NEW SYNTHESES WITH SULPHUR AND SELENIUM COMPOUNDS

A thesis submitted by

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'It is a better thing to travel hopefully than it is to arrive'

R. L. Stevenson

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ABSTRACT

The literature relating to sterically hindered olefins, and to the oxidation of disulphides and diselenides, is reviewed.

Monomeric selenoketones (selones) have been prepared from di-*t*-butyl ketone and (-)-1,3,3-trimethylnorbornan-2-one by heating their triphenylphosphoranylidenehydrazones with selenium. Although it was not possible to prepare tetra-*t*-butylethylene, the hindered olefin (-)-1,1',3,3,3',3'-hexamethyl-2,2'-binorbornylidene could be obtained in good yield *via* a two-fold extrusion reaction.

Treatment of cyclohexa-2,4-dienones with phosphorous pentasulphide or pentaselenide leads to rearrangement and fragmentation of the dienone, rather than the desired dienethiones or dieneselones.

Oxidation of diphenyl disulphide with two equivalents of *N*-chloro-*N*-sodio-4-methylbenzenesulphonamide affords a crystalline product; the possible structures are discussed. Similar treatment of diphenyl diselenide leads to an unstable intermediate, probably a selenoseleninamidine, which effects *trans*-1,2-selenoamination of cyclohexene at low temperatures, and decomposes with evolution of nitrogen at room temperature.

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PART I

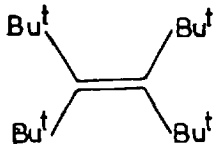
REVIEWS

A STERICALLY CROWDED OLEFINS

1. Theoretical Considerations

The olefinic bond is one of the most extensively documented functional groups in the literature of organic chemistry; however, the structure and reactivity of very hindered olefins did not attract much attention until quite recently[1].

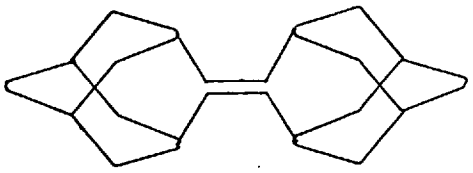
The structure of hindered olefins may provide useful insights into the nature of the double bond. Bulky substituents may be expected to distort the ideal ethylenic geometry in order to relieve non-bonded interactions; such distortions may involve bond stretching, alteration of bond angles, and twisting about the double bond. The latter effect is of particular interest, since in extreme cases the olefin may exhibit diradical rather than olefinic behaviour when the angle of twist about the double bond is too great to allow effective π-orbital overlap. Calculations based on a simple cosine potential curve related to vibrational frequencies suggest that the very hindered tetra-t-butylethylene (I),



(I)

which has not yet been synthesised, would have a 75° twist, implying substantial diradical character[2]. Such a diradical might well be stable, by analogy with the tri-t-butylmethyl radical[3]. The known olefins biadamantylidene (II) and 2,3-bis-(cis-4-chloro-1-methylcyclohexyl)-trans-2-butene (III), in contrast, display relatively low torsional effects (0°[4] and

16^{0}[5] respectively) despite significant non-bonded interactions.



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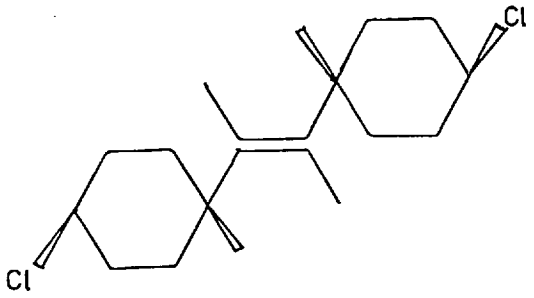
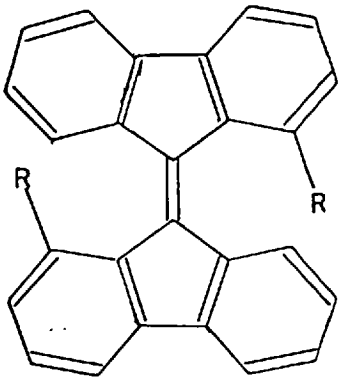


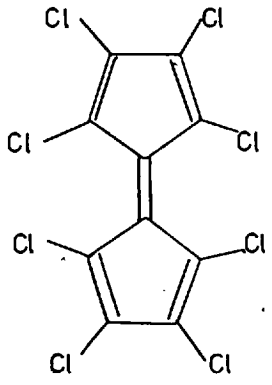
(III)

Some olefins whose formal structures require coplanarity of all parts of the molecule, have high torsion angles; examples are the bifluorenylidenes (IV) and substituted pentafulvalenes (V) (angles 43^{0}[6] and 41^{0}[7] respectively). However, in these



$R=CO_2CH(CH_3)_2$

(IV)

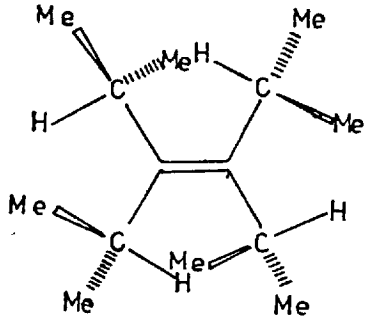


(V)

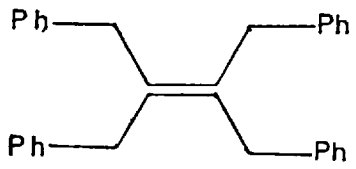
cases the olefinic bond itself is not as crowded as in compounds (I) to (III); furthermore, the structures offer considerable stabilisation for diradical intermediates, as evidenced by the low barrier to cis-trans isomerisation of (IV) (ΔG = 20-21 Kcal/mole)[8].

Another interesting steric phenomenon is the 'cogwheel' or 'gear' effect which is observed when the interactions between large groups present high energy barriers to rotation,

thus 'locking' the groups in certain preferred conformations. For example, the most stable conformation of hexaisopropylbenzene has the methine protons in the plane of the ring, with all the isopropyl groups pointing in the same direction around the ring[9]. A similar effect is observed in the case of tetraisopropylethylene (VI). The conformation shown, which has the minimum of steric interactions, has two non-equivalent pairs of methine protons. Accordingly, the proton n.m.r.



(VI)



(VII)

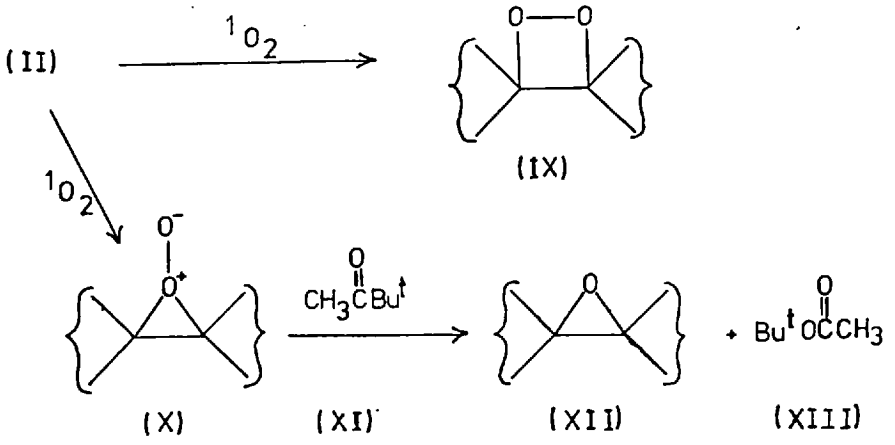
spectrum at low temperature shows two methyl doublets, which coalesce to one doublet at higher temperature[10a]. A similar effect is observed in the ^{13}C n.m.r. and laser Raman spectra[10b]. Tetrabenzylethylene (VII) does not exhibit a gear effect[11]; evidently the steric crowding is less severe in this case.

It has sometimes been found that the rates of electrophilic addition of substituted olefins tend to diminish with increasing bulk of the substituents[11,12], and the various attempts at rationalising such effects will not be discussed here. A more interesting phenomenon is that the steric bulk of the substituents may provide sufficient protection for an otherwise reactive intermediate to enable it to be trapped or even isolated. Biadamantylidene (II) has been particularly useful in this respect: for example, reaction with two moles

of bromine yields a salt which is believed to contain the brominium species (VIII)[13], postulated as the intermediate in the addition of bromine to olefins. However, no spectroscopic evidence for the structure (VIII) was provided, and the physical evidence would also be compatible with an inclusion complex of some kind.

(VIII)

Addition of singlet oxygen to the olefin (II) gave a stable dioxetane (IX), the first tetra-alkyl substituted dioxetane to be isolated[14]. The presence of an intermediate perepoxide (X) in this reaction was indicated by the formation of the dioxetane (IX), biadamantylidene oxide (XII), and t-butyl acetate (XIII) on reaction in the presence of t-butyl methyl ketone (XI)[15]. It is postulated that the ketone is



(X) (XI) (XII) (XIII)

oxidised by the perepoxide via a Baeyer-Villiger type reaction. However, this result does not necessarily mean that the perepoxide (X) is an intermediate in the formation of the dioxetane (IX).

Hindered olefins, therefore, are of interest to the physical chemist for the structural and mechanistic information they may provide; needless to say, they also offer a challenge to the ingenuity and skill of the synthetic chemist.

2. Synthetic Methods

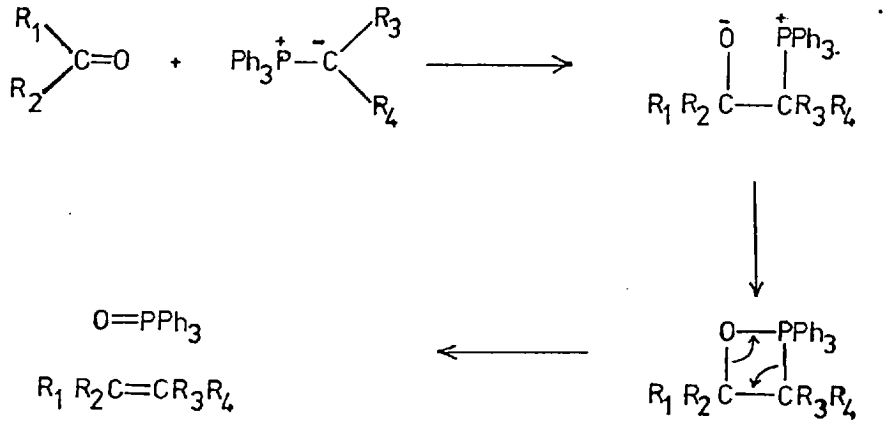
Olefins are most commonly made by rearrangement of other olefins, by addition to acetylenes, and by elimination, condensation or extrusion reactions[16]. Few of these reactions are applicable to hindered olefin synthesis, since the olefinic precursors themselves may present synthetic obstacles in extremely hindered cases. This review will be limited to some reactions which deal directly with the problem of carbon-carbon bond formation, and which are applicable to the synthesis of highly substituted olefins.

a Reactions of Ylids and Carbanions with Ketones and Aldehydes

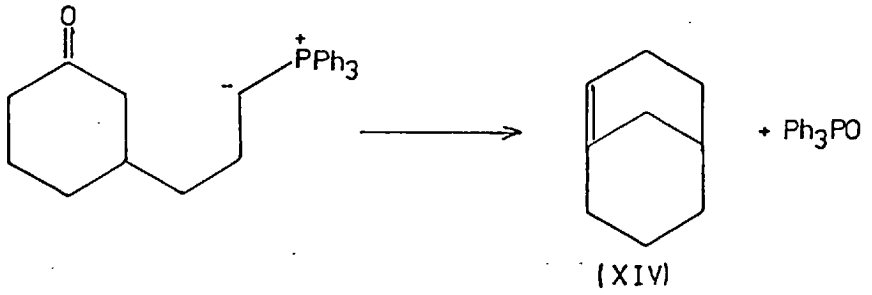
The most important recent olefin-forming process is the Wittig reaction, illustrated in Scheme 1[17]. This may be regarded as a consecutive condensation-elimination. The procedure is generally applied to di- or trisubstituted olefins, and very few tetrasubstituted olefins can be prepared in this way. Much of the work on the Wittig reaction has been directed towards improving the stereospecificity

under various conditions[17].

Scheme 1



However, the procedure can be used to prepare strained olefins, as in the recent synthesis of the cycloalkene (XIV)[18].



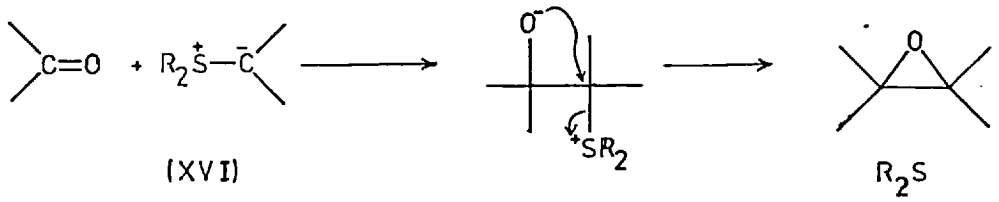
(XIV)

In cases where the substituents (R_3,R_4) on the ylid are capable of stabilising the negative charge, the ylid may be unreactive. This can be overcome by employing α--carbanions of phosphorous oxides (XVa)[19] or phosphonates (XVb)[20], in which the stabilising effect of the phosphorous substituent is diminished.

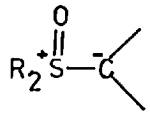
(XVa) (XVb)

Sulphonium (XVI) and sulphoxonium ylids (XVII) react with carbonyl compounds to give epoxides (Scheme 2)[21].

Scheme 2



(XVI)

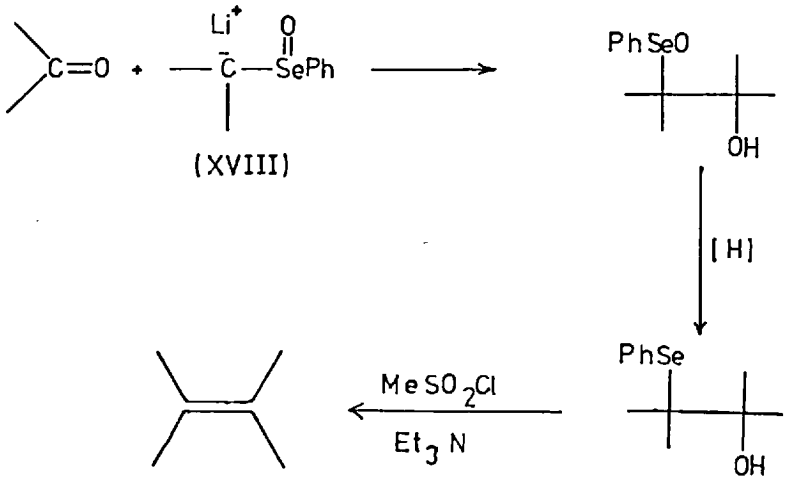


(XVII)

These reactions are in principle applicable to olefin synthesis, but research in this field has taken other directions[21]. The α-carbanions of sulphinamides[22], sulphoxides[23] and sulphoximides[24] undergo reactions similar to the Wittig and appear to be subject to the same steric limitations.

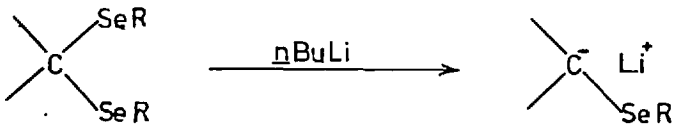
The condensation of α-lithiated selenoxides (XVIII) with ketones is a recent development[25].

Scheme 3



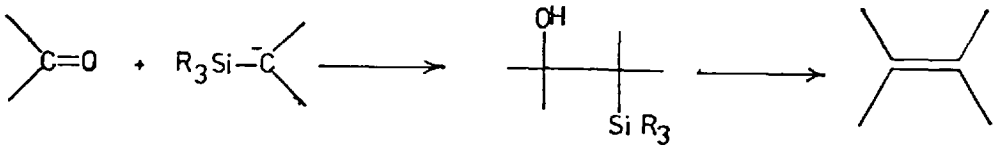
(XVIII)

The advantage of this procedure lies in the ease of removal of the selenoxide moiety (as compared with sulphoxide). The procedure shown in Scheme 3 can be short-circuited by the use of α-lithioselenides (XX), which are easily obtained from the corresponding selenoacetal (XIX)[26,27]; the methylselenoanions (XX, R=Me) are particularly reactive[27]. The conversion of the β-hydroxyselenides to olefins can also be effected by 4-methylbenzenesulphonic acid, perchloric acid or trifluoroacetic anhydride[26]. This reaction is believed to be a stereospecific anti-elimination. The steric limits of this procedure have yet to be explored.



(XIX) (XX)

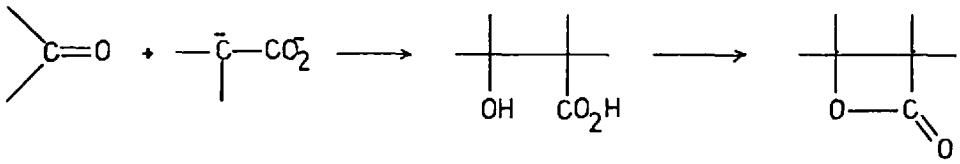
The analogous reaction of α-silyl anions (XXI) with ketones produces β-hydroxysilanes (XXII)[28]. The advantages of this procedure are (i) the strongly nucleophilic character of the anions (XXI), and (ii) the flexibility of the subsequent elimination.



(XXI) (XXII)

The conversion of the β-hydroxysilanes (XXII) to olefins proceeds via syn-elimination in base and anti-elimination in acid, so that olefins of either Z- or E-configuration may be produced, as required[29].

The β-anions of carboxylates (XXIII), which are readily available from carboxylic acids, react with ketones and aldehydes to give β-hydroxyacids (XXIV). These may be converted to β-lactones (XXV), which readily extrude carbon dioxide to afford the olefin[30]. This approach is especially



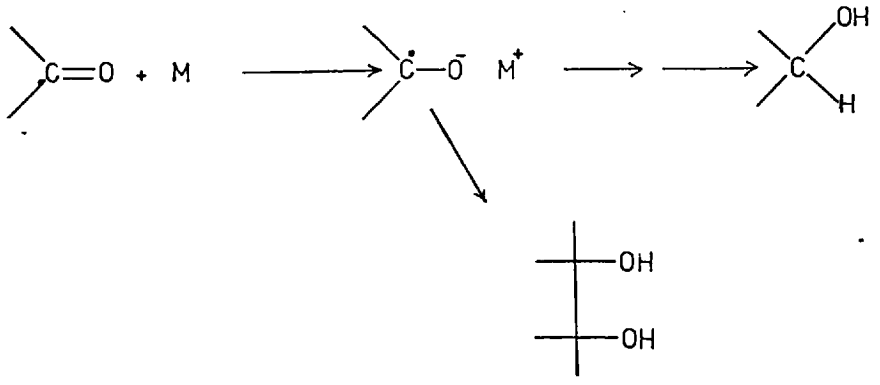
(XXIII) (XXIV) (XXV)

useful in view of the availability of the starting materials, and its proven applicability to the synthesis of tetra-substituted olefins, such as the mixed and symmetrical bis-(cycloalkylidenes)[30c].

All of the methods in this section require direct reaction between the carbon centres which are to be joined. In very hindered cases, such an approach is unlikely to be fruitful.

b The Pinacol Reduction

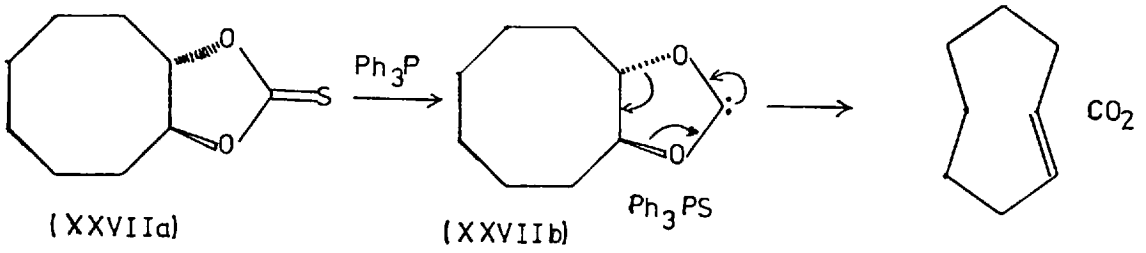
Metallic reduction of ketones in aprotic media frequently leads to pinacols (XXVI) via radical anion dimerisation. If magnesium, zinc or aluminium are used, the pinacols are the major products[31]. Since fairly hindered ketones can thus be coupled, this reaction might lead to a general olefin synthesis



(XXVI)

if the hydroxyl groups could be easily removed. The elegant, stereospecific method of Corey[32] (Scheme 4) involves the preparation of a thiocarbonate (XXVIIa), followed by treatment with a phosphine to give a carbene (XXVIIb) (or possibly an ylid) which loses carbon dioxide to give the olefin.

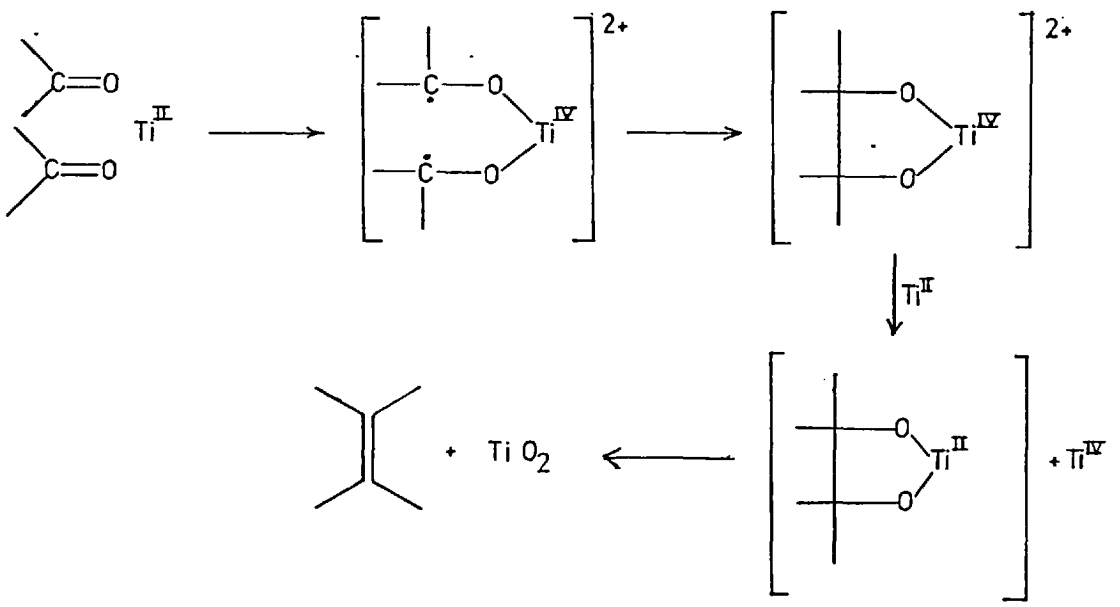
Scheme 4



(XXVIIa) (XXVIIb)

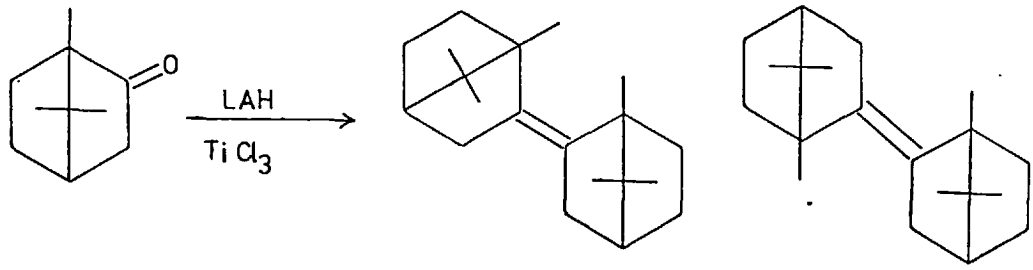
A new, inexpensive procedure for performing the coupling and deoxygenation steps consecutively (in one operation) employs a lithium aluminium hydride/titanium(III) chloride complex (McMurry's reagent)[33], in which the reducing species is believed to be titanium(II). Scheme 5 shows a plausible reaction pathway. The intermediate pinacols, which can be isolated from the reaction mixture, are deoxygenated

Scheme 5



under these conditions. Earlier work on titanium reagents using magnesium[34] or zinc[35] as the reducing agent, had indicated that although the coupling could be performed, the deoxygenation was only effective with pinacols derived from aryl ketones. This restriction does not apply to the McMurry reagent. Low valent tungsten species have been used to perform the same overall transformation, presumably via the same mechanism[36].

The titanium reagent has been used to prepare a number of tetrasubstituted olefins, including biadamantylidene (II), in an improved yield over the extrusion reaction previously used for its preparation[37] (see section 2.c). The reaction is not stereospecific: for example, d-(+)-camphor (XXVIII) gave an almost equal mixture of the cis- and trans--1,1',7,7,7',7'-hexamethyl-2,2'-binorbornylidenes (XXIX and XXX)[38].



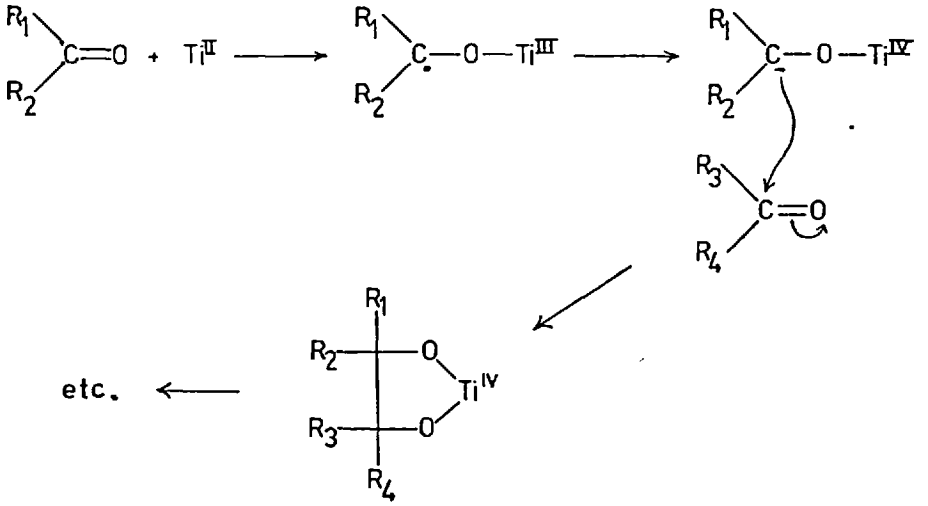
(XXVIII) (XXIX) (XXX)

Subsequent to McMurry's original work, it was shown that titanium(0) performs the same reaction with improved yields[39]. Recently the reaction was extended to the preparation of four-, five- and six-membered ring alkenes from the appropriate diketones, using either the original reagent[40] or a lithium aluminium hydride/cyclopentadienyl titanium(IV) chloride complex[41].

The pinacol reduction is most effective in the preparation of symmetrical pinacols, and hence symmetrical olefins. Attempts to couple two different ketones generally lead to all three pinacols, in an approximately statistical ratio[41]. However, it has proved possible to obtain high yields of unsymmetrical olefins in cases where one of the ketones is more readily reduced than the other[42]. If the radical anion formed from one ketone is reduced to a dianion before the other ketone is reduced at all, the reaction proceeds *via* an ionic mechanism (Scheme 6), and the unsymmetrical product predominates.

Gem-dihalides can also be coupled by metallic reduction in a similar process to give olefins, presumably *via* 1,2--dihalides[43]; the first synthesis of biadamantylidene (II) was achieved by reacting 2,2-dibromoadamantane with a zinc/copper couple[44]. However, this method appears to be very sensitive to moisture and impurities[37]. The McMurry reagent

Scheme 6[42]

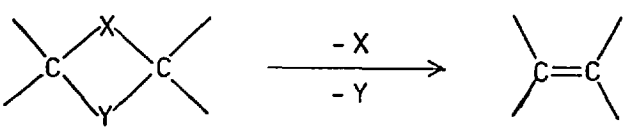


is reported to be extremely effective in this coupling reaction, as well as in the dehalogenation of 1,2-dihalides in general[45].

