Vinylidene Carbenes by α-Elimination from Haloallenes
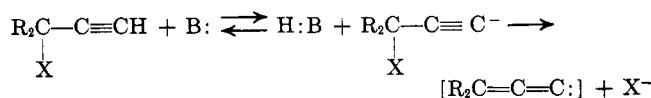
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1-Chloro-3-methyl-1,2-butadiene reacted with potassium *t*-butoxide and olefins to yield dimethylvinylidene-cyclopropanes. The relative rates of addition to olefins were found to be the same as those previously obtained with 3-chloro-3-methyl-1-butyne and potassium *t*-butoxide. Dimethylvinylidene carbene is presumed to be a common intermediate. The reported preparation of 3-bromo-1,1-diphenylpropadiene was shown to be erroneous.
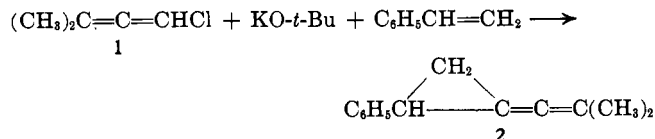
Terminal acetylenes with a good leaving group in the γ-position can react with bases by a γ-elimination mechanism to produce vinylidene carbenes as transient intermediates. Vinylidene carbenes have been shown
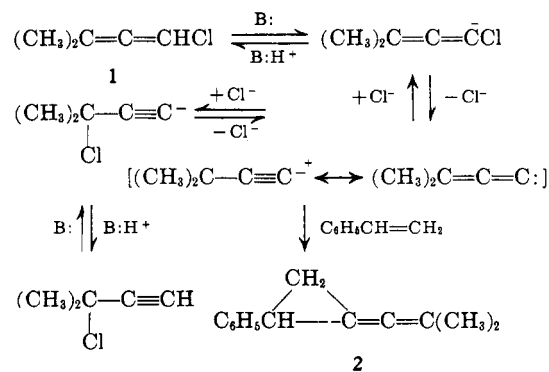
$$R_2C—C\equiv CH + B: \rightleftharpoons H:B + R_2C—C\equiv C^- \longrightarrow$$
$$\underset{X}{|} \qquad\qquad\qquad\qquad \underset{X}{|}$$
$$[R_2C=C=C:] + X^-$$

to react with alcohols to form acetylenic ethers,[1] with amines to form acetylenic amines,[2] with olefins to form vinylidenecyclopropanes,[3] with certain acetylide ions to form hexapentaenes,[3] and with bromide ion to form acetylenic bromide (and, possibly, allenic bromide).[4]

This paper describes our work on generation of vinylidene carbenes from haloallenes by α-elimination.

α-Elimination of Haloallenes.—The addition of 1-chloro-3-methyl-1,2-butadiene (1) to a slurry of potassium *t*-butoxide in styrene at 0° gave a rapid, exothermic reaction from which 1-dimethylvinylidene-2-phenyl-cyclopropane (2) was isolated in greater than 34% yield. Under identical conditions, the vinylidene-cyclopropane is formed from the isomeric 3-chloro-3-methyl-1-butyne in 49% yield.[3]

$$(CH_3)_2C=C=CHCl + KO\text{-}t\text{-}Bu + C_6H_5CH=CH_2 \longrightarrow$$
$$\mathbf{1}$$

$$\underset{\mathbf{2}}{C_6H_5CH\underset{\diagup\quad CH_2\quad\diagdown}{\underline{\qquad\qquad}}C=C=C(CH_3)_2}$$

Although the interconversion of allenic and propargylic compounds is a well-known reaction,[5] it is unlikely that **1** isomerizes to the acetylenic chloride under these conditions. Isomerization of allenic and propargylic systems occurs with Lewis acid catalysis[6] and under conditions of an SN2' reaction.[7] Isomerization of propargylic and allenic systems could occur in basic systems by a vinylidene carbene mechanism, if a large excess of the common ion is present in solution.[4] The possibility of rearrangement of **1** to the acetylenic chloride by such a mechanism is minimized under our reaction conditions because little chloride ion is in solution in the olefinic solvent and the large excess of olefin employed partitions the intermediate to form cyclopropane.

