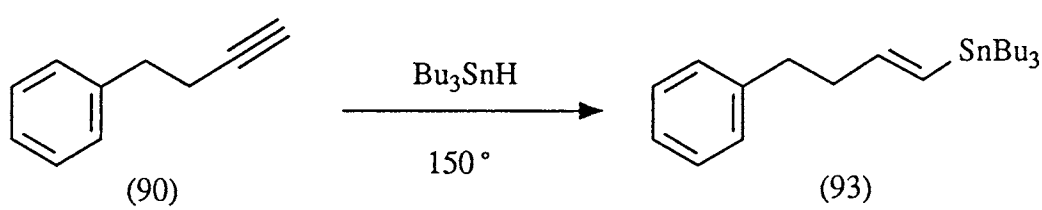
Moloney[19] found that in the styryl series of compounds (Scheme 53), the (*E*)-isomer (9) exchanged far more rapidly than the (*Z*)-isomer (91), both compounds giving the acetylene (10) as the major product. This result made the preparation of the (*E*)-isomer of (87) highly desirable. Since it could not be prepared by the above route, and a bromination-dehydrobromination sequence from the alkene (92) would result

in a complex mixture of (*E*), (*Z*), and allylic bromides, the thermal hydrostannylation of the acetylene (90) was investigated.

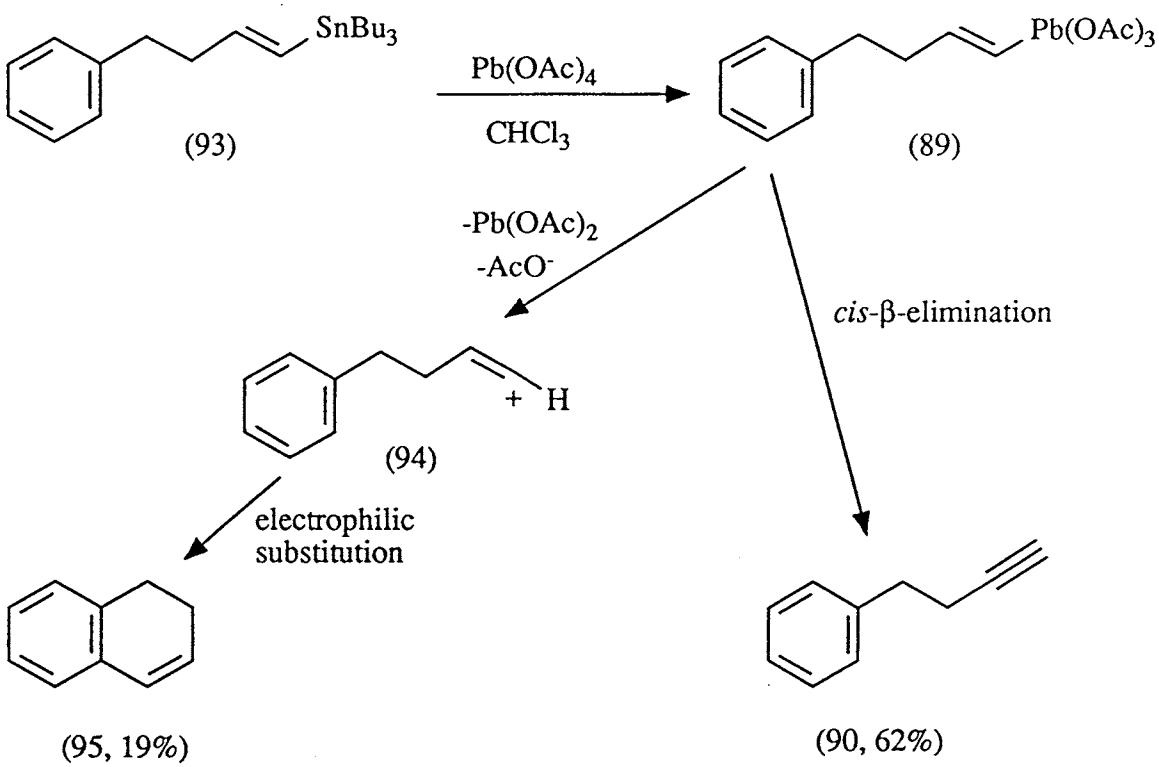


Scheme 53

Reaction of tributyltin hydride with (90) gave tributyl[(*E*)-4-phenyl-1-buten-1-yl]stannane (93) in excellent yield with the (*Z*)-isomer (87) only a minor component (19%), (Scheme 54). This stannane was found to react readily with lead tetraacetate and after 24 hours, the mixture was found to contain 1,2-dihydronaphthalene (95), in 19% yield, as well as the acetylene (90) in 62% yield (Scheme 55).



Scheme 54



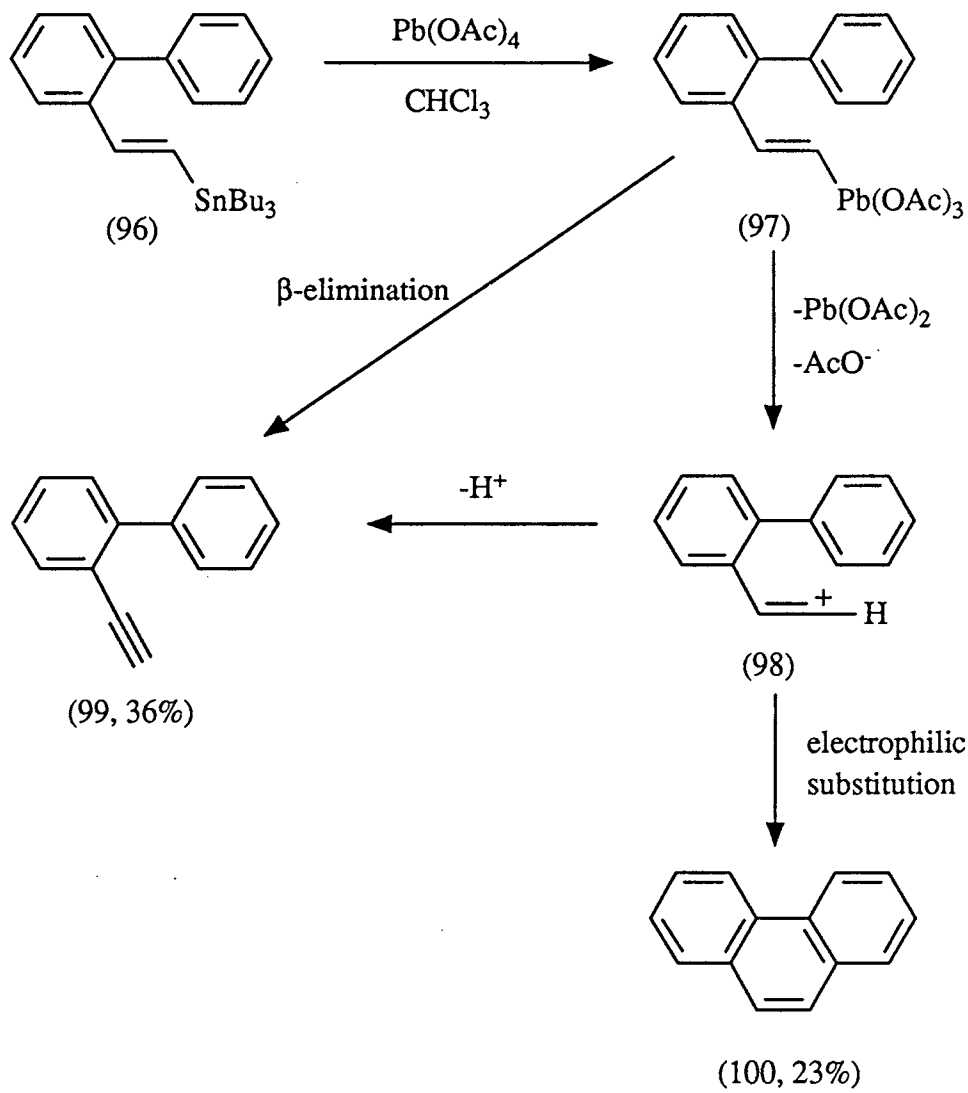
Scheme 55

It appears therefore, that the vinyllead triacetate (89) is decomposing to the vinyl cation (94), which is undergoing an intramolecular aromatic electrophilic substitution reaction. The formation of the acetylene (90) could be either by a *cis* β-elimination or a competing proton loss from the vinyl cation (94), of slightly faster rate. This is in contrast to the (*Z*)-vinyllead triacetates, which probably undergo a concerted elimination, as the proton and the lead group are in a favourable *trans* arrangement.

When lead tetraacetate was replaced by lead tetrabenzoate in the above reaction of (*E*)-stannane (93), there was an increase in the amount of cyclised material (95) formed to 36%, while there was a corresponding decrease in the amount of the acetylene (90), (43%). Since the total yield of compounds (90) and (95) did not decrease, and the yield of the cyclised material had increased at the expense of the acetylene, it appeared that the more electron-withdrawing tribenzoyloxyplumbyl group is most likely

increasing the rate of decomposition to the vinyl cation (94). Thus it appeared that the acetylene and dihydronaphthalene arise by two different pathways, and not from the same vinyl cation.

Further, when lead tetrapivalate was used in the above scheme, the exchange appeared to be extremely slow, and after the same period of time (24 hours), the yield of cyclised material (95) was reduced to 5%, while the elimination yielded 32% of the acetylene (90). This would suggest that the intermediate lead compound preferentially undergoes a slow *cis*-elimination.



Scheme 56

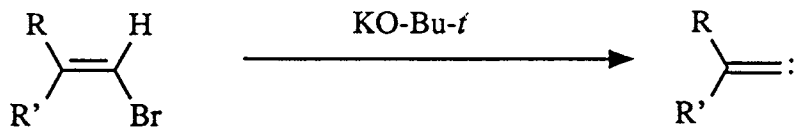
The second compound studied was tributyl[(*E*)-2-(*o*-phenylphenyl)-ethen-1-yl]stannane (96). This compound was found to react rapidly with lead tetraacetate to give an (*E*)-lead intermediate (97), readily observable by ^{1}H n.m.r. spectroscopy. The identified products were phenanthrene (100), (23% yield), the acetylene (99) (36% yield), and a small amount of butyl acetate (5%). This reaction appeared to be proceeding almost exactly as in the case above, and it is proposed that the cyclised product (100) was formed from the vinyl cation (98), which undergoes an intramolecular aromatic substitution (Scheme 56). Once again, it is possible that the acetylene (99) was formed either from the vinyl cation (98), or *via* a *cis* β-elimination.

The competing elimination reaction to give the acetylene (99) was again suppressed (20%) in an experiment in which lead tetrabenzoate replaced lead tetraacetate, and the yield of phenanthrene increased to 46%.

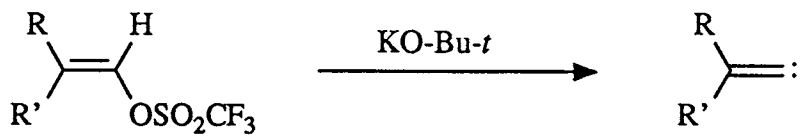
A second possibility here is that due to the very high energy of these primary vinyl cations, the reaction to give the cyclised material may not be proceeding *via* a fully developed cation, but rather by an attack of the aromatic π-system on the polarised vinylic system. Thus, the more electron-withdrawing tribenzoyloxyplumbyl group could be behaving as a better leaving group in an S_N2 sense, and increasing the rate of cyclisation, while the competing *cis*-elimination remains relatively unchanged in rate.

The assumption that vinyl cations are the reactive intermediates responsible for these rearrangements and decompositions, overlooks the possibility that some of the products are equally well explained by the intermediacy of alkylidenecarbenes. Several examples of these species have been described in the literature.[54,55,56] In general, these species are

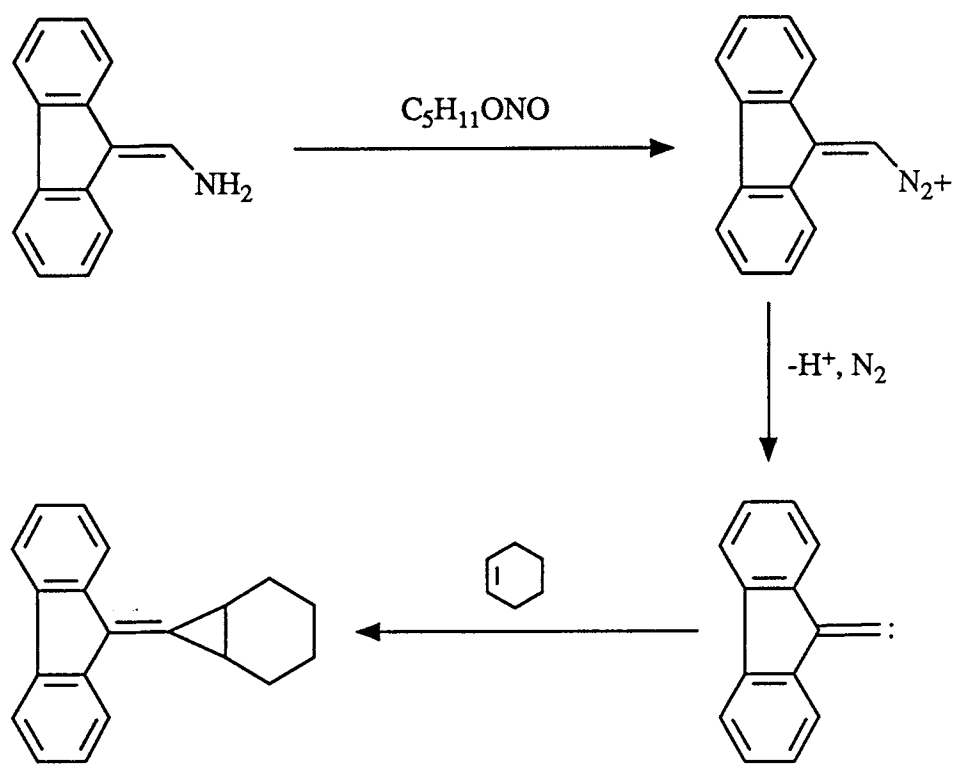
produced by α-elimination reactions of vinyl halides and enol triflates with bases, or *via* the decomposition of alk-1-enediazonium salts (Schemes 57-59).



Scheme 57

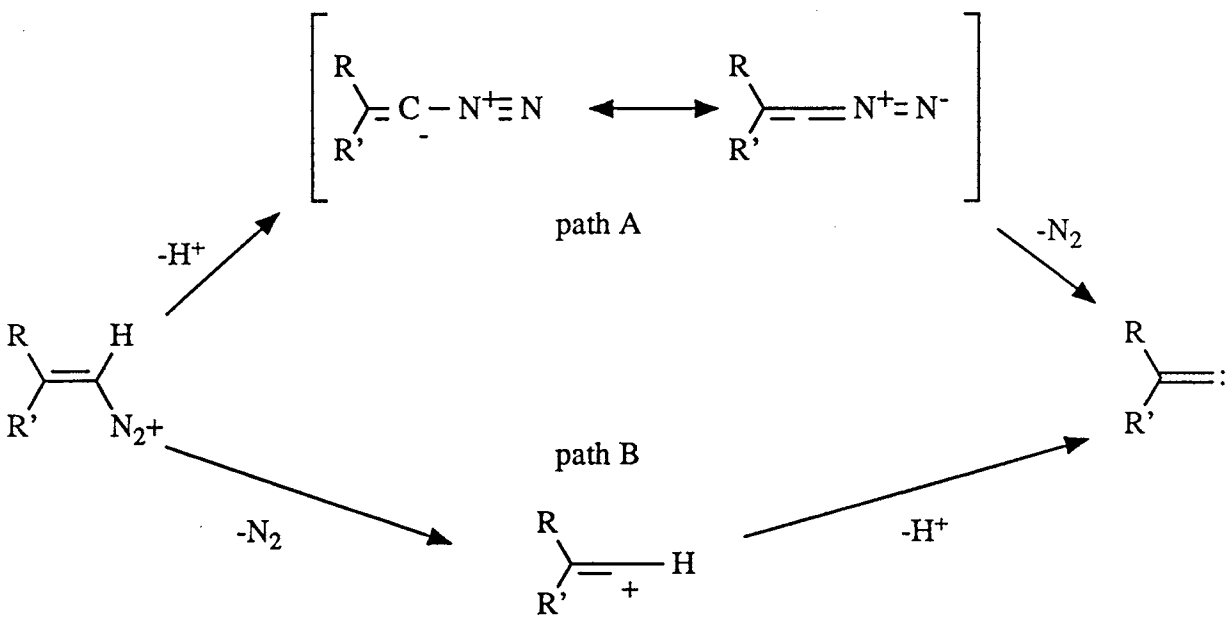


Scheme 58



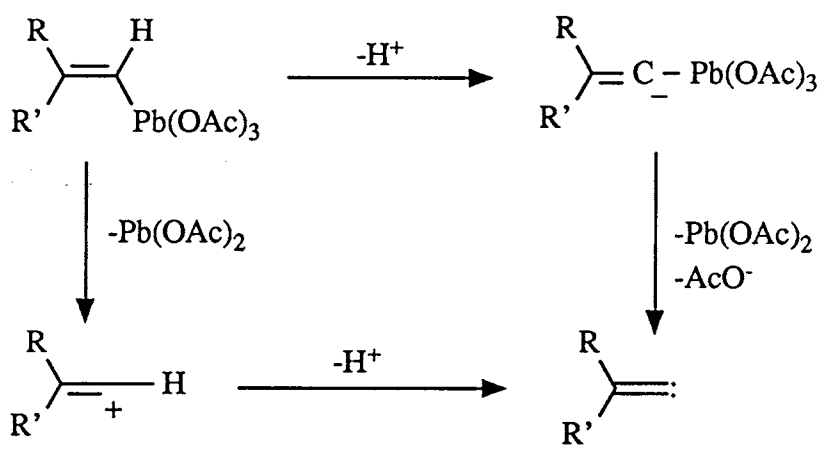
Scheme 59

Alk-1-enediazonium ion decompositions can be assumed to proceed *via* one of two possible pathways. Either the α-proton leaves first to give an α-diazocarbanion, followed by loss of nitrogen to give the carbene (Scheme 60, path A), or, the diazo group leaves first, giving the vinyl cation intermediate, followed by loss of a proton to give the same carbene (Scheme 60, path B). In spite of the considerable amount of work which has been done in this field[56], the exact mechanism is still unknown.



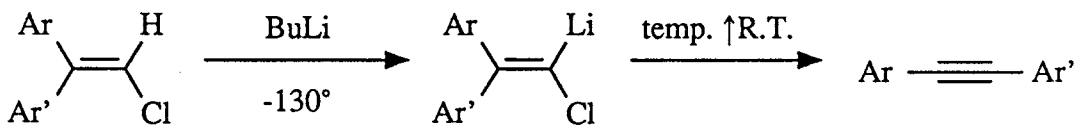
Scheme 60

If the lead compounds discussed here were mirroring this process, then we would have to invoke one of the same reaction pathways (Scheme 61).



Scheme 61

The reactions of the stannanes (56), (64), (66) and (70), and the mercury compound (57) discussed earlier could conceivably follow another route. In the Fritsch-Buttenberg-Weichell rearrangement (Scheme 62), where the groups at the β-carbon are aryl, it has been shown[57] that the lithiated compounds (101) are stable at low (-130°) temperatures and that only at higher temperatures do the compounds undergo an apparent α-elimination. The compounds do not decompose *via* a discreet alkylidenecarbene mechanism, but rather *via* an aryl migration coincident with loss of the halide ion.

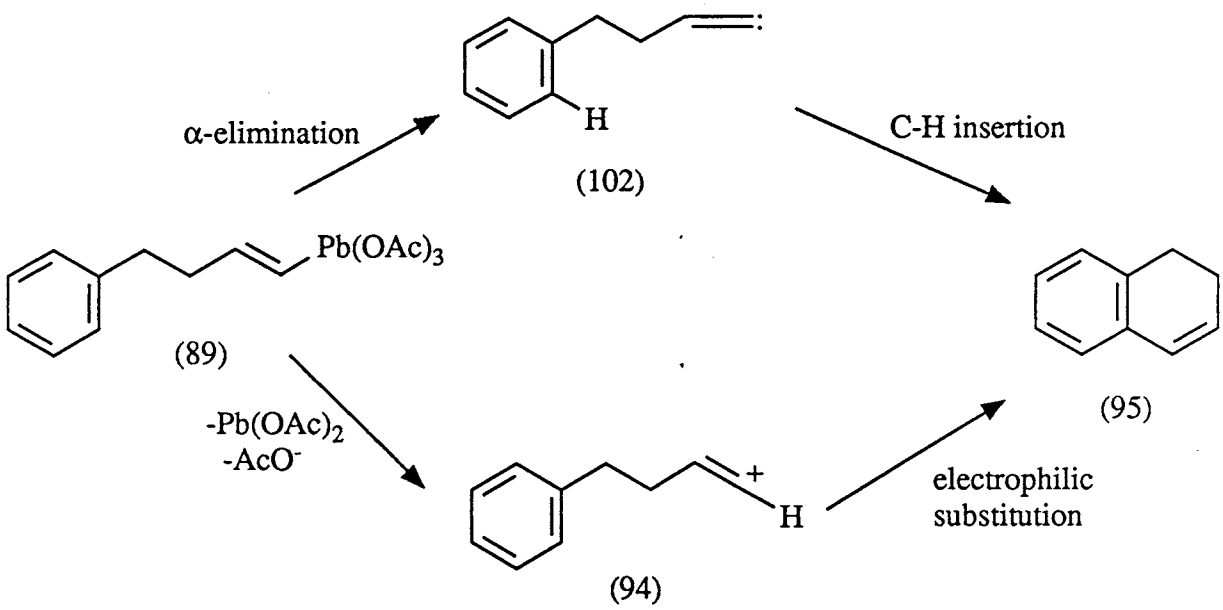


(101)

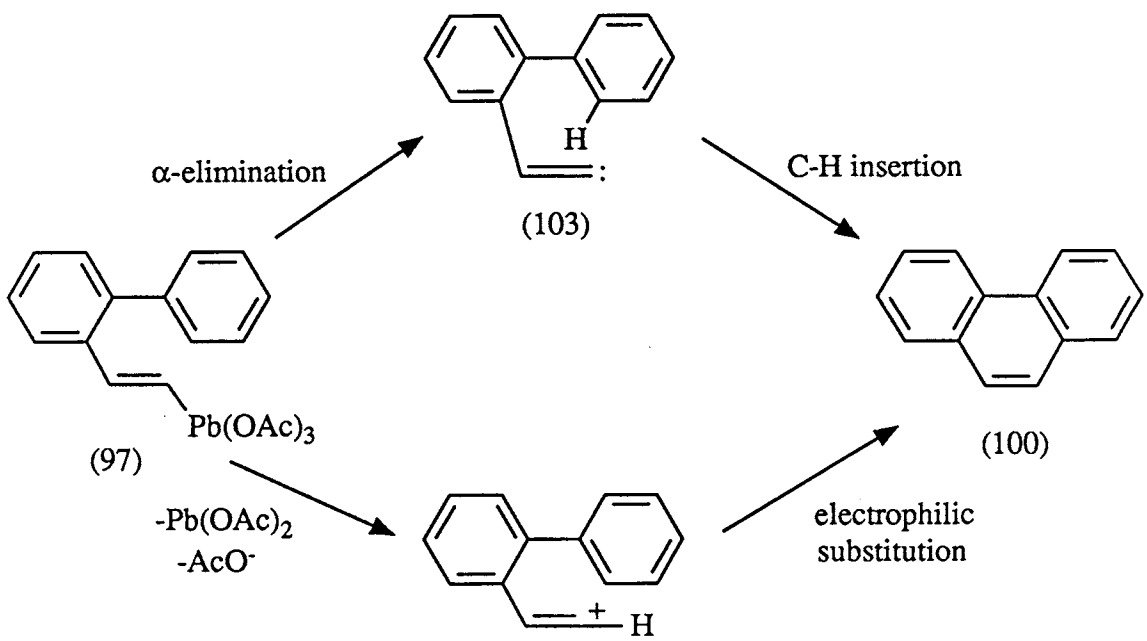
Scheme 62

In general, it is only in cases where the β-groups are alkyl or hydrogen that carbene mechanisms operate.[58]

The reactions of the lead compounds (89) and (97), which cyclised partially to 1,2-dihydronaphthalene and phenanthrene respectively, could, however, be pictured as proceeding *via* alkylidenecarbene pathways (Schemes 63, 64)



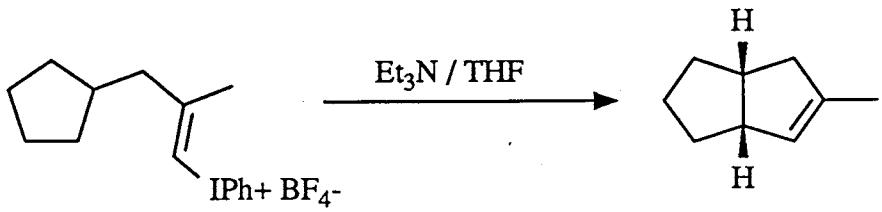
Scheme 63



Scheme 64

Both lead compounds (89) and (97) could undergo α-elimination reactions by either of the 2 pathways discussed above to give the respective alkylidenecarbenes (102) and (103), which insert into the aromatic C-H bonds to give the cyclised products, rather than through the respective vinyl cations (94) and (98). This type of reaction also has a precedent in the field of carbene chemistry, with the iodonium salt (104)

undergoing C-H insertion to give (105)[59] (Scheme 65).

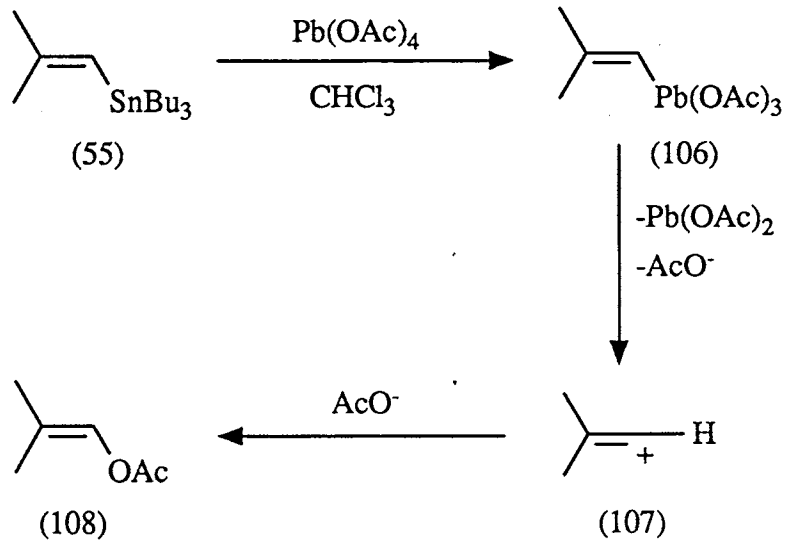


(104) (105)

Scheme 65

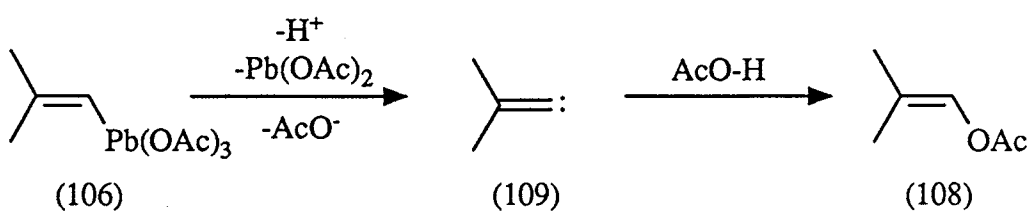
In nearly all the reports of the formation of vinylidenecarbenes from the vinyl halides and triflates, strong bases such as potassium *tert*-butoxide are used to generate the carbenes. In the case of vinyllead triacetates, the strongest possible base available is acetate ion, and it would appear unlikely that it could lead to α-elimination. In spite of this, it was thought that the carbene theory was potentially valid, so several experiments were devised to examine this possibility.

The stannane (55) had been prepared by Moloney[19] and was found to react readily with lead tetraacetate. When the reaction was performed on a ^{1}H n.m.r. spectroscopic scale in deuterochloroform, the tin-lead exchange could be seen to yield a new species, with a vinylic proton at δ 6.37, assumed to be the vinyllead triacetate (106) (see chapter 3). This was found to decompose with time to give the enol acetate (108). It was proposed that this lead compound decomposed to give the vinyl cation (107), before capturing acetate ion (Scheme 66).



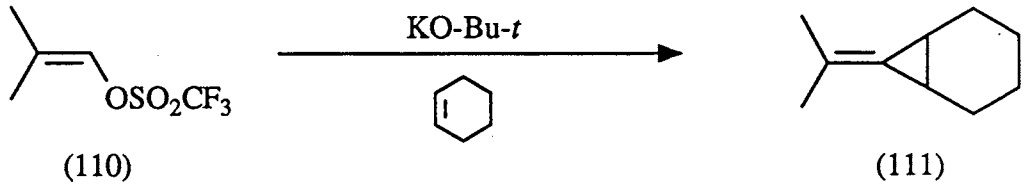
Scheme 66

It has been argued that it is extremely unlikely that this cation can form, due its high energy[27d], and thus it is possible that the reaction may proceed *via* the alkylidenecarbene (109), which reacts with acetic acid to yield the enol acetate (Scheme 67).



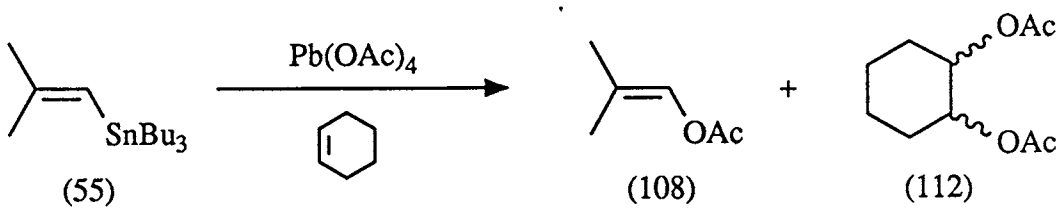
Scheme 67

It has been shown by Stang *et al.* that treatment of the enol triflate (110) with potassium *tert*-butoxide in the presence of cyclohexene produces the carbene addition product[60] (111), (Scheme 68). However, when the tin-lead exchange reaction of stannane (55) was conducted in the presence of varying amounts of cyclohexene, no insertion took place. The only products found were the enol acetate (108), and some diacetoxy cyclohexane (112), arising from oxidation of the cyclohexene by lead tetraacetate (Scheme 69).

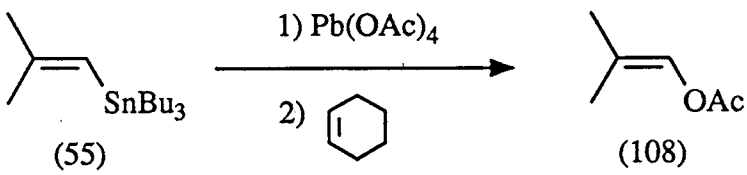


(110) (111)

Scheme 68



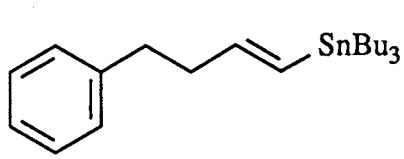
(55) (108) (112)



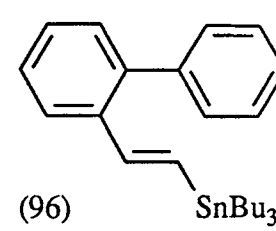
(55) (108)

Scheme 69

In order to minimise the oxidation of cyclohexene, the exchange reaction was carried out, and the cyclohexene added subsequently, at a time when the n.m.r. spectroscopic experiments (see Results and Discussion, Section 3) had shown the exchange to be complete, and the lead compound (106) at its most abundant (2 minutes). In none of these experiments was any of the carbene insertion product (111) observed. Similar experiments with stannanes (93) and (96), also failed to produce any carbene insertion products. The products obtained were the same as those obtained in the absence of cyclohexene.

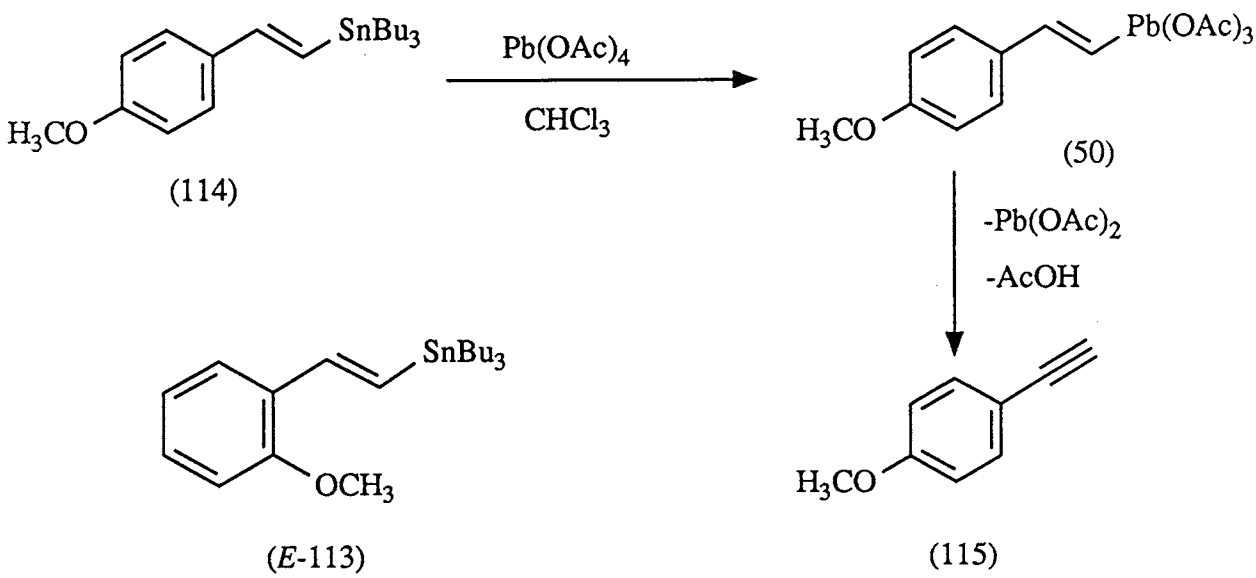


(93)



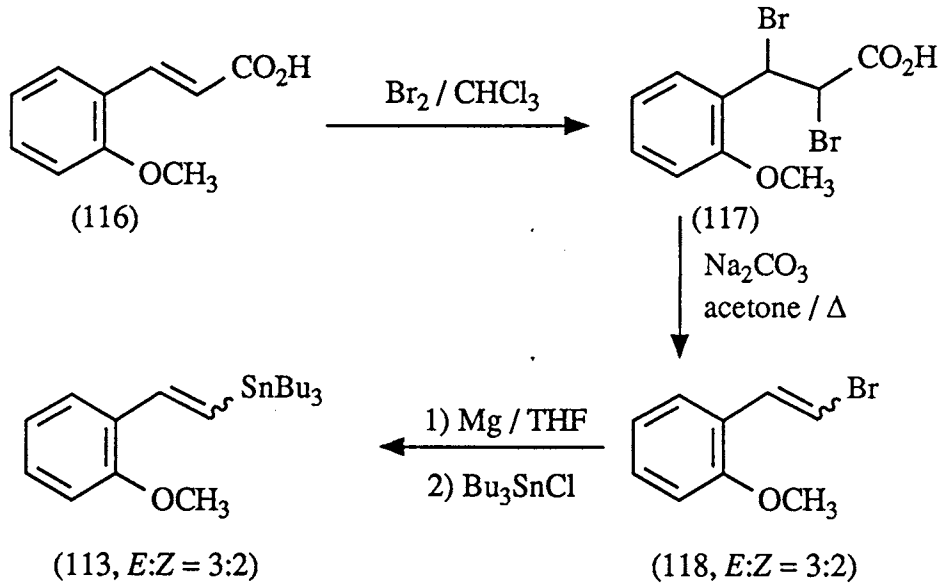
(96)

Another compound that helped to disprove the carbene theory was tributyl[(*E*)-2-(*o*-methoxyphenyl)ethen-1-yl]stannane (113). Interest in this compound originally arose because of the unusual stability of [(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]lead triacetate (50). Moloney[19] found that when this compound was prepared from the tributylstannane (114), it was relatively stable in chloroform solution. When the tin-lead exchange reaction was studied by ^{1}H n.m.r. spectroscopy, the acetylene (115) only began to appear after 1 hour (Scheme 70). For comparison, the electronically related stannane (113) was prepared.



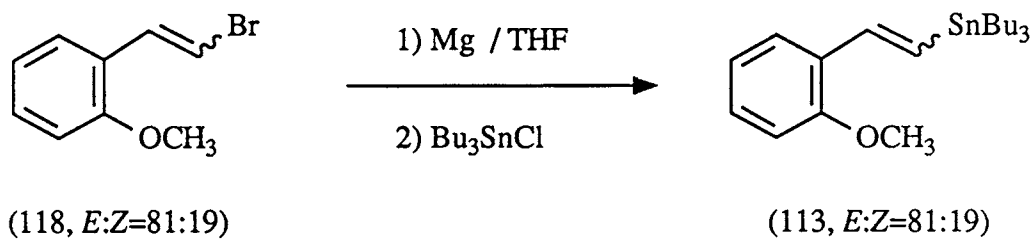
Scheme 70

The vinyl bromide (118), required for the synthesis of the stannane, could be prepared in a number of (*E*):(*Z*) isomer ratios. The bromination-decarboxylative debromination sequence from *o*-methoxycinnamic acid (116) gave a vinyl bromide mixture with an *E*:*Z* ratio of 3:2 (Scheme 71).



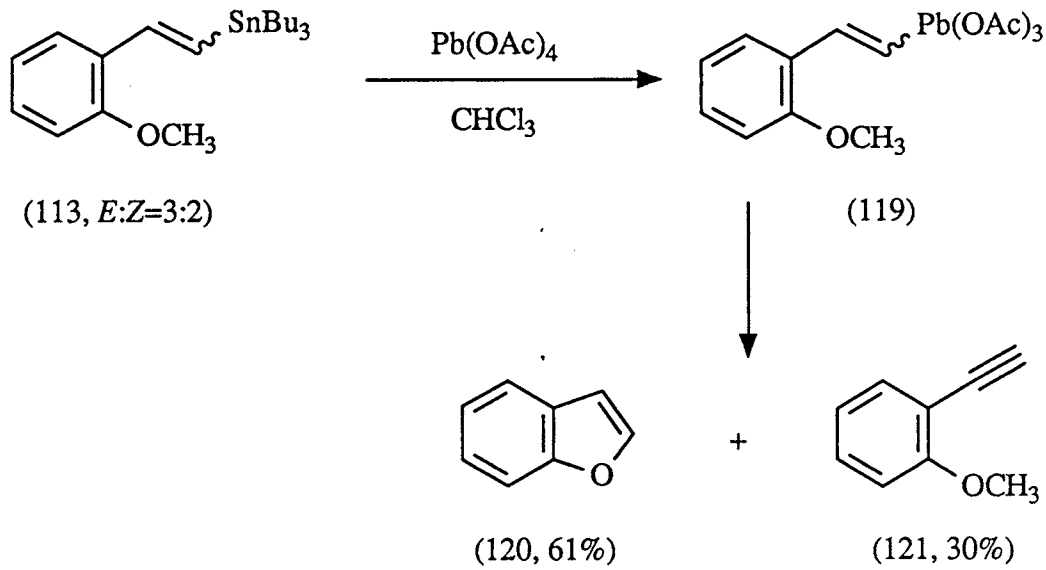
Scheme 71

This vinyl bromide could be isomerised to a mixture with an *E*:*Z* ratio of 81:19 by irradiation with a tungsten lamp in the presence of iodine. Both vinyl bromide mixtures were converted to the corresponding mixture of stannanes (113) with retention of their isomeric integrity (Scheme 72).



Scheme 72

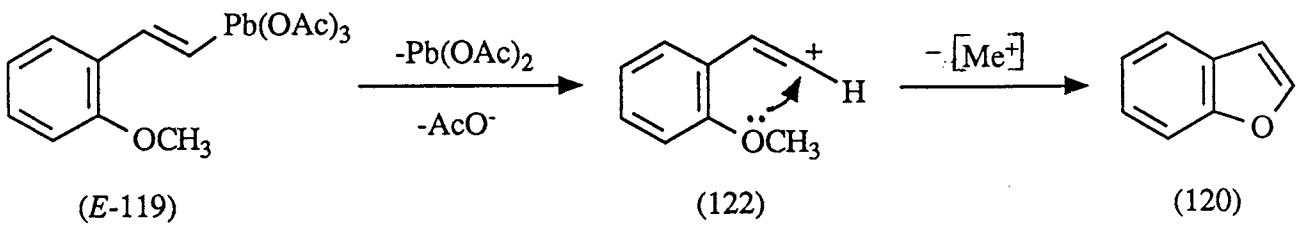
When a sample of the stannane (113, *E*:*Z*=3:2) was treated with lead tetraacetate and left for 24 hours, a 61% yield of benzofuran (120) was obtained, and this was accompanied by *o*-methoxyphenylacetylene (121, 30% yield) (Scheme 73). When the reaction was repeated on the mixture containing 81% of the (*E*)-isomer, there was an increase in the benzofuran yield to 84%.



(113, *E*:*Z*=3:2) (119)

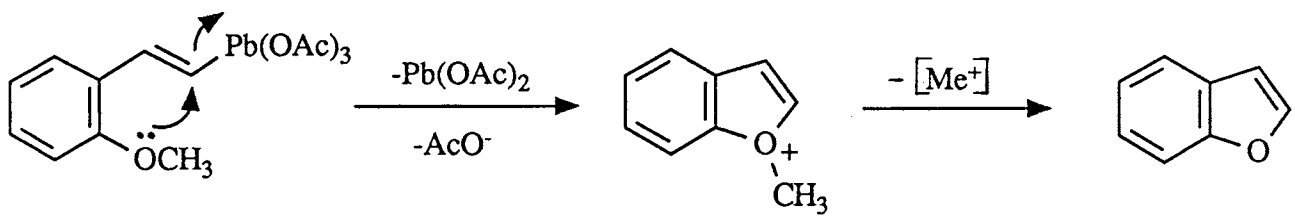
(120, 61%) (121, 30%)

Scheme 73



(*E*-119) (122) (120)

Scheme 74

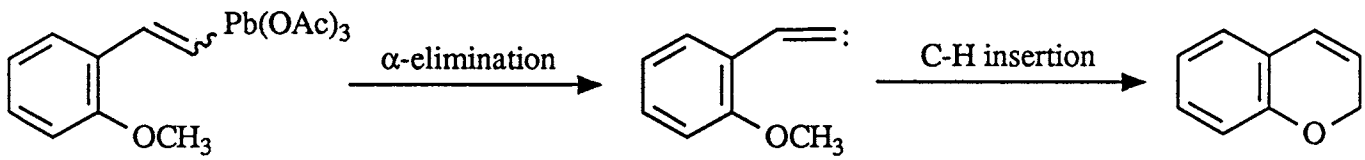


Scheme 75

It would appear that the *trans*-lead compound (*E*-119), derived from the *trans*-stannane (*E*-113), decomposes to the vinyl cation (122), and that the methoxyl group attacks the vinyl cation, with loss of the methyl group as methyl acetate, to give benzofuran (Scheme 74). A second possibility here is that the vinyl cation (122) implicated here, also primary, may not be fully formed, and the methoxyl oxygen acts as a nucleophile in an S_N2

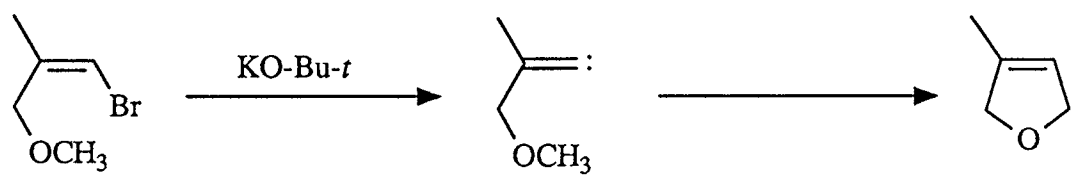
sense, attacking the vinylic carbon as the lead group is leaving (Scheme 75). In this case, however, the vinylic carbon must have significant cationic character for this reaction to occur, as such reactions are almost never observed in vinylic systems.

Had the intermediate been the alkylidenecarbene (124), then the carbene would have been expected to insert into the carbon-hydrogen bond of the methoxyl group, resulting in the formation of benzopyran (125) (Scheme 76). The insertion of an alkylidenecarbene (127) into a methoxyl C-H bond has been observed in the cyclisation of the vinyl bromide (126) when treated with potassium *tert*-butoxide[61] (Scheme 77).



(119) (124) (125)

Scheme 76

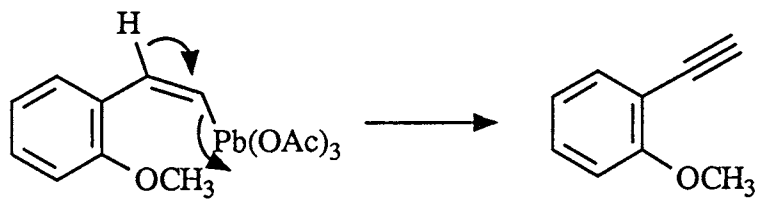


(126) (127) (128)

Scheme 77

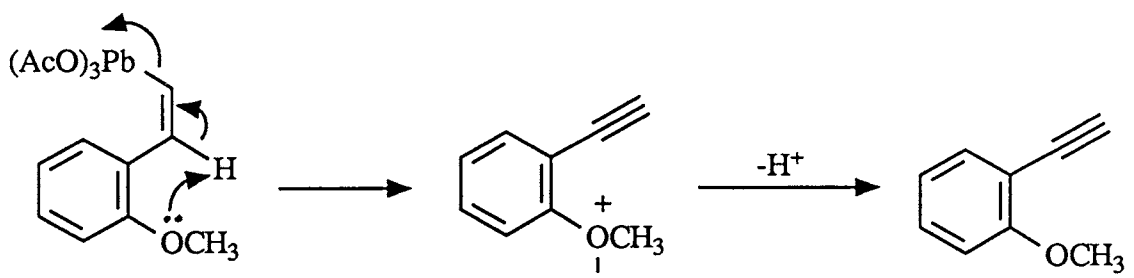
Interestingly, it seems that the *cis*-lead compound (*Z*-119), derived from the *cis*-stannane (*Z*-113), decomposes *via* one of three possible mechanisms to give the acetylene (121). The first, and most straightforward mechanism is a concerted β-elimination mechanism, without intermediate vinyl cation formation (Scheme 78). This elimination reaction may also be oxygen assisted as shown in Scheme 79. The third

possibility is that the reaction proceeds *via* the stepwise generation of the vinyl cation (122), followed by loss of a proton to give the acetylene (121) (Scheme 80). It is immediately apparent that the decompositions of the two isomeric lead compounds cannot be proceeding *via* the same vinyl cation (122), as this would lead to identical product ratios in the two experiments with different stannane isomer ratios. This point will be discussed later.



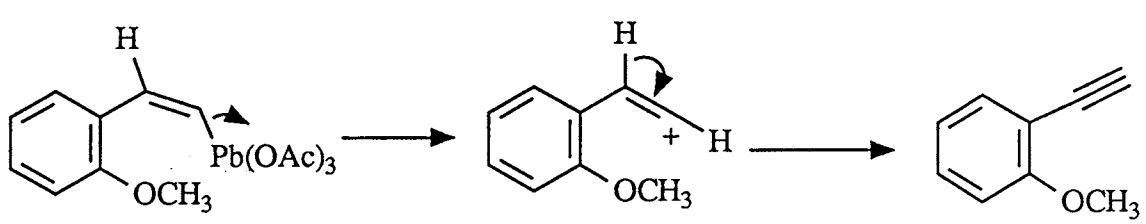
(Z-119) (121)

Scheme 78



(Z-119) (129) (121)

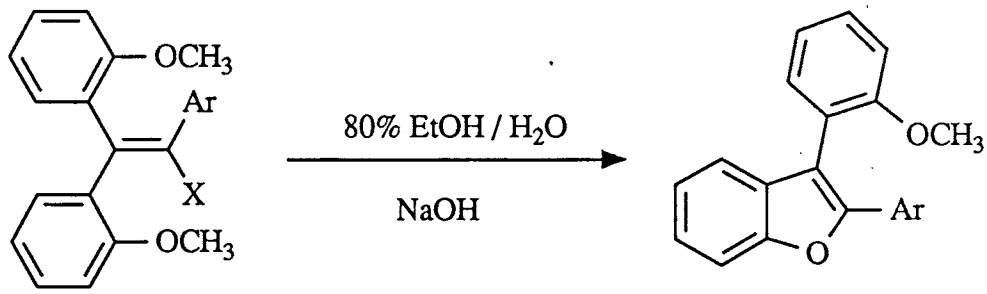
Scheme 79



(Z-119) (122) (121)

Scheme 80

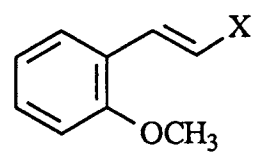
This reaction is also analogous to some solvolyses undertaken by Japanese workers[62]. Vinyl halides bearing two β-*o*-methoxyphenyl groups, and an α-aryl group were shown to undergo solvolyses to yield substituted benzofurans (Scheme 81).



