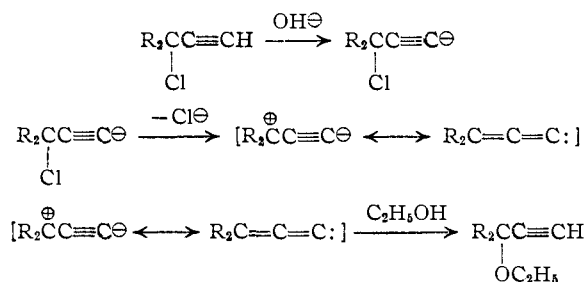# Carbenes from Derivatives of Ethynylcarbinols. The Synthesis of Alkenylidenecyclopropanes[1]

BY H. D. HARTZLER

Alkenylidenecyclopropanes have been synthesized in moderate yields by reactions of derivatives of ethynylcarbinols with base in the presence of olefins. A reaction scheme involving $\gamma$-elimination to give alkenylidene carbenes is proposed. Evidence for the formation of diarylvinylidene carbenes as intermediates in the formation of tetraarylhexapentaenes is given.
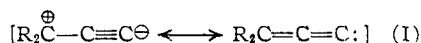
Ethynyldialkylcarbinyl chlorides undergo very slow solvolysis in aqueous ethanol at room temperature.[2-5] In acidic solution, isomerization of the chlorides to chloroallenes can occur.[3] In the presence of base, these tertiary acetylenic halides undergo a replacement reaction which is kinetically of second order.[2,4,5] The products are the unrearranged tertiary acetylenic ethers. Since a bimolecular displacement on the tertiary halide appears highly unlikely, the following mechanism was advanced[2]

$$R_2CC\equiv CH \xrightarrow{OH^\ominus} R_2CC\equiv C^\ominus$$
$$\underset{Cl}{|} \qquad\qquad \underset{Cl}{|}$$

$$R_2CC\equiv C^\ominus \xrightarrow{-Cl^\ominus} [R_2\overset{\oplus}{C}C\equiv C^\ominus \longleftrightarrow R_2C=C=C:]$$
$$\underset{Cl}{|}$$

$$[R_2\overset{\oplus}{C}C\equiv C^\ominus \longleftrightarrow R_2C=C=C:] \xrightarrow{C_2H_5OH} R_2CC\equiv CH$$
$$\underset{OC_2H_5}{|}$$

The rate-determining step of the reaction is presumed to be the loss of chloride ion from the acetylenic anion. Evidence in support of this scheme is found in the observations that the first step is reversible and very fast in comparison to the over-all rate of reaction,[6] and that no second-order reaction is observed when the ethynyl hydrogen is replaced with an alkyl group.[4] Additional evidence for the reaction sequence was obtained by the direct alkylation of amines with the tertiary acetylenic chlorides[5]

$$R_2CC\equiv CH + R'_2NH \longrightarrow R_2CC\equiv CH$$
$$\underset{Cl}{|} \qquad\qquad\qquad \underset{R'_2N}{|}$$
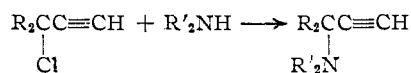
The purpose of the present work was to obtain more information concerning the nature of the highly unsaturated intermediate represented by the resonance hybrid I.

$$[R_2\overset{\oplus}{C}-C\equiv C^\ominus \longleftrightarrow R_2C=C=C:] \quad (I)$$

The addition of carbenes to olefins[7] has become the

most widely investigated reaction of carbenes, and has been shown to afford information concerning the electronic state[8-11] and relative reactivity[12-14] of the divalent carbon intermediates. Accordingly, this paper presents the demonstration of the reaction of I with olefins, and the following paper[15] describes the stereochemistry and relative rates of the olefin addition reactions.

## Results and Discussion

**Dialkylvinylidene Carbenes.**—The addition of 3-chloro-3-methyl-1-butyne (II) to a slurry of potassium $t$-butoxide in styrene resulted in the formation of a hydrocarbon, $C_{13}H_{14}$, in 48% yield. The hydrocarbon was assigned the structure of 1-(2-methylpropenylidene)-2-phenylcyclopropane (III) on the basis of spectroscopic and chemical evidence. The infrared spectrum of III showed strong absorption at 2020 cm.$^{-1}$ which may be attributed to the allenic group.[16] No evidence of additional unsaturation other than the aromatic ring was seen. The presence of the cyclopropane ring was suggested by absorption at 1030 cm.$^{-1}$ [17,18] The ultraviolet spectrum of III showed only strong end absorption with no maximum, thus demonstrating the absence of a conjugated alkenyl benzene. The nuclear magnetic resonance (n.m.r.) spectrum of III showed absorption due to the aromatic hydrogen at $\tau^{20} = 2.91$, methyl hydrogens at $\tau = 8.28$, benzylic hydrogen split into a quartet centered at $\tau = 7.25$, and the methylene hydrogens each split into partially resolved quartets centered at $\tau = 8.16$ and 8.60.

(1) Parts of this work were reported in preliminary form by H. D. Hartzler, J. Am. Chem. Soc., 81, 2024 (1959), and at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(2) G. F. Hennion and D. E. Maloney, J. Am. Chem. Soc., 73, 4735 (1951).

(3) A. N. Pudovik, J. Gen. Chem., U.S.S.R., 21, 1462, 1811 (1951); C. A., 46, 4467, 7033 (1952).

(4) A. Burawoy and E. Spinner, J. Chem. Soc., 3752 (1954).

(5) G. F. Hennion and K. W. Nelson. J. Am. Chem. Soc., 79, 2142 (1957).

(6) The results of deuterium exchange studies of Shiner and Wilson; private communication from Professor V. J. Shiner, Jr.

(7) W. von E. Doering and A. K. Hoffmann, J. Am. Chem. Soc., 76, 6162 (1954).

(8) P. S. Skell and A. Y. Garner, ibid., 78, 5430 (1956).

(9) R. M. Etter, H. S. Skovronek and P. S. Skell, ibid., 81, 1008 (1959).

(10) P. S. Skell and J. Klebe, ibid., 82, 247 (1960).

(11) K. R. Kopecky. G. S. Hammond and P. A. Leemakers, ibid., 83, 2397 (1961).

(12) W. von E. Doering and W. A. Henderson, Jr., ibid., 80, 5274 (1958).

(13) P. S. Skell and R. M. Etter, Chemistry & Industry, 624 (1958).

(14) G. L. Closs and G. M. Schwartz, J. Am. Chem. Soc., 82, 5729 (1960).

(15) H. D. Hartzler, ibid., 83, 4997 (1961).

(16) L. J. Bellamy. "The Infra-Red Spectra of Complex Molecules." John Wiley and Sons, Inc., New York, N. Y., 1954. pp. 52-53.

