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Study of resonance effects in allenic and related systems

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STUDY OF RESONANCE EFFECTS IN ALLENIC AND RELATED SYSTEMS

by

Robert Andrew Steinkamp - 1940 -

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The Final Ph.D. Thesis Examination of Robert Andrew Steinkamp

candidate for the degree of Doctor of Philosophy in

*** Chemistry ***

has been conducted in accordance with the regulations of the Graduate School. The undersigned, appointed to conduct this examination, agree that the candidate has successfully passed this examination.

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This dissertation is dedicated to
my son, Richard Andrew Steinkamp

ABSTRACT

In order to investigate the possibility of resonance effects through a non-coplanar substituted acetylene, synthesis of bis-(2,5,8-trimethyl-1-naphthyl)-acetylene was attempted. Condensation of acetylene with 2,5,8-trimethyl-1-tetralone to yield an acetylenic glycol followed by dehydration and dehydrogenation was expected to yield the desired non-coplanar acetylene. Comparison of its ultraviolet spectrum with that of di-1-naphthyl-acetylene would have suggested the true nature of the acetylene pi cloud. The acetylene condensation was unsuccessful, however.

Substituted allenes, which contain one sp hybridized carbon atom, were then successfully synthesized for a similar analysis of potential resonance effects. A series of para-substituted 4-phenyl-2-methylbutadienoic acids were synthesized and their pKa's determined in water solution. The pKa's of the para-methyl, para-chloro and para-hydrogen substituted allenic acids were identical, indicating that resonance effects are not transmitted through the allene function.

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INTRODUCTION

Many modern organic chemistry text books, Condon and Meislich[1] for example, state that the pi electron cloud of acetylene is cylindrically symmetrical. If this is true, then unsaturated groups bonded to both ends of a carbon-carbon triple bond might exhibit resonance effects regardless of their orientation with respect to each other. In other words even if the phenyl groups of diphenylacetylene (tolane) are forced to lie in perpendicular planes, they could still have continuous pi cloud overlap between them and perhaps exhibit resonance effects through the ethyne link.

Although tolane has been shown to be planar in the crystalline state,[2] a simple molecular orbital calculation (see Appendix I) indicates that the pi electron energy difference between the planar and non-planar conformations of tolane is very small, only 0.11β. Such a small energy difference suggests that little resonance energy would be lost upon rotation from a planar to a non-coplanar conformation. One therefore might expect to find an observable resonance effect through the ethyne link even in a non-coplanar tolane.

If the cylindrical symmetry attributed to the pi cloud of acetylene is true, then by analogy, circular symmetry of the pi cloud about the sp carbon in an allene would be expected. Due to the geometry of allene, 1,3-substituents

lie in perpendicular planes. Therefore an analysis of any electronic interactions between 1,3-unsaturated groups on an allene should indicate the true nature of the pi cloud about the sp hybridized carbon atom.

Based on the ideas stated above, the purpose of this problem was to investigate the possibility of resonance effects through non-coplanar acetylenes and allenes. Either analysis of any resonance effects or complete lack of any interactions between non-coplanar groups should help to clarify the true nature of the pi electron clouds about sp hybridized carbon atoms.

REVIEW OF LITERATURE

Countless volumes have been written on resonance effects particularly with respect to reactivity and spectra of organic compounds. The fact that N,N,2,6-tetramethylaniline fails to couple with phenyldiazonium chloride has been rationalized on the basis that the steric requirements of the methyl groups force the nitrogen atom into an orientation which does not permit delocalization (resonance) of the nitrogen p electrons with the phenyl ring.[3] Under such circumstances, the phenyl group is not sufficiently activated to react with a diazonium salt in a typical coupling reaction. This is a classical example of steric inhibition of resonance.

Another case of steric inhibition of resonance is evident when the ultraviolet spectra of biphenyl, benzene, bimesityl and mesitylene are compared. The ultraviolet spectra of benzene and biphenyl are quite dissimilar,[4] which is due to more extensive pi electron delocalization in the planar biphenyl. In the case of bimesityl though, its spectrum is almost identical (per aromatic ring) with mesitylene itself.[5] Here again, steric requirements of the methyl groups ortho to the ring junction cause the mesitylene rings of bimesityl to lie in different planes, thus inhibiting pi electron delocalization from ring to ring.[6]

Numerous studies comparing the relative abilities of carbon carbon triple and trans double bonds to transmit resonance effects are reported. Kochi and Hammond[7] examined

the solvolysis of benzyl tosylates and the saponification of ethyl benzoates having β-styryl and phenylethynyl groups as meta and para substituents.

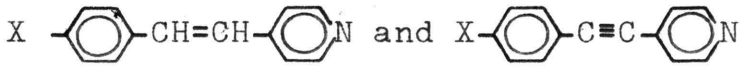
$$RC_6H_4CH_2OTOS \xrightarrow{^-OH} RC_6H_4CH_2OH + TOS^-$$

$$RC_6H_4CO_2C_2H_5 \xrightarrow{^-OH} RC_6H_4CO_2^- + C_2H_5OH$$

R = m - $C_6H_5CH{=}{=}CH^-$, p - $C_6H_5CH{=}{=}CH^-$,
m - $C_6H_5C \equiv C^-$, p - $C_6H_5C \equiv C^-$.

Analysis of their reaction rate data using the Hammett $\sigma\rho$ relationship showed that the p-phenylethynyl group exhibits a low conjugative aptitude, compared with the p-β-styryl group, toward electron deficient systems, i.e. tosylate solvolysis. However, the p-phenylethynyl group shows a higher conjugative aptitude than the corresponding p-β-styryl group toward ethyl benzoate hydrolysis. Inductive effects of the m-phenylethynyl and m-β-styryl groups are both small, although more pronounced in the m-phenylethynyl case. This result is in accord with an earlier study of inductive effects by Baker, Cooper and Ingold,[8] who attributed a greater electron attracting power to the acetylene function on the basis of isomer ratios from quantitative nitration of phenylpropiolic and cinnamic acids and their esters.

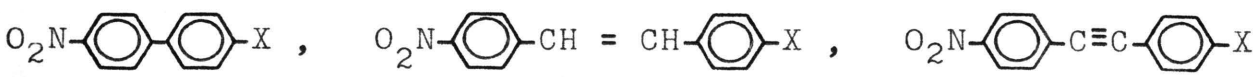
In 1960 Katritzky, Short and Boulton[9] reported a comprehensive study of the basicities of <u>para</u> substituted 4-styryl and 4-phenylethynyl pyridines. They prepared the following compounds and spectrophotometrically determined their pKa's.



X = OCH_3, CH_3, H, Cl, NO_2

The styryl substituted pyridines exhibited pKa values from 6.03 to 5.15 with a Hammett ρ value of 0.85. In the other case, the phenylethynyl substituted pyridines showed pKa's from 4.80 to 4.31 with a Hammett ρ value of 0.44. From these data they concluded that interaction between the phenyl ring substituents and the pyridine ring is small, but is significantly larger in the styryl than in the phenylethynyl compounds, indicating that the triple bond is a poorer conductor of resonance effects than is the double bond.

Berry, Brocklehurst and Buraway[10] also published a comparative study of resonance effects through double and triple bonds in 1960. They measured the K-band shift in the ultraviolet region on the following compounds:



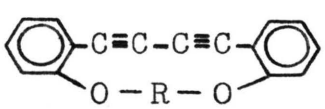
D* = 385 A° D* = 445 A° D* = 420 A°

X = H, NH_2

Since the observed shifts when X was changed from H to NH_2 (shown as D* in A^o) were very nearly the same for the three series of compounds, they concluded that in the case of the stilbene and tolane derivatives the interactions between the amino and nitro groups are nearly the same. They concluded further that transmission of polar effects through aliphatic unsaturated groups e.g. ethenyl and ethynyl, is greater than through a phenyl group.

As part of a study of field effects on the rates of saponification of propiolic acid esters, Roberts and Carboni[11] reported a Hammett ρ value of 1.91. This is nearly 50% larger than the corresponding value of 1.314 obtained for cinnamate ester hydrolyses in the same solvent,[12] suggesting that the triple bond of the propiolates transmits resonance effects better than the corresponding double bond of the cinnamates. A reinvestigation of ethyl phenylpropiolate saponification by Fuchs[13] established a Hammett ρ value of 1.10. Fuchs therefore states[13], "There is now no substantiated case in which the acetylene unit transmits electronic effects better than, or, as well as, a trans ethylenic unit."

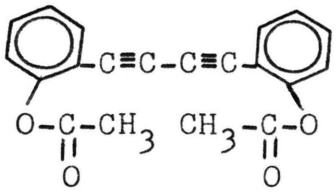
Nakagawa and Toda[14] investigated the physical properties and ultraviolet spectra of the two compounds shown below.



I R = $-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$

II R = $-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-$

As a control sample for spectral comparison they also synthesized the following open chain analog.



III

The ultraviolet spectra they obtained for compounds I, II and III are shown in Table I.

TABLE I

Ultraviolet Absorption Data of Compounds I, II and III[14]

Compound	Absorption Maxima mμ					
I			275 (113)	291 (290)	310 (535)	332 (541)
II	248.5 (267)		275 (122)	293 (171)	310 (216)	331 (174)
III	250 (479)	260 (483)	275 (240)	291 (337)	310 (445)	331 (398)

The underlined figure indicates inflection.

The figures in parentheses are ϵ max X 10^{-2}.

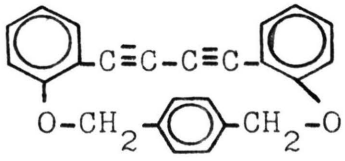
Their examination of Courtauld scale models of I and II indicated that I is a rigid molecule with the two phenyl rings tightly held in the same plane. However, the phenyl groups of II cannot exhibit a coplanar arrangement due to the length of the bridging chain.*

*Fisher-Taylor-Hirshfelder molecular model studies in this laboratory indicate that both I and II are flexible and may exhibit either a planar or non-planar conformation.

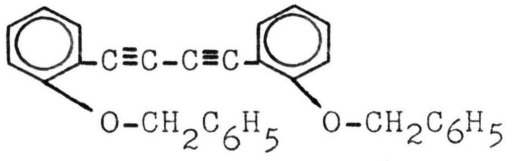
They felt that this situation is reflected in the closely related ultraviolet spectra of I, II and III. The observed decrease of extinction coefficients of the absorption maxima in the long wavelength region (290-340 mμ) are in the sequence I > III > II. This sequence is claimed to be a result of the importance of coplanar phenyl groups in effecting a change in the intensity of absorption.

Although it is not shown in the data in Table I, the authors[14] state that compound I exhibits a sharp ultraviolet absorption minimum near 260 mμ, the extinction coefficient of which is only one tenth that of II. Their interpretation is that it may be caused by a proximity effect of the bridging chain to the diacetylene linkage.

In a later paper Nakagawa and Toda[15] published the syntheses and ultraviolet spectra, Table II, of the following compounds.



IV



V

TABLE II

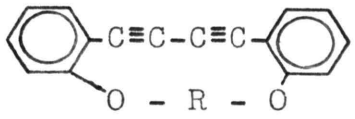
Ultraviolet Absorption Spectra of Compounds IV and V[16]

Compound	Absorption Maxima mμ				
IV	261 (322)	275 (105)	310 (189)	322 (208)	346 (127)
V	261 (287)	275 (130)	310 (212)	328 (323)	351 (285)

The underlined figures indicate shoulders.
The figures in parentheses are ϵ max X 10^{-2}.