(1) G. F. Hennion and D. E. Maloney, *J. Am. Chem. Soc.*, **73**, 4735 (1951).
(2) G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).
(3) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).
(4) V. J. Shiner, Jr., and J. W. Wilson, *ibid.*, **84**, 2402 (1962).
(5) A. Favorskiĭ and T. A. Favorskaya, *Compt. rend.*, **200**, 839 (1935); J. H. Ford, C. D. Thompson, and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 2619 (1935).
(6) T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953), and earlier references cited therein.
(7) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *ibid.*, **72**, 3542 (1950).

$$(CH_3)_2C=C=CHCl \underset{B:H^+}{\overset{B:}{\rightleftharpoons}} (CH_3)_2C=C=\bar{C}Cl$$
$$\mathbf{1}$$
$$(CH_3)_2C—C\equiv C^- \underset{-Cl^-}{\overset{+Cl^-}{\rightleftharpoons}} \qquad +Cl^- \uparrow \downarrow -Cl^-$$
$$\underset{Cl}{|}$$
$$[(CH_3)_2C—C\equiv C^{-+} \longleftrightarrow (CH_3)_2C=C=C:]$$

$$B: \uparrow \downarrow B:H^+ \qquad\qquad \downarrow C_6H_5CH=CH_2$$

$$(CH_3)_2C—C\equiv CH \qquad \underset{C_6H_5CH\underline{\qquad}C=C=C(CH_3)_2}{\overset{CH_2}{\diagup\quad\diagdown}}$$
$$\underset{Cl}{|}$$
$$\mathbf{2}$$

If the carbene is an intermediate in the reaction, its rates of reactions with olefins should be identical with those determined previously[8] for the same intermediate obtained from the isomeric acetylenic chloride.[9] Relative rates of reaction were determined by competition experiments in which a large excess of an olefin mixture was brought into reaction with potassium *t*-butoxide and **1**. Cyclohexene was used as a referent in these reactions and was arbitrarily given a rate of unity. The amounts of the two dimethylvinylidenecyclopropanes that were formed were determined by gas–liquid chromatography under conditions similar to those previously used with the acetylenic chloride.[8] Within experimental error, the relative rates of olefin addition in the two systems are identical. The experimental results are given in Table I.

TABLE I

RELATIVE RATES OF REACTION OF VINYLIDENE CARBENES WITH OLEFINS

	—log k/k_0—	
Olefin	$(CH_3)_2C=C=C:$[a]	$(CH_3)_2C=C=C:$[b]
$(CH_3)_2C=C(CH_3)_2$	1.2	1.3
$(CH_3)_2C=CHCH_3$	0.69	0.67
$CH_3CH_2(CH_3)C=CH_2$	0.62	0.70
⬡	0.00	0.00
$CH_3CH_2CH_2CH_2CH=CH_2$	-0.64	-0.60

[a] Carbene generated from $(CH_3)_2C=C=CHCl$ and potassium *t*-butoxide at -10°. [b] Carbene generated from $(CH_3)_2CCl—C\equiv CH$ and potassium *t*-butoxide at -10°.[8]

A recent report[10] disclosed the preparation of 1,1-diphenyl-3-bromopropadiene by dehydrobromination of 2,3-dibromo-1,1-diphenylpropene with potassium hydroxide in ethanol. Both the method of preparation
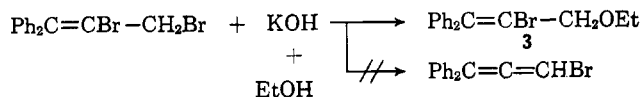
(8) H. D. Hartzler, *ibid.*, **83**, 4997 (1961).
(9) This would not be true if the carbene is complexed in solution and complexed differently in the two systems. While the former is probably the case, our results indicate the latter is not.
(10) V. I. Panseyich-Kolyada, *J. Gen. Chem. USSR*, **30**, 3854 (1960).