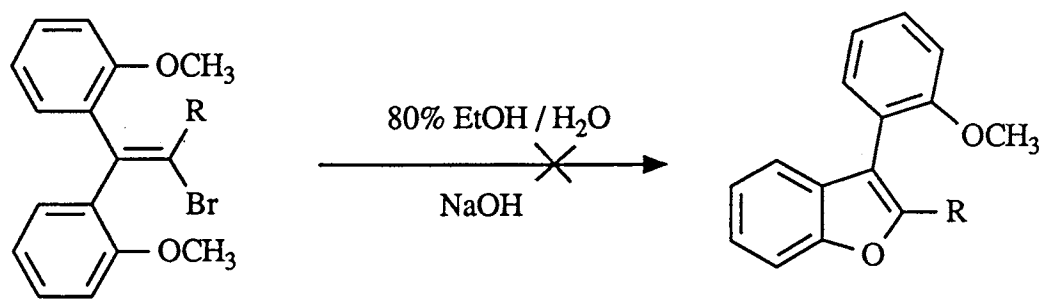
$X = Cl, Br;$ $Ar = Ph, p\text{-}MeOC_6H_4\text{-}$

Scheme 81

Although the directly analogous vinyl halides bearing only one β-*o*-methoxyphenyl group (130) were not examined by these workers, it was found that when the α-aryl substituent was absent, or had been replaced by a methyl group, there was no cyclisation, and indeed no solvolyses were observed in these cases (Scheme 82).



(130)

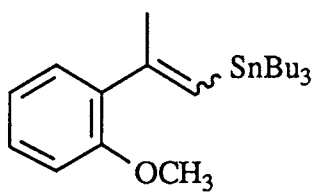


$R = H, CH_3$

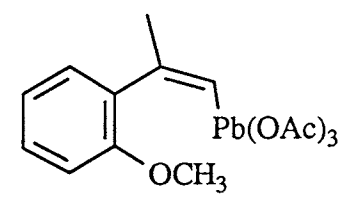
Scheme 82

This is in agreement with the observation that simple primary vinyl cations are not formed in solvolysis reactions. Thus it seems again, from the current work, that the triacetoxyplumbyl group is the best leaving group yet available for the study of vinyl cation chemistry.

To further examine the participation by a neighbouring methoxyl group, the mixture of isomeric stannanes (131) were produced. In this case, replacement of the β-proton by a methyl group removes the possibility of simple β-elimination in the derived (*Z*)-lead compound (*Z*-132).

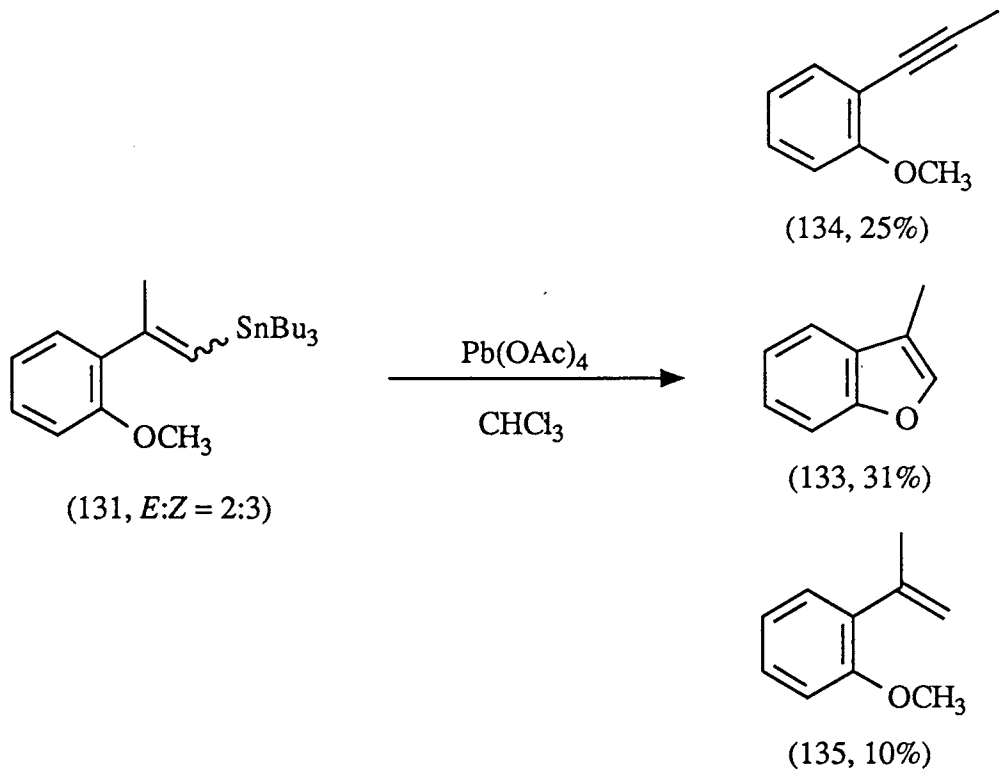


(131)



(Z-132)

It was envisaged, therefore, that it would be possible to obtain the cyclised material, 3-methylbenzofuran (133), from both *cis* and *trans* precursors. This, however, was not the case. When the reaction was carried out on a 2:3 mixture of the *E* and *Z*-isomers (131), the yield of 3-methylbenzofuran (133) was only 31% (36% when monitored by n.m.r. spectroscopy). The other product was the acetylene (134) which was obtained in 25% yield. Also present was butyl acetate (9%), and 2-(*o*-methoxyphenyl)propene (135) in 10% yield (Scheme 83). Due to the relatively low yields of the two main products, it was not clear which lead intermediate was the precursor of each one.



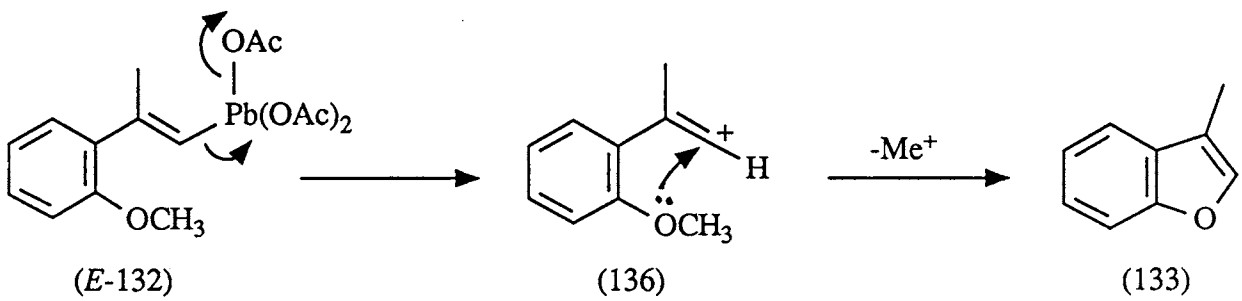
Scheme 83

The n.m.r. experiment yielded only a small amount of useful information. The initial exchange reaction was rapid only in the case of the (*E*)-isomer (*E*-131). The (*Z*)-isomer was much slower to exchange, and only one lead compound was observed; this was assigned to the (*E*)-lead compound (*E*-132). The low yields of (133) and (134) are most likely due to the oxidation of the products by lead tetraacetate, which was present due to the slow tin-lead exchange of the (*Z*)-stannane (*Z*-131).

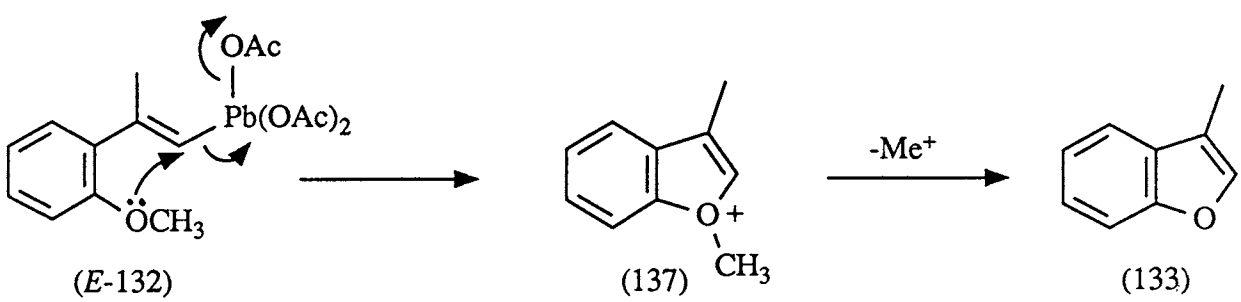
When a deuterochloroform solution of the above 2:3 mixture of the stannanes (131) was subjected to ultraviolet irradiation for 3 days under nitrogen, a 1:9 (*E*:*Z*) isomer mixture was obtained. Upon tin-lead exchange with lead tetraacetate, this mixture gave rise to a 72% yield of the acetylene (134), and a 4% yield of 3-methylbenzofuran (133). From these results, it would seem apparent that the two isomers are, once again decomposing by two different mechanisms; the (*E*)-isomer giving the 3-methylbenzofuran (133), and the (*Z*)-isomer giving rise to the acetylene

(134).

As in the case of the stannane (113), discussed earlier, it appears likely that the (*E*)-lead compound decomposes *via* either the stepwise generation of a primary vinyl cation (136), followed by ring closure onto the methoxyl oxygen (Scheme 84), or by an oxygen-assisted S_N2-like mechanism (Scheme 85).



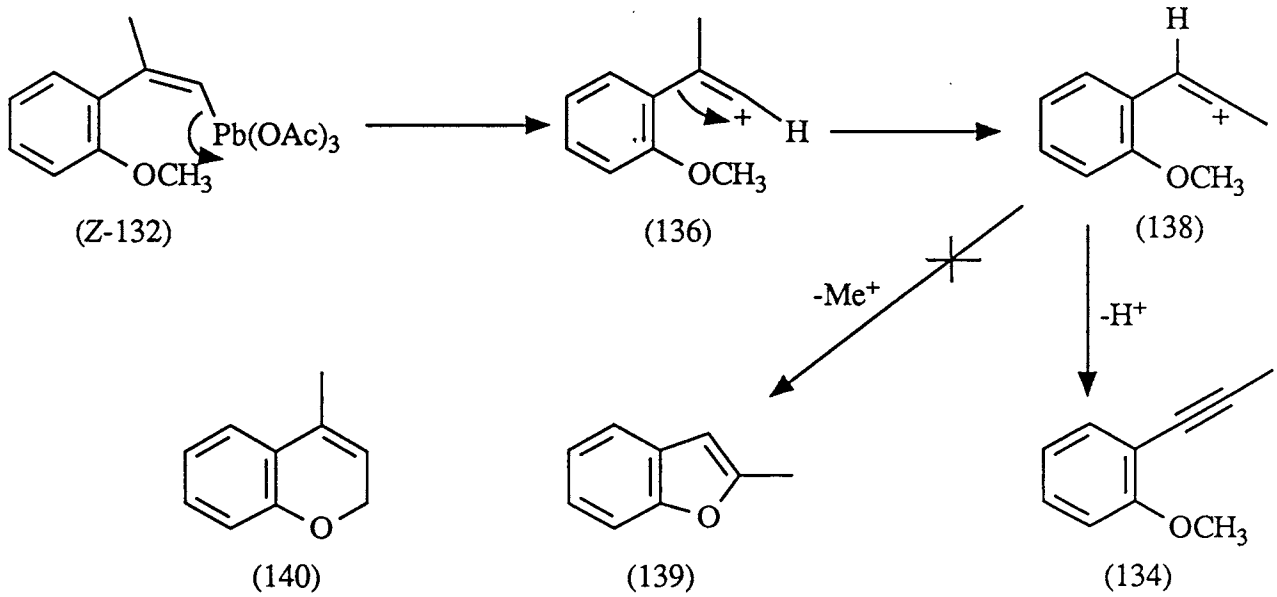
Scheme 84



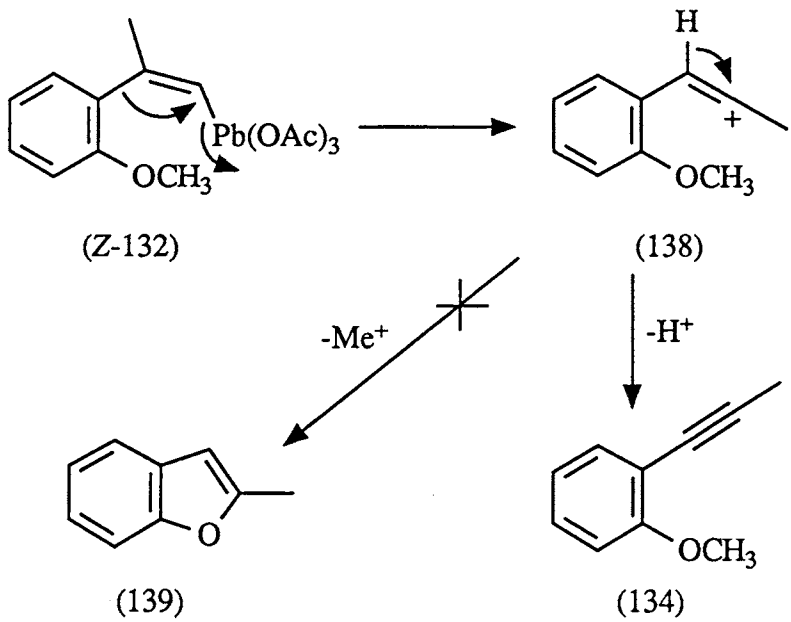
Scheme 85

The formation of the acetylene (134) from the (*Z*)-lead compound can also be rationalised in two ways. Either by a stepwise generation of primary vinyl cation (136), followed by an aryl shift, and loss of a proton (Scheme 86), or *via* a concerted aryl shift and loss of lead (Scheme 87). Clearly, as in the case of stannane (113) discussed above, the two lead compounds cannot both be decomposing *via* the same primary vinyl cation (136). Of special significance is the observation that no 2-methylbenzofuran (139) was found in the product mixture. This was

rigorously demonstrated by gas chromatography under a number of conditions (see Experimental). In addition, none of the alkylidenecarbene insertion product, the benzopyran (140), was observed.

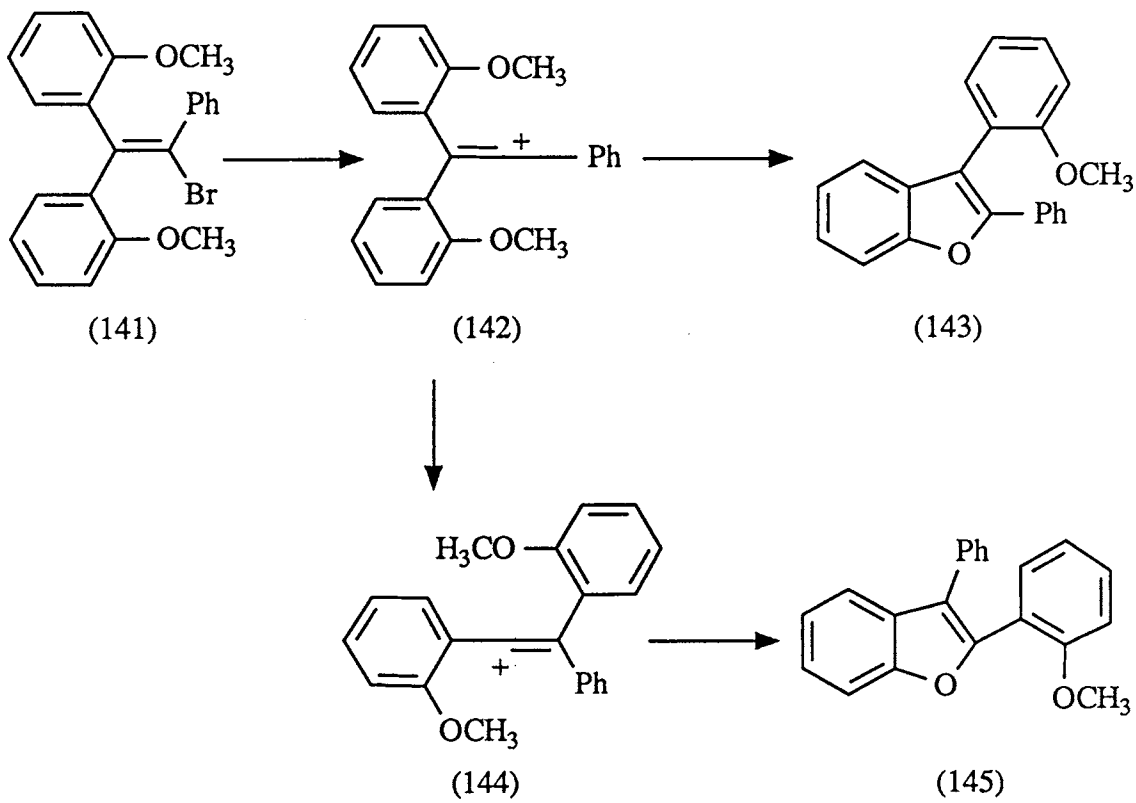


Scheme 86



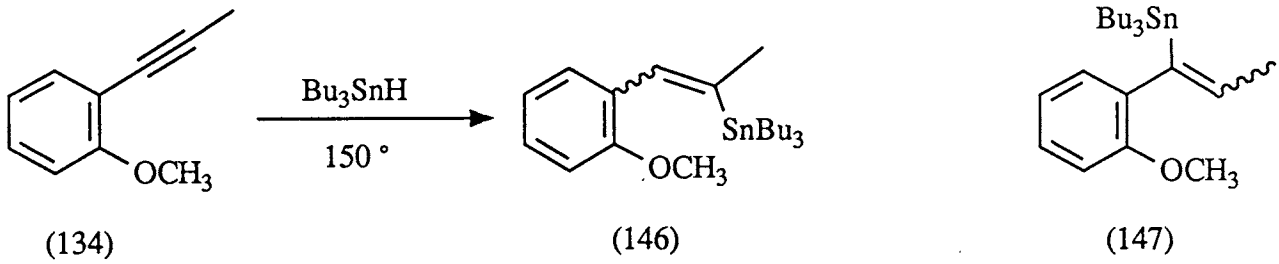
Scheme 87

This 1,2-aryl migration is also analogous to that observed in the solvolysis work discussed above[62]. When the vinyl bromide (141) was solvolysed, the major product was the benzofuran (143), as discussed earlier. However, there was also observed a small amount of the benzofuran (145), arising from a 1,2 aryl shift (Scheme 88).



Scheme 88

The next stannane studied was the methyl group was located on the α-carbon (146). This compound was prepared *via* the hydrostannylation of the acetylene (134). The initial experiment yielded the product with control of regiochemistry as desired; none of the α-aryl-β-methylstannane (147) was formed (Scheme 89).

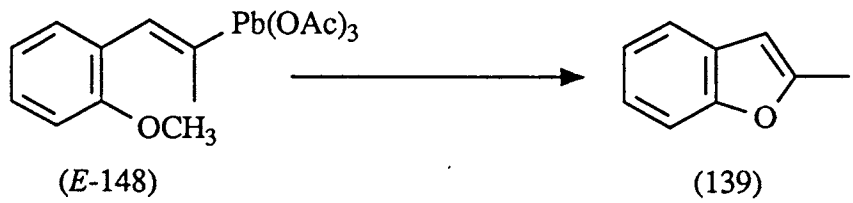


(134) (146) (147)

Scheme 89

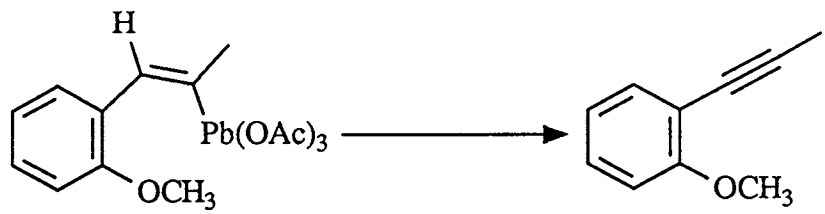
The compound was prepared in a 7:93 (*E*:*Z*) ratio as shown by n.O.e. difference spectroscopy. A series of experiments were undertaken to isomerise the mixture. When a solution of the stannane mixture (146) in deuterochloroform was irradiated with UV light through pyrex glass, an isomerisation to a 9:10 (*E*:*Z*) mixture occurred. This reaction took 3 days, but could be accelerated by the addition of a sensitiser such as benzophenone, or by performing the reaction on a solution of the stannane (146) in carbon tetrachloride in a quartz flask (16 hours). Irradiation in the presence of AIBN also isomerised the stannane to a 32:68 (*E*:*Z*) mixture, although this was accompanied by extensive decomposition.

The two mixtures were subjected to lead tetraacetate exchange reactions. The major product in both cases was the acetylene (134) in 64% and 27% yields respectively. 2-Methylbenzofuran (139) was formed in 7% and 20% yields. Both mixtures were also subjected to tin-lead exchange on a ^{1}H n.m.r. scale, but due to a relatively slow exchange, no intermediate lead compounds could be observed. In the second case, it was also found that there was a 33% yield of butyl acetate, arising from competing butyl-tin cleavage. From the results obtained it can be inferred that the (*E*)-lead compound (*E*-148) is decomposing once again to give the 2-methylbenzofuran (Scheme 90), whereas the (*Z*)-isomer (*Z*-148) is undergoing an elimination reaction to give the acetylene (134) (Scheme 91).



(*E*-148) (139)

Scheme 90



(*Z*-148) (134)

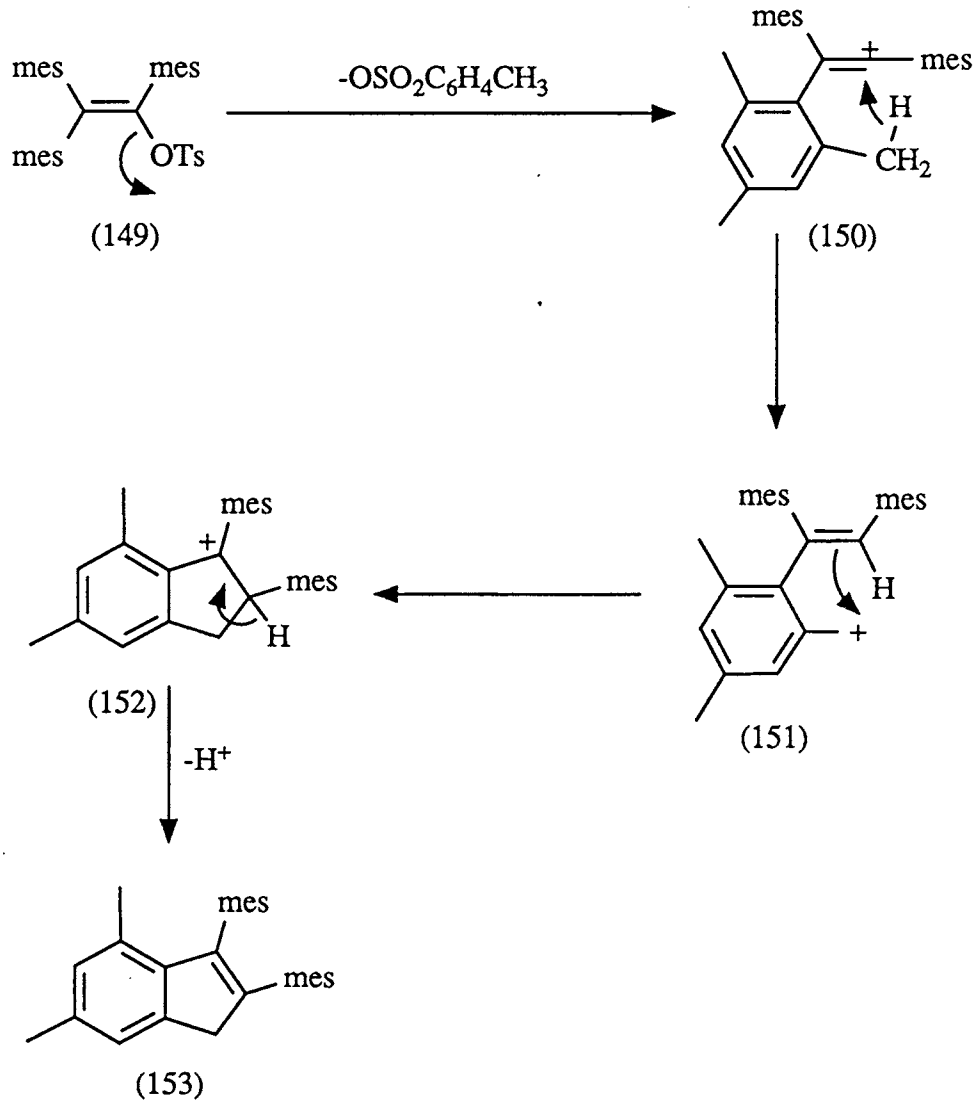
Scheme 91

The tin-lead exchange reactions of stannanes (113), (131), and (146) are best examined together. It would appear that the (*E*)-lead compounds in all cases cyclise to give the respective substituted benzofurans (120), (133), and (139). The fact that the (*E*)-α-methyl lead compound (*E*-148) cyclises to give 2-methylbenzofuran, and the rearranged cation (138), derived from the decomposition of the (*Z*)-β-methyl lead compound (*Z*-132), does not, indicates that the cyclisation to benzofurans is probably not proceeding *via* a discreet vinyl cation, but rather *via* the S_N2-like mechanism discussed above. The presence of the methyl group in stannane (*E*-146) appears not to affect the cyclisation in this case.

The decomposition mechanisms of the (*Z*)-lead compounds (*Z*-119), (*Z*-132), and (*Z*-148), are less clear, however. Assuming that the vinyl cation route is no longer excluded from these compounds, there are two possible mechanisms for their decomposition; the vinyl cation route, or a β-elimination (oxygen-assisted or otherwise) mechanism. The β-methyl lead

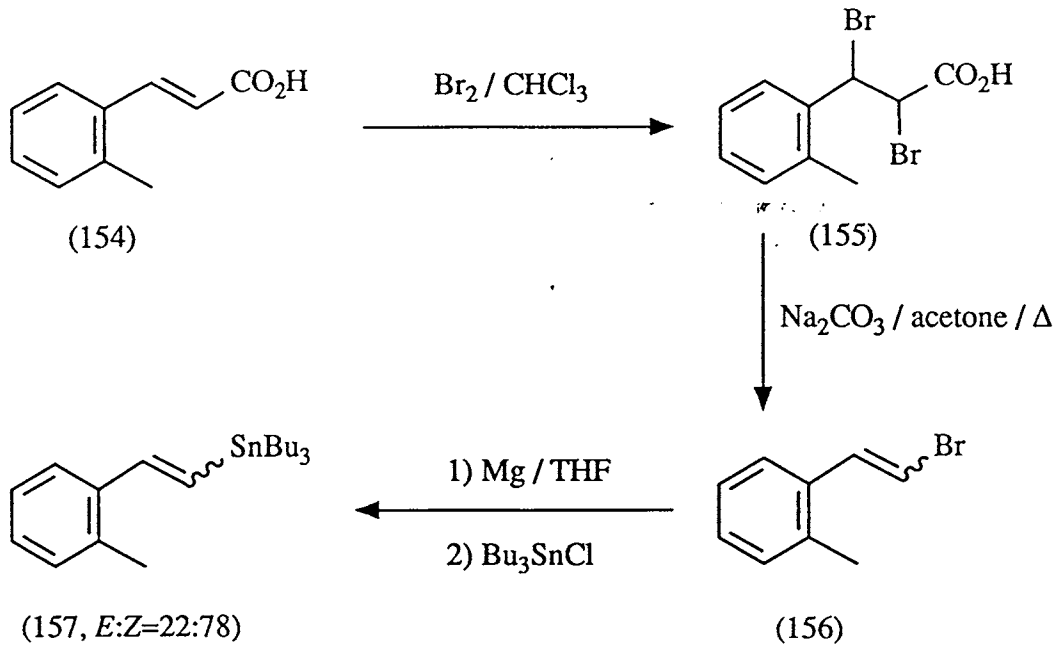
compound (*Z*-132) obviously proceeds through the vinyl cation (138), which then loses a proton too rapidly for cyclisation to compete. The lead compounds (*Z*-119) and (*Z*-148) however, have the lead group and β-proton in a *trans* arrangement, which is favourable for β-elimination reactions, and these probably decompose *via* such a mechanism, although at this stage, a vinyl cation route cannot be excluded.

The report of Biali and Rappoport[63] that trimesitylethenyl tosylate (149) cyclises upon solvolysis in benzene to give 2,3-dimesityl-4,6-dimethylindene (153) in 40% yield *via* a vinyl cation mechanism, prompted the study of a simpler system *via* vinyllead triacetate methodology. Biali and Rappoport[63] suggest that the tosylate solvolysed to the trimesitylvinyl cation (150), which abstracts a proton from one of the two *ortho* methyl groups on one of the β-mesityl groups, to generate a benzylic cation (151). This cation then undergoes an electrophilic addition to the vinylic system to produce the stabilised benzylic cation (152), which then yields the indene (153) by loss of a proton (Scheme 92).

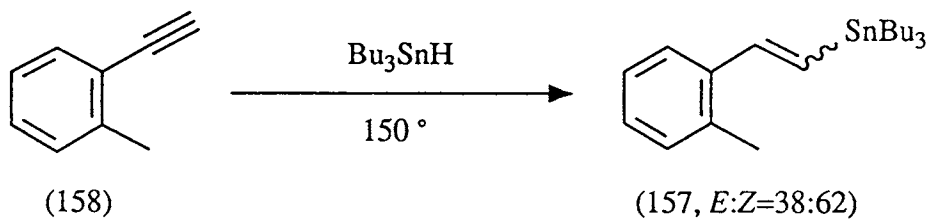


Scheme 92

In the present work, the stannane (157) was prepared as a mixture of isomers, which could be obtained in two *E*:*Z* isomeric ratios. The bromination-decarboxylative debromination sequence from *o*-methylcinnamic acid (154) followed by the Grignard route to the stannanes (157), gave an (*E*:*Z*) isomer ratio of 22:78 (Scheme 93).

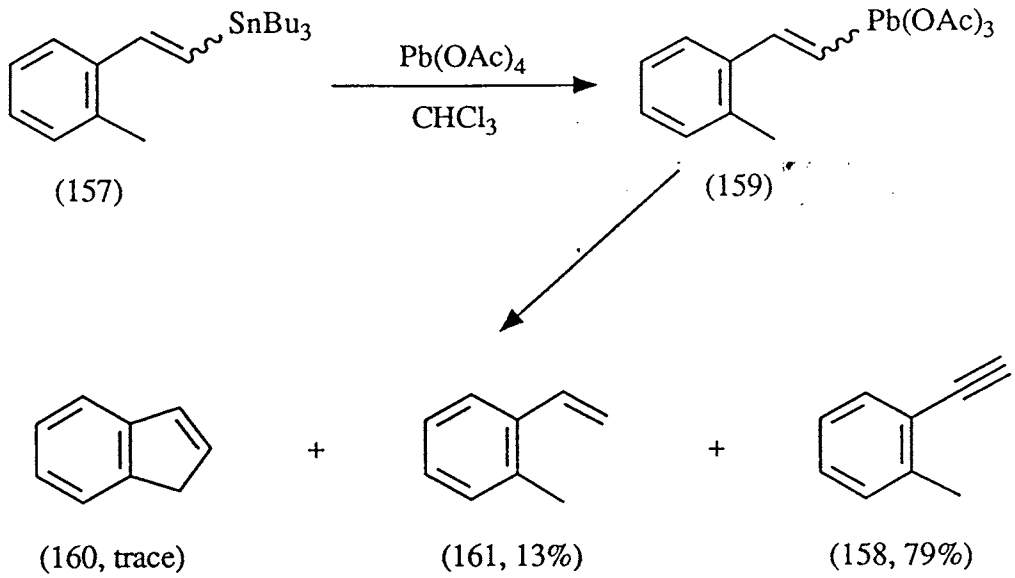


Scheme 93



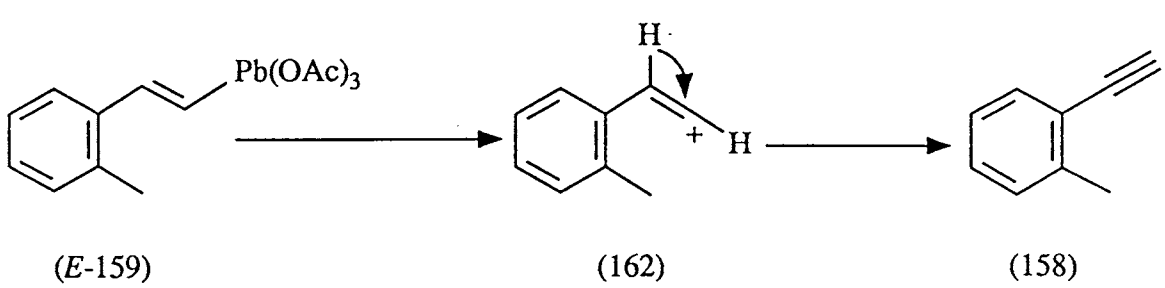
Scheme 94

The thermal hydrostannylation of *o*-methylphenylacetylene (158) also gave the mixture of stannanes (157) in a 38:62 (*E*:*Z*) isomer ratio (Scheme 94). Both of these isomer mixtures were subjected to tin-lead exchange with lead tetraacetate, but the major product in both cases was *o*-methylphenylacetylene (158), along with some *o*-methylstyrene (161), and butyl acetate (Scheme 95). Indene (160) was found in only trace (<1%) amounts from both of these reactions, with the slightly higher yield of indene from the mixture with the higher (*E*)-content. However, since the yields of indene obtained were far less than the experimental error, no conclusion can be made in this case.

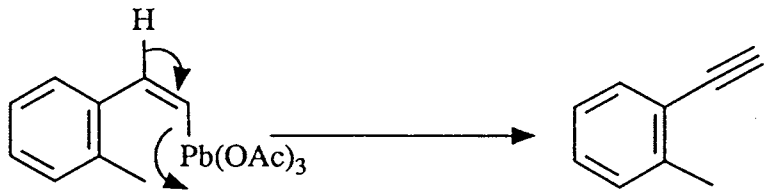


Scheme 95

It is apparent from this experiment that the sequence of steps required to form indene from the lead compounds (*E*-159) and (*Z*-159), are significantly slower than the competing simple eliminations of the vinyllead triacetates. As in the case of the *o*-methoxystyryl series of compounds studied above, the mechanism of the decomposition to the acetylene (158) is unclear, as both vinyl cation (Scheme 96), and β-elimination (Scheme 97) mechanisms may be operating. However, as a trace of indene is formed, the cation route is implied for at least the (*E*)-lead compound, as the lead group and β-proton are in a *cis* arrangement, which does not favour elimination.



Scheme 96



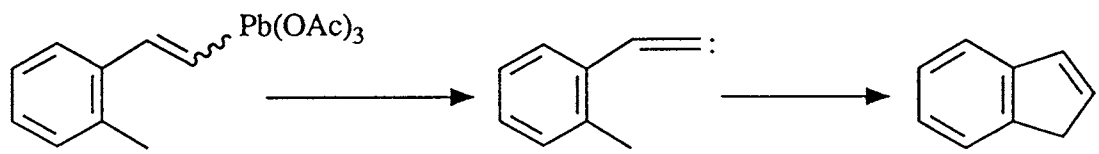
(Z-159) (158)

Scheme 97

The trimesityl case can only undergo either a degenerate 1,2-aryl migration, or react as in Scheme 92. Indeed, further work by Biali and Rappoport[63] indicated that the degenerate migrations are proceeding. By incorporating deuterium labelled methyl groups into the reagents, it was possible to show that significant skeletal rearrangement about the double bond took place.

When the solvolysis of the vinyl tosylate (149) was carried out in various alcohols (methanol, ethanol, and isopropanol), mixtures of indene (153) and the corresponding enol ethers were observed. Thus, in the absence of nucleophilic solvents, the vinyl cation (150) can only yield the indene (153).

Interestingly, the experiments with the stannanes (157), also show that the reaction is not of a carbene nature, as insertion of the carbene (163) into the benzylic methyl group would be expected to be a particularly facile reaction (Scheme 98).



(159) (163) (160)

Scheme 98

In conclusion, it can be seen that vinyllead tricarboxylates, and vinyllead triacetates in particular, have been shown to be reliable precursors for the study of vinyl cations, and that a wide range of such species can be observed using this methodology. In particular, the formation of primary vinyl cations, species which are almost never observed in conventional solvolysis reactions, have been generated by this method. The vinyllead tricarboxylates appear to generally yield the most stable possible vinyl cation before they lose protons to give acetylenes. In some cases it has been possible to isolate ring closed systems, and some of these may derive from primary vinyl cations. It has been shown quite rigorously that alkylidenecarbenes are not being formed in a number of these reactions, as the benzopyrans (125) and (140) were not observed in the reactions of the stannanes (220) and (257), and several attempts to trap alkylidenecarbenes with cyclohexene were unsuccesful.

SECTION 2

IMPROVEMENTS IN THE VINYLATION REACTION

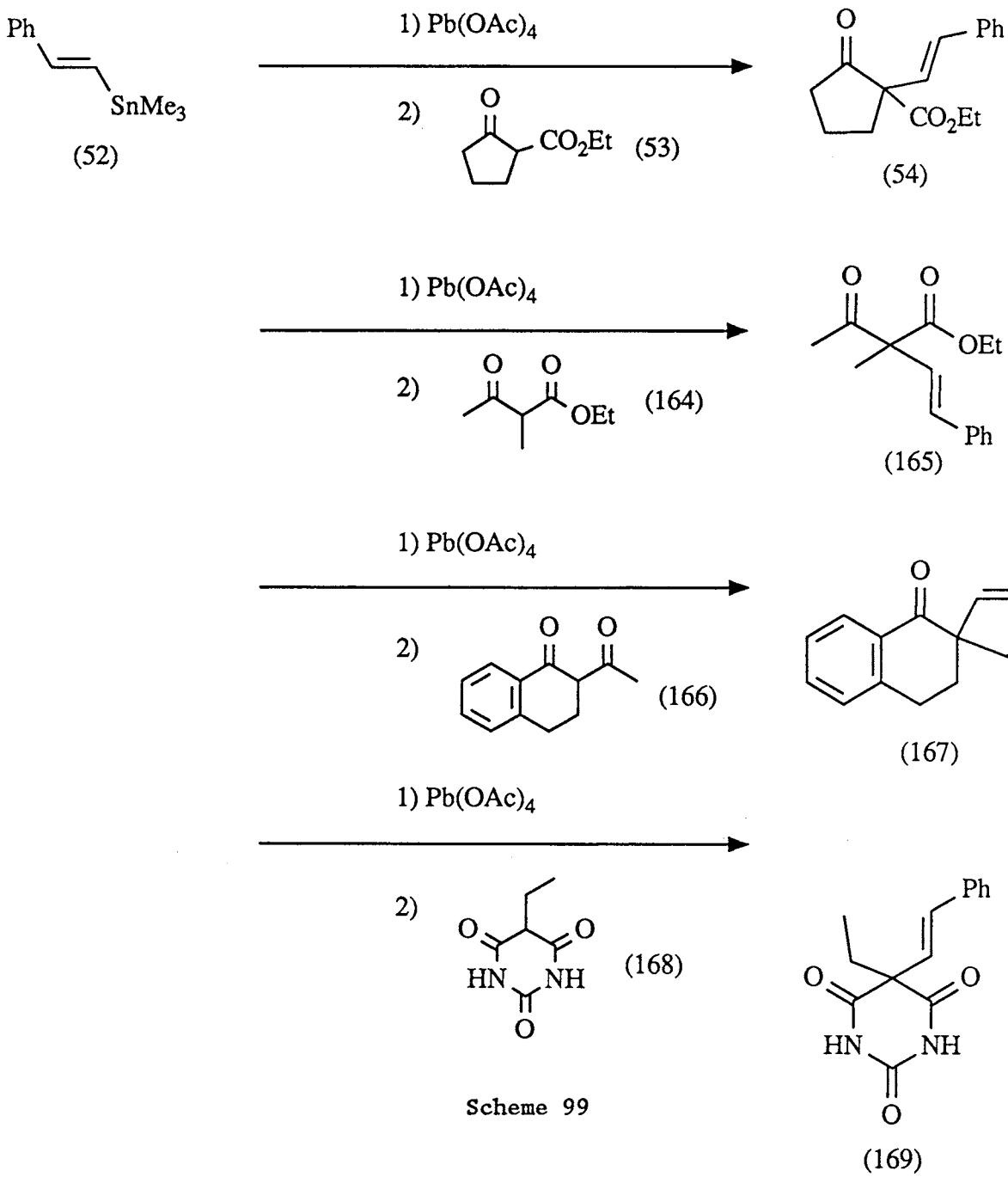
2.1. USE OF TRIMETHYLVINYLSTANNANES

Vinyllead triacetates, generated *in situ* by the treatment of vinylstannanes and vinylmercury compounds with lead tetraacetate, have been demonstrated to effect α-vinylation of β-dicarbonyl compounds in good yield,[19,21,22] as described earlier in the Introduction (Part 2). The best yields of α-vinyl-β-dicarbonyls were obtained with the use of divinylmercury compounds in chloroform/pyridine solution at room temperature, when the amount of pyridine used was between 3 and 5 equivalents.

As described earlier, the major drawback of this route was the formation, in the initial exchange, of one equivalent of a vinylmercury acetate, which was effectively a wasted vinyl residue. If a tributylvinylstannane was used, then the by-product, tributyltin acetate, was difficult to remove from the exchange mixtures. In addition, the reaction of tributylvinylstannanes with lead tetraacetate was often quite slow, resulting in reduced yields of the desired products.

Possibly the most significant finding in the earlier work[19] was the demonstration that the trimethylvinylstannane (52) could be employed in the vinylation sequence. This compound, when treated with lead tetraacetate followed by the β-keto ester (53), produced the product (54) in the highest yield (79%) obtained by any sequence. In addition, the by-product of the exchange, trimethyltin acetate, was much less soluble than tributyltin acetate and could readily be removed from the mixture.

Thus in the current work, it was sought to extend the use of this and other trimethylstannanes in the vinylation reaction. The first experiment performed was a duplicate of Moloney's[19] experiment. The stannane (52) gave a 75% yield of α-vinyl-β-keto ester (54), wholly in agreement with Moloney's result. In separate experiments, the stannane (52) was treated with lead tetraacetate, followed by the acyclic β-keto ester, ethyl methylacetoacetate (164), the β-diketone, 2-acetyl-1-tetralone (166), and 5-ethylbarbituric acid (168) (Scheme 99). The yields obtained were 29%, 62%, and 39% respectively.

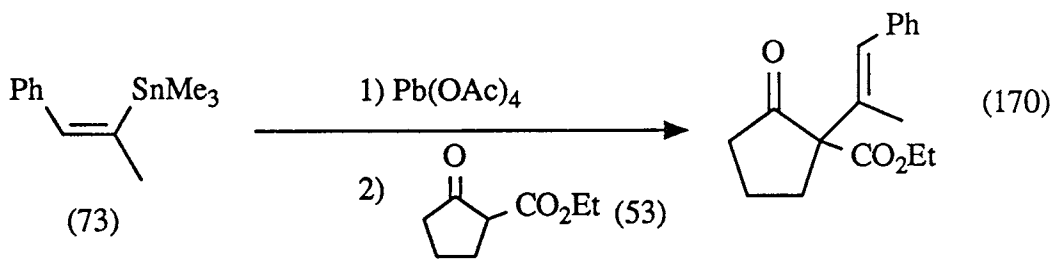


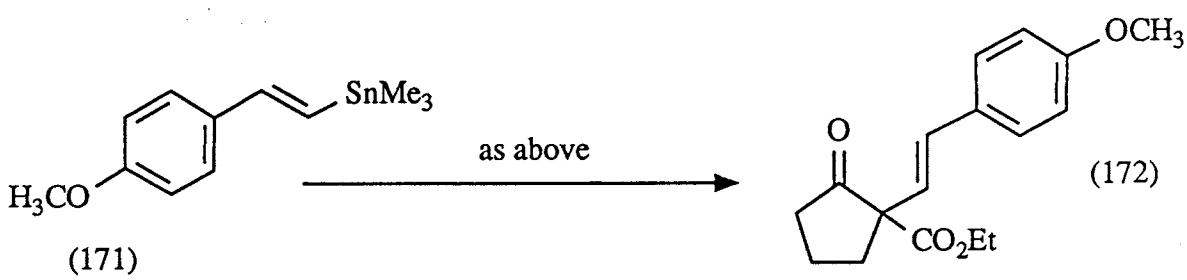
Scheme 99

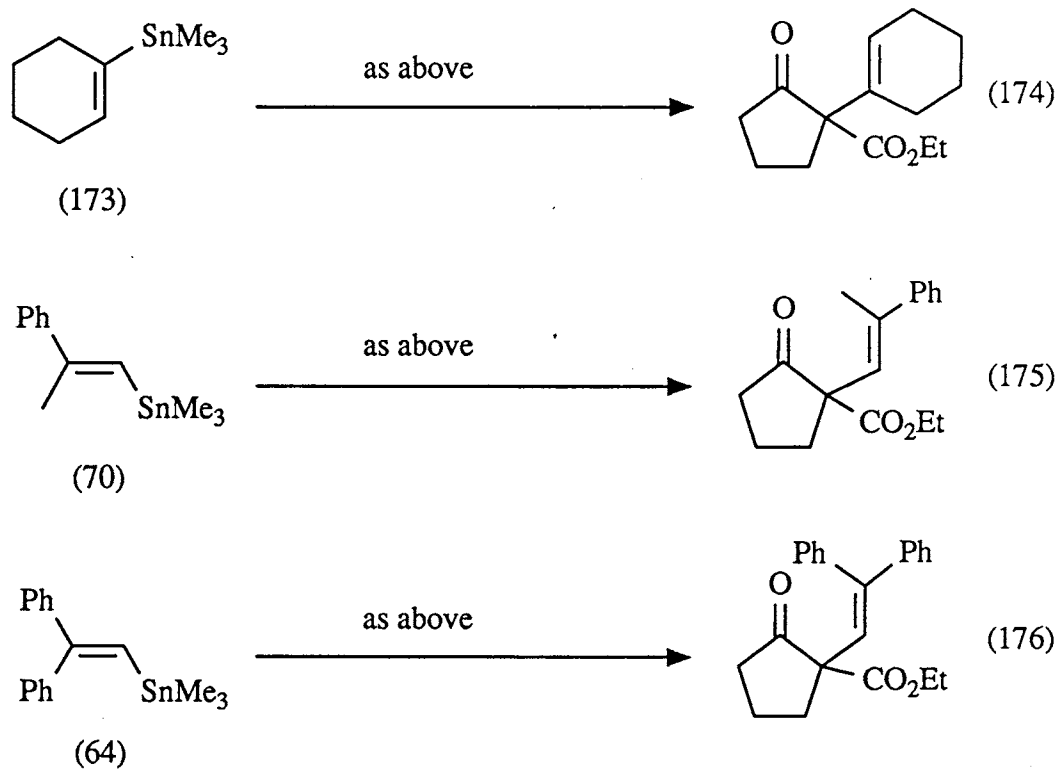
Although the yield of α-vinyl-β-keto ester (165) is low, it is worth noting that it is about the same as that obtained by Moloney[19] from the corresponding divinylmercury compound (7, 30%) and the tributylstannane (9, 24%) although both of these used excess lead tetraacetate (1.9 and 1.5 equivalents respectively) and 3 equivalents of pyridine. In the current work, it was found that pyridine did not improve the yields of the α-vinylated products derived from trimethylstannane (149), and in some cases reduced them.

It seemed therefore that the trimethylstannanes were in general as good as, or posssibly better vinyllead triacetate precursors than the tributylstannanes or the mercurials. In addition, they were more efficient both in the use of vinyl residues, and ease of work-up.

The reaction was then extended to a number of representative examples of trimethylstannanes (64,70,73,171, and 173, Scheme 100), whose analogous divinylmercury compounds had been studied by Moloney.[19] In cases where the corresponding tributylstannane had not been previously examined, comparison studies were carried out.







Scheme 100

Table 1. Reaction of trimethylvinylstannanes with lead tetraacetate and the β-keto ester (53), compared with the reactions of the corresponding divinylmercury compounds and tributylvinylstannanes.

$RSnMe_3$	product	yield (%)	R_2Hg	yield (%)	$RSnBu_3$	yield (%)
64	176	21†	57	59*	56	0
70	175	53	11	51*	66	42
73	170	10	177	11*	71	0
171	172	79(70)	178	52*	114	46*
173	174	48	34	54*	32	34

* Moloney[19]

† Sn-Pb exchange conducted at 0°, and vinylation at -40°

It can be seen from Table 1 that, in all the cases studied above, the yields obtained from the trimethylstannanes are superior to those obtained from the corresponding tributylstannanes, and similar to those of the corresponding divinylmercury compounds.

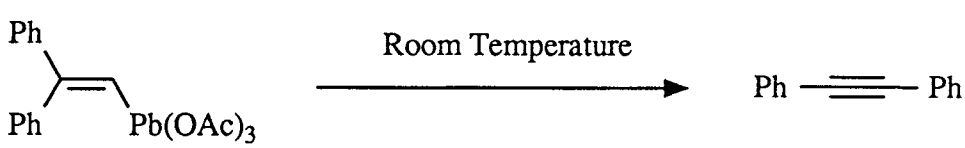
From the n.m.r. spectroscopic studies discussed in Section 3, it became evident that the higher yields of vinylated products probably resulted from the considerably faster exchange times involved for the trimethylstannanes than for the tributylstannanes; these were also fractionally faster than those of the divinylmercury compounds. The benefits of a fast exchange time are twofold. Firstly, there is less lead tetraacetate present in the mixture when the substrate is added, and hence its oxidation, which was reported by Moloney,[19] is suppressed. Secondly, there is less decomposition of the vinyllead triacetate prior to the addition of the substrate.