(17) Ibid., pp. 27-28.

(18) All of the alkenylidenecyclopropanes reported here exhibited strong absorption in this region with the exception of the allene derived from tetramethylethylene which has no hydrogen on the cyclopropane ring. This along with other compilations[19] of spectra of cyclopropane hydrocarbons suggests that the absorption in this region (1020-1030 cm.$^{-1}$) is a satisfactory diagnostic for cyclopropane hydrogen in hydrocarbons.

(19) H. E. Simmons and R. D. Smith, J, Am. Chem. Soc,, 81, 4256 (1959).

(20) G. V. D. Tiers. J. Phys. Chem., 62, 1151 (1958).

$$(CH_3)_2CC\equiv CH + C_6H_5CH=CH_2 \xrightarrow{KOt-C_4H_9} C_6H_5CH\text{—}C=C=C(CH_3)_2$$

II   Cl                                                        III (with CH$_2$ bridge)

$$III \xrightarrow[C_2H_5OH]{H_2/Pd} C_6H_5(CH_2)_3CH(CH_3)_2 \xleftarrow[KOH]{N_2H_4} C_6H_5CO(CH_2)_3CH(CH_3)_2$$

IV

III $\xrightarrow{O_3, C_2H_5OH}$

$$CH_3COCH_3 + C_6H_5CH\text{—}CCOOC_2H_5 \xrightarrow[2, H_3O^+]{1, NaOCH_3} C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}COOH + C_6H_5CH_2CH\overset{OH}{\overset{|}{C}}CH_2CH_2C_6H_5$$

V   OH                                        VI                      |
                                                                     COOH
                                                              VII   COCOOH
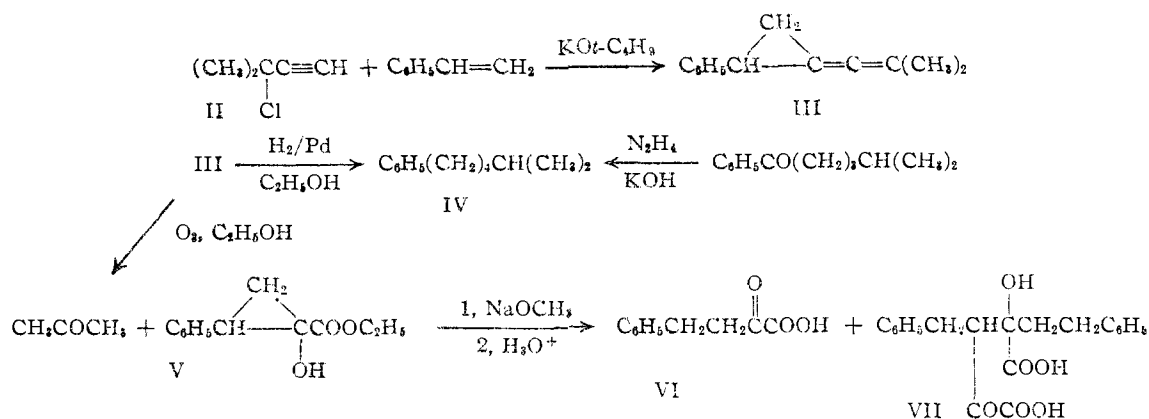
The two methylene hydrogens would be expected to be split into quartets since they are non-equivalent and would split each other as well as be split by the benzylic hydrogen. The situation is analogous to that of styrene oxide.[21] The combined spectral data are consistent only with the structure III.

Hydrogenation of III in 95% ethanol over palladium-on-carbon gave 5-methyl-1-phenylhexane (IV) in 89% yield. Compound IV was synthesized independently by a Wolff-Kishner reduction of 5-methyl-1-phenyl-1-hexanone. The two products had identical infrared spectra, and a mixture of their diacetamido derivatives gave no melting point depression. The diacetamido derivatives were prepared by the standard procedure[22] of nitration, reduction and acetylation. The pure diamide was obtained from III in 61% yield. The other possible products of hydrogenation, 2,4-dimethyl-1-phenylpentane and 5-methyl-2-phenylhexane, were also synthesized. The diacetamido derivatives of these hydrocarbons were shown to be different from that of IV. Hydrogenation of III could not be stopped without ring opening. There was no diminution in the rate of absorption of the third equivalent of hydrogen. When the hydrogenation was interrupted after the absorption of two equivalents of hydrogen, an examination of the infrared spectrum of the crude product indicated a complex mixture. A similar, facile ring opening during hydrogenation has been observed with methylenecyclopropane;[23] and hydrogenolysis of the cyclopropane ring appears to be a general reaction for vinyl- and alkylidenecyclopropanes.[24] The ease of ring hydrogenolysis suggests a conjugate addition of hydrogen, and the direction of ring opening may be rationalized along lines similar to those proposed by Ullman.[24] Addition of hydride ion to III would be expected to give a carbanion–metal complex of either structure A or B. Either species should very readily undergo ring cleavage to give the less-strained, benzylic carbanion A′ or B′. Further hydrogenation would lead ultimately to IV.

Ozonolysis of III in ethyl acetate solution produced a complex mixture of products. Acetone

(21) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 48–49.

(22) V. N. Ipatieff and L. Schmerling, J. Am. Chem. Soc., 59, 1056 (1937).

(23) J. T. Gragson, K. W. Greenlee, J. M. Derfer and C. E. Boord, ibid., 75, 3344 (1953).

(24) E. F. Ullman, ibid., 81, 5386 (1959).

was obtained in 65% yield and CO$_2$ in 6% yield. Traces of benzaldehyde and malonic acid were also identified, but the major product was an intractable oil. Most of the oil was soluble in dilute aqueous sodium hydroxide giving the red color typical of aldol condensation products. Ozonolysis of III in
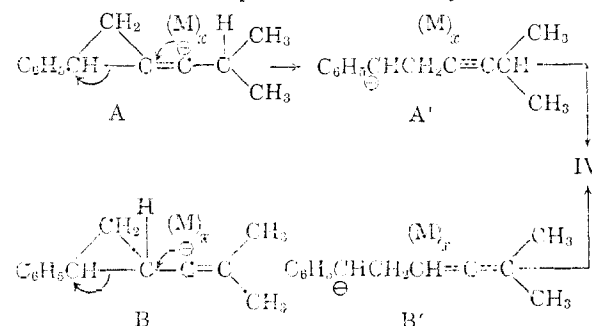


ethanol proved to be more useful. Traces of CO$_2$ were obtained when the ozonolysis was performed at 0°, while there was no evidence for CO$_2$ formation at −80°. Acetone was obtained in 73% yield and ethyl 1-hydroxy-2-phenylcyclopropanecarboxylate (V) in 40% yield. Compound V could have been contaminated by small amounts of an isomer, ethyl benzylpyruvate, but no 2,4-dinitrophenylhydrazine derivative could be obtained from V.

