[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PENNSYLVANIA STATE UNIVERSITY]

The Reactions of Bivalent Carbon Species. Addition of Dihalocarbenes to 1,3-Butadiene

BY ROBERT C. WOODWORTH AND PHILIP S. SKELL

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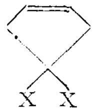
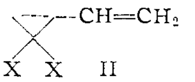
The reactions of dibromo- and dichlorocarbenes $:CBr_2$ and $:CCl_2$ to 1,3-butadiene are three center types of addition reactions producing 1,1-dihalo-2-vinylcyclopropanes. The structures of these products were demonstrated by conversion to the 2,2-dihalocyclopropanecarboxylic acids. The similarity of this addition reaction to heterolytic halogenation of 1,3-butadiene is discussed.

The reaction of 1,3-butadiene with dihalocarbenes $:CCl_2$ and $:CBr_2$ would be expected to produce 4,4-dihalocyclopentenes (I) by 1,4-addition or 1,1-dihalo-2-vinylcyclopropanes (II) by 1,2-addition.



I



II

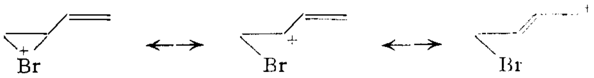
Dichloro- or dibromocarbene was generated in the presence of 1,3-butadiene by the action of base on chloroform or bromoform, respectively.[1,2] The major product from the reaction of 1,3-butadiene, bromoform and potassium *t*-butoxide is a heavy, sweet smelling, colorless liquid obtained in 70% yield. It rapidly discolors in air. The major product from the reaction of 1,3-butadiene, chloroform and potassium *t*-butoxide is a volatile, sweet smelling colorless liquid obtained in 50% yield. Since neither I nor II have been described previously, it was desirable that the homogeneity of the reaction products be established. Infrared spectra of fractions distilled from the reaction mixtures indicated that the dibromo product was contaminated only with unreacted bromoform. The dichloro product, however, contained an unknown contaminant boiling a few degrees lower than the main product. Careful fractional distillation of the contaminated material separated a small amount of the pure contaminant which proved to be 1,1-dichloro-2,2-dimethylcyclopropane, on comparison with the boiling point, refractive index and infrared spectrum reported for this compound.[2] This substance is formed in low yield in the reaction of chloroform with potassium *t*-butoxide in the presence of *t*-butyl alcohol,[2] probably by the addition of dichlorocarbene to isobutylene obtained by the dehydrating action of the dihalocarbenes on alcohols.[3] The bands observed in the infrared spectra of the successive fractions from the chloroform-1,3-butadiene reaction mixture can be explained by the major product and a single contaminant, 1,1-dichloro-2,2-dimethylcyclopropane.

Cleavage of the unsaturated bond with ozone was employed to prove the structures of the addition products. Ozonolysis of I should yield a dicarboxylic acid, and ozonolysis of II should yield a monocarboxylic acid. Ozonolysis of the dibromo- and dichloro-products yielded monocarboxylic acids with the correct analyses and neutral equivalents, respectively, for 2,2-dibromocyclopropanecarboxylic acid and 2,2-dichlorocyclopropanecarboxylic acid. The conclusion from these results is that both dibromo- and dichlorocarbene exhibit 1,2-addition to 1,3-butadiene and the products produced in this reaction have structure II.

Other instances of 1,2-additions to conjugated diolefins have been reported for the reactions of these olefins with diazoacetic esters in the presence of a copper catalyst to produce vinylcyclopropanecarboxylic esters.[4-8] Evidence which strongly suggests the intermediacy of a carbene in copper-catalyzed decompositions of diazo compounds has been presented.[9-12]

In the consideration of the heterolytic 1,4-additions of bromine and chlorine to 1,3-butadiene, Mislow and Hellman[13] have postulated that if 1,4-addition of X^+ produced a frontal halonium ion III, this would lead ultimately to a *cis*-1,4-dihalo-2-butene. However, since the products of bromination and chlorination of 1,3-butadiene were the *trans*-1,4-dihalo-2-butenes, these authors concluded that the intermediate halonium ion probably has structure IV.