Another point worthy of discussion here is the issue of the addition of pyridine to the vinylation reactions of trimethylvinylstannanes. In the current work, it has been found that, in those cases where it is possible for the vinyllead triacetate to undergo a β-elimination (either *trans* or *cis*) (i.e., where there is a proton in the β-position), the addition of the base, pyridine, increases the yield of the elimination products. This is in direct contrast to the results obtained previously for the divinylmercury compounds.[19,21,22] This is perhaps best explained by the "mercury effect" discussed earlier (Results and Discussion, Section 1). The observation that stannanes react with lead reagents to give acetylenes, whereas the lead compounds prepared from mercury compounds tend to be stable towards elimination, is pertinent to this work.

In the case of cyclohexenyltrimethylstannane (173), no elimination is possible, hence the presence of pyridine has a slightly beneficial effect.

In the absence of a carbon nucleophile, the stannane (70) decomposes *via* a vinyl cation mechanism (see Results and Discussion, Section 1) to the acetylene (67). It is believed that, since the vinylation reactions proceed without rearrangement, they do not proceed *via* a vinyl cation mechanism. Thus, in this case, the intermediate lead compound (12) is not affected by the presence of pyridine in the vinylation reaction, since elimination is only possible after the phenyl migration.

Of particular interest is the reaction of stannane (64). When the tin-lead exchange and vinylation reactions are carried out at room temperature, no vinylated product is observed. An n.m.r. spectroscopic examination of the reaction (Results and Discussion, Section 3) showed that the initial tin-lead exchange was rapid, but that the lead compound (58) generated in this manner was unstable, and decomposed to tolan very rapidly (Scheme 101, see Results and Discussion, Section 1). Indeed, it was too unstable for it to be seen in the n.m.r. spectrum.



(58) (62)

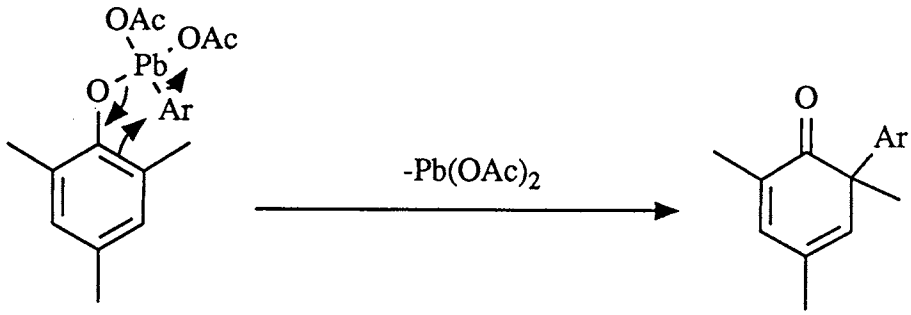
Scheme 101

The stannanes were known to exchange more slowly at reduced temperatures, but the behaviour of vinyllead triacetates at reduced temperatures was less clear. Moloney[19] had found that, in the case of the stannane (114), if the exchange mixture was chilled to 0° overnight, the

lead compound (50) could be isolated from the mixture by precipitation with cold dry light petroleum (see Results and Discussion, Section 1). However, if the lead compound was left at room temperature, decomposition to the acetylene (115) was apparent after 1 hour. At the conclusion of the current work a single experiment was performed to determine whether it would be possible to utilize low temperatures to enhance the yields of α-vinylated products, by slowing the decomposition of the intermediate lead compound in this manner.

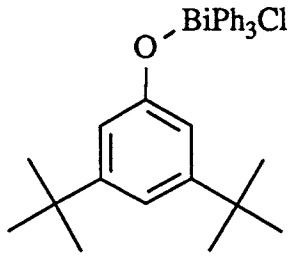
When the stannane (64) was treated with lead tetraacetate at 0° for 30 seconds, followed by immersion in an acetone/dry ice bath at -40° and addition of the β-keto ester (53), the mixture became very dark. The colour of the mixture changed to yellow on warming to room temperature, and gave the vinylated product (176) in low yield. Thus, it seems from this result, that the vinylating species can be "stabilized" by low temperatures, and used to greater effect in the vinylation reaction.

The mechanism of the vinylation is still unclear, as there are at least two possibilities. The first, proposed by Barton[64,65] for the analogous reaction of aryllead triacetates with phenols, involves an oxygen-bound lead group which rearranges with transfer of the aryl (or in this case, vinyl) residue (Scheme 102).

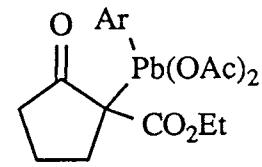


Scheme 102

Barton's evidence for this is based on the isolation[65] of an intermediate (179) of this type in the analogous reactions of organobismuth compounds with phenols. However, despite extensive work by his group,[64,65,66] no lead intermediates have been found.



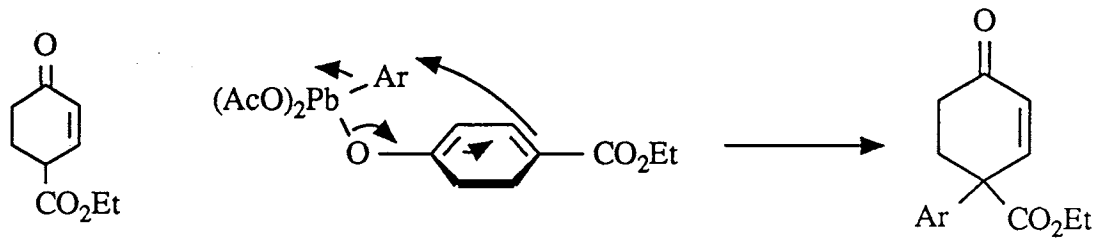
(179)



(180)

The second possibility, favoured in these laboratories, is the carbon-bound lead intermediate of the general type (180). Despite the fact that no intermediates of this type have been isolated, there is a significant body of evidence to support this mechanism.

The first evidence is that supplied by the work of Ackland and Pinhey[37,38,40,41] and later, Parkinson.[39] In that work, the arylation reaction of β-keto esters was extended to vinylogous systems. The key step in the synthesis of several alkaloids (see Introduction) was the addition of the aryl group to the C4 of the vinylogous β-keto ester (43). In this case, steric considerations indicate that the intermediate must be carbon-bound at C4. If the reaction involved an oxygen-bound lead species, then in the intermediate (181), transfer of the aryl group would have to take place across the nearly planar cyclohexadiene group to C4 (Scheme 103).

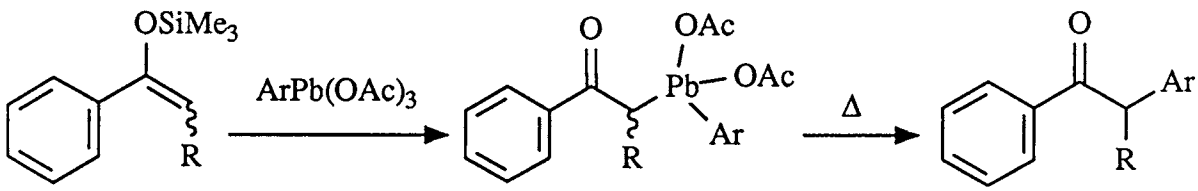


(43) (181) (182)

Scheme 103

Also, it has already been noted (see Introduction), that phenols react at both C2 and C4 with aryllead triacetates, and a similar transfer to that outlined above would have to be involved if the intermediate were an oxygen-bound lead compound.

In the study of reactions of enol trimethylsilyl ethers (183) with aryllead triacetates, Bell *et al.*,[8,67] found that it was possible to isolate compounds of the type (184). These are analogous to the intermediates proposed above, except that an α-alkoxycarbonyl group is absent. It was found that these compounds became less stable as the size of the substituent R increased, and that in several cases, the heating of these compounds gave rise to the α-arylated ketones (185) (Scheme 104).



(183) (184) (185)

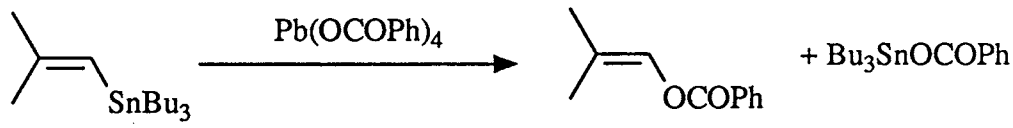
Scheme 104

Thus it is possible that the addition of an ester functionality, or other carbonyl group, to the α-position destabilizes the carbon-bound lead intermediate to such an extent that it decomposes rapidly even at room temperature. It is possible that the dark-coloured intermediate observed in the reaction of (64) with lead tetraacetate, and the β-keto ester (53) at -40° is a carbon-lead intermediate, that only decomposes as the temperature is raised.

2.2. USE OF ALTERNATIVE LEAD REAGENTS

Use of lead tetrabenzoate

The observation by Moloney,[19] that the stannane (55) reacts with lead tetrabenzoate "in an exchange reaction that was much more rapid than when lead tetraacetate was used", would appear to make it potentially useful in vinylation reactions, for the same reasons as outlined above. However, Moloney[19] only performed the one experiment with lead tetrabenzoate (Scheme 105).

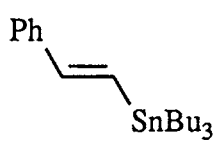


(55) (186)

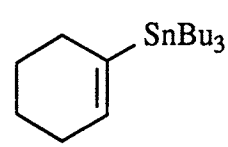
Scheme 105

Lead tetrabenzoate is prepared by the method of Hey *et al.*,[69] from a melt of benzoic acid and lead tetraacetate, with the acetic acid formed being distilled off under reduced pressure. In this manner, it is possible to produce material with a lead(IV) content of about 85-90%. The vinylation reactions of a representative number of tributyl and trimethylstannanes and divinylmercury compounds was then undertaken.

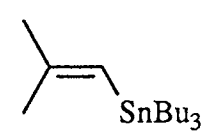
Vinylation reactions of tributylvinylstannanes with lead tetrabenzoate



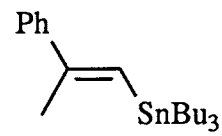
(9)



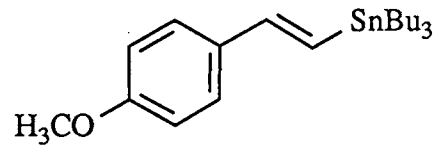
(32)



(55)



(66)



(114)

As can be seen from Table 2, the yields of vinylated products from the above tributylstannanes with lead tetrabenzoate (column 3) are in general quite significantly better than in the case of the corresponding lead tetraacetate reactions (column 4).

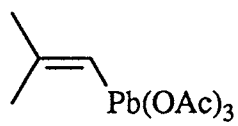
Table 2. Reaction of tributylvinylstannanes with lead tetrabenzoate and the β-keto ester (53), compared with the lead tetraacetate reactions.

$RSnBu_3$	Product	yield	yield from LTA reaction
9	54	65	55*
32	174	40	34
55	187	42	0*
66	175	32	42
114	172	47	46*

* Moloney[19]

An interesting result was the reaction of tributylstannane (55) with lead tetrabenzoate and the standard β-keto ester (53). Moloney[19] had found that this stannane, although known to exchange readily with lead tetraacetate, did not produce any α-vinylated-β-keto ester (187). This was confirmed in the current work. On the other hand, when lead tetrabenzoate was used, a 42% yield of the vinylated product (187) was

obtained. This point is puzzling as n.m.r. spectroscopic studies (Results and Discussion, Section 3) show that the lead compounds (106) and (188) are both formed readily from the stannane (55) and are relatively stable, only starting to decompose appreciably after 5 minutes.



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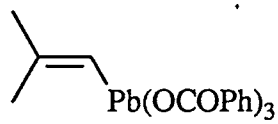

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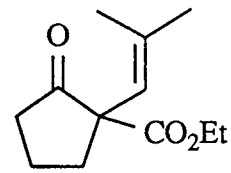
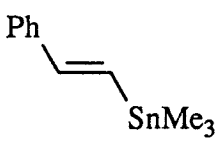
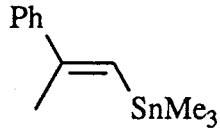


(187)

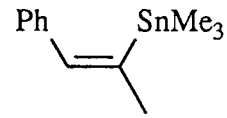
Vinylation reactions of trimethylvinylstannanes with lead tetrabenzoate



(52)



(70)



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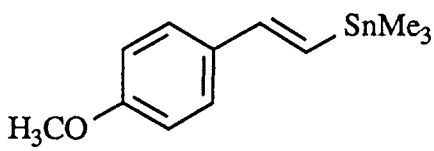

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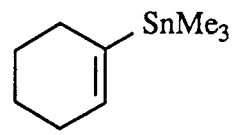


(173)

As can be seen from Table 3, the yields obtained on reacting the above trimethylstannanes with lead tetrabenzoate, followed by the addition of β-keto ester (53), were slightly higher than with lead tetraacetate. If, as was postulated above, the exchange speed is a major factor in these reactions, this result is not unexpected. The fact that trimethylstannanes undergo the fastest metal-lead exchange of the reagents yet examined, suggests that the use of the more reactive lead reagent will have only a marginal effect on yields.

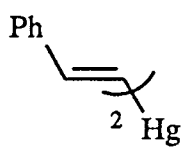
Table 3. Reaction of trimethylvinylstannanes with lead tetrabenzoate and the β-keto ester (53), compared with lead tetraacetate reactions.

$RSnMe_3$	Product	yield	yield from LTA reaction
52	54	84	79*
70	175	61	53
73	170	29	10
171	172	84	70(79**)
173	174	67	48

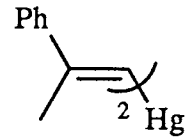
* Moloney[19]

** Yield determined by n.m.r. spectroscopy

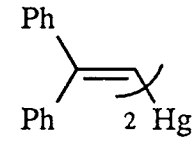
Vinylation reactions of divinylmercury compounds with lead tetrabenzoate



(7)



(11)



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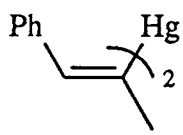

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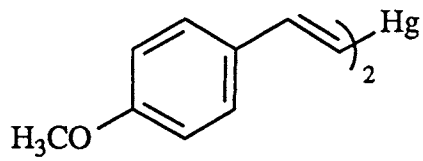
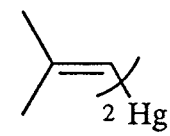


(178)



(189)

From the results outlined in Table 4, it can be seen that, in contrast to the results obtained above, the use of lead tetrabenzoate with the above divinylmercury compounds had no significant effect on the yields of α-vinyl-β-keto esters, and indeed in most cases they were lower.

Table 4. Reaction of divinylmercury compounds with lead tetrabenzoate and the β-keto ester (53), compared to the lead tetraacetate reactions.

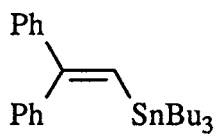
R_2Hg	Product	yield	yield from LTA rn.*
7	54	49	66
11	175	36	51
57	176	46	59
177	170	14	11
178	172	33	52
189	187	40	46

* Moloney[19]

This result is perhaps surprising, but would appear to indicate that the exchange speed is once again the most important factor in these vinylation reactions. As mercury-lead exchange is particularly fast with lead tetraacetate, the use of an even more reactive reagent has little or no effect.

Unsuccessful vinylation reactions.

It had been found previously[19] that several tributylvinylstannanes and divinylmercury compounds did not give any α-vinylated products when subjected to the vinylation procedure. This was usually attributed to a slow tin-lead or mercury-lead exchange. It was envisaged that by use of a combination of trimethylvinylstannanes and lead tetrabenzoate, that the rates of metal-metal exchange could be increased. However, when the reactions were attempted on stannanes (56,71, and 190-195), no vinylated products were obtained.



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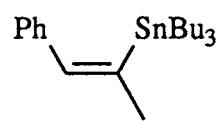

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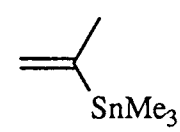
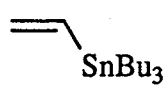


(190)



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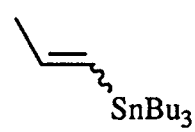
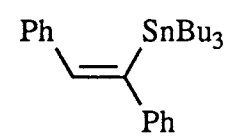


(192)



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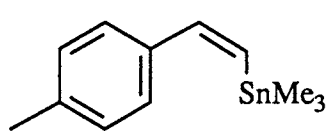
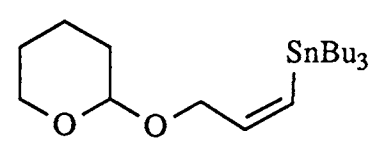


(194)



(195)

In view of the n.m.r. spectroscopic work discussed later (Results and Discussion, Section 3), it is perhaps not surprising that these experiments were unproductive, since the exchange times of trimethylvinylstannanes are similar to those of the divinylmercury compounds.

Use of lead tetrapivalate

It had been found previously by Roche[17] that lead tetrapivalate could be prepared in an analogous manner to lead tetrabenzoate. It was hoped that it could possibly be of use in the vinylation reaction; however, only a few experiments gave encouraging results in this area. In general, the yields obtained were lower than in the lead tetraacetate reactions, although in two cases a marked improvement was noted (Table 5).

Table 5. Reactions of miscellaneous stannanes with lead tetrapivalate and the β-keto ester (53), compared to the lead tetraacetate reactions.

$RSnR_3$	Product	yield	yield from LTA rn.
55	187	36	0*
73	170	42	10
173	174	14†	48†

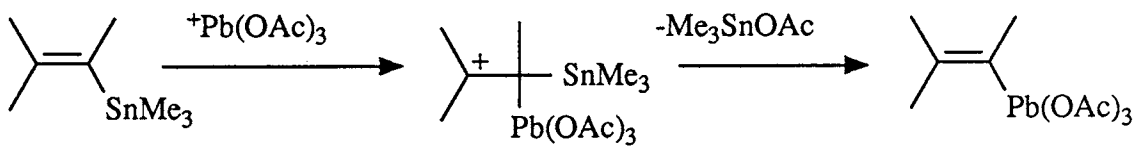
* Moloney[19]

† Pyridine (5 equivalents)

It has already been mentioned that the stannane (55) gave none of the product (187) with lead tetraacetate, but gave a 42% yield with lead tetrabenzoate. When this experiment was performed with lead tetrapivalate, the yield of (187) was 36%. Similarly stannane (73) afforded compound (170) in 10% yield with lead tetraacetate, 44% with lead tetrabenzoate, and 42% with lead tetrapivalate. In the n.m.r. spectroscopic work (Results and Discussion, Section 3), it had been found that the rates of metal-metal exchange with lead tetrapivalate were extremely variable; and that in some cases they were faster than for lead

tetraacetate, and in other cases they were slower. For this reason, work in this area was abandoned.

If the exchange reaction proceeds via an electrophilic substitution of the lead tricarboxylate cation (Scheme 106), then the use of ligands on lead which are more electron-withdrawing would make the cation more electrophilic, and the rate-determining step would be expected to be faster. Since benzoate is more electron-withdrawing than acetate, this could account for the faster reaction times, and higher yields. Thus an attempt was made to prepare lead reagents with greater electron-withdrawing ligands.



Scheme 106

Unfortunately, this was unsuccessful, as attempts to prepare such reagents by Hey's[68] method in the melt, using either chloroacetic acid, dichloroacetic acid or trichloroacetic acid, produced violent reactions with rapid expulsion of carbon dioxide. The free-radical decarboxylation of heavy metal salts of carboxylic acids is a well-documented reaction,[69,70] which in the above cases yielded only lead(II) salts. Similar results were obtained with *o*-chlorobenzoic acid, and *p*-nitrobenzoic acid, and with the use of solvents, in an attempt to moderate the reaction.

Thus it has been shown that the yields of α-vinyl-β-dicarbonyl compounds can be improved by the use of the faster exchanging trimethylvinylstannanes and the more electrophilic lead reagent, lead tetrabenzoate. The combination of these two approaches leads to the best yields yet obtained for a number of vinylation reactions, and also results in easier work-up procedures. Thus, these techniques increase the usefulness of organolead(IV) reagents in organic synthesis.

SECTION 3

N.M.R. OF VINYLLEAD TRICARBOXYLATES

As outlined in the Introduction, the purpose of this section of the current work was to demonstrate that the intermediates in the tin-lead exchange and mercury-lead exchange reactions were firstly, the same vinyllead triacetates, and secondly that these were formed with retention of configuration.

$(H_2=CH)_4Pb$

(196)

The magnetically active isotope of lead is ^{207}Pb with a relative abundance of 22.6% and a spin quantum number of $\frac{1}{2}$. The standard compound on which this work is based is tetravinyllead (196). This is a well-known compound which has been much studied in the petroleum industry as a potential anti-knock agent, and whose $^{207}Pb,H$ satellite couplings were first described by Cawley and Danyluk.[71] The couplings found for tetravinyllead are shown in Table 6. The general order in magnitude of the coupling constant is $J_{trans} > J_{geminal} > J_{cis}$.

Table 6. Proton-proton[72] and ^{207}Pb-proton[71] coupling constants for tetravinyllead (196).

$J_{Pb,H(gem)}$	$J_{Pb,H(cis)}$	$J_{Pb,H(trans)}$	$J_{H,H(gem)}$	$J_{H,H(cis)}$	$J_{H,H(trans)}$
212.4 Hz	161.7 Hz	330.1 Hz	2.02 Hz	12.13 Hz	19.57 Hz

Experimental factors dictated that the compounds studied should be the divinylmercury compounds, and the tributylvinylstannanes. Although it has been shown that trimethylvinylstannanes exchange faster than their tributyl analogues, they suffer from the significant problem that the insoluble trimethyltin acetate formed in the exchange hampers spectrometer resolution to such an extent as to make them largely impractical for this work. In only a few cases was it possible to observe the lead compounds derived from trimethylvinylstannanes (see Table 7), although it was possible to observe the disappearance of the starting stannanes, thus gaining a measure of the speed of the exchange.

The first lead compound studied was (*E*)-2-phenylethen-1-yllead triacetate (8). The exchange reactions of tributyl[(*E*)-2-phenylethen-1-yl]stannane (9) and bis[(*E*)-2-phenylethen-1-yl]mercury (7) were examined by ^{1}H (400 MHz) n.m.r. spectroscopy and were found to give the same intermediate vinyllead compound as shown in Figures 1 and 2. Both experiments gave intermediates with identical chemical shifts, and identical H–H (15.21 Hz) and ^{207}Pb–H (691.7 and 821.3 Hz) coupling constants (Figures 1a and 2a, and Table 7). The first point to be noted is that the H-H coupling has reduced from 19.78 Hz in the parent stannane (9) and 19.27 Hz in the parent divinylmercury compound (7). This was of some concern, as this could be explained by the intermediate being a *cis*-compound and not *trans*, as had been previously thought; however, later results showed that this was not the case, as two *cis*-lead compounds were observed, and these were found to have H-H couplings in the range 6-7 Hz, and ^{207}Pb-H coupling constants of approximately 1600 Hz (see Table 3-2). The ^{207}Pb-H couplings are also considerably larger than in tetravinyllead. This phenomenon has been noted before,[73] and is due to the more electron-withdrawing triacetoxyplumbyl group.

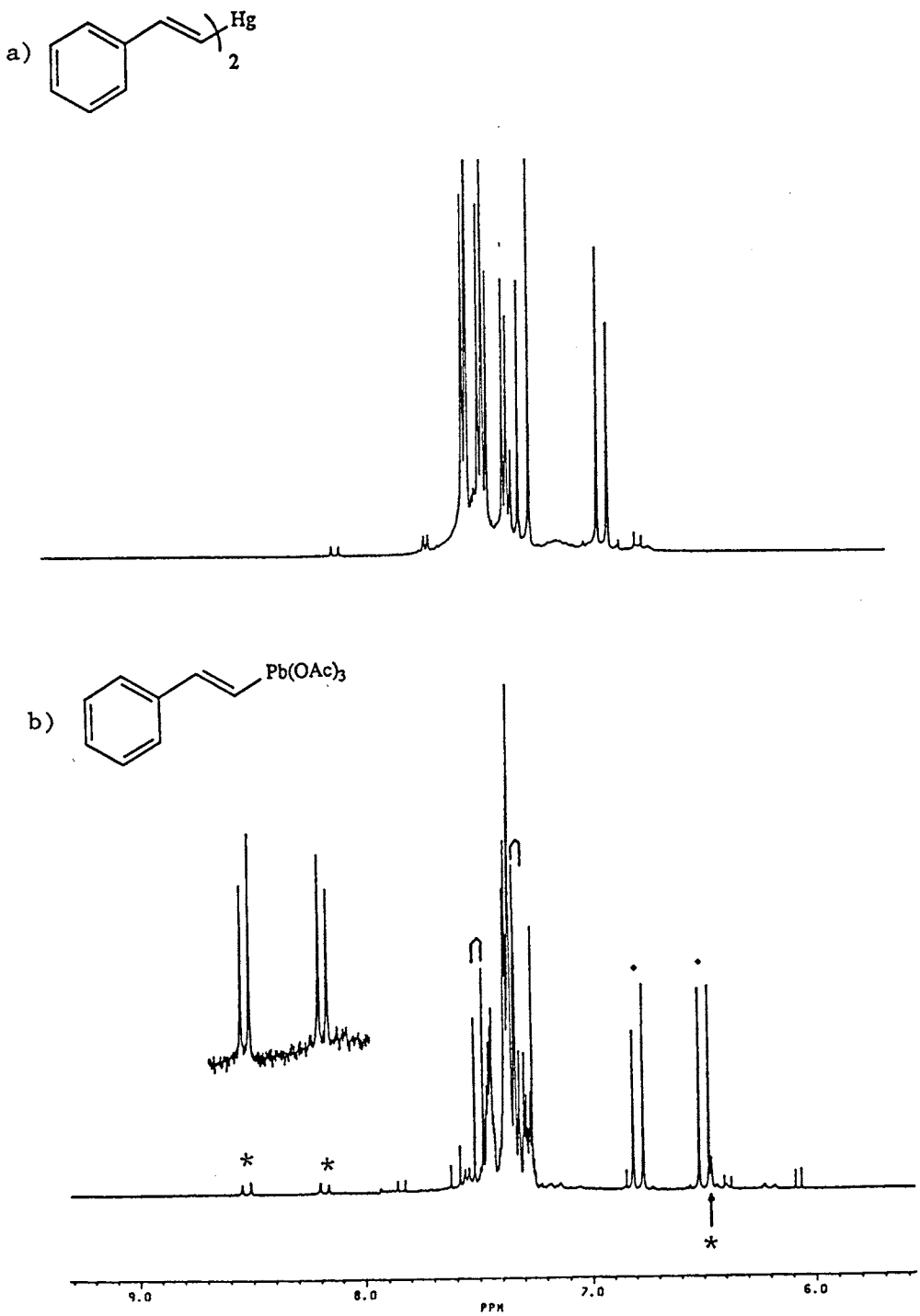


Figure 1. a) Bis[(*E*)-2-phenylethen-1-yl]mercury (7) before the addition of LTA. b) After the addition of LTA: *=Pb satellites, •=vinylmercury acetate (5).

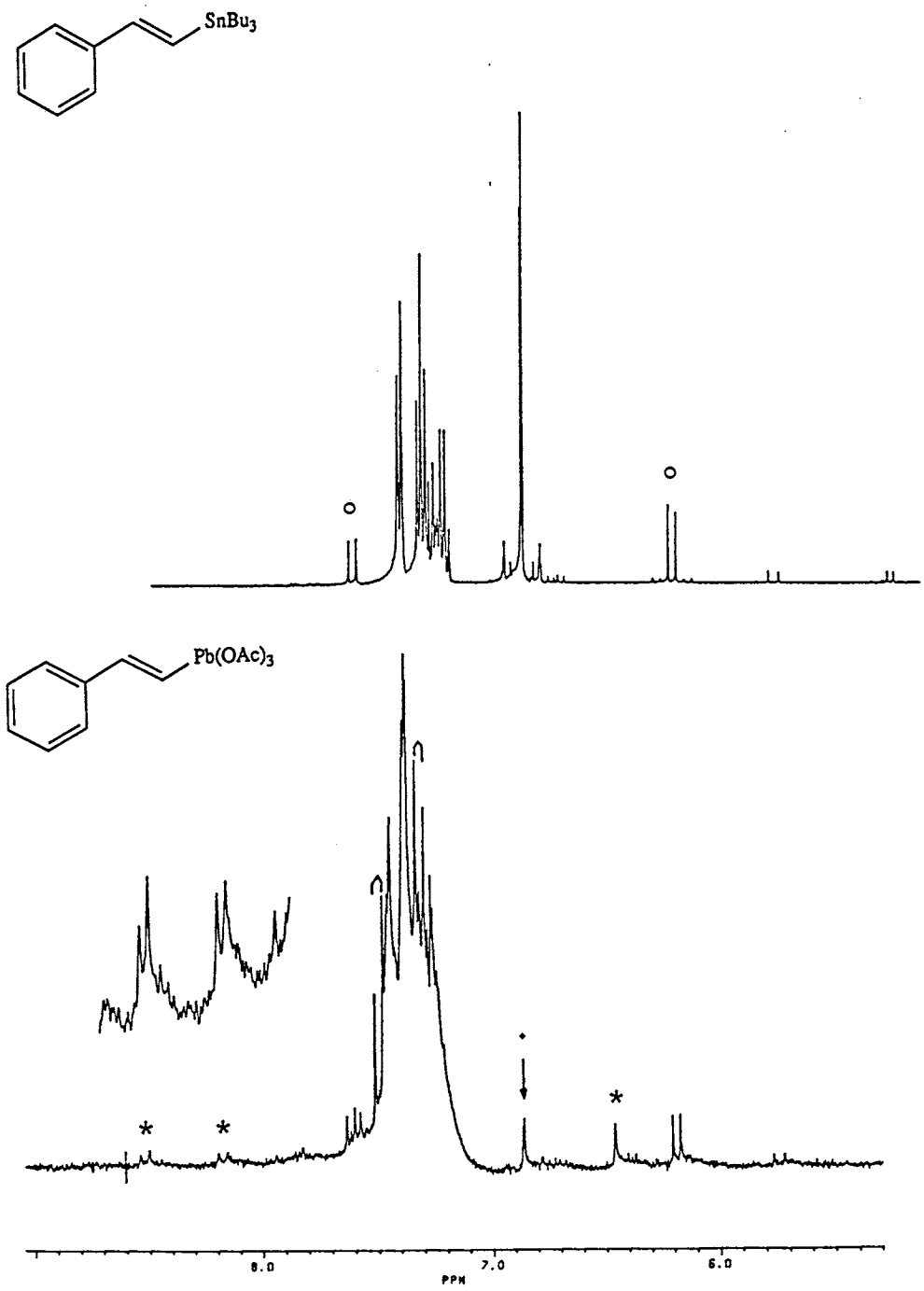
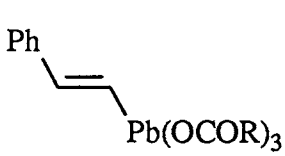


Figure 2. a) Tributyl[(*E*)-2-phenylethen-1-yl]stannane (9) before the addition of LTA. b) After the addition of LTA: *=Pb satellites, •=(*E*)-stannane, o=(*Z*)-stannane (91).

The assignments of the two vinylic protons are made on the basis of the magnitudes of the two ^{207}Pb-H couplings. By comparison with the standard compound, tetravinyllead, it can be seen that the larger of the two couplings should be to the geminal proton, while the smaller of the two should be to the proton *cis* to the lead group.

These spectra were obtained 2 minutes after the addition of lead tetraacetate, and from these it can easily be seen that the mercury-lead exchange was complete, while the tin-lead exchange was still proceeding, hence the broadening observed in several signals. Other points worthy of note here are that the contaminating *cis*-isomer of the stannane had not yet begun to react appreciably, and this is in accord with the general trend, that *cis*-compounds exchange slowly with lead reagents.[19] The lead satellites on the upfield side of the aromatic region are coincident, hence they appear as a broad line, and in the case of the mercury experiment they are partially hidden under the vinylic signal of the reaction by-product, (*E*)-styrylmercury acetate (5).

Other vinyllead triacetates and tricarboxylates studied are listed below. The results obtained from their n.m.r. spectra are summarised in Table 7.



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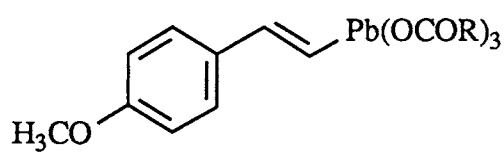
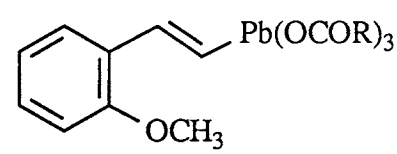
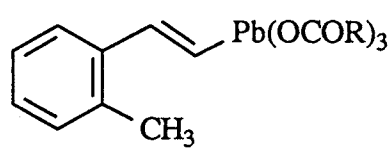
(197) R=Ph
(198) R=$C(CH_3)_3$



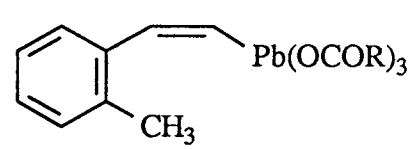
(50) R=CH_3
(199) R=Ph
(200) R=$C(CH_3)_3$



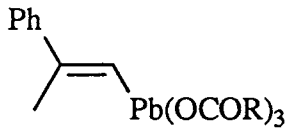
(*E*-119) R=CH_3



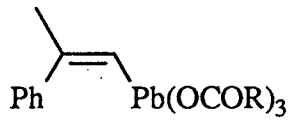
(*E*-159) R=CH_3
(201) R=Ph



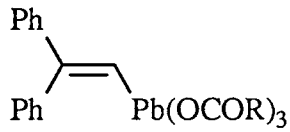
(Z-159) R=CH_3



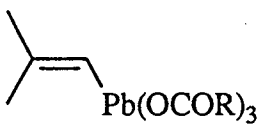
(*E*-12) R=CH_3
(202) R=Ph
(203) R=$C(CH_3)_3$



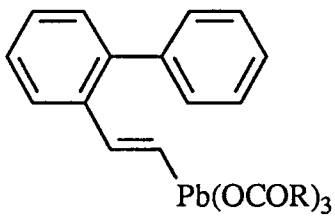
(*Z*-12) R=CH_3



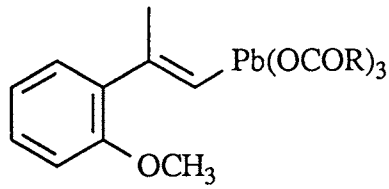
(58) R=CH_3
(204) R=Ph
(205) R=$C(CH_3)_3$



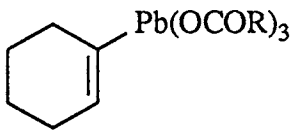
(106) R=CH_3
(188) R=Ph
(206) R=$C(CH_3)_3$



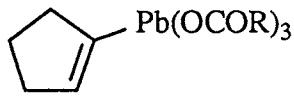
(97) R=CH_3



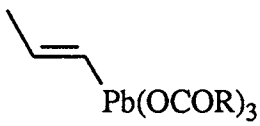
(*E*-132) R=CH_3



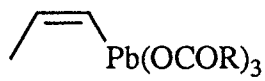
(33) R=CH_3
(207) R=Ph



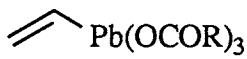
(29) R=CH_3
(208) R=Ph



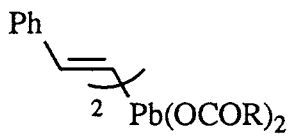
(*E*-209) R=CH_3



(Z-209) R=CH_3



(210) R=CH_3



(211) R=CH_3

Table 7. NMR spectroscopic data (run at 200 MHz, unless otherwise indicated) for the vinylic protons of vinyllead triacetates.

	J (Hz)		
Compound	H *gem* to Pb	H *cis* to Pb	H *trans* to Pb
(8)[a,g]	δ 7.50, $J_{H,H}$ 15.21	δ 7.32, $J_{H,H}$ 15.21	
	$J_{Pb,H}$ 821.3	$J_{Pb,H}$ 691.7	
(50)[b,g]	δ 7.37, $J_{H,H}$ 15.00	δ 7.25, $J_{H,H}$ 15.00	
	$J_{Pb,H}$ 831.3	$J_{Pb,H}$ 692.5	
(*E*-119)[c,g]	δ 7.72, $J_{H,H}$ 14.00	δ 7.44, $J_{H,H}$ 14.00	
	$J_{Pb,H}$ 926.5	$J_{Pb,H}$ 761.0	
(*E*-159)[c,g]	δ 7.39, $J_{H,H}$ 14.41	δ 7.59, $J_{H,H}$ 14.41	
	$J_{Pb,H}$ 866.7	$J_{Pb,H}$ 708.1	
(*Z*-159)[c,g]	δ 7.17, $J_{H,H}$ 6.48		δ 7.88, $J_{H,H}$ 6.48
	$J_{Pb,H}$ 871.0		$J_{Pb,H}$ 1599.0
(*E*-12)[a]	δ 6.89, $J_{Pb,H}$ 864.8		
(*Z*-12)[c]	δ 6.83, $J_{Pb,H}$ 854.8, $J_{CH3,H}$ 1.60		
(58)[d]	δ 7.33, $J_{Pb,H}$ 819.0		
(106)[a,g]	δ 6.37 $J_{Pb,H}$ 924.1		
(97)[c]	δ 7.42, $J_{H,H}$ 14.79	δ 7.27, $J_{H,H}$ 14.79	
	$J_{Pb,H}$ 860.0	$J_{Pb,H}$ 704.0	
(33)[e,g]		δ 6.17, $J_{Pb,H}$ 729.8	
(*E*-132)[c]	δ 7.03, $J_{Pb,H}$ 900.0		
(29)[c]		δ 6.37, $J_{Pb,H}$ 293.9	
(*E*-209)[c]	δ 7.84, $J_{H,H}$ 14.20	δ 7.50, $J_{H,H}$ 14.20	
	$J_{Pb,H}$ 931.0	$J_{Pb,H}$ 689.5	

Table 7 (Cont'd). NMR spectroscopic data for the vinylic protons of vinyllead triacetates.

	J (Hz)		
Compound	H *gem* to Pb	H *cis* to Pb	H *trans* to Pb
(*Z*-209)[c]	δ 7.74, $J_{H,H}$ 6.10		δ 7.77, $J_{H,H}$ 6.10
	$J_{Pb,H}$ 924.0		$J_{Pb,H}$ 1667.5
(210)[c]	δ 7.25, $J_{H,H}$ 15.49	δ 6.17, $J_{H,H}$ 15.49	δ 6.29, $J_{H,H}$ 7.10
	$J_{H,H}$ 7.10	$J_{H,H}$ 4.80	$J_{H,H}$ 4.80
	$J_{Pb,H}$ 952.5	$J_{Pb,H}$ 812.8	$J_{Pb,H}$ 1671.9
(211)[f]	δ 7.60, $J_{H,H}$ 16.21	δ 7.42, $J_{H,H}$ 16.21	
	$J_{Pb,H}$ 433.1	$J_{Pb,H}$ 339.9	

[a] Prepared from divinylmercury compound and tributylstannane.

[b] Prepared from tributylstannane, and trimethylstannane.

[c] Prepared from tributylstannane.

[d] Prepared from divinylmercury compound.

[e] Prepared from divinylmercury compound, tributylstannane and vinylmercury bromide.

[f] Prepared from boronic acid.[14]

[g] Run at 400 MHz.

The lead compound (210) is of particular importance, as it is the simplest vinyllead triacetate, and all three possible lead-proton coupling constants are present. Firstly, it can be seen that the large (1671.9 Hz) coupling constant is that to the proton *trans* to lead, and that the smallest (812.8 Hz) is that to the proton *cis* to lead. This confirms the assignments made above in the simple styryllead triacetate (8).

The simple variants of the styryl series display couplings in the same range as the parent compound. Of special note are (*E*-12) and (*Z*-12), which have only one vinylic proton, geminal to the lead, and these too, show couplings in the same range as that observed in the other styryl cases. These cases also serve to show that the original assignment was correct.

It is quite apparent from the results outlined in Table 7, that the substituents at the β-position influence the size of the coupling constant greatly. A close examination of the data shows that this effect is most important in the Pb-H(*gem*) coupling constant. Starting with vinyllead triacetate (210) itself, which has a coupling constant of 952.5 Hz, it can be clearly seen, that adding one methyl group β-to lead, as in (*E*-209), results in a drop in the coupling constant to 931.0 Hz (924.0 Hz in the (*Z*)-isomer). Adding a second methyl group in the β-position, as in compound (106), reduces the coupling constant further to 924.1 Hz, whilst replacing the methyl group with a phenyl group has an even greater effect, as in compound (8), resulting in a reduction to 821.3 Hz. When two phenyl groups occupy both β-positions, as in compound (58), then the coupling constant is reduced in magnitude even more (819.0 Hz). The introduction of one methyl group and one phenyl group, as in the isomers (*E*-12) and (*Z*-12), can be seen to have an intermediate effect.

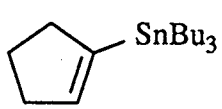
The effect of groups at the *ortho*-position in the styryl derivatives is also pronounced. The introduction of an *ortho*-methoxy substituent, as in compound (*E*-119), raises the coupling constant to 926.5 Hz, whilst *ortho*-methyl (*E,Z*-159) and *ortho*-phenyl (97) groups have a significant, if somewhat smaller effect. In contrast, the *para*-methoxystyryl compound (50) doesn't differ significantly from the simple styryl case.

Cyclohexen-1-yllead triacetate (33) has a ^3J coupling constant that is approximately the same as the $J_{Pb,H(cis)}$ coupling constants in the styryl compounds. However, compound (29) has a very much reduced ^3J coupling constant (293.9 Hz). This is thought to be due to the ring strain in the 5-membered ring. The same effect is observed in the parent stannanes (28) and (32), divinylmercury compounds (30)[19] and (34), vinylmercury bromides (212)[19] and (213) (Table 8), and also in simple cyclopentenes (5-7 Hz) and cyclohexenes (8.5-11 Hz).[74]

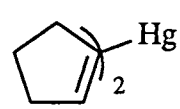
Table 8. $^3J_{X,H}$ coupling constants of metal-substituted cyclopentenes and cyclohexenes.

Compound	$J_{X,H}$ (Hz)
(28)	$J_{119Sn,H}$ 35.89, $J_{117Sn,H}$ 34.21
(32)	$J_{119Sn,H}$ 70.74, $J_{117Sn,H}$ 66.99
(30)	$J_{199Hg,H}$ 79*
(34)	$J_{199Hg,H}$ 136.21
(212)	$J_{199Hg,H}$ 150*
(213)	$J_{199Hg,H}$ 298.31

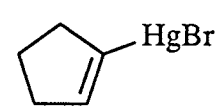
* Moloney[19]



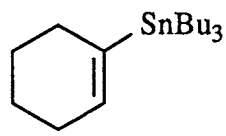
(28)



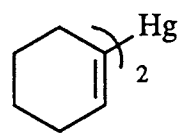
(30)



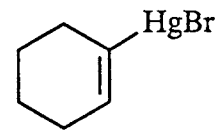
(212)



(32)

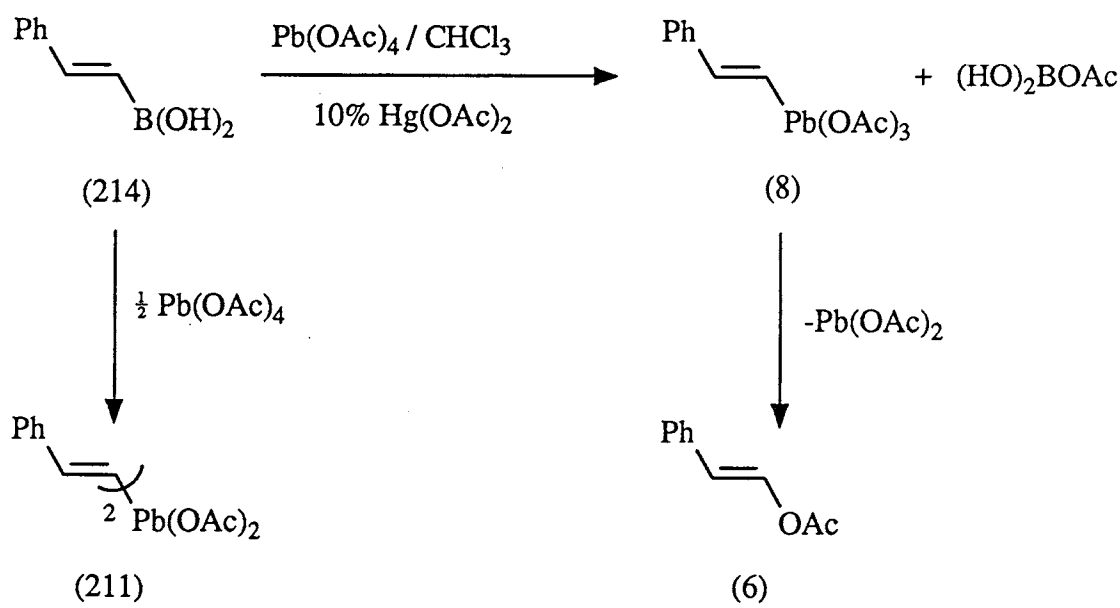


(34)



(213)

Bis[(*E*)-2-phenylethen-1-yl]lead diacetate (211) is the main product formed when (*E*)-2-phenylethen-1-ylboronic acid (214) is treated with lead tetraacetate.[14] Only in the presence of mercury(II) salts, such as mercury(II) acetate, does the boronic acid react normally to give the vinyllead triacetate (8), which then decomposes to the enol acetate (6) (Scheme 107). Bis[(*E*)-2-phenylethen-1-yl]lead diacetate (211) displays Pb-H coupling constants with a magnitude between those of tetravinyllead and vinyllead triacetates. This is once again consistent with the known effect of adding successive electron-withdrawing groups to the lead atom.[73] Also of note is the fact that the proton-proton coupling constant (16.21 Hz) is not as small as in the case of all the above styryllead triacetates.



Scheme 107

In addition to the above vinyllead triacetates, it was also possible to observe a number of vinyllead tribenzoates and tripivalates by monitoring the exchange reactions of the corresponding lead reagents, lead tetrabenzoate and lead tetrapivalate. The results obtained are summarised in Tables 9 and 10.

Table 9. NMR spectroscopic data for the vinylic protons of vinyllead tribenzoates (run at 200 MHz).

	J (Hz)		
Compound	H *gem* to Pb	H *cis* to Pb	H *trans* to Pb
(188)[a]	δ 6.58, $J_{Pb,H}$ 933.3		
(197)[b]	δ 7.68, $J_{H,H}$ 14.79	δ 7.51, $J_{H,H}$ 14.79	
	$J_{Pb,H}$ 819.8	$J_{Pb,H}$ 689.0	
(199)[c]	δ 7.57, $J_{H,H}$ 14.46	δ 7.45, $J_{H,H}$ 14.46	
	$J_{Pb,H}$ 829.5	$J_{Pb,H}$ 696.5	
(201)[a]	δ 7.58, $J_{H,H}$ 14.40	δ 7.78, $J_{H,H}$ 14.40	
	$J_{Pb,H}$ 869.4	$J_{Pb,H}$ 707.6	
(202)[d]	δ 7.10, $J_{Pb,H}$ 871.9		
(204)[b]	δ 7.60, $J_{Pb,H}$ 829.5		
(207)[d]		δ 6.34, $J_{Pb,H}$ 732.4	
(208)[a]		δ 6.54, $J_{Pb,H}$ 295.9	

[a] Prepared from tributylstannane.

[b] Prepared from divinylmercury compound.

[c] Prepared from tributylstannane and trimethylstannane.

[d] Prepared from tributylstannane and divinylmercury compound.

Table 10. NMR spectroscopic data for the vinylic protons of vinyllead tripivalates (run at 200 MHz, unless otherwise indicated).

	J (Hz)		
Compound	H *gem* to Pb	H *cis* to Pb	H *trans* to Pb
(198)[a]	δ 7.42, $J_{H,H}$ 14.89	δ 7.26, $J_{H,H}$ 14.89	
	$J_{Pb,H}$ 795.6	$J_{Pb,H}$ 696.5	
(200)[b]	δ 7.28, $J_{H,H}$ 14.86	δ 7.19, $J_{H,H}$ 14.86	
	$J_{Pb,H}$ 799.4	$J_{Pb,H}$ 662.2	
(203)[c]	δ 6.89, $J_{Pb,H}$ 834.7		
(205)[a]	δ 7.34, $J_{Pb,H}$ 789.7		
(206)[d]	δ 6.28, $J_{Pb,H}$ 879.0		

[a] Prepared from divinylmercury compound.

[b] Prepared from trimethylstannane.

[c] Prepared from tributylstannane and divinylmercury compound.

[d] Prepared from tributylstannane (run at 90 MHz).

The results obtained for the vinyllead tribenzoates and tripivalates differ only slightly from those obtained in the vinyllead triacetate series. It can be clearly seen that there is little change in the magnitude of the Pb-H coupling constants, with only a slight increase in magnitude in the tribenzoate series, and with a slight decrease in the tripivalate series. There is also a small but consistent downfield shift of the vinylic proton resonances in the tribenzoate series, accompanied by a small, but less consistent, upfield shift in the tripivalate series. These trends are easily accounted for, as they reflect the order of electron-withdrawing ability, with the tribenzoyloxyplumbyl group being

the most electron-withdrawing, and tripivaloyloxyplumbyl being the least electron-withdrawing.