The structure of V was established by its reaction with sodium methoxide to give benzylpyruvic acid (VI) and the aldol condensation product VII. Compound VI was oxidized with hydrogen peroxide to give β-phenylpropionic acid, and the structure of VII was confirmed by independent synthesis.[25] Benzylpyruvic acid has previously been obtained as the major product from the reaction of 2-hydroxy-3-phenyl-2-cyclobutenone (VIII) with base.[26] It was suggested[26] that VIII underwent a benzilic acid-type rearrangement to give the anion of 1-hydroxy-2-phenylcyclopropanecarboxylic acid (IX) which in turn ring opened in base to give the anion of VI.

The ring opening of V to give VI is analogous to the known conversion of cyclopropanol to propionaldehyde.[27]

The attack of ozone on III represents a preferential attack on the double bond bearing the methyl

(25) J. Bougalt. Compt. rend., 155, 477 (1912).

(26) L. Skattebøl and J. D. Roberts, J. Am. Chem. Soc., 80, 4085 (1958).
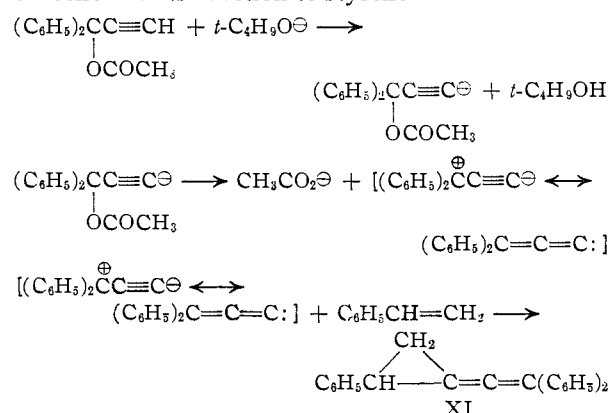
(27) J. K. Magrane, Jr., and D. L. Cottle, ibid., 64, 484 (1942); G. W. Stahl and D. L. Cottle, ibid., 65, 1782 (1943).

C₆H₅—◇=O → [C₆H₅CH——CCO₂⁻ with CH₃ and OH] →

VIII                IX

$$C_6H_5CH_2CH_2\overset{O}{\underset{||}{C}}CO_2^\ominus \rightarrow VI$$

groups. The attack at this position is favored at least by a factor of 3:1 in that acetone was isolated in 73% yield. The formation of V may be rationalized by the Criegee mechanism of ozonolysis[28] as is shown.

III $\xrightarrow{O_3}$ [C₆H₅CH—C=C ... structure with CH₃, O, CH₃] →

[C₆H₅CH—C=C structure with O—O⁻] + O=C(CH₃)₂

↓ C₂H₅OH

[C₆H₅CH—C=C structure with OC₂H₅, HO, O] → V

The addition of bromine and thiophenol to III gave oils which could not be crystallized. Upon standing, the bromine adduct evolved hydrogen bromide and blackened. There was no reaction between III and maleic anhydride.

The scope of the reaction of II with bases in the presence of olefins has not been extensively studied, but alkenylidenecyclopropanes have been obtained from cyclohexene, 2-methyl-1-butene, 2-methyl-2-butene, 1-hexene, 2,3-dimethyl-2-butene and cis and trans-2-butene.[15] The yields of allenes were 10–50%, but these are not optimum. Yields could probably be increased by using a higher ratio of olefin to II and by using potassium t-butoxide completely free of t-butyl alcohol. Potassium t-butoxide is the preferred base for the reaction. Sodium hydride dispersion in mineral oil was ineffective while butyllithium reacted with the alkenylidenecyclopropanes, and only poor yields of the allenes could be obtained.

With the exception of 1-(2-methylpropenylidene)-2,2,3,3-tetramethylcyclopropane (X), the alkenylidenecyclopropanes obtained from II and olefins are colorless liquids which air oxidize rapidly. Compound X is a low melting, air-stable solid which is

[(CH₃)₂ cyclopropane structure with CH₃, CH₃ ==C=C]

X

(28) P. S. Bailey, Chem. Revs., 58, 925 (1958).

characterized by extremely simple infrared and n.m.r. spectra. All of the alkenylidenecyclopropanes exhibit the characteristic allenic infrared absorption at 2020 ± 20 cm.⁻¹. This region is at slightly higher frequency than the frequency range normally cited[16] for allenes (1960–1980 cm.⁻¹). It is generally true that force constants of double bonds attached to a cyclopropane ring are increased above their acyclic values. Thus, a shift to higher frequencies has been observed for the double bond stretching frequency of methylenecyclopropane.[23] The frequency shift should not be as large with the allenes, for the stretching vibration of the allenic group involves mainly the motion of the central carbon atom. As a consequence, the compression of bond angles should not be as large with the alkenylidenecyclopropanes as it is with the alkylidenecyclopropanes. The shift above acyclic values is seen to be about 40 cm.⁻¹ in the case of the allenes as compared with a shift of 100 cm.⁻¹ for the olefins.

The spectrum of the alkenylidenecyclopropane obtained from cyclohexene is unusual in that there is a doublet at 2000 and 2030 cm.⁻¹. The splitting is not a result of the presence of two conformational isomers, for the relative intensities of the two bands were unaffected by temperature changes. The splitting is probably a result of Fermi resonance, although the coupled frequencies could not be determined from the spectrum. Splitting of the allenic band has been observed previously[29] and was suggested to be characteristic of an allene to which is attached a carboxyl, amide or ester group. The use of such a diagnostic would appear to be hazardous.

The formation of the alkenylidenecyclopropanes is most simply rationalized by the formation of the carbene I and its addition to the olefin.[30] Additional evidence for such a reaction course is given in the following paper.[15]

**Diarylvinylidene Carbenes.**—When acetic anhydride is added dropwise to a stirred slurry of powdered potassium hydroxide and diarylethynylcarbinols in ether, tetraarylhexapentaenes are formed in good yields.[31] The reaction sequence

$$Ar_2C-C\equiv CH + KOH + (CH_3CO)_2O \xrightarrow{(C_2H_5)_2O}$$
$$\underset{OH}{|}$$

$$Ar_2C=C=C=C=C=CAr_2$$

suggested by Cadiot[31] appeared unlikely in comparison with one involving carbenes, so the reaction was reinvestigated. An exothermic reaction ensues upon the addition of a solution of the acetate of diphenylethynylcarbinol in styrene to a slurry of potassium t-butoxide in styrene at −5°. The product was chromatographed on Florisil to give 1-diphenylvinylidene-2-phenylcyclopropane (XI) in 25% yield and 1,1,4,4-tetraphenyl-2-butyn-1,4-diol in 44% yield. Formation of the latter product is not unexpected since it has been shown[32] to be formed from diphenylethynyl carbinol and base.