McMurry has attempted at least one unsuccessful reaction with di-t-butyl ketone[42]; since he has not reported a synthesis of tetra-t-butylethylene (I), it may be assumed that the reaction fails in extremely hindered cases.

c Twofold Extrusion Reactions

A number of heterocycles can undergo extrusion reactions to form olefins[46]. Probably the best model systems are those of general structure (XXXI), where X and Y are easily

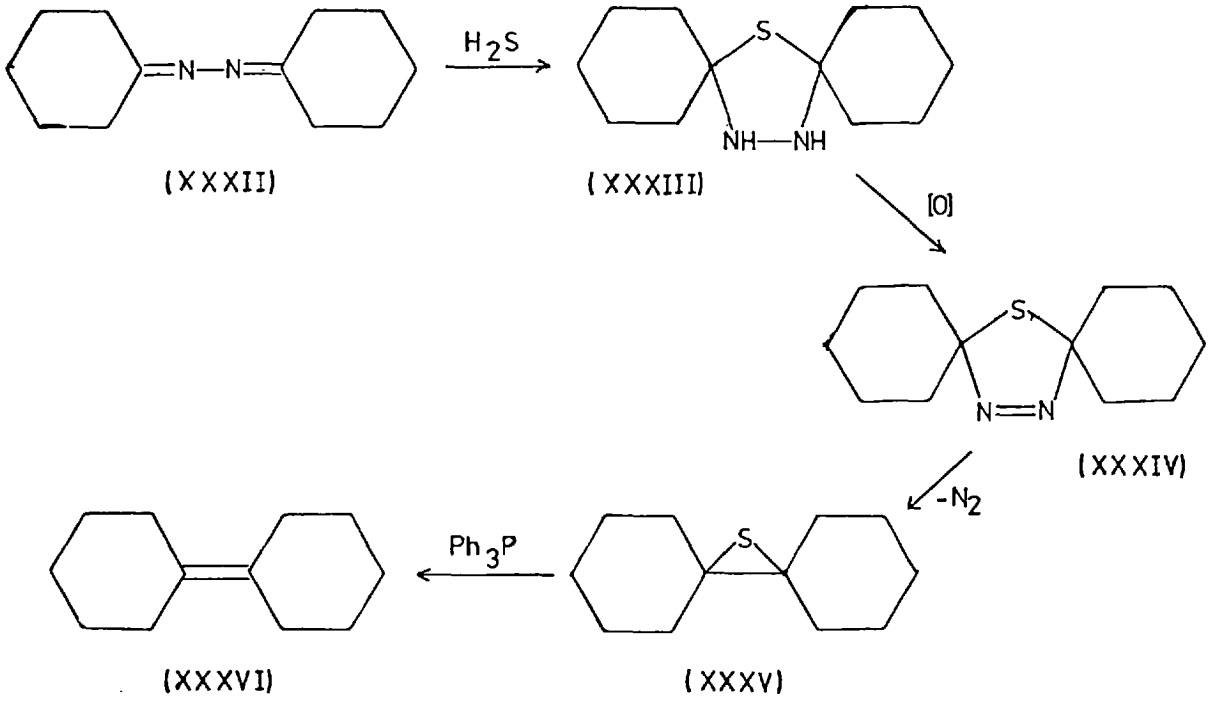


(XXXI)

X,Y = O, O_2, S, S_2, SO, SO_2, N_2, CO, CO_2, CS_2, N_2O, etc.

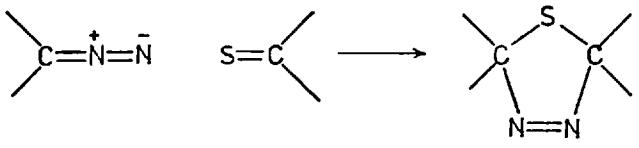
extrudable fragments, since this simplifies the problem of initially forming the carbon-carbon linkage. An investigation of a number of systems showed that 1,3-oxathiolan-5-ones (XXXIa, X=S, Y=-C(=O)-O-) and 1,3,4-thiadiazolines (XXXIb, X=S, Y=-N=N-) were the most promising[47a-c]. However, the oxathiolanones (XXXIa) only extrude in the desired manner if conjugating residues, such as phenyl groups, are present. The thiadiazoline system was more generally applicable. Thus, cyclohexanone azine (XXXII) reacted with hydrogen sulphide to form the 1,3,5-thiadiazolidine (XXXIII). Oxidation of (XXXIII) with lead tetraacetate led to the Δ^3-1,3,4-thiadiazoline (XXXIV), which lost nitrogen on heating to give the thiiran (XXXV). Triphenylphosphine removed the sulphur to afford bis(cyclohexylidene) (XXXVI) (Scheme 7)[47a-c,48a].

Scheme 7



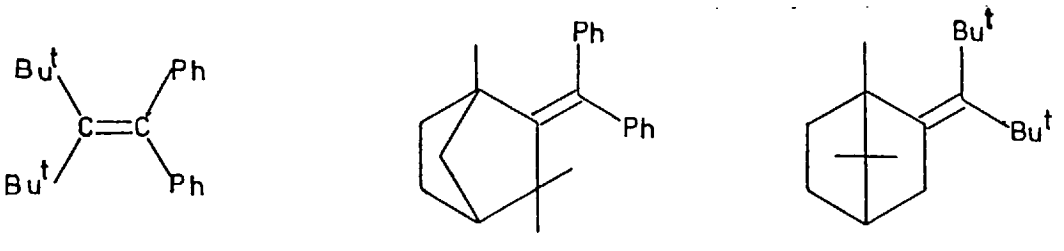
A similar route was used for the synthesis of cis- and trans-di-t-butylethylene[48b] and biadamantylidene (II)[37].

In very hindered substrates, the addition of hydrogen sulphide to azines does not occur. In such cases an alternative route to compounds of type (XXXIb) is provided by the cycloaddition of diazo-compounds (XXXVII) to thiones (XXXVIII). In general, compounds (XXXVII) and (XXXVIII) are somewhat unstable; however, their stability increases with



(XXXVII) (XXXVIII) (XXXIb)

increasing steric crowding, and this factor renders their use in hindered olefin synthesis particularly convenient. In this way it proved possible to synthesise a range of olefins, including 1,1-di-t-butyl-2,2-diphenylethylene (XXXIX), (+)-2-diphenylmethylene-1,3,3-trimethylnorbornane (XL) and (±)-2-di-t-butylmethylene-1,7,7-trimethylnorbornane (XLI)[47d]. These olefins are considerably more hindered than

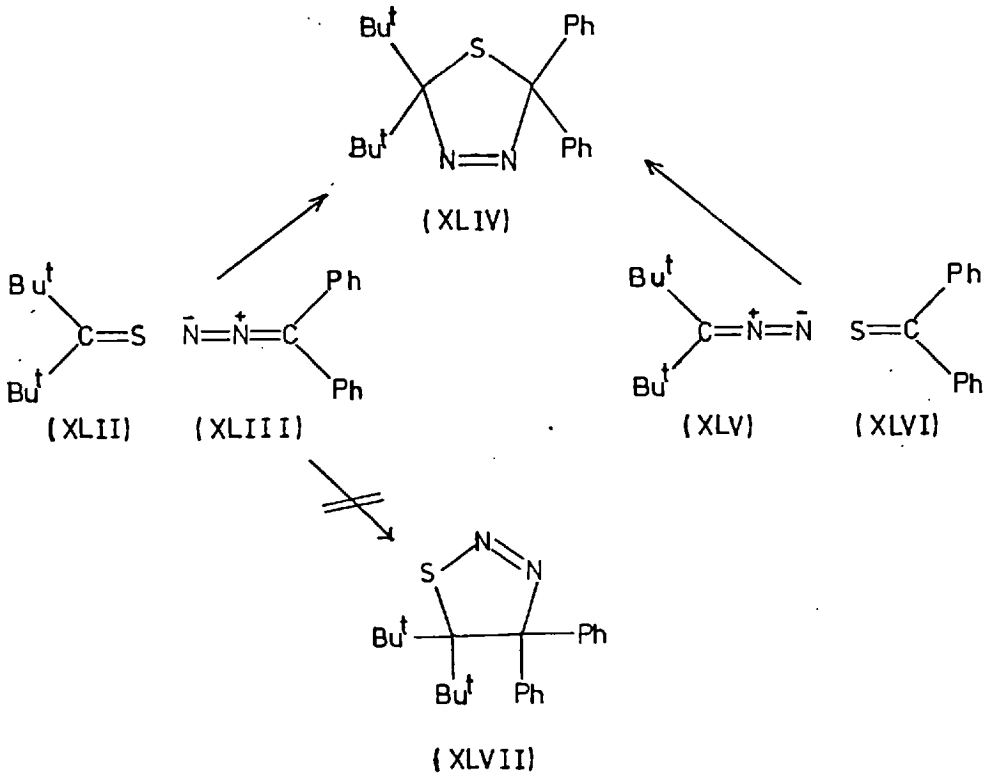


(XXXIX) (XL) (XLI)

any prepared by other methods. The intermediacy of the Δ^3--1,3,4-thiadiazolines (XXXIb) was proven by the isolation of the adduct (XLIV) from di-t-butyl thioketone (XLII) and diazodiphenylmethane (XLIII). Since the same adduct was

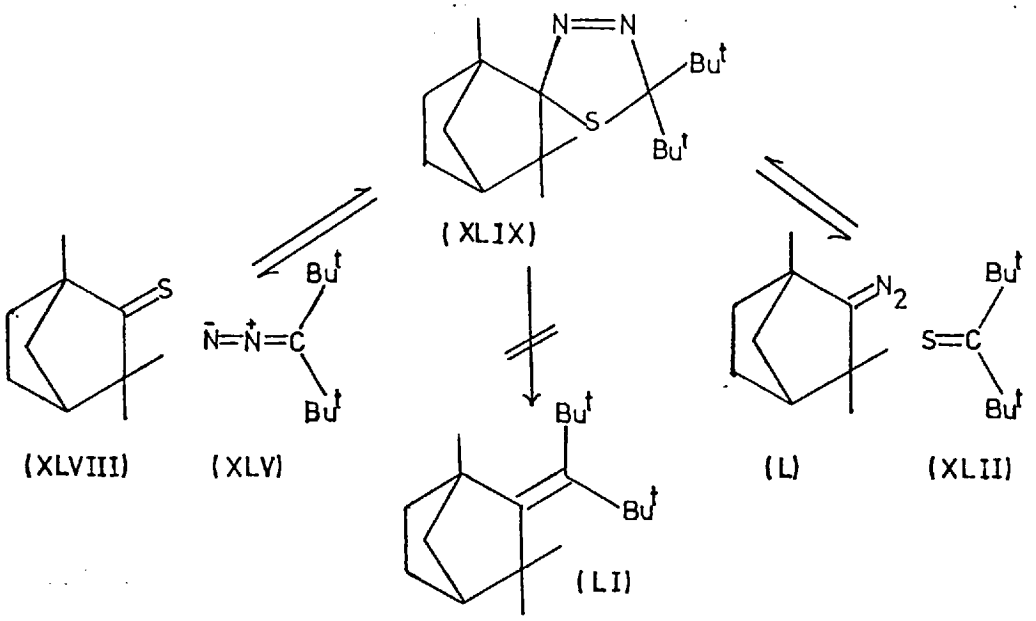
formed from diazodi-t-butylmethane (XLV) and thiobenzophenone (XLVI) (Scheme 8) the symmetrical structure (XLIV) must be correct[47d]. It was necessary to establish this, since alternative structures of the form (XLVII) had also been observed in other, less hindered cases[49].

Scheme 8

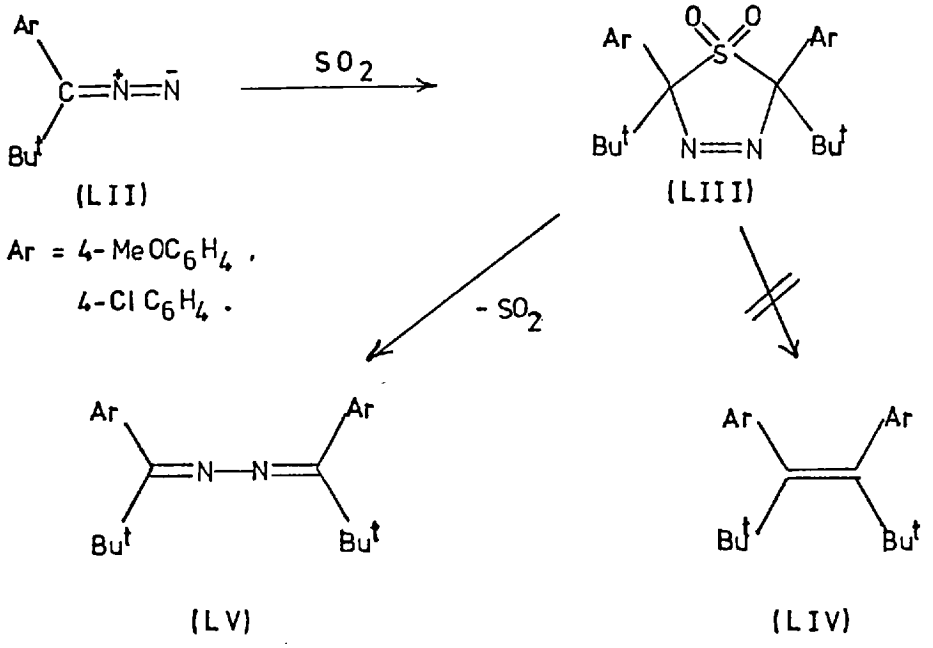


The limits of this particular approach are clearly defined by the unsuccessful reaction of diazo compound (XLV) with 1,3,3-trimethylnorbornane-2-thione (XLVIII) (Scheme 9)[36d]. No 2-di-t-butylmethylene-1,3,3-trimethylnorbornane (LI) was obtained, and the production of di-t-butyl thioketone (XLII) during the reaction indicated that although the adduct (XLIX) was probably formed, the reverse reactions occurred faster than loss of nitrogen to give thiiran. Tetra-t-butylethylene (I) could not be prepared by this method.

Scheme 9



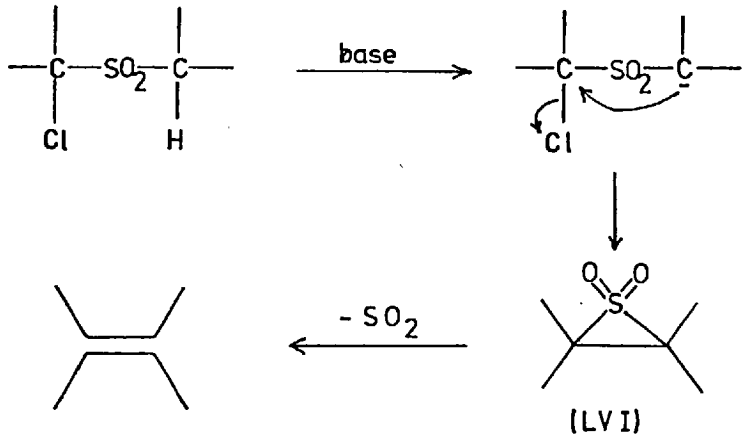
The reaction of sulphur dioxide with diazo compounds leads to olefins via twofold extrusion of Δ^3-1,3,4-thiadiazoline-1,1-dioxides (XXXIc, X=-$\overset{O}{\underset{O}{S}}$-, Y=-N=N-) which can be isolated in some cases[50]. The method, often referred to as the Staudinger-Pfenninger reaction[50a], is applicable to the synthesis of tetrasubstituted olefins[50c].



The hindered diazo-compounds (LII) reacted with sulphur dioxide to give the expected addition product (LIII) as a single (unspecified) isomer[51]. However, thermolysis did not in this case lead to the olefin (LIV), but to the azine (LV) via loss of sulphur dioxide. The scope of this reaction is also clearly limited.

It is suspected, though not proven, that thiiran-1,1--dioxides (LVI) are transient intermediates in the Staudinger--Pfenninger reaction. Such intermediates are also postulated for the Ramberg-Backlund reaction (Scheme 10)[52].

Scheme 10



Recently a modification of this reaction was discovered which dispenses with the need for α-halogenating the sulphone. Treatment with two equivalents of base affords the α,α'--dilithiosulphone, which is then oxidised with copper(II) to afford the thiiran-1,1-dioxide (LVI); extrusion as before leads to the olefin[53].

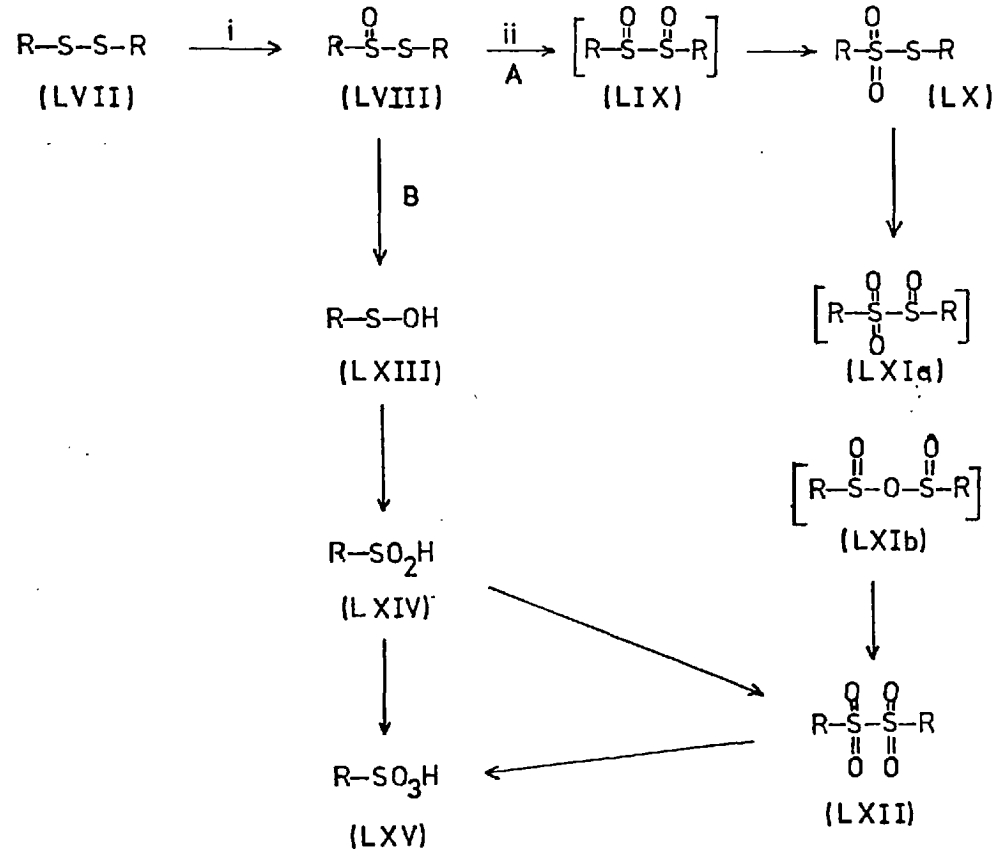
Despite some limitations, it is evident that extrusion reactions, particularly those of Barton, provide the best routes to hindered olefins.

B OXIDATION OF DISULPHIDES

1. General Remarks

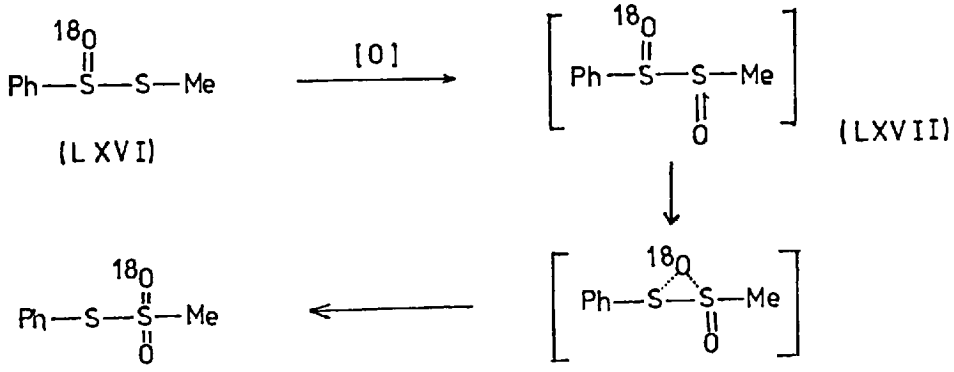
Disulphides have been oxidised with a wide variety of reagents; a number of products can be obtained, depending on the reaction conditions[54] (Scheme 11).

Scheme 11



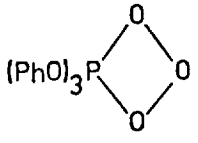
Strong oxidants, such as nitric acid[55], generally produce the sulphonic acid (LXV), and under such circumstances it is difficult to tell whether pathway A or B is followed. With milder oxidants, a clearer picture emerges. Treatment of a disulphide (LVII) with peracetic acid leads to the thiolsulphinate (LVIII)[56], which can in turn be

oxidised to the thiolsulphonate (LX) and the disulphone (LXII) in a stepwise process[57]. The intermediacy of the disulphoxide (LIX) in step (ii) has long been a source of controversy, but it is now accepted that such compounds probably have a very short lifetime. A recent study[58] has established the intermediacy of a disulphoxide (LXVII) in the oxidation of ^{18}O-labelled S-methyl benzenethiosulphinate (LXVI) with peracid. However, only 70% of the label is retained, indicating the possibility of alternative pathways.



(LXVI) (LXVII)

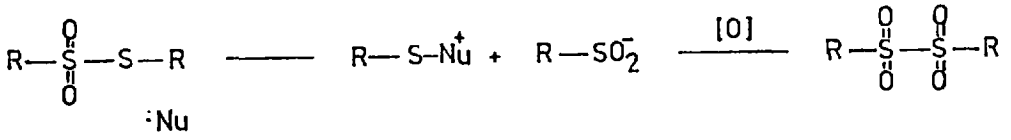
It is often difficult to produce the thiolsulphinate (LVIII) free of the thiolsulphonate (LX)[59]; for example, anhydrous hydrogen peroxide oxidation, catalysed by vanadium pentoxide, performs steps (i) and (ii) in rapid succession, so that only small amounts of thiolsulphinate can be isolated[60]. An improved procedure for step (i) employs triphenylphosphite ozonide (LXVIII) as the oxidant[61].



(LXVIII)

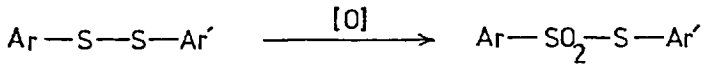
It is curious that the 'trioxide' species (LXI a and LXIb) have never been observed in the oxidation of thiolsulphonates (LX), although there is some kinetic evidence for such an intermediate[62]. Alternatively, the reaction may involve nucleophilic displacement on sulphur, producing a sulphinate anion, which may then be oxidatively coupled to give the disulphone (Scheme 12). There are precedents for

Scheme 12



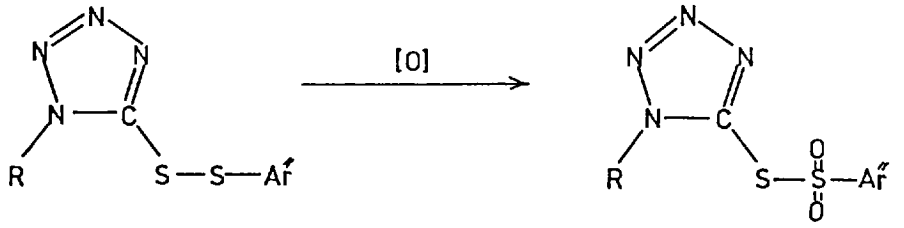
both the displacement[63] and oxidation[64,65] steps in this scheme; thus the reaction need not necessarily involve the sulphinyl sulphone (LXIa) or the sulphinic anhydride (LXIb) as intermediates.

Oxidation of unsymmetrical disulphides (R, R') generally leads to mixtures of symmetrical and unsymmetrical oxidation products[66,67], chiefly due to disproportionation of the starting materials under the reaction conditions. Not surprisingly, the unsymmetrical products are predominantly those in which oxidation has occurred at the sulphur atom adjacent to the more strongly electron-donating group. For example, the oxidation of unsymmetrical diaryl disulphides (LXIX)[66] and 1-substituted-5-tetrazolyl aryl disulphides (LXX)[68] with two equivalents of peracid leads in both cases to only one of the two possible unsymmetrical thiolsulphonates.



(LXIX)

Ar = Ph, 4-MePh, 2,4,6-$(Me)_3$Ph. Ar′ = 4-O_2NPh, 3-O_2NPh.

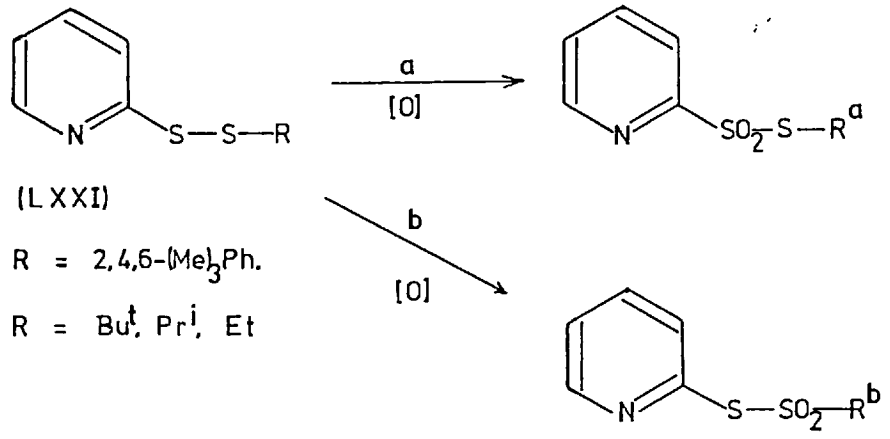


(LXX)

R = Ph, Me.

Ar″ = 4-MePh, 2,4,6-$(Me)_3$Ph.

In contrast, 2-pyridyl-2,4,6-trimethylphenyl disulphide (LXXIa) is oxidised at the sulphur atom attached to the pyridyl group[69].



(LXXI)

a: R = 2,4,6-$(Me)_3$Ph.

b: R = Bu^t, Pr^i, Et

This anomaly is ascribed to steric hindrance. However, the 2-pyridyl alkyl disulphides (LXXIb) are invariably oxidised at the sulphur atom attached to the alkyl group (even when R = t-butyl)[69].

The oxidation of t-butyl ethyl disulphide (LXXII) with one equivalent of peracid was originally believed to occur only at the sulphur atom next to the ethyl group, in view of the reported inertness of di-t-butyl disulphide[56]. However,

$$\underset{\text{(LXXII)}}{Bu^t\text{—S—S—Et}} \xrightarrow{[O]} \underset{\text{(LXXIII)}}{Bu^t\text{—SO—S—Et}} + \underset{\text{(LXXIV)}}{Bu^t\text{—S—SO—Et}}$$

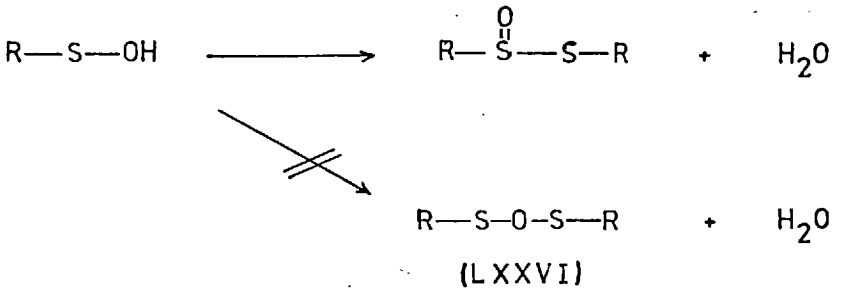
a re-examination of the reaction showed that a mixture of thiolsulphinates (LXXIII and LXXIV) was formed, with a 2:1 ratio in favour of the product (LXXIII) oxidised at the sulphur atom next to the t-butyl group[67].

2. Alternative Routes to Disulphide Oxidation Products

All of the species shown in route A of Scheme 11, with the exception of (LIX), may be prepared by the appropriate reactions of sulphenic (LXIII), sulphinic (LXIV) or sulphonic acids (LXV), or their derivatives. These reactions are often more convenient and give better yields of the pure products; furthermore, they are of wider application since unsymmetrical (R, R') compounds can be synthesised more conveniently. Thus, thiolsulphinates (LVIII) can in general be prepared by the reaction of thiols with sulphinyl chlorides (LXXV) in the presence of a base[59,67].