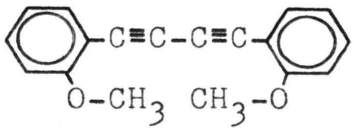
Here again the cyclic compound, IV, exhibits much lower intensity absorption in the long wavelength region compared with the open chain analog V. Scale models of IV and V indicate that they are both almost strain free.[16] The authors conclude[15] that the reduced absorption intensity of IV compared with V is due to a transannular interaction of pi electrons in the bridging chain with those of the diyne function. From infrared absorption data also published for IV and V,[16] Smith,[17] suggests that aromatic ring deformations are apparent, even though Nakagawa and Toda stated that models show IV to be almost strain free.[16]

In order to minimize transannular pi electron interaction between the diyne function and a bridging chain, the following compounds were synthesized and their spectra reported by Nakagawa and Toda.[18]



VI R = $-(CH_2)_4-$

VII R = $-(CH_2)_5-$



VIII

The ultraviolet absorption maxima of VI, VII and VIII[18] are shown in Table III.

TABLE III

Ultraviolet Absorption Maxima of Compounds VI, VII AND VIII

Compound	Absorption Maxima mμ				
VI	230 (345)	299 (122)	331 (201)	353 (199)	
VII	243 (218)	299 (161)	331 (317)	353 (365)	
VIII	259 (260)	273 (107)	310 (199)	326 (327)	348 (293)

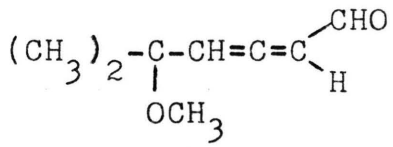
The underlined figure indicates a shoulder.

The figures in parentheses are ϵ max X 10^{-2}.

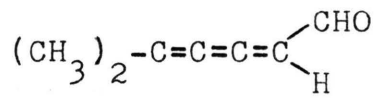
Examination of scale models of VI and VII indicated that the bridge of VI is too short to allow a strain-free conformation. The diacetylene linkage was forced to bend. Compound VII however seemed to exhibit very little ring strain and had an almost planar rigid structure. Again compound VIII was a planar open chain analog for spectral comparison. Comparison of the spectra of VI, VII AND VIII showed that the extinction coefficients in the long wavelength region lie in the order VII $>$ VIII $>$ VI. This sequence indicates that VII is a rigid and planar structure, thus increasing its transition probability compared to VIII.[18] The fact that VI exhibits the lowest extinction coefficients is believed to be due to bending of the diacetylene linkage thus causing a decreased transition probability.[18] Again sharp absorption minima near 260 mμ for both VI and VII were obvious in the published spectra,[18] and ascribed to a proximity effect between the bridge and the diacetylene linkage.

No further reports dealing with non-coplanar substituted acetylenes were found in the literature.

Diphenyl polyenes, cumulenes, $C_6H_5-(C=C)_n-C_6H_5$ show high intensity absorption in the ultraviolet region.[19] The wavelength and intensity of this absorption increase with the increase in length of the cumulene chain.[19] A specific case of this phenomenon is shown by comparing the $\pi \rightarrow \pi^*$ transitions in the ultraviolet region of the substituted cumulenes IX and X.



IX

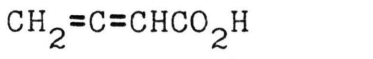


X

Compound IX exhibits a λ max = 227 mμ ϵ = 10,400 in isooctane solvent.[20] However, compound X which has one more cumulated double bond than IX exhibits a λ max (doublet) = 284 and 304 mμ ϵ = 24,000 in the same solvent.[21]

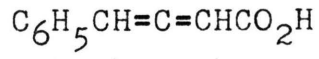
Comparison of the nmr spectra of allene and normal alkenes reveals that the vinyl protons of allene are shifted to higher field than are the protons of a = CH_2 in a non-cumulative alkene.[22] Whipple, Goldstein and Stewart[22] state that this shift to higher field could be explained by diamagnetic circulation in the cylindrically symmetrical pi electron distribution in the vicinity of the sp hybridized central carbon atom of allene. A similar argument, using electronic circulation within the cylindrical pi electron cloud of acetylene, has been used to explain diamagnetic shielding of acetylenic protons.[23]

Acidity determinations of allenic acids are scarce in the literature, however pKa's of the following two acids, XI and XII have been reported.[24]



XI

pKa = 3.69 (3.68)

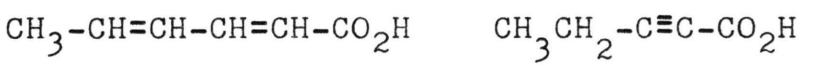


XII

pKa = 3.68 (3.71)

The numbers in parentheses are duplicate determinations.

Butadienoic acid(XI) has a pKa of 3.69 indicating that it is a stronger acid than XIII which has a pKa of 4.48,[24] but weaker than XIV which has a pKa of 2.61.[24]



XIII pKa = 4.48 (4.53)

XIV pKa = 2.61 (2.60)

Evidently the allene group shows some net electron-attracting powers intermediate between those of ethylenic and acetylenic groups. As is also shown in these data, acid XII has essentially the same pKa as XI, indicating that the phenyl group of XII has neither a mesomeric nor inductive effect on the acidity of the carboxyl group.

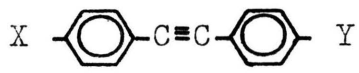
STATEMENT OF PROBLEM AND PLANNED SOLUTION

As indicated in the Review of Literature, many studies of resonance effects through acetylenes have been reported. Most of these studies however, dealt with comparing the relative abilities of ethylenic verses acetylenic linkages to conduct resonance effects. However, little agreement on the results seems to have come out of these studies. Only Nakagawa and Toda[14-18] handled systems in which the acetylenic link was flanked by non-coplanar unsaturated groups. All of their systems incorporated bridges in close proximity to the diyne function containing pi or non-bonding p electrons which prevented accurate interpretation of their spectral data. Also, their spectral interpretations were frequently based on questionable assumptions concerning strain and conformation of their systems.

If cylindrical symmetry of the pi cloud of acetylene[25] does exist, then unsaturated groups bonded to both ends of a carbon-carbon triple bond might exhibit resonance effects, continuous pi electron overlap, regardless of the orientation of the unsaturated groups with respect to each other. In other words, even if the aryl groups of a diarylacetylene are forced to lie in perpendicular planes, they might still be completely conjugated with each other and show resonance effects through the ethyne link.

In order to effectively study this hypothesis a suitably substituted non-coplanar diarylacetylene would have to be synthesized. It would be necessary that this compound have little or no bond strain to simplify spectral analysis. Also, any blocking groups to force aryl rings into different planes would have to be such that interactions between them and the acetylene link be minimized. Otherwise, accurate spectral interpretation would be impossible. The use of a bridging chain to force non-coplanarity in a diarylacetylene was ruled out because of the difficulties Nakagawa and Toda experienced in their work.

Orginally, it was anticipated that compounds such as a 2,2',6,6'-tetra-tert-butyldiphenylacetylene XV, where X and Y are substituents with opposite electronic effects, would be synthesized.

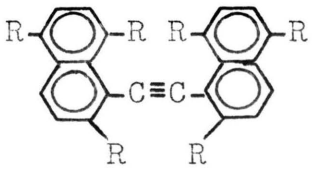


XV

The tert-butyl groups ortho to the acetylene link would force the phenyl groups into perpendicular planes, as shown by scale models of XV. By determining the effect, for example, of a para nitro group (X = NO_2) on the basicity of a para prime amino group (Y = NH_2), one could learn if the nitro group was conjugated with the amino group. Such an analysis would require that a base weakening effect be

found as compared to the potentially planar compound, 4-amino-4'-nitrodiphenylacetylene. If no base weakening effect were found, then obviously no resonance effects are transmitted through the triple bond of XV. Unfortunately, scale models of XV also indicated that the extreme bulk of the tert-butyl groups would make its synthesis almost impossible. The fact that 2,6-di-tert-butylphenol does not dissolve in aqueous sodium hydroxide solution appears to be due to the great bulk of the tert-butyl groups.[26] Therefore, better compounds were sought for synthesis.

Compounds of the following type, di-1-naphthylacetylenes, were then chosen for analysis.



XVI R = H

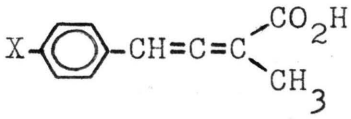
XVII R = CH_3

Scale model studies of both XVI and XVII indicated that they are essentially strain free. The methyl groups of XVII are large enough to prevent the naphthyl rings from being coplanar, but small enough to hopefully allow a reasonable synthesis. Also, since the methyl groups of XVII possess no non-bonding p or pi electrons, interactions between the blocking methyl groups and the acetylene link should be minimized. Comparison of the ultraviolet spectra of XVI

and XVII should give a strong indication as to whether or not pi electron overlap is continuous through the triple bond of the non-coplanar compound. If the ultraviolet spectra of XVI and XVII were very similar, then overlap must be continuous even though XVII is a non-coplanar compound. If the spectra were markedly different, then obviously overlap is not continuous. Therefore, it was planned to synthesize XVI and XVII and determine their ultraviolet spectra.

Allenes, which possess a central sp hybridized carbon atom, would be expected to exhibit circular symmetry of the pi cloud about the sp carbon, if the cylindrical symmetry attributed to the triple bond has an analog in the case of allene. Therefore, unsaturated 1,3-substituents on an allene might exhibit resonance effects, even though such substituents would lie in perpendicular planes due to the geometry of allene.[27] Since no studies of resonance effects in allenes were found in the literature, this investigation was undertaken.

Although many substituted allenes have been synthesized, none of them have had 1,3-substituents suitable for a study of resonance effects. We, therefore, proposed to synthesize a series of para substituted 4-phenyl-2-methylbutadienoic acids XVIII, and determine their pKa's.



XVIII

XVIIIa, X = OCH_3; XVIIIb, X = CH_3; XVIIIc, X = H;
XVIIId, X = Cl; XVIIIe, X = NO_2

If electronic effects of the nitro group of XVIIIe are transmitted through the allene system, then XVIIIe should be a much stronger acid than the unsubstituted XVIIIc. Similarly the methoxy substituted acid, XVIIIa, should be much weaker than XVIIIc if resonance effects are present. If all of the acids, XVIIIa-e, exhibit nearly the same acidities, then no resonance effects are present. Inductive effects would probably be negligible due to the extreme distance, nine atoms, between the carboxyl proton and X.[28] The possibility of mutual <u>pi</u> cloud polarization at the central allene carbon, could cause the acidities of XVIIIa-e to systematically vary, but not enough to be confused with a true resonance effect.[29]

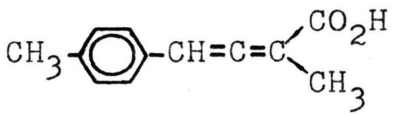
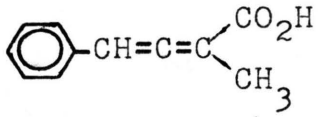
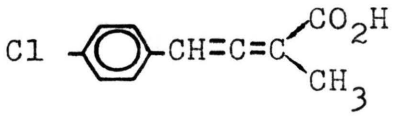
EXPERIMENTAL RESULTS

Trials to prepare the di-1-naphthylacetylenes XVI and XVII were unsuccessful. The reasons are discussed in detail in the Discussion section.

Three allenic acids, XVIIIb,c,d, were prepared and their pKa's determined as shown below in Table IV.

TABLE IV

pKa's of XVIIIb, XVIIIc and XVIIId

Compound	Number	pKa*	pKa**
	XVIIIb	4.16(4.13)	6.81
	XVIIIc	4.15(4.14)	6.38
	XVIIId	4.14(4.18)	—

*Determined by potentiometric titration in dilute water solution by the author. Numbers in parentheses are duplicate measurements.

**Determined by potentiometric titration by Dr. John O. Frohliger, Duquesne University, Pittsburgh, Pennsylvania in 75% ethanol-water solution.

DISCUSSION

In order to compare the ultraviolet spectra of a planar and a non-planar di-1-naphthylacetylene, XVI and XVII had to be synthesized. Although di-1-naphthylacetylene (XVI) is mentioned once in the literature in 1878,[30] the synthesis described was suspect. A more unequivocal synthesis similar to that chosen for the methylated dinaphthylacetylene XVII is shown in Chart I.

