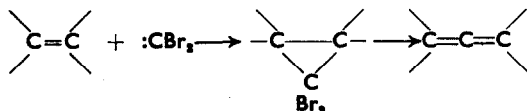


A TWO-STEP SYNTHESIS OF ALLENES FROM OLEFINS

W. VON E. DOERING and P. M. LAFLAMME
Sterling Chemistry Laboratory, Yale University

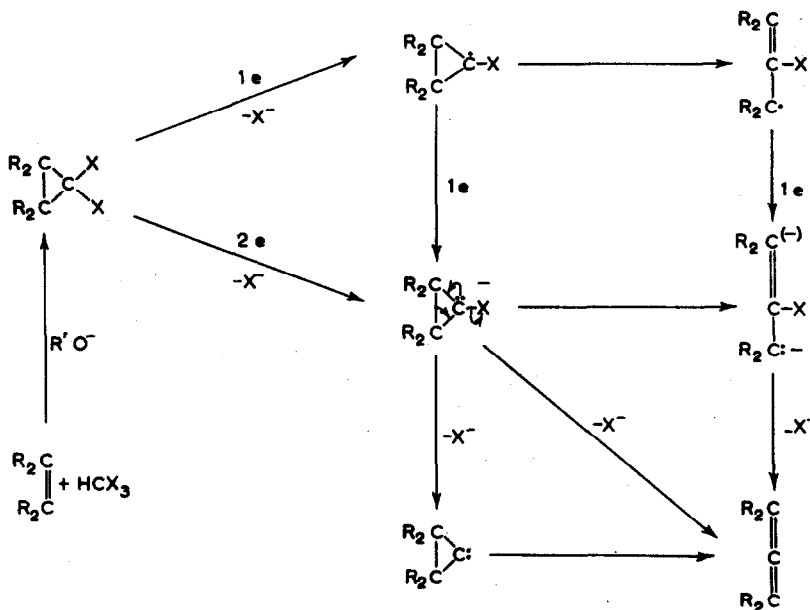
(Received 28 June 1957)

Abstract—In a two-step sequence, of which the first step involves addition of dibromocarbene to an olefin and the second involves reaction of the resulting substituted 1,1-dibromocyclopropane with magnesium or sodium, allenes are obtained. The overall structural change involves the insertion of



a single carbon atom between the two of the original double bond and therefore represents a novel way of increasing carbon chain lengths by one atom.

1,1-DIHALOCYCLOPROPANES are conveniently available in one step through the recently discovered reaction of Doering and Hoffmann in which an olefin is treated with haloform and alkoxide ion.^{1,2} Theoretical examination of the mechanistic possibilities leads to the prediction that reduction of these 1,1-dihalo-cyclopropanes by active metals may produce allenes. As depicted below, the accepting of two electrons, either in two steps or one, may lead to elimination of both halogen atoms as halide ion and cleavage of the cyclopropane ring to an allene.



¹ W. von E. Doering and A. K. Hoffmann *J. Amer. Chem. Soc.* **76**, 6162 (1954).

² Several examples giving additional support to the generality of the reaction have been carried out by P. S. Skell and O. Y. Garner *J. Amer. Chem. Soc.* **78**, 5430 (1956).

The chance of realizing the hypothetical reaction with the *dichloro* derivatives seems remote on the basis of the work of Gustavson³ who has found 1,1-dichloro-*cyclopropane* to be stable to sodium metal at 140°. Consistently, 1,1-dichloro-2,2,3-trimethyl-*cyclopropane* liberates no chloride ion on treatment with sodium metal at 180°, alone, in *bis*-(2-ethoxyethyl)ether and on alumina in the high surface form. Neither does lithium nor magnesium under a variety of conditions remove any halogen.

With dibromocyclopropane derivatives, however, it is possible to realize the reaction. Both magnesium and sodium are capable of converting substituted dibromocyclopropanes to allenes in varying yield. Thus, with magnesium in ether *cis*-1,1-dibromo-2,3-dimethyl-*cyclopropane* (from *cis*-butene and bromoform⁴) is converted to 2,3-pentadiene in low yield (16 per cent of theory). The identification follows from the presence in the i.r. of the 5.06 μ band characteristic of allenes⁵ and the coincidence of physical properties with those reported.⁶ By vapor phase chromatographic (v.p.c.) analysis this sample was found to be contaminated with 3 per cent of 2-pentyne. Reaction of 1,1-dibromo-2-*n*-propyl-*cyclopropane* with magnesium in ether yields 1,2-hexadiene (62 per cent of theory), identified by i.r. (5.09 μ), comparison of physical properties with those reported⁷ and oxidation to butyric acid. From 1,1-dibromo-2,2,3-trimethyl-*cyclopropane* in tetrahydrofuran, magnesium gives 2-methyl-2,3-pentadiene.