and the reported stability[11] of the bromoallene appeared surprising. The compound was of interest to us since it would be a useful intermediate to diphenylvinylidene carbene. In our hands the reaction gave an 87% yield of 2-bromo-3-ethoxy-1,1-diphenylpropene (3), rather

$$Ph_2C=CBr-CH_2Br + KOH \xrightarrow{\quad} \begin{array}{c} Ph_2C=CBr-CH_2OEt \\ \mathbf{3} \\ +\ EtOH \quad \not\longrightarrow Ph_2C=C=CHBr \end{array}$$

than the allene. The bromo ether has the same melting point reported for the bromoallene. Reaction of the dibromide with collidine in refluxing xylene, potassium t-butoxide in dimethyl sulfoxide, and butyllithium in hexane failed to give any of the bromoallene. From the latter reaction there was obtained a 9% yield of the coupling product, 2,5-dibromo-1,1,6,6-tetraphenyl-1,5-hexadiene.

Experimental[12]

1-Chloro-3-methyl-1,2-butadiene (1).—This chloroallene was prepared by the method of Jacobs, Teach, and Weiss.[13] The material used in the competition experiments distilled at 50–51° (105 mm.), n^{25}D 1.4744; lit.[17] b.p. 61–62° (175 mm.), n^{25}D 1.4739. Our sample was >98% pure by gas–liquid chromatographic analysis. The n.m.r. spectrum of the chloroallene showed the resonance of the vinyl hydrogen as a septuplet centered at τ 3.92 and the resonance of the methyl hydrogens as a doublet centered at τ 8.14. The coupling constant was ~3 c.p.s. An attempt was made to estimate the acidity of the vinyl hydrogen by measuring the C^{13} coupling constant, but this splitting could not be seen even after decoupling the methyl–vinyl splitting.

1-Dimethylvinylidene-2-phenylcyclopropane (2).—A slurry of 12 g. of potassium t-butoxide and 40 g. of styrene was stirred under nitrogen at 0°. Compound 1 (10.3 g.) was added dropwise with cooling. After addition, pentane (200 ml.) was added, and the mixture was filtered. Distillation of the filtrate gave 5.75 g. (34%) of 2, b.p. 68–73° (0.37 mm.), n^{25}D 1.5708; lit.[3] b.p. 78–80° (0.5 mm.), n^{25}D 1.5717–1.5722.

Competition Experiments with 1, Potassium t-Butoxide, and Olefins.—The olefins used were Phillips pure grade. Mixtures containing cyclohexene and another olefin (ca. 0.2 mole of total olefin) and 1.13 g. of potassium t-butoxide were stirred under nitrogen at −10° The allene 1 (1.10 g.) was added dropwise. Five minutes after addition, pentane (50 ml.) was added, and the mixture was filtered through Celite Filter Aid. The filtrates were concentrated under nitrogen and analyzed by gas–liquid chromatography. The column employed was a 2-m. tube packed with 20% triscyanoethylglyceryl ether on firebrick and was

(11) The corresponding chloroallene has never been isolated because of its very rapid dimerization. T. Nagase, Sci. Papers Inst. Phys. Chem. Res., 55, 165, 172 (1961); P. D. Landor and S. R. Landor, Proc. Chem. Soc., 77 (1962).

(12) Melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrometer, n.m.r. spectra on a Varian A-60 spectrometer, and ultraviolet spectra on a Cary Model 14 spectrometer.