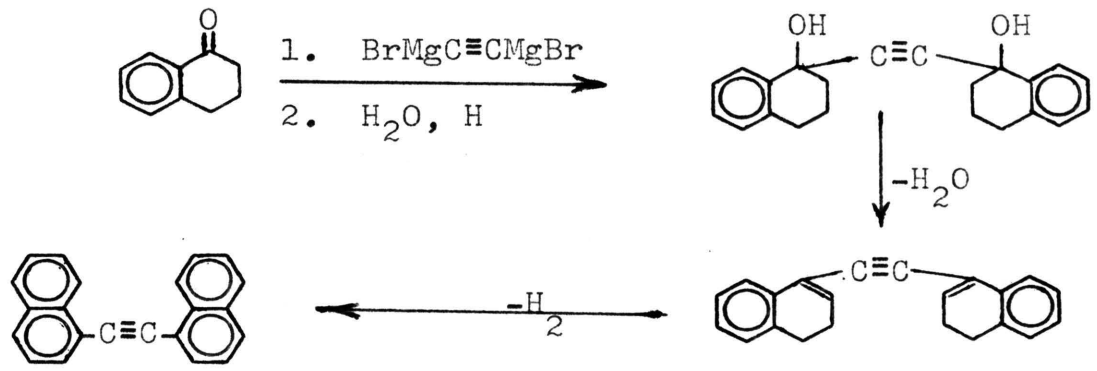


Chart I. Proposed Synthesis of Di-1-Naphthylacetylene

The condensation of acetylenedimagnesium bromide in a benzene or ether suspension with ketones is a common reaction which normally yields symmetrical acetylenic glycols as the major product.[31] One report,[32] however, using methylal solvent with a substituted 1-tetralone yielded a mono acetylenic alcohol. Two reports[33,34] of condensation of this reagent with 1-tetralone both state that the major product is the dehydration product, a dienyne, which was confirmed in this

laboratory. Although the yields were low, ca. 15%, sufficient material for dehydrogenation was prepared.

Dehydrogenation of the dienyne was first attempted by heating it with sulfur until hydrogen sulfide evolution became very slow. In several such attempts a resinous material soluble in benzene was produced. Chromatography of this material on neutral alumina invariably failed to separate any definable products; the resinous mass was always eluted in a small band. Further dehydrogenation attempts were done using chloranil, but decomposition always appeared to take place. Catalytic dehydrogenation techniques were not considered feasible, since aliphatic hydrogen atoms removed from the dienyne could possibly hydrogenate the triple bond. Since synthesis of the methylated dinaphthylacetylene eventually failed, no further trials to synthesize di-1-naphthylacetylene were attempted.

The proposed synthesis of bis-(2,5,8-trimethyl-1-naphthyl)-acetylene is shown in Chart 2.

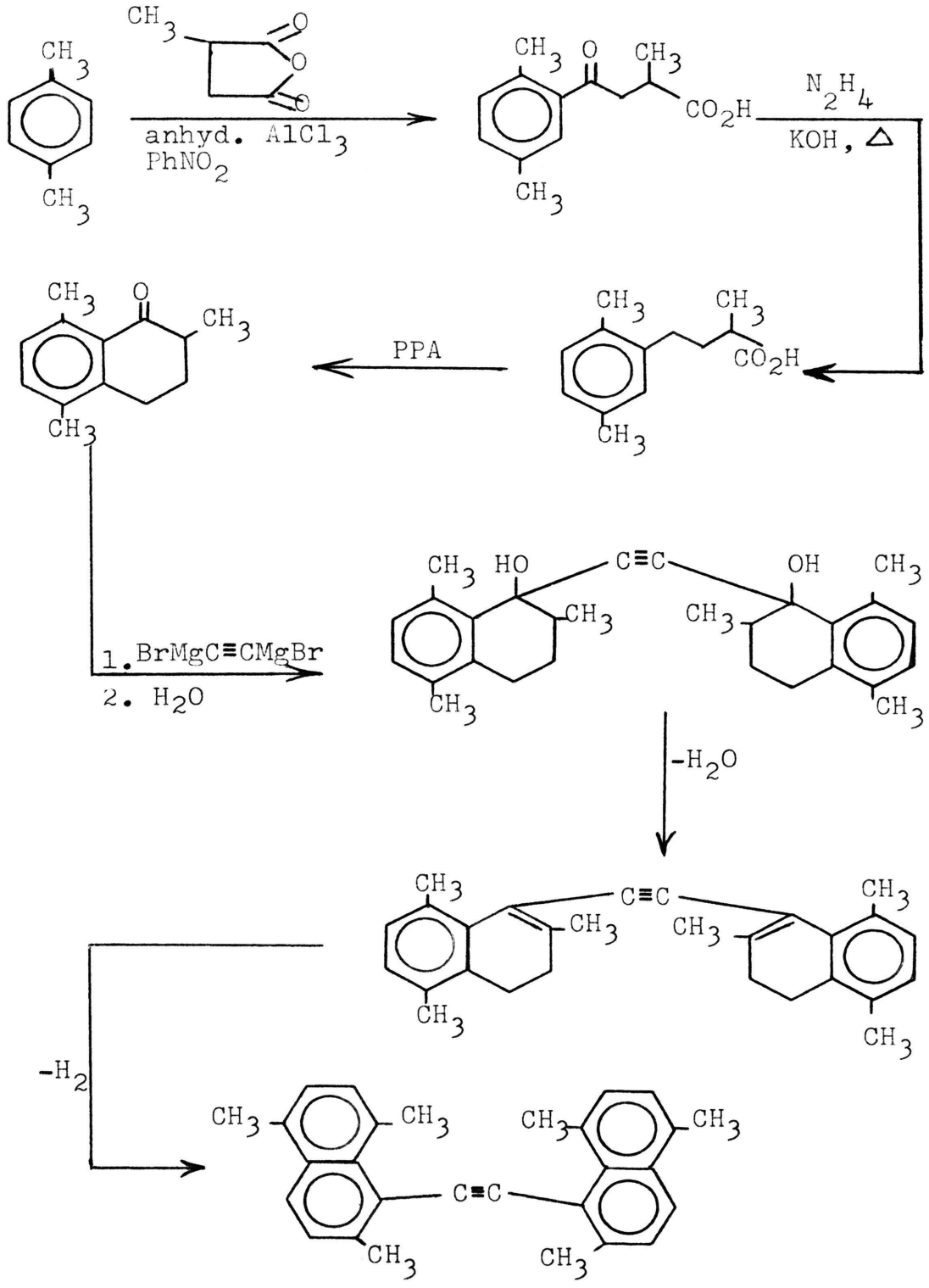


Chart 2. Proposed Synthesis of bis-(2,5,8-Trimethyl-1-Naphthyl)-Acetylene.

Although Friedel-Crafts reactions have been extensively studied and reviewed,[35] no report of reaction between p-xylene and pyrotartaric anhydride (methylsuccinic anhydride) was found in the literature. p-Xylene was chosen because only one aromatic substitution isomer is possible yielding a keto-acid product with the side chain ortho to a methyl group. Unfortunately, isomerism is possible in the side chain of the product, depending upon which acylonium ion derived from the anhydride attacks the aromatic ring.[35] Such isomerism can frequently be controlled by proper choice of the solvent.[35] Nitrobenzene, when used as the solvent, normally directs anhydride opening such that the α-methyl acid is the only isolable product,[35,36] but it also results in a more difficult work-up procedure.[35] Enamine alkylation[37] of 5,8-dimethyl-1-tetralone was not considered feasible, since the enamine must be coplanar with the ring being alkylated and the 8-methyl group of 5,8-dimethyl-1-tetralone would probably prevent coplanarity.

One report[38] using excess benzene as solvent for the reaction with pyrotartaric anhydride indicated a yield of 60% of the desired β-benzoyl-α-methylpropionic acid. Accordingly a small reaction was attempted using excess p-xylene as solvent. Since the anhydrous aluminum chloride is not really soluble in p-xylene,[35] stirring difficulties were encountered and the reaction never did proceed smoothly.

Another small-scale reaction between p-xylene and pyrotartaric anhydride was then run in sym-tetrachloroethane, in which anhydrous aluminum chloride is soluble.[35] Since no isomer separation or identification could be done easily on the keto-acid product, the Wolff-Kishner reduction was performed on the keto-acid. Vacuum distillation of the oily product yielded a colorless oil, which upon standing about three weeks turned purple and deposited about 25% of the material as large white crystals. The oil and crystals were separated and each cyclized with polyphosphoric acid. The resulting ketones had different nmr spectra. Deuteration of the ketone prepared from the white crystals with sodium methoxide-methanol-d (CH_3OD) showed that the desired 2-methyl ketone came from the white crystals, not the purple oil.

Since it was shown that the desired isomer was produced in poor yield using sym-tetrachloroethane as solvent, nitrobenzene was selected as a potentially better solvent. As described in the Experimental Section, nitrobenzene did indeed allow a reasonable yield of the desired isomer as determined by the production of 77.6 g of 2,5,8-trimethyl-1-tetralone.

The Wolff-Kishner reduction and cyclization with polyphosphoric acid both went smoothly following the procedure of Stetter, Schäfer and Spangenberger.[39]

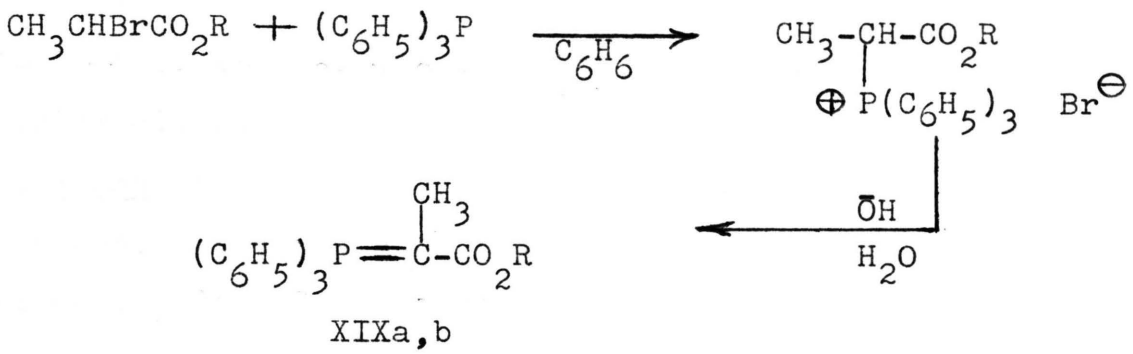
The condensation of 2,5,8-trimethyl-1-tetralone with acetylene posed the greatest problem in this synthesis. Model studies using 1-tetralone indicated that a small yield could be expected by using acetylenedimagnesium bromide as the condensing agent. However, no evidence for the desired reaction with the methylated ketone was obtained. Potassium hydroxide dispersed in an acetal saturated with acetylene[40] looked like a promising condensation technique based on model studies with simple ketones. Again, no evidence for the desired reaction of either 1-tetralone or 2,5,8-trimethyl-1-tetralone with this reagent was obtained. Instead only evidence for an aldol condensation in very poor yield was found in both cases. The tarry residues from reaction work-up exhibited both C=O and O-H stretch in their infrared spectra.

There are several explanations for the failure of the 1-tetralones to condense satisfactorily with acetylene. One is the possibility that under the conditions necessary for condensation, base-promoted enolization of the ketone took place, thus effectively removing the reactive carbonyl function. This does not seem too likely, however, since similarly substituted non-cyclic ketones (propiophenone and <u>iso</u>-butyrophenone) gave good yields of acetylenic glycols under identical conditions. Also, the deuteration study of 2,5,8-trimethyl-1-tetralone with sodium methoxide - methanol-d (CH_3OD) required three hours for complete replacement of the proton <u>alpha</u> to the carbonyl group. This certainly indicates that enolization is not a facile reaction.