(29) J. H. Wotiz and W. D. Celmer, J. Am. Chem. Soc., 74, 1860 (1952).

(30) The isomerization of II to (CH₃)₂C=C=CHCl, although possible under the reaction conditions, is not believed to be an intermediate reaction. Reactions of the chloroallene and base have been studied,³ and have been shown to differ in kind from those of II.

(31) P. Cadiot, Ann. Chim., [13] 1, 214 (1956).

(32) A. I. Zakharova, J. Gen. Chem. U.S.S.R., 11, 939 (1941); C. A., 37, 355 (1943).

$(C_6H_5)_2CC\equiv CH + KOtC_4H_9 + C_6H_5CH=CH_2 \longrightarrow$

$\underset{OCOCH_3}{|}$

$$C_6H_5CH\overset{CH_2}{\diagup\diagdown}C=C=C(C_6H_5)_2 + (C_6H_5)_2CC\equiv CC(C_6H_5)_2$$
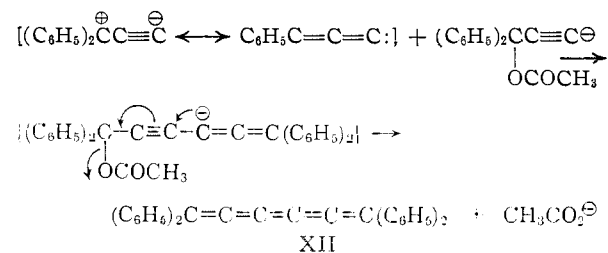$$\underset{XI}{} \qquad \underset{OH \quad OH}{|\quad|}$$

The structure of XI was confirmed by its infrared, ultraviolet and n.m.r. spectra. In the infrared, XI shows absorption due to the allenic group at 2000 cm.$^{-1}$. The ultraviolet spectrum of XI in ethanol showed absorption at 286 m$\mu$ ($\epsilon$ 1.8 $\times$ 10$^4$) and a shoulder at 225 m$\mu$ ($\epsilon$ 2.5 $\times$ 10$^4$). 1,1-Diphenyl-ethylene has a maximum at 250 m$\mu$ ($\epsilon$ 0.9 $\times$ 10$^4$). The n.m.r. spectrum of XI in deuteriochloroform provides unequivocal proof of its structure. In addition to the aromatic hydrogens ($\tau$ = 2.72 for C$_6$H$_5$ on the cyclopropane ring and $\tau$ = 2.83 for C$_6$-H$_5$ on the allenic carbon), the spectrum consists of three quartets of approximately equal area. The quartet for the benzylic hydrogen is centered at $\tau$ = 6.88 and the $\beta$-hydrogens are centered at $\tau$ = 7.80 and 8.17.

The most satisfactory explanation for the formation of XI is the formation of diphenylvinylidene carbene and its addition to styrene

$(C_6H_5)_2CC\equiv CH + t\text{-}C_4H_9O^\ominus \longrightarrow$

$\underset{OCOCH_3}{|}$

$$(C_6H_5)_2CC\equiv C^\ominus + t\text{-}C_4H_9OH$$
$$\underset{OCOCH_3}{|}$$

$(C_6H_5)_2CC\equiv C^\ominus \longrightarrow CH_3CO_2^\ominus + [(C_6H_5)_2\overset{\oplus}{C}C\equiv C^\ominus \longleftrightarrow$

$\underset{OCOCH_3}{|}$

$$(C_6H_5)_2C=C=C:]$$

$[(C_6H_5)_2\overset{\oplus}{C}C\equiv C^\ominus \longleftrightarrow$

$(C_6H_5)_2C=C=C:] + C_6H_5CH=CH_2 \longrightarrow$

$$C_6H_5CH\overset{CH_2}{\diagup\diagdown}C=C=C(C_6H_5)_2$$
$$\underset{XI}{}$$

Formation of the hexapentaene XII most likely occurs by reaction of the carbene with anion of the acetylenic acetate

$[(C_6H_5)_2\overset{\oplus}{C}C\equiv\overset{\ominus}{C} \longleftrightarrow C_6H_5C=C=C:] + (C_6H_5)_2CC\equiv C^\ominus$

$\underset{OCOCH_3}{|} \longrightarrow$

$[(C_6H_5)_2C\overset{\frown}{-}C\equiv\overset{\ominus}{C}-C=C=C(C_6H_5)_2] \longrightarrow$

$\underset{OCOCH_3}{\diagdown|}$

$(C_6H_5)_2C=C=C=C=C=C(C_6H_5)_2 + CH_3CO_2^\ominus$

$$XII$$

The reaction of the carbene with the acetylenic anion is reasonable in that alkenylidene carbenes are electrophilic species.[15] The direct dimerization of carbenes in solution appears to be an extremely unlikely reaction which probably does not occur to any significant extent.[33]

Dimerization reactions of carbenes in solution have been suggested by many workers; but in most cases alternate mechanisms are not only possible, but are more probable. This is particularly true

(33) W. Kirmse. Angew. Chem., 71, 537 (1959).

when nucleophiles are present in solution.[34] A recent example is given[35] in the explanation for the observed second-order kinetics for the reaction of alkali with 4-nitrobenzyl chloride to give 4,4'-dinitrostilbene. The suggested[35] reaction scheme included the rate-determining formation of 4-nitrophenylmethylene followed by its rapid dimerization. Since the anion derived from the 4-nitrobenzyl chloride will be present in greater concentration than the carbene, and since the carbene is an electrophilic reagent, the following sequence seems more probable[35a]
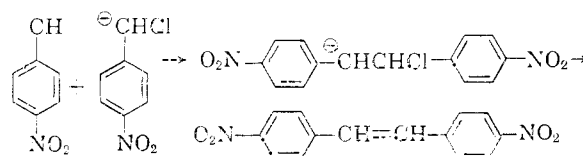


In contrast to reactions in solution, the dimerization of carbenes in the vapor phase is probable and has been observed for CH$_2$,[36] CF$_2$,[37] CF$_3$CH[38] and C$_3$F$_7$CH.[38]

**Vinylidene Carbene.**—The tertiary acetylenic halides or esters are more favorable systems for the formation of allenyl carbenes than are primary halides, because bimolecular nucleophilic displacement reactions are sterically hindered.[39] Elimination of halide ion from anions of the type R$_2$C(X)-C$\equiv$C$^\ominus$ should decrease in ease in the series R = C$_6$H$_5$, alkyl, hydrogen. The differences in rate of loss of halide ion, however, should not be as great as are those encountered in unimolecular or bimolecular $\beta$-elimination reactions of neutral halides, because in the transition state the extent of positive charge formation on the carbon bearing the leaving group will be much less in the acetylenic anion series. The simpler propargyl systems would be expected to react with nucleophiles by S$_N$2 or S$_N$2' mechanisms. Indeed, the absence of a deuterium isotope effect in the reaction of propargyl bromide with methoxide ion[40] indicates the probable absence of a $\gamma$-elimination reaction.