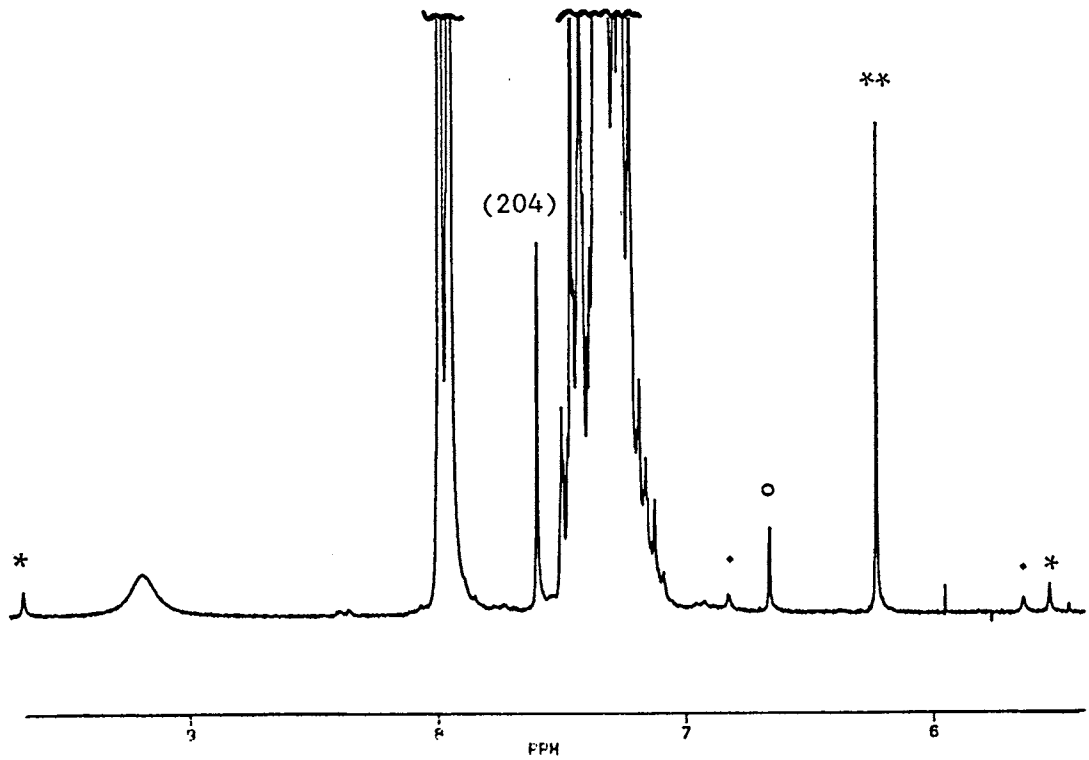


Figure 3. ^{1}H n.m.r. spectrum of (2,2-diphenylethenyl)lead tribenzoate (204) obtained from mercury compound (57) and LTB: *=Pb satellites, .=Hg satellites, o=starting material (57), **=2,2-diphenylethenylmercury benzoate (215)

Whilst the styryl series of lead compounds are readily analysed by virtue of the fact that the satellite spectra mirror the splitting patterns of the central peaks, more care must be exercised in interpreting the spectra obtained in the cases of compounds (*E*-12), (*Z*-12), (58), (106), (*E*-132), (188), (202), (203), (204), (205), and (206). In these cases, the satellites are only singlets symmetrically disposed around the central peak. In order to confirm that these peaks were, in fact satellites and not signals due to other compounds (especially in the cases where the parent peaks were located in the aromatic region), simple homonuclear decoupling experiments were carried out (Figures 3-5).

Decoupling each wing of the satellite spectrum in turn leads to collapse and disappearance of the other wing, confirming the electronic connectivity.

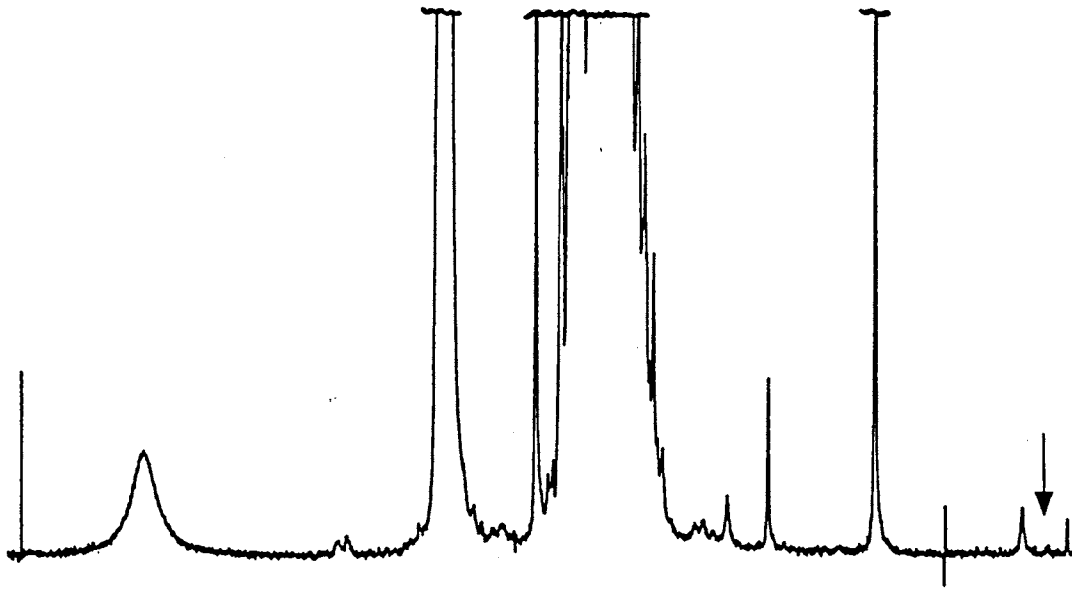


Figure 4. ^{1}H n.m.r. spectrum of (2,2-diphenylethenyl)lead tribenzoate (204) obtained from mercury compound (57) and LTB, with decoupling of the downfield satellite wing (δ 9.68).

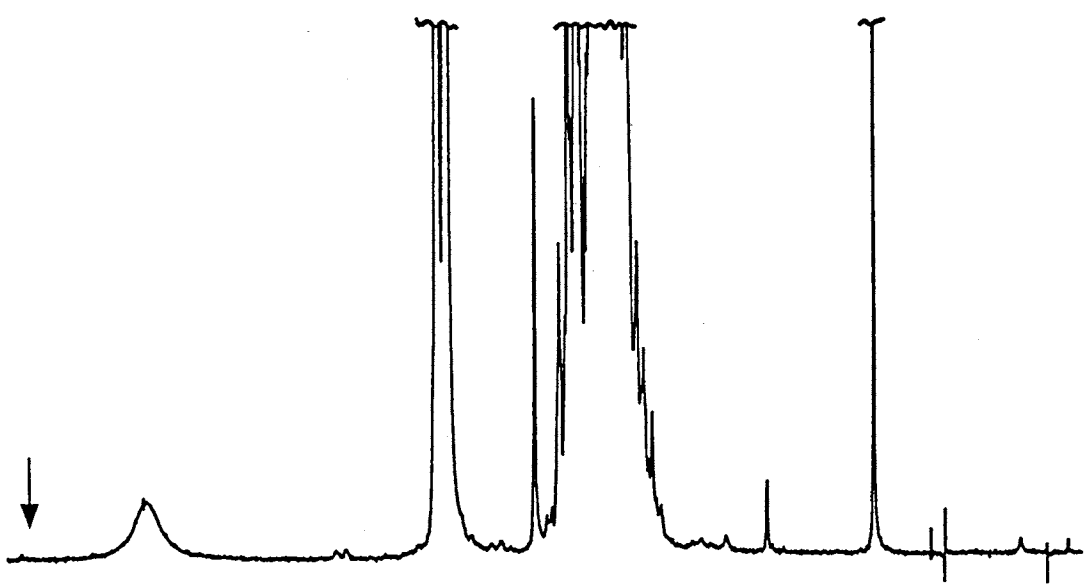


Figure 5. ^{1}H n.m.r. spectrum of (2,2-diphenylethenyl)lead tribenzoate (204) obtained from mercury compound (57) and LTB, with decoupling of the upfield satellite wing (δ 5.53).

^{13}C N.M.R. SPECTRA OF VINYLLEAD TRIACETATES AND RELATED COMPOUNDS.

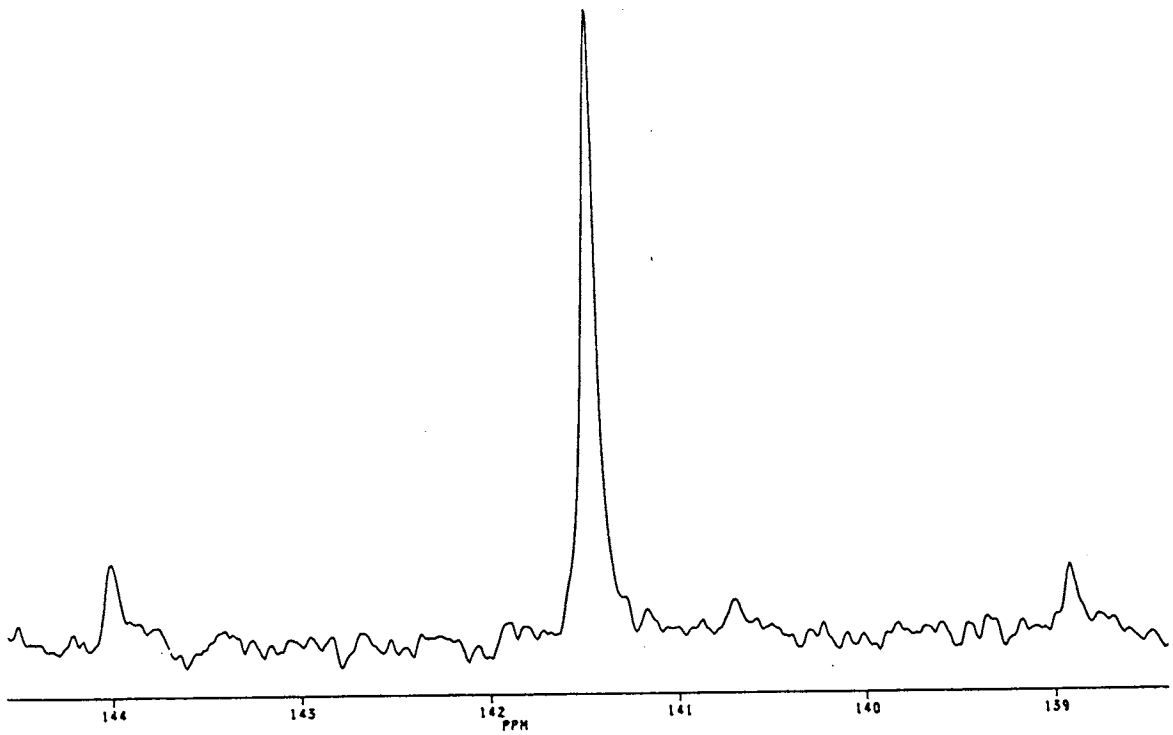


Figure 6. ^{13}C n.m.r. spectrum of cyclopentenyllead triacetate (29). Pictured is the tertiary vinylic carbon with $^{2}J_{Pb,C}$ 256.5 Hz

In a few of the cases studied above, it was possible to observe the ^{13}C n.m.r. spectra of vinyllead tricarboxylates. Cyclopenten-1-yllead triacetate (29) was found by Moloney[19] to be quite stable and it was even isolable in a semi-pure form. The ^{13}C n.m.r. spectrum was recorded, but in that work, no ^{207}Pb satellites could be seen. In the current work, it was found that the $^{2}J_{Pb,C}$ coupling constant to the β-vinylic carbon (δ 141.46) could be observed (Figure 6), however the $^{1}J_{Pb,C}$ coupling constant could not, due to the relatively low intensity of the parent ^{13}C peak of the quaternary C1 (δ 163.56). The $^{2}J_{Pb,C}$ coupling constant is only 256.5 Hz. Also observed was a $^{2}J_{Pb,C}$ coupling constant to the allylic carbon (δ 35.76) of 334.5 Hz. The second compound in this series, cyclopenten-1-yllead tribenzoate (208), was also found to have a small $^{2}J_{Pb,C}$ coupling constant to the β-vinylic carbon (δ 141.69, J 256.6 Hz) and

a slightly bigger $^{2}J_{Pb,C}$ coupling constant of 338.6 Hz to the allylic carbon. The signal for the quaternary carbon (δ 163.91) was once again of too low intensity for ^{207}Pb satellites to be visible. The relatively small size of the Pb-C coupling constant in these cases is due, as in the proton spectra discussed above, to the ring strain inherent in the 5-membered ring.

Two other compounds studied by ^{13}C n.m.r. spectroscopy were [(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]lead triacetate (50) and bis[(*E*)-2-phenylethen-1-yl]lead diacetate (211).

Lead compound (50) was found by Moloney[19] to be semi-isolable and was quite stable in solution, an n.m.r. sample of (50) was only observed to be decomposing to the acetylene (115) after 1 hour. The method used by Moloney[19] to isolate (50) was to perform the tin-lead exchange of the stannane (114) at room temperature, and chill the mixture to 0° overnight. In the current work, it was found that by simply performing the tin-lead exchange on an n.m.r. scale and following the reaction by ^{1}H and ^{13}C n.m.r. spectroscopy in an n.m.r. probe at 0°, it was possible to observe the ^{13}C n.m.r. spectrum of (50), and to extract a number of Pb-C coupling constants from the spectra obtained. The chief feature is the coupling constant of 1996 Hz to the α-vinylic carbon.

Bis[(E)-2-phenylethen-1-yl]lead diacetate (211) was found to exhibit a number of ^{207}Pb-^{13}C coupling constants, including 1273 Hz to the α-vinylic carbon, and 297.0 Hz to the aromatic quaternary carbon C3. The assignment of the large vinylic carbon-lead coupling constant to the β-vinylic carbon was made on the grounds of chemical shift, and a ^{13}C-^{1}H Heteronuclear Correlation experiment. This experiment showed that the carbon with this ^{207}Pb-^{13}C coupling constant was the same as that which bore the proton with the $J_{Pb,Hgem}$ of 433.1 Hz. On chemical shift grounds, it is proposed that

it is also the β-vinylic carbon in (50) above that has the large observed $^{207}Pb-^{13}C$ coupling constant. In neither of these two cases was it possible to observe any ^{207}Pb coupling to the β-vinylic carbon.

Very few vinyllead compounds have been reported in the literature, and only two have reported $^{207}Pb-^{13}C$ coupling constants.[75] Trivinyllead acetate has a reported ^1J coupling constant of 1272 Hz (chloroform), and tetravinyllead has a reported ^1J coupling constant of 454.1 Hz (tetrahydrofuran). In that work, no couplings to the β-carbons were reported. It is difficult to gauge from these results what trends occur in such systems, although it seems that there is no pronounced increase in the magnitude of the ^1J coupling constant in the transition from trivinyllead acetate through to systems bearing three acetate ligands. This is in direct contrast to the results obtained by Cox[75] for the aryl series as there is a fourfold increase in ^1J in the transition from tetraphenyllead ($^1J_{Pb,C}$ 480.9 Hz) to phenyllead triacetate ($^1J_{Pb,C}$ 2132 Hz).

It has been found[75] that the coordinating power of the solvent has a large effect on the ^1J coupling constant of aryllead(IV) compounds, but several experiments with lead compound (211) found that such effects were less pronounced in this case (Table 11).

Table 11. Solvent effects in ^{207}Pb–^{13}C, and ^{207}Pb–^{1}H coupling constants in bis[(*E*)-2-phenylethen-1-yl]lead diacetate (211).

	J (Hz)				
Solvent	$^{1}J_{Pb,C1}$	$^{3}J_{Pb,C3}$	$^{3}J_{H,H}$	$^{2}J_{Pb,Hgem}$	$^{3}J_{Pb,Hcis}$
$CDCl_3$	1273	297.0	16.40	433.1	339.9
$CDCl_3$ + THF	1412	310.2	16.30	430.7	348.9
$CDCl_3$ + DMSO-d_6	1539	321.8	16.00	425.9	355.9
DMSO-d_6	1644	331.8	16.25	422.6	366.3
$CDCl_3$ + pyridine-d_5	1687	352.9	16.40	429.1	367.9

^{1}H N.M.R. SPECTRA OF TRIBUTYL AND TRIMETHYLSTANNANES

Tin has ten naturally occurring isotopes, three of which have a spin quantum number of ½ (Table 12). Of these three, only ^{117}Sn and ^{119}Sn are often observed in n.m.r. spectroscopy, due to their relatively high natural abundance. Their effect on the ^{1}H n.m.r. spectra of organic molecules to which they are attached is to produce satellite spectra about the parent peaks. The relative sizes of these tin-proton coupling constants has been reviewed recently,[19] and was found to correspond with results obtained by earlier workers,[77,78] in that the sizes of these coupling constants vary in an unusual order,that being:

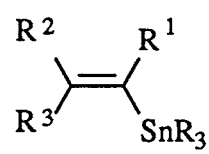
$$J_{Sn,Htrans} > J_{Sn,Hgem} > J_{Sn,Hcis}$$

The results of that review are summarised in Table 13.

Table 12. Naturally occurring tin isotopes.[76]

ISOTOPE	NATURAL ABUNDANCE (%)	I
112	0.96	0
114	0.66	0
115	0.35	½
116	14.30	0
117	7.61	½
118	24.03	0
119	8.58	½
120	32.85	0
122	4.72	0
124	5.94	0

Table 13. ^{1}H n.m.r. spectral data for vinylstannanes.



R^1	R^2	R^3	J (Hz)*			Reference
			$J_{Sn,R1}$	$J_{Sn,R2}$	$J_{Sn,R3}$	
Trimethylstannanes:						
H	H	Me			54	79
H	H	Bu	82	154		77

Table 13 (Cont'd). ^1H n.m.r. spectral data for vinylstannanes.

R^1	R^2	R^3	J (Hz)*			Reference
			$J_{Sn,R1}$	$J_{Sn,R2}$	$^nJ_{Sn,R3}$	
Trimethylstannanes (Cont'd):						
H	Et	H	84			77
H	H	Ph	66	148		77
H	Ph	H	74.5,71.5			77
Tributylstannanes:						
H	Ph	H	66.5,63.5			19
H	Me	Me	73.8			19
H	Ph	Ph	59.4,57.0			19
Ph	H	Ph		119.6,114.4		19
$-(CH_2)_3-$		H			35.2	19
$-(CH_2)_4-$		H			70	19
Me	H	H	42.0	137.4	62.4	19
H	H	Ph	56.6,56.0	136.8,130.4		19
H	p-$MeOC_6H_4$	H	67			19

* Where resolved, the couplings are quoted as $J_{119Sn,R}$,$J_{117Sn,R}$

In the present work a wide range of tributyl and trimethylstannanes were prepared. The ^1H n.m.r. spectra of these compounds yielded a large amount of information in the form of tin-proton coupling constants, and this is summarised in Table 14. The data obtained is both supplementary to, and consistent with that obtained in the previous reviews. The information obtained in this manner can be used as a supplement to normal

methods of the determination of the relative stereochemistry about the double bonds of these vinyltin compounds.

Table 14. ^1H n.m.r. spectral data for vinylstannanes.

R^1	R^2	R^3	J (Hz)*			Compound Number
			$J_{Sn,R1}$	$J_{Sn,R2}$	$J_{Sn,R3}$	
Tributylstannanes:						
H	H	Me	73.18,69.31	153.95,128.96		*Z*-192
H	Ph	Me	66,63		10	66
Me	H	Ph	42.8,39.1	125		71
H	$-(CH_2)_5-$		76			76
H	$Ph(CH_2)_2-$	H	79.02,76.02		66.51,63.51	93
H	H	H	82.48,77.98	146.96,140.96	73.49,69.88	191
H	*o*-$MeOC_6H_4$	H	73.20,70.00		64	*E*-113
H	*o*-PhC_6H_4	H	72.36,68.83		66.48,64.12	96
H	Me	*o*-$MeOC_6H_4$	71.58,67.98			*Z*-131
H	H	*o*-MeC_6H_4	65.69,62.69	136.70,131.10		*Z*-157
H	*o*-MeC_6H_4	H	72.29,68.99		63.62	*E*-157
Me	H	*o*-$MeOC_6H_4$		130.37		146
Trimethylstannanes:						
H	Ph	Me	72.14,69.42			*E*-70
H	Me	Ph	75.98,72.78			*Z*-70
Me	H	Ph	48,46	138		73
H	Ph	Ph	68.98,65.78			64
$-(CH_2)_5-$		H			78.06,74.39	173

* Where resolved, the couplings are quoted as $J_{119Sn,R}$,$J_{117Sn,R}$.

EXPERIMENTAL

GENERAL PROCEDURES

Melting points were determined on a Reichert Micro Melting Point Apparatus and are uncorrected. Ultraviolet spectra were recorded on a Hitachi Model 150-20 Double Beam Spectrophotometer as solutions in the indicated solvent. Infrared spectra were recorded on Perkin-Elmer 221 and 710B spectrometers or a Digilab FTS 20/80 Fourier Transform spectrometer from the neat liquid (sodium chloride plates) or as solutions in chloroform as indicated.

^{1}H n.m.r. spectra were recorded on Bruker WM 400 and AC 200F, Varian XL 400 and XL 100 Fourier Transform spectrometers and a Varian EM 390 spectrometer as solutions in deuterochloroform, using tetramethylsilane as an internal reference, except in the case of trimethylvinylstannanes which were referenced to either dibromomethane or 1,3,5-trinitrobenzene. Signals are reported in terms of chemical shift, intensity, multiplicity, coupling constants, and assignments, in that order. The following abbreviations for multiplicity are used: s, singlet; d, doublet; t, triplet; q, quartet; bs, broadened singlet; dt, doublet-of-triplets, *etc.*

^{13}C n.m.r. spectra were recorded on Bruker WM 400, AC 200F, Varian XL 400 and Jeol FX 60Q Fourier Transform spectrometers. Assignment of ^{13}C peaks was on the basis of multiplicities in the off-resonance decoupled spectra run on the Jeol FX 60Q instrument, or on the DEPT and APT spectra run on the Bruker WM 400 and AC 200F, and Varian XL 400 instruments respectively, in conjunction with comparison with calculated values of chemical shift.[74] Variable temperature (VT) n.m.r. spectra at temperatures between 60° and 130° were recorded in dideuterotetrachloroethane with hexamethyldisilane (HMDS, δ 0.00) as an internal reference.

Mass spectroscopy was carried out on a GEC-AEI MS 9 instrument for electron impact spectra, which was connected to a DS 55 data handling system (Release 4.00) for high resolution spectra. Chemical ionization mass spectra were recorded on a GEC-AEI MS 30 spectrometer, with methane as the ionizing gas. Peaks of intensity less than 10% of the base peak are not quoted, unless of special significance.

Microanalyses were performed by the Australian Mineral Development Laboratories, Melbourne, and Chemical and Micro Analytical Services Pty. Ltd., North Essendon. In those cases where satisfactory microanalyses could not be obtained, characterisation was made by means of high resolution mass spectroscopy and high field ^{1}H and ^{13}C n.m.r. spectroscopy.

Thin layer chromatography was conducted with Merck Kieselgel 60 PF_{254}, and preparative layer chromatography was conducted with Merck Kieselgel 60 $PF_{254 + 366}$, while for column chromatography Merck Kieselgel 60 (70-230 mesh) was used, and for flash chromatography,[80] Merck Kieselgel 60 (230-400 mesh) was used. Merck Kieselgel (60 PF_{254} gipshaltig) was used for preparative centrifugal (radial) chromatography with a Chromatotron Model 7924, Harrison Research U.S.A. with UV detection (Mineralight^{R} Lamp Model UV GL-58 with 254 nm only).

Analytical gas-liquid chromatography (GLC) was carried out on a Hewlett Packard 402 chromatograph, equipped with a flame ionization detector and a Hewlett Packard 3380A integrator, or on a Hewlett Packard 5890 chromatograph, equipped with a flame ionization detector and a Hewlett Packard 3393A integrator, and one of the following columns:

(a) HP 402 instrument

column 1. 2.5% FFAP on Chromasorb G-HP (100-120 mesh); 2.5 mm i.d. x 1.83 m.

column 2. 10% Carbowax 20M on Gas Chrom. Q (80-100 mesh); 2 mm i.d. x 1.5 m.

column 3. 3% OV-17 on Gas Chrom. Q (100-200 mesh); 2 mm i.d. x 1.5 m.

column 4. 10% Carbowax 20M on Gas Chrom. Q (80-100 mesh); 3 mm i.d. x 1.37 m.

Nitrogen (28-35 ml/min) was used as the carrier gas, with hydrogen (60 ml/min) and air (500 ml/min) as the combustion mixture.

(b) HP 5890 instrument

column 5. S.G.E. capilliary column BP1; 0.33 mm i.d. x 25 m (0.5 μm film thickness).

column 6. S.G.E. capilliary column BP 20; 0.22 mm i.d. x 25 m (0.33 μm film thickness).

column 7. S.G.E. capilliary column BP1; 0.22 mm i.d. x 25 m (0.25 μm film thickness).

column 8. S.G.E. capilliary column BP1; 0.22 mm i.d. x 50 m (1.0 μm film thickness).

column 9. S.G.E. capilliary column BP 20; 0.22 mm i.d. x 12 m (0.25 μm film thickness).

column 10. 3% OV-17 on Gas Chrom Q (100-120 mesh); 4 mm i.d. x 5 ft.

column 11. PORAPAK Q (100-120 mesh); 4 mm i.d. x 5 ft.

Helium (30 ml/min) was used as the carrier gas, with hydrogen (30 ml/min) and air (450 ml/min) as the combustion mixture.

The unknown concentration of a substance in solution was calculated from its known concentration in a standard solution of the authentic material, and the integrated peak areas obtained on injection of equal volumes of the two solutions. All integrals were referenced to an appropriate internal standard of known concentration in both solutions.

Analytical High Performance Liquid Chromatography (HPLC) was conducted on a Waters 6000 Chromatograph equipped with a Waters Differential Refractometer R401 and Waters Associates Model 450 Variable Wavelength Detector using a Whatman Partisil 5 column (4.6 mm i.d. x 25 cm). A flow rate of 1.5 ml/min was used.

Preparative HPLC was conducted on a Waters Model 510 Chromatograph equipped with a Waters Differential Refractometer R403 and an Instrumentation Specialities Company Model 226 UV Absorbance Monitor, and a Whatman Partisil 10 M20 column (22 mm i.d. x 50 cm). A flow rate of 13 ml/min was used.

The determination of product yields by ^{1}H n.m.r. spectroscopy was made using the following method: To a solution of a crude reaction mixture in deuterochloroform was added an accurately weighed quantity of an internal standard, usually 1,3,5-trinitrobenzene or dibromomethane, and the relevant peaks in the ^{1}H n.m.r. spectrum were integrated and compared. The accuracy of this method is 5-10%.

Tetrahydrofuran was predried over sodium and stored over sodium in the presence of benzophenone under nitrogen. Immediately prior to use the tetrahydrofuran was distilled into the reaction vessel under nitrogen. Chloroform for mercury-lead and tin-lead exchange reactions was washed with concentrated sulfuric acid and water, and dried over calcium chloride. It was refluxed over calcium sulfate, distilled from it and stored over type 4A molecular seives. Deuterochloroform for mercury-lead and tin-lead exchange reactions was passed through a short column of basic alumina and stored over type 4A molecular seives. All other solvents and reagents were purified in the usual manner,[81] and the purity of known substances was routinely determined by their melting/boiling points and their ^{1}H n.m.r. spectra.

Lead tetraacetate was obtained from Merck, and freed from excess acetic acid by drying under high vacuum immediately prior to use.

Bis[(*E*)-2-phenylethen-1-yl]lead diacetate (212) was kindly donated by Mrs. J. Morgan of these laboratories.

Unless otherwise stated, all compounds were obtained from chemical suppliers.

SYNTHESIS OF VINYL BROMIDES

Preparation of bromomethylenecyclohexane

Ethyl 2-(1-hydroxycyclohexyl)acetate was prepared according to the method of Vogel[82] in 38% yield, b.p. 60°/0.3 mmHg (lit.[82] 86-9°/2 mmHg). δ (90 MHz, $CDCl_3$) 1.25, 3H, t, $^3J_{CH2,CH3}$ 6.8 Hz, $-OCH_2CH_3$; 1.10-2.06, 10H, m, $-(CH_2)_5-$, 2.41, 2H, s, $-CH_2CO_2R$; 3.34, 1H, bs, OH; 4.09, 2H, q, $^3J_{CH3,CH2}$ 6.8 Hz, $-OCH_2CH_3$.

The above hydroxy ester (70 g, 0.376 mol) was refluxed with potassium hydroxide (56.5 g, 1.007 mol) in water (400 ml) for three hours and then cooled. The aqueous phase was washed with ether (150 ml) and acidified with concentrated hydrochloric acid to below pH 1. The mixture was extracted with ether (2x300 ml), and the combined ether extract was washed with brine (200 ml), and dried (Na_2SO_4). The solvent was removed to yield 2-(1-hydroxycyclohexyl)acetic acid (42 g, 71%) as an oil which crystallized on standing, m.p. 61° (lit.[83] 62-4°). δ (90 MHz, $CDCl_3$) 1.10-1.90, 10H, m, $-(CH_2)_5-$; 2.50, 2H, s, $-CH_2-CO_2H$; 6.08, 2H, bs, OH + COOH.

The crude hydroxy acid (24 g, 152 mmol) was refluxed with freshly distilled acetic anhydride (80 ml) for 4 hours, cooled, poured onto chipped ice (250 g) and the mixture was stirred for 1 hour. The product was collected at the pump, and dried in a vacuum dessicator to give cyclohexylideneacetic acid (15 g, 71%) as colourless crystals, m.p. 90.5-91° (lit.[84] 90-91°). δ (90 MHz, $CDCl_3$) 1.32-1.85, 6H, m, $3xCH_2$; 1.85-2.47, 2H, m, CH_2; 2.47-3.02, 2H, m, CH_2; 5.58, 1H, bs, =CH-; 9.30, 1H, bs, COOH. Analytical Gas-Liquid Chromatographic analysis (column 1, 190°) indicated that none of the endocyclic olefin (arising from

dehydration into the ring) was present.

Bromine (1.9 ml, 37 mmol) in dry chloroform (15 ml) was added over 90 minutes to a solution of cyclohexylideneacetic acid (5.01 g, 36 mmol) in dry chloroform (50 ml) at 0°. The solution was stirred for 16 hours at room temperature, and the solvent was removed under reduced pressure at room temperature, as the product sublimed readily. The crude 2-bromo-2-(1-bromocyclohexyl)acetic acid (10.60 g, 99%) had m.p. 130° (lit.[84] 135-6°). δ (90 MHz, $CDCl_3$) 1.00-2.68, 10H, m, $-(CH_2)_5-$; 4.62, 1H, s, -CHBr; 10.80, 1H, bs, COOH.

To anhydrous sodium carbonate (7.58 g, 72 mmol) was added a solution of 2-bromo-2-(1-bromocyclohexyl)acetic acid (10.6 g, 35 mmol) in acetone (150 ml). A mild effervescence was observed and the mixture was refluxed for 3 hours, cooled and the solvent was removed. The residue was extracted into ether (150 ml) and washed with water (100 ml), sodium carbonate solution (10%, 100 ml) and brine (100 ml). The ether extract was dried (Na_2SO_4), and the solvent was removed. The crude product was distilled (Kugelrohr), to yield bromomethylenecyclohexane (3.73 g, 60%) as a yellow oil, b.p. 50°/5 mmHg (lit.[85] 64-6°/10mmHg).
δ (90 MHz, $CDCl_3$) 1.33-1.73, 6H, m, $3xCH_2$; 1.93-2.47, 4H, m, $2xCH_2$; 5.75, 1H, bs, =CH-.

Preparation of *ethyl (E)-5-phenyl-2-pentenoate*

To a solution of (carbethoxymethylene)triphenylphosphorane (12.98 g, 37.3 mmol) in dry benzene (50 ml) was added 3-phenylpropanal (5 g, 37.3 mmol). The mixture was refluxed for 16 hours and the solvent was removed. The residue was purified by flash chromatography (ethyl acetate/light petroleum, 1:9) to yield *ethyl (Z)-5-phenyl-2-pentenoate*

(0.75 g, 10%) as a colourless oil, b.p. 110°/1.5 mmHg (Kugelrohr). (Found: C, 76.5; H, 8.3. $C_{13}H_{16}O_2$ requires C, 76.4, H, 7.9%). λ_{max} (ethanol) no peaks. υ_{max} (liquid film) 3028w, 2981w, 2928w, 1719s (C=O), 1645m, 1497w, 1454w, 1415w, 1161s, 1186m, 1031s, 823m, 749m, 690m cm^{-1}. δ (90 MHz, $CDCl_3$) 1.23, 3H, t, $^3J_{CH2,CH3}$ 7.2 Hz, $-OCH_2CH_3$; 2.50-3.13, 4H, m, 2xCH_2; 4.09, 2H, q, $^3J_{CH3,CH2}$ 7.2 Hz, $-OCH_2CH_3$; 5.66, 1H, dt, $^3J_{CH,CH}$ 11.4 Hz, $^4J_{CH2,CH}$ 1.2 Hz, $=CH-CO_2Et$; 6.12, 1H, dt, $^3J_{CH,CH}$ 11.4 Hz, $^3J_{CH2,CH}$ 6.9 Hz, $-CH_2-CH=$; 6.92-7.32, 5H, m, ArH. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 14.15, q, C1; 30.32, t, C6 or C7; 35.06, t, C6 or C7; 59.61, t, C2; 120.38, d, C4; 125.84, d, C11; 128.24, 2xd, C9 and C10; 141.09, s, C8; 148.36, d, C5; 165.96, s, C3. (*m/z*) 204(M^+, 10%), 159(9), 130(11), 91(100).

and *ethyl (E)-5-phenyl-2-pentenoate* (5.85 g, 77%) as a colourless oil, b.p. 113°/1.5 mmHg. (Found: C, 76.2; H, 8.1. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%). λ_{max} (ethanol) no peaks. υ_{max} (liquid film) 3028w, 2982m, 2938m, 1722s (C=O), 1655m, 1454m, 1368m, 1316m, 1267s, 1198s, 1148s, 1088m, 1042s, 974w, 749m, 699s cm^{-1}. δ (90 MHz, $CDCl_3$) 1.23, 3H, t, $^3J_{CH2,CH3}$ 7.3 Hz, $-OCH_2CH_3$; 2.25-2.88, 4H, m, 2xCH_2; 4.11, 2H, q, $^3J_{CH3,CH2}$ 7.3 Hz, $-OCH_2CH_3$; 5.74, 1H, dt, $^3J_{CH,CH}$ 15.3 Hz, $^4J_{CH2,CH}$ 1.6 Hz, $=CH-CO_2Et$; 6.91, 1H, dt, $^3J_{CH,CH}$ 15.3 Hz, $^3J_{CH2,CH}$ 6.3 Hz, $-CH_2-CH=$; 6.96-7.32, 5H, m, ArH; ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 14.15, q, C1; 33.63, t, C6 or C7; 34.28, t, C6 or C7; 59.87, t, C2; 121.94, d, C4; 125.97, d, C11; 128.30, 2xd, C9 and C10; 140.64, s, C8; 147.52, d, C5; 166.22, s, C3. (*m/z*) 204(M^+, 5%), 159(14), 158(10), 130(21), 92(14), 91(100), 65(11).

Preparation of *(E)-5-phenyl-2-pentenoic acid* (*E*-84)

Ethyl (*E*)-5-phenyl-2-pentenoate (2.75 g, 13.5 mmol) was refluxed with sodium hydroxide (1.4 g, 35 mmol) in water (50 ml) and methanol (5 ml) for 3 hours. The mixture was cooled and extracted with ether (50 ml). The aqueous phase was acidified with concentrated hydrochloric acid to below pH 1 and extracted with ether (3x50 ml). The combined ether extracts were dried (Na_2SO_4) and the solvent was removed to yield *(E)-5-phenyl-2-pentenoic acid* (2.205 g, 93%) as a colourless powder, m.p. 92-4°. (Found: C, 74.8; H, 7.2. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.9%). λ_{max} (ethanol) no peaks. υ_{max} (chloroform) 3400-2900bs (OH), 2941m, 1699s, 1654s (C=O), 1496w, 1445w, 1387m, 1312m, 1286m, 975m cm^{-1}. δ (90 MHz, $CDCl_3$) 2.33-2.93, 4H, 2xCH_2; 5.76, 1H, dt, $^3J_{CH,CH}$ 15.5 Hz, $^4J_{CH2,CH}$ 1.4 Hz, =*CH*-CO_2Et; 6.79-7.39, 6H, m, ArH and -CH_2-*CH*=; 9.80, 1H, bs, COO*H*. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 33.83, t, C4 or C5; 34.28, t, C4 or C5; 121.35, d,C2; 126.23, d, C9; 128.30, d, C7 or C8; 128.49, d, C7 or C8; 140.57, s, C6; 150.77, d, C3; 171.74, s, C1. (*m/z*) 176(M^+, 9%), 117(12), 91(100).

Preparation of *(Z)-5-phenyl-2-pentenoic acid* (84)

Ethyl (Z)-5-phenyl-2-pentenoate (0.25 g, 1.2 mmol) was refluxed with sodium hydroxide (0.13 g, 3.3 mmol) in water (5 ml) and methanol (0.4 ml) for 3 hours. The mixture was cooled and extracted with ether (3 ml). The aqueous phase was acidified with concentrated hydrochloric acid to below pH 1 and extracted with ether (3x5 ml). The combined ether extracts were dried (Na_2SO_4) and the solvent was removed to yield *(Z)-5-phenyl-2-pentenoic acid* (0.18 g, 82%) as a colourless oil, b.p. 103°/0.05 mmHg, which solidified on cooling to a colourless solid, m.p. 40-41°. (Found: C, 75.3; H, 7.0. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.9%).

λ_{max} (ethanol) no peaks. υ_{max} (chloroform) 3400-2800bs (OH), 3028m, 2928w, 2756w, 2588w, 1695s (C=O), 1641m, 1487w, 1454w, 1435m, 1303m, 1242s, 924m, 824w, 714w, 698m cm^{-1}. δ (90 MHz, $CDCl_3$) 2.43-3.17, 4H, 2xCH_2; 5.72, 1H, dt, $^3J_{CH,CH}$ 11.4 Hz, $^4J_{CH2,CH}$ 1.2 Hz, =C*H*-CO_2H; 6.27, 1H, dt, $^3J_{CH,CH}$ 11.4 Hz, $^3J_{CH2,CH}$ 6.9 Hz, =CH-; 6.88-7.37, 5H, m, ArH; 10.70, 1H, bs, COO*H*. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 30.45, t, C4 or C5; 34.80, t, C4 or C5; 119.61, d, C2; 125.90, d, C9; 128.24, 2xd, C7 and C8; 140.77, s, C6; 151.48, d, C3; 171.68, s, C1. (*m/z*) 176(M^+, 12%), 130(10), 117(10), 92(20), 91(100), 78(11), 65(24), 51(12), 39(16).

Preparation of *2,3-dibromo-5-phenylpentanoic acid* (85)

To a stirred solution of (*E*)-5-phenyl-2-pentenoic acid (2.13 g, 12 mmol) in dry chloroform (40 ml) was added a solution of bromine (0.8 ml, 15.6 mmol) in dry chloroform (10 ml) at room temperature over 30 minutes. The resulting mixture was stirred at room temperature for 6 hours and the solvent was removed to yield *2,3-dibromo-5-phenylpentanoic acid* (4.01 g, 99%) as a pale yellow powder. An analytical sample was obtained by recrystallization from carbon tetrachloride/light petroleum, m.p. 117-9°. (Found C, 39.6; H, 3.8. $C_{11}H_{12}Br_2O_2$ requires C, 39.3; H, 3.6%). λ_{max} (ethanol) no peaks. υ_{max} (chloroform) 3300-2900bs (OH), 3067m, 2986w, 2951s, 2860m, 2659s, 1732s (C=O), 1498m, 1455m, 1432m, 1284m, 1261s, 1150m, 1053m cm^{-1}. δ (90 MHz, $CDCl_3$) 1.88-3.16, 4H, m, 2xCH_2; 4.06-4.54, 2H, m, 2xCHBr†; 7.03-7.29, 5H, m, ArH; 8.49, 1H, bs, COOH. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$ + DMSO-d_6) 32.34, t, C4 or C5; 36.62, t, C4 or C5; 48.70, d, C3; 52.07, d, C2; 125.84, d, C9; 128.17, 2xd, C7 and C8; 139.73, s, C6; 168.87, s, C1. (*m/z*) 338(M^+ +4, 3%), 336(M^+ +2, 5), 334(M^+, 3), 257(2), 255(2), 239(2), 237(2), 175(33), 131(34), 129(21), 117(13), 92(28), 91(100), 82(17), 80(17), 65(29), 51(13), 44(17), 39(17).

Preparation of *(Z)-1-bromo-4-phenyl-1-butene* (86)

2,3-Dibromo-5-phenylpentanoic acid (1.5 g, 4.5 mmol) was refluxed with potassium carbonate (4 g, 28 mmol) in acetone (40 ml) for 3 hours with protection from light, cooled and the solvent was removed. The residue was partitioned between ether (50 ml) and water (50 ml). The ether layer was separated, washed with brine (50 ml), dried (Na_2SO_4), and the solvent was removed. The crude product was distilled (Kugelrohr) to give *(Z)-1-bromo-4-phenyl-1-butene* (0.80 g, 85%) as a colourless oil, b.p. 90°/1.5 mmHg. (Found : M^+, 210.0070, M^+-Br, 131.0854. $C_{10}H_{11}Br$ requires M^+, 210.0044, M^+-Br, 131.0861). λ_{max} (ethanol) 248 nm (ϵ 661). υ_{max} (liquid film) 3064m, 3027m, 2926m, 1621w, 1454m, 1305w, 1030w, 935m, 748m, 698s, 671w cm^{-1}. δ (400 MHz, C_6D_6)* 2.31-2.37, 2H, m, =CH-C*H*$_2$-; 2.43, 2H, bt, $^3J_{CH2,CH2}$ 7.20 Hz, Ph-C*H*$_2$-; 5.63, 1H, dt, $^3J_{CH,CH}$ 7.17 Hz, $^3J_{CH2,CH}$ 7.20 Hz, -CH$_2$-C*H*=; 5.80, 1H, dt, $^3J_{CH,CH}$ 7.17 Hz, $^4J_{CH2,CH}$ 1.37 Hz, =CHBr; 6.96-7.18, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 5.80 produced no n.O.e. at δ 2.35 (but produced a 6% n.O.e. at δ 5.63). Irradiation at δ 2.35 produced no n.O.e at δ 5.80 (but produced a 5% n.O.e. at δ 5.63). ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$)* 31.36, t, C3 or C4; 34.22, t, C3 or C4; 108.37, d, C2; 126.03, d, C8; 128.30, 2xd, C6 and C7; 133.76, d, C1; 141.03, s, C5. (*m/z*) 212(M^+ +2, <1%), 211(M^+ +1, 1), 210(M^+, <1), 209(M^+ -1, 1), 132(13), 131(77), 129(10), 104(10), 92(27), 91(100), 77(10), 65(22), 51(13), 39(17).

*Examination of both the ^1H and ^{13}C n.m.r. spectra of the (*Z*)-isomer indicated the presence of about 18% of *(E)-1-bromo-4-phenyl-1-butene* in the sample. δ (400 MHz, C_6D_6) 1.86, 2H, ddt, $^3J_{CH,CH2}$ 7.25 Hz, $^4J_{CH,CH2}$ 1.68 Hz, $^3J_{CH2,CH2}$ 7.75 Hz, =CH-C*H*$_2$-; 2.26, 2H, bt, $^3J_{CH2,CH2}$ 7.75 Hz, Ph-C*H*$_2$-; 5.63, 1H, dt, $^3J_{CH,CH}$ 13.75 Hz, $^4J_{CH2,CH}$ 1.68 Hz, =CHBr; 5.92, 1H, dt, $^3J_{CH,CH}$ 13.75 Hz, $^3J_{CH2,CH}$ 7.25 Hz, =C*H*-CH$_2$; 6.96-7.18, 5H, m, ArH.

Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 1.86 produced a 3% n.O.e. at δ 5.63 (also 2% at δ 5.92)· Irradiation at δ 5.63 produced a 2% n.O.e. at δ 1.86· ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 34.61, t, C3 or C4; 35.00, t, C3 or C4; 104.99, d, C2; 126.03, d, C8, 128.30, 2xd, C6 and C7; 137.00, d, C1; 140.77, s, C5.

Preparation of *o*-methylbenzaldehyde

A solution of *N*,*N*-dimethylformamide (27 ml, 0.350 mol) in dry ether (200 ml) was added slowly over 20 minutes to the Grignard reagent prepared from *o*-bromotoluene (40 ml, 0.333 mol) and magnesium turnings (9.7 g, 0.399 mol) in dry ether (400 ml). The solution was refluxed for 1 hour, cooled and quenched with hydrochloric acid (3 M, 400 ml). The ether layer was separated, washed with water (400 ml), and brine (100 ml), dried (Na_2SO_4), filtered and the solvent was removed by distillation. The residue was fractionally distilled to yield *o*-methylbenzaldehyde (24.51 g, 61%) as a colourless oil, b.p. 110°/ 40 mmHg (lit.[86] 199-200°).

Preparation of *o*-methylcinnamic acid (154)

Malonic acid (53.07 g, 0.51 mol) and *o*-methylbenzaldehyde (24.51 g, 0.20 mol) were refluxed in pyridine (100 ml) and piperidine (5 ml) for 3 hours. The mixture was then poured onto ice (200 g) and hydrochloric acid (10 M, 300 ml), and stirred at 0° for 30 minutes. The crude product was collected and dried at the pump, then crystallized from ethanol to yield *o*-methylcinnamic acid (23.7 g, 73%) as colourless needles, m.p. 173° (lit.[87] 174-5°). δ (90 MHz, $CDCl_3$ + DMSO-d_6) 2.56, 3H, s, CH_3; 6.25, 1H, d, $^3J_{CH,CH}$ 15.8 Hz, H2; 7.02-7.25, 3H, m, ArH; 7.49, 1H, m, ArH; 7.77, 1H, d, $^3J_{CH,CH}$ 15.8 Hz, H3; 9.8, 1H, vbs, COOH.

Preparation of *2,3-dibromo-3-(o-methylphenyl)propanoic acid* (155)

To a stirred solution of *o*-methylcinnamic acid (1.40 g, 8.6 mmol) in dry chloroform (10 ml) was added a solution of bromine (0.5 ml, 9.7 mmol) in dry chloroform (3 ml) over 30 minutes. The mixture was stirred at room temperature for 4 hours, washed with sodium bisulfite solution (5%, 50 ml), and brine (20 ml), dried (Na_2SO_4), filtered and the solvent was removed to yield *2,3-dibromo-3-(o-methylphenyl)propanoic acid* (2.53 g, 91%) as a pale yellow solid, m.p. 157-9°. (Found: C, 37.5; H, 3.1%. $C_{10}H_{10}Br_2O_2$ requires C, 37.3; H, 3.1%). λ_{max} (ethanol) 279(sh), 272(sh), 238, 202 nm (ϵ 1223, 1654, 4350, 21183). υ_{max} (chloroform) 3300-2700bs, 3039w, 2665w, 2574w, 1729s, 1495w, 1465w, 1424w, 1307w, 1276m, 1144m, 1039w, 919w, 873w, 674w, 656w, 606w, 531w, 504w cm^{-1}. δ (400 MHz, $CDCl_3$ + DMSO-d_6) 2.44, 3H, s, CH_3; 4.99, 1H, d, $^3J_{CH,CH}$ 11.70 Hz, H2; 5.65, 1H, d, $^3J_{CH,CH}$ 11.70 Hz, H3; 7.11-7.30, 3H, m, ArH; 7.45, 1H, m, ArH; 9.11, 1H, bs, COOH. Sample contained 13% of the other diastereomer (doublet at δ 5.50, $^3J_{CH,CH}$ 10.33 Hz, other peak was under H2 of major diastereomer, methyl group at δ 2.43). ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 19.78, CH_3; 45.78, 2xCHBr; 126.94, ArCH; 127.11, ArCH; 129.23, ArCH; 130.90, ArCH; 135.00, ArC; 137.22, ArC; 172.26, CO_2H. (*m/z*) 324(M^+ +4, <1%), 322(M^+ +2, 1%), 320(M^+, <1%), 198(15), 196(16), 162(10), 147(10), 120(10), 119(12), 118(15), 117(100), 116(42), 115(75), 91(34), 89(12), 82(15), 80(16), 65(10), 63(16), 51(13), 44(20), 39(19).