A more likely reason for failure of the methylated 1-tetralone to condense with acetylene is that the 2- and 8- methyl groups sterically hinder the carbonyl function enough to prevent reaction. In fact failure to form a semicarbazone can be used as a qualitative test to suggest the presence of 2- and 8-substituents on a 1-tetralone.[41,42] This does not, of course, account for the failure of 1-tetralone to condense with acetylene in the presence of dispersed potassium hydroxide.

In order to investigate the possibility of transmitting resonance effects through allenes, we decided to synthesize substituted butadienoic acids, XVIIIa-e and measure their pKa's. Earlier reports[43,44] indicated that allene carboxylic esters could be conveniently synthesized using a Wittig reagent plus an acid chloride. The Wittig ylid required is a stable crystalline compound which can be kept for a long time without decomposition[45]; the ylid is produced by addition of dilute sodium hydroxide to a water solution of a phosphonium halide.[46] Although two moles of ylid are required per mole of acid chloride, the by-product phosphonium chloride produced can be used to regenerate more ylid by treatment with dilute sodium hydroxide solution. The syntheses of the substituted butadienoic acids, XVIII a-e, are shown in Chart 3.

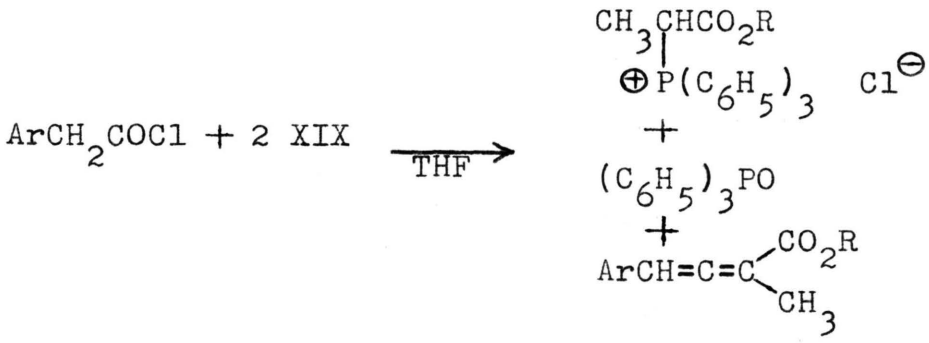
Ylid preparation:



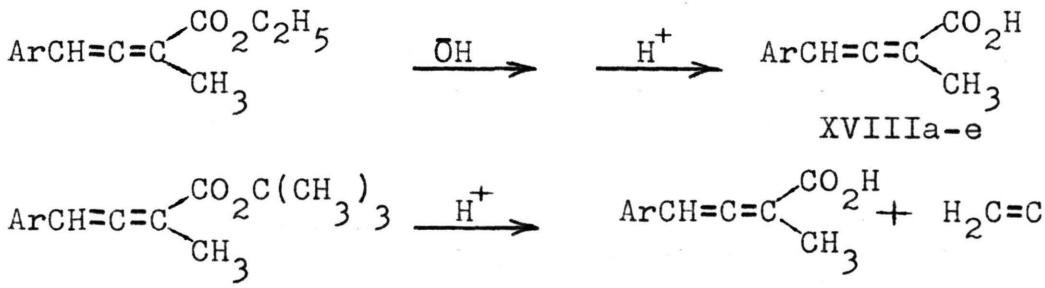
XIXa,b

XIXa, R = C_2H_5; XIXb, R = $-C(CH_3)_3$.

Allene ester preparation:



Allene ester hydrolysis:



XVIIIa-e

XVIIIa-e

XVIIIa, Ar = p-$CH_3OC_6H_4$; XVIIIb, Ar = p-$CH_3C_6H_4$;

XVIIIc, Ar = C_6H_5; XVIIId, Ar = p-ClC_6H_4;

XVIIIe, Ar = p-$NO_2C_6H_4$.

Chart 3. Synthesis of Para Substituted 4-Phenyl-2-Methyl-butadienoic Acids.

Bestman and Hartung[43] implied that almost any acid chloride could be used for reaction with the ylid XIXa to synthesize allene esters as long as there is at least one proton alpha to the acid chloride carbonyl group. Bestman[47] also stated, without giving conditions, that the allene esters thus produced could be smoothly hydrolyzed to the crystalline allene-carboxylic acids. When phenylacetyl chloride was allowed to react with XIXa however, the resulting ester was stable only in solution and polymerized upon evaporation of the solvent.[43] In spite of this problem syntheses of allene carboxylic acids using substituted phenylacetyl chlorides were attempted in this laboratory.

Syntheses of the allenic esters as shown in Chart 3 were done readily in this laboratory; however, hydrolysis of the allenic esters proved to be difficult. Basic hydrolysis of the allenic ethyl esters, except for one case, always produced non-acidic products containing no allene (=C=) stretch in their infrared spectra. These products were not characterized, but may be allene ester dimers, polymers or products from nucleophilic attack on the allene function. Such results are consistent with the observations of Eglington[48] and Harvey[49] that the sp carbon in allenic esters is extremely electrophilic, being more susceptible to Michael reactions than acrylates or propiolates. Furthermore Harvey[50] has observed extreme sensitivities toward polymerization in the absence of radical inhibitors.

In order to obviate the possibility of nucleophilic attack on the allene function, tert-butyl allenic esters were synthesized, since they can be smoothly hydrolyzed in acid solution.[51] The hydrolyses were carried out directly on the crude reaction mixtures, after removing the by-product phosphonium chloride, to always keep the esters in solution and thus retard polymerization. Radical inhibitors were also added before hydrolysis was attempted. As indicated in the Experimental Section, XVIIIb, XVIIIc and XVIIId were readily prepared using the tert-butyl ylid XIXb.

Hydrolysis of the methoxy substituted allene tert-butyl ester, however, was never affected in significant yield. As is shown in Table VI in the Experimental Section, numerous acid hydrolysis procedures were attempted yielding no isolable quantities of allene carboxylic acids. When very strong acids were used for hydrolysis, e.g. trifluoroacetic, 70% perchloric and toluenesulfonic, the reaction mixtures turned dark yellow within several minutes. Work-up of these reactions normally yielded only a trace of a non-allenic acidic material. The weaker acids shown in Table VI gave the same results after longer reaction times or after heating for a matter of minutes. In all cases infrared spectra of the non-acidic material produced exhibited little or no =C= or conjugated C=O stretching absorption. They did exhibit strong carbonyl (non-conjugated) absorption, however, at 1750 cm^{-1}.

For comparison purposes basic hydrolysis of a methoxy substituted allene ethyl ester was attempted. Again no allene acid was isolated, but the non-acidic material remaining after work-up yielded an infrared spectrum almost identical to that obtained from the acid hydrolysis of tert-butyl esters as described above. In another experiment a small amount of the crude methoxy substituted allene ethyl ester reaction mixture was allowed to evaporate to dryness. An infrared spectrum of this residue dissolved in methylene chloride exhibited no =C= stretch, but did show a broad C=O (conjugated) absorption around 1700 cm^{-1}. Assuming that the spectrum of the evaporation residue is representative of polymeric material, the products produced from both acid and basic hydrolysis are probably non-polymeric and have the same basic structures. A summary of these data is shown in Chart 4.

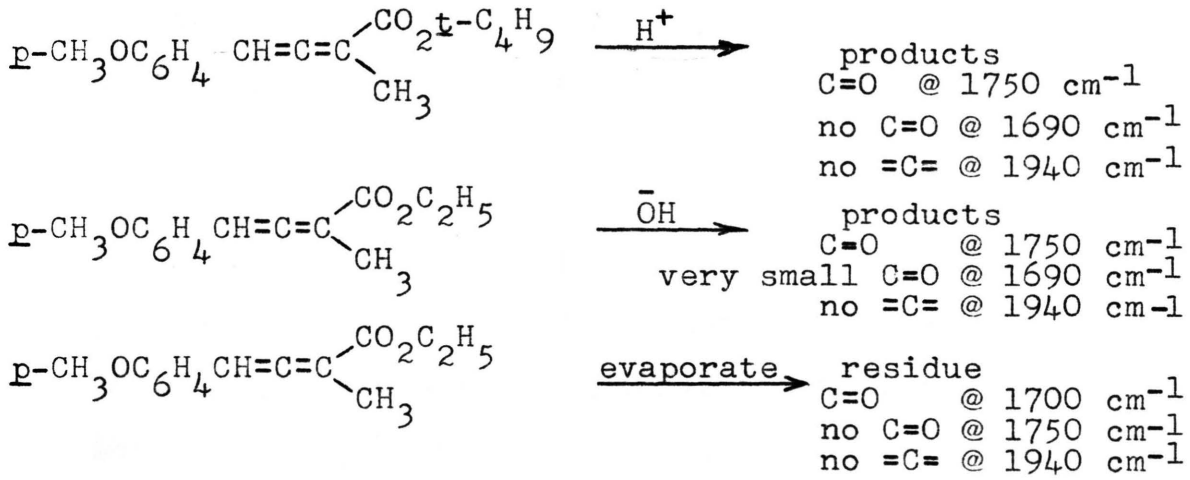


Chart 4. Summary of Data Concerning Products of Methoxy-Substituted Allene Carboxylic Ester Hydrolyses.

The 4-(4'nitrophenyl)-2-methylbutadienoic acid (XVIIIe) preparation was also unsuccessful. As explained in the Experimental section no evidence for formation of allenic products was obtained in several attempts. It appeared that the ylid in each attempt behaved as a general base to yield the purple colored solution, because treatment of a small sample of p-nitrophenylacetyl chloride with dilute sodium hydroxide under similar conditions also yielded a purple solution. This purple color was destroyed by addition of dilute acid, but could be regenerated upon neutralization with dilute base. No effort was made to elucidate the structure of the material responsible for the purple solutions produced.

The pKa's of XVIIIb-d were determined by potentiometric titration in dilute aqueous solution. The technique employed depended upon the fact that at half neutralization the pH of the solution of a weak acid equals its pKa. Therefore, the pH-meter used was calibrated to read 4.20, the pKa of benzoic acid,[52] with a benzoic acid-sodium benzoate buffer solution of the same concentration as the allene acid solutions titrated. As shown in the Experimental section the pKa's of XVIIIb-d are identical, since the precision of the method used was probably no better than ± 0.05 pKa unit. In order to check the procedure a known sample of trans-cinnamic acid was titrated under identical conditions. Since the pKa determined (4.42) was almost identical to the reported value 4.43,[52] the pKa's obtained for the allene acids are believed to be reliable.

Samples of acids XVIIIb-d were sent to Dr. John O. Frohliger at Duquesne University in Pittsburgh, Pennsylvania for independent determination of their pKa's. Dr. Frohliger attempted to determine their pKa's in 75% ethanol-water solution using a hydrochloric acid equilibration technique. As shown in the Experimental Results section he found a difference in acidities of XVIIIb and XVIIIc of about 0.4 pKa unit. He was unable to measure the pKa of XVIIId, since it apparently reacted immediately with his solvent. Because of this fact, the difference in acidities Dr. Frohliger found between XVIIIb and XVIIIc is questionable.

Further efforts to correlate the acidities of XVIIIb,c,d with their spectra were unsuccessful. As the data in the Experimental section show, no correlation between the Hammett σ_p values of the substituent "X" and the ultraviolet maxima is evident. The allenic protons of XVIIIb,c,d do exhibit a direct relationship between σ_p and their location in the nmr spectra, but this effect is probably due to the neighboring substituted phenyl group and has no relationship with the transmission of resonance effects through an allene. The carboxyl and methyl protons which should be a measure of such an effect, do not exhibit a correlation of σ_p with their chemical shift, again indicating that resonance effects do not appear to be transmitted through allenes.

EXPERIMENTAL

Boiling points and melting points are given in centigrade degrees and are uncorrected, unless so stated. Spectra were determined on a Varian A-56/60 nuclear magnetic resonance spectrometer using tetramethylsilane as an internal standard, a Beckman IR-5A infrared spectrophotometer and a Beckman DK-2A visible-ultraviolet spectrophotometer. Elemental analyses were performed by the Du-Good Chemical Laboratories of St. Louis, Missouri.