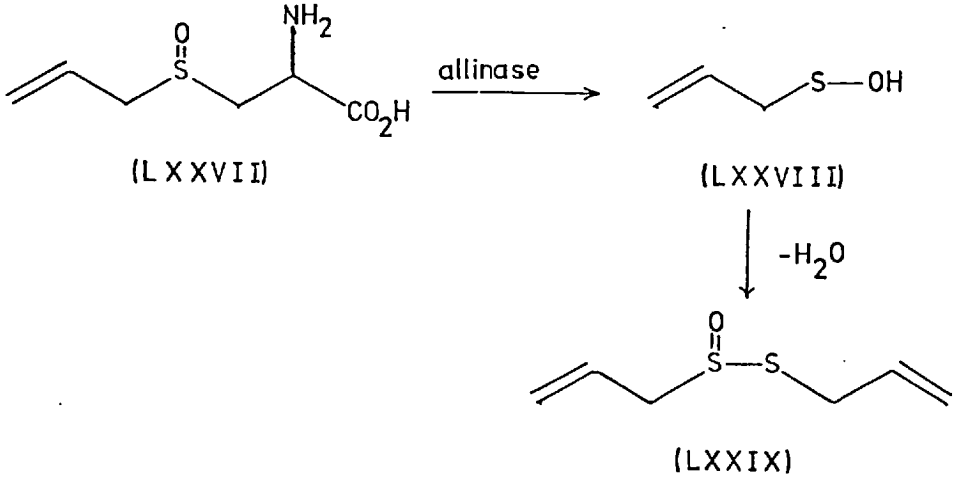
(LXXV) (LVIII)

Attempts at preparing free sulphenic acids (LXIII) have also produced thiolsulphinates by loss of water from two molecules of sulphenic acid[70, 71].



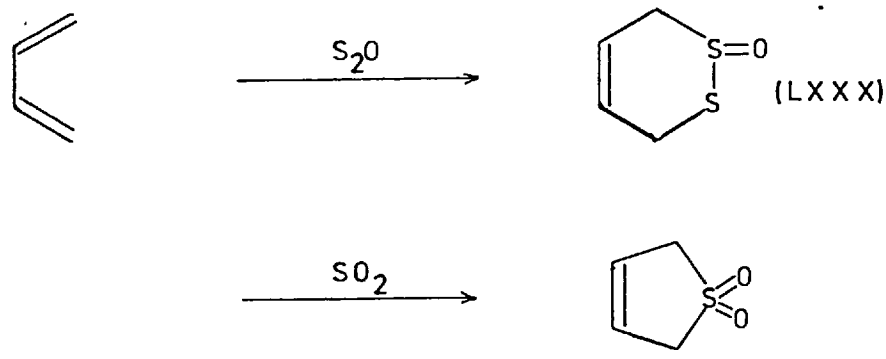
(LXXVI)

The isomeric 'sulphenic anhydrides' (LXXVI) have never been positively identified. The only known naturally-occurring thiolsulphinate is S-3-propenyl 3-propenethiosulphinate (allicin) (LXXIX), the antibacterial principle in garlic; it is believed to arise *in vivo* from 3-propenesulphenic acid (LXXVIII), which in turn is produced by enzyme-assisted decomposition of (+)-S-allyl-L-cysteine sulphoxide (alliin) (LXXVII)[72].

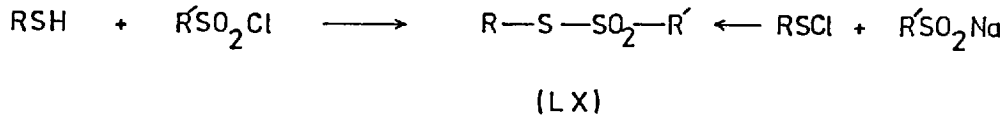


(LXXVII) (LXXVIII) (LXXIX)

Cyclic thiolsulphinates (LXXX) can be prepared by 1,4-addition of disulphur monoxide to 1,3-dienes[73], in interesting contrast to the reaction with sulphur dioxide[74].

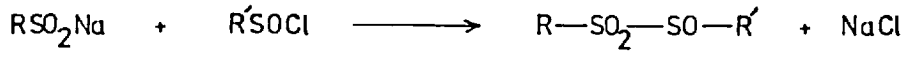


Thiolsulphonates (LX) are easily prepared by the reaction of thiols with sulphonyl chlorides in the presence of base, or by the reaction of sulphinate salts with sulphenyl chlorides[54].

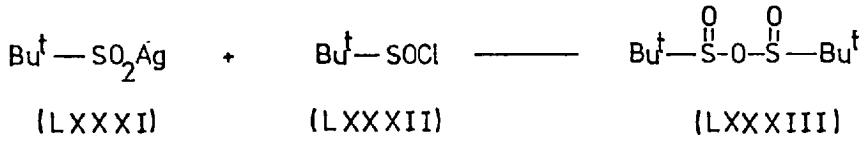


(LX)

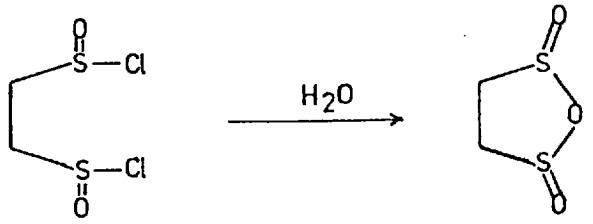
Sulphinyl sulphones (LXIa) can be prepared in a similar reaction from sulphinate salts and sulphinyl chlorides. It was originally believed that this reaction in fact gave rise to the isomeric sulphinic anhydrides (LXIb)[75];



but this was later refuted[76]. The existence of sulphinic anhydrides was only recently proven; t-butylsulphinic anhydride (LXXXIII) was prepared from silver t-butylsulphinate (LXXXI) and t-butylsulphinyl chloride (LXXXII)[77], while ethane-1,2-disulphinic anhydride (LXXXV) was prepared by controlled hydrolysis of ethane-1,2-disulphinyl chloride (LXXXIV)[78]. In both cases the absence of sulphone bands



(LXXXI) (LXXXII) (LXXXIII)



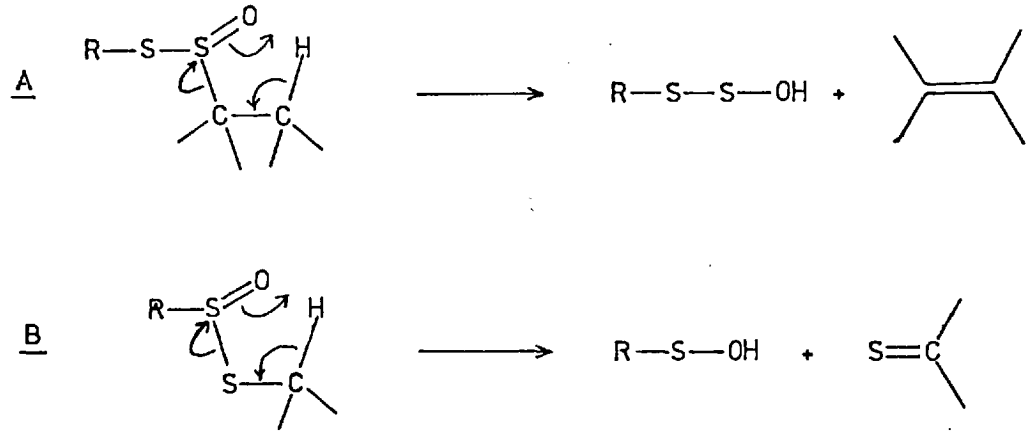
(LXXXIV) (LXXXV)

(approx. 7.4-7.7 μ) in the infra-red spectrum is the main evidence for the structure. In addition, the hydrolysis of t-butylsulphinic anhydride (LXXXIII) in dioxan/water is acid-catalysed, which would not be expected in the case of a sulphinyl sulphone[79]. The ^{1}H n.m.r. spectrum of the cyclic anhydride (LXXXV) shows a close double doublet, which would be compatible with either cis or trans orientation of the oxo groups[78].

Disulphones (LXII) have been prepared by oxidation of sulphinic acids (LXIV) with cobalt(III)[65] and with permanganate[64], or by the reaction of sulphonyl halides with sulphinates[80].

Thiolsulphinates in general are subject to disproportionation in solution, or even in the pure state if they are liquids[59,85]. The mechanisms are probably similar to Scheme 13; at all events, a simple oxygen transfer is unlikely. It is also possible for thiolsulphinates to undergo elimination in two ways (Scheme 14)[67]. Reaction A is analogous to the well-known β-elimination of sulphoxides[86]; reaction B has thus far only been observed in the mass spectrometer.

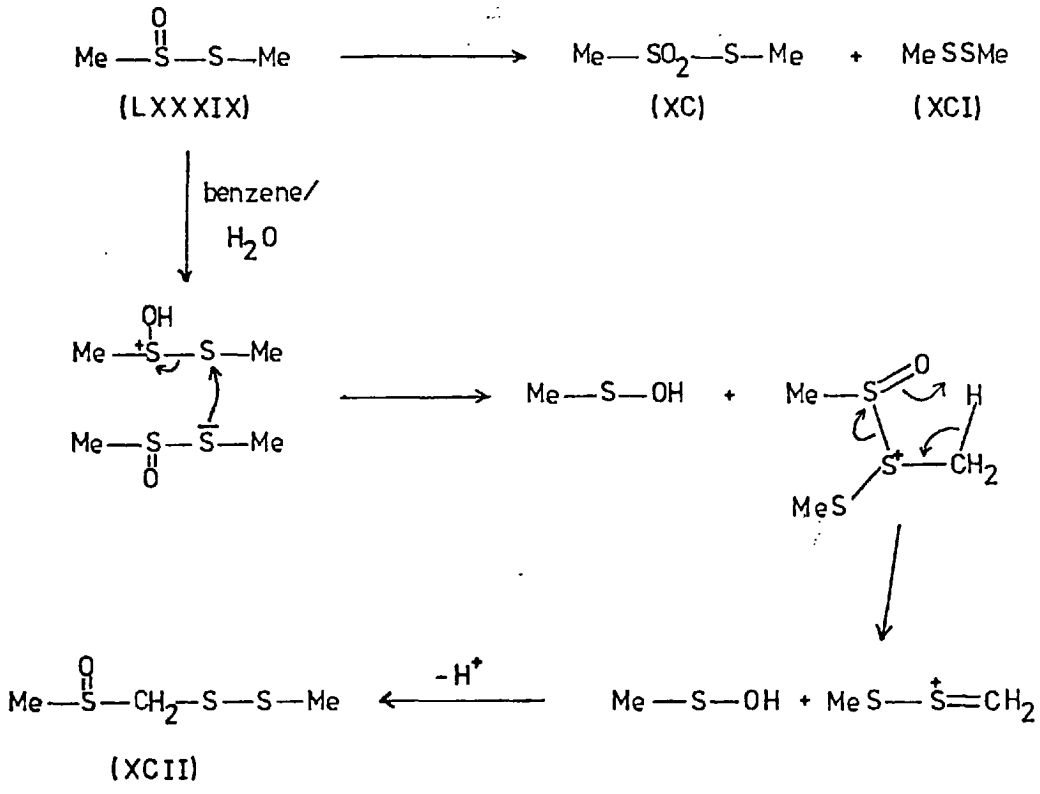
Scheme 14



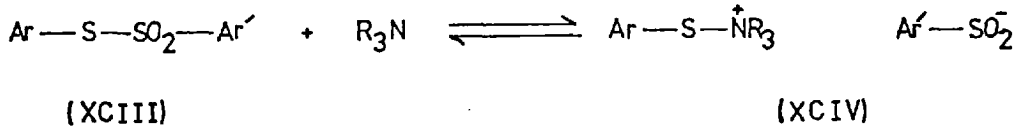
A study on the disproportionation reactions of S-methyl methanethiosulphinate (LXXXIX) has shown that processes similar to reaction B can occur under certain conditions (Scheme 15)[84]. In the pure state, or in aqueous acid, the products are S-methyl methanethiosulphonate (XC) and dimethyl disulphide (XCI). In moist benzene, however, methyl methanesulphinylmethyl disulphide (XCII) is obtained in 86% yield.

The susceptibility of thiolsulphonates to nucleophilic attack at the thiol sulphur is well known[63]. The reaction with thiols is essentially quantitative, and is used in analytical determination of thiolsulphonates[87].

Scheme 15

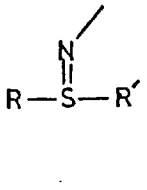


Recently it was demonstrated that the reversible reaction of arenethiolarenesulphonates (XCIII) with tertiary amines in ionising solvents produces arenethiotrialkylammonium salts (XCIV)[88].

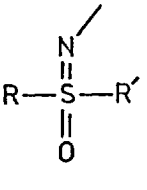


4. Imino Analogues of Disulphide Oxidation Products

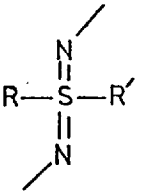
Sulphimides (XCV)[89a,e], sulphoximides (XCVI)[89b-e] and sulphondiimides (XCVII)[89e], the nitrogen analogues of sulphoxides and sulphones, are well known classes of compounds, with some synthetic importance. However, the



(XCV)



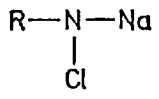
(XCVI)



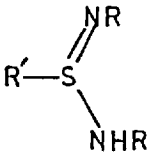
(XCVII)

nitrogen analogues of the compounds shown in Scheme 11 have received little attention.

Compounds (XCV) to (XCVII) can be made, *inter alia*, by oxidation of the appropriate precursor with an N-chloro--N-sodioamide (XCVIII)[90]. However, when this reaction is



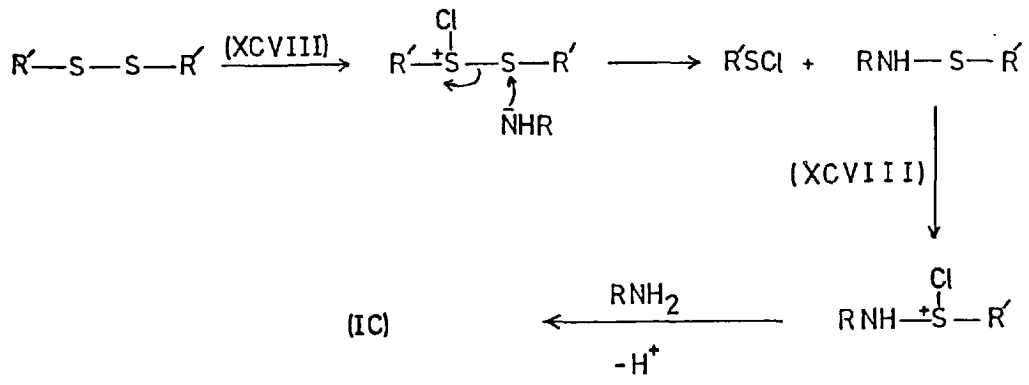
(XCVIII)



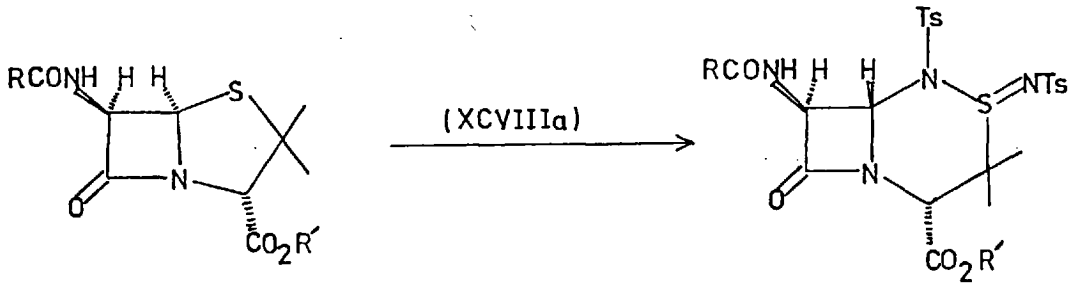
(IC)

applied to disulphides or thiols in protic solvents, the products are the corresponding sulphinamidines (IC) or their sodium salts[91]. A mechanism (Scheme 16) has been proposed for this reaction[91]. Compounds (IC) can also be obtained by similar oxidation reactions of sulphenyl chlorides[92], sulphenamides[93], thiolesters[94], xanthates[91e], and phenylthio- or ethylthioacetic acids[91a-c,95].

Scheme 16[90]

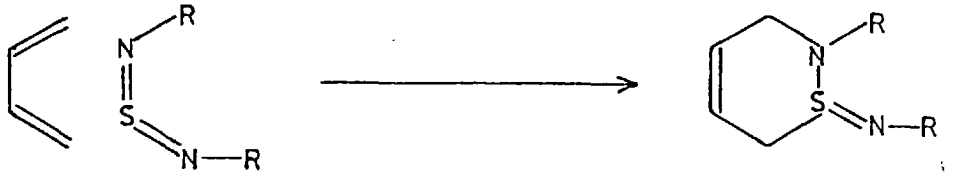


A cyclic sulphinamidine (CI) has been obtained by oxidation of the penicillin derivative (C) with Chloramine-T (XCVIIIa, R = 4-methylbenzenesulphonyl[96]).



(C) (CI)

Cyclic sulphinamidines (CIII) may also be prepared by 1,4--addition of sulphur diimides (CII) to 1,3-dienes[97] (cp. sulphur dioxide, Section B 2).

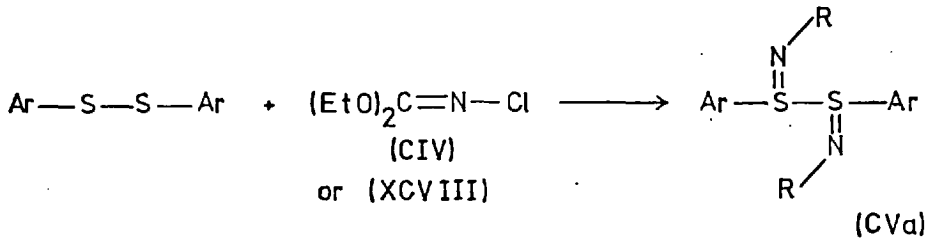


(CII) (CIII)

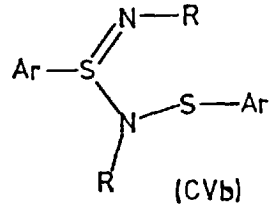
Disulphides have been reported to consume 10 equivalents of Chloramine-T in aqueous acid; however, the products were not identified[98].

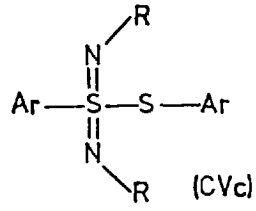
In contrast to the foregoing result, the reaction of aromatic disulphides with N-chloro-N-sodioamides (XCVIII) or N-chlorodiethyl iminocarbonate (CIV) in aprotic solvents is reported to give crystalline products with three possible structures (CV a,b,c)[99] (Scheme 17).

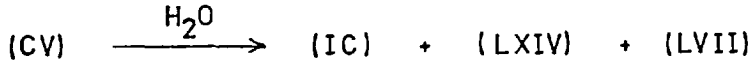
Scheme 17



R = 4-methylbenzenesulphonyl, carbethoxy.







Structure (CVb) has been tentatively assigned on the basis of the aqueous hydrolysis products, although the i.r. bands at 1285, 1245, and 1210 cm^{-1} in the carbethoxy compounds might suggest a sulphondiimidate structure such as (CVc).

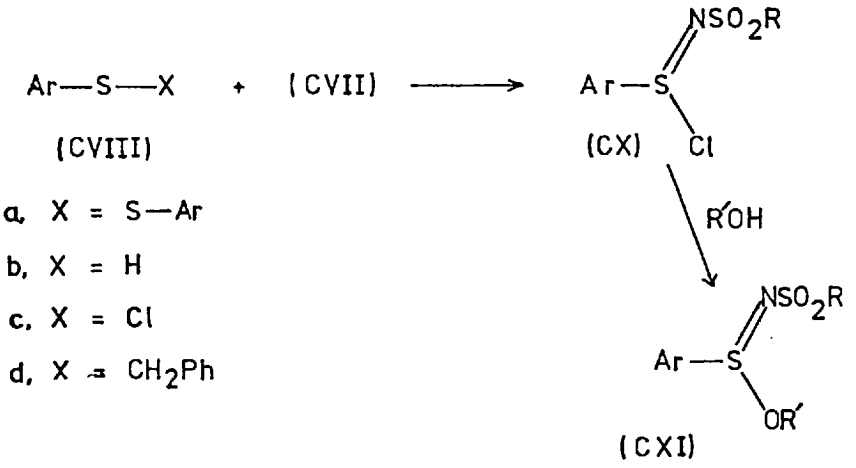
Compounds (CV) can also be prepared by oxidation of aromatic thiolate salts (CVI) with N,N-dichlorobenzene-sulphonamide (CVII, R = phenyl)[100].

$$4\ Ar{-}\bar{S}\ \overset{+}{Na} + R{-}SO_2{-}NCl_2 \longrightarrow (CV) + ArSSAr + 4\,NaCl$$

(CVI) (CVII)

Oxidation of disulphides (CVIIIa)[101,102], thiols (CVIIIb)[100], sulphenyl chlorides (CVIIIc)[101], and aryl benzyl sulphides (CVIIId)[101] with dichloramides (CVII), or the reaction of sulphenamides (CIX) with chlorine[103], leads to sulphinimidoyl chlorides (CX) (Scheme 18). Treatment

Scheme 18

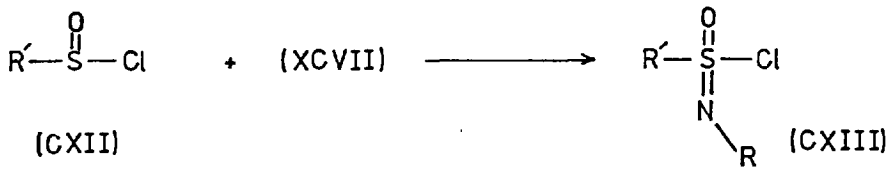


$$Ar{-}S{-}NH{-}SO_2R + Cl_2 \longrightarrow (CX)$$

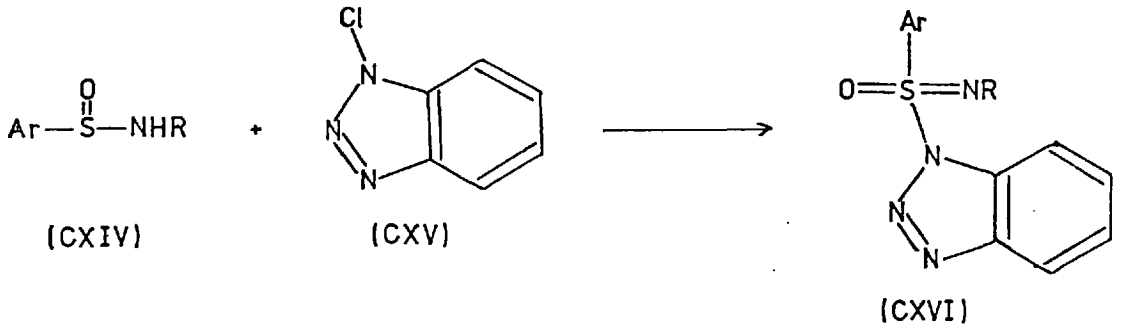
(CIX)

of the chlorides (CX) with alcohols leads to the corresponding sulphinimidates (CXI)[104], formal analogues of sulphinate esters.

Sulphonimidoyl chlorides (CXIII) can be prepared in a similar manner to the sulphinamidines (IC) by oxidation



of sulphinyl chlorides (CXII) with N-chloro-N-sodioamides (XCVIII)[105]. The sulphonimidamides (CXVI) were obtained by oxidation of sulphinamides (CXIV) with 1-chlorobenzotriazole



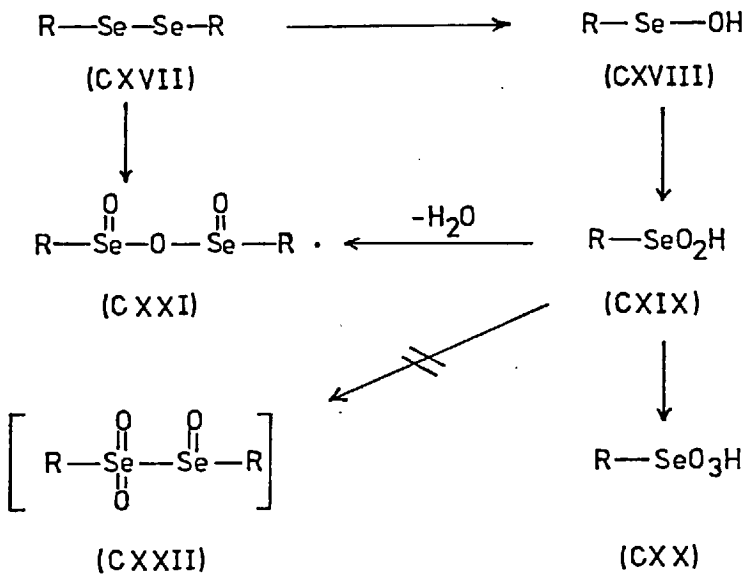
(CXV), presumably via an intermediate sulphonimidoyl chloride (CXIII)[105]. These chlorides (CXIII) could be prepared by reaction of the sulphinamides (CXIV) with chlorine[105a,b].

C OXIDATION OF DISELENIDES[107]

1. General Remarks

In contrast to the oxidation of disulphides, the oxidation of diselenides (CXVII) invariably causes fission of the Se-Se bond. The known oxidation products are shown in Scheme 19.

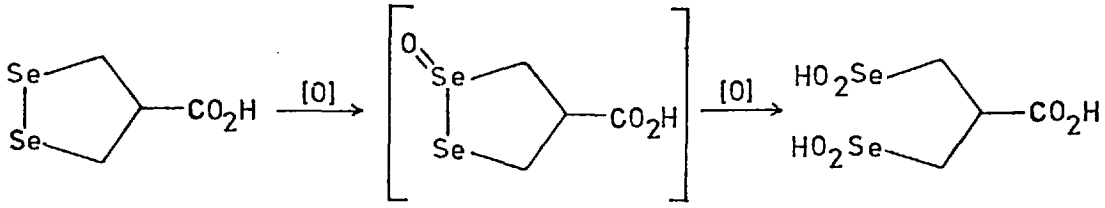
Scheme 19



An interesting feature is the stability of the seleninic anhydrides (CXXI), while the isomeric seleninyl selenones (CXXII) appear to be quite unknown (cp. sulphinic anhydride/sulphinyl sulphone isomerism, Section B 2).

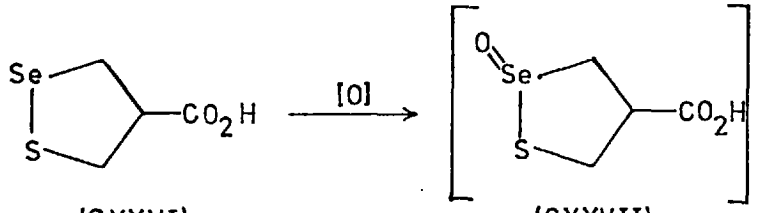
Mild oxidation, for example with hydrogen peroxide[108], gives the selenenic acid (CXVIII); further peroxide oxidation leads to the seleninic acid (CXIX)[109]. In the case of 1,2--diselenolan-4-carboxylic acid (CXXIII), oxidation gives rise to a band at 440 nm in the u.v. spectrum, which is believed to indicate the presence of an intermediate selenol-seleninate (CXXIV)[110]. However, only the diseleninic acid

(CXXV) could be isolated from the reaction.



(CXXIII) (CXXIV) (CXXV)

This study[110] also postulated the existence of a transient thiolseleninate (CXXVII) in the oxidation of 1-thia-2--selenolan-4-carboxylic acid (CXXVI), based on a similar observation; the final products were not identified. This is the only reported oxidation of a thiolselenenate.



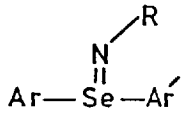
(CXXVI) (CXXVII)

Seleninic anhydrides (CXXI) are readily obtained by dehydration of seleninic acids, or directly from the diselenides with t-butyl peroxide or ozone[111]. Diphenyl seleninic anhydride (CXXI, R = phenyl) has recently attracted interest as a mild oxidising[112,113] and hydroxylating[114] agent.

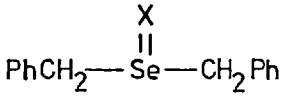
Selenonic acids (CXX) are produced by vigorous oxidation with chlorine water[115], permanganate[116], or fuming nitric acid[117]. They are unstable, and are readily reduced to the corresponding seleninic acid with hydrochloric acid[116,118].