(13) T. L. Jacobs, E. G. Teach, and D. Weiss, J. Am. Chem. Soc., 77, 6254 (1954).

operated at 102° (preheat 145°). Retention times were determined with authentic samples.[3] The product ratios were divided by the mole fraction ratios of the starting olefins to give the relative rates of addition. The logarithms of the rate ratios are given in Table I. Duplicate experiments were in agreement within 10%.

2,3-Dibromo-1,1-diphenylpropene.—Crude 1,1-diphenylpropene (106 g., m.p. 41–48°) in 150 ml. of ether was stirred in an ice bath while bromine (88 g.) was added. The solvent was removed under reduced pressure. The residual oil was dissolved in an ethanol–ether mixture and stirred with a solution of 22 g. of sodium hydroxide in 100 ml. of water. The layers were separated, and the ether-soluble product was distilled to give 128 g. (85%) of 2-bromo-1,1-diphenylpropene, b.p. 120–125° (0.5 mm.). The n.m.r. spectrum of the product showed only methyl and phenyl hydrogen.

A mixture of 63 g. of the bromoolefin, 41.4 g. of N-bromosuccinimide, 0.4 g. of benzoyl peroxide, and 200 ml. of carbon tetrachloride was heated at reflux for 3 hr. The succinimide was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue crystallized upon adding ethanol to give 74 g. (91%) of crude dibromide, m.p. 73–78°. Recrystallization from ethanol gave material which melted at 82–83°, lit.[11] m.p. 88–89°. The n.m.r. spectrum of the dibromide showed the resonances of the phenyl hydrogen at τ 2.74 and 2.78 and the methylene hydrogen at τ 5.68. The intensity ratio was 5:1.

2-Bromo-3-ethoxy-1,1-diphenylpropene (3).—A solution of 10 g. of potassium hydroxide in 30 ml. of ethanol was added to a stirred mixture of 10 g. of 2,3-dibromo-1,1-diphenylpropene in 40 ml. of ethanol. The mixture was heated at 70° for 30 min. Water (100 ml.) was added, and the product was extracted with ether. Distillation gave 6.75 g. of 3, b.p. 126° (0.4 mm.). Crystallization from ethanol gave pure 3, m.p. 62.4–63.4°, lit.[11] m.p. 60–61° for the bromoallene.

Anal. Calcd. for $C_{17}H_{17}BrO$: C, 64.4; H, 5.40; Br, 25.2. Found: C, 64.6; H, 5.32; Br, 25.3.

The infrared spectrum of 3 showed the presence of both saturated and unsaturated CH, conjugated C=C (6.15 μ), aromatic and C–O absorption (9.0 μ). There was no allenic absorption. The n.m.r. spectrum of 3 showed the resonances of the unsplit methylene at τ 5.70, the methylene of the ethoxy group (quartet) centered at τ 6.45, and the methyl triplet centered at τ 8.77.

2,5-Dibromo-1,1,6,6-tetraphenyl-1,5-hexadiene.—A solution of 17.6 g. of 2,3-dibromo-1,1-diphenylpropene in 100 ml. of ether was stirred at −5° while a solution of butyllithium in hexane (34 ml., 0.05 mole) was added. After 15 min., water was added, and the organic product was taken up in ether. Evaporation of the ether left a viscous oil. A crystalline solid (1.33 g.) was obtained when the residue was dissolved in 80 ml. of boiling methanol. Recrystallization from ethanol gave the pure diene (1.27 g., 9%), m.p. 167–168°.

Anal. Calcd. for $C_{30}H_{24}Br_2$: C, 66.2; H, 4.44; Br, 29.4; mol. wt., 544. Found: C, 66.6; H, 4.67; Br, 29.0; mol. wt. (b.p. in benzene), 585, 547.

In addition to the aromatic hydrogens, the n.m.r. spectrum showed the unsplit methylene at τ 7.05 with an intensity one-fifth that of the aromatic hydrogen. The infrared spectrum showed the absorption of the conjugated olefin and was completely consistent with the assigned structure.