Preparation of *(Z)-1-bromo-2-(o-methylphenyl)ethene* (156)

2,3-Dibromo-3-(*o*-methylphenyl)propanoic acid (1.5 g, 4.7 mmol) was refluxed with potassium carbonate (1.6 g, 11.6 mmol) in acetone (20 ml) for 3 hours, and the solvent was removed. The residue was partitioned between water (30 ml) and ether (30 ml). The ether layer was separated

and washed with brine (10 ml), dried (Na_2SO_4), filtered and the solvent was removed. The residue was distilled (Kugelrohr) to yield *(Z)-1-bromo-2-(o-methylphenyl)ethene* (0.69 g, 75%) as a pale yellow oil, b.p. 53°/0.8 mmHg. (Found: C, 54.9; H, 4.6. C_9H_9Br requires C, 54.9; H, 4.6%). λ_{max} (ethanol) 247, 206 nm (ϵ 10097, 20945) and υ_{max} (liquid film) 3071w, 3020w, 2973w, 2922w, 2859w, 1674w, 1615m, 1482m, 1459m, 1379w, 1317s, 1208w, 1159w, 1105w, 1048w, 1034w, 945w, 838w, 796m, 758s, 728w, 694w, 670w, 588w cm^{-1}. δ (200 MHz, $CDCl_3$) 2.23, 3H, s, CH_3; 6.46, 1H, d, $^3J_{CH,CH}$ 7.90 Hz, =*CH*Br; 7.09, 1H, d, $^3J_{CH,CH}$ 7.90 Hz, Ar*CH*=; 7.08-7.29, 3H, m, ArH; 7.54, 1H, m, ArH *ortho* to CH=CHBr. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 19.97, *C*H_3; 108.62, =*C*HBr; 125.61, Ar*C*H; 128.44, Ar*C*H; 128.86, Ar*C*H; 130.15, Ar*C*H; 132.19, Ar*C*H=; 135.66, Ar*C*; 136.33, Ar*C*. (*m/z*) 198(M^+ +2, 22%), 196(M^+, 24), 118(10), 117(100), 116(21), 115(70), 91(26), 89(10), 65(10), 63(11), 39(13).

Preparation of 1-bromo-2-(*p*-methylphenyl)ethene

p-Methylbenzaldehyde (40 g, 0.332 mol) and malonic acid (38 g, 0.365 mol) were refluxed in ethanol (100 ml) and pyridine (10 ml) for 16 hours, and half the ethanol was removed by distillation. The mixture was chilled to 5° and filtered at the pump. The product was dried in air and finally in a vacuum dessicator to give *p*-methylcinnamic acid (15.43 g, 39%) as colourless needles, m.p. 197° (lit.[88] 198-9°). δ (90 MHz, $CDCl_3$ + DMSO-d_6) 2.31, 3H, s, CH_3; 6.28, 1H, d, $^3J_{CH,CH}$ 15.9 Hz, H2; AA'BB' system: 7.08, 2H, d, J_{AB} + $J_{AB'}$ 7.8 Hz, ArH *ortho* to CH_3; 7.31, 2H, d, J_{AB} + $J_{AB'}$ 7.8 Hz, ArH *meta* to CH_3; 7.54, 1H, d, $^3J_{CH,CH}$ 15.9 Hz, H3; 10.12, 1H, bs, COOH.

Bromine (5.2 ml, 102 mmol) was added dropwise to a stirred solution of *p*-methylcinnamic acid (15.43 g, 95 mmol) in chloroform (400 ml) at room temperature. The mixture was stirred at room temperature for 20 hours and the solvent was removed to yield 2,3-dibromo-3-(*p*-methylphenyl)propanoic acid (29.2 g, 95%) as an unstable yellow solid. δ (90 MHz, $CDCl_3$ + DMSO-d_6) 2.31, 3H, s, CH_3; 4.74, 1H, d, $^3J_{CH,CH}$ 11.7 Hz, H2; 5.27, 1H, d, $^3J_{CH,CH}$ 11.7 Hz, H3; AA'BB' system: 7.08, 2H, d, $J_{AB} + J_{AB'}$ 8.1 Hz, ArH *ortho* to CH_3; 7.19, 2H, d, $J_{AB} + J_{AB'}$ 8.1 Hz, ArH *meta* to CH_3; 10.40, 1H, bs, COOH.

2,3-Dibromo-3-(*p*-methylphenyl)propanoic acid (29.2 g, 91 mmol) was refluxed with potassium carbonate (31.3 g, 226 mmol) in acetone (200 ml) for 3 hours. The solvent was removed and the residue was partitioned between ether (250 ml) and water (500 ml). The ether layer was separated and washed with brine (100 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled to yield 1-bromo-2-(*p*-methylphenyl)ethene (12.2 g, 68%) as a colourless oil, b.p. 126-130°/22 mmHg (lit.[89] 65°/0.5 mmHg). δ (90 MHz, $CDCl_3$) 2.26, 3H, s, CH_3; 6.21, 1H, d, $^3J_{CH,CH}$ 8.1 Hz, H1; 6.87, 1H, d, $^3J_{CH,CH}$ 8.1 Hz, H2; AA'BB' system: 7.03, 2H, d, $J_{AB} + J_{AB'}$ 7.8 Hz, ArH *ortho* to CH_3; 7.45, 2H, d, $J_{AB} + J_{AB'}$ 7.8 Hz, ArH *meta* to CH_3.

Preparation of (*Z*)-1-bromo-2-phenylethene

Bromine (4 ml, 78 mmol) was added dropwise over 1 hour to a stirred solution of cinnamic acid (9.5 g, 64 mmol) in dry chloroform (50 ml). The solution was stirred at room temperature for 2 hours, cooled to 0° and filtered. The precipitate was crystallized from chloroform to yield 2,3-dibromo-3-phenylpropanoic acid (17.1 g, 87%) as a colourless powder, m.p. 197° (lit.[53] 200°). δ (90 MHz, $CDCl_3$ + DMSO-d_6) 4.73, 1H, d, $^3J_{CH,CH}$

11.7 Hz, C*H*(Br)COOH; 5.26, 1H, d, $^3J_{CH,CH}$ 11.7 Hz, Ph-C*H*(Br)-; 7.07-7.39, 5H, m, ArH; 8.44, 1H, bs, COOH.

2,3-Dibromo-3-phenylpropanoic acid (17.1 g, 55 mmol) was refluxed with sodium hydrogencarbonate (15.4 g, 183 mmol) in acetone (250 ml) for 8 hours with protection from light, cooled and the solvent was removed. The residue was extracted into ether (150 ml) and the ether extract was washed with water (150 ml), and brine (50 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled (Kugelrohr) to yield (*Z*)-1-bromo-2-phenylethene (7.37 g, 73%) as a pale yellow oil. b.p. 118°/50 mmHg (lit.[90] 55-6°/2 mmHg). δ (90 MHz, $CDCl_3$) 6.29, 1H, d, $^3J_{CH,CH}$ 8.4 Hz, H1; 6.94, 1H, d, $^3J_{CH,CH}$ 8.4 Hz, H2; 7.12-7.37, 3H, m, ArH; 7.44-7.69, 2H, m, ArH.

Preparation of 1-bromo-2-methylpropene

Bromine (5.5 ml, 107 mmol) was added dropwise over 1 hour to a stirred solution of 3,3-dimethylacrylic acid (10 g, 100 mmol) in dry chloroform (100 ml) at room temperature. The mixture was stirred at room temperature for 15 hours and the solvent was removed. The crude product was crystallized from ethanol to yield 2,3-dibromo-3-methylbutanoic acid (22.19 g, 85%) as orange prisms, m.p. 105-6° (lit.[91] 106-7°). δ (90 MHz, $CDCl_3$) 1.93, 3H, s, CH_3; 2.03, 3H, s, CH_3; 4.60, 1H, s, -C*H*Br-; 9.80, 1H, bs, COOH.

2,3-Dibromo-3-methylbutanoic acid (22.19 g, 85 mmol) was refluxed with sodium carbonate (22.6 g, 213 mmol) in water (100 ml) for 1 hour and diluted with water (100 ml). The crude product was separated and washed with water (10 ml), dried ($CaCl_2$), and distilled over sodium to yield 1-bromo-2-methylpropene (5.03 g, 44%) as a colourless oil, b.p. 90-2°

(lit.[91] 90-1°). δ (90 MHz, $CDCl_3$) 1.83, 6H, m, 2xCH_3; 5.77, 1H, m, =CH-.

Preparation of (*Z*)-2-bromo-1-phenyl-1-propene

A solution of bromine (2 ml, 39 mmol) in carbon tetrachloride (8 ml) was added dropwise to a stirred solution of α-methylcinnamic acid (5 g, 31 mmol) in carbon tetrachloride (50 ml) at 5°. The mixture was stirred at room temperature overnight and the solvent was removed. The residue was crystallized from carbon tetrachloride/light petroleum to yield 2,3-dibromo-2-methyl-3-phenylpropanoic acid (6.18 g, 62%) as colourless needles, m.p. 138° (lit.[92] 137°). δ (90 MHz, $CDCl_3$) 2.08, 3H, s, CH_3; 5.70, 1H, s, CHBr; 7.17-7.61, 5H, m, ArH; 6.6-7.6, 1H, bs, COOH.

2,3-Dibromo-2-methyl-3-phenylpropanoic acid (3.5 g, 11 mmol) was refluxed with potassium carbonate (6 g, 43 mmol) in acetone (20 ml) for 3 hours and the solvent was removed. The residue was extracted into ether (150 ml) and washed with water (2x100 ml). The ether extract was dried (Na_2SO_4), the solvent was removed and the residue was distilled (Kugelrohr) to yield (*Z*)-2-bromo-1-phenyl-1-propene (1.96 g, 92%) as a colourless oil, b.p. 85°/0.44 mmHg (lit.[93] 226°). δ (200 MHz, $CDCl_3$) 2.47, 3H, d, $^4J_{CH,CH3}$ 1.40 Hz, CH_3; 6.70, 1H, bs, =CH-; 7.04-7.59, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.47 produced a 2% n.O.e. at δ 6.70. Irradiation at δ 6.70 produced a 4% n.O.e. at δ 2.47.

Preparation of (*E*)-1-bromo-2-(*p*-methoxyphenyl)ethene

Anisaldehyde (45 g, 0.33 mol) and malonic acid (75 g, 0.72 mol) were heated in pyridine (150 ml) and piperidine (2.5 ml) at 60° for 2 hours. The mixture was refluxed for 5 minutes, cooled and poured onto water (100 ml), and then acidified with hydrochloric acid (10 M, 300 ml) slowly with stirring. The precipitate was collected at the pump and crystallized from ethanol to yield (*E*)-*p*-methoxycinnamic acid (48.3 g, 82%) as colourless needles, m.p. 170° (lit.[94] 171-2°). δ (90 MHz, DMSO-d_6) 3.77, 3H, s, OCH_3; 6.33, 1H, d, $^3J_{CH,CH}$ 16.2 Hz, H2; 7.53, 1H, d, $^3J_{CH,CH}$ 16.2 Hz, H3; AA'BB' system: 6.93, 2H, d, J_{AB} + $J_{AB'}$ 8.7 Hz, ArH *ortho* to MeO; 7.60, 2H, d, J_{AB} + $J_{AB'}$ 8.7 Hz, ArH *meta* to MeO; 12.03, 1H, bs, COOH.

A solution of bromine (38 g, 0.24 mol) in glacial acetic acid (50 ml) was added dropwise over 1 hour to a stirred solution of (*E*)-*p*-methoxycinnamic acid (35.5 g, 0.2 mol) in glacial acetic acid (100 ml). The mixture was stirred at room temperature for 1 hour, chilled and the crude product was collected at the pump, and washed with chilled ether/light petroleum (1:1, 20 ml) to yield 2,3-dibromo-3-(*p*-methoxyphenyl)propanoic acid (40.35 g, 60%), m.p. 149° (lit.[94] 156-7°). δ (90 MHz, DMSO-d_6) 3.73, 3H, s, OCH_3; 5.06, 1H, d, $^3J_{CH,CH}$ 11.9 Hz, H2; 5.43, 1H, d, $^3J_{CH,CH}$ 11.9 Hz, H3; AA'BB' system: 6.83, 2H, d, J_{AB} + $J_{AB'}$ 8.7 Hz, ArH *ortho* to MeO; 7.40, 2H, d, J_{AB} + $J_{AB'}$ 8.7 Hz, ArH *meta* to MeO; 9.37, 1H, bs, COOH.

2,3-Dibromo-3-(*p*-methoxyphenyl)propanoic acid (20 g, 59 mmol) was refluxed with potassium carbonate (20 g, 145 mmol) in acetone (100 ml) for 8 hours, and the solvent was removed. The residue was partitioned between ether (100 ml) and water (100 ml). The ether layer was separated, dried (Na_2SO_4), and the solvent was removed. The crude product was crystallized

from ethanol to yield (*E*)-1-bromo-2-(*p*-methoxyphenyl)ethene (8.12 g, 64%) as colourless plates, m.p. 54° (lit.[94] 55.0-55.5°). δ (90 MHz, $CDCl_3$) 3.70, 3H s, OCH_3; 6.46, 1H, d, $^3J_{CH,CH}$ 13.8 Hz, H1; 6.92, 1H, d, $^3J_{CH,CH}$ 13.8 Hz, H2; AA'BB' system: 6.73, 2H, d, J_{AB} + $J_{AB'}$ 8.7 Hz, ArH *ortho* to MeO; 7.09, 2H, d, J_{AB} + $J_{AB'}$ 8.7 Hz, ArH *meta* to MeO.

Preparation of 1-bromo-2-(*o*-methoxyphenyl)ethene (118)

Malonic acid (16 g, 154 mmol) and *o*-methoxybenzaldehyde (10 g, 73 mmol) were refluxed in pyridine (35 ml) and piperidine 1.0 ml) for 3 hours. The mixture was cooled and poured onto a mixture of water (50 ml) and hydrochloric acid (10 M, 200 ml). The mixture was chilled to 0°, filtered and dried at the pump to give *o*-methoxycinnamic acid (116) (11.84 g, 90%) as colourless needles from ethanol, m.p. 182-4° (lit.[95] 182-3°). δ (90 MHz, DMSO-d_6) 3.83, 3H, s, OCH_3; 6.84, 1H, d, $^3J_{CH,CH}$ 16.2 Hz, H2; 6.83-7.13, 2H, m, ArH; 7.35, 1H, ddd, $^3J_{CH,CH}$ 8.7 Hz, $^3J_{CH,CH}$ 6.9 Hz, $^4J_{CH,CH}$ 1.5 Hz, ArH *para* to MeO; 7.62, 1H, dd, $^3J_{CH,CH}$ 6.9 Hz, $^4J_{CH,CH}$ 1.7 Hz, ArH *ortho* to acrylic acid group; 7.87, 1H, d, $^3J_{CH,CH}$ 16.2 Hz, H3.

Bromine (1.5 ml, 29 mmol) was added dropwise to a stirred suspension of *o*-methoxycinnamic acid (5.00 g, 28 mmol) in dry chloroform (60 ml) at 0°. The mixture was warmed to room temperature and stirred for 30 minutes. The solvent was removed to yield 2,3-dibromo-3-(*o*-methoxyphenyl)propanoic acid (117) (9.48 g, 100%) as a colourless powder, m.p. 130° and 175° (lit.[96] 134° and 177°). ^1H n.m.r. analysis showed this to be a mixture of two isomers as noted by Reimer and Howard.[96] δ (90 MHz, DMSO-d_6 + $CDCl_3$) 3.80, 3H, s, OCH_3; 3.82, 3H, s, OCH_3; 5.20, 1H, d, $^3J_{CH,CH}$ 9.9 Hz, -CHBr-; 5.28, 1H, d, $^3J_{CH,CH}$ 11.7 Hz, -CHBr-; 5.63, 1H, d, $^3J_{CH,CH}$ 9.9 Hz, -CHBr-; 5.73, 1H, d $^3J_{CH,CH}$ 11.7 Hz, -CHBr-; 6.75-7.12, 2H, m, ArH; 7.12-7.67, 2H, m, ArH.

The isomers were prepared in an approximately 2:1 ratio, with the isomer with the larger vicinal coupling constant (11.7 Hz) predominating. Variable temperature ^1H n.m.r. studies showed that the two isomers were diastereomers and not rotamers. The minor component could be slowly converted into the major component by heating in dideuterotetrachloroethane at 100°. This is in agreement with the result obtained by Reimer and Howard,[96] who were able to effect the conversion by heating the low-melting isomer above it's melting point. The n.m.r. experiment showed that no coalescence occurred, as would have been expected, had the two compounds been rotamers.

2,3-Dibromo-3-(*o*-methoxyphenyl)propanoic acid (9.48 g, 28 mmol) was refluxed with potassium carbonate (9.5 g, 69 mmol) in acetone (50 ml) for 5 hours. The solvent was evaporated and the residue was partitioned between water (100 ml) and ether (100 ml). The ether extract was washed with brine (50 ml), dried (Na_2SO_4), and the solvent was removed to yield 1-bromo-2-(*o*-methoxyphenyl)ethene (118) (4.51 g, 75%) as a colourless oil and a 3:2 mixture of (*E*) and (*Z*) isomers, b.p. 100°/0.7 mmHg (lit.[97] 139°/16 mmHg). δ (*E*)-isomer (400 MHz, $CDCl_3$) 3.84, 3H, s, OCH_3; 6.82-6.95, 2H, m, ArH; 6.90, 1H, d, $^3J_{CH,CH}$ 14.00 Hz, H1; 7.21-7.27, 2H, m, ArH; 7.31, 1H, d, $^3J_{CH,CH}$ 14.00 Hz, H2. δ (*Z*)-isomer (400 MHz, $CDCl_3$) 3.82, 3H, s, OCH_3; 6.44, 1H, d, $^3J_{CH,CH}$ 8.00 Hz, H1; 6.82-6.95, 2H, m, ArH; 7.21-7.27, 2H, m, ArH; 7.25, 1H, d, $^3J_{CH,CH}$ 8.00 Hz, H2.

Irradiation of the above 60:40 mixture (0.3 g) in carbon tetrachloride (5 ml) containing iodine (30 mg) for 3 hours, under a tungsten lamp, produced (118) in an *E*:*Z* isomer ratio of 81:19 (by 400 MHz ^1H n.m.r. spectroscopy).

Preparation of (*Z*)-1-bromo-2-(*o*-phenylphenyl)ethene

2-Iodobiphenyl was prepared by the method of Gilman, Kirby, and Kinney in 56% yield as a yellow oil, b.p. 110°/ 0.8 mmHg (lit.[98] 158°/ 6 mmHg).

A solution of dry *N*,*N*-dimethylformamide (9.0 ml, 0.117 mol) in dry ether (100 ml) was added to the Grignard reagent prepared from 2-iodobiphenyl (27.2 g, 0.097 mol) and magnesium turnings (3.5 g, 0.144 mol) in dry ether (250 ml). The solution was refluxed for 1 hour, and quenched with hydrochloric acid (3 M, 300 ml). The ether layer was separated, washed with sodium bisulfite solution (5%, 2x200 ml), water (2x200 ml), and brine (100 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled to yield 2-formylbiphenyl (15.35 g, 87%) as a pale yellow oil, b.p. 120°/ 1 mmHg (lit.[99] 150°/ 7 mmHg). δ (90 MHz, $CDCl_3$) 6.98-7.70, 9H, m, ArH. 10.25, 1H, s, C*H*O.

2-Formylbiphenyl (13.45 g, 74 mmol) and malonic acid (19.20 g, 184 mmol) were refluxed in pyridine (50 ml) and piperidine (5 ml) for 1.5 hours, cooled and poured onto a mixture of ice (100 g) and hydrochloric acid (10 M, 300 ml). The mixture was stirred for 30 minutes, filtered, washed with water (5x20 ml) and dried at the pump, and the residue was crystallized from ethanol to yield *o*-phenylcinnamic acid (8.65 g, 52%) as colourless needles, m.p. 208° (lit.[100] 202°). δ (90 MHz, $CDCl_3$ + DMSO-d_6) 6.28, 1H, d, $^3J_{CH,CH}$ 15.9Hz, H2; 7.06-7.80, 10H, m, ArH + COOH; 7.53, 1H, d, $^3J_{CH,CH}$ 15.9 Hz, H3.

A solution of bromine (2.0 ml, 39 mmol) in dry chloroform (10 ml) was added over 30 minutes to a stirred solution of *o*-phenylcinnamic acid (8.65 g, 39 mmol) in dry chloroform (200 ml),. The solution was stirred at room temperature for 16 hours, washed with sodium bisulfite solution (5%, 100 ml), and brine (80 ml), dried ($CaCl_2$), and the solvent was removed to yield 2,3-dibromo-3-(*o*-phenylphenyl)propanoic acid (14.09 g, 95%) as a pale yellow solid, m.p. 168-73° (lit.[101] 171°). δ (90 MHz, $CDCl_3$ + DMSO-d_6) 5.02, 1H, d, $^3J_{CH,CH}$ 11.7 Hz, H3; 5.42, 1H, d, $^3J_{CH,CH}$ 11.7 Hz, H2; 7.05-7.82, 10H, m, ArH + COOH.

2,3-Dibromo-3-(*o*-phenylphenyl)propanoic acid (14 g, 36 mmol) was refluxed with potassium carbonate (12 g, 87 mmol) in acetone (250 ml) for 3 hours, cooled, and the solvent was removed. The residue was partitioned between ether (200 ml) and water (200 ml). The ether layer was separated, washed with water (200 ml), and brine (100 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled (Kugelrohr) to yield (*Z*)-1-bromo-2-(*o*-phenylphenyl)ethene (7.43 g, 79%) as a colourless oil, b.p. 130° / 0.19 mmHg (lit.[101] 157°/ 0.5 mmHg). δ (90 MHz, $CDCl_3$) 6.23, 1H, d, $^3J_{CH,CH}$ 7.8 Hz, H1; 6.76, 1H, d, $^3J_{CH,CH}$ 7.8 Hz, H2; 7.10-7.60, 8H, m, ArH; 7.76, 1H, m, ArH. The sample was found to contain 28% of the (*E*)-isomer as shown by 2 doublets at δ 6.51 (H1) and δ 6.98 (H2), with $^3J_{CH,CH}$ 13.8 Hz.

Preparation of 1-bromo-2,2-diphenylethene

A solution of benzophenone (125 g, 0.686 mol) in dry ether (200 ml) was added with stirring at gentle reflux to the Grignard reagent prepared from methyl iodide (100 g, 0.705 mol) and magnesium turnings (18 g, 0.740 mol) in sodium-dried ether (300 ml). The mixture was refluxed for 1 hour , cooled and quenched with aqueous ammonium chloride solution (25%, 150

ml). The magnesium salts were dissolved with excess hydrochloric acid (3M). The ether layer was separated, with the aqueous phase being washed with ether (3x500 ml). The combined ether extracts were dried (Na_2SO_4), and the ether was removed. The residue was dehydrated directly by distillation over a catalytic amount of *p*-toluenesulfonic acid, to give 1,1-diphenylethene (59.3 g, 48%) as a colourless liquid, b.p. 95°/0.3 mmHg (lit.[102] 277°). δ (90 MHz, $CDCl_3$) 5.36, 2H, s, $=CH_2$; 7.08-7.43, 10H, m, ArH.

A solution of bromine (4.8 g, 30 mmol) in carbon tetrachloride (10 ml) was added dropwise over 30 minutes to a solution of 1,1-diphenylethene (5 g, 28 mmol) in carbon tetrachloride (50 ml). The solvent was removed by distillation and the residue heated on a steam bath under water pump vacuum for 2 hours. The crude product was distilled (Kugelrohr), b.p. 150°/0.1 mmHg to give 1-bromo-2,2-diphenylethene (6.21 g, 86%) as yellow crystals, m.p. 40° (lit.[103] 40-1°). δ (90 MHz, $CDCl_3$) 6.67, 1H, s, =CH-; 7.00-7.76, 10H, m, ArH.

Preparation of (*Z*)-1-bromo-1,2-diphenylethene

Potassium hydroxide (1.17 g, 21 mmol) was added to a solution of *d,l*-stilbene dibromide[104] (5.4 g, 21 mmol) in ethanol (35 ml). The mixture was refluxed for 1 hour, poured onto water (100 ml), and neutralized with hydrochloric acid (10 M). The mixture was extracted into ether (100 ml), washed with water (2x100 ml), and brine (50 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled (Kugelrohr) to yield (*Z*)-1-bromo-1,2-diphenylethene (3.23 g, 78%) as a pale yellow oil, b.p. 140°/1 mmHg (lit.[105] 187-191°/17 mmHg). δ (90 MHz, $CDCl_3$) 6.75-7.73, 10H, m, ArH; 7.11, 1H, s, =CH-.

Preparation of (*E*)-1-bromo-2-phenyl-1-propene

A solution of acetophenone (38 g, 0.32 mol) in dry ether (100 ml) was added dropwise to the Grignard solution prepared from magnesium turnings (10.00 g, 0.41 mol) and methyl iodide (50 g, 0.35 mol) in dry ether (150 ml). The mixture was refluxed for 2 hours and hydrochloric acid (3 M, 200 ml) was added dropwise. The ether layer was separated and the aqueous layer was extracted with ether (100 ml). The combined ether extracts were washed with water (200 ml), and brine (100 ml), dried (Na_2SO_4), and the solvent was removed to yield 2-phenyl-2-propanol (40.8 g, 95%) as a pale yellow oil.

The crude alcohol was refluxed wth a solution of oxalic acid (30 g, 0.33 mol) in water (300 ml) for 2 hours. The mixture was cooled and extracted with ether (2x100 ml). The combined ether extract was washed with water (200 ml), and brine (100 ml), dried (Na_2SO_4), and the solvent was removed.The residue was distilled to yield 2-phenylpropene (23.62g, 67%) as a colourless oil, b.p. 80°/50mmHg (lit.[106] 161°). δ (90 MHz, $CDCl_3$) 2.13, 3H, s, CH_3; 5.02, 1H, q, $^4J_{CH3,CH}$ 1.5 Hz, =CH-; 5.70, 1H, bs, =CH-; 7.00-7.47, 5H, m, ArH.

Bromine (11 ml, 0.215 mol) was added dropwise over 30 minutes to a stirred solution of 2-phenylpropene (23.5 g, 0.199 mol) in dry chloroform (200 ml). The solution warmed to 60° and was stirred at room temperature overnight. The solvent was removed to yield 1,2-dibromo-2-phenylpropane (51.0 g, 92%) as an unstable pale yellow oil. δ (90 MHz, $CDCl_3$) 2.32, 3H, s, CH_3; 4.02-4.38, 2H, m, CH_2; 7.15-7.58, 5H, m, ArH.

1,2-Dibromo-2-phenylpropane (51 g, 0.183 mol) was added dropwise to a refluxing solution of potassium hydroxide (20 g, 0.356 mol) in absolute ethanol (300 ml). The mixture was refluxed for 2 hours, cooled and filtered. The filtrate was evaporated and the residue was partitioned between ether (200 ml) and water (200 ml). The ether extract was washed with water (100 ml), and brine (100 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled and the distillate was found to be a mixture of isomers by ^1H n.m.r. spectroscopy. Flash chromatography (light petroleum) followed by radial chromatography (light petroleum) gave (*E*)-1-bromo-2-phenyl-1-propene (19.85, 55%) as a colourless oil, b.p. 60°/0.5 mmHg (lit.[107] 58°/0.6 mmHg). δ (100 MHz, $CDCl_3$) 2.20, 3H, d, $^4J_{CH,CH3}$ 1.30 Hz, CH_3; 6.44, 1H, q, $^4J_{CH3,CH}$ 1.30 Hz, =CH-; 7.20-7.50, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.20 produced no n.O.e. at δ 6.44. Irradiation at δ 6.44 produced no n.O.e. at δ 2.20.

Preparation of (*Z*)-1-bromo-2-(*o*-methoxyphenyl)propene

o-Methoxyacetophenone was prepared according to the method of Chakravarti, Haworth, and Perkin[108] in 90% yield as a colourless liquid, b.p. 85°/1 mmHg (lit.[108] 120-1°/13 mmHg). δ (90 MHz, $CDCl_3$) 2.55, 3H, s, CH_3; 3.82, 3H, s, OCH_3; 6.76-7.76, 4H, m, ArH.

Freshly sublimed potassium *tert*-butoxide (2.55 g, 23 mmol) was added under nitrogen to a stirred suspension of (bromomethyl)triphenylphosphonium bromide (9.91 g, 23 mmol) in dry tetrahydrofuran (50 ml) at -78°. The mixture was stirred at -78° for 1 hour and *o*-methoxyacetophenone (3.41 g, 23 mmol) in dry tetrahydrofuran (5 ml) was added at -78°. The mixture was stirred at -78° for 30 minutes, then warmed to room temperature. The solvent was removed and the residue

was partitioned between ether (200 ml) and hydrochloric acid (3 M, 150 ml). The ether extract was washed with hydrochloric acid (3 M, 150 ml), sodium carbonate solution (10%, 100 ml), and brine (100 ml), dried (Na_2SO_4), and the solvent was removed. Flash chromatography (light petroleum) followed by radial chromatography (ethyl acetate/light petroleum 1:999), and preparative HPLC (ethyl acetate/light petroleum 1:999), gave *(Z)-1-bromo-2-(o-methoxyphenyl)propene* (1.96 g, 38%) as a colourless oil, b.p. 115°/1.3 mmHg. (Found: C, 52.9; H, 4.8%. $C_{10}H_{11}BrO$ requires C, 52.9; H, 4.9). λ_{max} (ethanol) 279, 236(sh) nm (ϵ 2531, 5298). υ_{max} (liquid film). δ (200 MHz, $CDCl_3$) 2.06, 3H, d, $^4J_{CH,CH3}$ 1.60 Hz, CH_3; 3.80, 3H, s, OCH_3; 6.21, 1H, q, $^4J_{CH3,CH}$ 1.60 Hz, =CH-; 6.85, 1H, bd, $^3J_{CH,CH}$ 8.10 Hz, ArH *ortho* to MeO; 6.88, 1H, ddd, $^3J_{CH,CH}$ 7.32 Hz, $^3J_{CH,CH}$ 7.32 Hz, $^4J_{CH,CH}$ 1.08 Hz, ArH *para* to MeO; 7.09, 1H, dd, $^3J_{CH,CH}$ 7.32 Hz, $^4J_{CH,CH}$ 1.68 Hz, ArH *ortho* to C=CHBr; 7.25, 1H, ddd, $^3J_{CH,CH}$ 8.10 Hz, $^3J_{CH,CH}$ 7.32 Hz, $^4J_{CH,CH}$ 1.68 Hz, ArH *para* to C=CHBr. Stereochemistry confirmed by n.O.e difference spectroscopy. Irradiation at δ 2.06 produced a 4% n.O.e. at δ 6.21 (and a 1% n.O.e. at δ 7.09). Irradiation at δ 6.21 produced a 5% n.O.e. at δ 2.06 (and a 1% n.O.e. at δ 7.09). ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 23.80, *C*H_3; 55.55, O*C*H_3; 102.86, =*C*H-; 111.11, Ar*C*H *ortho* to MeO; 120.49, Ar*C*H; 128.92, Ar*C*H; 129.48, Ar*C*H; 129.59, C2 or C4; 140.61, C2 or C4; 155.88, Ar*C*OMe. (*m/z*) 228(M^+ +2, 17%), 226(M+, 17), 148(15), 147(100), 133(14), 132(97), 131(76), 130(11), 119(62), 115(27), 104(15), 103(27), 102(11), 91(65), 89(19), 79(10), 78(18), 77(43), 75(11), 74(10), 65(11), 63(33), 62(13), 51(40), 50(19), 43(13), 41(18), 39(34), 38(11). This sample contained 35% of *(E)-1-bromo-2-(o-methoxyphenyl)propene* as shown by the following: δ (200 MHz, $CDCl_3$) 2.13, 3H, d, $^4J_{CH,CH3}$ 1.36 Hz, CH_3; 3.78, 3H, s, OCH_3; 6.24, 1H, q, $^4J_{CH3,CH}$ 1.36 Hz, =CH-; 6.9-7.5, 4H, m, ArH. Stereochemistry confirmed by n.O.e difference spectroscopy. Irradiation at δ 2.13 produced no n.O.e. at δ 6.24. Irradiation at δ 6.24 produced no n.O.e. at δ 2.13 (but

produced a 3% n.O.e. at δ 7.11). ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 20.43, CH_3; 55.36, OCH_3; 106.13, =CH-; 110.83, ArCH *ortho* to MeO; 120.52, ArCH; 129.04, ArCH; 129.33, ArCH; 130.89, C2 or C4; 140.90, C2 or C4; 156.44, ArCOMe.

SYNTHESIS OF TRIBUTYLVINYLSTANNANES

General Method

The Grignard solution prepared from magnesium turnings (1.1 equiv.) and the vinyl bromide (3-4 mmol) in dry tetrahydrofuran (15 ml) was decanted from the excess magnesium turnings by double-ended needle. Tri-*n*-butyltin chloride was titrated into the dark Grignard solution until it decolourised. The resulting solution was stirred at room temperature for 1 hour and the solvent was removed. The residue was partitioned between water (30 ml) and ether (30 ml). The ether layer was separated and washed with brine (50 ml), dried (Na_2SO_4) and the solvent was removed. The residue was distilled (Kugelrohr) to yield the pure tributyl(vinyl)stannane.

The following compounds were prepared according to the above general procedure:

(i) Tributyl[(*E*)-2-phenylethenyl]stannane (9) was prepared in 74% yield as a colourless oil, b.p. 180°/0.9 mmHg (lit.[109] 130-2°/0.1 mmHg). δ (400 MHz, $CDCl_3$) 0.87-1.07, 15H, m, 3xCH_2 and 3xCH_3; 1.28-1.47, 6H, m, 3xCH_2; 1.47-1.65, 6H, m, 3xCH_2; 6.83, 1H, d, $^3J_{CH,CH}$ 19.78 Hz, $^2J_{119Sn,CH}$ and $^2J_{117Sn,CH}$ give average of 64.90 Hz, H1; 6.88, 1H, d, $^3J_{CH,CH}$ 19.78 Hz, H2; 7.18-7.44, 5H, m, ArH. This sample contained approximately 20% of the (*Z*)-isomer as shown by a pair of doublets at δ 6.18 (with $^3J_{CH,CH}$ 14.20 Hz, $^2J_{119Sn,CH}$ 57.81 Hz, $^2J_{117Sn,CH}$ 55.78 Hz, H1) and δ 7.61 (with $^3J_{CH,CH}$ 14.20 Hz, $^3J_{119Sn,CH}$ 137.93 Hz, $^3J_{117Sn,CH}$ 131.84 Hz, H2).

(ii) *Tributyl[(E)-2-(o-methoxyphenyl)ethenyl]stannane* (*E*-113) was prepared in 77% yield as a yellow oil, b.p. 220°/2 mmHg. (Found: C, 59.7; H, 8.5; $^{120}SnM^{+}$-Bu, 367.1068; $^{119}SnM^{+}$-Bu, 366.1097. $C_{21}H_{36}OSn$ requires C, 59.6; H, 8.6%; $^{120}SnM^{+}$-Bu, 367.1084; $^{119}SnM^{+}$-Bu, 366.1095). λ_{max} (ethanol) 349, 301, 255, 204 nm (ϵ 1964, 5522, 10336, 22207). υ_{max} (liquid film) 2057s, 2926s, 2872w, 2853m, 1599m, 1485m, 1464m, 1435w, 1377w, 1335w, 1292m, 1244s, 1180m, 1161w, 1116w, 1049w, 1032w, 993w, 831w, 750s, 673w cm^{-1}. δ (400 MHz, $CDCl_3$) 0.86–1.00, 15H, m, 3x$SnCH_2$ + 3xCH_3; 1.35, 6H, m, 3xCH_2; 1.56, 6H, m, 3xCH_2; 3.83, 3H, s, OCH_3; 6.81, 1H, d, $^{3}J_{CH,CH}$ 19.60 Hz, $^{2}J_{119Sn,CH}$ 73.20 Hz, $^{2}J_{117Sn,CH}$ 70.00 Hz, H1; 6.85, 1H, bd, $^{3}J_{CH,CH}$ 8.4 Hz, ArH *ortho* to MeO; 6.93, 1H, dd, $^{3}J_{CH,CH}$ 7.6 Hz, $^{3}J_{CH,CH}$ 7.6 Hz, ArH *para* to MeO; 7.19, ddd, $^{3}J_{CH,CH}$ 8.4 Hz, $^{3}J_{CH,CH}$ 7.6 Hz, $^{4}J_{CH,CH}$ 1.6 Hz, ArH *para* to CH=CHSnBu_3; 7.27, 1H, d, $^{3}J_{CH,CH}$ 19.60 Hz, $^{3}J_{119Sn,CH}$ and $^{3}J_{117Sn,CH}$ give average of 64 Hz, H2; 7.51, 1H, dd, $^{3}J_{CH,CH}$ 7.6 Hz, $^{4}J_{CH,CH}$ 1.6 Hz, ArH *ortho* to CH=CHSnBu_3. This sample contained approximately 19% of the (*Z*)-isomer as shown by; δ 3.82, 3H, s, OCH_3; 6.24, 1H, d, $^{3}J_{CH,CH}$ 13.50 Hz, $^{2}J_{119Sn,CH}$ 64.0 Hz, $^{2}J_{117SnCH}$ 62.0 Hz, H1(*Z*); 7.69, 1H, d, $^{3}J_{CH,CH}$ 13.50 Hz, H2(*Z*). ^{13}C n.m.r. spectrum (100 MHz, $CDCl_3$) 9.01, $^{1}J_{119Sn,C}$ 343.32 Hz, $^{1}J_{117Sn,C}$ 328.06 Hz, C4; 13.69, C1; 27.28, C2 or C3; 29.13, C2 or C3; 55.49, C13; 110.97, C5; 120.58, C6; 125.98, Ar*C*H; 128.45, Ar*C*H; 129.85, Ar*C*H; 140.41, 2 peaks, Ar*C*H + C8; 156.28, C7. (*m/z*) 371(15%), 369(17), 368(19), 367(100), 366(39), 365(74), 364(31), 363(45), 311(22), 309(16), 271(14), 269(34), 268(13), 267)(24), 265(13), 255(13), 253(18), 251(12), 235(12), 225(14), 223(16), 221(10), 213(12), 211(10), 179(12), 177(23), 175(16), 155(10), 134(12), 121(18), 120(19), 119(28), 118(18), 117(17), 91(28), 57(51), 56(18), 55(13), 51(10).

This compound was also prepared as 60:40 mixture of (*E*) and (*Z*)-isomers from the corresponding 60:40 mixture of (*E*) and (*Z*)-vinyl bromides.

(iii) *Tributyl[(Z)-2-(2-methoxyphenyl)propen-1-yl]stannane* (*Z*-131) was prepared in 86% yield as a pale yellow oil, b.p. 190°/0.4 mmHg. (Found: C, 59.4;* H, 9.1; $M^+(^{120}Sn)$-1, 437.1870; $M^+(^{120}Sn)$-Bu, 381.1237; $M^+(^{118}Sn)$-Bu, 379.1226; $M^+(^{116}Sn)$-Bu, 377.1236. $C_{22}H_{38}OSn$ requires C, 60.4; H, 8.8%; $M^+(^{120}Sn)$-1, 437.1866; $M^+(^{120}Sn)$-Bu, 381.1240; $M^+(^{118}Sn)$-Bu, 379.1235; $M^+(^{116}Sn)$-Bu, 377.1236). λ_{max} (ethanol) 278 nm (ϵ 2931). υ_{max} (liquid film) 2956s, 2925s, 2872w, 2854m, 1592m, 1488m, 1464m, 1434w, 1376w, 1341w, 1293w, 1270w, 1239m, 1181w, 1113w,1072w, 1032w, 961w, 818w, 753m cm^{-1}. δ (200 MHz, $CDCl_3$) 0.55, 6H, t, $^3J_{CH_2,CH_2}$ 8.13 Hz, $^2J_{119Sn,CH_2}$ and $^2J_{117Sn,CH_2}$ give average of 52 Hz (relative area, 18%), 3x$SnCH_2$-; 0.83, 9H, t, $^3J_{CH_2,CH_3}$ 7.31 Hz, 3xCH_3; 1.09-1.44, 12H, m, 6xCH_2; 2.21, 3H, d, $^4J_{CH,CH_3}$ 1.47 Hz, =C(CH_3)-; 3.80, 3H, s, OCH_3; 5.97, 1H, q, $^4J_{CH_3,CH}$ 1.47 Hz, $^2J_{119Sn,CH}$ 71.58 Hz, $^2J_{117Sn,CH}$ 67.98 Hz (relative area, 16%), =CH-; 6.82, 1H, dd, $^3J_{CH,CH}$ 8.22 Hz, $^4J_{CH,CH}$ 1.12 Hz, ArH *ortho* to MeO; 6.88, 1H, ddd, $^3J_{CH,CH}$ 7.40 Hz, $^3J_{CH,CH}$ 7.40 Hz, $^4J_{CH,CH}$ 1.12 Hz, ArH *para* to MeO; 7.03, 1H, dd, $^3J_{CH,CH}$ 7.40 Hz, $^4J_{CH,CH}$ 2.00 Hz, ArH *ortho* to (CH_3)C=CHSn; 7.22, 1H, ddd, $^3J_{CH,CH}$ 8.22 Hz, $^3J_{CH,CH}$ 7.40 Hz, $^4J_{CH,CH}$ 2.00 Hz, ArH *para* to (CH_3)C=CHSn. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.21 produced a 4% n.O.e. at δ 5.97. Irradiation at δ 5.97 produced a 9% n.O.e. at δ 2.21. This sample contained 40% of the (*E*)-isomer as shown by: δ 2.14, 3H, d, $^4J_{CH,CH_3}$ 0.80 Hz, CH_3; 3.78, 3H, s, OCH_3; 5.83, 1H, q, $^4J_{CH_3,CH}$ 0.80 Hz, $^2J_{119Sn,CH}$ and $^2J_{117Sn,CH}$ give average of 69.98 Hz (relative area, 16%), =CH-. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.14 produced a no n.O.e. at δ 5.83. Irradiation at δ 5.83 produced a no n.O.e. at δ 2.14. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 9.97, $^1J_{119Sn,CH_2}$ 345.01 Hz, $^1J_{117Sn,CH_2}$ 330.01 Hz, C4; 13.64, C1; 27.36, C2 or C3; 28.00, C7(Me); 29.01, C2 or C3; 55.09, OCH_3; 110.23, C5; 120.35, ArCH; 128.20 ArCH; 128.44, ArCH; 129.53, ArCH; 135.19, C6; 154.70, C8; 156.79, C9. (*m/z*) 438(M^+, 0.2%), 437 (M^+-1, 1), 385(10), 383(10),

382(13), 381(62), 380(25), 379(46), 378(20), 377(27), 227(12), 225(10), 43(16). * It is proposed that this low carbon analysis is due to the moisture sensitivty of this compound. Sealed samples of this compound start to produce precipitates of bis(tributyltin)oxide after 16 hours.

Ultraviolet irradiation of a solution of this stannane (0.013 g, 2.97×10^{-5} mmol) in deuterochloroform (0.4 ml) for 3 days produced a mixture of *cis* and *trans*-isomers in a ratio of 9:1.

(iv) *Tributyl[(E)-2-(o-phenylphenyl)ethen-1-yl]stannane* (96) was prepared in 68% yield as a colourless oil, b.p. 200°/0.2 mmHg. (Found : C, 66.7; H, 8.4; $(^{120}Sn)M^+-1$, 469.1912; $(^{120}Sn)M^+-Bu$, 413.1277. $C_{26}H_{38}Sn$ requires C, 66.6; H, 8.2%; $(^{120}Sn)M^+-1$, 469.1917; $(^{120}Sn)M^+-Bu$, 413.1291. λ_{max} (ethanol) 262(sh), 237, 208 nm (ϵ 13742, 18171, 24295). υ_{max} (liquid film) 3061w, 3021w, 2957s, 2926s, 2871m, 2853m, 1596w, 1465m, 1376w, 1180w, 1073w, 993w, 874w, 772w, 744m, 701m, 668w cm^{-1}. δ (400 MHz, $CDCl_3$) 0.75-0.98, 15H, m, 3xSn-CH_2- + 3xCH_3, 1.23-1.39, 6H, m, 3xCH_2; 1.39-1.50, 6H, m, 3xCH_2; 6.81, 1H, d, $^3J_{CH,CH}$ 19.41 Hz, $^3J_{119Sn,CH}$ 72.36 Hz, $^3J_{117Sn,CH}$ 68.83 Hz, Ar-*CH*=; 6.89, 1H, d, $^3J_{CH,CH}$ 19.41 Hz, $^2J_{119Sn,CH}$ 66.48 Hz, $^2J_{117Sn,CH}$ 64.12 Hz, =*CH*-Sn-; 7.22-7.50, 8H, m, ArH; 7.65, 1H, d, $^3J_{CH,CH}$ 7.33 Hz, ArH. ^{13}C n.m.r. spectrum (100 MHz, $CDCl_3$) 9.62, $^1J_{119Sn,C}$ 343.93 Hz, $^1J_{117Sn,C}$ 325.98 Hz, C4; 19.68, C1; 125.65, C16; 126.89, C5; 127.28, Ar*C*H; 127.38, Ar*C*H; 127.86, C14 or C15; 129.84, C14 or C15; 129.97, Ar*C*H; 130.83, Ar*C*H; 137.28, ArC; 140.22, ArC; 140.87, ArC; 145.35, C6. (*m/z*) 471(M^++1, 2%), 470(M^+, 3), 469(7), 467(5), 465(3), 418(10), 417(29), 416(10), 415(31), 414(45), 413(91), 412(71), 411(84), 410(60), 409(70), 358(11), 357(32), 356(14), 355(26), 354(12), 353(16), 309(10), 307(12), 305(11), 303(10), 301(31), 300(15), 299(43), 298(20), 297(35), 296(12), 295(18), 273(33), 272(16), 271(27), 270(14), 269(19), 251(11), 181(16), 180(29), 179(100), 178(75), 177(44), 176(24), 175(23), 173(10), 165(23),

152(20), 151(10), 125(13), 123(17), 121(64), 120(37), 119(54), 118(30), 117(32), 116(11), 57(15), 41(33). (Note: this Grignard reaction appears to proceed with considerable inversion of configuration at the double bond. A mixture of the vinyl bromides (*E*:*Z* = 28:72) resulted in the stannane with *E*:*Z* = 91:9. No reason for this inversion could be found, as all other stannane preparations attempted in this work were found to give retention of configuration, within the errors of n.m.r. integrals).

(v) *Tributyl(cyclohexylidenemethyl)stannane* (76) was prepared in 75% yield as a colourless oil, b.p. 200°/0.2 mmHg (lit.[110] no b.p. given). λ_{max} (ethanol) 281, 260, 250 nm (ϵ 109, 652, 967). υ_{max} (liquid film) 2956s, 2926s, 2872w, 2854m, 1606m, 1457m, 1367w, 1072w, 958w, 874w, 808m, 690w, 665w cm^{-1}. δ (400 MHz, $CDCl_3$) 0.88–1.11, 15H, m, 3xSn–CH_2 and 3xCH_3; 1.35–1.51, 6H, m, 3xCH_2 (butyl); 1.51–1.63, 6H, m, 3xCH_2 (butyl); 1.63–1.72, 6H, m, –$(CH_2)_3$–; 2.21, 2H, m, =C(CH_2–)–; 2.35, 2H, m, =C(CH_2–)–; 5.37, 1H, m, $^2J_{119Sn,CH}$ and $^2J_{117Sn,CH}$ give average of 76 Hz (relative area, 17%), =CH–. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 10.26, t, C4; 13.76, q, C1; 26.49, t, C9; 27.40, t, C3; 28.96, 2xt, C8 and C10; 29.35, t, C2; 37.92, t, C7 or C11; 40.26, t, C7 or C11; 118.43, d, C5; 159.34, s, C6. All data in agreement with literature[113] values.

(vi) Tributyl(1-propen-1-yl)stannane (192) was prepared as a mixture of (*E*) and (*Z*)-isomers in 68% yield as a colourless oil, b.p. 75°/0.12 mmHg (lit.[111] 90–2°/0.4 mmHg). δ (200 MHz, $CDCl_3$) 0.70–1.70, 27H, m, $SnBu_3$; (*Z*)-isomer: 1.76, 3H, dd, $^3J_{CH,CH3}$ 6.48 Hz, $^4J_{CH,CH3}$ 1.32 Hz, CH_3; 5.82, 1H, dq, $^3J_{CH,CH}$ 12.49 Hz, $^4J_{CH3,CH}$ 1.32 Hz, $^2J_{119Sn,CH}$ 73.18 Hz, $^2J_{117Sn,CH}$ 69.31 Hz, H1; 6.59, 1H, dq, $^3J_{CH,CH}$ 12.49 Hz, $^3J_{CH3,CH}$ 6.68 Hz, $^3J_{119Sn,CH}$ 153.95 Hz, $^3J_{117Sn,CH}$ 128.96 Hz, H2. (*E*)-isomer: 1.84, 3H, bd, $^3J_{CH,CH3}$ 4.52 Hz, CH_3; 5.88, 1H, bd, $^3J_{CH,CH}$ 18.44 Hz, H1; 6.00, 1H, dq, $^3J_{CH,CH}$ 18.44 Hz, $^3J_{CH3,CH}$ 4.52 Hz, H2.

(vii) *Tributyl[(Z)-1-phenylpropen-2-yl]stannane* (71) was prepared in 72% yield as a colourless oil, b.p. 180°/0.1 mmHg. (Found: C, 62.0; H, 8.8. $C_{21}H_{36}Sn$ requires C, 61.9; H, 8.9%). λ_{max} (ethanol) 249 nm (ϵ 8065). υ_{max} (liquid film) 2940m, 2710w, 1710w, 1600w, 1460w, 1380w, 1075w, 870w, 740w cm^{-1}. δ (400 MHz, $CDCl_3$) 0.72, 6H, t, $^3J_{CH_2,CH_2}$ 8.00 Hz, 3x$SnCH_2$-; 0.83, 9H, t, $^3J_{CH_2,CH_3}$ 6.00 Hz, 3xCH_3; 1.23, 6H, m, 3xCH_2; 1.34, 6H, m, 3xCH_2; 2.10, 3H, d, $^4J_{CH,CH_3}$ 1.80 Hz, $^3J_{^{119}Sn,CH_3}$ 42.80 Hz, $^3J_{^{117}Sn,CH_3}$ 39.10 Hz, =C(CH_3); 7.26, 1H, bs, $^3J_{^{119}Sn,CH}$ and $^3J_{^{117}Sn,CH}$ give average of 125 Hz, =CH-; 7.04-7.50, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.10 produced a 3% n.O.e at 7.26. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 10.58, t, C4; 13.70, q, C1; 27.40, t, C2 or C3; 28.05, q, C6; 29.15, t, C2 or C3; 126.55, 127.71, 127.97, 3xd, C9,10,11; 140.96, d, C7; 142.00, s, C8; 144.47, s, C5. (*m/z*) 355(21%), 352(26), 351(M^+-Bu, 100), 350(54), 349(81), 348(41), 347(51), 295(18), 237(42), 235(31), 121(26), 119(22), 118(27), 117(33).