III



IV

The affinity of the dihalocarbenes for olefins with electron-releasing substituents[14] and the stereochemical evidence for a singlet state (no unpaired electrons) for carbenes[12] led to the postulate

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[1] J. Hine, THIS JOURNAL, **72**, 2438 (1950); J. Hine and A. M. Dowell, *ibid.*, **76**, 2688 (1954); J. Hine, A. M. Dowell and J. E. Singley, *ibid.*, **78**, 479 (1956).

[2] W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6163 (1954).

[3] J. Hine, E. L. Politzer and H. Wagner, *ibid.*, **75**, 5607 (1953).

[4] C. von der Heide, *Ber.*, **37**, 2101 (1904).

[5] H. Staudinger, O. Muntwyler, L. Ruzicka and S. Seibt, *Helv. Chim. Acta*, **7**, 390 (1924).

[6] P. C. Guha and G. D. Hazra, *J. Indian Inst. Sci.*, **22A**, 263 (1939).

[7] (a) I. G. M. Campbell and S. H. Harper, *J. Chem. Soc.*, 283 (1945); (b) S. H. Harper and H. W. B. Reed, *ibid.*, 779 (1955).

[8] M. Matsui, Japanese Patent, 1769 (1952); *C. A.*, **48**, 2093*h* (1954).

[9] I. A. D'yakonov, *Zhur. Obshchei Khim.*, **19**, 1734 (1949).

[10] P. Yates, THIS JOURNAL, **74**, 5376 (1952).

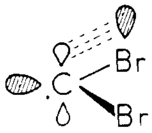
[11] M. S. Kharasch, T. Rudy, W. Nudenberg and G. Büchi, *J. Org. Chem.*, **18**, 1030 (1953).

[12] P. S. Skell and R. C. Woodworth, THIS JOURNAL, **78**, 4496 (1956).

[13] K. Mislow and H. M. Hellman, *ibid.*, **73**, 244 (1951); K. Mislow, *ibid.*, **75**, 2512 (1953); H. M. Hellman, J. W. Hellman and K. Mislow, *ibid.*, **76**, 1175 (1954).

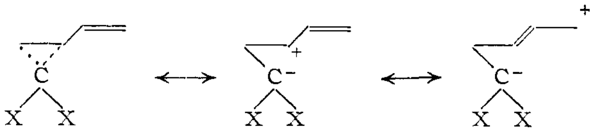
[14] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

that carbenes may be considered as sp^2-hybridized species, which by virtue of their vacant *p*-orbital exhibit electrophilic behavior predominantly.



IV

From this point of view one might have anticipated that the 2-electron deficient species $:CX_2$ and Br^+ would show similar behavior toward 1,3-butadiene. The intermediate complex in the reactions of dihalocarbenes with 1,3-butadiene may be described by V, in which bonding to both carbons of the double bond is developed simultaneously.



V

The electron-seeking character of the carbenes leads to the suggestion that electron-withdrawing (halogen) substituents on the 1,3-butadiene system will result in cyclopropane formation at the unsubstituted double bond, while electron-donating (alkyl) substituents will direct this addition to the substituted double bond. In partial confirmation of this prediction can be cited the failure to obtain an adduct when dichlorocarbene is generated in the presence of hexachloro-1,3-butadiene. Also it has been reported that carbethoxycarbene adds to the terminal double bond of 1-phenyl-1,3-butadiene[4] and the γ,δ-olefinic linkage of sorbate and α-methylsorbate esters.[7] In contradiction of an earlier report[5] the major product obtained from the reaction of carbethoxycarbene with isoprene is the ethyl ester of 2-methyl-2-vinylcyclopropanecarboxylic acid.[15]

Experimental

Procedure.—Solvent-free potassium *t*-butoxide was prepared by dissolving potassium metal in anhydrous *t*-butyl alcohol (dried by distillation from potassium *t*-butoxide). The excess alcohol was removed by distillation and then by pumping to an ultimate pressure of 2 mm. at a temperature of 95°. The dry cake was pulverized mechanically and the flask fitted with a stirrer, thermocouple and dropping funnel. The flask was cooled in a freezing carbon tetrachloride–Dry Ice-bath. The haloform was added to a slurry of the potassium *t*-butoxide in liquid 1,3-butadiene at such a rate that the reaction temperature never exceeded −10°. The haloform was added at a rate of approximately 0.5 mole per hour to avoid excessive temperature rise as a result of the rapid exothermic reaction. The reactants were stirred for an additional hour after the haloform addition was complete and then diluted with pentane and water. The organic layer was separated, washed with cold water, dried over anhydrous sodium sulfate, the solvent removed by distillation and the residue distilled to obtain the reaction products.