2. Imino Analogues of Diselenide Oxidation Products

A number of diaryl selenimides (CXXVIII) have been synthesised by reaction of diaryl selenides with



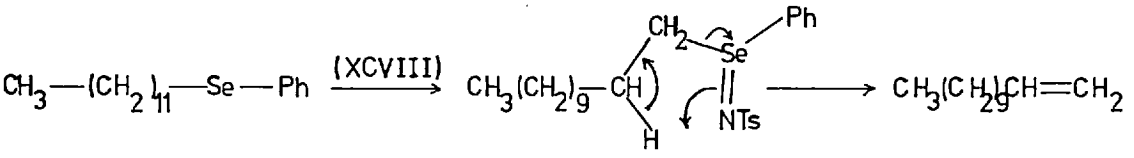
(CXXVIII)



(CXXIX)

a, X = NH
b, X = O

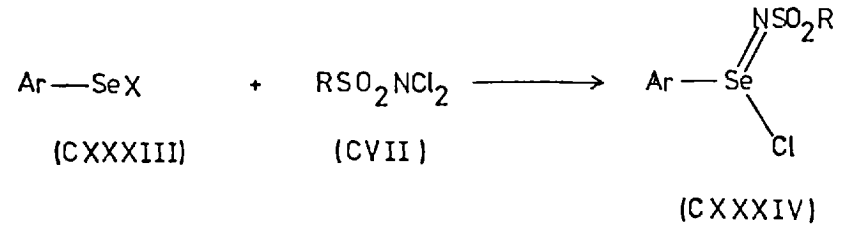
Chloramine-T, but their chemistry has not been extensively investigated [119]. Dibenzyl selenimide (CXXIXa) and selenoxide (CXXIXb) are converted to the corresponding selenide upon treatment with triphenylphosphine[120]. Treatment of dodecyl phenyl selenide (CXXX) with Chloramine-T (XCVIIIa, R = 4-methylbenzenesulphonyl) in a phase transfer



(CXXX) (CXXXI) (CXXXII)

system leads to 1-dodecene (CXXXII), presumably via α-elimination of the selenimide (CXXXI)[121].

Nitrogen analogues of the compounds shown in Scheme 19 are rarely documented. Seleninimidoyl chlorides (CXXXV) can be obtained by reaction of dichloramides (CVII) with diselenides (CXXXIIIa), silyl selenides (CXXXIIIb), selenenyl chlorides (CXXXIIIc), or aryl



(CXXXIII) (CVII) (CXXXIV)

a, X = Se—Ar

b, X = SiR_3

c, X = Cl

d, X = Cl_3

selenium trichlorides (CXXXIIId)[122]. It is possible to convert the imidoyl chlorides (CXXXIV) to seleninimidates and seleninimidamides[122], but no details have been published.

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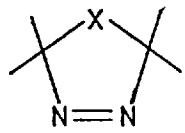
PART II

RESULTS AND DISCUSSION

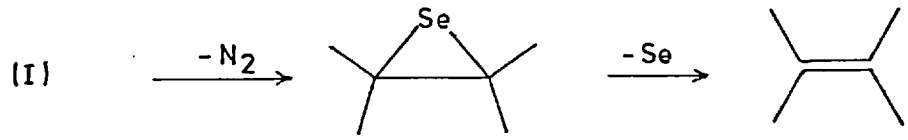
A OLEFIN SYNTHESIS VIA THIONES AND SELENOKETONES

In order to extend the scope of olefin synthesis by twofold extrusion, the possibility of using Δ^3-1,3,4--selenadiazolines (I) was examined. The radius of the



(I) X = Se
(II) X = S

selenium atom is greater than that of sulphur[1]; hence the hindered carbon centres would be held further apart in compounds of type (I) than in those of type (II), thereby reducing steric interactions in the formation of (I). Extrusion of nitrogen from a Δ^3-1,3,4-selenadiazoline would give the corresponding episelenide, which would in turn decompose to the olefin by the loss of selenium[2].



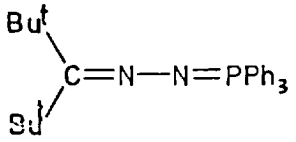
By analogy with the preparation of compounds (II), the best route to compounds (I) appeared to be the cycloaddition of selenoketones (selones) to diazo-compounds. Thus, the first synthetic objective was a route to reasonably stable, monomeric selenoketones.

Prior to this work, the only selenoketones reliably reported were those which are ligand-stabilised or resonance--stabilised by conjugation with an electron-donating heteroatom[3]. An earlier report[4] describing the preparation of

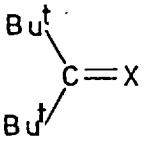
dimeric selenoketones from ketones with hydrogen selenide was later refuted[5]; the products of this reaction are the corresponding diselenides.

During the course of some attempted syntheses of selenoketones (see Section B) it became clear that reagents such as hydrogen selenide or sodium hydrogen selenide, led almost invariably to diselenides rather than the selenoketones. Accordingly, it was decided that elemental selenium (Se^0) would be a better reagent; reaction with a carbenoid species such as a diazo-compound should give a selenoketone, which would hopefully be inert to further reaction with either selenium or the carbene. In the event, this simple approach led to the only successful synthesis for selenoketones.

Diazodi-t-butylmethane can be obtained by treatment of the appropriate tosylhydrazone with base[6]. However, the diazo-compound can be generated *in situ* by thermal decomposition of di-t-butyl ketone triphenylphosphoranylidenehydrazone (III); this method is less drastic and more convenient, since phosphoranylidenehydrazones are stable, crystalline compounds obtainable in high yield from the corresponding hydrazones by the method of Bestmann and Fritzsche[7].



(III)

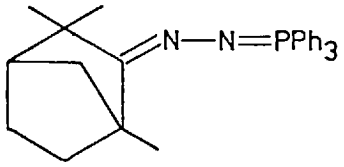


(IV) X = Se

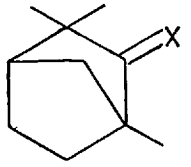
(V) X = S

Di-t-butyl selenoketone (IV) was obtained in 35% yield by heating di-t-butyl ketone triphenylphosphoranylidene-hydrazone (III) with selenium and a trace of tri-n-butyl-amine. The product was a distillable blue liquid with a

mild, slightly unpleasant odour. Similar treatment of (-)-1,3,3-trimethylnorbornan-2-one triphenylphosphoranylidenehydrazone (VI) gave (-)-1,3,3-trimethylnorbornan-2--selone (selenofenchone) (VII), which was continuously distilled from the reaction mixture and isolated in 28% yield as bright blue crystals with a camphoraceous odour.



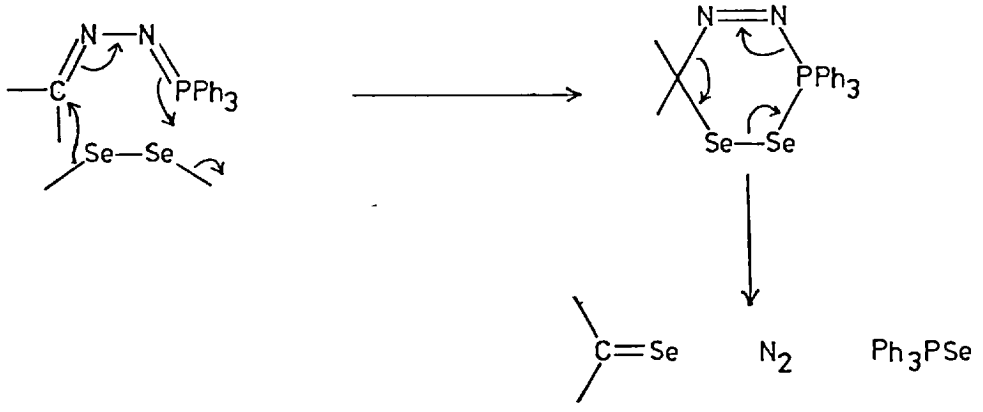
(VI)



(VII) X = Se, (VIII) X = S

This curious reaction is not a simple carbene reaction, since diazodi-t-butylmethane and selenium alone give only a trace amount of the selenoketone. It is reasonable to suggest that the sp^2 carbon is attacked by some nucleophilic selenium species, and that triphenylphosphine activates the elemental selenium, possibly by opening the Se_n chains. Alternatively, the reaction may involve a Diels-Alder-type cycloaddition, followed by disproportionation (Scheme 1).

Scheme 1

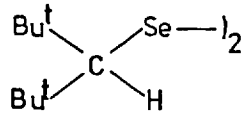


Either mechanism is supported by the formation of triphenylphosphine selenide as a by-product, and by the fact that an excess of selenium is required for the best yields. The phosphoranylidene hydrazones employed must be free of hydrazone, or the selenoketones are reduced to selenols as fast as they are formed.

Subsequent to the first publication of this synthesis[8], the selone (IV) was prepared by a modification of the method (tri-n-octylamine instead of tri-n-butylamine) and in improved yield[9].

The selenoketones are remarkably stable thermally and were recovered intact after prolonged heating under argon at 150°. Their inertness is attributed to the absence of enolisable hydrogens and to the steric protection afforded by the adjacent bulky alkyl groups.

Treatment of the selenoketone (IV) with sodium borohydride effected quantitative reduction to the selenol, which underwent rapid oxidation to bis(1-t-butyl-2,2-dimethylpropyl)diselenide (IX) on work-up in air.



(IX)

The synthesis of other selenoketones was also attempted. When benzophenone triphenylphosphoranylidenehydrazone (X)[7], or adamantanone triphenylphosphoranylidenehydrazone (XI)* was

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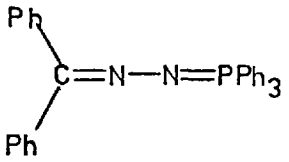
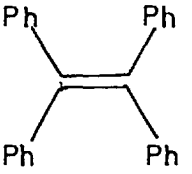
*Adamantanone hydrazone, prepared for the first time, decomposed to adamantanone azine at an appreciable rate, especially under oxidising conditions. Hence (XI) could not be obtained free of azine; however, the result justifies the experiment.

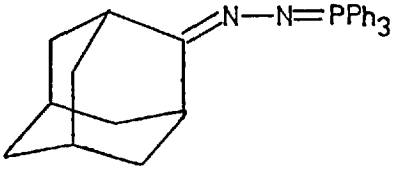
heated with selenium in the usual manner, the respective products were tetraphenylethylene (XII) and biadamantylidene (XIII). The selenoketones may be postulated as



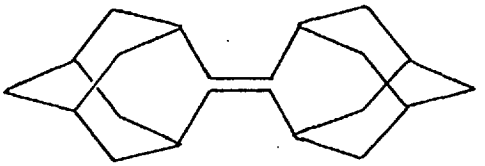
(X)



(XII)



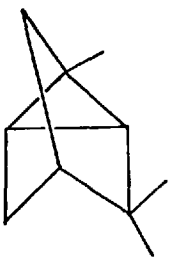
(XI)



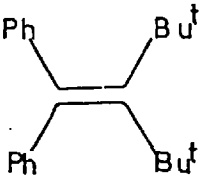
(XIII)

intermediates in the formation of the olefins, since it is known that thiones react with triphenylphosphoranylidene-hydrazones to give olefins via an extrusion process[6]. The synthesis is therefore restricted to selenoketones whose further reaction with the starting material is sufficiently slow, for steric or other reasons, to enable them to be isolated.

The reaction could not be extended to telluroketones. Pyrolysis of the fenchone derivative (VI) in the presence of tellurium under vacuum gave 1,3,3-trimethyl-[2.2.1.$0^{2,6}$]--tricycloheptane (XIV) as the only identifiable product; this presumably arises from a carbenoid insertion reaction.



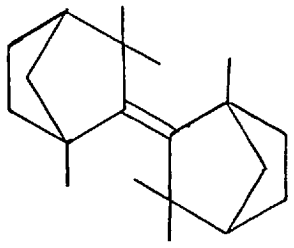
(XIV)



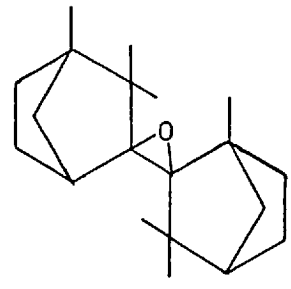
(XV)

Dr. T. G. Back of this department established that di-t-butylselenoketone (IV) was more reactive than the corresponding thione towards diazodiphenylmethane, and underwent a similar reaction to give 3,3-dimethyl-1,1--diphenyl-2-t-butylbut-1-ene (XV) via an intermediate of type (I). However, he was unable to induce cycloaddition of the selenoketone (IV) with diazodi-t-butylmethane by extremes of temperature, by high pressure (8500 atm) or by photolysis. In all cases the products were those attributable to decomposition of the diazo-compound, while the selenoketone was recovered intact. Attempted cycloaddition of the selenoketone with di-t-butylsulphine[6] or with di-t-butylketene was likewise unsuccessful. It was not possible to couple the selenoketone by photolysis or by reduction.

Accordingly, it was decided to investigate the synthesis of the 2,2′-binorbornylidene (XVI) derived from 1,3,3-trimethylnorbornan-2-one (fenchone). This could be regarded as a "tied-back" tetra-t-butylethylene, in which steric hindrance is reduced by the linking of the alkyl groups into a bicyclic structure.



(XVI)



(XVII)

The phosphoranylidenehydrazone (VI) was heated with selenium to give the olefin (XVI) in 24% yield as a single isomer, shown by X-ray diffraction to have the E-configuration[10]. The selenoketone (VII) was an intermediate in this process; it can be isolated from the mixture under these conditions by vacuum distillation. When the phosphoranylidenehydrazone (VI) was heated with the thione (VIII), the same isomer of the olefin was obtained in high yield. Hence, the use of the selenoketone (VII) instead is not advantageous in this preparation. The olefin (XVI) undergoes ozonolysis to give 1,3,3-trimethylnorbornan-2-one (fenchone) and reacts with 3-chloroperbenzoic acid to afford the corresponding epoxide (XVII) in high yield. No reaction was observed when a solution of the olefin (XVI) was exposed to a stream of air for one week.

Although the olefin (XVI) ought to be the most hindered olefin yet prepared, it nonetheless displays some aspects of typical olefinic behaviour, and it does not behave as a diradical. These results are understandable on considering the structure, as determined by X-ray diffraction (Table 1). The deviation from planarity in the double bond system is only 11.8^0, significantly less than for the olefin (XV). Most of the strain appears to be relieved by $C(sp^2)$-$C(sp^3)$ bond stretching, and by the "pushing back" of the 1 and 1′ methyl groups. The double bond is not significantly stretched. Therefore, normal olefinic behaviour would be expected, except inertness to bulky electrophiles.

The olefin (XV) was previously reported[6] to be inert to the normal olefinic reagents. However, we found that it underwent ozonolysis readily to give benzophenone and di-t-

Table 1

Structural Data of Hindered Olefins

	Binorbornylidene[10] (XVI)	Di-t-butyldiphenyl-ethylene[11] (XV)	Normal values[12]
$C(sp^2)=C(sp^2)$ distance	1.349 Å	1.360 Å[a]	1.335 Å
$C(sp^2)-C(sp^3)$ distance	1.565 Å	1.572 Å[b]	1.501 Å
α-C-methyl bond angle	122°[c]	118-122°	109.5°
Torsion angle of double bond	11.8°	24°	0°

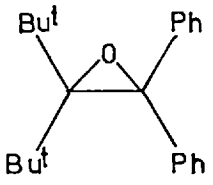
a cp. 1.347 A (calculated) for 1,1-diphenylethylene[13]

b $C(sp^2)-C$(phenyl) distances averaged 1.505 A

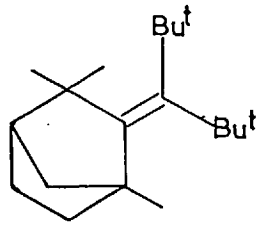
c The angles for the gem-dimethyl groups averaged 114.7°

-butyl ketone, and was oxidised to the corresponding epoxide (XVIII) in high yield with 3-chloroperbenzoic acid. It would appear that (XV) is in fact a more "hindered" olefin than (XVI), judging by the greater torsion and stretching of the double bond, and by the much slower rate of reaction (qualitative) with 3-chloroperbenzoic acid.

Attempts were made to prepare 2-di-t-butylmethylene--1,3,3-trimethylnorbornane (XIX) via the reactions of (i) the triphenylphosphoranylidenehydrazone (VI) with di-t-butyl thioketone (V) or selenoketone (IV); and (ii) di-t-butyl ketone triphenylphosphoranylidenehydrazone (III) with 1,3,3--trimethylnorbornane-2-thione (VIII). In each case, the



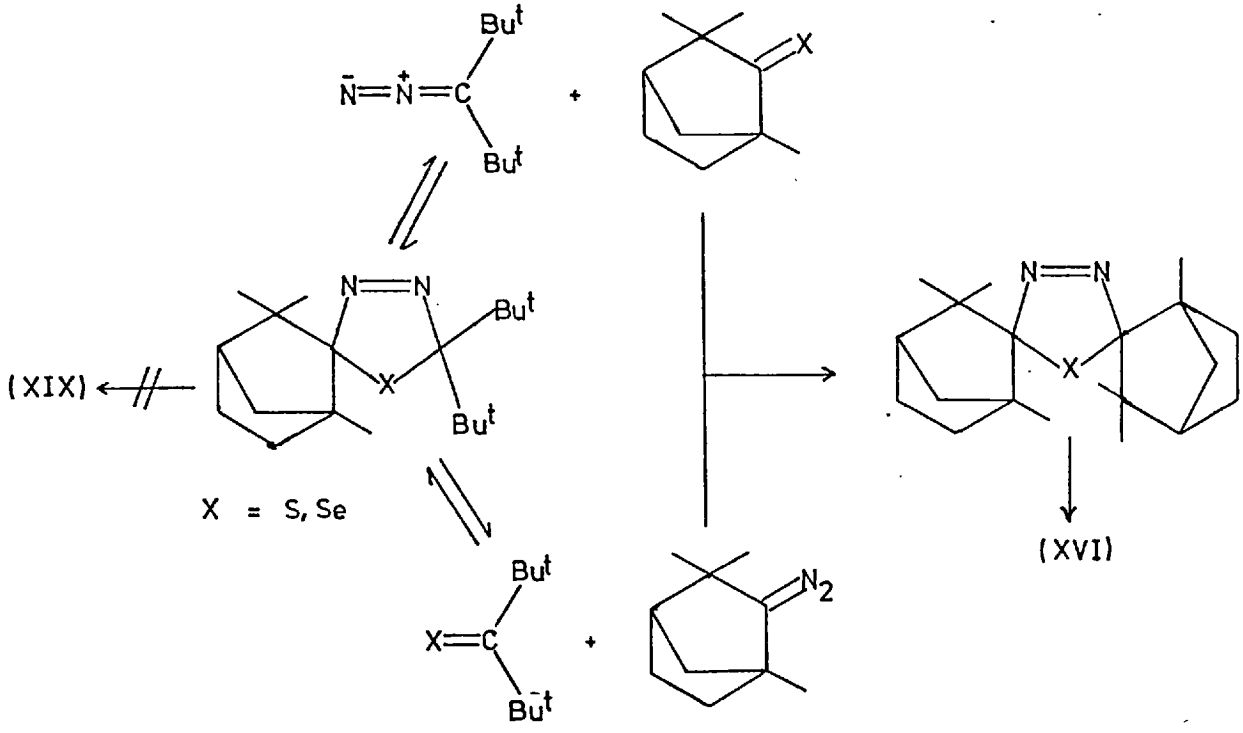
(XVIII)



(XIX)

binorbornylidene (XVI) was the only olefin isolated. Hence, 1,3,4-selena- and thiadiazolines are intermediates in these reactions and must exist in equilibrium with both possible pairs of diazo-compounds and seleno- or thioketones, as illustrated in Scheme 2. This scheme is supported by the formation of di-t-butyl thioketone (V) in reaction (ii).

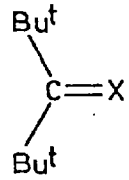
Scheme 2



B MISCELLANEOUS ATTEMPTED SELENOKETONE SYNTHESES

1. Nucleophilic Displacements

Although it has been shown[5] that the reaction of ketones with hydrogen selenide leads to diselenides and not to selenoketones, the observation of a blue colour in one such experiment indicated that this approach might reward investigation. Since di-t-butyl ketone (XX) and the corresponding imine (XXI) were inert to hydrogen selenide[14], diazodi-t-butylmethane (XXII) was chosen as an appropriate substrate. Pyrolysis of the triphenylphosphoranylidene-hydrazone (III) under continuous vacuum caused the diazo--compound (XXII) to distil into a cold trap, in nearly quantitative yield, thus establishing a new, more convenient synthesis of (XXII). Unfortunately, reaction with either hydrogen selenide or sodium hydrogen selenide led to the



(XX) X = O

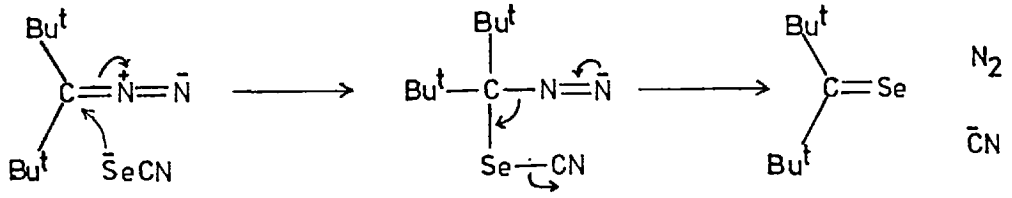
(XXI) X = NH

(XXII) X = N_2

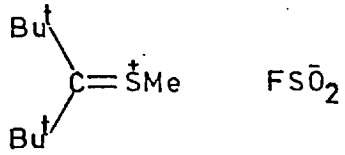
diselenide (IX) in a rapid reaction showing no evidence of intermediate selenoketone.

Potassium selenocyanate is a highly nucleophilic reagent with wide application in selenium chemistry[15]; it was therefore hoped that the reaction sequence shown in Scheme 3 might be feasible. Instead, the diazo-compound (XXII) decomposed slowly in the presence of selenocyanate without apparently undergoing nucleophilic attack.

Scheme 3



Di-t-butyl thioketone (V) did not react with methyl iodide or with triethyloxonium fluoroborate, but formed a colourless solid on treatment with methyl fluorosulphonate. It was proposed that the salt, probably of the form (XXIV), would be more reactive to nucleophiles than the diazo--compound (XXII). However, reaction with selenocyanate gave an immediate precipitate of selenium, suggesting that



(XXIV)

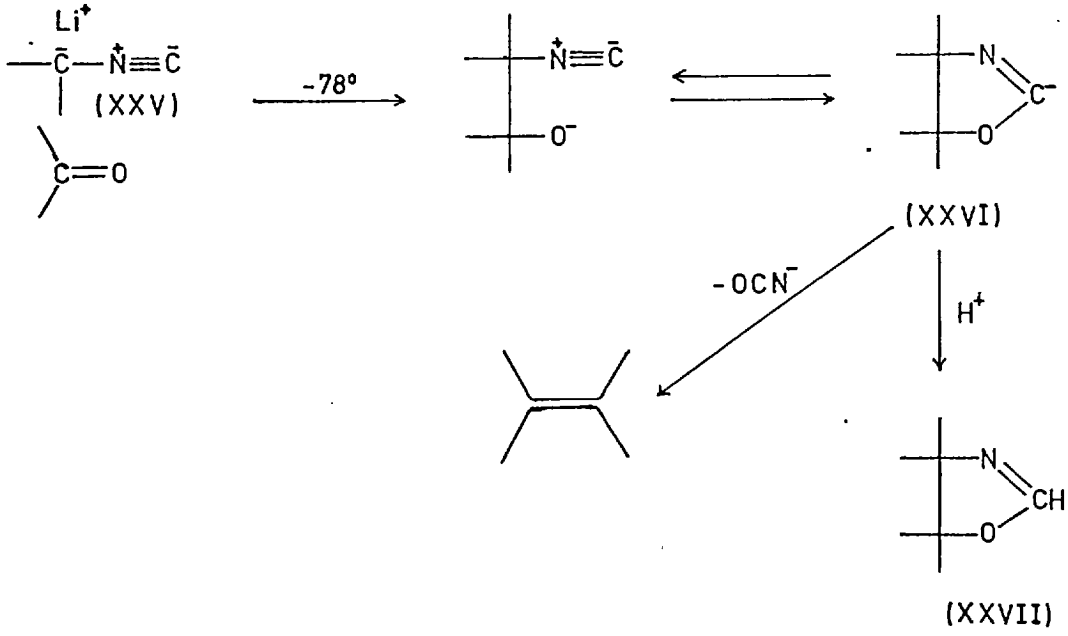
attack had occurred through the nitrogen end of the selenocyanate anion. Attempted reactions with seleno-benzoic acid and triphenylphosphine selenide were equally unsuccessful. In view of the fact that (XXIV) reacts with water to give only partial conversion to the ketone (XX), together with a number of other, unidentified products (n.m.r.), it was concluded that the scope of this route would be severely limited.

2. α-Lithiated Isonitriles

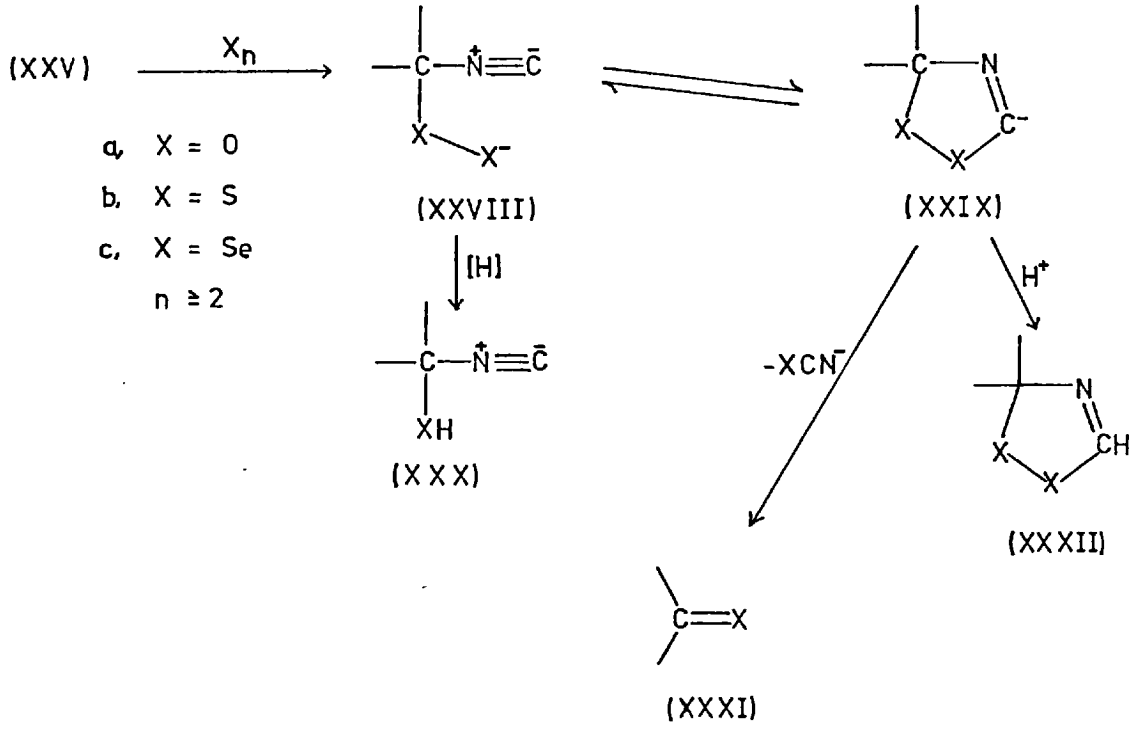
Much attention has been focused lately on the synthetic applications of α-lithiated isonitriles (XXV)[16]. In particular, their ability to react with a wide range of carbonyl compounds leads to a useful general synthesis of Δ^2-1,3-oxazoles (XXVII) (Scheme 4). It has been noted[17] that if the intermediate anion (XXVI) is allowed to warm to room temperature, loss of cyanate ion occurs to give an olefin.