This stannane was also prepared in 85% yield by the reaction of tributyltin hydride with 1-phenylpropyne (67) at 100°.

(viii) *Tributyl[(Z)-4-phenyl-1-buten-1-yl]stannane* (87) was prepared in 78% yield as a colourless oil, b.p. 200°/0.8 mmHg with data as described for the *E/Z* mixture below.

(ix) Tributyl[(*Z*)-1,2-diphenylethen-1-yl]stannane (193) was prepared in 66% yield as ayellow oil, b.p. 200°/0.9 mmHg (lit.[112] 220°/5 mmHg). δ (200 MHz, $CDCl_3$) 0.69, 6H, t, $^3J_{CH_2,CH_2}$ 8.25 Hz, $^2J_{^{119}Sn,CH_2}$ 51.99 Hz, $^2J_{^{117}Sn,CH_2}$ 50.49 Hz (relative area, 16%), 3x$SnCH_2$; 0.78, 9H, t, $^3J_{CH_2,CH_3}$ 7.10 Hz, 3xCH_3; 1.20-2.10, 12H, m, 6xCH_2; 7.08-7.34, 10H, m, ArH; 7.40, 1H, s, $^3J_{^{119}Sn,CH}$ 119.96 Hz, $^3J_{^{117}Sn,CH}$ 114.56 Hz (relative area, 20%) H2.

(x) *Tributyl[(E)-2-phenyl-1-propen-1-yl]stannane* (66) was prepared in 64% yield as a pale yellow oil, b.p. 150°/0.05 mmHg (Found; C, 62.0; H, 9.3. $C_{21}H_{36}Sn$ requires C, 61.9; H, 8.9%). λ_{max} (ethanol) 254 nm (ϵ 12922). υ_{max} (liquid film) 2930s, 1600w, 1495w, 1460m, 1380w, 1270w, 1200w, 1075w, 870w, 750m cm^{-1}. δ (400 MHz, $CDCl_3$) 0.90, 9H, t, $^3J_{CH_2,CH_3}$ 7.2 Hz, 3xCH_3; 0.98, 6H, t, $^3J_{CH_2,CH_3}$ 9 Hz, 3x$SnCH_2$; 1.33, 6H, m, 3xCH_2; 1.37–1.59, 6H, m, 3xCH_2; 2.21, 3H, d, $^4J_{CH,CH_3}$ 0.68 Hz, $^4J_{^{119}Sn,CH_3}$ and $^4J_{^{117}Sn,CH_3}$ give average of 10 Hz, =C(CH_3)–; 6.28, 1H, q, $^4J_{CH_3,CH}$ 0.68 Hz, $^2J_{^{119}Sn,CH}$ 66 Hz, $^2J_{^{117}Sn,CH}$ 63 Hz, =CH–; 7.20–7.48, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.21 produced no n.O.e at δ 6.28, irradiation at δ 6.28 produced no n.O.e. at δ 2.21. This sample contained 18% of the (*Z*)-isomer as shown by a doublet at δ 2.26 with $^4J_{CH,CH_3}$ 1.47 Hz; and a quartet at δ 5.87, with $^4J_{CH_3,CH}$ 1.47 Hz, and $^2J_{^{119}Sn,CH}$ and $^2J_{^{117}Sn,CH}$ giving an average of 65 Hz. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.26 produced a 3% n.O.e. at δ 5.87. Irradiation at δ 5.87 produced a 9% n.O.e. at δ 2.26. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) 10.45, t, C4; 13.57, q, C1; 24.13, q, C7; 27.33, t, C2 or C3; 29.35, t, C2 or C3; 125.64, d, C11; 126.94, d, C5; 127.78, d, C9 or C10; 128.04, d, C9 or C10; 143.80, s, C8; 151.87, s, C6. (*m/z*) 355 (22%), 352(25), 351(100), 350(54), 349(92), 348(30), 347(63), 295(43), 293(36), 291(33), 279(31), 277(24), 269(38), 267(29), 239(31), 237(54), 236(22), 235(45), 234(26), 233(35), 197(29), 195(29), 193(20), 177(45), 175(22), 121(25), 118(25), 117(24), 77(33), 57(40).

(xi) Tributyl(2,2-diphenylethen-1-yl)stannane (56) was obtained in 61% yield as a colourless liquid, b.p. 160°/0.1 mmHg (lit.[19] 220–30°/1 mmHg). δ (90 MHz, $CDCl_3$) 0.47–1.93, 27H, m, 3x$CH_2CH_2CH_2CH_3$; 6.54, 1H, s, $^2J_{^{119}Sn,CH}$ and $^2J_{^{117}Sn,CH}$ give average of 58 Hz, =CH–; 6.68–7.59, 10H, m, ArH.

(xii) Tributyl(2-methyl-1-propen-1-yl)stannane (55) was prepared in 76% yield as a colourless oil, b.p. 115°/0.8 mmHg (lit.[109] 104-5°/0.4 mmHg). δ (400 MHz, $CDCl_3$) 0.85-0.98, 15H, m, 3xSn-CH_2 + 3xCH_3; 1.25-1.40, 6H, m, 3xCH_2; 1.44-1.55, 6H, m, 3xCH_2; 1.76, 3H, bs, $^4J_{119Sn,CH3}$ and $^4J_{117Sn,CH3}$ give average of 9.50 Hz, CH_3 *cis* to Sn; 1.90, 3H, d, $^4J_{CH,CH3}$ 1.50 Hz, CH_3 *trans* to Sn; 5.44, 1H, bs, $^2J_{119Sn,CH}$ and $^2J_{117Sn,CH}$ give average of 73.62 Hz.

(xiii) *Tributyl[(Z)-2-(o-methylphenyl)ethen-1-yl]stannane* (*Z*-157) was prepared in 86% yield as a pale yellow oil, b.p. 180°/ 0.6 mmHg. (Found: C, 62.1; H, 8.8; $C_{21}H_{36}Sn$ requires C, 61.9; H, 8.9%). λ_{max} (ethanol) 248, 202 nm (ε 7460, 24073). υ_{max} (liquid film) 3063w, 3018w, 2959s, 2927s, 2872w, 2855w, 1600w, 1566w, 1479w, 1463m, 1459m, 1418w, 1377w, 1292w, 1182w, 1073w, 989w, 875w, 756w, 740w, 692w, 666w, 555w cm^{-1}. δ (400 MHz, $CDCl_3$) 0.70, 6H, t, $^3J_{CH2,CH2}$ 8.29 Hz, $^2J_{119Sn,CH2}$ and $^2J_{117Sn,CH2}$ give average of 52.11 Hz (relative area, 18%), 3xSnCH_2-; 0.83, 9H, t, $^3J_{CH2,CH3}$ 7.11 Hz, 3xCH_3; 1.15-1.26, 6H, m, 3xCH_2; 1.26-1.42, 6H, m, 3xCH_2; 2.26, 3H, s, ArCH_3; 6.23, 1H, d, $^3J_{CH,CH}$ 13.50 Hz, $^2J_{119Sn,CH}$ 65.69 Hz, $^2J_{117Sn,CH}$ 62.69 Hz (relative area, 17%), =CHSn; 7.07-7.19, 3H, m, ArH; 7.47, 1H, bd, $^3J_{CH,CH}$ 7.59 Hz, ArH; 7.65, 1H, d, $^3J_{CH,CH}$ 13.50 Hz, $^3J_{119Sn,CH}$ 136.70 Hz, $^3J_{117Sn,CH}$ 131.10 Hz (relative area, 16%), ArCH=. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 9.80, $^1J_{119Sn,CH2}$ 342.00 Hz, $^1J_{117Sn,CH2}$ 329.94 Hz, C4; 12.77, C1; 18.74, ArCH_3; 26.38, C2 or C3; 28.13, C2 or C3; 124.81, Ar*C*H; 126.33, Ar*C*H; 126.58, Ar*C*H; 128.54, Ar*C*H; 132.29, C5; 134.85, C7 or C8; 140.56, C7 or C8; 146.16, C6. (*m/z*) 408(M^+, 0.2%), 355(14), 353(13), 352(15), 351(81), 350(33), 349(63), 348(25), 347(36), 295(13), 293(11), 269(14), 267(10), 239(11), 237(20), 235(20), 233(12), 211(11), 177(11), 121(15), 119(12), 118(11), 117(17), 115(16), 91(10), 58(11), 43(27), 41(14). This sample contained 22% of the (*E*)-isomer as shown by n.m.r.: δ (400 MHz, $CDCl_3$) 0.91, 9H, t, $^3J_{CH2,CH3}$ 7.11 Hz, 3xCH_3; 0.97, 6H, t, $^3J_{CH2,CH2}$ 8.29 Hz,

$^{2}J_{119Sn,CH2}$ and $^{2}J_{117Sn,CH2}$ give average of 66.32 Hz (relative area, 14%), 3x$SnCH_2$–; 1.26–1.42, 6H, m, 3xCH_2; 1.49–1.64, 6H, m, 3xCH_2; 2.36, 3H, s, $ArCH_3$; 6.71, 1H, d, $^{3}J_{CH,CH}$ 19.50 Hz, $^{3}J_{119Sn,CH}$ 72.29 Hz, $^{3}J_{117Sn,CH}$ 68.99 Hz (relative area, 13%), =CHSn; 7.07–7.19, 5H, m, ArH + ArCH=. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 8.79, $^{1}J_{119Sn,CH2}$ 342.00 Hz, $^{1}J_{117Sn,CH2}$ 329.94 Hz, C4; 12.83, C1; 18.74, $ArCH_3$; 26.38, C2 or C3; 28.28, C2 or C3; 124.33, Ar*C*H; 125.16, Ar*C*H; 126.40, Ar*C*H; 129.30, Ar*C*H; 130.34, C5; 133.78, C7 or C8; 137.55, C7 or C8; 143.30, C6. (*m/z*) 408(M^+, 0.2%), 355(14), 353(13), 352(15), 351(81), 350(33), 349(63), 348(25), 347(36), 295(13), 293(11), 269(14), 267(10), 239(11), 237(20), 235(20), 233(12), 211(11), 177(11), 121(15), 119(12), 118(11), 117(17), 115(16), 91(10), 58(11), 43(27), 41(14).

(xiv) Tributyl[(*Z*)-2-phenylethenyl]stannane (91) was prepared in 81% yield as a colourless oil, b.p. 180°/0.9 mmHg (lit.[109] 130–2°/0.1 mmHg). δ (90 MHz, $CDCl_3$) 0.85–1.95, 27H, m, 3x$CH_2CH_2CH_2CH_3$; δ 6.18, 1H, d, $^{3}J_{CH,CH}$ 14.20 Hz, $^{2}J_{119Sn,CH}$ 57.81 Hz, $^{2}J_{117Sn,CH}$ 55.78 Hz, H1; 7.2–7.60,5H, m, ArH; 7.61, 1H, d, $^{3}J_{CH,CH}$ 14.20 Hz, $^{3}J_{119Sn,CH}$ 137.93 Hz, $^{3}J_{117Sn,CH}$ 131.84 Hz, H2.

Other Methods

Preparation of tributyl(cyclopenten-1-yl)stannane (28)

The title compound was prepared via the method of Moloney[19] in 38% yield as a pale yellow oil, b.p. 150°/1 mmHg (lit.[19] 115–25°/0.6 mmHg). δ (200 MHz, $CDCl_3$) 0.76–0.99, 15H, m, 3x$SnCH_2$ + 3xCH_3; 1.18–1.89, 12H, m, 6xCH_2; 5.89, 1H, m, $^{3}J_{119Sn,CH}$ 35.89 Hz, $^{3}J_{117Sn,CH}$ 34.21 Hz, =CH–.

Preparation of tributyl[(*E*)-2-phenylethen-1-yl]stannane (9)

To freshly distilled phenylacetylene (2 ml, 18.2 mmol) was added tributyltin hydride (4.8 ml, 17.8 mmol). The mixture was stirred at 100° for 16 hours, and distilled to yield tributyl[(*E*)-2-phenylethenyl]stannane (6.7 g, 95%) as a colourless oil, b.p. 200°/1.2 mmHg (lit.[109] 130-2°/0.1 mmHg). This sample was free of the (*Z*)-isomer by 90 MHz ^{1}H n.m.r. spectroscopy, and had data identical to that reported above.

Preparation of tributyl(ethenyl)stannane (191)

To a stirred solution of tri-*n*-butyltin chloride (3 g, 9.2 mmol) in dry tetrahydrofuran (10 ml) under nitrogen at 0° was added a solution of vinylmagnesium bromide in tetrahydrofuran (1.0 M, 18 ml, 18 mmol). The mixture was warmed to room temperature, refluxed for 18 hours then cooled to 0°. Ammonium chloride (1 g, 19 mmol) was added and the mixture was stirred for 30 minutes. The solution was diluted with light petroleum (30 ml) and filtered through celite. The solvent was removed and the residue was distilled (Kugelrohr) to yield tributyl(ethenyl)stannane (2.07 g, 71%) as a colourless oil, b.p. 105°/2 mmHg (lit.[113] 95°/1.5 mmHg). δ (200 MHz, $CDCl_3$) 0.71-1.69, 27H, m, $3x(CH_2CH_2CH_2CH_3)$; 5.65,1H, dd, J_{gem} 20.69 Hz, $^3J_{CH,CH}$ 3.75 Hz, $^3J_{119Sn,CH}$ 73.49 Hz, $^3J_{117Sn,CH}$ 69.88 Hz (relative area, 16%), =CH- *cis* to Sn; 6.15, 1H, dd, J_{gem} 14.10 Hz, $^3J_{CH,CH}$ 3.75 Hz, $^3J_{119Sn,CH}$ 146.96 Hz, $^3J_{117Sn,CH}$ 140.96 Hz (relative area, 16%), =CH- *trans* to Sn; 6.47, 1H, dd, $^3J_{CH,CH}$ 20.69 Hz, $^3J_{CH,CH}$ 14.10 Hz, $^2J_{119Sn,CH}$ 82.48 Hz, $^2J_{117Sn,CH}$ 77.98 Hz (relative area, 16%) =CH-Sn.

Preparation of *tributyl[(E)-2-(o-methylphenyl)ethen-1-yl]stannane* (*E*-157)

To freshly distilled *o*-methylphenylacetylene (1.7 g, 15 mmol) was added freshly distilled tri-*n*-butyltin hydride (3.9 ml, 14 mmol). The mixture was heated to 90° for 3 hours and room temperature overnight. The mixture was Kugelrohr distilled to yield *tributyl[2-(o-methylphenyl)-ethen-1-yl]stannane* as a mixture of isomers (*E*:*Z* = 38:62) with data as given above under the corresponding (*Z*)-isomer.

Preparation of *tributyl[(E)-4-phenyl-1-buten-1-yl]stannane* (93)

To 4-phenyl-1-butyne (2.00 g, 15.4 mmol) was added tri-*n*-butyltin hydride (4.10 ml, 15.2 mmol) dropwise. The mixture was stirred at 90° for 5 hours and distilled to yield *tributyl[(E)-4-phenyl-1-buten-1-yl]stannane* (5.83 g, 91%) as a colourless oil, b.p. 200°/0.8 mmHg. (Found: C, 57.6;* H, 9.6; $M^+(^{120}Sn)$-Bu, 365.1259; $M^+(^{118}Sn)$-Bu, 363.1246; $M^+(^{116}Sn)$-Bu, 361.1276. $C_{22}H_{38}Sn$ requires: C, 62.7; H, 9.1%; $M^+(^{120}Sn)$-Bu, 365.1291; $M^+(^{118}Sn)$-Bu, 363.1285; $M^+(^{116}Sn)$-Bu, 361.1287). λ_{max} (ethanol) 260, 203 nm (ϵ 45, 19262). υ_{max} (liquid film) 3028w, 2957s, 2927s, 2872m, 2854m, 1599w, 1525w, 1497w, 1455w, 1376w, 1073w, 989w, 749w, 698w, 669w cm^{-1}. δ (400 MHz, $CDCl_3$) 0.84-0.96, 15H, m, 3x$SnCH_2$ + 3xCH_3; 1.31, 6H, tq, $^3J_{CH_2,CH_2}$ 7.20 Hz, $^3J_{CH_3,CH_2}$ 7.36 Hz, 3xCH_2CH_3; 1.42-1.54, 6H, m, 3x$SnCH_2CH_3$; 2.44, 2H, m, =CH-CH_2-; 2.71, 2H, m, Ph-CH_2-; 5.91, 1H, dt, $^3J_{CH,CH}$ 18.75 Hz, $^4J_{CH_2,CH}$ 1.00 Hz, $^2J_{119Sn,CH}$ 79.02 Hz, $^2J_{117Sn,CH}$ 76.02 Hz, =*CH*-Sn; 6.01, 1H, dt, $^3J_{CH,CH}$ 18.75 Hz, $^3J_{CH_2,CH}$ 5.75 Hz, $^3J_{119Sn,CH}$ 66.51 Hz, $^3J_{117Sn,CH}$ 63.51 Hz, =*CH*-CH_2-; 7.13-7.29, 5H, m, ArH. ^{13}C n.m.r. spectrum (100 MHz, $CDCl_3$) 9.42, $^1J_{119Sn,C}$ 345.10 Hz, $^1J_{117Sn,C}$ 325.09 Hz, C4; 13.70, C1; 27.32, C2 or C3; 29.11, C2 or C3; 35.52, C8; 39.57, $^3J_{119Sn,C}$ and $^3J_{117Sn,C}$ give average of 73.35 Hz, C7; 125.67, C12; 128.20, C10 or C11; 128.48, C10 or C11; 142.11, C9; 148.03, C5 or C6; 148.47, C5 or C6.

(*m/z*, high pressure) 422(M^+, <1%), 421(M^+-1,2), 370(22), 369(53), 368(21), 367(49), 366(58), 365(100), 364(79), 363(95), 362(71), 361(79), 360(15), 359(14), 357(21), 313(19), 311(17), 310(16), 309(53), 308(53), 307(49), 306(27), 305(37), 262(25), 257(17), 255(23), 254(12), 253(53), 252(32), 251(55), 250(41), 249(58), 248(23), 247(33), 223(17), 221(13), 211(14), 209(12), 207(12), 197(24), 195(18), 193(11), 179(31), 178(11), 177(40), 176(16), 175(32), 173(16), 161(12), 159(11), 147(14), 145(12), 132(14), 131(53), 129(27), 125(19), 123(26), 121(57), 120(45), 119(55), 118(37), 117(43), 116(12), 91(67), 65(13), 56(21). This sample contained approximately 19% of the (*Z*)-isomer (19) as shown by signals at δ 2.34, 2H, ddt, $^3J_{CH,CH_2}$ 7.20 Hz, $^4J_{CH,CH_2}$ 1.15 Hz, $^3J_{CH_2,CH_2}$ 8.08 Hz, =CH-CH_2-, δ 5.84, 1H, dt, $^3J_{CH,CH}$ 12.38 Hz, $^4J_{CH_2,CH}$ 1.15 Hz, =C*H*Sn, and δ 6.55, 1H, dt, $^3J_{CH,CH}$ 12.38 Hz, $^3J_{CH_2,CH}$ 7.20 Hz, =C*H*-CH_2-. * No reason could be found for this low carbon analysis. Several attempts at microanalysis produced widely ranging carbon and hydrogen analyses (C, 53.5; H, 4.9, C, 53.7; H, 5.0; C, 55.7; H, 7.3).

Preparation of tributyl(cyclohexen-1-yl)stannane (32)

The title compound was prepared by the method used by Lambert, Wang and Teranova[114] for the analagous trimethylstannane in 69% yield as a colourless oil, b.p. 180°/0.75 mmHg (lit.[19] no b.p. given). λ_{max} (ethanol) no peaks. υ_{max} (liquid film) 2957s, 2927s, 2872m, 2855m, 1612w, 1464m, 1458w, 1376w, 1071w cm^{-1}. δ (200 MHz, $CDCl_3$) 0.85, 6H, t, $^3J_{CH_2,CH_2}$ 8.50 Hz, $^2J_{119Sn,CH_2}$ and $^2J_{117Sn,CH_2}$ give average of 49.00 Hz (relative area, 15%), 3xSnCH_2; 0.89, 9H, t, $^3J_{CH_2,CH_3}$ 7.00 Hz, 3xCH_3; 1.20-1.54, 12H, m, 6xCH_2; 1.59, 4H, m, 2x ring CH_2; 2.06, 2H, m, =C-CH_2; 2.15, 2H, m, =CH-CH_2; 5.80, 1H, tt, $^3J_{CH_2,CH}$ 3.60 Hz, $^4J_{CH_2,CH}$ 2.00 Hz, $^3J_{119Sn,CH}$ 70.74 Hz, $^3J_{117Sn,CH}$ 66.99 Hz (relative area, 19%), =CH-. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 8.82, $^1J_{119Sn,C}$ 327.95 Hz, $^1J_{117Sn,C}$ 312.95 Hz, Sn-CH_2;

13.71, CH_3; 22.74, CH_2; 23.76, CH_2; 27.43, Bu-CH_2; 27.54, CH_2; 29.23, Bu-CH_2; 31.92, CH_2; 137.11, =CH-; 141.14, =CSn-. (*m/z*) 370(M^+-2, 1%) 318(17), 316(15), 315(16), 314(100), 313(37), 312(76), 311(30), 310(44), 263(12), 261(11), 259(69), 258(24), 257(53), 256(20), 255(31), 213(10), 207(17), 205(19), 203(100), 202(32), 201(99), 200(34), 199(69), 198(10), 197(20), 179(22), 177(28), 176(10), 175(21), 125(12), 123(16), 121(65), 120(29), 119(50), 118(24), 117(31), 82(11), 81(19), 79(44), 67(32), 57(10), 55(12), 54(22), 53(14), 41(29), 39(28), 32(25). All data consistent with the literature.[19]

Preparation of *tributyl[(Z)-(o-methoxyphenyl)propen-2-yl]stannane* (146)

To freshly distilled 1-(*o*-methoxyphenyl)propyne (0.90 g, 6.2 mmol) was added tri-*n*-butyltin hydride (1.6 ml, 5.9 mmol). The mixture was stirred at 100° for 16 hours, cooled and distilled to yield *tributyl[(Z)-(o-methoxyphenyl)propen-2-yl]stannane* (2.01 g, 75%) b.p. 195°/ 0.4 mmHg. (Found: C, 59.4;* H, 9.2; M^+(^{120}Sn)-Bu, 381.1239; M^+(^{118}Sn)-Bu, 379.1238; M^+(^{116}Sn)-Bu, 377.1238. $C_{22}H_{38}OSn$ requires C, 60.4; H, 8.8%; M^+(^{120}Sn)-Bu, 381.1240; M^+(^{118}Sn)-Bu, 379.1235; M^+(^{116}Sn)-Bu, 377.1236). λ_{max} (ethanol) 283, 245 nm (ϵ 3713, 8719). υ_{max} (liquid film) 2957s, 2927s, 2872w, 2854m, 1597w, 1486m, 1465m, 1435w, 1376w, 1286w, 1246s, 1177w, 1160w, 1112w, 1072w, 1050w, 1031w, 867w, 752m, 670w cm^{-1}. δ (200 MHz, $CDCl_3$) 0.69, 6H, t, $^3J_{CH_2,CH_2}$ 8.06 Hz, $^2J_{119Sn,CH_2}$ and $^2J_{117Sn,CH_2}$ give average of 52.39 Hz (relative area, 16%), 3xSn-CH_2; 0.83, 9H, t, $^3J_{CH_2,CH_3}$ 7.00 Hz, 3xCH_3; 1.06-1.70, 12H, m, 6xCH_2; 2.12, 3H, d, $^4J_{CH,CH_3}$ 1.70 Hz, $^3J_{119Sn,CH_3}$ 43.09 Hz, $^3J_{117Sn,CH_3}$ 39.95 Hz (relative area, 16%), =(CH_3)Sn; 3.81, 3H, s, OCH_3; 6.80, 1H, bd, $^3J_{CH,CH}$ 8.40 Hz, ArH *ortho* to MeO; 6.87, 1H, dd, $^3J_{CH,CH}$ 7.44 Hz, $^3J_{CH,CH}$ 7.44 Hz, ArH *para* to MeO; 6.95, 1H, dd, $^3J_{CH,CH}$ 7.44 Hz, $^4J_{CH,CH}$ 1.60 Hz, ArH *ortho* to -CH=CSn; 7.21, 1H, ddd, $^3J_{CH,CH}$ 8.40 Hz, $^3J_{CH,CH}$ 7.44 Hz, $^4J_{CH,CH}$ 1.60 Hz, ArH *para* to -CH=CSn; 7.23, 1H,

bs, $^{4}J_{CH3,CH}$ 1.70 Hz, =CH-. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.12 produced a 7% n.O.e. at δ 7.23. Irradiation at δ 7.23 produced a 6% n.O.e. at δ 2.12. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 10.45, $^{1}J_{119Sn,CH2}$ 335.14 Hz, $^{1}J_{117Sn,CH2}$ 321.66 Hz, 3xSn-CH_2; 13.64, 3xCH_3; 27.38, 3xCH_2; 28.00, =C(Sn)-CH_3; 29.05, 3xCH_2; 55.30, OCH_3; 109.88, =CH-; 120.22, Ar*C*H; 128.22, Ar*C*H; 129.25, Ar*C*H; 130.63, Ar*C*-CH=; 136.94, Ar*C*H; 144.52, =*C*(CH_3)Sn-; 157.13, Ar*C*OMe. (*m/z*) 385(17%), 383(16), 382(17), 381(M^+-Bu, 100), 380(36), 379(78), 378(31), 377(41), 325(5), 323(5), 309(20), 307(20), 267(14), 265(10), 225(22), 223(11), 213(14), 211(11), 197(21), 195(13), 194(10), 193(13), 181(14), 179(57), 178(19), 177(81), 176(11), 175(34), 149(19), 148(40), 145(11), 137(11), 135(31), 134(11), 133(26), 132(14), 131(97), 124(17), 123(27), 122(13), 121(77), 120(82), 119(100), 118(65), 117(26), 116(34), 115(41), 105(23), 103(19), 91(97), 89(17), 83(15), 79(16), 77(37), 69(21), 65(10), 63(17), 57(20), 56(19), 55(16), 53(16), 51(17), 50(20), 44(14), 43(14), 41(71), 39(57). * It is proposed that this low carbon analysis is due to the moisture sensitivty of this compound. Sealed samples of this compound start to produce precipitates of bis(tributyltin)oxide after 16 hours.

Ultraviolet irradiation of a solution of this stannane (0.100 g, 0.23 mmol) in deuterochloroform (0.4 ml) for 3 days produced a mixture of *cis* and *trans*-isomers in a ratio of 10:9

Preparation of tributyl[(*Z*)-3-(2-dihydropyranyloxy)propen-1-yl]stannane (195)

To 3-(2-dihydropyranyloxy)propyne[115] (2 g, 14.2 mmol) was added tributyltin hydride (3.9 ml, 14.4 mmol). The mixture was stirred at 100° for 3 hours, cooled and distilled to yield tributyl[(*Z*)-3-(2-dihydropyranyloxy)propen-1-yl]stannane (5.23 g, 85%) as a colourless oil, b.p. 185°/1 mmHg (lit.[116] 140-2°/0.1 mmHg). δ (200 MHz, $CDCl_3$) 0.75- 1.00, 15H, m, 3x$SnCH_2$ + 3xCH_3; 1.20-1.96, 18H, m, 9xCH_2; 3.51, 1H, m, 1x$H_{6'}$; 3.83, 1H, m, 1x$H_{6'}$; 3.87, 1H, ddd, $^2J_{CH,CH}$ 12.60 Hz, $^3J_{CH,CH}$ 6.82 Hz, $^3J_{CH,CH}$ 1.08 Hz, 1xH_3; 4.23, 1H, ddd, $^2J_{CH,CH}$ 12.60 Hz, $^3J_{CH,CH}$ 5.83 Hz, $^3J_{CH,CH}$ 1.08 Hz, 1xH_3; 4.65, 1H, dd, $^3J_{CH,CH}$ 4.3 Hz, $^3J_{CH,CH}$ 3.8 Hz, $H_{2'}$; 6.10, 1H, dd, $^3J_{CH,CH}$ 12.98 Hz, $^4J_{CH2,CH}$ 1.08 Hz, H1; 6.66, 1H, ddd, $^3J_{CH,CH}$ 12.98 Hz, $^3J_{CH,CH}$ 6.82 Hz, $^3J_{CH,CH}$ 5.83 Hz, $^3J_{119Sn,CH}$ 67.41 Hz, $^3J_{117Sn,CH}$ 64.55 Hz (relative area, 16%), H2. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 10.29, $^1J_{119Sn,CH2}$ 334.13 Hz, $^1J_{117Sn,CH2}$ 327.74 Hz, 3x$SnCH_2$; 13.61, 3xCH_3; 19.46, CH_2; 25.45, CH_2; 27.24, $^3J_{Sn,CH2}$ 55.86 Hz, 3xCH_2; 29.06, $^2J_{Sn,CH2}$ 19.32 Hz, 3xCH_2; 30.63, CH_2; 62.10, OCH_2CH_2-; 70.46, OCH_2-CH=; 98.09, CH; 132.38, $^1J_{119Sn,C}$ 361.26 Hz, $^1J_{117Sn,C}$ 346.07 Hz, Sn-CH=; 144.41, =CH-.

SYNTHESIS OF TRIMETHYLVINYLSTANNANES

i) Method A

To a solution of the vinyl bromide (20 mmol) in sodium-dried ether (40 ml) at -78° under a nitrogen atmosphere was added butyllithium (1 equiv.). The solution was warmed to -20° and stirred for 1 hour. The mixture was cooled again to -78° and a solution of trimethyltin chloride (1 equiv.) in sodium-dried ether (20 ml) was added over 15 minutes. The mixture was stirred at -78° for 1 hour and allowed to warm to room temperature overnight. The solution was filtered through celite and the solvent was removed. Distillation gave the pure trimethyl(vinyl)stannane.

ii) Method B

The Grignard solution prepared from the vinyl bromide (20 mmol) and magnesium turnings (1.1 equiv.) in dry tetrahydrofuran (25 ml) was refluxed for 1 hour and decanted from the excess magesium via double-ended needle. To the stirred solution was titrated a solution of trimethyltin chloride (1 equiv.) in dry tetrahydrofuran (15 ml) until the solution decolourised. The mixture was stirred for 16 hours, diluted with light petroleum (40 ml) and filtered through Celite. The filtrate was evaporated and the residue distilled (Kugelrohr) to yield the pure trimethyl(vinyl)stannane.

The following compounds were prepared according to the above general procedures:

(i) *Trimethyl(2,2-diphenylethen-1-yl)stannane* (64) was prepared via method A in 62% yield as a colourless oil, b.p. 130°/0.2 mmHg (lit.[117] 116-8°/0.2 mmHg). λ_{max} (ethanol) 297, 288, 280, 272, 266 nm (ϵ 18195, 16408, 24740, 22350, 22443). υ_{max} (liquid film) 3081w, 3058m, 3032w, 2966m, 2916m, 1664m, 1602m, 1499s, 1443s, 1277w, 1071m, 1027m, 914m, 832w, 756s, 701s cm^{-1}. δ (400 MHz, $CDCl_3$) -0.08, 9H, s, $^2J_{119Sn,CH3}$ 55.78 Hz, $^2J_{117Sn,CH3}$ 53.23 Hz (relative area, 18%), $-SnMe_3$; 6.67, 1H, s, $^2J_{119Sn,CH}$ 68.98 Hz, $^2J_{117Sn,CH}$ 65.78 Hz (relative area, 15%), =CH-; 7.21-7.40, 8H, m, ArH; 7.54, 2H, m, ArH. ^{13}C n.m.r. spectrum (15 MHz, $CDCl_3$) -8.44, q, C1; 127.20, d, C7 or C11; 127.85, d, C7 or C11; 127.98, d, ArC; 128.17, d, ArC; 129.27, d, C2; 131.48, 2xd, 2xArC; 142.72, s, C4 or C8; 144.04, s, C4 or C8; 158.51, s, C3. (*m/z*) 329($R^{120}Sn^+Me_2$, 26%), 328(10), 327(20), 326(8), 325(12), 299(3), 179(31), 178(100), 177(13), 176(25), 152(10), 151(10), 105(17), 89(17), 77(12), 76(16).

(ii) Trimethyl[(*E*)-2-phenylethen-1-yl]stannane (52) was prepared via method B in 42% yield as a pale yellow oil, b.p. 80°/0.7 mmHg (lit.[118] 110-4°/3.5 mmHg). δ (90 MHz, $CDCl_3$) 0.25, 9H, s, $^2J_{119Sn,CH3}$ 56 Hz, $^2J_{117Sn,CH3}$ 53 Hz, $SnMe_3$; 6.92, 2H, s, $^2J_{119Sn,H1}$ and $^2J_{117Sn,H1}$ give an average of 75 Hz, $^3J_{119Sn,H2}$ and $^3J_{117Sn,H2}$ give an average of 111 Hz, 2x=CH-; 7.08-7.58, 5H, m, ArH.

(iii) [(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]trimethylstannane (171) was prepared via method B in 86% yield as a colourless oil, b.p. 120°/0.9 mmHg (lit.[117] m.p. 34-5°, b.p. 104°/0.6 mmHg). δ (200 MHz, $CDCl_3$) 0.10, 9H, s, $^2J_{119Sn,CH3}$ 55.40 Hz, $^2J_{117Sn,CH3}$ 53.19 Hz, $SnMe_3$; 3.68, 3H, s, OCH_3; 6.60, 1H, d, $^3J_{CH,CH}$ 19.40 Hz, H1; 6.74, 1H, d, $^3J_{CH,CH}$ 19.40 Hz, H2; AA'BB' system: 6.75, 2H, d, $J_{AB} + J_{AB'}$ 8.80 Hz, ArH *ortho* to MeO; 7.25, 2H, d, $J_{AB} + J_{AB'}$ 8.80 Hz, ArH *meta* to MeO.

(iv) *Trimethyl[(Z)-1-phenyl-1-propen-2-yl]stannane* (73) was prepared via method B in 82% yield as a colourless oil, b.p. 110°/0.4 mmHg. (Found: C, 51.7; H, 6.3; $C_{12}H_{18}Sn$ requires C, 51.3; H, 6.5%). λ_{max} (ethanol) 343 nm (ϵ 10329). υ_{max} (liquid film) 3075w, 3060w, 3022w, 2978w, 2935m, 2905m, 2875w, 2844w, 2363w, 1712w, 1592w, 1577w, 1490m, 1441m, 1187w, 1072w, 1022w, 978w, 916w, 851m, 770s, 747s, 698s cm^{-1}. (400 MHz, $CDCl_3$) 0.03, 9H, s, $^2J_{119Sn,CH3}$ 54 Hz, $^2J_{117Sn,CH3}$ 52 Hz (relative area , 16%), $SnMe_3$; 2.15, 3H, d, $^4J_{CH,CH3}$ 1.75 Hz, $^3J_{119Sn,CH3}$ 48 Hz, $^3J_{117Sn,CH3}$ 46 Hz (relative area, 18%), CH_3; 7.18-7.39, 5H, m, ArH; 7.29, 1H, m, $^3J_{119Sn,CH}$ and $^3J_{117Sn,CH}$ give average of 138 Hz, =CH-; Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.15 produced an 8% n.O.e. at δ 7.29 (also 6% at δ 0.03). Irradiation at δ 7.29 produced a 3% n.O.e. at δ 2.15 (also 4% at δ 0.03). Irradiation at δ 0.03 produced a 2% n.O.e. at δ 7.20. ^{13}C n.m.r spectrum (15 MHz, $CDCl_3$) -8.25, q, $^1J_{C1,H1}$ 128.3 Hz, $^1J_{119Sn,C1}$ 343.67 Hz*, $^1J_{117Sn,C1}$ 327.69 Hz*, C1; 27.21, dq, $^3J_{C3,H4}$ 9.8 Hz, $^1J_{C3,H3}$ 120.5 Hz, $^2J_{119Sn,C3}$ and $^2J_{117Sn,C3}$ give average of 48.99 Hz*, C3; 126.62, d, $^1J_{C8,H8}$ 161.0 Hz, C8; 127.85, d, $^1J_{C,H}$ 159.6 Hz, C6 or C7; 127.98, d, $^1J_{C,H}$ 159.6 Hz, C6 or C7; 141.03, d, $^1J_{C4,H4}$ 148.2 Hz, $^2J_{119Sn,C4}$ and $^2J_{117Sn,C4}$ give average of 27.48 Hz*, C4; 141.16, s, C5; 144.34, s, $^1J_{119Sn,C2}$ 444.58 Hz*, $^1J_{117Sn,C2}$ 425.59 Hz*, C2 (*- These values determined at 50 MHz). (*m/z*, chemical ionization) 282(M^+,<1%), 271(17), 269(14), 268(12), 267($R^{120}Sn^+Me_2$, 100), 266(35), 265(75), 264(26), 263(45), 165(13), 41(11).

(v) Trimethyl[(*Z*)-2-(*p*-methylphenyl)ethen-1-yl]stannane (194) was prepared via method B in 53% yield as a pale yellow liquid, b.p. 80°/0.2 mmHg (lit.[117] 89°/0.35 mmHg). δ (90 MHz, $CDCl_3$) -0.10, 9H, s, $^2J_{119Sn,CH3}$ and $^2J_{117Sn,CH3}$ give average of 54.0 Hz (relative area, 16%), $SnMe_3$; 2.13, 3H, s, CH_3; 5.90 1H, d, $^3J_{CH,CH}$ 13.5 Hz, H1; 6.53-7.27, 4H, m, ArH; 7.33, 1H, d, $^3J_{CH,CH}$ 13.5 Hz, H2.

(vi) Trimethyl[(*E*)-2-phenyl-1-propen-1-yl]stannane (70) was prepared via method B in 83% yield as a colourless oil, b.p. 130°/13 mmHg (lit.[119] 125°/12 mmHg). δ (200 MHz, $CDCl_3$) 0.19, 9H, s, $^2J_{^{119}Sn,CH_3}$ 55.18 Hz, $^2J_{^{117}Sn,CH_3}$ 52.54 Hz (relative area, 17%), $SnMe_3$; 2.18, 1H, bs, CH_3; 6.22, 1H, bs, $^2J_{^{119}Sn,CH}$ 72.14 Hz, $^2J_{^{117}Sn,CH}$ 69.42 Hz (relative area, 18%), =CH-; 7.09-7.47, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.18 produced no n.O.e. at δ 6.22, but produced a 4% n.O.e. at δ 0.19, and a 3% n.O.e. at δ 7.44. Irradiation at δ 6.22 produced no n.O.e. at δ 2.18, but produced a 4% n.O.e. at δ 0.19, and a 9% n.O.e. at δ 7.44. This sample contained 18% of the (*Z*)-isomer: -0.18, 9H, s, $^2J_{^{119}Sn,CH_3}$ 54.60 Hz, $^2J_{^{117}Sn,CH_3}$ 52.00 Hz, $SnMe_3$; 2.21, 3H, d, $^4J_{CH,CH_3}$ 1.50 Hz, CH_3; 5.85, 1H, q, $^4J_{CH_3,CH}$ 1.50 Hz, $^2J_{^{119}Sn,CH}$ 75.98 Hz, $^2J_{^{117}Sn,CH}$ 72.78 Hz, =CH-; 7.09-7.47, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.21 produced a 2% n.O.e. at δ 5.85 (also 7% at δ -0.18, 4% at δ 7.44). Irradiation at δ 5.85 produced a 13% n.O.e at 2.21 (also 25% at δ -0.18).

(vii) Trimethyl(propen-2-yl)stannane (190) was prepared by method B in 32% yield as a colourless oil, b.p. 130° (lit.[120] 123.5-4.5°/760 mmHg). δ (90 MHz, $CDCl_3$) 2.20, 3H, bs, CH_3; 5.00, 1H, m, and 5.30, 1H, m, $=CH_2$.

Other methods.

Preparation of (Cyclohexen-1yl)trimethylstannane (173)

The title compound was prepared by the method of Lambert, Wang and Teranova[114] in 66% yield as a colourless oil, b.p. 60°/5 mmHg (lit.[114] 88°/12 mmHg). δ (200 MHz, $CDCl_3$) 0.85, 9H, s, $^2J_{^{119}Sn,CH_3}$ 53.18 Hz, $^2J_{^{117}Sn,CH_3}$ 51.09 Hz (relative area 18%), $^1J_{^{13}C,CH_3}$ 128.06 Hz, $SnMe_3$; 1.63,

4H, m, 2xCH_2; 2.08, 2H, m, =C-CH_2-; 2.18, 2H, m, =C-CH_2-; 5.83, 1H, m, $^3J_{119Sn,CH}$ 78.06 Hz, $^3J_{117Sn,CH}$ 74.39 Hz (relative area, 17%), =CH-. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) -10.68, $SnMe_3$; 22.48, CH_2; 23.49, CH_2; 27.28, =C-CH_2; 30.69, =C-CH_2; 136.73, =CH-; 140.72, =C(Sn)-

SYNTHESIS OF VINYLMERCURY BROMIDES

General method

To magnesium turnings (1.1 equiv.) was added 5 ml of a solution of the vinyl bromide (10 mmol) in dry tetrahydrofuran (20 ml) and 1,2-dibromoethane (3 drops). Once initiation had occurred, the remainder of the solution was added over 30 minutes at a gentle reflux. The solution was then refluxed for a further 1 hour and the dark Grignard solution was decanted (double-ended needle) from the excess magnesium and added dropwise over 1 hour to a stirred solution of mercuric bromide (1.1 equiv.) in dry tetrahydrofuran (20 ml). The mixture was refluxed for a further 1 hour and stirred overnight at room temperature. The mixture was centrifuged, and the precipitate of magnesium bromide was washed with tetrahydrofuran (2x30 ml), centrifuged and decanted. The washings were combined and the solvent was removed to yield the crude vinylmercury bromide, which was crystallised from an appropriate solvent.

The following compounds were prepared according to the above general procedure:

(i) (*E*)-2-phenylethenylmercury bromide was obtained in 32% yield as colourless needles from ethanol, m.p. 203° (lit.[121] 203-4°). δ (200 MHz, $CDCl_3$) 6.81, 1H, d, $^3J_{CH,CH}$ 19.48 Hz, H1; 7.16, 1H, d, $^3J_{CH,CH}$ 19.48 Hz, H2; 7.15-7.47, 5H, m, ArH.

(ii) 2-Methylpropen-1-ylmercury bromide was obtained in 35% yield as colourless needles from light petroleum, m.p. 89° (lit.[122] 91-93.5°). δ (200 MHz, $CDCl_3$) 1.93, 3H, d, $^4J_{CH,CH_3}$ 1.25 Hz, $^4J_{^{199}Hg,CH_3}$ 4.26 Hz, *trans*-CH_3; 1.97, 3H, s, $^4J_{^{199}Hg,CH_3}$ 33.69 Hz, *cis*-CH_3; 5.52, 1H, bs, $^2J_{^{199}Hg,CH}$ 283.74 Hz, =CH-. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 5.52 produced an 8% n.O.e. at δ 1.93. Irradiation at δ 1.93 produced a 3% n.O.e at δ 5.52. Irradiation at δ 1.97 produced no n.O.e. at δ 5.52.

(iii) (*E*)-2-phenyl-1-propen-1-ylmercury bromide was obtained in 35% yield as pale yellow needles from cyclohexane/light petroleum, m.p. 175° (lit.[19] 175-6.5°). δ (200 MHz, DMSO-d_6) 2.28, 3H, s, $^4J_{^{199}Hg,CH_3}$ 36 Hz, CH_3; 6.22, 1H, bs, $^2J_{^{199}Hg,CH}$ 212 Hz, =CH-; 7.10-7.50, 5H, m, ArH. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.28 produced no n.O.e. at δ 6.22. Irradiation at δ 6.22 produced no n.O.e. at δ 2.28.

(iv) 2,2-Diphenylethenylmercury bromide was obtained in 55% yield as a pale yellow powder from cyclohexane, m.p. 152-5° (lit.[123] 157°). δ (200 MHz, $CDCl_3$) 6.47, 1H, s, $^2J_{^{199}Hg,CH}$ 234 Hz, =CH-; 7.10-7.56, 10H, m, ArH.

(v) (*E*)-2-(*p*-methoxyphenyl)ethen-1-ylmercury bromide was prepared in 26% yield as pale yellow plates from chloroform, m.p. 222° (lit.[19] 220-2°). δ (200 MHz, $CDCl_3$ + DMSO-d_6) 3.78, 3H, s, OCH_3; 6.59, 1H, d, $^3J_{CH,CH}$ 17.82 Hz, $^2J_{^{199}Hg,CH}$ 248 Hz, H1; 6.80, 1H, d, $^3J_{CH,CH}$ 17.82 Hz, $^3J_{^{199}Hg,CH}$ 284

Hz, H2; AA'BB' system: 6.85, 2H, d, J_{AB} + $J_{AB'}$ 8.73 Hz, ArH *ortho* to MeO; 7.31, 2H, d, J_{AB} + $J_{AB'}$ 8.73 Hz, ArH *meta* to MeO.

Other methods

Preparation of cyclohexen-1-ylmercury bromide (214)

To hydrazine hydrate (40 g, 0.8 mol) and barium oxide (2 g) at 60° was added cyclohexanone (20 g, 0.2 mol) dropwise over 90 minutes. The mixture was diluted with water (100 ml) and extracted into ether (3x100 ml). The ether extract was dried over sodium hydroxide overnight at 0°, filtered and evaporated.

The residue of crude cyclohexanone hydrazone was added dropwise over 30 minutes to a stirred solution of cupric acetate (2 g, 11 mmol) and mercuric acetate (56 g, 0.176 mol) in warm water (500 ml). As the hydrazone was added the solution darkened to a grey suspension of mercury(I)acetate, followed by metallic mercury at the completion of the addition. The hot solution was filtered, cooled, and potassium bromide (9.8 g, 83 mmol) was added. The crude product was collected, washed with water (3x50 ml) and dried at the pump, followed by drying overnight in a vacuum dessicator. The crude product was extracted into light petroleum (150 ml) using a Soxholet extractor, and the residue was recrystallized from light petroleum to yield cyclohexen-1-ylmercury bromide (3.79 g, 5%) as colourless leaflets, m.p. 174° (lit.[124] 174-5°). δ (200 MHz, $CDCl_3$) 1.65, 4H, m, 2xCH_2; 2.19, 2H, m, CH_2; 2.33, 2H, m, $^3J_{^{199}Hg,CH2}$ 40.29 Hz (relative area 16%), CH_2; 5.66, 1H, tt, $^3J_{CH2,CH}$ 2.02 Hz, $^4J_{CH2,CH}$ 1.80 Hz, $^3J_{^{199}Hg,CH}$ 298.31 Hz (relative area 15%), =CH-.

SYNTHESIS OF VINYLMERCURY ACETATES

General method

To a stirred solution of the vinylmercury bromide (3 mmol) in dry tetrahydrofuran (40 ml) was added silver acetate (1 equiv.) and the mixture was stirred overnight at room temperature in the dark, filtered through celite, and the solvent was removed. The crude product was crystallised from an appropriate solvent.

The following compounds were prepared according to the above general procedure:

(i) (*E*)-2-phenylethen-1-ylmercury acetate (5) was obtained in 59% yield as a colourless powder from *n*-heptane, m.p. 145° (lit.[19] 146-8°). δ (200 MHz, $CDCl_3$) 2.06, 3H, s, $OCOCH_3$; 6.50, 1H, d, $^3J_{CH,CH}$ 17.99 Hz, $^2J_{199Hg,CH}$ 240.93 Hz (relative area, 17%), =C*H*-Hg; 6.81, 1H, d, $^3J_{CH,CH}$ 17.99 Hz, $^3J_{199Hg,CH}$ 293.91 Hz (relative area, 17%), ArC*H*=; 7.24-7.45, 5H, m, ArH.

(ii) (*E*)-2-phenyl-1-propen-1-ylmercury acetate (13) was prepared in 74% yield as colourless needles from chloroform/cyclohexane, m.p. 122° (lit.[19] 125-8°). δ (90 MHz, $CDCl_3$) 2.10, 3H, s, $OCOCH_3$; 2.42, 3H, d, $^4J_{CH,CH3}$ 1.2 Hz, CH_3; 6.26, 1H, bs, $^2J_{199Hg,CH}$ 234.0 Hz, =CH-; 6.95-7.67, 5H, m, ArH.

(iii) Cyclohexen-1-ylmercury acetate (216) was prepared in 56% yield as colourless plates from cyclohexane, m.p. 112-3° (lit.[124] 116-116.5°). δ (200 MHz, $CDCl_3$) 1.49-1.79, 4H, m, 2xCH_2; 2.08, 3H, s, $OCOCH_2$; 2.14-2.37, 4H, m, 2xCH_2; 5.67, 1H, m, $^3J_{199Hg,CH}$ 301.42 Hz (relative area, 16%), =CH-.