Ozonolyses were carried out in pentane solution, the viscous ozonide separating from the solution as it formed. The ozonides were decomposed in the presence of hydrogen peroxide and sulfuric acid and then refluxed to ensure complete oxidation of the aldehydes.

Reaction of 1,3-Butadiene with Chloroform and Potassium *t*-Butoxide.—The quantities of reactants were 239 g. (4.4 moles) of 1,3-butadiene, 170 g. (1.42 moles) of chloroform and 1.6 moles of potassium *t*-butoxide (from 62 g. of potassium metal). The products were distilled at atmospheric pressure to obtain 103 g. of material boiling at 115–123°, $n^{25}D$ 1.4662–1.4720. These fractions were combined and redistilled through a 50–100 plate column (24 in. × 8 mm. Podbielniak Mini-cal column packed with Hastelloy Heli-grid). The major portion of the product was separated as a fraction boiling constant at 122.5° (730 mm.), $n^{25}D$ 1.4720–1.4722. This product was identified as 1,1-dichloro-2-vinylcyclopropane. The foreruns were recombined and distilled through the same column to separate approximately 3 g. of 1,1-dichloro-2,2-dimethylcyclopropane, a middle fraction boiling at 115.8–116.7° (729 mm.), $n^{25}D$ 1.4450. These physical properties compare favorably with those reported by Doering and Hoffmann[2] (b. 118–120°, $n^{20}D$ 1.4461). The infrared spectrum of this substance appeared to be identical with that reported.[2] All of the fractions obtained between the 1,1-dichloro-2,2-dimethylcyclopropane and the 1,1-dichloro-2-vinylcyclopropane were examined by obtaining their infrared spectra on the neat liquid. All of the bands in the spectra were attributable to these two products, no other bands being evident. The total weight of 1,1-dichloro-2-vinylcyclopropane obtained was 98.5 g. (51%).

Anal. Calcd. for $C_5H_6Cl_2$: C, 43.83; H, 4.42. Found: C, 44.28; H, 4.41.

Ozonolysis of 1,1-Dichloro-2-vinylcyclopropane to 2,2-Dichlorocyclopropanecarboxylic Acid.—From the ozonolysis of 10.0 g. of 1,1-dichloro-2-vinylcyclopropane, there was obtained 8.0 g. of a crude viscous liquid monobasic acid (neutral equivalent 196 and pK_a 3.47) which crystallized from heptane. Recrystallization from hexane raised the melting point to 75–76°. Titrations of the pure acid indicated a monobasic acid, pK_a 3.50, 3.51 (23°, 0.01, 0.005 *M*).

Anal. Calcd. for $C_4H_4Cl_2O_2$: C, 30.86; H, 2.59; neut. equiv., 155. Found: C, 31.16; H, 2.55; neut. equiv., 151, 159, 155.

The *p*-bromophenacyl ester of this acid (recrystallized from ethanol) melted at 122–123°.

Anal. Calcd. for $C_{12}H_9BrCl_2O_3$: C, 40.92; H, 2.58. Found: C, 41.11; H, 2.63.

Reaction of 1,3-Butadiene with Bromoform and Potassium *t*-Butoxide.—The reactants were 152 g. (2.81 moles) of 1,3-butadiene, 125 g. (0.495 mole) of bromoform and 0.51 mole of potassium *t*-butoxide (from 20 g. of potassium metal). The products from this reaction were distilled in vacuum through a Vigreux column to separate a forerun of bromoform (identified through its infrared spectrum) and a fraction boiling 69.5–70.0° (26 mm.), $n^{25}D$ 1.4520, which was identified as 1,1-dibromo-2-vinylcyclopropane. A total of 67 g. of product was obtained (64% of theory, taking into account the recovered bromoform). This product darkens rapidly on contact with air.

Anal. Calcd. for $C_5H_6Br_2$: C, 26.58; H, 2.68. Found: C, 26.61; H, 2.52.