Simple carbanions, such as those adjacent to carboxamide, ester, and carboxylate groups, react with oxygen to give hydroperoxides[18,19], or with sulphur to give thiols[20]. It may reasonably be expected that α-metallated isonitriles would undergo similar reactions. Scheme 5 shows how further transformations might parallel those in Scheme 4. Thus it should be possible to establish routes to α-hydroxy-, α-thiol- and α-selenoisonitriles (XXX), ketones, thioketones and

Scheme 4



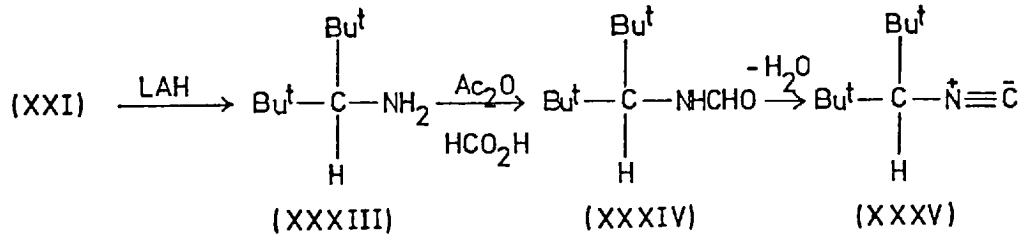
Scheme 5



selenoketones (XXXI), and 3H-1,2,4-dioxa-, dithia- and diselenazoles (XXXII) from isonitriles.

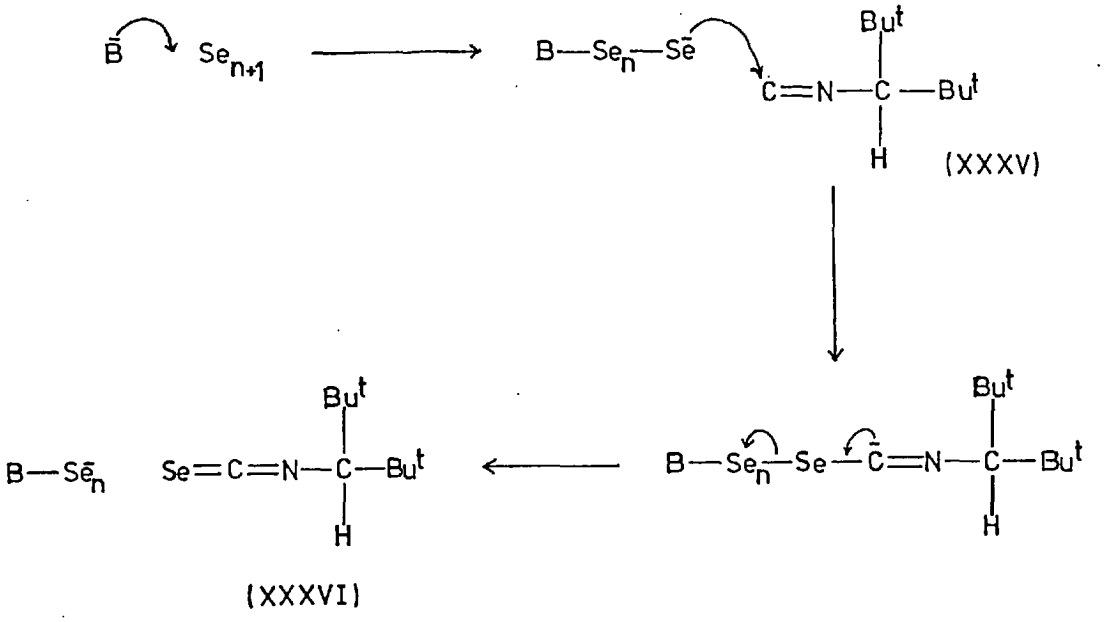
However, before this impressive scheme can be put into practice, the isonitrile in question must be α-metallated. In general, this can only be done if there is a substituent present to stabilise the negative charge. Lithium 2,2,4,4-tetramethylpiperidine can be used to force the reaction of unsubstituted alkyl isonitriles, but with n-butyl lithium nucleophilic attack at the isonitrile carbon predominates. With the latter reagent only methyl and cyclopropyl isonitriles can be α-metallated, i.e. those in which the protons of the parent hydrocarbons are as acidic as those of methane on the Cram acidity scale[16].

This requirement is not met by 3-isocyano-2,2,4,4--tetramethylpentane (XXXV), the precursor required for the synthesis of di-t-butyl selenoketone. The isonitrile (XXXV),



easily obtainable from di-t-butyl ketone imine (XXI) by reduction, N-formylation and dehydration, could not be α-metallated with n-butyl lithium under a variety of conditions. Addition of selenium to a mixture of isonitrile (XXXV) and n-butyl lithium or lithium diisopropylamide led to the isoselenocyanate (XXXVI) in good yield. A probable mechanism is shown in Scheme 6 ; this would also explain

Scheme 6

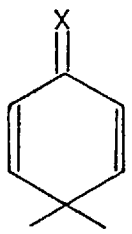


a recent report on the preparation of isoselenocyanates from isonitriles and selenium in the presence of tertiary amine[21].

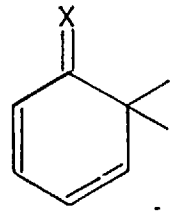
This route may be useful in preparing selenoketones from less hindered isonitriles with more acidic α-protons, but such selenoketones would be of no use in preparing hindered olefins. The route was not, therefore, explored in any depth.

C CYCLOHEXADIENONES

Cyclohexa-2,5-diene-1-thiones (XXXVIIb) are easily prepared by the action of phosphorous pentasulphide on the corresponding cyclohexa-2,5-dienones (XXXVIIa)[22]. We decided to attempt the synthesis of the analogous selenoketones (XXXVIIc), and also of cyclohexa-2,4-diene-1-thiones (XXXVIIIb) and -1-selenoketones (XXXVIIIc).



(XXXVII)



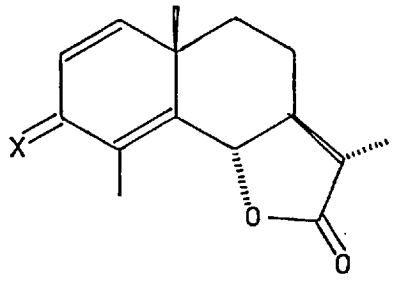
(XXXVIII)

a, X = O
b, X = S
c, X = Se

The first of these objectives was rapidly abandoned, when it was discovered that α-santonin (XXXIXa) was unreactive to either phosphorous pentaselenide or aluminium triselenide under a variety of conditions. Since α-santonin

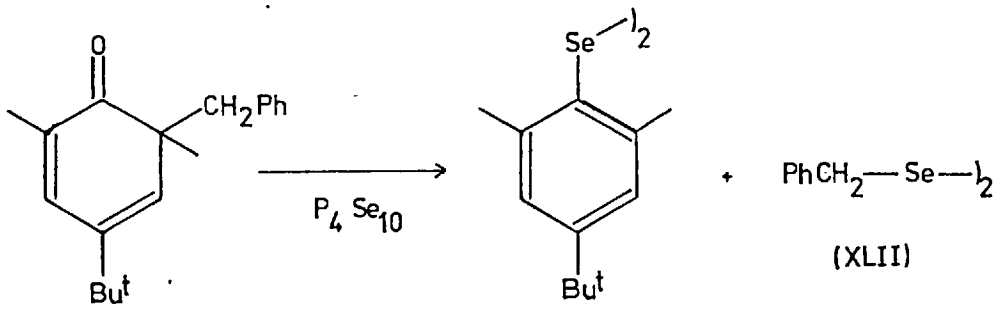
(XXXIX)

a, X = O
b, X = S



is known[22] to give thio-α-santonin (XXXIXb) with phosphorous pentasulphide, it can be concluded that the reagents used are not sufficiently reactive.

In contrast, 6-benzyl-4-t-butyl-2,6-dimethylcyclohexa-2,4-dienone (XL) reacted smoothly with phosphorous



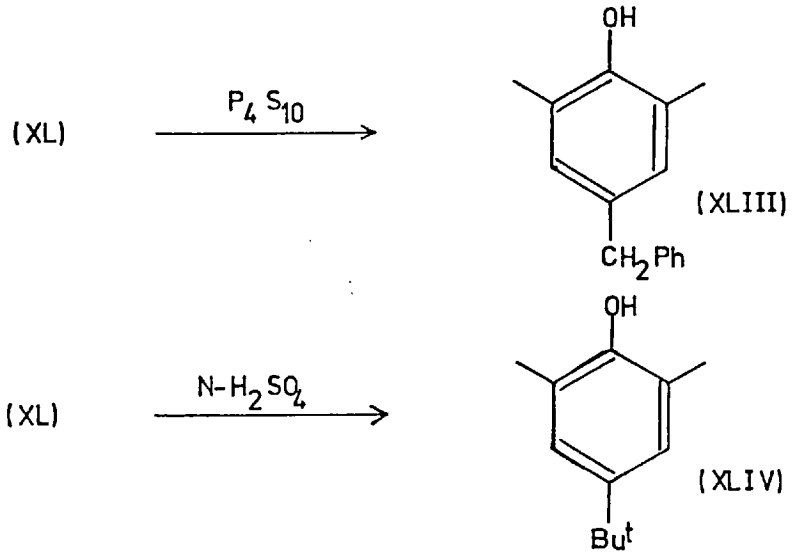
(XL)

(XLI)

(XLII)

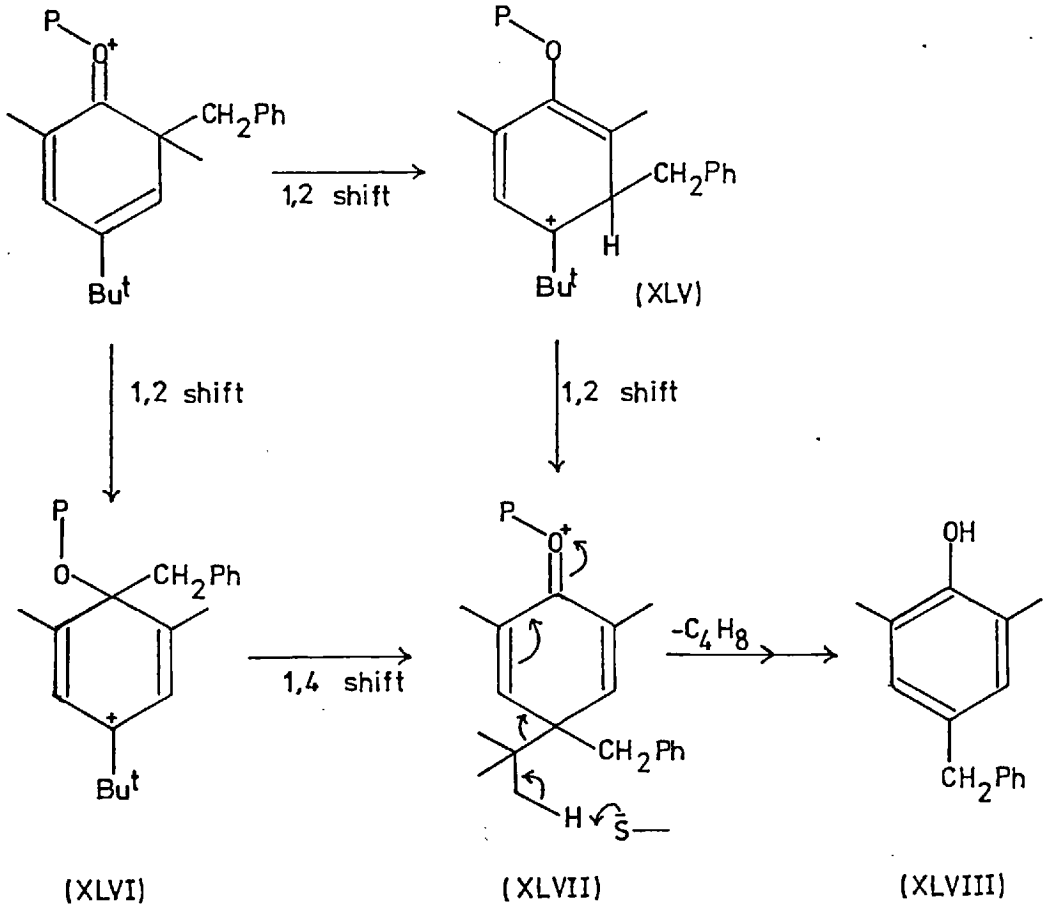
pentaselenide in refluxing benzene to give bis(4-t-butyl--2,6-dimethylphenyl) diselenide (XLI) and dibenzyl diselenide (XLII) in almost equal amounts. It seems probable that selenide ion, generated during the replacement of oxygen by selenium, attacks the benzylic carbon, thus restoring the aromatic system. It is therefore unlikely that this reaction will be useful in cyclohexadieneselenoketone synthesis.

The reaction of dienone (XL) with phosphorous pentasulphide took an entirely different course. The absence



of strong u.v. absorptions in the crude product indicated that no thione had been formed, and the alkaline extract afforded 4-benzyl-2,6-dimethylphenol (XLIII) as the only phenolic product. This curious rearrangement must proceed either by two consecutive 1,2 shifts, or by consecutive 1,2 and 1,4 shifts (Scheme 7). The rearrangement does not occur with phosphorous pentaselenide (vide supra), presumably because the selenide counter ion is more nucleophilic than sulphide and is therefore able to attack the benzylic substituent. At the same time, it is puzzling that the

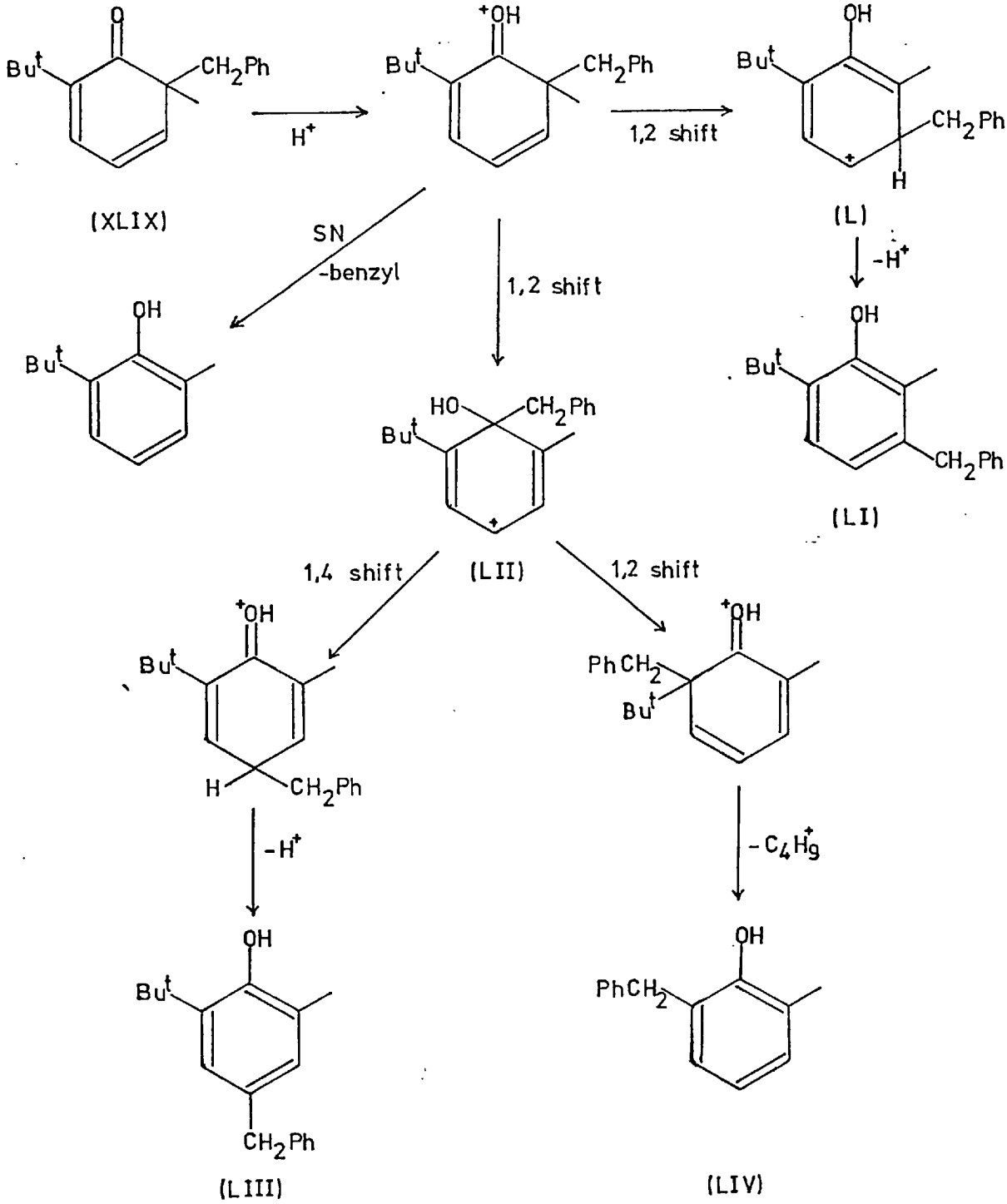
Scheme 7



sulphide counter ion is so eager to remove a proton from a methyl group in (XLVII), yet so loath to remove one from an allylic position in (XLVII); the steric factor seems insufficient to account for this. On the evidence available, the intermediate (XLVI) must be preferred.

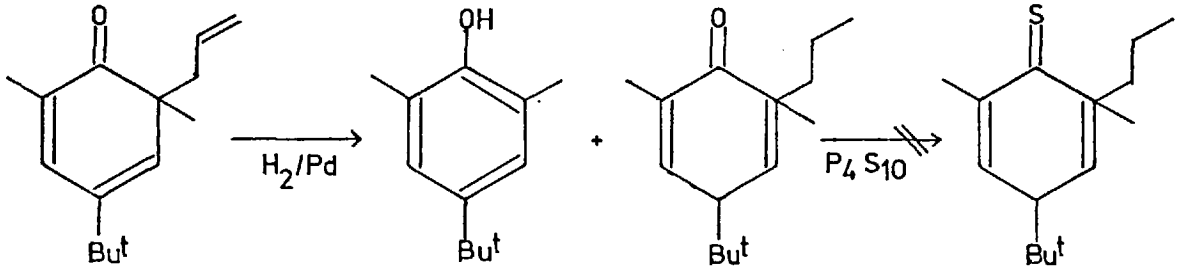
Miller[23] has postulated an intermediate (LII), similar to (XLVI), in the acid-catalysed rearrangement of 6-benzyl--2-t-butyl-6-methylcyclohexa-2,4-dienone (XLIX) (Scheme 8). The formation of 2-benzyl-6-methylphenol (LIV) sets a precedent for rearomatisation via loss of isobutene, while the formation of 4-benzyl-2-t-butyl-6-methylphenol (LIII) is most likely to proceed via the intermediate (LII). The alternative intermediate (L) is much less hindered than the analogous (XLV) and readily loses a proton to give

Scheme 8[23]


But
CH2Ph
H+
1,2 shift
SN
-benzyl
1,2 shift
-H+
1,4 shift
1,2 shift
-H+
-C4H9
(XLIX)
(L)
(LI)
(LII)
(LIII)
(LIV)

3-benzyl-6-t-butyl-2-methylphenol (LI). In our case, the acid-catalysed rearrangement of the dienone (XL) gave 4-t-butyl-2,6-dimethylphenol (XLIV) as the only phenolic product.

Since the benzyl group is clearly prone to sigmatropic shifts, a less mobile substituent is required. Accordingly, 4-t-butyl-2,6-dimethyl-6-n-propylcyclohexa-2,4-dienone (LVI) was synthesised by hydrogenation of 6-allyl-4-t-butyl-2,6--dimethylcyclohexadienone (LV). The yield is poor, since hydrogenolysis of the allyl-ring carbon bond predominates.

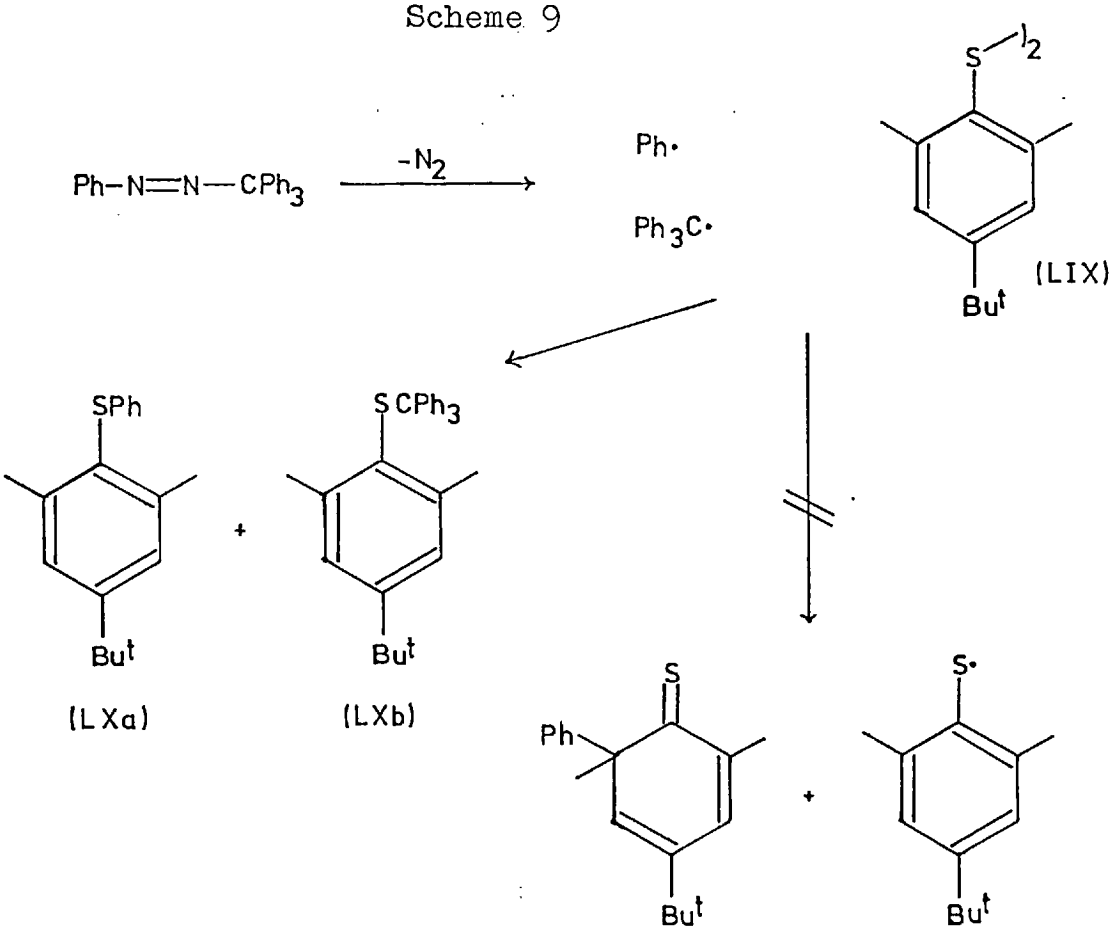


(LV) (XLIX) (LVI) (LVII)

Treatment of the dienone (LVI) with phosphorous pentasulphide resulted in complete destruction of the dienone chromophore, with no evidence for the formation of dienethione (LVII). The complex mixture of products was not investigated.

Finally, the azo-compound (LVIII) was thermally decomposed in the presence of the disulphide (LIX), in the hope that the phenyl radicals generated would attack the aromatic ring of the disulphide (Scheme 9). However, the only products observed were the thioethers (LXa and LXb) arising from radical attack on sulphur.

Scheme 9



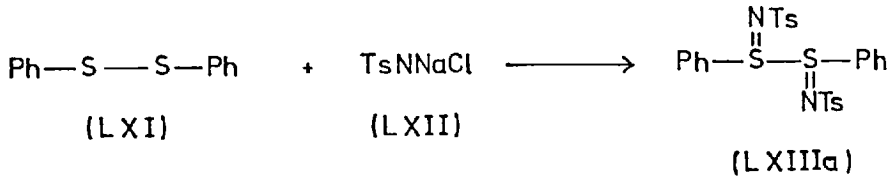
D OXIDATION OF DISULPHIDES AND DISELENIDES

The report of a fragmentation of thiolsulphinates to give sulphenic acids and thiones (see Review, Section B 2) led us to investigate the possibility of synthesising thiones and selenoketones by this route.

1. Disulphides

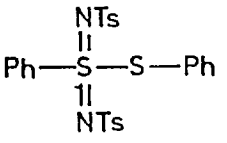
In view of the substantial amount of research that has already been done on oxidation of disulphides (Review, Section B), it was felt that an investigation of the 'oxidative imination' of disulphides with Chloramine-T (N-chloro-N-sodio-4-methylbenzenesulphonamide) (LXII) would be more original. It was found that diphenyl disulphide

(LXI) reacted with Chloramine-T (LXII) in acetone to give a crystalline product of formula $(PhSSPh)(TsN)_2$, m.p. 125-

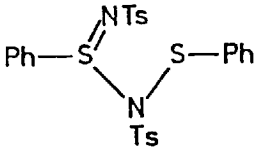


(LXI) (LXII) (LXIIIa)

Ts = 4-methylbenzenesulphonyl



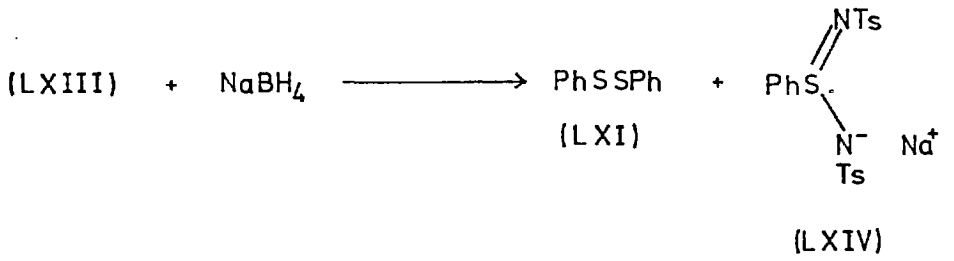
(LXIIIb)



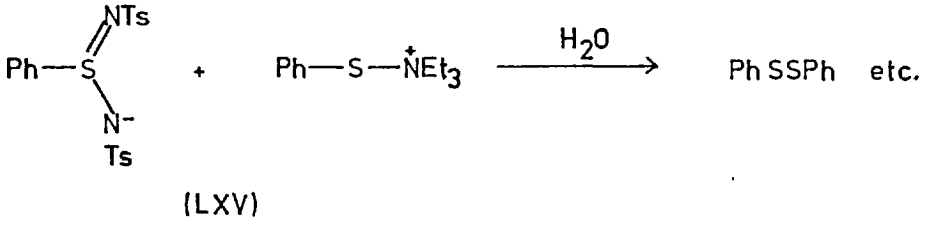
(LXIIIc)

-130° d. Recrystallisation lowered the m.p. to 121-124° d, possibly owing to the presence of different isomers (LXIII a,b,c) which may have interconverted during crystallisation. Levchenko et al[24] have been unable to establish which of the three isomers is formed in this reaction, mainly owing to the presence of strong S=O bands which overshadow the S=N bands in the infra-red spectrum; we observed the same difficulty with the adduct (LXIII). However, the disulphimide structure (LXIIIa) can now be ruled out in view of the chemical evidence. Sodium borohydride reduced the adduct (LXIII) to give, upon work up, diphenyl disulphide (LXI) and the sodium salt of the benzenesulphinamidine (LXIV). Thus one of the sulphur atoms in the adduct (LXIII) has

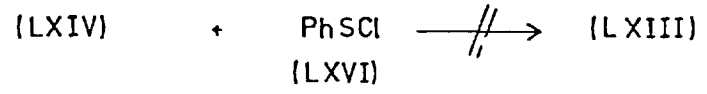
not been oxidised.



The adduct (LXIII) acts as a sulphenylating agent, reacting irreversibly with triethylamine in dichloromethane to give diphenyl disulphide (LXI), probably <u>via</u> hydrolysis of the salt (LXV).

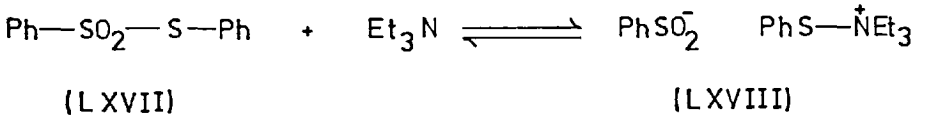


The irreversibility of this reaction may explain the failure of the attempted synthesis of (LXIII) by reaction of the sulphinamidine salt (LXIV) with benzenesulphenyl chloride (LXVI).