In our hands sodium reacts best in the form of its high surface dispersion on alumina. Under reduced pressure without solvent, 1,1-dibromo-2-*n*-propyl-*cyclopropane* is converted in excellent yield (96 per cent of theory) to a mixture of C₆H₁₀ hydrocarbons. Separation by v.p.c. gives three components, the major one (64 per cent) being 1,2-hexadiene and the two minor ones apparently being acetylenes. The more reactive metal has thus effected the allene-acetylene interconversion, a reaction well recognized as the result of the action of strong bases.^{8a} No extensive effort has been made to define the conditions necessary to minimize the isomerization.

No choice between the modes of cleavage formulated above can be made with assurance. The first scheme depicts the opening of an intermediate *cyclopropyl* radical to the corresponding allyl radical. Although this kind of change occurs at higher temperature, it does not occur in the low-temperature photochemical chlorination of *cyclopropane*⁸ to *cyclopropyl* chloride. Accordingly, the radical scheme does not seem particularly attractive. The second scheme, involving cleavage of the *cyclopropyl* carbanion to the allyl carbanion, also seems unlikely, in view of the failure of *cyclopropyl* carbanion itself to isomerize.^{9,10} It becomes far more attractive if ring opening and loss of halide ion be assumed to occur *simultaneously*.

The carbene mechanism will be tested partially by examining the irradiation of diazocyclopropane. The necessary condition that 1,1-dihalides and active metals

³ G. Gustavson *J. Prakt. Chem.* [2] 42, 496 (1890); [2] 43, 396 (1891).

⁴ W. von E. Doering and P. M. LaFlamme *J. Amer. Chem. Soc.* 78, 5447 (1956).

^{5a} T. L. Jacobs, R. Akawic and R. G. Cooper *J. Amer. Chem. Soc.* 72, 1272 (1950).

^{5b} J. H. Wotiz *J. Amer. Chem. Soc.* 73, 692, 5503 (1951); 74, 1860 (1952); *J. Organ. Chem.* 22, 207 (1957).

⁶ American Petroleum Institute Research Project 44 *Selected Values of Properties of Hydrocarbons and Related Compounds* Table 11a (Part I) Carnegie Institute of Technology, Department of Chemistry, Pittsburgh, Penn. (1952).

⁷ G. F. Hennion and J. J. Sheehan *J. Amer. Chem. Soc.* 71, 1964 (1949).

⁸ J. D. Roberts and P. W. Dirstine *J. Amer. Chem. Soc.* 67, 1281 (1945).

⁹ J. D. Roberts and V. C. Chambers *J. Amer. Chem. Soc.* 73, 3176 (1951).

¹⁰ V. A. Slabey *J. Amer. Chem. Soc.* 74, 4928 (1952).

should give carbenes appears to be fulfilled. In unpublished work, methylene iodide and finely divided zinc-copper couple react with *cis*- and *trans*-butene to give *cis*-1,2-dimethylcyclopropane, *cis*-pentene and 2-methyl-2-butene and *trans*-1,2-dimethylcyclopropane, *trans*-pentene and 2-methyl-2-butene respectively. These reactions are comparable to that of diazomethane with *cis*- and *trans*-butene.⁴

To the previously known conversions of the double bond through the 1,1-dibromocyclopropane group to a methyl ethane group¹ and to a cyclopropane ring,^{1,4} this reaction adds the conversion to an allene in only two steps by the insertion of a single carbon atom between the two of the original olefin. These transformations of the 1,1-dibromocyclopropanes are potentially useful in synthesis and are summarized below:

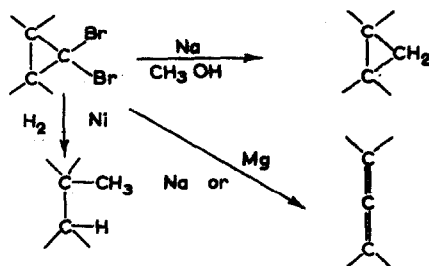
Examination of the behavior of some bicyclic dibromocyclopropanes obtained from bromoform and cyclic olefins is in progress and will be reported later. This investigation has been supported since its inception in the fall of 1954 by a much appreciated grant from the Research Corporation, New York City.