Ozonolysis of 1,1-Dibromo-2-vinylcyclopropane to 2,2-Dibromocyclopropanecarboxylic Acid.—From the ozonolysis of 19.4 g. of 1,1-dibromo-2-vinylcyclopropane, 10.0 g. of crude acid was obtained. Recrystallization of this acid from hexane gave a product whose melting point was 94–95°. Titration curves indicated this acid was a monobasic acid, pK_a 3.48, 3.57 (24°, 0.01, 0.005 *M*).

Anal. Calcd. for $C_4H_4Br_2O_2$: neut. equiv., 244. Found: neut. equiv., 242, 240.

The Reaction of Hexachloro-1,3-butadiene with Chloroform and Potassium *t*-Butoxide.—To a suspension of 0.43 mole of potassium *t*-butoxide in 133 g. of hexachloro-1,3-butadiene and 250 ml. of *n*-pentane, 40 g. of chloroform was added. Unreacted hexachloro-1,3-butadiene was recovered. The same result was obtained when potassium *t*-butoxide was added to a chloroform-hexachlorobutadiene mixture.

Infrared Spectra.—The following infrared spectra were obtained for the neat liquids in a 0.0235-mm. cell using NaCl optics, recording wave length in microns. 1,1-Dichloro-2-vinylcyclopropane: 3.27(m) 3.37(mw) 4.80(vw) 4.92(vw) 5.45(w) 5.54(vw) 5.73(vw) 6.11(ms) 6.31(vw) 6.99(m) 7.03(ms) 7.57(mw) 7.73(mw) 8.20(s) 8.36(m) 8.97(vs)

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[15] I. A. Dyakonov and V. F. Myznikova, *C. A.*, **47**, 4293e (1955).

9.32(m) 9.55(ms) 9.82(s) 10.15(s) 10.90(vs) 11.38(m) 13.00–13.10(vs) 14.86(s) 15.02(ms).

1,1-Dibromo-2-vinylcyclopropane: 3.27(m) 3.37(mw) 3.43(m) 3.52(mw) 4.80(vw) 4.93(vw) 5.45(w) 5.81(vw) 6.13(m) 6.99(m) 7.05(m) 7.58(w) 7.73(mw) 8.24(m) 8.41(m) 9.03(vs) 9.55(ms) 9.89(s) 10.16(vs) 10.85–10.90(vs) 11.56(mw) 12.73(w) 13.93(vs).

1,1-Dichloro-2,2-dimethylcyclopropane: 3.37(ms) 3.40(s) 3.45(s) 3.50(m) 3.68(w) 6.30(w) 6.85(s) 6.92(ms) 6.97(s) 7.21(m) 7.27(ms) 7.52(vw) 7.62(w) 7.80(w) 7.94(mw) 8.22(w) 8.94(s) 9.06(s) 9.40(vs) 9.62(s) 9.96(ms) 10.34(m) 11.00(w) 11.20(w) 11.64(ms) 12.25(w) 12.70(m) 13.19(vs) 14.12(vw) 14.95(vw).

UNIVERSITY PARK, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Confirmation of the Intramolecular Nature of the Hofmann "Haloamide" Reaction by Double Labeling

BY THOMAS J. PROSSER AND ERNEST L. ELIEL

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Treatment of a mixture of m-$DC_6H_4CONH_2$ and $C_6H_5CON^{15}H_2$ with sodium hypochlorite gave a mixture of m-$DC_6H_4NH_2$ and $C_6H_5N^{15}H_2$ free of m-$DC_6H_4N^{15}H_2$ as established by mass spectrometry. The degree of labeling of the substrates and the sensitivity of the analytical method are such that it can be stated with confidence that the Hofmann reaction is at least 96% intramolecular.

The reaction of an amide with hypohalite to give an amine or derivative thereof, *e.g.*, $RCONH_2 + NaOBr \rightarrow RNH_2 + CO_2 + NaBr$, is known as the Hofmann haloamide reaction.[1,2] This reaction, as well as several other related ones,[3] has long been considered to be intramolecular. Evidence for this is entirely stereochemical and comes from the fact that amides in which the R-group is asymmetric at the point of attachment—such as $C_6H_5CH(CH_3)CONH_2$—yield amines in which configuration is retained and optical activity almost completely preserved,[4] even where activity is due to restricted rotation in a biphenyl system,[5] and that geometric configuration of the R-group is also preserved[6] in the rearrangement of R from carbon to nitrogen which must occur in the Hofmann haloamide reaction. Moreover, the reaction proceeds normally at bridgehead carbon atoms.[7]

While the stereochemical evidence for retention of configuration is thus overwhelming, it is not so convincing that this constitutes proof for the intramolecular nature of the rearrangement, especially in view of the fact that certain intermolecular reactions involving carbanion intermediates have recently been shown to involve retention of optical[8] and geometrical[9] configuration and that carbanion reactions may proceed normally at bridgehead carbon atoms.[10] An independent proof of the intramolecular nature of the Hofmann haloamide reaction thus seemed desirable.