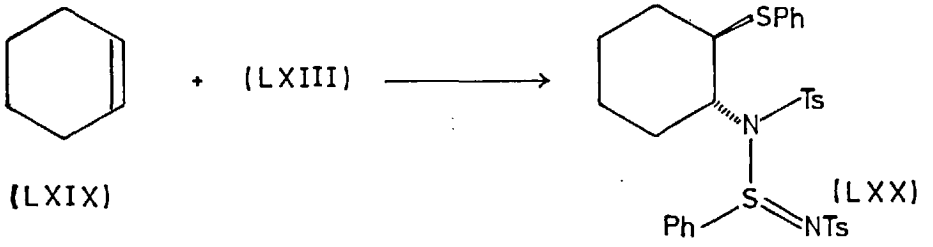
The reversible reaction of thiolsulphonates (LXVII) with triethylamine in polar solvents gives rise to sulphinate salts (LXVIII)[25], similar to the proposed salts (LXV). However, the thiolsulphonate reaction fails in dichloromethane, indicating that the sulphide group in thiol-

sulphonates (LXVII) is more strongly bonded than in the adduct (LXIII).



(LXVII) (LXVIII)

The evidence available does not make it possible to choose between the sulphinamidine (LXIIIc) and the thiosulphondiimide structure (LXIIIb). Dr. D. Ferreira of this department has observed that the addition of the adduct (LXIII) to cyclohexene (LXIX) gives a sulphinamidine



(LXIX) (LXX)

(LXX). This suggests that the sulphinamidine ion (LXIV) forms bonds on nitrogen more readily than on sulphur, which would favour the structure (LXIIIc).

The oxidation of di-t-butyl disulphide (LXXIa) and dibenzyl disulphide (LXXIb) with (LXII) gave intractable mixtures; bis(α-diphenylmethyl) disulphide (LXXIc) underwent a substitution reaction to give a low yield of

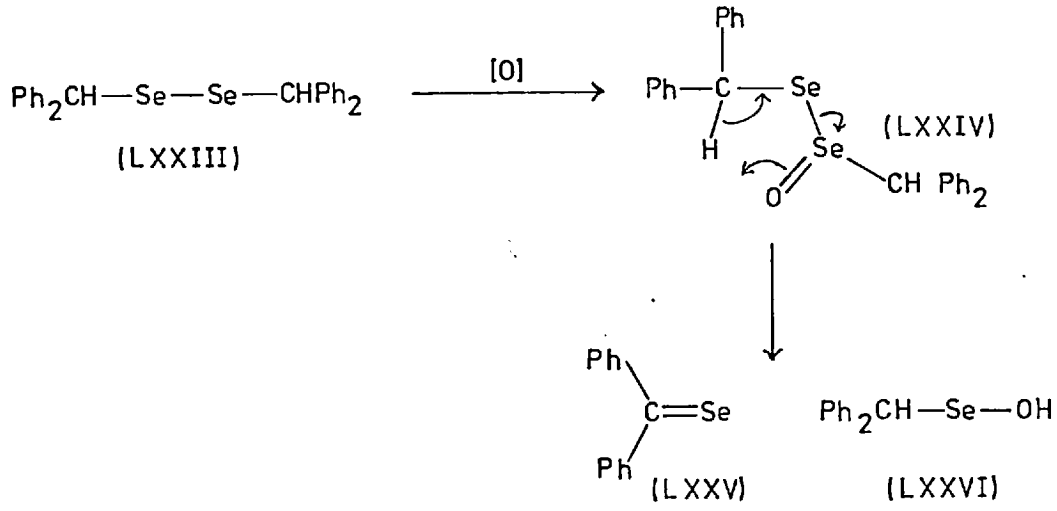
(LXXI) (LXXII)

a, R = Bu^t
b, R = CH_2Ph
c, R = $CHPh_2$

N-(4-methylbenzenesulphonyl) diphenylmethylamine (LXXII). These disappointing results forestalled further investigation of the structure of the adduct (LXIII) and the mechanism of its formation.

2. Diselenides

It was hoped that oxidation of bis(α-diphenylmethyl) diselenide (LXXIII) with 3-chloroperbenzoic acid would lead to a selenolseleninate (LXXIV) which might then undergo



elimination to give selenobenzophenone (LXXV) and a selenenic acid (LXXVI). The only identifiable products of the reaction are benzophenone and the starting diselenide, indicating that although the α-proton is removed during the course of the reaction, the selenoketone (LXXV) is probably oxidised or hydrolysed as rapidly as it is formed. However, the result does not establish the intermediacy of (LXXV). It is interesting to note that photolysis of the diselenide (LXXIII) in the presence of oxygen also leads to benzophenone. A free radical mechanism has been proposed for the very similar photolysis of dibenzyl diselenide (LXXVII) to give benzaldehyde (LXXVIII)[26].

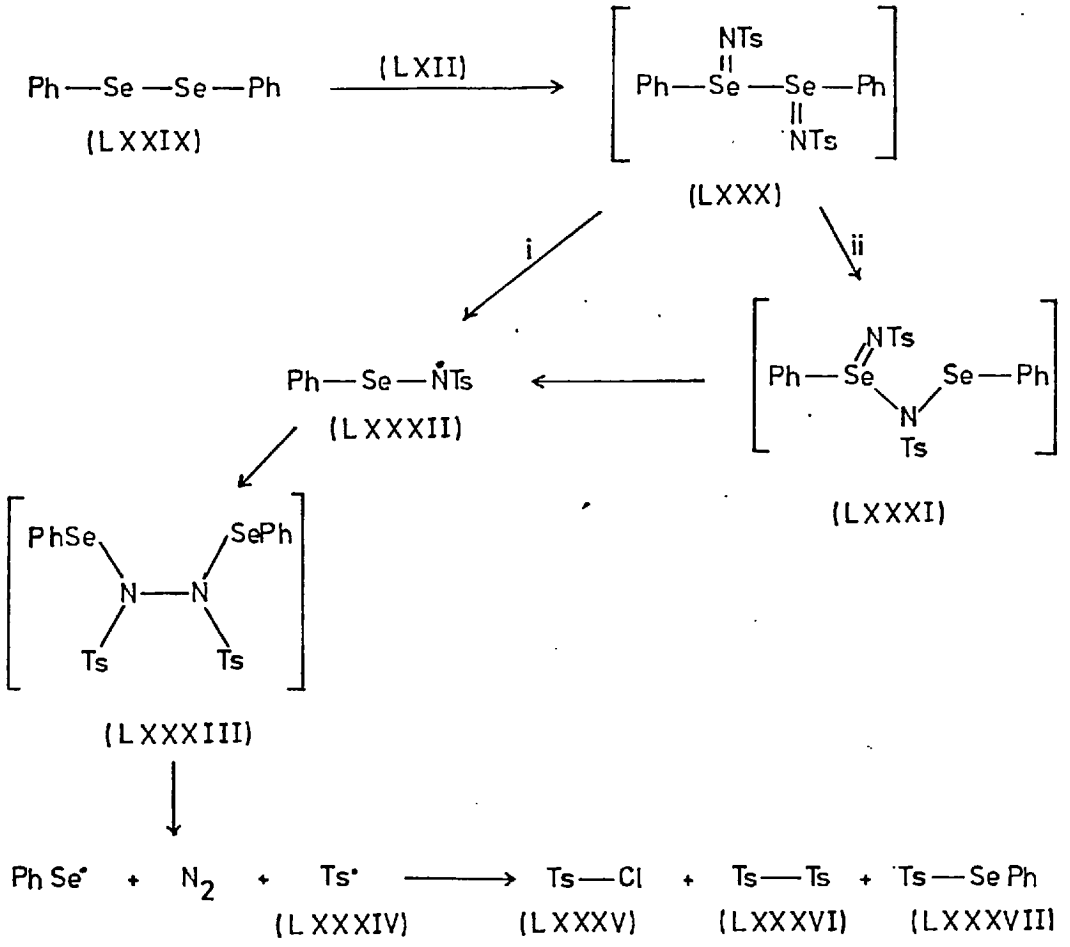
$$\underset{\text{(LXXVII)}}{PhCH_2—Se—Se—CH_2Ph} \xrightarrow[h\nu]{O_2} \underset{\text{(LXXVIII)}}{PhCHO} + Se$$

It was clear from these two experiments that the oxidation of diselenides would require extensive investigation, and was in any event unlikely to lead to selenoketones. The 'oxidative imination' reaction did not seem to offer any advantages over straightforward oxidation, but the investigation was nonetheless carried out for the purpose of comparison with the disulphide case.

Accordingly, diphenyl diselenide (LXXIX) was treated with Chloramine-T (LXII) at room temperature in dichloromethane. A vigorous reaction occurred, accompanied by effervescence. The products were 4-methylbenzenesulphonyl chloride (LXXXV), bis(4-methylphenyl) disulphone (LXXXVI) and Se-phenyl 4-methylbenzeneselenosulphonate (LXXXVII) (Scheme 10), strongly suggesting that a free radical reaction was occurring.

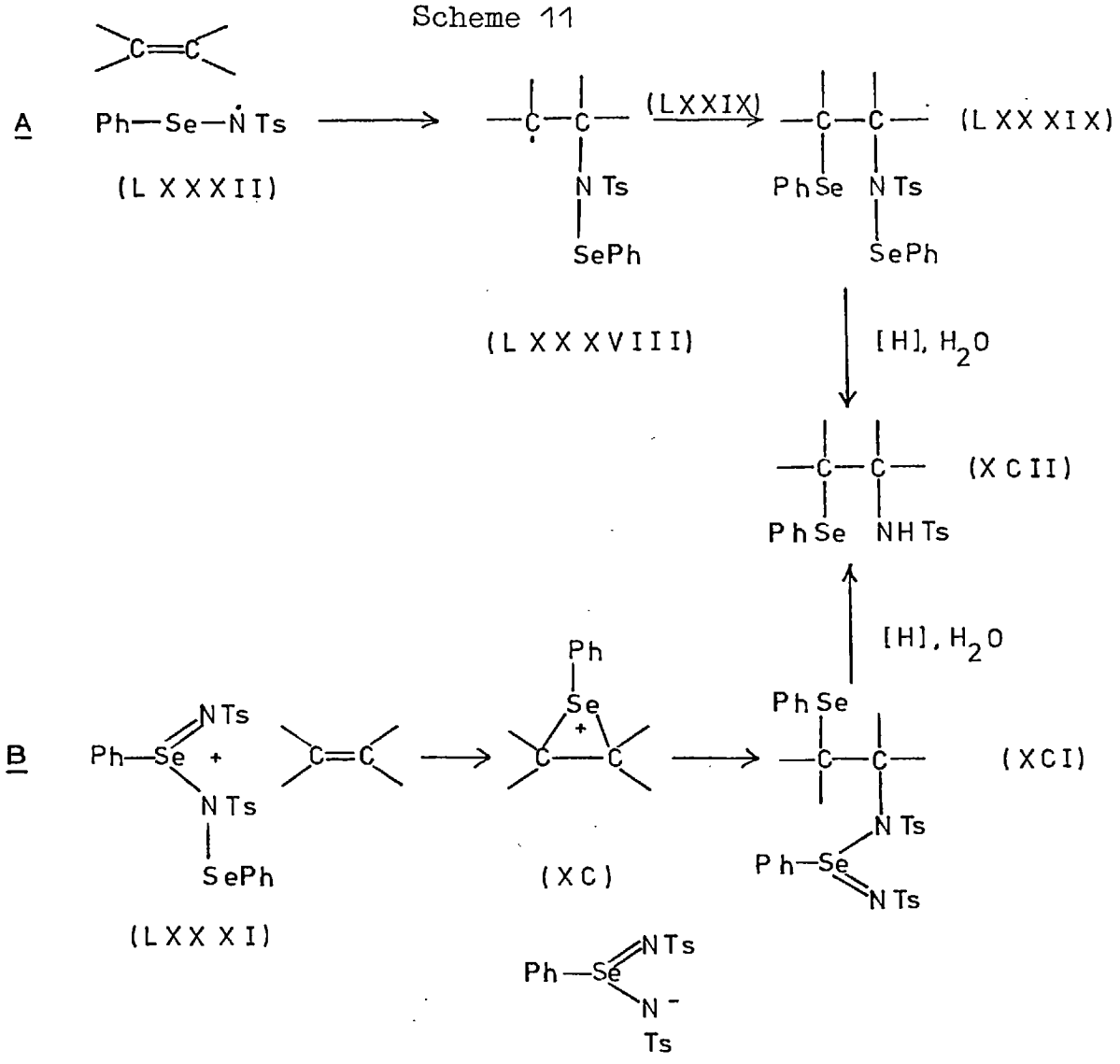
It seems reasonable to suggest that the diselenide is oxidised twice to afford, in the first instance, a diselenimide (LXXX). This may then fragment to give a nitrogen-centred radical (LXXXII), either directly (route i) or after rearrangement to the selenoseleninamidine (LXXXI) (route ii). Dimerisation of the radical (LXXXII) would lead to the tetrasubstituted hydrazine (LXXXIII) which would in turn decompose to afford nitrogen, phenyl selenide radical and 4-methylbenzenesulphonyl radical (LXXXIV).

Scheme 10



The products formed are consistent with the intermediacy of the sulphonyl radical (LXXXIV), but little can be deduced concerning the earlier intermediates along the reaction pathway. In an attempt to trap these intermediates, the reaction was performed in the presence of a number of olefins. There are two possible reaction pathways (Scheme 11). If the radical intermediate (LXXXII) is trapped (route A), the product of addition to the olefin will be the selenenamide (LXXXIX). In this case one would expect a mixture of cis- and trans-addition products; attachment of the amide function to the less hindered end of an unsymmetrical olefin;

Scheme 11

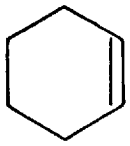
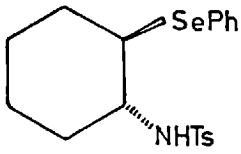
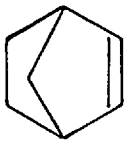
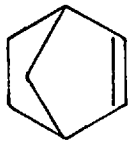


and sensitivity of the reaction to the presence of molecular oxygen.

Alternatively, ionic addition of the selenoseleninamidine (LXXXI) to an alkene (route B) would lead to a β-(phenylseleno) seleninamidine (XCI) via an intermediate selenonium species (XC). Here one would expect exclusive Markownikoff trans-addition, and failure of the reaction with electron-deficient olefins. The results of the reactions with a variety of alkenes are presented in Table 2.

Table 2

Reactions of Diphenyl Diselenide (LXXIX) with Chloramine-T (LXII) in the Presence of Various Olefins

Olefin	Product	Yield (%)
 (LXIX)	 (XCVII)	30
$CH_3(CH_2)_5CH{=}CH_2$ (XCIII)	$CH_3(CH_2)_6CH_2NHTs$ (XCVIII)	45[a]
$CH_2{=}CH{-}C{\equiv}N$ (XCIV)	$PhSeCH_2CH_2CN$ (IC)	15
$Ph{-}CH{=}CH_2$ (XCV)	$PhCHCH_2SePh$ $NHTs$ (C)	62
 (XCVI)	 . (PhSe) . (Ts) (CI)	25[b]

a The intermediate amidoselenide was not characterised, but was deselenated with nickel boride.

b Two isomers were obtained, neither of which was fully characterised.

The reaction with cyclohexene (LXIX) was investigated to find the conditions for optimum yield based on the olefin. Anhydrous acetonitrile was chosen as solvent for the reactions in view of its polarity, which would assist ionic reactions, and its inertness to most radical species. Detailed results are listed in the Experimental, Section D, from which the following observations can be made:

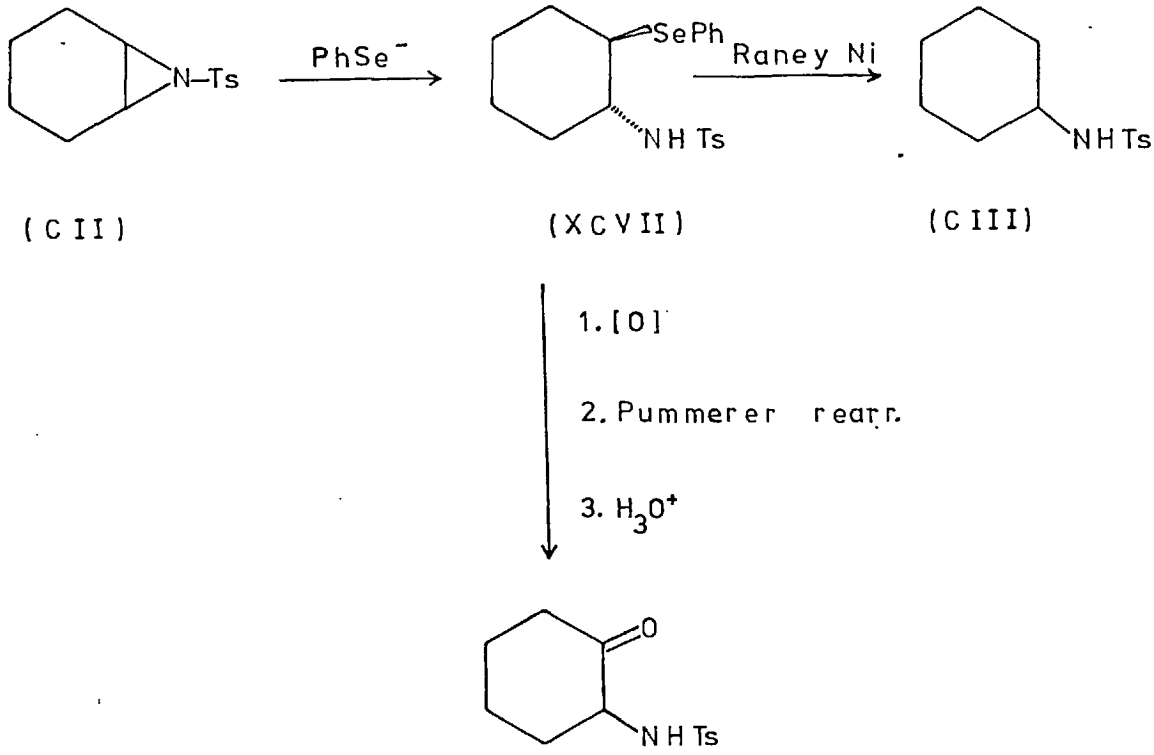
(1) The initial product of addition is a very polar, unstable compound which could not be isolated. Treatment with sodium borohydride gave the amidoselenide (XCVII), which might arise from either a selenenenamide (LXXXIX) or seleninamidine (XCI). (2) The trans-1,2-amidoselenide (XCVII) is obtained, with only very small amounts of cis--product. This supports the ionic mechanism. (3) At temperatures near or below 0^0, no evolution of nitrogen is observed, and the yields are improved. This is consistent with route B, Scheme 11, assuming that the selenoseleninamidine (LXXXI) is more stable at lower temperature; however, it could also be argued that the radicals (LXXXII) are produced more slowly at lower temperature, thus improving the efficiency of the trapping reaction (route A). (4) An excess of Chloramine-T (LXII) reduces the yield, probably by oxidation of the product selenide (XCVII). (5) A large excess of diselenide (LXXIX) also reduces the yield, probably because the effect of the oxidant is dissipated. (6) The best ratio of reactants is 1:2:2 for alkene:Chloramine-T:diphenyl diselenide. This represents a greater amount of diselenide (LXXIX) than required by

the stoichiometry of the reaction. However, the diselenide (LXXIX) is only partially soluble in acetonitrile at 0^0, so it is difficult to draw conclusions from this. (7) The reaction is not inhibited by the presence of oxygen, nor are the yields significantly improved when the reaction is performed under an inert atmosphere. This strongly indicates that intermediate carbon radicals such as (LXXXVIII) are not involved. (8) The addition reaction fails when Chloramine-T trihydrate is used instead of the anhydrous reagent, although in both cases the diselenide is consumed. In this case, the failure of route B could be attributed to hydrolysis of the selenoseleninamidine (LXXXI); it is less easy to see how water would interfere with the radical pathway.

The structure and stereochemistry of the amido-selenide (XCVII) derived from cyclohexene, were established by the reactions shown in Scheme 12. (The synthesis of (XCVII) from N-(4-methylbenzenesulphonyl) cyclohexyl-aziridine (CII) and phenyl selenide, was performed by Dr. D. Ferreira.)

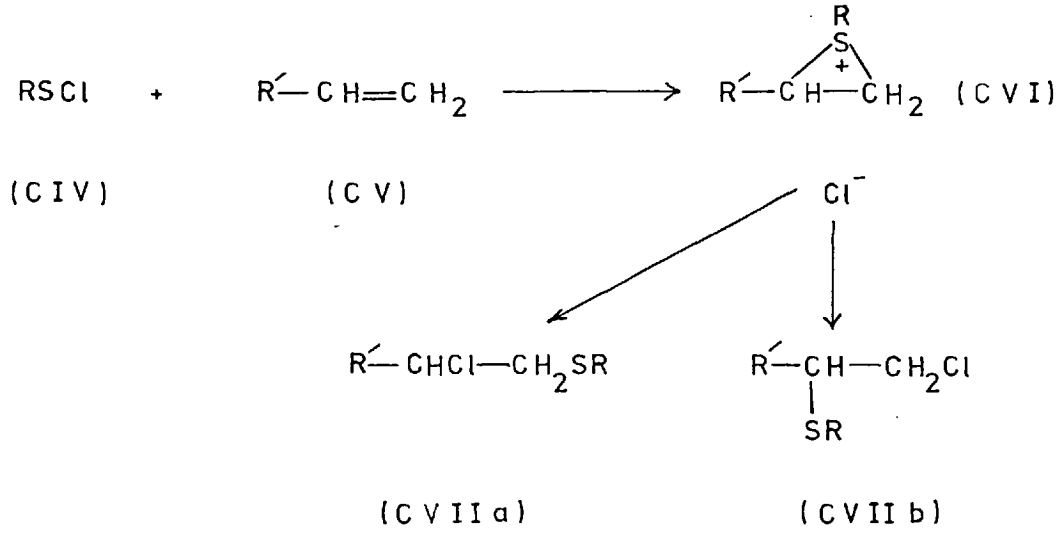
The reaction product (XCVIII) from 1-octene appeared to favour the radical mechanism, since the amide function is attached to the terminal carbon. However, anti--Markownikoff addition by an ionic mechanism cannot be ruled out. This result can be compared with that obtained for the addition of sulphenyl chlorides (CIV) to terminal olefins (CV, R'= alkyl)[27]. It is proposed that the reaction proceeds via an intermediate sulphonium ion (CVI), and that the ratio of addition products (CVIIa and CVIIb)

Scheme 12



(CII) (XCVII) (CIII)

depends on the relative rates of reaction of the chloride ion at the 1- and 2-positions in (CVI). The anti-Markownikoff adduct (CVIIb) predominates, and the effect becomes more marked with increasing size of R'. Similar product distributions are observed with benzeneselenenyl chloride[28] and β-methylselenium trichloride[29].



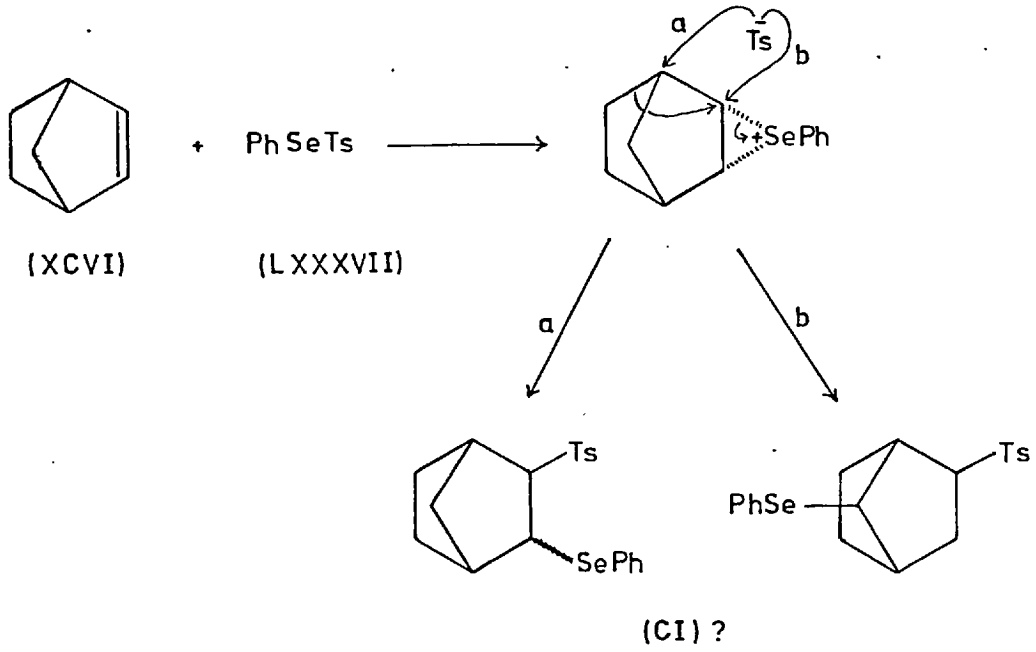
(CIV) (CV) (CVIIa) (CVIIb)

It is interesting to note that addition of sulphenyl chlorides (CIV) to styrene (CV, R'= phenyl) leads to the Markownikoff addition product (CVIIa, R'= = phenyl)[27]. In this case the electronic effect determines the course of the reaction. Our selenium reagent also adds to styrene to give a Markownikoff addition product (C); this is strong evidence for an ionic mechanism.

Acrylonitrile (XCIV) would not be expected to undergo electrophilic addition, since the olefinic bond is electron--deficient; the failure of the reaction to give an amido-selenide addition product is therefore in accordance with an electrophilic addition mechanism. The product obtained in this case is 3-phenylselenopropionitrile (IC), which probably arises from nucleophilic attack of phenyl selenide anion, generated during the work up with sodium boro-hydride.

The reaction with norbornene (XCVI) gives two compounds which appear to be isomeric 4-methylphenyl phenylselenonorbornyl sulphones. It seems likely that these products arise from addition of Se-phenyl 4-methyl-benzeneselenosulphonate (LXXXVII), which is present in the reaction mixture, to norbornene (XCVI), via the mechanism shown in Scheme 13. The products (CIa and CIb) were not considered interesting enough to warrant full characterisation. It is curious, however, that the seleno-seleninamidine (LXXXI) which should be a better source of electrophilic selenium, does not react with the alkene more rapidly than the selenosulphonate (LXXXVII).

Scheme 13



The reaction of diphenyl diselenide with Chloramine-T gave no addition products when performed in the presence of cholesteryl benzoate, α-pinene or stilbene.

The reaction of Chloramine-T (LXII) with dibenzyl diselenide (LXXVII) closely parallels the reaction with diphenyl diselenide. Reaction in the presence of cyclo-

$$PhCH_2—Se—Se—CH_2Ph \quad + \quad (LXII) \longrightarrow Ts—Cl \quad + \quad Ts—Ts$$

(LXXVII) (LXXXV) (LXXXVI)

hexene (LXIX) gave a seleniferous product which could be deselenated with nickel boride to give N-cyclohexyl-4--methylbenzenesulphonamide (CIII). The extension of the reaction to other diselenides is probably quite feasible, but not of great significance.

In conclusion, the reaction of Chloramine-T (LXII) with diphenyl diselenide appears to give rise to a

selenoseleninamidine (LXXXI). This compound decomposes at room temperature, generating nitrogen, phenyl selenide radicals, and 4-methylbenzenesulphonyl radicals. At lower temperatures, the amidine (LXXXI) effects stereospecific *trans* 1,2-aminoselenation of simple olefins, probably *via* an electrophilic addition reaction.

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PART III

EXPERIMENTAL

M.p.s were determined with a Reichert hot-stage apparatus.

I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer and u.v. spectra with a Unicam SP 800B spectrometer.

^{1}H N.m.r. spectra were recorded with a Varian T60 instrument (tetramethylsilane as an internal reference) and ^{13}C spectra were obtained with a Varian XL 100 spectrometer through the cooperation of Dr. L. Phillips (Department of Chemistry, Imperial College).

Mass spectra were recorded with an A.E.I. MS9 instrument.

Rotations were measured on a Perkin-Elmer 141 polarimeter.

Selenium analyses were performed by the method of Gould[1].

'Light petroleum' refers to the fraction b.p. 40-60° C, and 'petroleum' to the fraction b.p. 60-80° C.

A OLEFIN SYNTHESIS VIA THIONES AND SELENOKETONES

Di-t-butyl Ketone Hydrazone

2,2,4,4-Tetramethylpentane-3-imine[2] (30.8 g) and hydrazine hydrate (42.0 g) were refluxed for 18 h in 2,2′-oxydiethanol (50 ml). The mixture was then cooled to room temperature and poured into cold water (300 ml). The resulting solid was filtered off, dried, and recrystallized from methanol-water to provide the hydrazone as plates (88%), m.p. 67-68.5° (lit[3]. 68-69°).