$HC\equiv CCH_2Br + CH_3O^\ominus \longrightarrow HC\equiv CCH_2OCH_3 + Br^\ominus$
$(D) \qquad\qquad\qquad\qquad (D)$
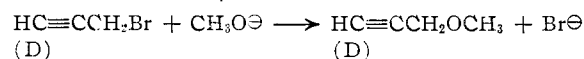
It has been suggested[41] that the reaction of phenothiazine, propargyl bromide and sodium hydride in dimethylformamide to give N-(1-propynyl)-phenothiazine proceeds by way of the allenyl carbene. This appears surprising in that the mode of reaction

(34) J. Hine and A. M. Dowell, Jr., J. Am. Chem. Soc., 76, 2688 (1954).

(35) S. B. Hanna, Y. Iskander and Y. Riad, J. Chem. Soc., 217 (1961).

(35a) NOTE ADDED IN PROOF.—4,4'-Dinitrostilbenes also are products of the $\alpha$-elimination of 4-nitrobenzyldimethylsulfonium tosylate. The sulfur isotope effect suggests that the carbene is formed and reacts with anion rather than carbene: cf., C. G. Swain and E. R. Thornton. J. Am. Chem. Soc., 83, 4033 (1961).

(36) W. F. Ross and G. B. Kistiakowsky, J. Am. Chem. Soc., 56, 1112 (1934).

(37) R. D. Chambers, H. C. Clark and C. J. Willis, ibid., 82, 5298 (1960).

(38) R. Fields and R. N. Haszeldine. Proc. Chem. Soc., 22 (1960).

(39) No S$_N$2 reaction is observed for the tertiary halides (CH$_3$)$_3$-CClC$\equiv$CR when R is an alkyl group; cf. ref. 4.

(40) Unpublished work of T. L. Jacobs and W. Maya: private communication from Professor Jacobs.

(41) H. E. Zaugg. L. R. Swett and G. R. Stone, J. Org. Chem., 23 1389 (1958).

of the dimethylallenyl carbene with amines[5] would lead one to expect the isomeric N-(2-propynyl)-phenothiazine. More conclusive evidence for the formation of a carbene from propargyl bromide has been obtained in this work.

When propargyl bromide is added to a stirred slurry of potassium $t$-butoxide in styrene at 25° a moderately exothermic reaction ensues. No vinylidenecyclopropane has been isolated, but 1-ethynyl-2-phenylcyclopropane (XIII) has been obtained in 8% yield. The infrared and n.m.r. spectra of XIII indicate that it is a mixture of cis and trans isomers. The structure of XIII was established by hydration to 1-acetyl-2-phenylcyclopropane (XIV)[42] and cleavage of XIV with sodium hydroxide and bromine to 2-phenylcyclopropanecarboxylic acid.

$$HC\equiv CCH_2Br + C_6H_5CH=CH_2 + KOtC_4H_9 \longrightarrow$$
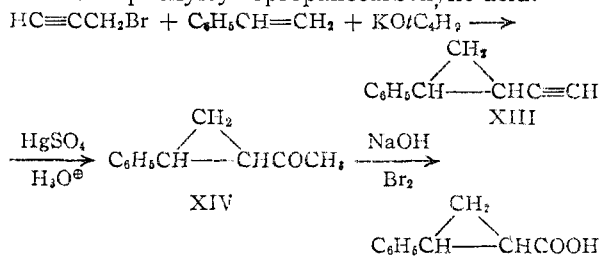


Compound XIII might have been formed in a variety of ways, but the two most likely paths appear to be: (1) the formation of a vinylidenecyclopropane by way of a vinylidene carbene and a rearrangement of the allene to XIII in the basic medium; (2) an $\alpha$-elimination reaction to form propargylene[10] which would add to styrene to give XIII. The allene–acetylene isomerization reaction is well-known,[43] but, alternatively, the $\alpha$-elimination of primary halides to give carbenes has recently had ample illustration.[44-47]
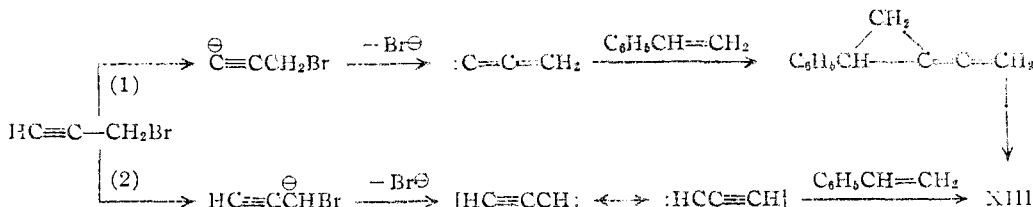


Preliminary evidence that the reaction proceeds at least in part through path 1 has been obtained in the reaction of propargyl bromide, potassium $t$-butoxide and cis-2-butene. The products resulting from the addition of the base to a mixture of the halide and olefin include allenic and acetylenic hydrocarbons. The lability of the allene has, to date, precluded its separation and identification.

### Experimental[48]

**Materials.**—3-Chloro-3-methyl-1-butyne was prepared by the method of Hennion and Nelson.[5] The chloride was re-

distilled immediately before use, b.p. 75–76°, $n^{25}D$ 1.4143. Propargyl bromide (Aldrich) was distilled before use (b.p. 83°, $n^{25}D$ 1.4899). Potassium $t$-butoxide was prepared by the method of Johnson, et al.,[49] the excess alcohol being removed by codistillation with benzene. This technique gives a 1:1 complex of alkoxide and alcohol. Cyclohexene (Eastman Kodak Co.) was washed with aqueous sodium hydroxide, dried, and distilled under nitrogen through a spinning-band column; $n^{25}D$ 1.4438. Styrene (Eastman Kodak Co.) was used without purification. The other olefins used were analyzed by vapor phase chromatography: 2-methyl-1-butene (Phillips), 99+%; 2-methyl-2-butene (Matheson), 95%; 1-hexene (Phillips), 99+%; and tetramethylethylene, 98%.