The most convincing evidence for the intramolecular nature of any reaction comes from study of the products obtained in the reaction when carried out on a mixture of two substrates A–B and A′–B′. If only products corresponding to A–B and A′–B′ are obtained in a reaction involving rupture of the A–B bond, then the reaction is intramolecular; but if products corresponding to A–B′ and A′–B are also obtained, then the reaction is at least in part intermolecular. In fact this criterion may well be considered an operational definition of the terms "intramolecular" and "intermolecular." In the case of the Hofmann haloamide reaction, an appropriate experiment would be to rearrange a mixture of $RCONH_2$ and $R'CON^{15}H_2$, cleanly separate the two chemically distinct products RNH_2 and $R'NH_2$ (labeled or unlabeled), and demonstrate by conventional degradation to nitrogen gas and isotope ratio measurements of the latter[11] that RNH_2 contains no excess of the N^{15} isotope. There are, however, two difficulties with such a procedure. One is the need for rigorous purification of RNH_2, to eliminate the possibility of contamination with $R'N^{15}H_2$. This difficulty can be obviated by carrying out the N^{15} analysis by direct mass spectrometry[12] of RNH_2 at reduced ionizing voltage[13]—provided RNH_2 and $R'NH_2$ are not isomeric. The second difficulty is concerned with the need of choosing $RCONH_2$ and $R'CONH_2$ so

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[1] A. W. Hofmann, *Ber.*, **14**, 2725 (1881). We prefer to include the word "haloamide" since at least two other reactions—the alkylation of amines and the degradation of quaternary ammonium salts—are commonly associated with Hofmann's name.

[2] For a review see E. S. Wallis and J. F. Lane in R. Adams, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 267–306.

[3] *Cf.* D. J. Cram in M. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 251–253.

[4] E. S. Wallis and S. C. Nagel, THIS JOURNAL, **53**, 2787 (1931); C. L. Arcus and J. Kenyon, *J. Chem. Soc.*, 916 (1939).

[5] F. Bell, *ibid.*, 835 (1934); E. S. Wallis and W. W. Moyer, THIS JOURNAL, **55**, 2598 (1933).

[6] W. A. Noyes, *et al.*, *Am. Chem. J.*, **16**, 503 (1894); **24**, 290 (1900); **27**, 425 (1902); THIS JOURNAL, **32**, 1669 (1910); **36**, 118 (1914); **39**, 2692 (1917); J. Weir, *J. Chem. Soc.*, **99**, 1270 (1911).

[7] P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939).

[8] R. L. Letsinger, *ibid.*, **72**, 4842 (1950); D. J. Cram, J. Allinger and L. Langemann, *Chemistry & Industry*, 919 (1955). The cases cited by A. N. Nesmeyanov, O. A. Reutov and S. S. Poddubnaya, *Doklady Akad. Nauk S.S.S.R.*, **88**, 479 (1953), *C. A.*, **48**, 2632b (1954), and S. Winstein, T. G. Traylor and C. S. Garner, THIS JOURNAL, **77**, 3741 (1955), may or may not be pertinent here.

[9] *Cf.* E. Eliel in M. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 154–155.

[10] W. v. E. Doering and L. K. Levy, THIS JOURNAL, **77**, 509 (1955).

[11] D. W. Wilson, A. O. C. Nier and S. P. Reimann, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Mich., 1946, pp. 20–22, 31–39.

[12] *Cf.* H. W. Washburn in W. G. Berl's "Physical Methods of Chemical Analysis," Vol. I, Academic Press, Inc., New York, N. Y., 1950, pp. 618–620: E. L. Eliel, T. J. Prosser and G. W. Young, *J. Chem. Ed.*, **34**, 72 (1957).

[13] D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950).