Di-t-butyl Ketone Azine

Diazodi-t-butylmethane (154 mg) and copper(I) iodide (10 mg) were stirred for 0.5 h. The orange colour was rapidly discharged and the white solid residue was taken up in dichloromethane (10 ml). The solution was washed with water (10 ml), dried ($MgSO_4$), and concentrated, and the residue crystallized from ether to give white needles of the azine (50%), m.p. 67.5-69.5°, ν_{max} ($CHCl_3$) 1565, 1480, 1390, 1370, and 1000 cm^{-1}, ν_{max} (CCl_4) 1480, 1390, 1370, 1215, and 1060 cm^{-1}, δ (CCl_4) 1.30 (s) and 1.26 (s), λ_{max} (cyclohexane) 242 (ε 5900) and 260 nm (600), m/e 280 (M^+) and 223 ($M - C_4H_9$) (Found: C, 77.3; H, 12.9; N, 9.9. $C_{18}H_{36}N_2$ requires C, 77.1; H, 12.9; N, 10.0%).

Adamantanone Hydrazone

The title compound, prepared (57%) from adamantanone by the method of Newkome and Fishel[4], had m.p. 68.5-69°, (CCl_4) 5.0-4.5br (2H, s, exch. D_2O), 3.05 (1H, m), and 1.88 br (12H, s), m/e 164 (M^+).

Di-t-butyl Ketone Triphenylphosphoranylidenehydrazone (III) (with Dr. F. S. Guziec) and Congeners

A modification of the procedure of Bestmann and Fritzsche[5] was employed. Bromine (12.8 g) in dry benzene (100 ml) was added over 30 min to a stirred, cooled (ice-water) solution of triphenylphosphine (21.0 g) in dry benzene (250 ml). After stirring for 30 min, di-t-butyl ketone hydrazone (12.5 g) and triethylamine (17.8 g) in dry benzene (80 ml) were added over 1 h. After 5 h at room temperature, the mixture was filtered and evaporated in vacuo. The resulting yellow oil was crystallized from chloroform-petroleum to afford compound (III) as two crops of yellow crystals (82%), m.p. 109-110°, ν_{max} ($CHCl_3$) 1485, 1445, 1390, and 1360 cm^{-1}, δ($CDCl_3$) 7.9-7.3 (15 H, complex), 1.60 (9 H, s), and 1.12 (9 H, s) (Found: C, 77.7; H, 7.8; N, 6.6; P, 7.5. $C_{27}H_{33}N_2P$ requires C, 77.9; H, 8.0; N, 6.7; P, 7.4%).

Similarly, the following were prepared from the corresponding hydrazones: (-)-1,3,3-trimethylnorbornan-2-one triphenylphosphoranylidenehydrazone (VI) (90%), m.p. (from) 123-137°, $[\alpha]_D^{23}$ -41.1° (c 0.6 in $CHCl_3$), δ(CCl_4) 7.50-7.05 (15 H, complex) and 2.0-0.9 (16 H, complex, singlets at 1.50, 1.42, and 1.05), m/e 426 (M^+) and 262 ($M - C_{10}H_{16}N_2$) (Found: C, 79.2; H, 7.15; N, 6.9; P, 7.2. $C_{28}H_{31}N_2P$ requires C, 78.85; H, 7.3; N, 6.6; P, 7.25%); adamantanone triphenylphosphoranylidenehydrazone (XI) (55%), m.p. (from) 143-145°, δ(CCl_4) 7.9-7.2 (15 H, complex), 2.5br (2 H, s), and 1.9br (12 H, s), m/e 424 (M^+).

Di-t-butyl Selenoketone (IV) (with Dr. F. S. Guziec and Dr. T. G. Back)

(a) A vigorously stirred mixture of di-t-butyl ketone triphenylphosphoranylidenehydrazone (9.99 g), selenium (3.78 g), and tri-n-butylamine (12 drops) was heated for 21 h at 120° C under nitrogen. Gas was evolved. The mixture was cooled to room temperature, taken up in light petroleum, and filtered through a short column of silica gel. The light petroleum was evaporated off under reduced pressure at room temperature and the resulting oil was distilled *in vacuo* into a solid CO_2-acetone trap to provide di-t-butyl selenoketone (IV) as a blue liquid (35%), b.p. 83-85° at 30 mmHg, ν_{max} (film) 2970, 1490, 1395, 1365, 1055, 970, and 785 cm^{-1}, λ_{max} (cyclohexane) 230 (ε 2800), 268 (7200), and 710 nm (21), δ (CCl_4) 1.53 (s) (Found: C, 53.2; H, 9.0; Se, 38.2%; M^+, 206.057 8. $C_9H_{18}Se$ requires C, 52.7; H, 8.8; Se, 38.5%; M^+, 206.057 3).

(b) The preceding procedure was followed except that volatile material was distilled from the reaction vessel into a solid CO_2-acetone trap every 90 min by reducing the pressure (to 20 mmHg). When no more distillate was obtained, the temperature was raised to 150° C and the procedure was continued at 1 mmHg. The combined volatile material was redistilled to provide four fractions. The first afforded pure 2,3,4,4-tetramethylpent-1-ene, b.p. 57-58° at 90 mmHg, ν_{max} (film) 3075, 1785, 1640, and 890 cm^{-1} (lit.[6] 3076, 1785, and 891 cm^{-1}), δ (CCl_4) 4.72 (1 H, s), 4.62 (1 H, s), 1.87 (1 H, q, J 7 Hz), 1.70 (3 H, s), 1.00 (3 H, d, J 7 Hz), and 0.88 (9 H, s), m/e 126 (M^+). The second contained additional olefin of lower purity, b.p. 64-67° at 110 mmHg, redistilled

with b.p. 124-126° (lit[7]. 125-126°) at 754 mmHg (32% total). The third furnished diazodi-t-butylmethane[2] (12%) containing a significant amount of the olefin and a trace of the selone. The last fraction afforded pure selenoketone (23%), b.p. 83-85° at 30 mmHg.

(c) Di-t-butyl ketone triphenylphosphoranylidene-hydrazone (2.08 g) and selenium (0.79 g) were heated at 165°C and 5 mmHg. Volatile material was continuously distilled into a solid CO_2-acetone trap at 5 mmHg. Diazodi-t--butylmethane was collected first (40%), followed by the selenoketone (20%). N.m.r. analysis revealed the purity of the products as ca. 90 and 85%, respectively.

Reduction of Di-t-butyl Selenoketone (IV) with sodium borohydride

The selenoketone (IV) (103 mg) in ethanol (25 ml) was added to sodium borohydride (38 mg) in ethanol (25 ml). The blue colour rapidly changed to pale yellow, and after 20 h the ethanol was removed under reduced pressure. The residue was taken up in petroleum (100 ml), dried, concentrated *in vacuo*, and crystallized from petroleum-methanol to provide bis(1-t-butyl-2,2-dimethylpropyl)diselenide (IX) (99%), m.p. 56.5°, ν_{max} ($CHCl_3$) 1480, 1390, and 1370 cm^{-1}, δ (CCl_4) 3.08 (2 H, s), and 1.25 (36 H, s), m/e 414 (M^+) (Found: C, 52.85; H, 9.3. $C_{18}H_{38}Se_2$ requires C, 52.4; H, 9.3%).

Stability of Di-t-butyl Selenoketone (IV) (performed by Dr. T. G. Back)

The selenoketone (52 mg) was placed in a sealed glass tube under argon and heated for 24 h at 150°C. No reaction

was observed.

1,3,3-Trimethylnorbornane-2-selone (Selenofenchone) (VII)

Trimethylnorbornan-2-one triphenylphosphoranylidene-hydrazone (VI) (3.41 g) and selenium (1.62 g) were heated at 160° C with stirring at 5 mmHg pressure. A bright blue liquid was distilled into a solid CO_2-acetone cold trap. Redistillation and recrystallization from ether at -30° C gave the blue crystalline selenoketone (VII) (28%), m.p. 41-47°, ν_{max} (CCl_4) 1470, 1450, 1380, 1360, 1080, and 1050 cm^{-1}, δ (CCl_4) 2.6-1.0 (complex, singlets at δ 1.43, 1.22, and 1.13), λ_{max} (cyclohexane) 616 (ε 42), 272 (9600), and 224 nm (3700), m/e 216 (M^+) (Found: C, 56.15; H, 7.5; Se, 36.7. $C_{10}H_{16}Se$ requires C, 55.8; H, 7.5; Se, 36.7%).

A sample of the selone (VII) was heated in a sealed tube under argon at 150° C for 24 h without decomposition (n.m.r.).

(-)-1,1',3,3,3',3'-Hexamethyl-2,2'-binorbornylidene (Fenchylidenefenchane) (XVI)

(a) (-)-1,3,3-Trimethylnorbornan-2-one triphenylphosphoranylidene hydrazone (VI) (3.41 g) and selenium (1.62 g) were heated at 160° C with stirring under dry nitrogen for 24 h. The cooled residue was extracted with hot petroleum and the extract concentrated and chromatographed on silica (100 g). Elution with petroleum gave an oil (0.5 g). Repeated recrystallization from petroleum at -30° C gave a single isomer of the olefin (XVI) (24%), m.p. 125-127°, $[\alpha]_D^{23}$ -240.0° (c 0.3 in EtOH), ν_{max} (CCl_4)

1470, 1450, 1390, and 1365 cm^{-1}, δ (CCl_4) 2.1-0.9 (complex, singlets at δ 1.50, 1.32, and 1.25), m/e 272 (M^+), 257 ($M - CH_3$), and 242 ($M - C_2H_6$) (Found: C, 87.7; H, 12.1. $C_{20}H_{32}$ requires C, 88.2; H, 11.8%).

(b) The hydrazone (VI) (2.13 g) and (-)-1,3,3-trimethylnorbornane-2-thione[2] (0.84 g) were treated (24 h) and worked up as in (a). Elution with petroleum gave the olefin (XVI) (72%), m.p. 110-115° C, $[\alpha]_D^{23}$ -174° (c 0.6 in EtOH), n.m.r. and i.r. spectra identical to those for the single isomer. Repeated recrystallization from hot ethanol gave material of m.p. 120-125° and $[\alpha]_D^{23}$ -225.0° (c 0.6 in EtOH).

Ozonolysis of the Binorbornylidene (XVI)

Ozone was bubbled through a solution of the olefin (0.54 g) in dry dichloromethane (10 ml) at -25° C. After 2.5 h, the starting material was entirely consumed (t.l.c.). The solution was washed with 5% sodium iodide and 5% sodium thiosulphate, dried ($MgSO_4$), and concentrated to an oil (0.7 g). T.l.c. indicated the presence of a complex mixture containing 1,3,3-trimethylnorbornanone (identified by i.r. and n.m.r.).

1,1",3,3,3",3"-Hexamethyldispiro norbornane-2,2'-oxiran-3',2"-norbornane (Fenchylidenefenchane oxide) (XVII)

The olefin (XVI) (0.54 g) was added with stirring to a solution of m-chloroperbenzoic acid (0.69 g) in chloroform (10 ml). After 1 h, the solution was washed with aqueous potassium carbonate, dried ($MgSO_4$), and concentrated, and the residue was crystallized from carbon tetrachloride

to give the epoxide (XVII) (>90%), m.p. 117-118°, $[\alpha]_D^{23}$ +65.0° (c 0.5 in cyclohexane), ν_{max} (CCl_4) 1465, 1455, 1390, 1370, 1210, 950, 910, and 870 cm^{-1}, δ (CCl_4) 2.2-0.9 (complex, singlets at δ 1.17, 1.13, and 1.05), m/e 288 (M^+) and 273 ($M - CH_3$) (Found: C, 83.05; H, 11.45. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%).

2,2-Diphenyl-3,3-di-t-butyloxiran (XVIII)

1,1-Diphenyl-2,2-di-t-butylethylene[2] (XV) (0.29 g) was added with stirring to a solution of m-chloroperbenzoic acid (0.69 g) in chloroform (10 ml). After 16 h at room temperature, the solution was refluxed for 4 h, washed with aqueous potassium carbonate, dried ($MgSO_4$), and concentrated, and the residue was crystallized from ethanol to give the epoxide (XVIII) (>90%), m.p. 152-153°, ν_{max} (CCl_4) 1480, 1455, 1395, 1370, 1240, 1230, 950, 885, and 865 cm^{-1}, δ (CCl_4) 7.5-6.8 (10 H, complex) and 1.02 (18 H, s), m/e 308 (M^+) and 251 ($M - C_4H_9$) (Found: C, 85.8; H, 9.25. $C_{22}H_{28}O$ requires C, 85.7; H, 9.15%).

Attempted Preparation of 2-Di-t-butylmethylene-1,3,3-trimethylnorbornane (XIX)

(a) The hydrazone (VI) (2.13 g) and di-t-butyl thioketone[2] (V) (0.79 g) were treated (24 h) and worked up as for the preparation of the olefin (XVI). Elution with petroleum gave the olefin (XVI) (isomeric mixture) (59% based on (VI)), m.p. 70-75°, $[\alpha]_D^{23}$ -189.6° (c 0.6 in EtOH), i.r. and mass spectra identical to those for the single isomer, δ (CCl_4) 2.1-0.9 (complex, singlets at δ 1.50, 1.42,

1.32, 1.25, and 1.18) (Found: C, 88.2; H, 11.8. Calc. for $C_{20}H_{32}$: C, 88.2; H, 11.8%).

A portion was recrystallized from hot ethanol to m.p. 82-87° and $[\alpha]_D^{23}$ -231.3° (c 0.6 in EtOH). A further portion was recrystallized from petroleum at -30° to m.p. 120-125°, $[\alpha]_D^{23}$ -230.8° (c 0.6 in EtOH), n.m.r. data identical to those for the single isomer.

(b) Di-t-butyl ketone triphenylphosphoranylidene-hydrazone (III) (2.08 g) and (-)-1,3,3-trimethylnorbornane--2-thione (VIII) (0.84 g) were treated (24 h) and worked up as in (a). Elution with petroleum gave the olefin (XVI) (isomeric mixture) (28% based on (VIII)), di-t-butyl thioketone (30%), and the starting thione (36%).

(c) (performed by Dr. T. G. Back) Di-t-butyl seleno-ketone (IV) (205 mg) and (-)-1,3,3-trimethylnorbornan-2--one triphenylphosphoranylidenehydrazone (VI) (426 mg) were heated for 19 h at 185° C in a sealed glass tube. Chromatography on silica gel (petroleum) furnished the binorbornylidene (XVI) as a mixture of isomers (76%), identical (i.r., n.m.r., and t.l.c.) with an authentic sample. Further elution (chloroform) afforded crude triphenylphosphine selenide (75%), which was recrystallized from chloroform-methanol; m.p. 188--189° (lit[8]. 184-185°). The presence of a large amount of 1,1-dimethyl-2-t-butylcyclopropane was also observed (n.m.r.). When the reaction was performed for 15 h at 120° C, starting material was detected (n.m.r. and t.l.c.).

Attempted Preparation of Selenobenzophenone

Benzophenone triphenylphosphoranylidenehydrazone[5] (X) (3.8g) and selenium (1.3 g) were treated under the conditions

used for trimethylnorbornane-2-selone. No distillate was observed, and the evolution of nitrogen ceased after 2 h. The cooled mixture was taken up in chloroform; the solution was filtered and concentrated, and the residue chromatographed on silica (200 g). Elution with 50% benzene-petroleum gave tetraphenylethylene (XII) (84%), m.p. 227° (lit[9]. 223--224°), identical to an authentic sample.

Attempted Preparation of Selenoadamantanone

Adamantanone triphenylphosphoranylidenehydrazone (XI) (1.7 g) and selenium (0.63 g) were treated under the conditions used for trimethylnorbornane-2-selone. No distillate was observed. After 4 h the mixture was cooled and taken up in chloroform; the solution was filtered and concentrated to an oil (0.32 g). Preparative t.l.c. (silica; petroleum) gave adamantylideneadamantane (XIII) (24%), m.p. 189-190° (lit[10]. 184-187°), m/e 268 (M^+).

Attempted Preparation of 1,3,3-Trimethylnorbornane-2--telluroketone (Tellurofenchone)

The triphenylphosphoranylidenehydrazone (VI) (2.13 g) and tellurium (1.28 g) were treated under the conditions used for trimethylnorbornane-2-selone (VII). After 4 h the cold trap contained almost pure 1,3,3-trimethyl-[2.2.1.$0^{2,6}$]--tricycloheptane (XIV) (50%), i.r. and n.m.r. identical to published spectra[33], m/e 136 (M^+).

B MISCELLANEOUS ATTEMPTED SYNTHESES OF SELENOKETONES

Diazodi-t-butylmethane (with Dr. T. G. Back)

Di-t-butyl ketone triphenylphosphoranylidenehydrazone (III) (8.00 g) was heated for 2 h at 160° C and 0.3 mmHg. Volatile material was continuously distilled into a solid CO_2-acetone trap to provide the pure diazo-compound (XXII) (100%) as an orange liquid with i.r. and n.m.r. spectra identical to those of an authentic sample[2].

Reactions of Diazodi-t-butylmethane (XXII)

(a) With Sodium Hydrogen Selenide

The diazo-compound (XXII) (1.54 g) was added dropwise to a solution of sodium hydrogen selenide[11] (1.03 g) in ethanol at room temperature. After the reaction had subsided (approx. 5 min) the solution was poured into water (100 ml) and extracted with light petrol (3x50 ml). The combined organic extracts were dried and concentrated to give bis(2,2--dimethyl-1-t-butylpropyl) diselenide (IX) (25%).

(b) With Hydrogen Selenide

A stream of argon carrying hydrogen selenide (generated by the action of water on aluminium triselenide) was passed into a solution of the diazc-compound (0.77 g) in ethanol. The solution immediately became paler, with some effervescence; after 0.5 h, no diazo-compound remained (i.r.). Removal of solvent gave the diselenide (IX) (14%).

(c) With Potassium Selenocyanate

The diazo-compound (50 mg) and potassium selenocyanate (144 mg) were heated at 90° C with stirring. After 3 h, n.m.r. indicated the presence of starting material (XXII) (80%),

di-t-butyl ketone azine (10%) and 2,3,4,4-tetramethyl--pent-1-ene (10%).

Reaction of Di-t-butyl Thioketone (V) with Methyl Fluorosulphonate

The thioketone (V) (154 mg) was stirred with methyl fluorosulphonate (0.5 ml) for 0.5 h at room temperature. Volatile materials were removed under vacuum, leaving a colourless solid.

(a) treatment with potassium selenocyanate:

The solid was suspended in dichloromethane (5 ml) and potassium selenocyanate (288 mg) was added. An immediate red precipitate appeared. The mixture was filtered and concentrated to a yellowish oil which contained no di-t--butyl selenoketone (n.m.r.).

(b) treatment with selenobenzoic acid:

The solid was taken up in pyridine (5 ml) and treated with selenobenzoic acid (0.5 g) at room temperature. No reaction was observed after 1 h. The solution was refluxed for 15 min, giving a red precipitate ; no di-t-butyl thioketone (V) or di-t-butyl selenoketone (IV) was produced.

(c) treatment with triphenylphosphine selenide:

The solid was taken up in THF (10 ml) and treated with triphenylphosphine selenide (0.68 g) at room temperature. No reaction was observed.

(d) treatment with water:

The solid was stirred with water (10 ml) for 16 h. The mixture was diluted with water (50 ml) and extracted with ether (2x50 ml), and the combined ethereal extracts were

dried and concentrated to an oil containing di-t-butyl ketone with other unidentified material (n.m.r.).

N-(2,2-Dimethyl-1-t-butylpropyl) formamide (XXXIV)

2,2,4,4-Tetramethylpentane-3-imine (XXI) (14 g) in dry ether (50 ml) was added to a suspension of lithium aluminium hydride (1.7 g) in dry ether (50 ml). The mixture was stirred at room temperature for 24 h and refluxed for 2 h. After cooling, water (1.7 ml), 15% sodium hydroxide (5 ml), and water (5 ml) were cautiously added in succession, and the mixture was filtered, concentrated, and distilled to give the amine (XXXIII) (83%), b.p. 79-81° at 40 mmHg, $\delta(CCl_4)$ 2.15 (1 H, s) and 1.00 (18 H, s).

Formic acid (60 ml) was added dropwise to acetic anhydride (60 ml) at 0° C, followed by 3-amino-2,2,4,4-tetramethylpentane (10.7 g). The solution was stirred for 0.5 h, heated on a steam-bath for a further 0.5 h, and concentrated under reduced pressure. The residual oil was taken up in dichloromethane (100 ml) and stirred vigorously with 10% sodium hydrogen carbonate (150 ml) for 3.5 h. The layers were separated, and the aqueous layer washed with dichloromethane (2x50 ml). The combined organic fractions were dried and concentrated to a solid, which was crystallized from ether at -30° C to give the formamide (XXXIV) (93%), m.p. 89-91°, ν_{max} (CCl_4) 3450, 1680, 1375, and 1250 cm^{-1}, $\delta(CCl_4)$ 8.16 (1 H, J 2 Hz, collapses to singlet upon D_2O exch.), 8.0 (1 H, m, exch. D_2O), 3.87 (2 H, d, J 11 Hz, collapses to singlet upon D_2O exch.), and 1.03 (18 H, s), m/e 171 (M^+) (Found: C, 70.15; H, 12.3; N, 8.2. $C_{10}H_{21}NO$ requires C, 70.1; H, 12.35; N, 8.2%).

3-Isocyano-2,2,4,4-tetramethylpentane (XXXV)

The foregoing formamide (XXXIV) (3.4 g) in pyridine (10 ml) and dichloromethane (25 ml) was treated with phosgene (4 g) in dichloromethane (20 ml) at 0°C. After stirring for 0.5 h and refluxing for 0.5 h, dichloromethane (50 ml) was added, and the mixture was washed with water (100 ml), N-hydrochloric acid (50 ml), and 10% sodium hydrogen carbonate (50 ml), dried ($MgSO_4$), and concentrated. Distillation afforded the isocyanide (XXXV) (72%), b.p. 60--62° at 5 mmHg, ν_{max} (CCl_4) 2120, 1470, 1400, and 1375 cm^{-1}, δ (CCl_4) 3.07 (1 H, t, J_{NH} 2 Hz) and 1.10 (18 H, s), m/e 138 (M - CH_3) (Found: C, 77.9; H, 12.3; N, 9.1. $C_{10}H_{19}N$ requires C, 78.4; H, 12.5; N, 9.1%).

3-Isoselenocyanato-2,2,4,4-tetramethylpentane (XXXVI)

3-Isocyano-2,2,4,4-tetramethylpentane (XXXV) (0.3 g) in THF at -80°C was treated with n-butyl lithium (2.4 mmol) in pentane under argon. After 5 min, selenium (0.4 g) was added with stirring, and the mixture allowed to warm to room temperature overnight. Removal of solvent, followed by preparative t.l.c. (silica; hexane) afforded di-n-butyl diselenide (54%) and the isoselenocyanate (XXXVI) (75%), m.p. 45°, ν_{max} (CCl_4) 2140 vs, 1400, and 1275 cm^{-1}, δ (CCl_4) 3.30 (1 H, s) and 1.15 (18 H, s), λ_{max} (cyclohexane) 250 nm (ε 9400), m/e 233 (M^+) (Found: C, 51.9; H, 8.1; N, 6.0. $C_{10}H_{19}NSe$ requires C, 51.7; H, 8.25; N, 6.0%). The use of lithium di-isopropylamide instead of n-butyl lithium gave a 72% yield of the isoselenocyanate. Addition of the base to the isonitrile, followed by quenching with D_2O (after

2-4 h) and recovery of starting material indicated no incorporation of deuterium at the α-position (n.m.r., mass spectrum).

C CYCLOHEXADIENONES

Phosphorous Pentaselenide[12]

Red phosphorus (0.34 g) and selenium (1.98 g) were thoroughly mixed in a mortar under an inert atmosphere, sealed in a Carius tube under vacuum, heated at 490° for 15 h and allowed to cool to room temperature over 8 h. The tube was opened cautiously under an inert atmosphere, and the glassy black solid was ground to a purplish powder which was used without further purification.

6-Benzyl-4-t-butyl-2,6-dimethyl-2,4-cyclohexadienone (XL)[13]

The reaction of sodium 4-t-butyl-2,6-dimethylphenolate with benzyl chloride in toluene gave, after chromatography, the dienone (XL) (45%), b.p. 112-120° at 0.25 mmHg (lit.[13] b.p. 101-104° at 0.2-0.4 mmHg).

Reaction of Dienone (XL) with Phosphorous Pentasulphide

The dienone (XL) (0.54 g) in dry benzene (5 ml) was stirred with phosphorous pentasulphide (1 g) at room temperature in the dark. After 2 h, the mixture was filtered and extracted with Claisen alkali[14]. Concentration of the benzene fraction gave an intractable oil. Acidification of the alkaline extract, followed by extraction with dichloromethane, concentration and crystallization of the organic extract gave 4-benzyl-2,6-dimethylphenol (XLIII)

(49%), m.p. 65-66°, ν_{max} (CCl_4) 3620, 1605, 1490, 1195, and 1150 cm^{-1}, δ (CCl_4) 7.05 (5 H, s), 6.64 (2 H, s), 4.05 (1 H, broad s, exch. D_2O), 3.74 (2 H, s) and 2.14 (6 H, s), m/e 212 (M^+) (Found: C, 84.72; H, 7.68. $C_{15}H_{16}O$ requires C, 84.87; H, 7.59%).

Reaction of Dienone (XL) with Phosphorous Pentaselenide

The dienone (XL) (0.54 g) in dry benzene (5 ml) was stirred with phosphorous pentaselenide (1 g) at 60° in the dark for 24 h, followed by reflux for a further 4 h, after which starting material was still present. Preparative t.l.c. of the organic residue afforded dibenzyl diselenide (15%), m.p. 85-90° (lit.[11] m.p. 92-94°) and bis(4-t-butyl--2,6-dimethylphenyl) diselenide (XLI) (16%), m.p. 129-130°, δ (CCl_4) 6.90 (4 H, s), 2.22 (12 H, s), and 1.28 (18 H, s), m/e 482, 480 (M^+) and 241, 239 ($\frac{1}{2}M^+$) (Found: C, 60.66; H, 7.03. $C_{24}H_{34}Se$ requires C, 60.00; H, 7.13%).

Reaction of Dienone (XL) with Aqueous Acid

The dienone (XL) (54 mg) was dissolved in N-sulphuric acid (in 10% aqueous methanol) (10 ml) and allowed to stand for 48 h. The solution was poured into ether (50 ml) and extracted with Claisen alkali (50 ml). The alkaline extract was acidified with concentrated hydrochloric acid, and extracted with dichloromethane (2x50 ml). The combined organic extracts were dried and concentrated to give 4-t-butyl-2,6-dimethylphenol (XLIV) (20%).

4-t-Butyl-2,6-dimethyl-6-n-propylcyclohexadien-2-one (LVI)

The sodium salt of 4-t-butyl-2,6-dimethylphenol was treated with allyl bromide by the method of Miller[15] to give a mixture of 6-allyl-4-t-butyl-2,6-dimethylcyclohexadien-2-one and 4-t-butyl-2,6-dimethylphenyl allyl ether. The oil (2.1 g) was taken up in light petroleum (20 ml) and stirred with 10% Pd/C at room temperature under 1 atm. in the dark. After absorption of 10 mmol H_2, the mixture was filtered, concentrated and chromatographed (silica, 80% petrol/$CHCl_3$) to give a clear yellow oil contaminated with starting material. Washing with Claisen alkali gave pure dienone (LVI) (2%), ν_{max} ($CHCl_3$) 1660, 1645, 1585, 1455, and 1370 cm^{-1}, δ (CCl_4) 6.87 (1 H, m), 5.80 (1 H, m), 1.84 (3 H, s), 1.3-0.7 (19 H, complex, sharp singlet at δ 1.15), λ_{max} (cyclohexane) 310 nm (ε 7700), m/e 220 (M^+) and 205 (M - CH_3) (Found: C, 81.75; H, 11.1. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%).

Reaction of Dienone (LVI) with Phosphorous Pentasulphide

The dienone (LVI) (110 mg), phosphorous pentasulphide (550 mg) and sodium hydrogen carbonate (250 mg) were stirred in benzene in the dark at room temperature for 24 h. The u.v. band at 310 nm disappeared and was replaced by a broad band of lower ε at 270-280 nm. The complex mixture (t.l.c.) was not identified.

1-t-Butyl-3,5-dimethylbenzene[16]

1,3-Dimethylbenzene and t-butyl chloride reacted in the presence of aluminium trichloride to give 1-t-butyl-

-3,5-dimethylbenzene (86%), b.p. 83-89° at 12 mmHg (lit.[16] b.p. 77-78° at 8 mmHg).