1-Tetralone. - Alpha-tetralone was prepared following the procedure given in Organic Syntheses, Coll. Vol. IV.[53] The product, a colorless liquid boiling at 148-150° (25 mm) [lit.[53] bp 143-145° (20 mm)], amounted to 126 g (72%).

1,1' - Ethynylene-bis-3,4-dihydronaphthalene. - Ethylmagnesium bromide was prepared from 6 g of magnesium turnings and 30 g of ethyl bromide in 150-ml of absolute ether. To this solution 250-ml of dry benzene was added and the ether removed by distillation. After the solution cooled to room temperature, acetylene, purified by bubbling through concentrated sulfuric acid, was bubbled into the solution for 3 hr. yielding acetylenedimagnesium bromide as a light grey suspension. Thirty grams of alpha-tetralone dissolved in 80-ml of dry benzene was allowed to drip into this suspension over a period of 30 minutes. After refluxing 15 hr. the reaction mixture was cooled and poured onto ice and dilute hydrochloric

acid. The benzene layer was separated and evaporated under vacuum yielding a dark brown oily residue which upon addition of petroleum ether (30-60°) gave a dark yellow precipitate mp 113-123°. Recrystallization from petroleum ether (60-110°) yielded 4.5 g (15%) of yellow plates mp 120-124°, [lit.[34] mp 120-121°, lit.[33] mp 124°]. Dehydration of the expected acetylene glycol apparently took place during hydrolysis.

Di-1-naphthylacetylene. - Rapid evolution of hydrogen sulfide resulted from heating 2.0 g of 1,1' - ethynylene-bis-3,4-dihydronaphthalene with 4.5 g of elemental sulfur for one hour at 150-200°. Chromatography on neutral alumina of the resulting tarry residue yielded no identifiable products.

Two and five tenths grams of 1,1'-ethynylene-bis-3,4-dihydronaphthalene and 13.3 g of chloranil were refluxed for 7 hr. in 50-ml of xylene. Decomposition appeared to take place, since a penetrating odor similar to hydrogen chloride was evident after one hour of reflux. After cooling, 50-ml of petroleum ether (30-60°) was added to the reaction mixture, which was then filtered. The dark residue on the filter was washed with 4% potassium hydroxide and water and then dissolved in ethyl acetate, which was then washed with dilute sodium hydroxide, dried over Drierite and evaporated. Picric acid in boiling chloroform was added to a chloroform solution of the oily product, resulting in a yellow precipitate mp 186°. Decomposition of this picrate with dilute ammonium hydroxide yielded no isolable organic products.

4-(2,5-Dimethylphenyl)-2-methyl-3-one-butanoic acid. - A mixture of 220 g of p-xylene and 240 g of pyrotartaric anhydride (α-methylsuccinic anhydride) in 600-ml of dry nitrobenzene was added with stirring to a solution of 650 g of anhydrous aluminum chloride in 1800-ml of dry nitrobenzene at 0-6°. The reaction mixture was held at ice-bath temperature overnight and then allowed to stand for one week at room temperature with occasional shaking. After pouring the reaction mixture onto ice drenched with dilute hydrochloric acid the nitrobenzene was removed by steam distillation. The resulting dark crystalline upper layer was dissolved in sodium carbonate solution using steam distillation to hasten the solution and also to remove last traces of nitrobenzene. Acidification of this dark alkaline solution with cold dilute hydrochloric acid yielded a brown solid which was decolorized in ether solution with Norit. Evaporation of the ether gave a tan solid which was recrystallized twice from ethanol-water yielding 270 g (61%) of white needles mp 118.0-119.6°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; mol. wt. 220. Found: C, 70.76; H, 7.38; mol. wt. (neutralization equivalent), 218.

4-(2,5-Dimethylphenyl)-2-methylbutanoic acid. - Two hundred and seventy grams of the keto-acid prepared above (4-(2,5-dimethylphenyl)-2-methyl-3-one-butanoic acid) were added to a warm solution of 350 g of 98% sodium hydroxide in 3-l of diethyleneglycol. Then 200-ml of 95% hydrazine in water was added and the reaction mixture refluxed for

10 hours at 126° by means of methanol addition. Distillation was then begun to remove methanol, water and excess hydrazine until the pot temperature reached 196°. It was allowed to reflux at that temperature for 16 hr. After cooling and acidification with cold dilute hydrochloric acid the resulting dark oil was dissolved in ether, dried over Drierite and the ether evaporated yielding 232 g (96% crude) of black foul smelling oil.

A small sample of this oil was repeatedly recrystallized from methanol-water yielding an analytical sample mp 55.0-55.8° (cor.).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79; mol. wt. 206. Found: C, 75.78; H, 8.96; mol. wt. (neutralization equivalent), 207.

2,5,8-Trimethyl-1-tetralone. - Two hundred and twenty grams of the black oil prepared above was added with stirring to about one kilogram of polyphosphoric acid pre-heated to 70°. After all of the organic acid was added the temperature was rapidly raised to 100° and held between 95-100° with stirring for about one half hour. The reaction mixture was then poured into ice water and the oily layer resulting was dissolved in ether, washed with water, dilute sodium bicarbonate and water, filtered through Drierite and evaporated. Vacuum distillation of the residue from evaporation yielded 77.6 g (42%) of 2,5,8-trimethyl-1-tetralone, colorless oil bp 111-112° (0.6 mm).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.89; H, 8.67.

The product exhibits infrared absorption at 1680 cm^{-1} (conj. C=O) determined in carbon tetrachloride. Its nmr spectrum in carbon tetrachloride exhibits a doublet at 1.09 ppm (2-methyl protons), a singlet at 2.12 ppm (5-methyl protons), a singlet at 2.48 ppm (8-methyl protons), a poorly resolved quartet at 2.68 ppm (2-proton) and another quartet at 6.87 ppm (aromatic protons). The region from 1.4-2.0 ppm shows several small and poorly resolved peaks.

A small sample of this material was dissolved in deuteriomethanol (CH_3OD) in which the nmr spectrum again exhibited a methyl doublet around one part per million. After addition of a small piece of sodium metal to this sample the methyl doublet began to collapse and after 3 hr. only a singlet was evident. This clearly shows that the methyl group in question is located on the 2 position not the 3 position as might be anticipated from the synthesis.

Acetaldehyde di-n-butyl acetal. - Six hundred grams (54%) of the di-n-butyl acetal of acetaldehyde was prepared according to the procedure in Vogel[53] starting with 445-ml of paraldehyde, 2,320-ml of n-butyl alcohol and 50 g of p-toluenesulfonic acid. The product boiled at 183-186°, [lit.[54] 186.5-187.5°].

Condensation of ketones with acetylene using potassium hydroxide dispersed in an acetal. - The general procedure for condensation required that 85% potassium hydroxide pellets be dispersed in di-n-butyl acetal of acetaldehyde by heating the mixture to 150° and then cooling to 80° using a Tru-Bore stirrer for agitation.[40] Acetylene, purified by passage through concentrated sulfuric acid and a bed of Drierite mixed with potassium hydroxide pellets, was then bubbled into the flask for about one and one half hours while holding the temperature between 75-85°. After cooling the flask and adding the ketone the acetylene flow was discontinued. The reaction mixture was then stirred for the described times at the temperatures shown in Table V before being poured into ice water. The resulting organic layers were separated, treated with several grams of Dry Ice, dried over Drierite and vacuum distilled to remove solvent and unreacted ketone. In all cases the distillation residue was weighed and if its infrared spectrum exhibited hydroxyl stretching but no C≡C, ≡C-H and C=O stretch, then the residue was assumed to be the desired acetylene glycol. A summary of the results of these experiments is shown in Table V.

TABLE V

Condensation of Acetylene with Ketones to Yield Acetylenic Glycols in Acetal Solvent

Ketone	g Ketone	g KOH	ml-Solv.	Ketone Add. Temp. °C	React. Temp. °C	React. Time Hours	% Yield
propio-phenone	26.8	13.4	55	- 5	25	7	30
	26.8	13.4	50	10	25	19	30
	53	26	100	-10	25	96	41
	26.8	26.8	100	- 8	25	24	53
	26.8	26.8	100	- 5	25	40	77
iso - butyro-phenone	29.6	28	100	-40	25	96	71
alpha - tetralone	14.6	14	50	-10	25	96	0
	14.6	14	50	-40	25	48	0
	14.6	28	55	-40	0- 5	40	0
	14.6	15	55	12	45-50	36	0
2,5,8-trimethyl-1-tetralone	18.8	15	55	-40	25	24	0
	9.4	15	55	0	25	72	0
	9.4	15	55	0	55	72	0
	9.4	15	55	0	0	72	0
	9.4	15	55	-76	-76	168	0

Attempted condensation of 2,5,8-trimethyl-1-tetralone with acetylenedimagnesium bromide. - Acetylenedimagnesium bromide was prepared as previously described (page 33) from 4.8 g of magnesium turnings and 21.8 g of ethyl bromide in 250-ml of dry benzene. To this suspension 18.8 g of 2,5,8-trimethyl-1-tetralone was added and the reaction mixture then held at reflux for 24 hr. After hydrolysis with ice and dilute hydrochloric acid the organic layer was vacuum distilled to remove benzene and unreacted ketone. An infrared spectrum of the trace of red oil remaining showed no evidence of the desired acetylene glycol.

p-Methoxyphenylacetyl chloride. - Two hundred and fifty grams of p-methoxyphenylacetic acid and 500 g of thionyl chloride were allowed to stand at room temperature for 2 hr., one hour at 40-50° and one hour at reflux. After removing the last traces of excess thionyl chloride under aspirator vacuum, the dark residue was vacuum distilled yielding about two hundred grams (72%) of p-methoxyphenylacetyl chloride as a colorless oil bp 121-125° (5-6 mm), [lit.[55] bp 121-122° (5 mm)].

p-Methylphenylacetyl chloride. - A mixture of 50-ml of thionyl chloride and 50 g of p-methylphenylacetic acid was allowed to stand overnight at room temperature and then refluxed for 3 hrs. Excess thionyl chloride was removed on a steam bath under aspirator vacuum. The dark colored

residue was vacuum distilled yielding 48.7 g (87%) of p-methylphenylacetyl chloride as a colorless oil bp 123° (25 mm).

p-Chlorophenylacetic acid. - Two hundred grams of p-chlorophenylacetonitrile were refluxed for 3 hrs. with a mixture of 300-ml water and 300-ml of concentrated sulfuric acid. The resulting solution and precipitate were poured into 2-l of ice water and filtered. The precipitate was dissolved in dilute sodium carbonate solution and extracted with ether. The acid was reprecipitated from the sodium carbonate solution with dilute hydrochloric acid. Attempted recrystallization from water and water-ethanol resulted in an oil so the p-chlorophenylacetic acid was used without further purification. Yield, 145 g (64%), mp 103-105°, [lit.[56] mp 105-106°].

p-Chlorophenylacetyl chloride. - A mixture of 120 g of the p-chlorophenylacetic acid prepared above and 110-ml of thionyl chloride was allowed to stand overnight at room temperature and then refluxed for 3 hrs. The excess thionyl chloride was removed under aspirator vacuum and the resulting dark residue was vacuum distilled yielding 70 g (52%) of p-chlorophenylacetyl chloride as a pale purple oil bp 128-133° (25 mm), [lit.[57] 120° (14 mm)].

p-Nitrophenylacetyl chloride. - A solution of 100 g of p-nitrophenylacetic acid and 250 g of thionyl chloride in 200-ml of absolute ether was refluxed for one hour and then allowed to stand for 45 hr. at room temperature with occasional shaking. The ether and excess thionyl chloride were removed under aspirator vacuum and the residue triturated with petroleum ether (30-60°) which yielded 103.5 g (94%) of crude product mp 42-46°. Recrystallization from ligroine-petroleum ether (30-60°) yielded p-nitrophenylacetyl chloride as white needles mp 45-46°, [lit.[58] mp 46-47°].