**1-(2-Methylpropenylidene)-2-phenylcyclopropane (III).**—A flask containing styrene (80 g.) was flushed with dry nitrogen for 30 minutes, and potassium $t$-butoxide (37.2 g., 0.20 mole of 1:1 complex with $t$-butyl alcohol) was added. The slurry was stirred and cooled to −10°. 3-Chloro-3-methyl-1-butyne (20.6 g., 0.20 mole) was added over a 30-minute period with the temperature maintained at −10 to 0°. The mixture became dark red-brown during the addition. Stirring was continued for 3 hours. Excess styrene and $t$-butyl alcohol were removed under reduced pressure. Pentane (250 ml.) was added to the residue, and it was filtered. The solid was washed three times with 50-ml. portions of pentane, and the combined filtrates were distilled through a semi-micro spinning-band column.[50] The allene (16.3 g., 0.96 mole, 48%) distilled at 78–80° at 0.5 mm., $n^{25}D$ 1.5717–1.5722. The initial distillate was colorless, but it yellowed slightly upon exposure to air.

*Anal.* Calcd. for $C_{13}H_{14}$: C, 91.76; H, 8.30. Found: C, 91.71; H, 8.29.

**Hydrogenation of III.**—The allene (3.40 g., 0.020 mole) was hydrogenated at atmospheric pressure in 95% ethanol (40 ml.) with 5% palladium-on-carbon (0.12 g.) as catalyst. Hydrogen absorption was quantitative (1.34 l. at S.T.P., 0.0598 mole). After removal of the catalyst, the solution was distilled through a 3-inch concentric tube, tantalum wire, spiral column to give 3.13 g. (0.178 mole, 89% yield) of 5-methyl-1-phenylhexane (IV), b.p. 55–58° at 1.0 mm., $n^{25}D$ 1.4836.

*Anal.* Calcd. for $C_{13}H_{20}$: C, 88.55; H, 11.45. Found: C, 88.05; H, 11.74.
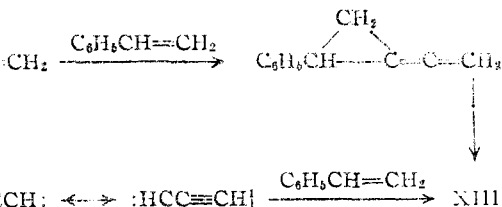
The diacetamido derivative of III was prepared according to the procedure of Ipatieff and Schmerling.[22] After two recrystallizations from 95% ethanol the diamide melted at 205–206°, reported[51] 206.5–207°, yield 61%.

*Anal.* Calcd. for $C_{17}H_{24}N_2O_2$: C, 70.31; H, 9.03; N, 9.65. Found: C, 70.21; H, 8.87; N, 9.49.

**Alternate Synthesis of IV.**—The Friedel–Crafts reaction of the acid chloride of 5-methylhexanoic acid,[52] benzene and aluminum chloride gave 5-methyl-1-phenyl-1-hexanone in 62% yield (b.p. 73–75° at 1.5 mm., $n^{25}D$ 1.5072; semicarbazone, m.p. 143.5–144.5° from 50% ethanol; reported[53] b.p. 145–148° at 18 mm., $n^{20}D$ 1.5067; semicarbazone, m.p. 144–145°).

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The ketone was reduced by the Huang-Minlon variation of the Wolff–Kishner reaction.[54] The ketone (2.75 g., 0.01145 mole) was heated at 200° for 3 hours with 1.17 g. of 85% aqueous hydrazine, 1.8 g. of potassium hydroxide and 25 ml. of triethylene glycol. Water and excess hydrazine were collected in a Dean-Stark trap. The cooled solution was neutralized with dilute hydrochloric acid and extracted with ether. The combined ether extracts were dried over anhydrous sodium sulfate and distilled to give 5-methyl-1-phenylhexane (IV), 1.99 g., 0.0113 mole, 78% yield, b.p. 54–56° at 1.0 mm., $n^{25}$D 1.4838. The diacetamido derivative melted at 205–206°. A mixture with the sample prepared above also melted at 205–206°. The preparation of IV by this reaction sequence has recently been reported,[51] b.p. 111–114° at 17 mm., $n^{25}$D 1.4823, m.p. of diacetamido derivative 206.5–207°.

5-Methyl-2-phenylhexane.—The hydrocarbon was prepared essentially according to the method of Klages.[55] The Grignard reaction between acetophenone and isoamyl bromide gave 5-methyl-2-phenyl-2-hexanol, b.p. 79–80° at 0.5 mm., $n^{25}$D 1.5036 (reported[56] b.p. 135–137° at 15 mm., $n^{19}$D 1.50596) in 54% yield. Dehydration was accomplished by heating the alcohol (7.90 g., 0.041 mole) in 60 ml. of benzene with 0.61 g. of p-toluenesulfonic acid under a water separator. When evolution of water ceased, the benzene solution was washed with aqueous potassium carbonate solution and with water. After drying the benzene solution over anhydrous sodium sulfate, the solvent was removed. The crude olefin was hydrogenated in ethanol solution using palladium-on-carbon catalyst. Distillation of the hydrogenation product gave 6.17 g., 85%, of 5-methyl-2-phenylhexane, b.p. 93–95° at 7 mm., $n^{25}$D 1.4829, reported[51] b.p. 223°.

Preparation of the diacetamido derivative in the usual way gave material of m.p. 185–186° after two recrystallizations from 60% ethanol.

Anal. Calcd. for $C_{17}H_{26}N_2O_2$: C, 70.31; H, 9.03; N, 9.65. Found: C, 70.30; H, 9.24; N, 9.33.

2,4-Dimethyl-1-phenylpentane.—2,4-Dimethyl-1-phenyl-2-pentanol[57] was dehydrated by heating 4.05 g. (0.021 mole) of the alcohol with 0.2 g. of p-toluenesulfonic acid in 30 ml. of benzene under a water separator. When water evolution ceased, the benzene solution was washed with aqueous potassium carbonate solution and water and dried over anhydrous sodium sulfate. The benzene was removed under reduced pressure and the crude olefin was hydrogenated in ethanol solution over palladium-on-carbon. Distillation of the hydrogenation product gave 2,4-dimethyl-1-phenylpentane, 2.16 g., 59%, b.p. 102–104° at 11 mm., $n^{25}$D 1.4839.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.55; H, 11.45. Found: C, 88.47; H, 11.61.

The diacetamido derivative was prepared, and it melted at 202–204° after two recrystallizations from 50% ethanol.

Anal. Calcd. for $C_{17}H_{26}N_2O_2$: C, 70.31; H, 9.03; N, 9.65. Found: C, 70.12; H, 9.18; N, 9.39.

The melting point of a mixture of this diamide with the diacetamido derivative of 5-methyl-1-phenylhexane was depressed; the mixture melted at 193–197°.