1-Bromo-4-t-butyl-2,6-dimethylbenzene[17]

1-t-Butyl-3,5-dimethylbenzene reacted with bromine to give the title compound (79%), m.p. 35-45° (lit.[17] m.p. 48-50°).

Bis(4-t-butyl-2,6-dimethylphenyl) disulphide (LIX)

1-Bromo-4-t-butyl-2,6-dimethylbenzene (2.4 g) and ethyl bromide (2.2 g) in dry ether (40 ml) were added to magnesium ribbon (0.7 g) under ether (10 ml) and stirred under gentle reflux for 1 h. Sulphur (0.96 g) was added and refluxing continued for a further hour. The mixture was poured onto ice (100 ml) and N-hydrochloric acid (100 ml) was added. The layers were separated and the aqueous layer washed with ether (2x100 ml). The combined ethereal layers were dried and concentrated to a yellow oil (1.8 g). Chromatography (alumina, light petrol) gave starting material (6%), followed by the disulphide (LIX) (55%), m.p. 127-128° C (crystallised from ethanol), δ (CCl_4) 6.87 (4 H, s), 2.17 (12 H, s) and 1.27 (18 H, s), m/e 386 (M^+) and 193 ($M - C_{12}H_{17}S$) (Found: C, 74.66; H, 8.89; S, 16.64. $C_{24}H_{34}S_2$ requires C, 74.56; H, 8.86; S, 16.58%).

Phenylazotriphenylmethane (LVIII)

The reaction of phenylhydrazine and α-chlorotriphenylmethane gave 1-phenyl-2-triphenylmethylhydrazine (36%), m.p. 130-133°C (lit.[18] m.p. 134-135°C). Oxidation of the hydrazine with hydrogen peroxide gave (LVIII) (54%), m.p. 108-110°C (lit.[18] m.p. 110-112°C).

Reaction of Disulphide (LIX) with Phenylazotriphenylmethane (LVIII)

The disulphide (LIX) (0.39 g) and the azo-compound (LVIII) (0.70 g) were refluxed in petrol (10 ml) under nitrogen for 24 h. Preparative t.l.c. (silica, petrol) of the reaction mixture gave starting disulphide (LIX) (42%), 4-t-butyl-2,6-dimethylphenyl phenyl sulphide (LXa) (recrystallised from methanol) (18%), m.p. 66-66.5°C, $\delta(CCl_4)$ 7.3-6.7 (7 H, complex), 2.40 (6 H, s) and 1.31 (9 H, s), m/e 270 (M^+) and 255 ($M - CH_3$) (Found: C, 79.77; H, 8.03; S, 12.09. $C_{18}H_{22}S$ requires C, 79.94; H, 8.20; S, 11.86%) and 4-t-butyl-2,6-dimethylphenyl triphenylmethyl sulphide (LXb) (recrystallised from ether at -30°C) (18%), m.p. 146-147°C, $\delta(CCl_4)$ 7.15 (15 H, broad s), 6.81 (2 H, s), 1.90 (6 H, s) and 1.25 (9 H, s), m/e 243 ($M - C_{12}H_{17}S$) and 193 ($M - C_{19}H_{15}$) (Found: C, 85.23; H, 7.24; S, 7.24. $C_{31}H_{32}S$ requires C, 85.27; H, 7.39; S, 7.34%).

Attempted Preparation of α-Selenosantonin

α-Santonin (XXXIXa) (61 mg) in benzene (1.5 ml) was stirred with phosphorous pentaselenide (238 mg) at room temperature. After 12 h, no reaction had occurred. The

mixture was refluxed 4 h, with no change in the t.l.c.

The reaction was similarly unsuccessful in pyridine. In dimethylacetamide and acetonitrile, the only seleniferous products were N,N-dimethylselenoacetamide and selenoacetamide, respectively. Aluminium triselenide was ineffective.

D OXIDATIONS OF DISULPHIDES AND DISELENIDES

The trivial name Chloramine-T, for N-chloro-N-sodio--4-methylbenzenesulphonamide, is used throughout.

Reaction of Diphenyl Disulphide (LXI) with Chloramine-T (LXII)

Diphenyl disulphide (218 mg) and anhydrous Chloramine--T (456 mg) were stirred in dry acetone (5 ml) for 2 h. The solvent was removed under reduced pressure, and the residue was taken up in dichloromethane (20 ml) and filtered through Celite. Ether (20 ml) was added, and the solution was concentrated to give a pale yellow crystalline product (LXIII) $(PhSSPh)(TsN)_2$ (66%), m.p. 125-130° d, ν_{max} (Nujol) 2990-2890, 1470, 1390, 1175, 1155, 1100, 1020, 900 and 680 cm^{-1}, δ ($CDCl_3$) 7.9-6.9 (18 H, complex) and 2.45 (6 H, s), m/e 387 (M - $C_7H_7NO_2S$) (Found: C, 55.82; H, 4.70; N, 4.99. $C_{26}H_{24}N_2O_4S_4$ requires C, 56.09; H, 4.35; N, 5.03%).

Repeated crystallisation from dichloromethane/ether gave a somewhat paler yellow compound, m.p. 121-124° d, with identical i.r., n.m.r. and m.s. (Found: C, 56.0; H, 4.3;

N, 4.95; S, 22.7. $C_{26}H_{24}N_2O_4S_4$ requires C, 56.1; H, 4.35; N, 5.05; S, 23.05%).

Reactions of the Adduct (LXIII)

(a) With Sodium Borohydride

A suspension of the adduct (LXIII) (278 mg) in ethanol (5 ml) was treated with sodium borohydride (20 mg) and stirred for 15 min. The clear solution was concentrated to an oil, taken up in dichloromethane (40 ml) and filtered through Celite. Ether (20 ml) was added, and the solution was concentrated to give S-phenyl-S-(N-sodio-4-methylbenzenesulphonamido)-N-(4-methylbenzenesulphonyl) sulphimide (LXIV) (88%), m.p. 228-230° (lit.[19] m.p. 226°), δ (d_6-Me_2CO) 7.8-7.0 (13 H, complex) and 2.35 (9 H, s). The mother liquor was concentrated and crystallised from methanol to give diphenyl disulphide (LXI) (77%).

(b) With Anhydrous Hydrogen Chloride

A suspension of the adduct (LXIII) (557 mg) in dry benzene was treated with a stream of dry hydrogen chloride for 15 min. The starting material dissolved almost immediately, giving a bright yellow solution. Removal of benzene and crystallisation from chloroform gave 4-methylbenzenesulphonamide (67%).

(c) With Triethylamine

A solution of the adduct (LXIII) (278 mg) in dichloromethane (5 ml) was treated with triethylamine (100 mg). T.l.c. (silica; benzene) showed immediate disappearance of the starting material (R_f = 0 - 4), and the appearance of diphenyl disulphide (R_f > 9) and a heavy spot at the

origin. The starting material is not regenerated upon acidification with glacial acetic acid.

The adduct showed no reaction with absolute ethanol or with anhydrous sodium carbonate under these conditions.

(d) In Refluxing Benzene

The adduct (LXIII) (278 mg) was refluxed in dry benzene for 4 h. The dark orange solution was concentrated to a gum; preparative t.l.c. (silica; benzene) showed a complex mixture, from which was isolated N,N-bis(phenylthio)--4-methylbenzenesulphonamide (15%), m.p. 97-100° (lit.[20] m.p. 97.5-98°), δ ($CDCl_3$) 8.0-7.0 (14 H, complex) and 2.37 (3 H, s), m/e 387 (M^+).

Oxidation of Diphenyl Disulphide (LXI) with 3-Chloroperbenzoic Acid (cf. reference 21)

Diphenyl disulphide (436 mg) in dichloromethane (5 ml) was treated with 3-chloroperbenzoic acid (89%) (850 mg) in dichloromethane (15 ml). The starting material was immediately consumed (t.l.c.). The mixture was washed with 5% sodium carbonate (3x50 ml), dried, concentrated and chromatographed (silica; benzene) to afford S-phenyl benzenethiosulphonate (LXVII) (46%), m.p. 42° (lit.[21] m.p. 45-46°), and S-phenyl benzenethiosulphinate (13%), m.p. 66-67° (lit.[21] m.p. 68.5-70°).

Reaction of S-Phenyl Benzenethiosulphonate (LXVII) with Triethylamine

The thiolsulphonate (25 mg) in dichloromethane (1 ml) was treated with triethylamine (1 drop). After 24 h the mixture was unchanged (t.l.c.).

Benzenesulphenyl Chloride (LXVI)

A solution of diphenyl disulphide (5.45 g) in carbon tetrachloride (50 ml) with a few drops of triethylamine was cooled in an ice bath and treated dropwise with sulphuryl chloride (3.4 g). After 0.5 h the solvent was removed under reduced pressure, and the residue was distilled to give benzenesulphenyl chloride (74%) as a red oil, b.p. 38-40° at 0.6 mmHg (lit.[22] b.p. 58-60° at 3 mmHg).

Attempted Preparation of the Adduct (LXIII)

Benzenesulphenyl chloride (72 mg) in acetone (5 ml) was added dropwise to a solution of S-phenyl-S-(N-sodio--4-methylbenzenesulphonamido)-N-(4-methylbenzenesulphonyl) sulphimide (LXIV) (235 mg) in acetone (5 ml) with immediate disappearance of the orange colour. After 2 h, the acetone was removed under reduced pressure, and the mixture was taken up in dichloromethane (20 ml) and filtered through Celite. Ether (20 ml) was added, and the mixture was crystallised to give 4-methylbenzenesulphonamide (>95%).

Bis(α-diphenylmethyl) Disulphide (LXXIc)[24]

The reaction of diazodiphenylmethane with hydrogen sulphide gave the disulphide (LXXIc) (18%), m.p. 150--152° (lit.[25] m.p. 151-152°).

Oxidation of Bis(α-diphenylmethyl) Disulphide (LXXIc) with Chloramine-T (LXII) in Acetone

The same procedure was employed as for diphenyl disulphide. The reaction produced a gum, of which the only identifiable component was N-(4-methylbenzene-sulphonyl)-α-aminodiphenylmethane (LXXII) (7%), m.p. 153-154° (lit.[23] m.p. 155-156°), separated by preparative t.l.c. (silica; benzene).

In the reactions with dibenzyl disulphide and di-t-butyl disulphide, the products could not be crystallised, and showed a complex mixture on t.l.c. (silica; benzene).

Bis(α-diphenylmethyl) Diselenide (LXXIII)

Sodium selenide was prepared in ethanol from selenium (6 g) and sodium borohydride (2 g) under nitrogen[11]. After removal of ethanol, chlorodiphenylmethane (5.1 g) in 25% aqueous THF (50 ml) was added, and stirred for 48 h. The mixture was poured into water (100 ml) and extracted with dichloromethane (2x100 ml); the combined organic extracts were dried, concentrated and crystallised from ethanol to give the diselenide (LXXIII) (54%), m.p. 120-124° (lit.[26] m.p. 120-123°).

Dibenzyl Diselenide (LXXVII)[11]

The reaction of benzyl chloride with sodium hydrogen selenide in ethanol gave dibenzyl diselenide (LXXVII) (67%), m.p. 88-91° (lit.[11] m.p. 92-94°).

Oxidations of Bis(α-diphenylmethyl) Diselenide (LXXIII)

(a) By Photolysis

The diselenide (246 mg) in dry acetonitrile (50 ml), exposed to the atmosphere, was irradiated with a 40 W tungsten lamp at room temperature for 4 days. Considerable selenium deposition was observed. Removal of solvent under reduced pressure, followed by preparative t.l.c. (silica; 10% benzene/petrol) gave the starting material (32%) and benzophenone (22%), identified by i.r., n.m.r. and t.l.c..

(b) With 3-Chloroperbenzoic Acid

The diselenide (246 mg) in chloroform (10 ml) at 4^0 was treated dropwise with 3-chloroperbenzoic acid (89%) (86 mg) in chloroform (5 ml) over 1 h. The solution turned pale green, then deep orange. After stirring for a further 1 h, the solution was concentrated under reduced pressure ($T < 30^0$). Preparative t.l.c. as before gave starting material (30%) and benzophenone (20%).

Reactions of Diselenides with Chloramine-T

(a) Diphenyl Diselenide (LXXIX)

The diselenide (312 mg) in dichloromethane (5 ml) was treated with anhydrous Chloramine-T (456 mg) in portions; vigorous frothing followed each addition. The mixture was concentrated under reduced pressure, and preparative t.l.c. (silica; benzene) gave 4-methylbenzenesulphonyl chloride (LXXXV) (8% based on Chloramine-T), m.p. 66-67^0, mixed m.p. 65-66^0; bis(4-methylphenyl) disulphone (LXXXVI) (<1%), m.p. 220-222^0 (lit.,[27] m.p. 222^0), m/e 310 (M^+); and

Se-phenyl-4-methylbenzeneselenosulphonate (LXXXVII) (37%), m.p. 77-79°, δ ($CDCl_3$) 7.6-7.0 (9 H, complex) and 2.42 (3 H, s), m/e 312 (M^+) (Found: C, 49.9; H, 4.0. $C_{13}H_{12}O_2SSe$ requires C, 50.15; H, 3.9%).

(b) Dibenzyl Diselenide (LXXVII)

The same procedure was followed as in (a); the evolution of gas was somewhat slower. Column chromatography (silica; dichloromethane) gave 4-methylbenzenesulphonyl chloride (10%) and bis(4-methylphenyl) disulphone (5%), together with a seleniferous oil.

(c) Bis(α-diphenylmethyl) Diselenide (LXXIII)

The diselenide (246 mg) in dichloromethane (5 ml) at room temperature was treated with anhydrous Chloramine-T (114 mg). No evolution of gas was observed. After stirring for 4 h, t.l.c. (silica; chloroform) showed the appearance of at least six new components. The only isolable product by preparative t.l.c. was N-(4-methylbenzenesulphonyl)-α--aminodiphenylmethane (LXXII) (12%), m.p. 153-154° (lit.,[23] m.p. 155-156°).

Reaction of Diphenyl Diselenide (LXXIX) with Chloramine-T (LXII) in the Presence of Cyclohexene (LXIX)

(a) Chloramine-T (LXII) (912 mg) was added to a solution of the diselenide (312 mg) in redistilled cyclohexene (10 ml). After 3 h stirring, no reaction was observed (t.l.c.). Dichloromethane (3 ml) was added, whereupon an immediate reaction occurred, with complete consumption of the diselenide and the appearance of a seleniferous spot at the t.l.c. origin (silica; benzene). The mixture was filtered

through Celite and concentrated under reduced pressure to give a greenish-yellow foam. Treatment with ethanol (30 ml) and sodium borohydride (156 mg) for 1 h gave a pale yellow suspension which was poured into water (100 ml) and extracted with dichloromethane (3x50 ml). The combined organic extracts were dried, concentrated and separated by preparative t.l.c. (silica; benzene) to give trans-2--(4-methylbenzenesulphonamido)-1-phenylselenocyclohexane (XCVII) (52% based on diselenide), m.p. 133-134°, ν_{max} ($CHCl_3$) 3360, 3250, 2910, 1600, 1400, 1330, 1155, 1090 and 890 cm^{-1}, δ ($CDCl_3$) 8.0-7.1 (9 H, complex), 5.5-5.3 (1 H, m, exch. D_2O), 3.3-2.9 (2 H, m), 2.41 (3 H, s) and 2.4-1.1 (8 H, complex), m/e 409 (M^+) and 252 (M - C_6H_5Se) (Found: C, 55.75; H, 5.7; N, 3.15. $C_{19}H_{23}NO_2SSe$ requires C, 55.9; H, 5.7; N, 3.45%).

(b) At different temperatures

The diselenide (312 mg) and cyclohexene (82 mg) in dry acetonitrile (5 ml) were cooled to the desired temperature. Chloramine-T (456 mg) was added, and the mixture was stirred for 1 h at the bath temperature before warming to room temperature over 2-4 h. Ethanol (5 ml) and sodium borohydride (80 mg) were added, and stirring continued for 15 min. The mixture was poured into dilute hydrochloric acid (50 ml) and extracted with dichloromethane (2x50 ml); the combined organic extracts were dried, concentrated and chromatographed on a column (silica; dichloromethane) to afford the aminoselenide (XCVII), m.p. (from) 131-135°, recrystallised from ethanol.

Table 3

Effect of the Temperature on the Reaction of Diphenyl Diselenide/Chloramine-T/Cyclohexene

Temperature (°C)	Yield (%)	Remarks
25	18	
0-5	30-35	
-5	40	Argon atmosphere; tenfold scale; cis-isomer separated *
-42	27	Nitrogen atmosphere

* The crude aminoselenide from the column was extracted with hot petrol (3x50 ml); preparative t.l.c. (silica; benzene) of the extracts afforded cis-2-(4-methylbenzenesulphonamido)-1-phenylselenocyclohexane (0.85%), m.p. 110--113°, ν_{max} (Nujol) 3370, 1600, 1385, 1320-1300, 1170, 1090, 1070 and 745 cm^{-1}, δ ($CDCl_3$) 8.0-7.1 (9 H, complex), 5.4--5.2 (1 H, m, exch. D_2O), 3.5-3.2 (2 H, m), 2.37 (3 H, s) and 2.3-1.1 (8 H, complex), m/e 409 (M^+) and 252 (M - C_6H_5Se) (Found: C, 55.65; H, 5.8; N, 3.25. $C_{19}H_{23}NO_2SSe$ requires C, 55.9; H, 5.7; N, 3.45%).

(c) With varying amounts of Chloramine-T (LXII)

The diselenide (312 mg) and cyclohexene (82 mg) in acetonitrile (5 ml) were cooled in an ice bath; Chloramine-T was added, and the mixture was allowed to warm to room temperature with stirring over 2 h before reduction and work up as in (b).

Table 4

Effect of Chloramine-T on Product Formation

Chloramine-T (mole equivalents)	Yield (%)
1	15
2	30
4	20

(d) With varying amounts of Diselenide (LXXIX)

Procedure (c) was employed, using 2 mmoles of Chloramine-T.

Table 5

Effect of Diselenide on Product Formation

Diphenyl Diselenide (mole equivalents)	Yield (%)
1	30
2	45
5	39

(e) Under oxygen

Procedure (c) was employed, using the molar ratio 1:2:10 for diphenyl diselenide:Chloramine-T:cyclohexene. The reaction was performed under a slow stream of oxygen. The aminoselenide (XCVII) was obtained in 55% yield (based on diselenide).

(f) With Chloramine-T trihydrate

Procedure (c) was employed, using a molar ratio of 1:2:1 for diphenyl diselenide:Chloramine-T trihydrate: cyclohexene. The only seleniferous product was diphenyl diselenide (>90%).

Diphenyl diselenide was routinely recovered (30-70%) from reactions (a) to (f) by column chromatography.

Reactions of Trans-2-phenylseleno-(4-methylbenzenesulphonamido) cyclohexane (XCVII)

(a) With Hydrogen Peroxide[28]

The amidoselenide (XCVII) (204 mg) in THF (15 ml) was treated with 30% hydrogen peroxide (1.2 g). T.l.c. (silica; benzene) showed immediate disappearance of starting material. Magnesium sulphate (5 g) was added, and the mixture was stirred for 16 h, filtered, poured into 10% sodium thiosulphate (50 ml) and extracted with dichloromethane (2x50 ml). The combined organic extracts were dried, concentrated and crystallised to afford 4-methylbenzenesulphonamide (56%). The mother liquor was concentrated to an oil (50 mg) containing further sulphonamide and a component with ν_{max} ($CHCl_3$) 1770 cm^{-1}, δ ($CDCl_3$) 4.37 (t, J 7 Hz). Since the desired elimination reaction had evidently not occurred, the reaction was abandoned at this stage.

(b) With Benzoyl Peroxide[29]/Acetic Anhydride

The amidoselenide (XCVII) (204 mg) in dichloromethane (10 ml) was treated with a dry solution of benzoyl peroxide (360 mg) in dichloromethane (5 ml). The starting material was immediately consumed (t.l.c.). The solution was washed

with 10% sodium thiosulphate (50 ml), dried, concentrated to an oil, and refluxed with acetic anhydride (15 ml) for 4 h. Water (50 ml) was added, and the solution cooled to room temperature over 1 h with stirring. After extraction with dichloromethane (2x50 ml), the combined organic extracts were dried and concentrated to an oil (0.2 g). Preparative t.l.c. (silica; benzene) gave 2-(4-methylbenzenesulphonamido)-cyclohexanone (29%), m.p. 137-138° (lit.[30] m.p. 136-137°), ν_{max} ($CHCl_3$) 3300, 2910-2880, 1720, 1605, 1355 and 1160 cm^{-1}, δ ($CDCl_3$) 7.70 (2 H, d, J 8 Hz), 7.27 (2 H, d, J 8 Hz), 6.0-5.7 (1 H, m, exch. D_2O), 4.0-3.5 (1 H, m), 2.44 (3 H, s) and 2.4-1.2 (8 H, complex), m/e 287 (M^+) (Found: C, 58.49; H, 6.32; N, 5.24. $C_{13}H_{17}NO_3S$ requires C, 58.41; H, 6.41; N, 5.24%).

(c) With Raney Nickel[31]

The amidoselenide (XCVII) (204 mg) in ethanol (10 ml) was stirred with Raney nickel (1 g) for 16 h at room temperature. The mixture was filtered through Celite and the solvent was carefully distilled and analysed for benzene (82%) by g.l.c. (Carbowax, 30°). The residue was crystallised from ethanol to give N-cyclohexyl-4-methylbenzenesulphonamide (CIII) (76%), m.p. 85° (lit.[32] m.p. 86-87°), identical (mixed m.p., t.l.c. (silica; benzene)) to authentic material.

(d) With Chloramine-T

The amidoselenide (XCVII) (204 mg) in dry acetone (10 ml) was treated with anhydrous Chloramine-T (250 mg). The starting material was immediately consumed (t.l.c.). Removal of solvent gave an oily residue, from which only

4-methylbenzenesulphonamide (97 mg) could be isolated by crystallisation.

(e) With Lithium Aluminium Hydride

The amidoselenide (XCVII) (204 mg) in dry ether (10 ml) was refluxed 24 h with lithium aluminium hydride (40 mg). T.l.c. (silica; benzene) indicated that no reaction had occurred.

(f) With Aqueous Acid

The amidoselenide (XCVII) (204 mg) was refluxed in a mixture of N-sulphuric acid (10 ml) and ethanol (2 ml) for 24 h. T.l.c. (silica; benzene) indicated that no reaction had occurred.

Reaction of Diphenyl Diselenide with Chloramine-T in the Presence of Other Olefins

Procedure (c) for cyclohexene was employed, using a molar ratio of 1:2:1 for alkene:Chloramine-T:diphenyl diselenide.

(i) Norbornene (XCVI)

After the usual reduction and work up, preparative t.l.c. (silica; benzene) gave two isomeric phenylselenonorbornyl 4-methylphenyl sulphones (CI) : A (22%), m.p. 104-107°, ν_{max} (Nujol) 1385, 1300, 1150, 1095, 750, 720 and 700 cm^{-1}, m/e 406 (M^+), 250 ($M - C_7H_8O_2S$) and 222 ($M - C_9H_{12}O_2S$) (Found: C, 59.33; H, 5.63. $C_{19}H_{22}O_2SSe$ requires C, 59.25; H, 5.47%). B (3%), m.p. 153-154°, ν_{max} (Nujol) 1385, 1300, 1155, 1150, 1090, 740, 730 and 695 cm^{-1}, m/e 406 (M^+) and 249 ($M - C_6H_5Se$).

(ii) 1-Octene (XCIII)

After the usual reduction and work up, column chromatography (silica; dichloromethane) gave a (4-methylbenzenesulphonamido)-phenylselenooctane as a clear oil (55%), δ ($CDCl_3$) 7.9-7.0 (9 H, complex), 5.3--4.9 (1 H, m), 3.3-2.7 (3 H, complex), 2.42 (3 H, s) and 2.0-0.7 (13 H, complex), m/e 439 (M^+).

The oil was taken up in ethanol (15 ml) and water (10 ml) and treated under nitrogen with nickel(II) chloride hexahydrate (2.38 g), boric acid (6.2 g) and sodium borohydride (0.8 g)[34]. After the reaction had subsided, the mixture was refluxed for 3 h, cooled, and filtered through Celite. The filter and the aqueous filtrate were washed with ether (100 ml and 2x100 ml, respectively); the combined ethereal fractions were washed with water (100 ml), dried and concentrated to give N-(1-octyl)-4-methylbenzenesulphonamide (XCVIII) (45%), m.p. 49-53°, mixed m.p. 47-53° (lit.,[35] m.p. 56°), identical (i.r., n.m.r.) to an authentic sample.

(iii) Acrylonitrile

After the usual reduction and work up, column chromatography (silica; benzene) gave 3-phenylseleno-propionitrile (IC) (15%), identical (i.r., n.m.r.) to an authentic sample.

(iv) Styrene

After the usual reduction and work up, column chromatography (silica; dichloromethane) gave 1-(4-methyl-benzenesulphonamido)-1-phenyl-2-phenylselenoethane (C) (62%), m.p. 90-92° (crystallised from ethanol), ν_{max}

(Nujol) 3270, 1330, 1165, 795 and 710 cm^{-1}, δ ($CDCl_3$) 7.7-6.9 (14 H, complex), 5.90 (1 H, d, J 6 Hz, exch. D_2O), 4.40 (1 H, q, J 6 Hz, collapses to triplet upon D_2O exch.), 3.15 (2 H, broadened d, J 6 Hz) and 2.25 (3 H, s), m/e 430 (M^+) (Found: C, 58.37; H, 4.94; N, 3.23. $C_{21}H_{21}NO_2SSe$ requires C, 58.60; H, 4.92; N, 3.25%).

The amidoselenide (C) (107 mg) reacted with Raney nickel in ethanol to give 1-(4-methylbenzenesulphonamido)--1-phenylethane (42%), m.p. 79-80° (lit.,[36] m.p. 81-82°).

(v) α-Pinene, Cholesteryl Benzoate and trans-1,2-Diphenylethylene

In the above cases, no seleniferous components were observed in the reaction product, apart from diphenyl diselenide.

Reaction of Dibenzyl Diselenide (LXXVII) with Chloramine-T (LXII) in the Presence of Cyclohexene

Procedure (c) for diphenyl diselenide/cyclohexene was employed, using a molar ratio of 1:2:1 for cyclohexene: Chloramine-T: dibenzyl diselenide. Reduction and work up in the usual way, followed by column chromatography (silica, dichloromethane) gave 1-benzylseleno-2-(4-methylbenzenesulphonamido)-cyclohexane as a yellowish oil (46%), m/e 423 (M^+). The oil was taken up in ethanol (15 ml) and water (10 ml) and treated under nitrogen with nickel(II) chloride hexahydrate (2.38 g), boric acid (6.2 g) and sodium borohydride (0.8 g). After the reaction had subsided, the mixture was refluxed for 3 h, cooled and worked up as in the case of 1-octene. The product was

N-cyclohexyl-4-methylbenzenesulphonamide (CIII) (35% overall), m.p. 81-86° (crystallised from petrol).

Preparation of N-substituted-4-methylbenzenesulphonamides

The following sulphonamides were prepared by reaction of the appropriate amine with equimolar amounts of 4-methylbenzenesulphonyl chloride and triethylamine in ether:
N-cyclohexyl-4-methylbenzenesulphonamide (CIII) (51%), m.p. 85-86° (lit.[32] m.p. 86-87°).
N-(1-octyl)-4-methylbenzenesulphonamide (XCVIII) (63%), m.p. 53-54° (lit.[35] m.p. 56°).

3-Phenylselenopropionitrile (IC)

Acrylonitrile (XCIV) (212 mg) and diphenyl diselenide (624 mg) in ethanol (10 ml) were treated under nitrogen with sodium borohydride (80 ml). After stirring for 4 h, the mixture was poured into dilute hydrochloric acid and extracted into dichloromethane (2x50 ml). The combined organic extracts were dried, concentrated, chromatographed (silica; benzene) and distilled to give 3-phenylselenopropionitrile (IC)(25%), b.p. 118-120° at 0.2 mmHg, ν_{max} (film) 3030, 2920, 2250, 1575, 1475, 1435, 1260, 1020, 735 and 690 cm^{-1}, δ ($CDCl_3$) 7.8-7.2 (5 H, complex) and 3.3-2.5 (4 H, complex symmetrical A_2B_2 system), m/e 211 (M^+) (Found: C, 51.34; H, 4.59; N, 6.52. C_9H_9NSe requires C, 51.44; H, 4.32; N, 6.67%).

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