(iv) 2,2-Diphenylethenylmercury acetate (255) was prepared in 24% yield as colourless needles from cyclohexane, m.p. 127-9° (lit.[125] 130°). δ (200 MHz, $CDCl_3$) 2.02, 3H, s, $OCOCH_3$; 6.25, 1H, s, $^2J_{^{199}Hg,CH}$ 240.43 Hz, =CH-; 7.21-7.34, 5H, m, ArH; 7.34-7.47, 5H, m, ArH.

SYNTHESIS OF DIVINYLMERCURY COMPOUNDS

(a) General methods

Method A. To a stirred solution of sodium hydroxide (20 equiv.) in distilled water (4 ml) was added stannous chloride (1.5 equiv.) in distilled water (10 ml); then a suspension of the vinylmercury bromide (2-3 mmol) in water (10 ml) and ethanol (10 ml), added over 1 hour. The mixture was stirred overnight at room temperature, diluted with water and extracted into ether (3x40 ml). The combined ether extracts were dried (Na_2SO_4) and the solvent was removed to yield the crude product. Distillation (Kugelrohr) or crystallisation gave the pure divinylmercury compound.

Method B. To a solution of the vinylmercury bromide (1 g) in acetone (50 ml) was added a solution of potassium iodide (4 g) in acetone (60 ml) and water (7 ml). The mixture was stirred at room temperature for 3 hours, filtered, dried and crystallized to give the pure divinylmercury compound

The following compounds were prepared according to the above general procedure:

(i) Bis[(*E*)-2-phenylethen-1-yl]mercury (7) was obtained via Method B in 60% yield as colourless needles from heptane, m.p. 138-140° (lit.[19] 136-40°). δ (400 MHz, $CDCl_3$) 6.78, 1H, d, $^3J_{CH,CH}$ 19.27 Hz, H2; 7.14, 1H, d, $^3J_{CH,CH}$ 19.27 Hz, H1; 7.18-7.54, 5H, m, ArH. This sample contained approximately 15% of the (*Z*)-isomer as characterised by a pair of doublets at δ 6.63 and δ 7.97 with $^3J_{CH,CH}$ 13.18 Hz.

(ii) Bis(cyclohexen-1-yl)mercury (34) was obtained via Method A in 87% yield as a colourless liquid, b.p. 120°/0.1 mmHg (lit.[124] 170°/10 mmHg). δ (400 MHz, $CDCl_3$) 1.54, 2H, m, CH_2; 1.62, 2H, m, CH_2; 2.07-2.27, 4H, m, 2xCH_2; 5.51, 1H, m. $^3J_{^{199}Hg,CH}$ 136.21 Hz (relative area, 16%), =CH-.

(iii) Bis[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]mercury (178) was prepared via Method B in 70% yield as colourless plates from toluene, m.p. 174° (lit.[19] 172-6°). δ (200 MHz, $CDCl_3$) 3.83, 3H, s, OMe; 6.75, 1H, d, $^3J_{CH,CH}$ 19.51 Hz, $^3J_{^{199}Hg,CH}$ 143 Hz (relative area, 16%), H2; 7.01, 1H, d, $^3J_{CH,CH}$ 19.51 Hz, $^2J_{^{199}Hg,CH}$ 116 Hz (relative area, 16%), H1; AA'BB' system: 6.88, 2H, d, $J_{AB} + J_{AB'}$ 8.65 Hz, ArH *ortho* to MeO; 7.36, 2H, d, $J_{AB} + J_{AB'}$ 8.65 Hz, ArH *meta* to MeO.

(iv) Bis(2,2-diphenylethenyl)mercury (57) was prepared via Method A in 44% yield as colourless needles from ether, m.p. 139° (lit.[126] 140.5°). δ (200 MHz, $CDCl_3$) 6.66, 1H, s, $^2J_{^{199}Hg,CH}$ 114.86 Hz, =CH-; 7.13-7.34, 10H, m, ArH.

(v) Bis[(*E*)-2-phenylpropen-1-yl]mercury (11) was prepared via Method B in 89% yield as a colourless powder from cyclohexane/light petroleum, m.p. 144° (lit.[19] 141-3°). δ (200 MHz, $CDCl_3$) 2.42, 3H, bs, $^4J_{^{199}Hg,CH_3}$ 17.78 Hz (relative area, 15%), CH_3; 6.65, 1H, bs, $^2J_{^{199}Hg,CH}$ 105.50 Hz (relative area, 15%), 7.18-7.53, 5H, m, ArH.

(vi) Bis(2-methylpropen1-yl)mercury (189) was prepared via Method A in 44% yield as a colourless oil, b.p. 135°/0.4 mmHg (lit.[19] 150°/1 mmHg). δ (200 MHz, $CDCl_3$) 1.89, 3H, d, $^4J_{CH,CH3}$ 1.19 Hz, *trans*-CH_3; 1.92, 3H, bs, *cis*-CH_3; 5.83, 1H, bs, $^2J_{199Hg,CH}$ 117.56 Hz; =CH-. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 1.89 produced a 2% n.O.e. at δ 5.83. Irradiation at δ 1.92 produced no n.O.e. at δ 5.83. Irradiation at δ 5.83 produced a 8% n.O.e. at δ 1.89.

Other methods.

Preparation of bis[(*Z*)-1-phenylpropen-2-yl]mercury (177)

The Grignard reagent prepared from (*Z*)-2-bromo-1-phenylpropene (5.00 g, 25 mmol) and magnesium turnings (0.74 g, 30 mmol) in tetrahydrofuran (25 ml) was decanted at room temperature via a double-ended needle onto a solution of mercuric bromide (4.5 g, 12 mmol) in tetrahydrofuran (10 ml). The mixture was refluxed for 1 hour and stirred at room temperature overnight. The solution was filtered through celite, the solvent was removed and the residue was recrystallised from cyclohexane/light petroleum to give the title compound (3.679 g, 70%), m.p. 126-7° (lit.[19] 125-8°) δ (200 MHz, $CDCl_3$) 2.11, 3H, d, $^4J_{CH,CH3}$ 1.74 Hz, $^3J_{199Hg,CH3}$ 92.40 Hz (relative area, 17%), CH_3; 7.13-7.41, 5H, m, ArH; 7.64, 1H, bq, $^4J_{CH3,CH}$ 1.74 Hz, $^3J_{199Hg,CH}$ 226.10 Hz (relative area, 18%), =CH-. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 2.11 produced an 11% n.O.e. at δ 7.64. Irradiation at δ 7.64 produced an 8% n.O.e. at δ 7.64 (and 5% at δ 7.34).

MISCELLANEOUS SYNTHESES

Preparation of (carbethoxymethylene)triphenylphosphorane

Triphenylphosphine (20.02 g, 76.3 mmol) and ethyl bromoacetate (8.5 ml, 76.3 mmol) in dry benzene (40 ml) were refluxed for 30 minutes and stirred at room temperature for 1 hour. The product was collected at the pump, washed with dry benzene (2x20 ml) and dried at the pump to give (carbethoxymethyl)triphenylphosphonium bromide (32 g, 98%), m.p. 154° (lit.[127] 158°).

The above phosphonium salt (32 g, 75 mmol) in water (800 ml) was titrated with sodium hydroxide (3M, 25 ml) to above pH 10 and stirred for 30 minutes. (Carbethoxymethylene)triphenylphosphorane (23.72 g, 91%) was collected and dried at the pump as a colourless powder, m.p. 116-7° (lit.[127] 117°). δ (90 MHz, $CDCl_3$) 1.00, 3H, bt, $^3J_{CH_2,CH_3}$ 7.5 Hz, $-OCH_2CH_3$; 2.82, 1H, bs, =CH-; 3.89, 2H, q, $^3J_{CH_3,CH_2}$ 7.5 Hz, $-OCH_2CH_3$; 7.20-7.74, 15H, m, ArH.

Preparation of (bromomethyl)triphenylphosphonium bromide

Triphenylphosphine (30 g, 114 mmol) and dibromomethane (44.6 g, 257 mmol) were refluxed in sodium-dried benzene (100 ml) for 24 hours and chilled to 0°. The mixture was filtered at the pump and the residue was washed with cold, dry benzene (3x20 ml) to give (bromomethyl)triphenylphosphonium bromide (19.97 g, 40%) as a grey powder, m.p. 238-9° (lit.[85] 241°).

Preparation of triethylphosphonoacetate

Triethylphosphite (21 g, 126 mmol) and ethyl bromoacetate (21.1 g, 126 mmol) were stirred at 130° for 2 hours. The mixture was distilled to yield triethylphosphonoacetate (26.12 g, 92%) as a colourless oil, b.p. 80°/0.08 mmHg (lit.[128] 152-3°/20mmHg). δ (90 MHz, $CDCl_3$) 1.14-1.50, 9H, m, 3x-OCH_2CH_3; 2.92, 2H, d, $^2J_{P,H}$ 21 Hz, CH_2; 3.93-4.34, 6H, m, 3x-OCH_2CH_3

Preparation of 3-phenylpropanal

To a solution of 3-phenylpropanoic acid (5 g, 33 mmol) in dry benzene (50 ml) was added oxalyl chloride (4 ml, 47 mmol) at room temperature under nitrogen. The mixture was stirred at room temperature for 1 hour, and the solvent was removed to yield 3-phenylpropanoyl chloride (5.41 g, 96%) as a colourless oil. δ (90 MHz, $CDCl_3$) 2.80-3.33, 4H, m, 2xCH_2; 6.97-7.50, 5H, m, ArH.

A solution of 2,6-dimethylpyridine (3.6 g, 34 mmol), palladium on charcoal catalyst (100 mg) in dry tetrahydrofuran (150 ml) was flushed with dry hydrogen and cooled to 0°. 3-Phenylpropanoyl chloride (5.41 g, 32 mmol) was added and the uptake of hydrogen monitored until 1 equivalent (780 ml) had been consumed. The solution was filtered through Celite, the solvent was removed and the residue extracted into ether (80 ml). The ether extract was washed with hydrochloric acid (3M, 2x80 ml), sodium carbonate solution (10%, 2x80 ml), and brine (50 ml), dried (Na_2SO_4), and the solvent was removed. The crude product was distilled to yield 3-phenylpropanal (3.47 g, 78%) as a colourless oil, b.p. 60°/1 mmHg (lit.[129] 105°/13 mmHg). δ (90 MHz, $CDCl_3$) 2.36-3.01, 4H, m, 2xCH_2; 6.82-7.32, 5H, m, ArH; 9.60, 1H, bs, -CHO.

Preparation of *o*-phenylphenylacetylene (99)

o-Phenylphenylacetylene was prepared according to the method of Faseeh and Zaheer[101] in 79% yield as a colourless liquid, b.p. 110°/1 mmHg (lit.[101] 137°/ 3 mmHg). δ (90 MHz, $CDCl_3$) 2.91, 1H, s, ≡CH; 7.00-7.67, 9H, m, ArH.

Preparation of 4-phenyl-1-butyne (90)

To the Grignard solution prepared from magnesium turnings (5.5 g, 0.23 mol) and benzyl bromide (25 ml, 0.21 mol) in dry ether (200 ml) was added a solution of allyl bromide (19 ml, 0.22 mol) in dry ether (50 ml). The mixture was stirred for 16 hours at room temperature and hydrochloric acid (3M, 200 ml) was added. The ether phase was separated and washed with sodium bisulfite solution (5%, 50 ml), water (100 ml), and brine (30 ml), dried (Na_2SO_4), and the solvent was removed. The crude product was distilled (Kugelrohr) to yield 4-phenyl-1-butene (16.66 g, 60%) as a colourless oil, b.p. 100°/24 mmHg (lit.[130] 64°/10 mmHg). δ (200 MHz, $CDCl_3$) 2.37, 2H, m, CH_2; 2.70, 2H, bt, $^3J_{CH_2,CH_2}$ 7.2 Hz, Ph-CH_2; 4.97, 1H, ddt, $^3J_{CH,CH}$ 10.27 Hz, $^2J_{CH,CH}$ 1.88 Hz, $^4J_{CH_2,CH}$ 1.25 Hz, =C(*H*)H *trans* to CH_2; 5.04, 1H, ddt, $^3J_{CH,CH}$ 16.91 Hz, $^2J_{CH,CH}$ 1.88 Hz, $^4J_{CH_2,CH}$ 1.50 Hz, =C(*H*)H *cis* to CH_2; 5.85, 1H, ddt, $^3J_{CH,CH}$ 16.91 Hz, $^3J_{CH,CH}$ 10.27 Hz, $^3J_{CH_2,CH}$ 6.51 Hz, =C*H*-CH_2; 7.06-7.35, 5H, m, ArH

Bromine (0.8 ml, 15.6 mmol) was added dropwise to a stirred solution of 4-phenyl-1-butene (1.94 g, 14.7 mmol) in dry chloroform (20 ml) over 10 minutes. The mixture was stirred for 1 hour, and the chloroform solution was washed with sodium bisulfite solution (5%, 100 ml), dried ($CaCl_2$) and the solvent was removed to yield 1,2-dibromo-4-phenylbutane as a pale yellow oil.

1,2-Dibromo-4-phenylbutane (all of the above) was added dropwise over 30 minutes to a suspension of sodium amide prepared from sodium (0.8 g, 35 mmol), liquid ammonia (200 ml) and ferric chloride hexahydrate (2 mg) was added. The mixture was stirred at -33° for 2 hours with periodic topping-up of the liquid ammonia. Ammonium chloride (2g, 37 mmol) was slowly added, and the ammonia allowed to evaporate. The residue was then partitioned between water (100 ml) and ether (100 ml). The ether layer was separated, washed with brine (50 ml), dried (Na_2SO_4), and the solvent was removed. The crude product was purified by flash chromatography (light petroleum) to yield 4-phenyl-1-butyne (0.49 g, 26%) as a colourless oil, b.p. 110°/17 mmHg (Kugelrohr) (lit.[131] 72-8°/11 mmHg). δ (200 MHz, $CDCl_3$) 1.97, 1H, t, $^4J_{CH_2,CH}$ 2.66 Hz, ≡CH; 2.48, 2H, dt, $^4J_{CH,CH_2}$ 2.66 Hz, $^3J_{CH_2,CH_2}$ 7.50 Hz, $CH_2C\equiv$; 2.84, 2H, bt, $^3J_{CH_2,CH_2}$ 7.50 Hz, Ph-CH_2-; 6.85-7.35, 5H, m, ArH.

Preparation of *o*-methoxyphenylacetylene (121)

o-Methoxyphenylacetylene was prepared according to the method of Barton and Groh[132] in 67% yield as a colourless liquid, b.p. 130°/20 mmHg (lit.[132] 80-2°/1 mmHg). δ (90 MHz, $CDCl_3$) 2.15, 1H, s, ≡CH; 3.81, 3H, s, OCH_3; 6.8-7.4, 4H, m, ArH.

Preparation of 1-(*o*-methoxyphenyl)propyne (134)

1-(*o*-Methoxyphenyl)propyne was prepared according to the method of Barton and Groh[132] in 75% yield as a pale yellow oil, b.p. 150°/19 mmHg (lit.[132] 115-7°/9 mmHg). δ (200 MHz, $CDCl_3$) 2.09, 3H, s, CH_3; 3.86, 3H, s, OCH_3; 6.79-6.96, 2H, m, ArH *ortho* and *para* to OCH_3; 7.22, 1H, ddd, $^3J_{CH,CH}$ 7.98 Hz, $^3J_{CH,CH}$ 7.98 Hz, $^4J_{CH,CH}$ 1.75 Hz, ArH *para* to C≡C; 7.37, 1H, dd, $^3J_{CH,CH}$ 7.48 Hz, $^4J_{CH,CH}$ 1.75 Hz. ArH *ortho* to C≡C.

Preparation of 1-phenylpropyne (67)

Butyllithium (2.3 M, 9 ml, 20.7 mmol) was added dropwise to a stirred solution of phenylacetylene (2.00 g, 19.6 mmol) in dry tetrahydrofuran (60 ml) under nitrogen at -80°. The mixture was stirred at -80° for 20 minutes, and methyl iodide (1.3 ml) was then added dropwise. The mixture was allowed to warm to room temperature, stirred for 1 hour and quenched with ammonium chloride solution (10%, 40 ml). The mixture was extracted into ether (100 ml), washed with water (100 ml), and brine (30 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled (Kugelrohr) to yield 1-phenylpropyne (2.09 g, 92%) as a colourless oil, b.p. 105°/18 mmHg (lit.[133] 74-5°/14 mmHg). δ (90 MHz, $CDCl_3$) 2.00, 3H, s, CH_3; 7.03-7.53, 5H, m, ArH.

Preparation of *o*-methylphenylacetylene (158)

o-Methylphenylacetylene was prepared according to the method of Tirpak, Hollingsworth, and Wotiz[134] in 21% yield, b.p. 80°/20 mmHg (lit.[134] 42-4°/6 mmHg). δ (90 MHz, $CDCl_3$) 2.41, 3H, s, CH_3; 3.19,1H, s, ≡CH; 6.85-7.22, 3H, m, ArH; 7.35, 1H, m, ArH.

Preparation of (*E*)-1-phenyl-1-propene (74)

A solution of benzaldehyde (3.85 g, 36 mmol) in dry ether (30 ml) was added dropwise to the Grignard solution prepared from ethyl bromide (4 g, 37 mmol) and magnesium turnings (1.06 g, 44 mmol) in dry ether (50 ml). The mixture was refluxed for 1 hour, cooled, and quenched with hydrochloric acid (3M, 50 ml). The ether layer was separated, washed with water (2x100 ml), and sodium carbonate solution (10%, 100 ml), dried (Na_2SO_4), and the solvent was removed to yield 1-phenyl-1-propanol (4.7 g,

96%) as a colourless oil. δ (90 MHz, $CDCl_3$) 0.85, 3H, t, $^3J_{CH_2,CH_3}$ 7.2 Hz, CH_3; 1.72, 2H, dq, $^3J_{CH,CH_2}$ 6.5 Hz, $^3J_{CH_3,CH_2}$ 7.2 Hz, CH_2; 2.28, 1H, bs, OH; 4.45, 1H, t, $^3J_{CH_2,CH}$ 6.5 Hz, C*H*OH; 7.18, 5H, m, ArH.

1-Phenyl-1-propanol (4.70 g, 35 mmol) was refluxed with sulfuric acid (20%, 100 ml) for 45 minutes, cooled, and extracted into ether (100 ml). The ether extract was separated and washed with water (100 ml), sodium carbonate solution (10%, 100 ml), and brine (50 ml), dried (Na_2SO_4), and the solvent was removed. The residue was purified by flash chromatography (light petroleum) to yield (*E*)-1-phenyl-1-propene (1.178 g, 29%) as a colourless oil, b.p. 85°/28 mmHg (lit.[135] 74°/13 mmHg). δ (200 MHz, $CDCl_3$) 1.83, 3H, dd, $^3J_{CH,CH_3}$ 6.28 Hz, $^4J_{CH,CH_3}$ 1.24 Hz, CH_3; 6.19, 1H, dq, $^3J_{CH,CH}$ 15.83 Hz, $^3J_{CH_3,CH}$ 6.28 Hz, =C*H*-CH_3; 6.37, 1H, dq, $^3J_{CH,CH}$ 15.83 Hz, $^4J_{CH_3,CH}$ 1.24 Hz, Ph-C*H*=; 7.08-7.34, 5H, m, ArH.

Preparation of 1,2-dihydronaphthalene (95)

A solution of α-tetralone (3.95 g, 27 mmol) in sodium-dried ether (20 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (5.13 g, 135mmol) in sodium-dried ether (80 ml) under nitrogen. The mixture was refluxed for 3 hours, cooled and quenched successively with methanol (10 ml), water (100 ml) and hydrochloric acid (10M) until all inorganic salts were dissolved. The ether layer was separated, washed with brine (100 ml), dried (Na_2SO_4), and the solvent was removed to yield 1,2,3,4-tetrahydro-1-naphthol (4.01 g, 100%) as a colourless oil. δ (90 MHz, $CDCl_3$) 1.53-3.03, 7H, m, 3xCH_2 + OH; 5.19, 1H, m, C*H*-OH; 6.72-7.35, 4H, m, ArH.

The above alcohol (4.01 g, 27 mmol) was refluxed with freshly distilled acetic anhydride (100 ml) for three hours, cooled and poured onto chipped ice (100 g). The slurry was stirred for 1 hour and extracted with ether (100 ml). The ether layer was washed with sodium carbonate solution (10%, 2x100 ml), and brine (100 ml), dried (Na_2SO_4), and the solvent was removed. The crude product was purified by flash chromatography (light petroleum/ethyl acetate, 1:1) followed by distillation (Kugelrohr) to give 1,2-dihydronaphthalene (2.18 g, 62%) as a colourless oil, b.p. 65°/3 mmHg (lit.[136] 84°/12 mmHg). δ (90 MHz, $CDCl_3$) 2.15-2.40, 2H, m, CH_2; 2.75, 2H, t, $^3J_{CH_2,CH_2}$ 8.3 Hz, Ar-C*H*$_2$-; 5.92, 1H, dt, $^3J_{CH,CH}$ 9.6 Hz, $^3J_{CH_2,CH}$ 4.1 Hz, =C*H*-CH$_2$-; 6.35, 1H, dt, $^3J_{CH,CH}$ 9.6 Hz, $^4J_{CH_2,CH}$ 1.6 Hz, Ar-C*H*=; 6.77-7.20, 4H, m, ArH.

Preparation of benzofuran (120)

Benzofuran was prepared according to the method of Burgstahler and Worden[137] in 46% yield as a colourless liquid, b.p. 80°/60 mmHg (lit.[137] 97.5-99°/80 mmHg). δ (90 MHz, $CDCl_3$) 6.67, 1H, m, H3; 7.00-7.65, 5H, m, ArH + H2.

Preparation of 3-methylbenzofuran (133)

3-Methylbenzofuran was prepared according to the method of Elvridge and Foster[138] in 4% yield as a colourless oil, b.p. 85°/13 mmHg (lit.[138] 90°/23 mmHg). δ (200 MHz, $CDCl_3$) 2.21, 3H, d, $^4J_{CH,CH_3}$ 1.35 Hz, CH_3; 7.17-7.54, 4H, m, ArH; 7.38, 1H, q, $^4J_{CH_3,CH}$ 1.35 Hz, H2.

Preparation of 4-methyl-3-chromene (140)

A solution of 4-chromanone (0.5 g, 3.4 mmol) in dry ether (10 ml) was added under nitrogen to the Grignard solution prepared from methyl iodide (2 ml, 32 mmol) and magnesium turnings (0.9 g, 37 mmol) in dry ether (10 ml). The mixture was refluxed for 1 hour and then quenched with hydrochloric acid (3 M, 25 ml). The two-phase mixture was stirred at room temperature for 1 hour, and the ether layer was separated. The ether extract was washed with sodium bisulfite solution (5%, 5x20 ml), water (20 ml), and brine (20 ml), dried (Na_2SO_4), and the solvent was removed. Flash chromatography (ethyl acetate/light petroleum, 1:20) followed by distillation gave 4-methyl-3-chromene (0.247 g, 50%) as a colourless oil, b.p. 95°/12 mmHg (lit.[139] 109-110°/17 mmHg). δ (200 MHz, $CDCl_3$) 2.00, 3H, dt, $^4J_{CH,CH3}$ 1.65 Hz, $^5J_{CH2,CH3}$ 1.75 Hz, CH_3; 4.72, 2H, dq, $^3J_{CH,CH2}$ 3.65 Hz, $^5J_{CH3,CH2}$ 1.75 Hz, CH_2-O; 5.54, 1H, tq, $^3J_{CH2,CH}$ 3.65 Hz, $^4J_{CH3,CH}$ 1.65 Hz, =CH-; 6.72-7.17, 4H, m, ArH.

Preparation of 3-chromene (125)

A solution of 4-chromanone (1.00 g, 6.7 mmol) in dry ether (5 ml) was added under nitrogen to a refluxing suspension of lithium aluminium hydride (1.00g, 26 mmol) in dry ether (50 ml). The mixture was refluxed for 2 hours, stirred at room temperature overnight, and quenched successively with water (5 ml) and hydrochloric acid (3 M, 50 ml). The mixture was stirred at room temperature for 30 minutes, and the ether layer was separated. The ether extract was washed with water (100 ml), and brine (20 ml), dried (Na_2SO_4), and the solvent was removed. The residue was heated in dry dimethylsulfoxide (5 ml) at 100° for 24 hours, cooled, and poured onto water (100 ml). The mixture was extracted into light petroleum (30-40°, 50 ml). The organic layer was washed with water

(10x50 ml), and brine (20 ml), dried (Na_2SO_4), filtered, and the solvent was removed. The residue was distilled (Kugelrohr) to yield 3-chromene (0.37 g, 40%) as a colourless oil, b.p. 120°/30 mmHg (lit.[140] 51-3°/1.2 mmHg). δ (200 MHz, $CDCl_3$) 4.77, 2H, dd, $^3J_{CH,CH_2}$ 3.50 Hz, $^4J_{CH,CH_2}$ 1.90 Hz, CH_2; 5.71, 1H, dt, $^3J_{CH,CH}$ 9.90 Hz, $^3J_{CH_2,CH}$ 3.50 Hz, CH_2-*CH*=; 6.38, 1H, dt, $^3J_{CH,CH}$ 9.90 Hz, $^4J_{CH_2,CH}$ 1.90 Hz, Ar-*CH*=; 6.66-7.14, 4H, m, ArH.

Preparation of lead tetrabenzoate

Lead tetrabenzoate was prepared according to the method of Hey, Stirling and Williams[68] in 81% yield as a pale yellow amorphous powder after recrystallization from dry benzene, m.p. 182-3° (lit.[68] 185°). Before use this material was analysed for lead(IV) by the method of Hey, *et al.*[68]

Preparation of lead tetrapivalate

Lead tetrapivalate was prepared according to the method of Roche[17] in 54% yield as a white amorphous powder after recrystallization from dry dichloromethane, m.p. 190-3° (dec.) (lit.[17] 190° (dec.)).

SYNTHESIS OF ENOL ACETATES

General methods

Method A. The ketone or aldehyde (5 g) was refluxed with isopropenyl acetate (1.5 equiv.) and *p*-toluenesulfonic acid (0.1 equiv.) for 16 hours. Acetone and excess isopropenyl acetate were distilled out of the reaction mixture, and the residue was partitioned between pentane (50 ml) and sodium carbonate solution (10%, 50 ml). The pentane extract was separated, dried (Na_2SO_4), and the solvent was removed. The residue was distilled (Kugelrohr) or crystallised from an appropriate solvent to yield the pure enol acetate.

Method B. The ketone or aldehyde (10 g) was refluxed with crystallised sodium acetate (0.35 equiv.) in acetic anhydride (3.5 equiv.) for 16 hours, and the mixture was cooled and diluted with ether (50 ml). The organic phase was washed with water (2x30 ml), and sodium carbonate solution (10%, 30 ml), dried (Na_2SO_4), and the solvent was removed. The residue was distilled (Kugelrohr) or crystallised from an appropriate solvent to yield the pure enol acetate.

The following compounds were prepared according to one of the above general procedures:

(i) Cycloheptenyl acetate (80) was prepared from cycloheptanone according to Method A in 53% yield as a pale yellow liquid, b.p. 55°/2 mmHg (lit.[141] 64°/4 mmHg). δ (90 MHz, $CDCl_3$) 1.35–1.85, 6H, m, 3xCH_2; 2.06, 3H, s, $OCOCH_3$; 1.85–2.41, 4H, m, 2xCH_2; 5.37, 1H, t, $^3J_{CH2,CH}$ 7.2 Hz, =CH–.

(ii) (*Z*)-1,2-Diphenylethenyl acetate (*E*,*Z*-217) was prepared from deoxybenzoin according to Method B in 27% yield. It was obtained as colourless needles from methanol, m.p. 100° (lit.[142] 101°). δ (90 MHz, $CDCl_3$) 2.21, 3H, s, $OCOCH_3$; 6.59, 1H, s, =CH-; 6.95-7.59, 10H, m, ArH.

(iii) 2,2-Diphenylethen-1-yl acetate (63) was prepared from diphenylacetaldehyde[143] according to method B in 52% yield, as a pale yellow oil, b.p. 230°/1.0 mmHg (Kugelrohr), that solidified on cooling, m.p 55° (lit.[144] m.p. 58°). δ (200 MHz, $CDCl_3$) 2.14, 3H, s, $OCOCH_3$; 7.19-7.40, 10H, m, ArH; 7.62, 1H, s, =CH-.

(iv) (*E/Z*)-1-Phenylpropen-2-yl acetate (*E*,*Z*-16) was prepared from phenylacetone according to Method A in 88% yield as pale yellow oil, b.p. 80°/1 mmHg (lit.[145] 67-9°/0.8 mmHg). δ (90 MHz, $CDCl_3$) 1.98-2.30, 6H, m, CH_3 + OAc; 6.18, 5.87, total 1H, bs, (*E*) and (*Z*)- =CH-; 6.69-7.36, 5H, m, ArH;

(v) 2-Phenylpropen-1-yl acetate (17) was prepared from 2-phenylpropanal according to Method A in 60% yield (as a 5:1 mixture of (*E*) and (*Z*)-isomers), as a pale yellow liquid, b.p. 110-112°/2 mmHg (lit.[146] 120-2°/8 mmHg). δ (200 MHz, $CDCl_3$) (*E*)-isomer: 2.10, 3H, d, $^4J_{CH,CH3}$ 1.40 Hz, CH_3; 2.19, 3H, s, $OCOCH_3$; 7.13-7.56, 5H, m, ArH; 7.52, 1H, q, $^4J_{CH3,CH}$ 1.40 Hz, =CH. (*Z*)-isomer: 2.01, 3H, d, $^4J_{CH,CH3}$ 1.50 Hz, CH_3; 2.19, 3H, s, $OCOCH_3$; 7.13-7.56, 5H, m, ArH, 7.24, 1H, q, $^4J_{CH3,CH}$ 1.50 Hz.

(vi) 2-Methylpropen-1-yl acetate (108) was prepared from isobutyraldehyde according to Method B in 17% yield by Dr. M. Moloney of these laboratories, b.p. 124° (lit.[147] m.p. 122-8°). δ (90 MHz, $CDCl_3$) 1.60-1.71, 6H, m, 2xCH_3; 2.11, 3H, s, $OCOCH_3$; 6.80, 1H, bs, =CH.

(vii) Cyclopenten-1-yl acetate (31) was prepared from cyclopentanone according to Method A in 37% yield, as a colourless liquid, b.p. 160° (lit.[148] 84-7°/69 mmHg). δ (200 MHz, $CDCl_3$) 1.83-2.05, 2H, m, CH_2; 2.13, 3H, s, $OCOCH_3$; 2.28-2.52, 4H, m, $2xCH_2$; 5.40, 1H, m, =CH-.

(viii) Cyclohexen-1-yl acetate (35) was prepared from cyclohexanone according to Method A in 79% yield, as a very pale yellow liquid, b.p. 188° (lit.[149] 78°/20 mmHg). δ (200 MHz, $CDCl_3$) 1.48-1.66, 2H, m, CH_2; 1.66-1.83, 2H, m, CH_2; 1.99-2.18, 4H, m, $2xCH_2$; 2.11, 3H, s, $OCOCH_3$; 5.36, 1H, m, =CH-.

VINYLATION REACTIONS OF VINYLLEAD TRICARBOXYLATES WITH β-KETO ESTERS AND β-DIKETONES

General Method.

A solution of the stannane or mercurial (3-4 mmol) in dry chloroform (5 ml) was added to the lead reagent (3.3-4.4 mmol, 1.1 equivalents) in dry chloroform (10 ml) at room temperature. The mixture was stirred at room temperature for the indicated period, and the β-dicarbonyl compound was added. The mixture was stirred at room temperature overnight, diluted with ether (20 ml), and filtered. The filtrate was washed with sodium carbonate solution (10%, 3x20 ml), water (20 ml), and brine (20 ml), dried (Na_2SO_4), filtered and the solvent was removed. In those cases where pyridine was used, additional washes with hydrochloric acid (1 M, 3x20 ml) were carried out. The pure α-vinylated-β-dicarbonyl compound was then obtained by chromatography as indicated.

In each case, the optimum yield and conditions are quoted, and the yields obtained by this and other routes are tabulated.

1) Ethyl 1-[(*E*)-1-phenylpropen-2-yl]-2-oxocyclopentanecarboxylate (170)

The title compound was prepared from the trimethylstannane (73) and lead tetrapivalate (30 seconds exchange time) and ethyl 2-oxocyclopentanecarboxylate (53) in 42% yield as a colourless oil after radial chromatography (ethyl acetate/light petroleum, 1:49). δ (200 MHz, $CDCl_3$) 1.27, 3H, t, $^3J_{CH_2,CH_3}$ 7.10 Hz, OCH_2CH_3; 1.82-2.74, 6H, m, $3xCH_2$; 1.91, 3H, d, $^4J_{CH,CH_3}$ 1.33 Hz, CH_3; 4.23, 2H, q, $^3J_{CH_3,CH_2}$ 7.10 Hz, OCH_2CH_3; 6.37, 1H, bs, =CH-; 7.09-7.40, 5H, m, ArH. The sample contained 30% of the (*Z*)-isomer as shown by a doublet at δ 1.88, $^4J_{CH,CH_3}$ 1.55 Hz, a

broadened singlet at δ 6.62, and an ester methylene quartet at δ 4.24, $^{3}J_{CH3,CH2}$ 7.10 Hz. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 14.10, $OCH_2\mathit{C}H_3$; 29.70, $=C(\mathit{C}H_3)-$; 29.37, 33.39, 38.03, 3x$\mathit{C}H_2$; 61.71, $O\mathit{C}H_2CH_3$; 66.71, C1;126.83, Ar*C*H; 128.07, Ar*C*H; 129.08, Ar*C*H; 130.58, =*C*H-; 135.17, Ar*C*; 137.33, $=\mathit{C}(CH_3)-$; 171.50, $\mathit{C}O_2Et$; 214.10, C2. All data consistent with that reported in the literature.[19]

Table 15. Yields of α-vinyl-β-dicarbonyl compound (170) obtained by all other routes.

organometallic reagent	lead reagent	yield of (260)
73	LTP	42
73	LTA	10
73	LTB	29
177	LTB	14

(73)= Trimethyl[(*Z*)-1-phenylpropen-2-yl]stannane.

(177)= Bis[(*Z*)-1-phenylpropen-2-yl]mercury.

2) Ethyl 1-[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]-2-oxocyclopentane-carboxylate (172)

The title compound was obtained from trimethylstannane (171) and lead tetrabenzoate (5 minutes exchange time) and ethyl 2-oxocyclopentanecarboxylate (53) in 84% yield as a colourless liquid after flash chromatography (ethyl acetate/light petroleum, 1:9), b.p. 250°/ 1 mmHg (lit.[19] no b.p. given). λ_{max} (ethanol) 208, 268 nm (ε 13007, 17321). υ_{max} (liquid film) 3037w, 2963m, 2838w, 1751s, 1727s, 1608m, 1512s, 1465w, 1366m, 1305w, 1284w, 1251s, 1175m, 1108w, 1032m, 971w, 823w,

557w cm^{-1}. δ (200 MHz, $CDCl_3$) 1.25, 3H, t, $^3J_{CH2,CH3}$ 7.20 Hz, OCH_2CH_3; 1.92-2.45, 5H, m, $2xCH_2$ + $H_{5\alpha}$ or $H_{5\beta}$; 2.71, 1H, dt, $^2J_{CH,CH}$ 13.19 Hz, $^3J_{CH2,CH}$ 7.10 Hz, $H_{5\alpha}$ or $H_{5\beta}$; 3.78, 3H, s, OCH_3; 4.19, 2H, q, $^3J_{CH3,CH2}$ 7.20 Hz, OCH_2CH_3; 6.26, 1H, d, $^3J_{CH,CH}$ 16.43 Hz, =CH-; 6.48, 1H, d, $^3J_{CH,CH}$ 16.43 Hz, ArCH=; AA'BB' system: 6.85, 2H, d, J_{AB} +J'_{AB}, 8.70 Hz, ArH *ortho* to OCH_3; 7.32, 2H, d, J_{AB} + J_{AB}, 8.70 Hz, ArH *meta* to OCH_3. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 13.96, OCH_2CH_3; 19.44, 33.35, 37.37, $3xCH_2$; 55.15, OCH_3; 61.67, OCH_2CH_3; 62.69, C1; 113.86, Ar*C*H *ortho* to OCH_3; 123.39, =*C*H-; 127.65, Ar*C*H *meta* to OCH_3; 129.09, Ar*C*-CH=; 159.37, Ar*C*OCH_3; 170.34, *C*O_2Et; 212.50, C2. (*m/z*) 288(M^+, 11%), 242(22), 232(10), 215(24), 214(13), 187(43), 160(15), 159(100), 158(16), 145(11), 144(25), 128(19), 127(14), 121(17), 116(17), 115(40), 55(26). All data consistent with that reported in the literature.[19]

Table 16. Yields of α-vinyl-β-dicarbonyl compound (172) obtained by all other routes.

reagent	lead reagent	pyridine (eq.)	yield of (172)	yield of (115)
171	LTB	0	84	
171	LTA	0	70	
171	LTA	3	65*	34*
114	LTB	0	47	
178	LTB	0	33	

(171)= Trimethyl[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]stannane.

(114)= Tributyl[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]stannane.

(178)= Bis[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]mercury.

(115)= *p*-Methoxyphenylacetylene

* Yield determined by n.m.r. spectroscopy.

3) Ethyl 1-(2-methylpropen-1-yl)-2-oxocyclopentanecarboxylate (187)

The title compound was prepared from tributylstannane (55) and lead tetrabenzoate (2 minutes exchange time) and ethyl 2-oxocyclopentanecarboxylate (53) in 42% yield as a colourless liquid after flash chromatography (ethyl acetate/light petroleum, 1:9) followed by radial chromatography (ethyl acetate/light petroleum, 1:19). λ_{max} (cyclohexane) 230 nm (ϵ 4987). υ_{max} (liquid film) 2959s, 2927s, 2873w, 1754s, 1726s, 1645w, 1621m, 1606w, 1573w, 1451m, 1354s, 1268m, 1175m, 1128w, 1026w, 719m, 688w cm^{-1}. δ (200 MHz,$CDCl_3$) 1.25, 3H, t, $^3J_{CH_2,CH_3}$ 7.10 Hz, OCH_2CH_3; 1.64, 3H, d, $^4J_{CH,CH_3}$ 1.40 Hz, CH_3 *trans* to =CH-; 1.76, 3H, d, $^4J_{CH,CH_3}$ 1.60 Hz, CH_3 *cis* to =CH-; 1.98, 3H, m, $C(4)H_2$ + $H_{5\alpha}$ or $H_{5\beta}$; 2.18-2.53, 2H, m, $C(3)H_2$; 2.74, 1H, m, $H_{5\alpha}$ or $H_{5\beta}$; 4.18, 2H, m, q, $^3J_{CH_3,CH_2}$ 7.10 Hz, OCH_2CH_3; 5.29, 1H, m, =CH-. Stereochemistry confirmed by n.O.e. difference spectroscopy. Irradiation at δ 5.29 produced a 5% n.O.e. at δ 1.76, and a 2% n.O.e. at δ 1.98. Irradiation at δ 2.74 produced a 14% n.O.e. at δ 1.98. Irradiation at δ 1.76 produced a 2% n.O.e. at δ 5.29. Irradiation at δ 1.64 produced no n.O.e. at δ 5.29. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 14.12, OCH_2CH_3; 19.33, CH_2; 19.68, CH_3; 26.46, CH_3; 36.55, CH_2; 36.94, CH_2; 60.28, C1; 61.45, OCH_2CH_3; 121.74, =CH-; 138.75, -C=CH-; 170.71, CO_2Et; 213.08, C2. All data consistent with that reported in the literature.[19]

Table 17. Yields of α-vinyl-β-dicarbonyl compound (187) obtained by all other routes.

organometallic reagent	lead reagent	yield of (187)
55	LTB	42
55	LTP	36
55	LTA	0
189	LTB	40

(55)= Tributyl(2-methylpropen-1-yl)stannane.

(189)= Bis(2-methylpropen-1-yl)mercury.

4) Ethyl 2-methyl-2-[(*E*)-2-phenylethen-1-yl]-3-oxobutanoate (165)

The title compound was prepared from trimethylstannane (52) and lead tetraacetate (5 minutes exchange time) and ethyl 2-methylacetoacetate (164) in 29% yield as a colourless oil after column chromatography (ethyl acetate/light petroleum, 1:9) followed by radial chromatography (ethyl acetate/light petroleum, 1:24). λ_{max} (hexane) 221, 254 nm (ϵ 5872, 6532). δ (90 MHz, $CDCl_3$) 1.27, 3H, t, $^3J_{CH2,CH3}$ 7.1 Hz, OCH_2CH_3; 1.57, 3H, s, CH_3; 2.23, 3H, s, $COCH_3$; 4.21, 2H, q, $^3J_{CH2,CH3}$ 7.1 Hz, OCH_2CH_3; 6.43, 1H, d, $^3J_{CH,CH}$ 16.5 Hz, Ph-C*H*=; 6.77, 1H, d, $^3J_{CH,CH}$ 16.5 Hz, =CH-; 7.13-7.53, 5H, m, ArH. All data consistent with that reported in the literature.[19]

5) 2-Acetyl-2-[(*E*)-2-phenylethen-1-yl]-1-tetralone (167)

The title compound was prepared from trimethylstannane (52) and lead tetraacetate (5 minutes exchange time) and 2-acetyl-1-tetralone (166) in 62% yield as a yellow oil after column chromatography (ethyl acetate/light petroleum, 1:9) followed by radial chromatography (ethyl acetate/light petroleum, 1:49). λ_{max} (ethanol) 207, 254, 284(sh), 292(sh) nm (ϵ 27428, 18285, 4839, 4638). υ_{max} (chloroform) 3063w, 3053w, 3010w, 2938w, 2853w, 1711s, 1677s, 1601s, 1487w, 1455w, 1356w, 1302m, 1295m, 1234m, 1181w, 1157w, 1122w, 1064w, 971w, 930w, 913w, 897w, 693w cm^{-1}. δ (200 MHz, $CDCl_3$) 2.25, 3H, s, CH_3; 2.80-3.15, 4H, m, 2xCH_2; 6.44, 1H, d, $^3J_{CH,CH}$ 16.58 Hz, Ph-C*H*=; 6.76, 1H, d, $^3J_{CH,CH}$ 16.58 Hz, =CH-; 7.08-7.59, 8H, m, ArH; 8.10, 1H, dd, $^3J_{CH,CH}$ 7.99 Hz, $^4J_{CH,CH}$ 1.20 Hz, ArH *ortho* to -C(O)-. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 25.86, CH_2; 27.93, CH_3; 30.57, CH_2; 66.01, C2; 126.53, 2xAr*C*H; 126.84, 2xAr*C*H; 128.02, Ar*C*H; 128.10, Ar*C*H; 128.63, 2xAr*C*H; 128.84, Ar*C*H; 131.81, Ar*C*; 132.86, =*C*H-; 133.99, =*C*H-; 136.34, Ar*C*; 143.58, Ar*C*; 195.94, C=O; 203.89, C=O. All data consistent with that of an authentic sample.[150]

6) Ethyl 1-[(*E*)-2-phenylethen-1-yl]-2-oxocyclopentanecarboxylate (54)

The title compound was prepared from the trimethylstannane (52) and lead tetrabenzoate (5 minutes exchange time) and ethyl 2-oxocyclopentanecarboxylate (53) in 84% yield after flash chromatography (ethyl acetate/light petroleum, 1:9) followed by radial chromatography (ethyl acetate/light petroleum, 1:19). λ_{max} (ethanol) 206, 254, 292 nm (ϵ 10514, 11973, 1246). υ_{max} (liquid film) 3027w, 2960m, 2932w, 2871w, 1753s, 1729s, 1449w, 1233s, 1174m, 1117w, 1028w, 989w, 747m, 694w cm^{-1}. δ (200 MHz, $CDCl_3$) 1.27, 3H, t, $^3J_{CH2,CH3}$ 7.10 Hz, OCH_2CH_3; 1.82-2.50, 5H, m, 2xCH_2 + $H_{5\alpha}$ or $H_{5\beta}$; 2.73, 1H, ddd, $^2J_{H5\alpha,H5\beta}$ 13.30 Hz, $^3J_{CH,CH}$ 7.17 Hz,

$^3J_{CH,CH}$ 6.87 Hz, $H_{5\alpha}$ or $H_{5\beta}$; 4.20, 2H, q, $^3J_{CH3,CH2}$ 7.10 Hz, OCH_2CH_3; 6.40, 1H, d, $^3J_{CH,CH}$ 16.36 Hz, =CH-; 6.53, 1H, d, $^3J_{CH,CH}$ 16.36 Hz, Ar-CH=; 7.21-7.53, 5H, m, ArH. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 14.06, CH_3; 19.55, 33.42, 37.51, 3xCH_2; 61.87, OCH_2CH_3; 62.88, C1; 125.82, Ar*C*H; 126.56, Ar*C*H; 127.93, =*C*H-; 128.56, Ar*C*H; 131.68, =*C*H-; 136.40, Ar*C*; 170.27, CO_2Et; 214.69, C2. All data consistent with that reported in the literature.[19]

Table 18. Yields of α-vinyl-β-dicarbonyl compound (54) obtained by all other routes.

organometallic reagent	lead reagent	yield of (54)
52	LTB	84
9	LTB	65
7	LTB	49

(52)= Trimethyl[(*E*)-2-phenylethen-1-yl]stannane.

(9)= Tributyl[(*E*)-2-phenylethen-1-yl]stannane.

(7)= Bis[(*E*)-2-phenylethen-1-yl]mercury.

7) 5-Ethyl-5-[(*E*)-2-phenylethen-1-yl]barbituric acid (169)

The title compound was prepared from trimethylstannane (52) and lead tetraacetate (5 minutes exchange time) and 5-ethylbarbituric acid (168) in 39% yield as a colourless solid after column chromatography (ethyl acetate) and recrystallization from chloroform, m.p. 167° (lit.[19] 169-72°). λ_{max} (ethanol) 256 nm (ϵ 15290). υ_{max} (chloroform) 3383w, 2845w, 1739s, 1712s, 1413w, 1351w, 1308w, 967w cm^{-1}. δ (200 MHz, $CDCl_3$) 0.92, 3H, t, $^3J_{CH2,CH3}$ 7.40 Hz, CH_3; 2.25, 2H, q, $^3J_{CH3,CH2}$ 7.40 Hz, CH_2;

6.20, 1H, d, $^{3}J_{CH,CH}$ 16.21 Hz, Ph-C=C*H*-; 6.62, 1H, d, $^{3}J_{CH,CH}$ 16.21 Hz, Ph-C*H*=CH-; 7.18-7.44, 5H, m, ArH; 10.47, 2H, bs, 2xNH. ^{13}C n.m.r. spectrum (50 MHz,$CDCl_3$) 9.62, *C*H_3; 30.06, *C*H_2; 58.70, C5; 126.51, Ar*C*H; 127.21, Ar*C*H or =*C*H-; 128.19, Ar*C*H or =*C*H-; 128.46, Ar*C*H; 132.07, =*C*H-; 135.51, Ar*C*; 149.57, C2; 170.98, C4 and C6. All data consistent with that reported in the literature.[19]

8) Ethyl 1-[(*E*)-2-phenylpropen-1-yl]-2-oxocyclopentanecarboxylate (175)

The title compound was prepared from the trimethylstannane (70) and lead tetrabenzoate (2 minutes exchange time) and ethyl 2-oxocyclopentanecarboxylate (53) in 61% yield as a colourless oil after p.l.c. (chloroform) followed by radial chromatography (ethyl acetate/light petroleum, 1:19). λ_{max} (cyclohexane) 245 nm (ϵ 9204). υ_{max} (liquid film) 2963m, 1755s, 1723s, 1600w, 1446w, 1405w, 1367w, 1223s, 1161m, 1113w, 1028w, 759m, 700 cm^{-1}. δ (200 MHz, $CDCl_3$) 1.24, 3H, t, $^{3}J_{CH2,CH3}$ 7.10 Hz, OCH_2CH_3; 1.93-2.61, 5H, m, 2xCH_2 + $H_{5\alpha}$ or $H_{5\beta}$; 2.06, 3H, d, $^{4}J_{CH,CH3}$ 1.36 Hz, CH_3; 2.85, 1H, m, $H_{5\alpha}$ or $H_{5\beta}$; 4.19, 2H, q, $^{3}J_{CH3,CH2}$ 7.10 Hz, OCH_2CH_3; 5.88, 1H, q, $^{4}J_{CH3,CH}$ 1.36 Hz, =CH-; 7.14-7.45, 5H, m, ArH. Stereochemistry confirmed by n.O.e difference spectroscopy. Irradiation at δ 2.06 produced no n.O.e. at δ 5.88 (1% at δ 2.85, 3% at δ 7.44). Irradiation at δ 5.88 produced no n.O.e. at δ 2.06 (10% at δ 7.44). ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 13.95, CH_3; 17.87, CH_3; 19.34, 36.37, 36.87, 3xCH_2; 61.56, OCH_2CH_3; 61.79, C1; 124.96, Ar*C*H or =*C*H-; 125.76, 2xAr*C*H; 127.19, Ar*C*H or =*C*H-; 128.04, 2xAr*C*H; 140.90, Ar*C* or =*C*(CH_3)-; 143.21, Ar*C* or =*C*(CH_3)-; 170.25, *C*O_2Et; 212.46, C2. All data consistent with that reported in the literature.[19]

Table 19. Yields of α-vinyl-β-dicarbonyl compound (175) obtained by all other routes.

organometallic reagent	lead reagent	yield of (175)
70	LTB	61
70	LTA	53
11	LTB	36
66	LTA	42

(70)= Trimethyl[(*E*)-2-phenylpropen-1-yl]stannane.