Ozonolysis of III in Ethanol.—The allene III (8.53 g., 0.050 mole) was ozonized at 0° in absolute ethanol (125 ml.). A barium hydroxide trap was used to collect any carbon dioxide evolved. About 0.056 mole of ozone was consumed. Only 0.29 g. (0.0015 mole, 3% yield) of barium carbonate was produced. The ethanol solvent was removed from the ozonolysis residue under reduced pressure and collected in a trap at −70°. Addition of an aqueous ethanolic solution of 2,4-dinitrophenylhydrazine followed by removal of most of the solvent yielded acetone 2,4-dinitrophenylhydrazone, m.p. 125–126°, 7.32 g., 0.032 mole, 65% yield.

The ozonolysis residue gave a negative test for peroxide (potassium iodide) and was distilled. Distillation yielded unchanged allene, b.p. 70–85° at 1.0 mm., 0.49 g., and ethyl 1-hydroxy-2-phenylcyclopropanecarboxylate (V), b.p. 110–113° at 1.0 mm., 4.18 g., 0.020 mole, 40% yield, $n^{25}$D 1.5355.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.19; H, 6.89.

There was a distillation residue of 4.58 g. The infrared spectrum of V showed sharp hydroxyl absorption at 3420 cm.$^{-1}$ and the ester carbonyl at 1730 cm.$^{-1}$. Absorption at 1025 cm.$^{-1}$ can probably be attributed to cyclopropyl hydrogen, although other bands are present in this region. The spectrum was completely consistent with the assigned structure.

Hydrolysis of V.—The ester (2.20 g., 0.011 mole) was added to a solution of sodium methoxide prepared from 0.38 g. of sodium and 20 ml. of methanol. After standing for an hour at room temperature, the solution was acidified and extracted with three 25-ml. portions of ether. The combined ether solutions were extracted with dilute sodium bicarbonate solution. Acidification of the bicarbonate solution yielded a hydroxy acid (VII), m.p. 159.5–160° dec. after recrystallization from 3:1 benzene–petroleum ether, 1.48 g., 0.0083 mole, 76% yield.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66; neut. equiv., 178. Found: C, 67.56; H, 5.74; neut. equiv., 179.

The infrared spectrum of VII showed broad OH absorption at 3350 and 3250 cm.$^{-1}$ and carbonyl absorption at 1770 and 1720 cm.$^{-1}$. The identification of VII as 3-benzyl-4-carboxyl-4-hydroxy-2-oxo-6-phenylhexanoic acid was confirmed by its synthesis from benzylpyruvic acid.[25] A mixture of VII with the authentic sample decomposed at 159–160°. The infrared spectra of the two samples were identical.

The mother liquor from the recrystallization of VII was examined, and another acid which was slightly soluble in petroleum ether was obtained. The material was crystallized from water to given an oily solid, m.p. 36–40°, 0.15 g., 8%. The solid was benzylpyruvic acid (reported[58] m.p. 46–48°). Oxidation of the keto acid (0.32 g.) in 3 ml. of acetic acid with 1 ml. of 30% hydrogen peroxide gave β-phenylpropionic acid, m.p. 47–48° from petroleum ether. A mixture with an authentic sample also melted at 47–48°.

7-(2-Methylpropenylidene)-bicyclo[4,1,0]heptane.—A mixture of cyclohexene (33.6 g.) and potassium t-butoxide (18.6 g. of a 1:1 complex with t-butyl alcohol) was stirred under nitrogen at −10°; II (10.3 g.) was added dropwise so that the reaction temperature was maintained between −10 and 0°. The mixture was stirred for 20 minutes after addition, pentane (100 ml.) was added, and the mixture was filtered. The filtrate was distilled through a spinning-band column, and the allene was collected at 84–87° at 12 mm., $n^{25}$D 1.5215–1.5218, 3.85 g., 26% yield.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.27; H, 10.89.

The infrared spectrum of this allene was unusual in one respect. A doublet was present in the allene region. There were peaks at 2000 and 2030 cm.$^{-1}$.

1-(2-Methylpropenylidene)-2-ethyl-2-methylcyclopropane.—2-Methyl-1-butene and the acetylenic chloride under similar conditions gave a 36% yield of the allene, b.p. 77–78.5° at 45 mm., $n^{25}$D 1.4780–1.4790.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.27; H, 11.87.

1-(2-Methylpropenylidene)-2-butylcyclopropane.—1-Hexene and the acetylenic chloride gave a 12% yield of the allene, b.p. 84–87° at 44 mm., $n^{25}$D 1.4801–1.4815.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.51; H, 12.09.

1-(2-Methylpropenylidene)-2,2,3-trimethylcyclopropane.—2-Methyl-2-butene and the acetylenic chloride gave a 23% yield of the allene, b.p. 67–70° at 46 mm., $n^{25}$D 1.4736–1.4747.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.84; H, 11.92.

1-(2-Methylpropenylidene)-2,2,3,3-tetramethylcyclopropane.—Tetramethylethylene and the acetylenic chloride gave a 47% yield of the allene, b.p. 80° at 55 mm., m.p. 48.6–49.3°.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.51; H, 12.25.

Diphenylethynylcarbinol.[59]—Higher yields of the carbinol are obtained by using lithium acetylide rather than potas-

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(55) A. Klages, Ber., 35, 2633 (1902).

(56) P. Schorigen, ibid., 41, 2711 (1908).

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(58) W. Wislicenus and M. Münzesheimer, Ber., 31, 551 (1898); W. Wislicenus, ibid., 31, 3133 (1898).

(59) Procedure of A. Logothetis; private communication from Dr. Logothetis.

sium acetylide as described[60] in the published procedure. Liquid ammonia (600 ml.) containing 0.2 g. of ferric chloride was stirred while lithium wire (4.0 g.) was added in portions. When hydrogen evolution ceased, acetylene was passed through solid carbon dioxide–acetone and alumina traps into the reaction for 2 hours. A solution of 91 g. of benzophenone in 300 ml. of ether was added dropwise over 2 hours while acetylene was still being passed through the solution. The mixture was allowed to evaporate overnight. The residue was distributed between ether and aqueous ammonium chloride. The ether solution was dried and distilled. The alcohol (95 g., 87%) was collected at 121–127° at 0.5 mm., m.p. 45–46°. Recrystallization from heptane gave material, m.p. 47–48° (reported[60] m.p. 49°), yield 85.1 g. (78%).