α-Carbethoxyethylidenetriphenylphosphorane (XIXa). - This ylid was prepared by a modification of the procedure of Isler et.al.[46] One hundred and forty six grams of triphenylphosphine, 100 g of ethyl-2-bromopropionate and about one gram of trimethylphenylammonium iodide (catalyst) were dissolved in 600-ml of dry benzene and heated at 60-70° for 45 hr. After vacuum evaporation of the benzene, the semi-solid residue was distributed between water and ether. Dilute sodium hydroxide was dripped into the aqueous phase while stirring vigorously until the solution was barely alkaline to phenolphthalein. The resulting yellow precipitate was filtered, washed with water, dried on a clay plate overnight and recrystallized from ethyl acetate-ligroine, yielding 72 g (36%) of crude ylid mp 161-162°. Several recrystallizations from ethyl acetate-ligroine yielded pure ylid mp 164° (cor.), [lit.[46] mp 156-157°, lit.[59] 161-164°].

Anal. Calcd. for $C_{23}H_{23}O_2P$: C, 76.23; H, 6.39. Found: C, 76.29; H, 6.32.

The infrared spectrum in methylene chloride solvent exhibited strong absorption around 1600 cm^{-1}, C=O stretch. An nmr spectrum in methylene chloride was also consistent with the expected structure.

It appears that the melting point, crystalline structure and color of this ylid reported by Isler et.al.[46] were really those of triphenylphosphine oxide. Their elemental analysis was consistent with the ylid however.

2-Bromo-tert-butylpropionate. - This compound was prepared by the method of Korst.[60] Three different solutions of 153 g of 2-bromopropionic acid, 100-ml of absolute ether and 10-ml of concentrated sulfuric acid were placed in 16 oz soda bottles and cooled to about -20°. Approximately 200-ml of liquid iso-butylene was added to each, the bottles capped and shaken and allowed to stand at room temperature for 48 hr. The bottles were then cooled to about -20°, opened and poured into ice-water containing about 300 g of potassium carbonate. After the excess iso-butylene boiled away, the aqueous phase was separated from the ether layer and repeatedly extracted with ether. The ether solutions were combined, extracted once with 10% potassium carbonate solution, once with water and dried over anhydrous potassium carbonate. The ether was then

evaporated and the residue vacuum distilled yielding 438 g (71%) of 2-bromo-tert-butylpropionate bp 76-77° (25 mm), [lit.[61] bp 51-52° (10 mm)].

α-Carbo-tert-butoxyethylidenetriphenylphosphorane (XIXb).- A solution of 580 g of triphenylphosphine and one gram of trimethylphenylammonium iodide in about three liters of benzene was distilled until the distillate and solution were clear. After cooling to room temperature 438 g of 2-bromo-tert-butylpropionate dried over anhydrous potassium carbonate was added and the solution refluxed for six days. The white solid resulting was filtered and dissolved in water. Dropwise addition of 10% sodium hydroxide to this water solution while stirring vigorously precipitated the ylid as a yellow solid which was filtered, washed with water and dried to constant weight on a clay plate: yield 722 g (95%, crude). Recrystallization from ethyl acetate yielded 491 g (60%) of pure ylid mp 168-169° (cor.).

Anal. Calcd. for $C_{25}H_{27}PO_2$: C, 76.90; H, 6.97. Found: C, 77.03; H, 7.24

An infrared spectrum of this material in methylene chloride solvent exhibited a strong absorption around 1600 cm^{-1}, carbonyl stretch. An nmr spectrum in methylene chloride was also consistent with the expected structure.

4-Phenyl-2-methylbutadienoic acid (XVIIIc). -

From ethyl ylid (XIXa)

A solution of 4.6 g of phenylacetyl chloride in 10-ml of dry tetrahydrofuran was added dropwise to a stirred solution of 21.7 g of α-carbethoxyethylidenetriphenylphosphorane (XIXa) in 70-ml of dry tetrahydrofuran. The white phosphonium chloride precipitated within a few minutes. After refluxing for about one half hour the reaction mixture was cooled, filtered and the precipitate washed with 20-ml of tetrahydrofuran. The tetrahydrofuran solutions were combined and stirred overnight at room temperature with 90-ml of 2M sodium hydroxide. Separation and acidification of the water phase with dilute hydrochloric acid yielded 0.3 g of yellow-white solid mp 95-107°, which exhibited a medium infrared absorption in methylene chloride solvent at 1940 cm^{-1} (=C=). Attempted recrystallization of this acid from benzene and ethanol-water lead to what appeared to be yellow polymerization products. Treatment of a tetrahydrofuran solution of another identical reaction mixture with dilute sodium hydroxide under a nitrogen atmosphere also lead to yellow non-allenic and unidentified products.

From tert-butyl ylid (XIXb).

A solution of 6.96 g of phenylacetyl chloride in 20-ml of tetrahydrofuran was added dropwise to a stirred solution of 35.1 g of α-carbo-tert-butoxyethylidenetriphenylphosphorane (XIXb) in 200-ml of tetrahydrofuran. After about 75% of the

acid chloride was added, the phosphonium chloride began to precipitate. The solution was refluxed for one hour, cooled and about one gram of 2,6-di-tert-butylphenol (anti-oxidant) was added.[50] After filtration the precipitate (19.1 g, quantitative yield) was washed with 50-ml of tetrahydrofuran. To the combined tetrahydrofuran solutions a cooled mixture of 200-ml of water made up to 300-ml total volume with concentrated sulfuric acid was added with stirring over a period of about ten minutes. Gentle boiling occurred during the beginning of the water-sulfuric acid addition. Stirring at room temperature was continued for 36 hr. The reaction mixture was then poured into a mixture of 300-ml of ether and 300-ml of water and extracted. The aqueous phase was further extracted twice with 100-ml portions of ether. Prolonged extractions of the combined ether phases with dilute sodium bicarbonate solution dissolved the allene acid in the aqueous phase as its carboxylate anion. Addition of dilute hydrochloric acid to the sodium bicarbonate solution precipitated 5.85 g (74%) of crude 4-phenyl-2-methylbuta-dienoic acid (XVIIIc) mp 111-114°.

Purification of the acid was very tedious. The acid was redissolved in ether and extracted with dilute sodium bicarbonate solution. Acidification of this extract with 1-2% hydrochloric acid was stopped when the allene acid just began to precipitate in a sizeable quantity (about 100 mg). This initial precipitate was filtered and discarded. Acidification

of the filtrate continued until the solution began to foam slightly. This point of the acidification was also marked by a distinct change in the precipitate from small granules to curds. When the solution was filtered at this point, the precipitated product was significantly purer (mp 115-117°) than when acidification was continued to completion (mp 112-116°). Reprecipitation of the acid by the method just described twice more resulted in 3.04 g (39%) of pure 4-phenyl-2-methylbutadienoic acid mp 121.0-121.6° dec.

Anal. Calcd, for $C_{11}H_{10}O_2$: C, 75.84; H, 6.19; mol. wt. 174. Found: C, 75.80; H, 6.01; mol. wt. (neutralization equivalent) 174.

Structural proof was afforded by its nmr spectrum in deuterochloroform which showed the 2-methyl group as a doublet at 2.04 ppm (J = 3cps), the 4-proton as a quartet at 6.6 ppm (J = 3 cps), the aromatic protons at 7.36 ppm and carboxyl group proton at 9.24 ppm. An infrared spectrum in chloroform solvent showed O-H stretching absorption in the 3300-2700cm^{-1} region, =C= at 1930 cm^{-1}, C=O at 1680 cm^{-1} and monosubstituted phenyl ring at 686 cm^{-1}.

4-(4'-Methylphenyl)-2-methylbutadienoic acid (XVIIIb). - This material was prepared from 7.59 g of p-methylphenylacetyl chloride and 35.1 g of α-carbo-tert-butoxyethylidenetriphenylphosphorane (XIXb) using a procedure

identical to that described earlier for the preparation of 4-phenyl-2-methylbutadienoic acid (XVIIIc). The crude XVIIIb formed amounted to 4.87 g (57%), mp 114-115°. Purification by triple reprecipitation as described for XVIIIc yielded 1.14 g (13%) of pure 4-(4'-methylphenyl)-2-methylbutadienoic acid mp 119.0-120.2° dec.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.53; H, 6.42; mol. wt. 188. Found: C, 76.53; H, 6.48; mol. wt. (neutralization equivalent) 188.

The nmr spectrum of XVIIIb in deuteriochloroform showed the 2-methyl group as a doublet at 1.98 ppm (J = 2 cps), the 4'-aromatic methyl group at 2.34 ppm as a singlet, the 4-proton as a quartet at 6.59 ppm (J = 2 cps) and the aromatic protons at 7.24 ppm. Further structural proof was afforded by an infrared spectrum in chloroform which showed O-H stretch in the 3300-2700 cm^{-1} region, =C= at 1940 cm^{-1}, C=O at 1680 cm^{-1} and 1,4-substituted phenyl at 841 cm^{-1}.

4-(4'-Chlorophenyl)-2-methylbutadienoic acid (XVIIId). - This compound was prepared from 8.51 g of p-chlorophenylacetyl chloride and 35.1 g of α-carbo-tert-butoxyethylidenetriphenylphosphorane (XIXb) by a procedure identical to that described earlier for 4-phenyl-2-methylbutadienoic acid (XVIIIc). The crude XVIIId produced amounted to 6.07 g (64%), mp 109-116°. Purification by triple reprecipitation as described for XVIIIc yielded 1.50 g (16%) of pure 4-(4'-chlorophenyl)-2-methylbutadienoic acid mp 125-126° dec.

Anal. Calcd. for $C_{11}H_9ClO_2$: C, 63.32; H, 4.35; mol. wt. 209. Found: C, 63.19; H, 4.52; mol. wt. (neutralization equivalent) 212.

The nmr spectrum of XVIIId in deuteriochloroform showed the 2-methyl protons as a doublet at 2.03 ppm (J = 4 cps), the 4-proton as a quartet at 6.59 ppm (J = 3 cps), aromatic protons at 7.37 ppm and the carboxyl group proton at 8.47 ppm. Further structural proof was provided by its infrared spectrum in chloroform which exhibited O-H strech in the 3300-2700cm^{-1} region, =C= at 1930 cm^{-1}, C=O at 1680 cm^{-1} and 1,4-substituted phenyl at 844 cm^{-1}.

Attempted preparation of 4-(4'methoxyphenyl)-2-methyl-butadienoic acid (XVIIIa). - A solution of 2.76 g of p-methoxyphenylacetyl chloride in 20-ml of dry tetrahydrofuran was added dropwise to a stirred solution of 11.7 g of α-carbo-tert-butoxy-ethylidenetriphenylphosphorane (XIXb) in 90-ml of dry tetrahydrofuran. This reaction mixture was refluxed for one hour, cooled to room temperature, the phosphonium chloride (6.4 g, quantitative yield) removed by filtration and washed with 20-ml of tetrahydrofuran. An infrared spectrum of the crude reaction mixture exhibited =C= at 1940 cm^{-1}, C=O at 1690 cm^{-1} and 1,4-substituted phenyl at 843 cm^{-1}. No evidence for unreacted acid chloride or ylid was present.

Hydrolysis of the tert-butyl-4-(4'-methoxyphenyl)-2-methylbutadienoate was attempted by adding the quantities

of acid shown in Table VI directly to filtered crude reaction mixtures prepared as stated above and stirring at room temperature for the given times. Work-up consisted of extraction of the acidified reaction mixtures with ether, extraction of the ether with dilute sodium bicarbonate and acidification of this solution with dilute hydrochloric acid. As summarized in Table VI acid hydrolysis was not successful; only 50% sulfuric acid yielded sufficient product for infrared identification, but this technique never did reach a preparative scale on repeated attempts.