EXPERIMENTAL*

Preparation of allenes from 1,1-dibromocyclopropanes

(1) With magnesium

(a) *2,3-Pentadiene from cis-1,1-dibromo-2,3-dimethylcyclopropane*. *cis*-Dibromo-2,3-dimethylcyclopropane (45.6 g, 0.20 mole) in 100 ml of anhydrous ether was added dropwise to a stirred mixture of 24.3 g (1.00 g atom) of magnesium and 200 ml of ether in a 500-ml, 3-necked flask equipped with mechanical stirrer, dry-ice condenser and Ascarite drying tube. The reaction started easily on warming and was essentially complete after 2 hr under gentle reflux. A magnesium bromide-ether phase separated



midway through the addition. The reaction mixture was carefully hydrolyzed with ice-water. The ether phase was separated and later united with three 25 ml portions of ether used to extract the aqueous phase. Following addition of a trace of hydroquinone, the dried (magnesium sulfate) ether solution was fractionated through a 10 in. helix-packed column giving (1) b.p. 40–46°; 1.80 g; (2) b.p. 46.0–48.0°; 0.60 g and (3) b.p. 48–49.0°; 1.60 g. The infra-red spectrum of (3) showed a very strong

* Boiling points are uncorrected. Infra-red spectra were taken with a Perkin-Elmer Model 21 infra-red spectrophotometer with sodium chloride optics, samples neat of 0.1 and 0.025 mm thickness. V.p.c. (vapor phase chromatographic) analyses were made with a Perkin-Elmer Model 154 instrument, using a 2 m "A" column. Elementary analyses were performed by Schwarzkopf Microanalytical Laboratory, 56–19 37th Avenue, Woodside 77, New York.

peak at 5.06μ . Redistillation afforded 2,3-pentadiene; b.p. $48-48.5^\circ/771 \text{ mm}$; $n_D^{25} 1.4202$, $d_4^{25} 0.7020$ (reported⁶ b.p. $48.27^\circ/760 \text{ mm}$, $n_D^{25} 1.4251$); MR_D : found: 24.38; calcd: 23.30¹¹ (Found: C, 88.0; H, 12.0. C_6H_8 requires C, 88.2; H, 11.8 per cent).

Examination of the crude material by means of v.p.c. at 10 lb of He and 25° indicated 96.9 per cent, 2,3-pentadiene and 3.1 per cent of 2-pentyne, having an infra-red spectrum identical to that of an authentic sample obtained from the Farchan Research Laboratories, Cleveland, Ohio. Bromine in carbon tetrachloride was standardized against pure 2-methyl-2-butene. The allene (112.85 mg) in a sealed ampoule was crushed under carbon tetrachloride and titrated against a blank. The sample absorbed 5.250 ml of $0.282 + 0.011 \text{ M}$ bromine solution, or 0.89 mole of bromine per mole of hydrocarbon. This result agrees with that of Acree and La Forge¹² who found that the same compound under similar conditions absorbed 0.85 mole of bromine.

(b) *1,2-hexadiene from 1,1-dibromo-2-n-propylcyclopropane*. From 1-pentene, bromoform and potassium *t*-butylate, 1,1-dibromo-2-*n*-propylcyclopropane (b.p. $72^\circ/12 \text{ mm}$; $n_D^{25} 1.5023$) was prepared in 55 per cent of the theoretical yield through the kindness of Mr. Wm. A. Henderson, Jr. of this laboratory. A solution of 24.2 g (0.10 mole) of this dibromide in 25 ml of ether was added slowly to 2.67 g (0.11 atom) of magnesium in 25 ml of ether. The reaction was worked up as before giving 2.65 g (45 per cent) of material, b.p. $74-75^\circ$, and 11.23 g of recovered starting material. The yield based on unrecovered starting material was 62 per cent of theory. Analysis by v.p.c. of the crude material indicated it to be 92 per cent 1,2-hexadiene. A pure sample obtained by v.p.c. possessed a very strong peak in the infra-red at 5.09μ ; b.p. 75° ; $n_D^{20} 1.4276$ (unreported⁷ b.p. $74.6-74.8^\circ$; $n_D^{25} 1.4282$) (Found: C, 87.6; H, 12.0. C_6H_{10} requires C, 87.7; H, 12.3). Using the procedure of Hennion and Sheehan⁷ 0.25 g of the diene was oxidized with alkaline permanganate to an acid from which a *p*-bromophenacyl ester was prepared, m.p. $61-62^\circ$; mixed m.p. with an authentic sample of *p*-bromophenacyl-butyrate was $62-63^\circ$.