**Diphenylethynylcarbinyl Acetate.**—The preparation of the acetate is given because it represents a considerable improvement over the published[31] procedure. A suspension of sodium hydride (2.70 g. of 53% dispersion in mineral oil) in 100 ml. of benzene was stirred while diphenylethynylcarbinol (12.5 g., 0.06 mole) was added. The mixture was heated at reflux for 30 minutes, then cooled in ice. Acetic anhydride (6.20 g.) was added, and the mixture was stirred for 30 minutes. The precipitated sodium acetate was filtered and the filtrate was concentrated to give 10.88 g. (73%) of the crude acetate (m.p. 72–77°). Recrystallization from hexane gave 9.3 g. of acetate, m.p. 78.6–80°. This material could be purified by sublimation to give material of m.p. 80.3–81.8°, reported[31] m.p. 80–81°.

**Tetraphenylhexapentaene.**—The cumulene was prepared by adding a solution of diphenylethynylcarbinyl acetate (2.50 g.) in 5 ml. of ether to a slurry of potassium *t*-butoxide (1.20 g.) in 10 ml. of ether. The dark reaction product was distributed between water and ether. The red cumulene remained suspended and was collected by filtration. The crude material (1.06 g.) was purified by dissolving in hot chloroform and precipitating with acetic acid. This procedure gave 0.86 g. (50%) of cumulene, m.p. 202–205° dec. (reported[31] m.p. 204–206° and 290–302°[61]). The absorption spectra are in agreement.[61] We obtained $\lambda_{max}$ 487 m$\mu$ ($\epsilon$ 7.7 × 10⁴), a shoulder at 430 m$\mu$ ($\epsilon$ 2.4 × 10⁴), $\lambda$ 367 m$\mu$ ($\epsilon$ 1.2 × 10⁴), $\lambda$ 288 m$\mu$ ($\epsilon$ 3.3 × 10⁴), $\lambda$ 273 m$\mu$ ($\epsilon$ 3.3 × 10⁴), and $\lambda$ 253 m$\mu$ ($\epsilon$ 4.8 × 10⁴).

**1-Diphenylvinylidene-2-phenylcyclopropane (XI).**—A solution of diphenylethynylcarbinyl acetate (2.50 g., 0.010 mole) in 15 ml. of styrene was added dropwise to a stirred slurry of 1.7 g. of potassium *t*-butoxide (alcohol-free) in 15 ml. of styrene. Reaction temperature was maintained between 0 and 10° while the mixture was stirred for 30 minutes. All volatile materials were removed under reduced pressure. The residue was distributed between ether and water. The ether-soluble material was chromatographed on Florisil. The allene XI was eluted with pentane. The crude allene was crystallized from methanol to give material of m.p. 91.2–91.8° after softening at 89.4° (0.73 g., 25%).

*Anal.* Calcd. for C₂₃H₁₈: C, 93.84; H, 6.16. Found: C. 93.34; H, 6.38.

The allene absorption of XI was at 2000 cm.⁻¹ in the infrared. The ultraviolet spectrum of XI in ethanol showed absorption at 286 m$\mu$ ($\epsilon$ 1.8 × 10⁴) and a shoulder at 225 m$\mu$ ($\epsilon$ 0.9 × 10⁴). The n.m.r. spectrum of XI in deuteriochloroform showed the aromatic hydrogens at $\tau$ = 2.72 and 2.83, the benzylic hydrogen split into a quartet centered at

$\tau$ = 6.88, and the methylene hydrogens split into quartets centered at $\tau$ = 7.80 and 8.17.

The chromatogram yielded crystalline material when eluted with ether. The crude material (1.35 g.) upon recrystallization from benzene gave tetraphenyl-2-butyn-1,4-diol, 0.86 g., 44%, m.p. 195–196°, reported[62] m.p. 193°.

*Anal.* Calcd. for C₂₈H₂₂O₂: C, 86.12; H, 5.68. Found: C, 86.33; H, 5.92.

**1-Ethynyl-2-phenylcyclopropane (XIII).**—A slurry of potassium *t*-butoxide (37.8 g.) in styrene (83 g.) was stirred under nitrogen. Propargyl bromide (24 g.) was added dropwise while the temperature was kept at 25–30°. The mixture was stirred for 2 hours, pentane (200 ml.) was added, and the mixture was filtered. A small amount of hydroquinone was added to the filtrate, and it was distilled through a spinning band column; XIII was collected at 81–83° at 8 mm., 2.35 g., 8%, $n^{25}$D 1.5501. The infrared spectrum of XIII showed absorption at 3280 (acetylenic CH), 2120 (C≡C) and 1030 cm.⁻¹ (cyclopropyl hydrogen). There was no allenic absorption.

*Anal.* Calcd. for C₁₁H₁₀: C, 92.91; H, 7.09. Found: C, 93.01; H, 7.18.

A mixture containing XIII (1.42 g.) in 6 ml. of 70% aqueous acetic acid with one drop of sulfuric acid and 0.02 g. of mercuric sulfate was stirred at 60–70° for 3 hours. The heterogeneous mixture became nearly homogeneous after 30 minutes. The warm mixture was filtered and the filtrate was neutralized with 10% aqueous sodium carbonate solution. The oil which separated could not be crystallized. Half of the oil was used to form a semicarbazone which melted at 132–134° alone and at 132–135° in mixture with the semicarbazone of 1-acetyl-2-phenylcyclopropane.[42] The remaining portion of oil was stirred in 15 ml. of 20% aqueous sodium hydroxide solution containing 1.0 g. of bromine. After 24 hours an oily acid was separated. The acid was crystallized from water; m.p. 89–90°, reported m.p. 90°,[42] 93°[63] for 2-phenylcyclopropanecarboxylic acid.

**Propargyl Bromide and *cis*-2-Butene.**—A solution of *n*-butyllithium (0.10 mole) in hexane was added to 50 ml. of decahydronaphthalene. The hexane was removed in a stream of dry nitrogen. The decahydronaphthalene solution was added dropwise to a solution of 12 g. (0.10 mole) of propargyl bromide, 28 g. of *cis*-2-butene and 50 ml. of decahydronaphthalene. The mixture was stirred for an hour with the temperature maintained at 25–30°. Water was added and the hydrocarbon layer was separated and dried over anhydrous magnesium sulfate. Rapid distillation through a short Vigreux column gave a fraction, b.p. 68–85° (3.25 g.). The infrared spectrum of this cut showed the presence of both allenic and acetylenic unsaturation. Redistillation of this cut through a spinning-band column gave 1.35 g. of material, b.p. 84–85°. The infrared spectrum of this material showed acetylenic CH (3300 cm.⁻¹), C≡C (2130 cm.⁻¹), allene (1970 cm.⁻¹) and cyclopropyl hydrogen (1025 cm.⁻¹). Vapor phase chromatographic (v.p.c.) analysis indicates that the cut is largely composed of three hydrocarbons. These have not been completely separated. The intensity of the allenic absorption in the infrared is increased in one of the v.p.c. cuts.

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(63) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).