TABLE VI

Ester Hydrolysis Techniques Attempted To Prepare 4-(4'-Methoxyphenyl)-2-Methylbutadienoic Acid (XVIIIa)

Acid Used	Quantity of Acid	Contact Time	% Yield
trifluoroacetic	5-ml	3 hrs.	0
trifluoroacetic	5-ml	30 min.	0
70% perchloric	1-ml	5 min.	0
toluenesulfonic	2 g	3 hrs.	0
50% sulfuric	120-ml	24 hrs.	trace
33% sulfuric	120-ml	24 hrs.	0
25% sulfuric	120-ml	24 hrs.	0
12% sulfuric	120-ml	30 hrs.	0
oxalic	3 g	48 hrs.	0
maleic	5 g	96 hrs.	0

Attempted preparation of 4-(4'nitrophenyl)-2-methyl-butadienoic acid (XVIIIe). - A solution of 3.0 g of p-nitrophenylacetyl chloride in 20-ml of dry tetrahydrofuran was added dropwise to a stirred solution of 11.7 g of α-carbo-tert-butoxyethylidenetriphenylphosphorane (XIXb) in 100-ml of dry tetrahydrofuran. The reaction mixture at the beginning of the acid chloride addition was yellow due to the ylid but gradually became a light red wine color and eventually at the end of the addition a deep purple color. No phosphonium chloride precipitate was evident at the end of the acid chloride addition or at the end of a one hour reflux period. Another 24 hrs. reflux did produce 1.4 g (22%) of the white phosphonium chloride. An infrared spectrum of the crude filtered reaction mixture showed no evidence for allene ester or unreacted p-nitrophenylacetyl chloride. These same results were duplicated several times. Another reaction was run by adding the ylid to the acid chloride, reverse addition, with similar results. More of the phosphonium chloride (3.3 g 51%) was produced, but no allene ester or unreacted p-nitrophenylacetyl chloride was detected in an infrared spectrum of the crude reaction mixture.

Determination of pKa's. - The pKa's of XVIIIb-d and cinnamic acid were determined in dilute aqueous solution by means of potentiometric titration using a Beckman Zeromatic II pH-meter with glass and calomel electrodes. The pH-meter was calibrated to read 4.20 before and after each trial using an equimolar (1.3×10^{-4} M) aqueous solution of benzoic acid and

sodium benzoate. A standardization trial using approximately 8 mg of benzoic acid dissolved in 500-ml of boiled UMR nuclear reactor pool water was then run by adding portions of a 0.00917M sodium hydroxide solution from a micro-buret and noting the pH one minute after each addition. Twenty five to thirty points were read to furnish data for a plot of pH verses milliliters of base consumed from which the end-point was determined. The fraction of base consumed at each point was then calculated and the pH verses this fraction was plotted on an expanded-scale graph paper. An identical procedure was used to get similar graphs for duplicate trials with allene acids XVIIIb-d and for one trial with trans-cinnamic acid.

The allene acid samples were prepared by stirring about 12 mg of each acid with 500-ml of water for two hours at room temperature. The solutions (about 1.3×10^{-4} M) were then filtered to remove any undissolved material, adjusted to 25°C and then titrated as explained for the benzoic acid sample. pKa's were calculated for each acid from Equation 1.

Equation 1: $pKa'' = pKa' - (pH' - pH'')$

pKa'' is the pKa at a given point for an unknown acid.

pKa' is the pKa of benzoic acid, 4.202[52].

pH' is the pH of the benzoic acid sample at a given fraction titrated.

pH'' is the pH of the unknown acid at the same fraction titrated as that for benzoic acid.

The pKa's reported below in Table VII are averages of pKa'' for each trial computed from about twenty points between 0.200 and 0.700 fraction titrated. The data are given in Appendix II.

TABLE VII

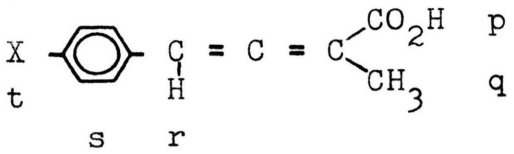
Summary of Calculated pKa's

Trial	XVIIIb	XVIIIc	XVIIId	trans-cinnamic acid
1	4.16	4.15	4.14	4.42
2	4.13	4.14	4.18	

Attempts to correlate acidities of XVIIIb,c,d with spectral data. - The nmr spectra of XVIIIb,c,d were obtained with 0.287M solutions of these acids in dimethylsulfoxide; the data in ppm are shown in Table VIII.

TABLE VIII

nmr Spectra of XVIIIb,c,d in Dimethylsulfoxide



Compound	X	Type of Protons p	q (doublet)	r (quartet)	s	t
XVIIIb	CH_3	12.53	1.86 (4)	6.73 (4)	7.26	2.34
XVIIIc	H	12.62	1.93 (4)	6.77 (4)	7.43	--
XVIIId	Cl	12.57	1.93 (4)	6.81 (4)	7.47	--

Numbers in parentheses are coupling constants given in cps.

The ultraviolet spectra of XVIIIb,c,d were obtained from equimolar acetonitrile solutions; the data are shown in Table IX.

TABLE IX

Ultraviolet Spectra of XVIIIb,c,d in Acetonitrile

Compound	max, mu		
XVIIIb	251 (25,000)	282 (2,400)	292 (1,500)
XVIIIc	246 (24,000)	279 (2,000)	288 (1,250)
XVIIId	253 (28,000)	284 (2,700)	295 (1,500)

Numbers in parentheses are extinction coefficients.

CONCLUSION

Although synthetic problems forced a study of resonance effects in non-coplanar acetylenes to be postponed, it is still a worthwhile problem to solve even in the light of the results obtained for allenes. The fact that allenes, which possess only one sp hybridized carbon atom, do not transmit resonance effects makes the acetylene problem that much more intriguing, since acetylenes possess two sp hybridized carbon atoms. Hopefully, further studies will answer this question.

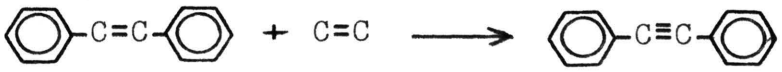
Since the acidities of the three allene carboxylic acids synthesized were essentially the same, the only conclusion to be drawn from this is that resonance effects are not transmitted through the allene function. In view of this result interpretations resting upon cylindrical symmetry of the pi cloud in an allene must be viewed sceptically.

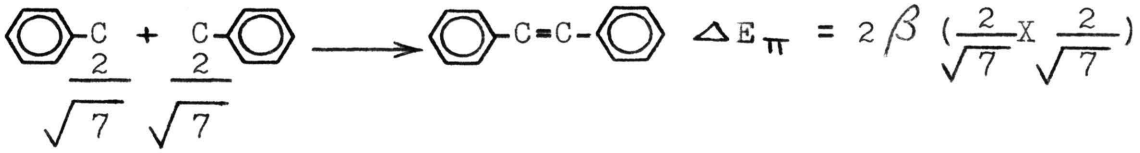
APPENDIX I

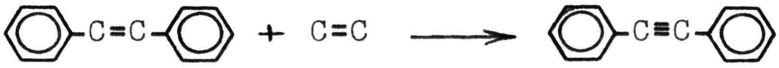
Simplified Molecular Orbital Calculations of Pi Electron Energies of Planar and Non-planar Conformations of Tolane

Use of the Dewar RS technique[62,63] to estimate pi electron energies of planar and non-planar tolane conformations is shown below.

Planar: represented by a stilbene plus an ethylene pi system.

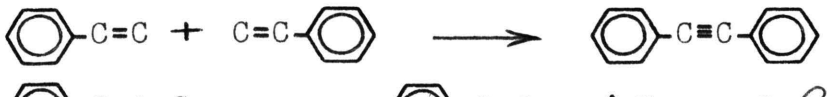


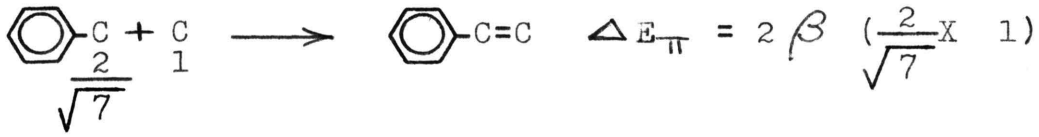


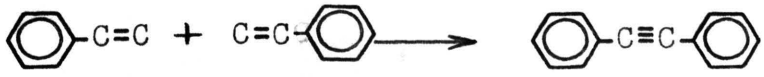


$$\Delta E_{\pi} = 2\beta \left(\frac{2}{\sqrt{7}} X \frac{2}{\sqrt{7}}\right) + 2\beta = 3.14\beta$$

Non-planar: represented by two independent styrene pi systems







$$\Delta E_{\pi} = 2\beta \left(\frac{2}{\sqrt{7}} X\ 1\right) X\ 2 = 3.03\beta$$

Difference between planar and non-planar =

$$3.14\beta - 3.03\beta = 0.11\beta$$

APPENDIX II

Data for Calculation of pKa's of XVIIIb-d and trans-Cinnamic Acid

Benzoic Acid Calibration Data

ml base consumed	pH	ml base consumed	pH
0.00	3.64	4.40	4.34
0.30	3.68	4.70	4.42
0.50	3.71	5.00	4.54
0.80	3.73	5.30	4.65
1.20	3.78	5.60	4.81
1.80	3.86	5.90	4.97
2.00	3.88	6.20	5.18
2.30	3.92	6.50	5.43
2.60	3.98	6.80	5.81
2.90	4.02	7.00	6.01
3.20	4.06	7.20	6.34
3.50	4.13	7.40	6.78
3.80	4.19	7.60	7.18
4.10	4.24	7.90	7.60

7.46-ml required for neutralization

Data for XVIIIb, Trial 1

ml base consumed	pH	ml base consumed	pH
0.00	3.63	4.70	4.54
0.50	3.68	5.00	4.69
1.00	3.73	5.30	4.89
1.50	3.80	5.60	5.09
2.00	3.87	5.90	5.36
2.30	3.91	6.20	5.64
2.60	3.97	6.50	6.02
2.90	4.02	6.70	6.41
3.20	4.07	6.90	6.98
3.50	4.13	7.00	7.11
3.80	4.21	7.10	7.21
4.10	4.30	7.20	7.28
4.40	4.40	7.40	7.42

6.88-ml required for neutralization.

average pKa between 0.20 and 0.70 fraction titrated = 4.16.

Data for XVIIIb, Trial 2

ml base consumed	pH	ml base consumed	pH
0.00	3.58	4.40	4.37
0.50	3.63	4.70	4.49
1.00	3.69	5.00	4.65
1.50	3.75	5.30	4.80
2.00	3.81	5.60	5.01
2.30	3.87	5.90	5.23
2.60	3.92	6.20	5.48
2.90	3.97	6.50	5.76
3.20	4.02	6.80	6.18
3.50	4.09	7.00	6.65
3.80	4.17	7.20	7.01
4.10	4.25	7.40	7.27

7.06-ml required for neutralization.

Average pKa between 0.200 and 0.575 fraction titrated = 4.13.

Data for XVIIIc, Trial 1

ml base consumed	pH	ml base consumed	pH
0.00	3.63	4.70	4.44
0.50	3.68	5.00	4.59
1.00	3.73	5.30	4.76
1.30	3.76	5.60	4.96
1.60	3.80	5.90	5.19
1.90	3.83	6.20	5.45
2.20	3.87	6.50	5.74
2.50	3.91	6.80	6.22
2.80	3.98	7.10	6.95
3.10	4.02	7.30	7.23
3.40	4.08	7.50	7.43
3.70	4.13	7.70	7.54
4.00	4.21	7.90	7.66
4.30	4.30		

7.17-ml required for neutralization.

Average pKa between 0.200 and 0.675 fraction titrated = 4.15.

Data for XVIIIc, Trial 2

ml base consumed	pH	ml base consumed	pH
0.00	3.64	5.00	4.39
0.50	3.68	5.30	4.50
1.00	3.72	5.60	4.63
1.50	3.77	5.90	4.77
2.00	3.82	6.20	4.96
2.30	3.86	6.50	5.20
2.60	3.91	6.80	5.42
2.90	3.94	7.10	5.70
3.20	3.99	7.40	6.11
3.50	4.03	7.60	6.60
3.80	4.09	7.70	6.77
4.10	4.17	7.90	7.05
4.40	4.23	8.00	7.20
4.70	4.30		

7.72-ml required for neutralization.