(c) *2-Methyl-2,3-pentadiene from 1,1-dibromo-2,2,3-trimethylcyclopropane*. From powdered potassium *t*-butylate (1 mole), bromoform (1 mole) and 300 g of 2-methyl-2-butene, 1,1-dibromo-2,2,3-trimethylcyclopropane (b.p. $63-66^\circ/15 \text{ mm}$) was prepared in 53 per cent yield by the usual reaction. A solution of 24.2 g (0.1 mole) of this dibromide in 50 ml of tetrahydrofuran (dried by distillation from Grignard) was treated with 4.86 g (0.2 g atom) of magnesium in dry tetrahydrofuran. Hydrolysis with water caused separation of a hydrocarbon phase which was washed repeatedly with water and dried over magnesium sulfate. Distillation gave 1.72 g of starting material and 2.75 g (34 per cent) of 2-methyl-2,3-pentadiene; b.p. 72.5° (reported¹³ b.p. $71.5-72.5^\circ$); $n_D^{25} 1.4350$; showing a weak peak at 5.09μ . (Found: C, 87.9; N, 12.0. C_6H_{10} requires C, 87.7; H, 12.3 per cent). The qualitative test for allenes described by Bouis¹⁴ in which the allene is added to an ethanolic mercuric chloride solution was positive, a copious white precipitate being formed.

¹¹ Using the value 0.44 for the system $C=C=C$ given by T. L. Jacobs and W. F. Brill *J. Amer. Chem. Soc.* **75**, 1316 (1953).

¹² F. Acree and F. B. La Forge *J. Organ. Chem.* **5**, 430 (1940).

¹³ S. Lebedew and B. Mereschkowski *J. Russ. Phys. Chem. Soc.* **45**, 1249 (1913); *Chem. Zentr.* **1**, 1409 (1914); *Chem. Abstr.* **8**, 3204 (1914).

¹⁴ M. Bouis *C. R. Acad. Sci., Paris* **182**, 788 (1925).

(II) With sodium

(b) *1,2-Hexadiene from 1,1-dibromo-2-n-propylcyclopropane*. High-surface sodium on alumina was prepared as follows. Chromatographic alumina (80–200 mesh, 103 g) was dried at 500° for 15 hr, cooled and placed in a 3-necked, 500 ml flask where it was further dried at 200° for 2 hr at 1 mm with stirring. The flask was cooled to 150° and, under nitrogen, 14.0 g (0.61 g atom) of sodium was added. Stirring was continued until a dark gray dispersion formed. An additional funnel and an exit tube connected to a trap at –78° were attached. At 5 mm, 24.2 g (0.1 mole) of 1,1-dibromo-2-n-propylcyclopropane was added dropwise with stirring at room temperature. The reaction was moderated by intermittent cooling to avoid the distillation of starting material. After the addition had been completed, pumping and stirring were continued one more hour. The crude product (7.64 g, 95.6 per cent) was examined by v.p.c. and appeared to be a mixture of 1,2-hexadiene (63.5 per cent) and two other components (26.5 and 10.0 per cent respectively) which had infrared peaks at 4.5 μ and were probably 1-hexyne and 2-hexyne.

(b) *2,3-Pentadiene from trans-1,1-dibromo-2,3-dimethylcyclopropane*. A suspension of 14.0 g (0.61 g atom) of sodium on 70 g of alumina was prepared as above. Into the same apparatus, 100 ml of *cis*-decalin (dried by distillation from sodium-on-alumina) was put. Thereupon, a solution of 57.0 g (0.25 mole) of *trans*-1,1-dibromo-2,3-dimethylcyclopropane in 50 ml of *cis*-decalin was added dropwise with stirring over a period of 2.5 hr at 25 mm and room temperature. The exothermic reaction was cooled intermittently to maintain the contents at 35°. After an additional hour, the trap had collected 17.6 g of liquid, from which 7.46 g (44 per cent) of nearly pure 2,3-pentadiene b.p. 48.0–48.5°, was obtained by distillation.