(11)= Bis[(*E*)-2-phenylpropen-1-yl]mercury.

(66)= Tributyl[(*E*)-2-phenylpropen-1-yl]stannane.

9) Ethyl 1-(cyclohexen-1-yl)-2-oxocyclopentanecarboxylate (174)

The title compound was prepared from the trimethylstannane (173) and lead tetrabenzoate (15 minutes exchange time) and ethyl 2-oxocyclopentanecarboxylate (53) in 67% yield as a colourless liquid after flash chromatography (ethyl acetate/light petroleum, 1:9), followed by radial chromatography (ethyl acetate/light petroleum, 1:19) and distillation, b.p. 100°/0.75 mmHg (lit.[19] no b.p. given). λ_{max} (cyclohexane) no peaks. υ_{max} (liquid film) 2978w, 2935s, 2861w, 2673w, 1750s, 1728s, 1676m, 1449m, 1405w, 1346w, 1254m, 1234m, 1174m, 1140w, 1102m, 1023m, 1005w, 967w, 922w, 855w, 558m cm^{-1}. δ (200 MHz, $CDCl_3$) 1.26, 3H, bt, $^3J_{CH2,CH3}$ 7.20 Hz, OCH_2CH_3; 1.49-1.76, 4H, m, $2xCH_2$; 1.76-2.01, 4H, m, $2xCH_2$; 2.01-2.16, 2H, m, CH_2; 2.24, 1H, ddd, $^2J_{CH,CH}$ 13.30 Hz, $^3J_{CH,CH}$ 5.95 Hz, $^3J_{CH,CH}$ 5.95 Hz, $H_{5\alpha}$ or $H_{5\beta}$; 2.31, 2H, m, CH_2; 2.49, 1H, ddd, $^2J_{CH,CH}$ 13.30 Hz, $^3J_{CH,CH}$ 8.40 Hz, $^3J_{CH,CH}$ 6.65 Hz, $H_{5\alpha}$ or $H_{5\beta}$; 4.16, 1H, dq, $^2J_{CH,CH}$ 12.60 Hz, $^3J_{CH3,CH}$ 7.20 Hz, and 4.22, 1H, dq, $^2J_{CH,CH}$ 12.60 Hz,

$^{3}J_{CH3,CH}$ 7.20 Hz, $-OCH_2CH_2$; 5.54, 1H, m, =C*H*. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 13.96, OCH_2CH_3; 19.13, 21.79, 22.75, 25.36, 25.87, 32.60, 37.84, 7xCH_2; 61.30, OCH_2CH_3; 67.07, C1; 125.42, *C*H=C; 132.95, *C*=CH; 170.68, CO_2Et; 212.90, C2. (*m/z*) 236(M^+, 3%), 209(28), 208(100), 181(17), 180(93), 179(23), 163(58), 162(43), 161(13), 152(27), 151(23), 149(11), 148(11), 136(19), 135(36), 134(58), 133(24), 121(16), 120(31), 119(23), 107(48), 106(35), 105(40), 93(29), 92(23), 91(75), 81(25), 80(15), 79(79), 78(23), 77(48), 67(40), 65(25), 55(60), 53(29), 52(13), 51(19). All data consistent with that reported in the literature.[19]

Table 20. Yields of α-vinyl-β-dicarbonyl compound (174) obtained by all other routes.

reagent	lead reagent	exchange time	pyridine (eq.)	yield of (174)
173	LTB	15 min.	0	67
173	LTB	10	0	65
173	LTB	5	0	58
173	LTB	1	0	39
173	LTB	15	5	46
173	LTP	15	5	14
173	LTA	15	5	48
173	LTA	1	0	26
173	LTP	1	0	5*
32	LTA	15	5	34
32	LTB	15	0	40
32	LTB	15	5	38

(173)= (Cyclohexen-1-yl)trimethylstannane.

(32)= (Cyclohexen-1-yl)tributylstannane.

* Yield determined by GLC (column 5 200°).

10) Ethyl 1-(2,2-diphenylethenyl)-2-oxocyclopentanecarboxylate (176)

The title compound was prepared from divinylmercury compound (57) and lead tetrabenzoate (5 minutes exchange time) and ethyl 2-oxocyclopentanecarboxylate (53) in 46% yield as a pale yellow oil after p.l.c. (chloroform) followed by radial chromatography (ethyl acetate/light petroleum, 1:19). λ_{max} (cyclohexane) 233, 252, 257 nm (ϵ 9312, 10085, 10085). υ_{max} (liquid film) 3031w, 1753s, 1724s, 1595w, 1494w, 1445w, 1404w, 1368w, 1315w, 1231s, 1110w, 1032m, 703s cm^{-1}. δ (200 MHz, $CDCl_3$) 1.22, 3H, t, $^3J_{CH_2,CH_3}$ 7.12 Hz, OCH_2CH_3; 1.54-2.52, 6H, m, 3xCH_2; 4.00, 1H, dt, $^2J_{CH,CH}$ 12.39 Hz, $^3J_{CH_3,CH}$ 7.12 Hz and 4.05, 1H, dt, $^2J_{CH,CH}$ 12.39 Hz, $^3J_{CH_3,CH}$ 7.12 Hz, OCH_2CH_3; 6.41, 1H, s, =CH-; 7.11-7.44, 10H, m, ArH. ^{13}C n.m.r. spectrum (50 MHz, $CDCl_3$) 13.97, CH_3; 19.53, 36.29, 37,02, 3xCH_2; 61.77, OCH_2CH_2; 63.07, C1; 126.70, Ar*C*H; 127.40, Ar*C*H; 127.53, Ar*C*H; 127.59, Ar*C*H; 128.00, Ar*C*H; 128.04, Ar*C*H; 130.09, =*C*H-; 139.42, Ar*C*; 142.45, Ar*C*; 144.56, =*C*$(Ph)_2$; 169.66, CO_2Et; 213.11, C2. All data consistent with that reported in the literature.[19]

Table 21. Yields of α-vinyl-β-dicarbonyl compound (176) obtained by all other routes.

organometallic reagent	lead reagent	yield of (176)
57	LTB	46
64	LTA	21*
64	LTA	0†

(57)= Bis(2,2-diphenylethenyl)mercury.

(64)= Trimethyl(2,2-diphenylethenyl)stannane.

* Reaction performed at -40°.

† Reaction performed at room temperature.

REACTIONS OF TRIALKYLVINYLSTANNANES WITH LEAD TETRACARBOXYLATES

(i) Trimethyl-[(*Z*)-1-phenyl-1-propen-2-yl]stannane (73)

A solution of trimethyl[(*Z*)-1-phenyl-1-propen-2-yl]stannane (0.188 g, 0.67 mmol) in dry chloroform (1 ml) was added to a stirred solution of lead tetraacetate (0.297 g, 0.67 mmol) in dry chloroform (2 ml) under nitrogen at room temperature. The mixture was stirred at room temperature for 20 hours, filtered through Celite, and the volume was made up to 10 ml. Gas chromatographic analysis was carried out on column 5 using a temperature program of 100° for three minutes, followed by a temperature increase of 20°/min. to 230°, which was maintained for 10 minutes. 1-Phenylpropyne (67) was formed in 51% yield, (*E*)-1-phenylpropene (74) in 12% yield, (*Z*)-1-phenyl-1-propen-2-yl acetate (*Z*-16) in 5% yield, and (*E*)-1-phenyl-1-propen-2-yl acetate (*E*-16) in 1% yield.

(ii) Tributyl(cyclohexylidenemethyl)stannane (76)

Tributyl(cyclohexylidenemethyl)stannane (0.19 g, 0.4 mmol, 1.3 equivalents) was added to a stirred solution of lead tetraacetate (0.135 g, 0.3 mmol) in dry chloroform (3 ml) under nitrogen at room temperature. The mixture was stirred at room temperature for 16 hours, filtered through Celite and the volume was made up to 10 ml. Gas chromatographic analysis,

carried out on column 2 at 150° indicated the formation of cyclohepten-1-yl acetate (83) in 79% yield.

(iii) Tributyl(2,2-diphenylethenyl)stannane (56)

(a) Tributyl(2,2-diphenylethen-1-yl)stannane (0.205 g, 0.44 mmol, 1.1 equivalents) was added to a stirred solution of lead tetraacetate (0.18 g, 0.41 mmol) in dry chloroform (3 ml) under nitrogen at room temperature. The mixture was stirred at room temperature for 16 hours, filtered through Celite and the volume was made up to 10 ml. Gas chromatographic analysis, carried out on column 3 at 160° indicated the formation of diphenylacetylene (tolan, 62) in 30% yield.

(b) Compound (56) (0.418 g, 0.89 mmol, 1.6 equivalents) was added to a stirred solution of lead tetraacetate (0.25 g, 0.56 mmol) in dry chloroform (3 ml) under nitrogen at room temperature. The mixture was stirred at 55° for two hours, and at 30° for 14 hours. The mixture was filtered through Celite and the volume was made up to 10 ml. Gas chromatographic analysis on column 3 at 160° indicated the formation of tolan (62) in 34% yield.

(c) Compound (56) (0.22 g, 0.47 mmol, 1.6 equivalents) was added to a stirred solution of lead tetraacetate (0.135 g, 0.3 mmol) in dry chloroform (3 ml) and dry pyridine (0.1 ml, 4.2 equivalents) under nitrogen at room temperature. The mixture was stirred at room temperature for 16 hours, filtered through Celite, and the volume was made up to 10 ml. Gas chromatographic analysis on column 3 at 160° indicated the formation of tolan (62) in 40% yield.

(d) Compound (56) (0.14 g, 0.30 mmol, 1.6 equivalents) was added to a stirred solution of lead tetraacetate (0.085 g, 0.19 mmol) in dry chloroform (3 ml) and dry pyridine (0.065 ml, 4 equivalents) under nitrogen at room temperature. The mixture was stirred at 45° for 16 hours, cooled, filtered through Celite and the volume was made up to 10 ml. Gas chromatographic analysis on column 3 at 160° indicated the formation of tolan (62) in 17% yield.

(e) Compound (56) (0.264 g, 0.56 mmol) was added to a stirred solution of lead tetraacetate (0.155 g, 0.35 mmol) in dry chloroform (4 ml) and triethylamine (0.05 ml, 0.36 mmol) under nitrogen at room temperature. The mixture was stirred at room temperature for 24 hours. No precipitate of lead salts was observed. Glacial acetic acid (4 drops) was added and the mixture was stirred for 24 hours, then filtered through Celite. Gas chromatographic analysis on column 3 at 160° indicated the formation of 1,1-diphenylethene (65) in 32% yield.

(f) Compound (56) (0.195 g, 0.42 mmol) was added to a stirred solution of lead tetraacetate (0.185 g, 0.42 mmol) and mercury(II) acetate (0.045 g, 0.14 mmol, 0.34 equivalents) in dry chloroform (5 ml) under nitrogen at room temperature. The mixture was stirred for 24 hours, then filtered through Celite. Gas chromatographic analysis on column 3 at 160° indicated the formation of tolan (62) in 23% yield.

In all the above cases neither of the isomeric enol acetates (*E*,*Z*-219) nor the enol acetate (63) were detected.

(iv) Trimethyl(2,2-diphenylethenyl)stannane (64)

Trimethyl(2,2-diphenylethenyl)stannane (0.165 g, 0.48 mmol) was added to a stirred solution of lead tetraacetate (0.210 g, 0.47 mmol) in dry chloroform (5 ml) under nitrogen at room temperature. The mixture was stirred at room temperature for 16 hours, filtered through Celite, and the volume was made up to 10 ml. Gas chromatographic analysis on column 3 at 160° indicated the formation of diphenylacetylene (62) in 90% yield, and 1,1-diphenylethene (65) in 4% yield.

(v) Tributyl[(*E*)-4-phenyl-1-buten-1-yl)]stannane (93)

(a) A solution of tributyl[(*E*)-4-phenyl-1-buten-1-yl)]stannane (1.063 g, 2.5 mmol) in dry chloroform (1 ml) was added to a stirred solution of lead tetraacetate (1.119 g, 2.5 mmol) in dry chloroform (5 ml). The mixture was stirred at room temperature for 24 hours, filtered and the volume was made up to 10 ml. Analytical GLC on column 5 at 100° indicated the formation of 4-phenyl-1-butyne (90) in 62% yield, and 1,2-dihydronaphthalene (95) in 19% yield.

(b) A solution of stannane (93) (0.24 g, 0.57 mmol) in dry chloroform (1 ml) was added to a stirred solution of lead tetrabenzoate (0.40 g, 0.58 mmol) in dry chloroform (2 ml). The mixture was stirred at room temperature for 24 hours, filtered and the volume was made up to 10 ml. Analytical GLC on column 5 at 100° indicated the formation of 4-phenyl-1-butyne (90) in 43% yield, and 1,2-dihydronaphthalene (95) in 36% yield.

(c) A solution of stannane (93) (0.286 g, 0.68 mmol) in dry chloroform (1 ml) was added to a stirred solution of lead tetrapivalate (0.415 g, 0.68 mmol) in dry chloroform (2 ml). It was noted that unlike the lead tetraacetate and lead tetrabenzoate experiments above, no precipitate of lead (II) pivalate formed immediately, and only a slight precipitate was present after 24 hours. The mixture was stirred at room temperature for 24 hours, filtered and the volume was made up to 10 ml. Analytical GLC on column 5 at 100° indicated the formation of 4-phenyl-1-butyne (90) in 32% yield, and 1,2-dihydronaphthalene (95) in 5% yield.

(vi) Tributyl[(*E*)-2-(*o*-phenylphenyl)ethen-1-yl]stannane (96)

(a) A solution of tributyl[(*E*)-2-(*o*-phenylphenyl)ethen-1-yl]stannane (0.7464 g, 1.59 mmol) in dry chloroform (1 ml) was added to a stirred solution of lead tetraacetate (0.7052 g, 1.59 mmol) in dry chloroform (8 ml). The mixture was stirred at room temperature for 5 days, filtered, and the volume was made up to 10 ml. Analytical GLC on column 5 at 200° indicated the formation of phenanthrene (100) in 23% yield, and ^{1}H n.m.r analysis indicated the formation of *o*-phenylphenylacetylene (99) in 36% yield and butyl acetate in 4% yield.

(b) A solution of stannane (96) (0.1289 g, 0.27 mmol) in dry chloroform (1 ml) was added to a stirred solution of lead tetrabenzoate (0.1900 g, 0.27 mmol) in dry chloroform (2 ml). The mixture was stirred at room temperature for 5 days, filtered, and the volume was made up to 10 ml. Analytical GLC on column 5 at 200° indicated the formation of phenanthrene (100) in 46% yield, and ^{1}H n.m.r analysis indicated the formation of *o*-phenylphenylacetylene (99) in 20% yield and butyl benzoate in 5% yield.

(c) A solution of stannane (96) (0.2176 g, 0.46 mmol) in dry chloroform (1 ml) was added to a stirred solution of lead tetrapivalate (0.2837 g, 0.46 mmol) in dry chloroform (1 ml). The mixture was stirred at room temperature for 5 days, filtered, and the volume was made up to 10 ml. Analytical GLC on column 5 at 200° indicated the formation of phenanthrene (100) in 20% yield, and ^{1}H n.m.r analysis indicated the formation of *o*-phenylphenylacetylene (99) in 0.5% yield.

(vii) Tributyl[(*Z*)-2-(*o*-methylphenyl)ethen-1-yl]stannane (*Z*-157)

(a) A solution of tributyl[(*Z*)-2-(*o*-methylphenyl)ethen-1-yl]stannane (containing 22% *E*-isomer) (0.1377 g, 0.34 mmol) in dry deuterochloroform (1.0 ml) was added to lead tetraacetate (0.1499 g, 0.34 mmol) in an n.m.r. tube. ^{1}H n.m.r. analysis (90 MHz) showed that after 24 hours, the only recognisable products were *o*-methylphenylacetylene (158), which was formed in 79% yield, and *o*-methylstyrene (161, 13%). No trace of the cyclised material, indene (160), could be seen. The mixture was filtered, and the volume was made up to 10 ml. Analytical GLC on column 7 at 150° indicated the presence of indene (160) in 0.1% yield.

(b) A solution of stannane (*Z*-157) (1.00 g, 2.5 mmol) in dry chloroform (10 ml) was added to lead tetraacetate (1.10 g, 2.5 mmol) and mercuric acetate (80 mg, 0.25 mmol). The mixture was stirred overnight, filtered and the volume was made up to 25 ml. Analytical GLC on column 7 at 150° indicated the presence of indene (160) in only 0.1% yield again, although a host of other products, including the acetylene (158) and styrene (161) were observed.

(c) A solution of stannane (*E*-157) (containing 38% *E*-isomer) (1.76 g, 4.3 mmol) in dry deuterochloroform (10 ml) was added to lead tetraacetate (1.92 g, 4.3 mmol). The mixture was stirred at room temperature for 16 hours, filtered and the volume was made up to 25 ml. GLC analysis on column 7 at 150° indicated the formation of the acetylene (158) in 63% yield, and indene (160) in 0.5% yield.

(d) A solution of stannane (*Z*-157) (4.59 g, 11 mmol) in dry chloroform (10 ml) was added to a stirred solution of lead tetraacetate (5.00 g, 11 mmol) in dry chloroform (30 ml). The mixture was stirred overnight, filtered, and the filtrate was fractionally distilled to yield *o*-methylphenylacetylene (158), b.p. 80°/20 mmHg (lit.[134] 42-4°/6 mmHg) (0.73 g, 56%).

(e) Glacial acetic acid (0.025 g, 0.42 mmol) was added to a solution of stannane (*Z*-157) (0.173 g, 0.42 mmol) in dry deuterochloroform (0.3 ml). The mixture was shaken and n.m.r. spectra were recorded at intervals (90 MHz). The results are entered in Table 22.

Table 22. Protodemetallation of (*Z*-157) with acetic acid.

time (hours)	yield of alkene (161)
1	50
12	88
24	95
36	100

(viii) Tributyl[(*E*)-2-(*o*-methoxyphenyl)ethen-1-yl]stannane (*E*-113)

(a) A solution of lead tetraacetate (57 mg, 0.128 mmol) in dry deuterochloroform (0.25 ml) was added to a solution of tributyl[(*E*)-2-(*o*-methoxyphenyl)ethen-1-yl]stannane[r] (*E*:*Z* = 81:19, 54 mg, 0.127 mmol) in dry deuterochloroform (0.45 ml). The mixture was analysed by ^{1}H n.m.r. spectroscopy (400 MHz) and found to yield benzofuran (120) in 84% yield. The (*Z*)-isomer exchanged much more slowly than the (*E*)-isomer and it appeared that the unreacted lead tetraacetate oxidised the benzofuran rather than exchanging with the (*Z*)-stannane, since the amount of (*Z*)-stannane remained unchanged throughout the experiment. No *o*-methoxyphenylacetylene (121) was seen in the n.m.r. spectrum.

(b) A solution of the stannanes (113) (*E*:*Z* = 60:40, 2.339 g, 5.5 mmol) in dry chloroform (15 ml) was added to lead tetraacetate (2.451 g, 5.5 mmol). The mixture was stirred at room temperature overnight, filtered, and the volume was made up to 25 ml. GLC analysis on column 5 at 100° showed the formation of benzofuran (120) in 61% yield, and n.m.r. analysis showed the formation of *o*-methoxyphenylacetylene (121) in 30% yield.

(ix) Tributyl[(*Z*)-2-(*o*-methoxyphenyl)propen-1-yl]stannane (*Z*-131)

(a) A solution of tributyl[(*Z*)-2-(*o*-methoxyphenyl)propen-1-yl]stannane (*Z*:*E* = 3:2) (0.7530 g, 1.72 mmol) in dry chloroform (5 ml) was added to lead tetraacetate (0.7636 g, 1.72 mmol). The mixture was stirred overnight, filtered, and the volume was made up to 10 ml with chloroform. The mixture was analysed by GLC using column 6 (and a temperature program of 120° for 18.5 min, followed by a rate of 25°/min up to 250° which was maintained for 30 minutes) and found to contain a 25% yield of 1-(*o*-methoxyphenyl)propyne (134) and a 31% yield of 3-methylbenzofuran

(133). Neither 2-methyl benzofuran (139) or 4-methyl-3-chromene (140) was found. Further analysis showed the presence of methyl acetate, ethyl acetate, butyl acetate, and acetic acid. The absence of 2-methylbenzofuran (139) was rigorously proven by the following procedure: Analysis of the two isomeric benzofurans (133) and (139) on columns 5 and 7 at a range of temperatures between 100° and 250° could not resolve the two peaks. Changing to a longer column with the same solid support (column 8), also could not distinguish between the two isomers. The use of a different column (6) with the above temperature program however, resulted in the two isomers having sufficiently different retention times (2-methylbenzofuran (139), 9.938 min; 3-methylbenzofuran (133), 10.240 min) for analytical accuracy. Mixed injections the two standard compounds in a variety of isomer ratios, indicated that the two could be baseline resolved under the indicated conditions, regardless of the ratio of products. The shorter version of column 6 (column 9) was also found to separate the two compounds sufficently well for analysis, although with less efficiency.

(b) When the above reaction was repeated on a ^1H n.m.r scale, there was found to be a 9% yield of butyl acetate, arising out of competing butyl-tin cleavage of the starting stannane.

(c) A solution of stannanes (131, *Z*:*E* = 3:2) (0.3104 g, 0.71 mmol) in dry chloroform (0.5 ml) was added to lead tetraacetate (0.3130 g, 0.71 mmol) and mercuric acetate (0.0112 g, 0.035 mmol) in dry chloroform (2 ml). The mixture was stirred at room temperature overnight, filtered, and the volume was made up to 10 ml with chloroform. GLC analysis on column 6 as in (i) showed the formation of 1-(*o*-methoxyphenyl)propyne (134) in 24% yield and 3-methylbenzofuran (133) in 33% yield.

(d) A solution of stannanes (131, *E*:*Z* = 9:1) (0.013 g, 2.97×10^{-5} mmol) in dry deuterochloroform (0.4 ml) was added to a solution of lead tetraacetate (0.014 g, 3.16×10^{-5} mmol) in dry deuterochloroform (0.3 ml). The mixture was shaken and ^1H n.m.r. spectra were recorded. After 3 hours, the mixture was filtered, and the volume was made up to 10 ml with chloroform. GLC analysis on column 6 as in (i) showed the formation of 1-(*o*-methoxyphenyl)propyne (134) in 72% yield and 3-methylbenzofuran (133) in 4% yield.

(x) Tributyl[(*Z*)-1-phenylpropen-2-yl]stannane (71)

A solution of tributyl[(*Z*)-1-phenylpropen-2-yl]stannane (0.10 g, 0.25 mmol) in dry chloroform (3 ml) was added to lead tetraacetate (0.11g, 0.25 mmol). The mixture was stirred at room temperature for 8 days, filtered, the internal standard (1-methylnaphthalene) was added, and the mixture was made up to 10 ml. Gas chromatographic analysis on column 4 at 150° indicated the formation of 1-phenylpropyne (67) in 56% yield, (*Z*)-1-phenyl-1-propen-2-yl acetate (*Z*-16) in 1.3% yield, and (*E*)-1-phenyl-1-propen-2-yl acetate (*E*-16) in 0.6% yield.

(xi) Tributyl[(*E*)-2-phenylpropen-1-yl]stannane (66)

A solution of tributyl[(*E*)-2-phenylpropen-1-yl]stannane (0.34 g, 0.83 mmol) in dry chloroform (5 ml) was added to lead tetraacetate (0.37 g, 0.83 mmol). The mixture was stirred at room temperature for 5 days, filtered, the internal standard (1-methylnaphthalene) was added, and the volume was made up to 10 ml. Gas chromatographic analysis on column 4 at 150° indicated the formation of 1-phenylpropyne (67) in 77% yield and (*E*)-1-phenylpropen-2-yl acetate (*E*-16) in 10% yield.

(xii) Trimethyl[(*E*)-2-phenylpropen-1-yl]stannane (70)

A solution of trimethyl[(*E*)-2-phenylpropen-1-yl]stannane (1.25 g, 4.5 mmol) in dry chloroform (5 ml) was added to a stirred solution of lead tetraacetate (1.98 g, 4.5 mmol) in dry chloroform (10 ml). The mixture was stirred at room temperature for 16 hours, filtered and the solvent was removed under reduced pressure in the cold. The residue was distilled to yield 1-phenylpropyne (67) (0.43 g, 83%), b.p. 105°/18 mmHg (lit.[133] 74-5°/14 mmHg).

(xiii) Tributyl[(*Z*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane (*Z*-146)

(i) A solution of tributyl[(*Z*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane containing 7% of the (*E*)-isomer by ^{1}H n.m.r. spectroscopy (0.458 g, 1.05 mmol) in dry chloroform (0.5 ml) was added to a stirred solution of lead tetraacetate (0.464 g, 1.05 mmol) in dry chloroform (2 ml). The mixture was stirred overnight, filtered, and the volume was made up to 10 ml with chloroform. The mixture was analysed by GLC using column 6 (and a temperature program of 120° for 18.5 min, followed by a rate of 25°/min up to 250° which was maintained for 30 minutes) and found to contain a 65% yield of 1-(*o*-methoxyphenyl)propyne (134) and a 7% yield of 2-methylbenzofuran (139)

(ii) A solution of lead tetraacetate (0.102 g, 0.23 mmol) in dry deuterochloroform (2 ml) was added to a solution of tributyl[(*Z*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane containing 45% of the (*E*)-isomer by ^{1}H n.m.r. spectroscopy (0.100 g, 0.23 mmol) in dry deuterochloroform (0.4 ml). The reaction was followed by ^{1}H n.m.r. spectroscopy, and found to yield 2-methylbenzofuran (139) in 20% yield, and 1-(*o*-methoxyphenyl)propyne (134) in 27% yield.

ATTEMPTED CARBENE TRAPPING EXPERIMENTS

(i) Tributyl(2-methylpropen-1-yl)stannane (55)

A solution of tributyl(2-methylpropen-1-yl)stannane (212) (3.46 g, 10 mmol) in dry chloroform (10 ml) was added to lead tetraacetate (4.45 g, 10 mmol) in dry chloroform (10 ml), and the mixture was stirred at room temperature for 2 minutes (metal-metal exchange complete by n.m.r. spectroscopy). Freshly distilled cyclohexene (1.1 ml, 108 mmol) was then added, and the mixture was stirred at room temperature for 24 h. The mixture was filtered, and the filtrate was concentrated at room temperature to 3 ml. Analysis by FTIR showed no absorption at 1776 cm^{-1}, which is present in the cyclopropane derivative (111);[60] the only carbonyl absorption was at 1736 cm^{-1}, due to isobutenyl acetate (108). Analysis by ^1H NMR spectroscopy showed the presence of enol acetate (108), tributyltin acetate, and cyclohexene; there were no signals at δ 1.75, which have been assigned to the methyl groups of compound (111).[151]

(ii) Tributyl[(*E*)-4-phenylbuten-1-yl]stannane (93)

A solution of tributyl[(*E*)-4-phenylbuten-1-yl]stannane (0.19 g, 0.45 mmol) in dry chloroform (5 ml) was added to lead tetraacetate (0.20 g, 0.45 mmol). The mixture was stirred at room temperature for 2 minutes, and freshly distilled cyclohexene (1 ml, 9.8 mmol) was added. The mixture was stirred at room temperature overnight, filtered, and the solvent was removed. ^1H n.m.r. analysis of the crude product indicated the formation of 4-phenyl-1-butyne (90) and 1,2-dihydronaphthalene (95), as well as tributyltin acetate. No products arising out of carbene insertion reactions were observed. Radial chromatography (light petroleum) gave the acetylene (90) in 50% yield, and 1,2-dihydronaphthalene (95) in 15% yield.

Tributyl[(*E*)-2-(*o*-phenylphenyl)ethen-1-yl]stannane (96)

A solution of tributyl[(*E*)-2-(*o*-phenylphenyl)ethen-1-yl]stannane (0.79 g, 1.7 mmol) in dry chloroform (4 ml) was added to a stirred solution of lead tetraacetate (0.75 g, 1.7 mmol) in dry chloroform (12 ml). The mixture was stirred at room temperature for 2 minutes, and freshly distilled cyclohexene (2 ml, 19.6 mmol) was added. The mixture was stirred at room temperature overnight, filtered, and the solvent was removed. ^{1}H n.m.r. analysis of the crude product indicated the formation of *o*-phenylphenylacetylene (99) and phenanthrene (100), as well as tributyltin acetate. No products arising out of carbene insertion reactions were observed. Radial chromatography (light petroleum) gave the acetylene (99) in 29% yield, and phenanthrene (100) in 18% yield.

ANALYSIS OF VINYLLEADTRICARBOXYLATES BY ^{1}H N.M.R. SPECTROSCOPY

General Method

The exchange reactions were generally carried out on scales of about 50 mg of the stannane or mercurial in dry deuterochloroform (0.4 ml). N.m.r. spectra were recorded such that sufficient signal-to-noise was obtained, that the tin or mercury satellites were clearly visible. When Fourier transform n.m.r. spectrometers were used, this involved commonly about 64 scans. It was important to limit sample size, otherwise the exchange reaction produced an almost solid sample, and the resolution was poorer. After the suitable parameters had been determined, the sample was treated with a solution of the lead reagent in the minimum possible volume

of solvent. Spectra were recorded as rapidly as possible for the first 10 minutes, after which spectra were recorded after 1 hour and 24 hours. It was generally found that the resolution deteriorated immediately after the addition, but that it recovered after a few minutes. Thus if the lead comound was relatively stable, it was possible to get very clean spectra. However, if the vinyllead compound was at all unstable, then the first obtained spectrum, generally of lesser quality, had to be used.

The following vinyllead tricarboxylates were studied by the general method.

Vinyllead triacetates:

(i) (*E*)-2-phenylethen-1-yllead triacetate (8) was prepared from the tributylstannane (9) and the divinylmercury compound (7). 400 MHz ^1H n.m.r. analysis showed resonances at δ 7.50 and δ 7.32 with $^3J_{CH,CH}$ 15.21 Hz, and $J_{^{207}Pb,H\,gem}$ 821.3 Hz, and $J_{^{207}Pb,H\,cis}$ 691.7 Hz respectively.

When the lead compound (8) was prepared from the divinylmercury compound (7), there was also formed one equivalent of the corresponding vinylmercury acetate (5), as shown by resonances at δ 6.50 and δ 6.81 with $^3J_{CH,CH}$ 17.99 Hz.

(ii) (*E*)-2-(*p*-methoxyphenyl)ethen-1-yllead triacetate (50) was prepared from the tributylstannane (114) and trimethylstannane (171). 400 MHz ^1H n.m.r. analysis showed resonances at δ 7.37 and δ 7.25 with $^3J_{CH,CH}$ 15.00 Hz, and $J_{^{207}Pb,H\,gem}$ 831.3 Hz, and $J_{^{207}Pb,H\,cis}$ 692.5 Hz respectively.

(iii) (*E*)-2-(*o*-methoxyphenyl)ethen-1-yllead triacetate (*E*-119) was prepared from the tributylstannane (*E*-113). 400 MHz ^{1}H n.m.r. analysis showed resonances at δ 7.72 and δ 7.44 with $^3J_{CH,CH}$ 14.00 Hz, and $J_{^{207}Pb,Hgem}$ 926.5 Hz, and $J_{^{207}Pb,Hcis}$ 761.0 Hz respectively. Also observed was an AA'BB' system: 6.90, 2H, d, $J_{AB} + J_{AB'}$ 8.58 Hz, ArH *ortho* to MeO; 7.40, 2H, d, $J_{AB} + J_{AB'}$ 8.58 Hz, ArH *meta* to MeO.

(iv) (*E*)-2-phenylpropen-1yllead triacetate (*E*-12) was prepared from the stannane (66) and the divinylmercury compound (11). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 6.89 with $J_{^{207}Pb,gem}$ 864.8 Hz.

When the lead compound (*E*-12) was prepared from the divinylmercury compound (11), there was also formed one equivalent of the corresponding vinylmercury acetate (13) as shown by a resonance at δ 6.26 with $^2J_{^{199}Hg,CH}$ 234.0 Hz.

(v) (*Z*)-2-phenylpropen-1-yllead triacetate (*Z*-12) was prepared from the stannane (*Z*-66). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 6.83 with $J_{^{207}Pb,Hgem}$ 871.0 Hz.

(vi) 2-Methylpropen-1yllead triacetate (106) was prepared from the tributylstannane (55) and the divinylmercury compound (189). 400 MHz n.m.r. analysis showed a resonance at δ 6.37 with $J_{^{207}Pb,Hgem}$ 924.1 Hz.

When the lead compound (106) was prepared from the divinylmercury compound (189), there was also formed one equivalent of the corresponding vinylmercury acetate (218) as shown by a resonance at δ 5.31 with $^2J_{^{199}Hg,CH}$ 273.48 Hz.

(vii) (*E*)-2-(*o*-methyphenyl)ethen-1-yllead triacetate (*E*-159) was prepared from tributylstannane (*E*-157). 400 ^{1}H n.m.r. analysis showed resonances at δ 7.39 and δ 7.59 with $^{3}J_{CH,CH}$ 14.41 Hz and $J_{207Pb,Hgem}$ 866.7 Hz and $J_{207Pb,Hcis}$ 708.1 Hz respectively. Also observed was a methyl resonance at δ 2.32.

(viii) (*Z*)-2-(*o*-methyphenyl)ethen-1-yllead triacetate (*Z*-159) was prepared from tributylstannane (*Z*-157). 400 ^{1}H n.m.r. analysis showed resonances at 7.17 and 7.88 with $^{3}J_{CH,CH}$ 6.48 Hz and $J_{207Pb,Hgem}$ 871.0 Hz and $J_{207Pb,Htrans}$ 1599.0 Hz respectively. Also observed was a methyl resonance at δ 2.42.

(ix) 2,2-Diphenylethen-1-yllead triacetate (58) was prepared from divinylmercury compound (57). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 7.33 with $J_{207Pb,Hgem}$ 819.0 Hz.

Also formed was one equivalent of the corresponding vinylmercury acetate (59) as shown by a resonance at δ 6.25 with $^{2}J_{199Hg,CH}$ 240.43 Hz.

(x) (*E*)-2-(*o*-phenylphenyl)ethen-1-yllead triacetate (97) was prepared from tributylstannane (96). 200 MHz ^{1}H n.m.r. analysis showed resonances at δ 7.42 and δ 7.27 with $^{3}J_{CH,CH}$ 14.79 Hz and $J_{207Pb,Hgem}$ 860.0 Hz and $J_{207Pb,Hcis}$ 704.0 Hz respectively.

(xi) Cyclohexenyllead triacetate (33) was prepared from the tributylstannane (32), the divinylmercury compound (34) and the vinylmercury bromide (214). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 6.17 with $J_{207Pb,Hcis}$ 729.8 Hz.

When the lead compound (33) was prepared from the divinylmercury compound (34), there was also formed one equivalent of the corresponding vinylmercury acetate (218) as shown by a resonance at δ 5.67 with $^{2}J_{^{199}Hg,CH}$ 301.42 Hz.

(xii) (*E*)-2-(*o*-methoxyphenyl)propen-1-yllead triacetate (*E*-132) was prepared from the tributylstannane (*E*-131). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 7.03 with $J_{^{207}Pb,H\,gem}$ 900.0 Hz.

(xiii) Cyclopenten-1-yllead triacetate (29) was prepared from the tributylstannane (28). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 6.37 with $J_{^{207}Pb,H\,cis}$ 293.9 Hz.

(xiv) (*E*)-propen-1-yllead triacetate (*E*-209) was prepared from tributylstannane (*E*-192). 200 MHz ^{1}H n.m.r. analysis showed resonances at δ 7.84 with $^{3}J_{CH,CH}$ 14.20 Hz, $^{4}J_{CH_3,CH}$ 1.48 Hz and $J_{^{207}Pb,H\,gem}$ 931.0 Hz; δ 7.50 with $^{3}J_{CH,CH}$ 14.20 Hz, $^{3}J_{CH_3,CH}$ 6.80 Hz, and $J_{^{207}Pb,H\,gem}$ 931.0 Hz and $J_{^{207}Pb,H\,cis}$ 689.5 Hz; δ 2.04 with $^{3}J_{CH,CH_3}$ 6.80 Hz, and $^{4}J_{CH,CH_3}$ 1.48 Hz.

(xv) (*Z*)-propen-1-yllead triacetate (*Z*-209) was prepared from tributylstannane (*Z*-192). 200 MHz ^{1}H n.m.r. analysis showed resonances at δ 7.74 with $^{3}J_{CH,CH}$ 6.10 Hz, and $J_{^{207}Pb,H\,gem}$ 924.0 Hz; δ 7.77 with $^{3}J_{CH,CH}$ 6.10 Hz, $^{3}J_{CH_3,CH}$ 5.00 Hz, and $J_{^{207}Pb,H\,trans}$ 1667.5 Hz.

(xvi) Ethenyllead triacetate (210) was prepared from tributylstannane (191). 200 MHz ^{1}H n.m.r. analysis showed resonances at δ 7.25, $^{3}J_{CH,CH}$ 15.49 Hz, $^{3}J_{CH,CH}$ 7.10 Hz, $J_{^{207}Pb,H\,gem}$ 952.2 Hz; δ 6.17, $^{3}J_{CH,CH}$ 15.49 Hz, $^{2}J_{CH,CH}$ 4.80 Hz, $J_{^{207}Pb,H\,cis}$ 812.8; δ 6.29, $^{3}J_{CH,CH}$ 7.10 Hz, $^{2}J_{CH,CH}$ 4.80 Hz, $J_{^{207}Pb,H\,trans}$ 1671.9 Hz.

(xvii) Bis[(*E*)-2-phenylethenyl]lead diacetate (211) was found (200 MHz ^{1}H n.m.r analysis) to have resonances at δ 7.60 and δ 7.42 with $^3J_{CH,CH}$ 16.21 Hz, and $J_{^{207}Pb,H\,gem}$ 433.1 Hz, and $J_{^{207}Pb,H\,cis}$ 339.9 Hz respectively.

Unsuccessful ^{1}H n.m.r. experiments with lead tetraacetate:

The following compounds failed to give recognisable vinyllead triacetate intermediates:

trimethyl(2,2-diphenylethen-1-yl)stannane (56),

tributyl[(*Z*)-1-phenylpropen-2-yl]stannane (71),

trimethyl[(*Z*)-1-phenylpropen-2-yl]stannane (73),

tributyl(cyclohexylidenemethyl)stannane (76),

tributyl[(*Z*)-4-phenyl-1-buten-1-yl]stannane (87),

tributyl[(*Z*)-2-phenylethen-1-yl]stannane (91),

tributyl[(*E*)-4-phenyl-1-buten-1-yl]stannane (93),

tributyl[(*Z*)-2-(*o*-methoxyphenyl)propen-1-yl]stannane (*Z*-131),

tributyl[(*E*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane (*E*-146),

tributyl[(*Z*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane (*Z*-146),

bis[(*Z*)-1-phenylpropen-2-yl]mercury (177),

bis[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]mercury (178),

trimethyl(propen-2-yl)stannane (190),

tributyl[(*Z*)-1,2-diphenylethen-1-yl]stannane (193), and

tributyl[(*Z*)-3-(2-dihydropyranyloxy)propen-1-yl]stannane (195).

Vinyllead tribenzoates:

(i) (*E*)-2-phenylethen-1-yllead tribenzoate (197) was prepared from divinylmercury compound (7). 200 MHz ^{1}H n.m.r analysis showed resonances at δ 7.68 and δ 7.51 with $^3J_{CH,CH}$ 14.79 Hz and $J_{207Pb,Hgem}$ 819.8 Hz and $J_{207Pb,Hcis}$ 689.0 Hz respectively.

Also formed was one equivalent of the corresponding vinylmercury benzoate (219) as shown by resonances at δ 6.51 and δ 6.79 with $^3J_{CH,CH}$ 17.96 Hz.

(ii) (*E*)-2-(*p*-methoxyphenyl)ethen-1-yllead tribenzoate (199) was prepared from the tributylstannane (114) and trimethylstannane (171). 200 MHz ^{1}H n.m.r. analysis showed resonances at δ 7.57 and δ 7.45 with $^3J_{CH,CH}$ 14.46 Hz and $J_{207Pb,Hgem}$ 829.5 Hz and $J_{207Pb,Hcis}$ 696.5 Hz respectively.

(iii) (*E*)-2-(*o*-methylphenyl)ethen-1-yllead tribenzoate (201) was prepared from the stannane (*E*-157). 200 MHz ^{1}H n.m.r analysis showed resonances at δ 7.58 and δ 7.78 with $^3J_{CH,CH}$ 14.40 Hz, and $J_{207Pb,Hgem}$ 869.4 Hz and $J_{207Pb,Hcis}$ 707.6 Hz respectively. Also observed was a methyl resonance at δ 2.40.

(iv) Cyclohexen-1-yllead tribenzoate (207) was prepared from tributylstannane (32) and divinylmercury compound (34). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 6.34 with $J_{207Pb,Hcis}$ 732.4 Hz.

When the lead compound (207) was prepared from the divinylmercury compound (34), there was also formed one equivalent of the corresponding vinylmercury benzoate (220) as shown by a resonance at δ with $^2J_{199Hg,CH}$ Hz.

(v) Cyclopenten-1-yllead tribenzoate (208) was prepared from tributylstannane (28). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 6.54, with $J_{^{207}Pb,Hcis}$ 295.9 Hz.

(vi) 2,2-Diphenylethen-1-yllead tribenzoate (204) was prepared from divinylmercury compound (57). 200 MHz ^{1}H n.m.r analysis showed a resonance at δ 7.60 with $J_{^{207}Pb,Hgem}$ 829.5 Hz.

Also formed was one equivalent of the corresponding vinylmercury benzoate (215) as shown by a resonance at δ 6.23 with $^2J_{^{199}Hg,CH}$ 238.74 Hz (relative area, 17%).

(vii) (*E*)-2-phenylpropen-1-yllead tribenzoate (202) was prepared from tributylstannane (66) and divinylmercury compound (11). 200 MHz ^{1}H n.m.r. analysis showed a resonance at δ 7.10 with $J_{^{207}Pb,Hgem}$ 871.9 Hz.

When the lead compound (203) was prepared from the divinylmercury compound (11), there was also formed one equivalent of the corresponding vinylmercury benzoate (221) as shown by a resonance at δ 6.02 with $^2J_{^{199}Hg,CH}$ 243.54 Hz (relative area, 17%).

(viii) 2-methylpropen-1-yllead tribenzoate (188) was prepared from the stannane (55). 200 MHz ^{1}H n.m.r analysis showed a resonance at δ 6.58 with $J_{^{207}Pb,Hgem}$ 933.3 Hz. Also observed were methyl resonances at δ 2.00 and δ 2.20.

Unsuccessful ^1H n.m.r. experiments with lead tetrabenzoate:

The following compounds failed to give recognisable vinyllead tribenzoate intermediates:

trimethyl[(*Z*)-2-phenylethen-1-yl]stannane (*Z*-52),

trimethyl(2,2-diphenylethen-1-yl)stannane (56),

tributyl[(*Z*)-1-phenylpropen-2-yl]stannane (71),

trimethyl[(*Z*)-1-phenylpropen-2-yl]stannane (73),

tributyl(cyclohexylidenemethyl)stannane (76),

tributyl[(*Z*)-4-phenyl-1-buten-1-yl]stannane (87),

tributyl[(*E*)-4-phenyl-1-buten-1-yl]stannane (93),

tributyl[(*E*)-2-(*o*-phenylphenyl)ethen-1-yl]stannane (96),

tributyl[(*Z*)-2-(*o*-methoxyphenyl)propen-1-yl]stannane (*Z*-131),

tributyl[(*E*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane (*E*-146),

tributyl[(*Z*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane (*Z*-146),

bis[(*Z*)-1-phenylpropen-2-yl]mercury (177),

bis[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]mercury (178),

trimethyl(propen-2-yl)stannane (190),

tributylethenylstannane (191),

tributyl[(*E*,*Z*)-propen-1-yl]stannane (192),

tributyl[(*Z*)-1,2-diphenylethen-1-yl]stannane (193), and

tributyl[(*Z*)-3-(2-dihydropyranyloxy)propen-1-yl]stannane (195),

Vinyllead tripivalates:

(i) 2-Methylprop-1-en-1-yllead tripivalate (206) was prepared from the tributylstannane (55). 90 MHz n.m.r. analysis showed this compound to be relatively stable, and it only began to decompose after 2 hours. δ (90 MHz, $CDCl_3$) 1.22, 27H, s, $3xOCOC(CH_3)_3$; 1.97, 3H, s, CH_3; 2.05, 3H, s, CH_3; 6.28, 1H, bs, $^2J_{207Pb,Hgem}$ 879.0 Hz.

(ii) (*E*)-2-phenylethen-1-yllead tripivalate (198) was prepared from divinylmercury compound (7). 200 MHz ^1H n.m.r. analysis showed resonances at δ 7.42 and δ 7.26 with $^3J_{CH,CH}$ 14.89 Hz, and $J_{207Pb,Hgem}$ 795.6 Hz and $J_{207Pb,Hcis}$ 696.5 Hz respectively.

Also formed was one equivalent of the corresponding vinylmercury pivalate (222) as shown by resonances at δ 6.50 and δ 6.79 with $^3J_{CH,CH}$ 18.00 Hz.

(iii) (*E*)-2-(*p*-methoxyphenyl)ethen-1-yllead tripivalate (200) was prepared from trimethylstannane (171). 200 MHz ^1H n.m.r analysis showed resonances at δ 7.28 and δ 7.19 with $^3J_{CH,CH}$ 14.86 Hz, and $J_{207Pb,Hgem}$ 799.4 Hz, and $J_{207Pb,Hcis}$ 662.2 Hz.

(iv) (*E*)-2-phenylpropen-1-yllead tripivalate (203) was prepared from tributylstannane (66) and divinylmercury compound (11). 200 MHz ^1H n.m.r. analysis showed a resonance at δ 6.89 with $J_{207Pb,Hgem}$ 834.7 Hz.

When the lead compound (203) was prepared from the divinylmercury compound (11), there was also formed one equivalent of the corresponding vinylmercury pivalate (223) as shown by a resonance at δ 6.02 with $^2J_{199Hg,CH}$ 239.94 Hz.

(v) 2,2-Diphenylethen-1-yllead tripivalate (205) was prepared from divinylmercury compound (57). 200 MHz ^{1}H n.m.r analysis showed a resonance at δ 7.34 with $J_{^{207}Pb,H_{gem}}$ 789.7 Hz.

Also formed was one equivalent of the corresponding vinylmercury pivalate (224) as shown by a resonance at δ 6.22 with $^2J_{^{199}Hg,CH}$ 234.84 Hz.

Unsuccessful ^{1}H n.m.r. experiments with lead tetrapivalate:

The following compounds failed to give recognisable vinyllead tripivalate intermediates:

trimethyl[(*Z*)-2-phenylethen-1-yl]stannane (*Z*-52),
trimethyl(2,2-diphenylethen-1-yl)stannane (64),
tributyl[(*Z*)-1-phenylpropen-2-yl]stannane (71),
trimethyl[(*Z*)-1-phenylpropen-2-yl]stannane (73),
tributyl(cyclohexylidenemethyl)stannane (76),
tributyl[(*Z*)-4-phenyl-1-buten-1-yl]stannane (87),
tributyl[(*E*)-4-phenyl-1-buten-1-yl]stannane (93),
tributyl[(*E*)-2-(*o*-phenylphenyl)ethen-1-yl]stannane (96),
tributyl[(*Z*)-2-(*o*-methoxyphenyl)propen-1-yl]stannane (*Z*-131),
tributyl[(*E*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane (*E*-146),
tributyl[(*Z*)-1-(*o*-methoxyphenyl)propen-2-yl]stannane (*Z*-146),
bis[(*Z*)-1-phenylpropen-2-yl]mercury (177),
bis[(*E*)-2-(*p*-methoxyphenyl)ethen-1-yl]mercury (178),
trimethyl(propen-2-yl)stannane (190),
tributylethenylstannane (191),
tributyl[(*E*,*Z*)-propen-1-yl]stannane (192),
tributyl[(*Z*)-1,2-diphenylethen-1-yl]stannane (193), and
tributyl[(*Z*)-3-(2-dihydropyranyloxy)propen-1-yl]stannane (195).

APPENDIX

Table 23. GLC retention times for standard compounds.

Compound	Column	Temperature (°C)	Retention Time (min)
(174)	5	200	4.93
(67)	4	150	2.30
(67)	5	100	3.92
(*E*-16)	4	150	11.47
(*E*-16)	5	100	7.06
(*Z*-16)	4	150	11.47
(*Z*-16)	5	100	6.85
(74)	5	100	3.80
(80)	2	150	6.68
(62)	3	160	3.11
(65)	3	160	1.66
(63)	3	160	5.92
(*E*,*Z*-219)	3	160	8.43
(90)	5	100	3.94
(95)	5	100	6.25
(100)	5	150	6.51
(99)	5	150	3.38
(158)	7	150	2.44
(161)	7	150	2.51
(160)	7	150	2.75

Table 23 (Cont'd). GLC retention times for standard compounds.

Compound	Column	Temperature (°C)	Retention Time (min)
(120)	5	100	3.02
(121)	5	100	5.62
(133)	6	120	10.24
(139)	6	120	9.40
(134)	6	120	22.99

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