Average pKa between 0.200 and 0.675 fraction titrated = 4.14.

Data for XVIIId, Trial 1

ml base consumed	pH	ml base consumed	pH
0.00	3.61	4.10	4.59
0.50	3.67	4.40	4.82
1.00	3.73	4.70	5.05
1.50	3.81	5.00	5.33
2.00	3.90	5.30	5.73
2.30	3.97	5.60	6.25
2.60	4.01	5.80	6.79
2.90	4.10	6.00	7.18
3.20	4.18	6.20	7.41
3.50	4.30	6.40	7.62
3.80	4.43		

5.93-ml required for neutralization.

Average pKa between 0.200 and 0.550 fraction titrated = 4.14.

Data for XVIIId, Trial 2

ml base consumed	pH	ml base consumed	pH
0.00	3.66	3.80	4.59
0.50	3.72	4.10	4.83
1.00	3.79	4.40	5.07
1.50	3.87	4.70	5.34
2.00	3.96	5.00	5.66
2.30	4.02	5.20	5.90
2.60	4.11	5.40	6.30
2.90	4.20	5.60	6.87
3.20	4.30	5.80	7.22
3.50	4.43	6.00	7.41

5.54-ml required for neutralization.

Average pKa between 0.200 and 0.500 fraction titrated = 4.18.

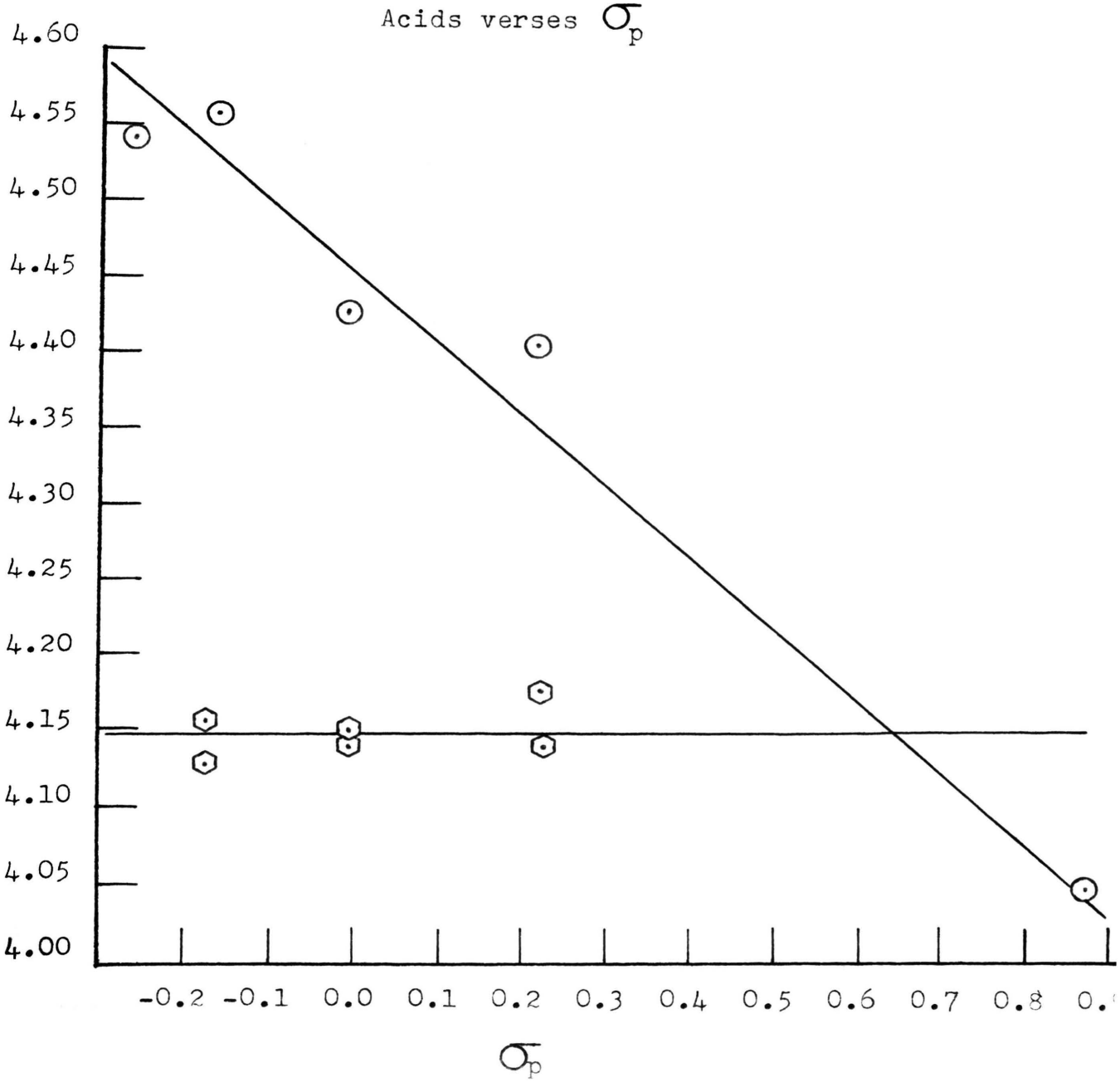
Data for trans-Cinnamic Acid

ml base consumed	pH	ml base consumed	pH
0.00	3.92	4.10	4.73
0.50	3.97	4.40	4.89
1.00	4.02	4.70	5.07
1.50	4.07	5.00	5.28
2.00	4.16	5.30	5.56
2.30	4.20	5.60	5.81
2.60	4.26	5.90	6.40
2.90	4.33	6.10	6.78
3.20	4.41	6.30	7.06
3.50	4.50	6.50	7.24
3.80	4.62	6.70	7.39

6.18-ml required for neutralization.

Average pKa between 0.200 and 0.700 fraction titrated = 4.42.

pKa's of Allene Carboxylic Acids XVIIIb,c,d and trans-Cinnamic Acids verses σ_p



⊙ = pKa's of substituted trans-cinnamic acids[52]

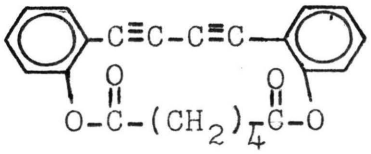
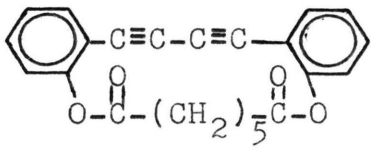
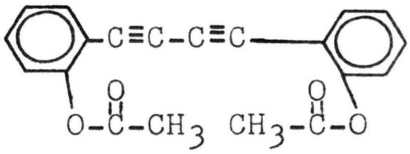
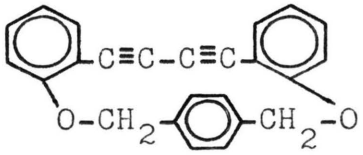
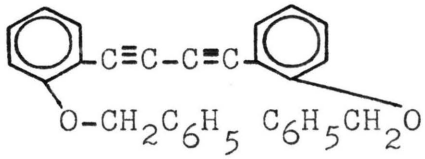
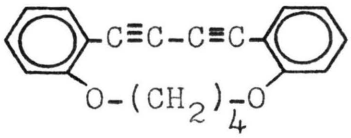
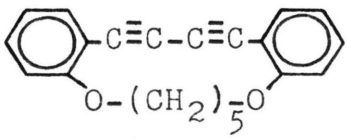
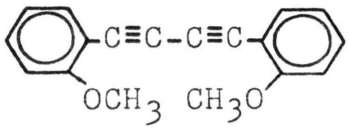
⊙ = pKa's of allene acids determined in these laboratories, April 1967.

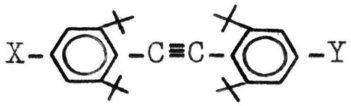
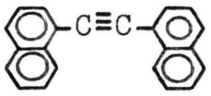
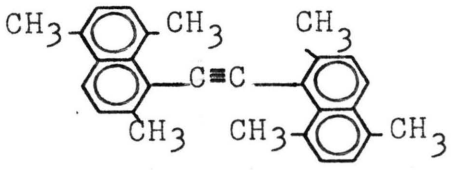
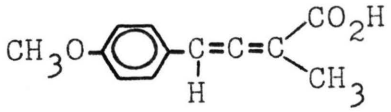
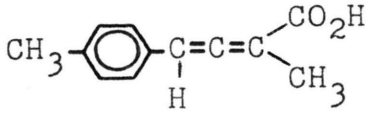
σ_p = -0.268 for p-CH_3O-, -0.170 for p-CH_3-, 0.000 for p-H-,[3] 0.226 for p-Cl-, 0.778 for p-NO_2-.[64]

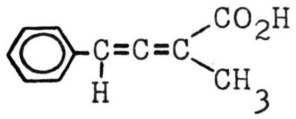
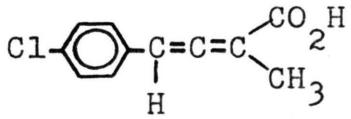
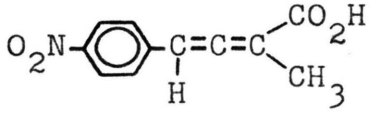
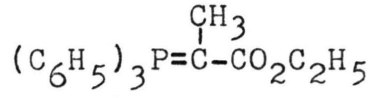
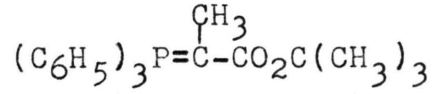
Figure 1. pKa's of XVIIIb,c,d and trans-Cinnamic Acid vs. σ_p.

APPENDIX III

Name and Structure of Compounds Numbered in This Dissertation

Number	Structure	Name
I		diphenyldiacetylene-o,o'-hexanedioate
II		diphenyldiacetylene-o,o'-heptanedioate
III		o,o'-diacetoxydiphenyl-diacetylene
IV		o,o'-p-xylydioxy-diphenyldiacetylene
V		o,o'-dibenzyloxydiphenyl-diacetylene
VI		o,o'-butanedioxy-diphenyldiacetylene
VII		o,o'-pentanedioxy-diphenyldiacetylene
VIII		o,o'-dimethoxydiphenyl-diacetylene

Number	Structure	Name
IX	$(CH_3)_2$-C(OCH$_3$)-CH=C=CHCHO	5-methoxy-5-methyl-2,3-hexadienal
X	$(CH_3)_2C{=}C{=}C{=}CHCHO$	5-methyl-2,3,4-hexatrienal
XI	$CH_2{=}C{=}CHCO_2H$	butadienoic acid
XII	$C_6H_5CH{=}C{=}CHCO_2H$	4-phenylbutadienoic acid
XIII	$CH_3CH{=}CH{-}CH{=}CHCO_2H$	trans, trans - 2,4-hexadienoic acid
XIV	$CH_3CH_2C{\equiv}C{-}CO_2H$	2-pentynoic acid
XV		p-X, p'-Y-2,2',6,6'-tetra-tert-butyldiphenyl-acetylene
XVI		di-1-naphthylacetylene
XVII		bis-(2,5,8-trimethyl-1-naphthyl)-acetylene
XVIII$_a$		4-(4'-methoxyphenyl)-2-methylbutadienoic acid
XVIII$_b$		4-(4'-methylphenyl)-2-methylbutadienoic acid

Number	Structure	Name
XVIIIc		4-phenyl-2-methylbutadienoic acid
XVIIId		4-(4'-chlorophenyl)-2-methylbutadienoic acid
XVIIIe		4-(4'-nitrophenyl)-2-methylbutadienoic acid
XIXa		α-carbethoxyethylidene-triphenylphosphorane
XIXb		α-carbo-tert-butoxy-ethylidenetriphenyl-phosphorane

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