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

The Stereochemistry of Carbene–Olefin Reactions. Reactions of Dibromocarbene with the *cis*- and *trans*-2-Butenes

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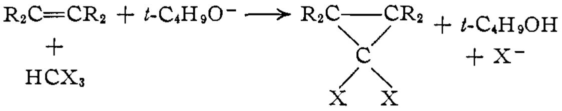
The reaction of dibromocarbene, $:CBr_2$, with *cis*- or *trans*-2-butene is stereospecific and produces the *cis*- or *trans*-1,1-dibromo-2,3-dimethylcyclopropane from the respective olefin. The mechanistic implications are discussed.

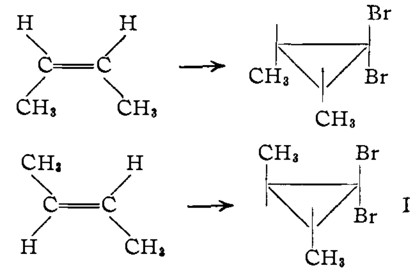
During the first decade of this century, carbenes (uncharged disubstituted carbons, $R_2C:$) received much consideration by J. U. Nef and his students. Although their efforts to introduce carbene intermediates into numerous reaction mechanisms were notably unsuccessful, during the intervening years sporadic reports from various laboratories have indicated a continuing interest and an accumulation of evidence indicative of carbene intermediates.[1] The recent studies reported by Hine[1l] have demonstrated that when haloforms react with strong bases they lose the elements H and X and leave a reactive dihalocarbene intermediate. Doering and Hoffman[1t] showed that these carbenes react readily with olefins to produce cyclopropane derivatives.

$$HCX_3 + B^- \rightleftharpoons BH + :CX_3^-$$

$$:CX_3^- \rightleftharpoons X^- + :CX_2{}^{2}$$



Since the study of the addition reactions of $\cdot CCl_3$ radical to the *cis*- and *trans*-2-butenes[3] helped to define the details of radical–olefin interactions, the study of dihalocarbene additions to these olefins held promise of being similarly rewarding. The reaction of *cis*- or *trans*-2-butene (1.0 mole) and alcohol-free potassium *t*-butoxide (0.4 mole) with bromoform (0.3 mole) was carried out at temperatures between −10 and −24°. The infrared spectra of the recovered 2-butenes were identical with those of the starting materials and showed no evidence of isomerization. Isolation of the 3,3-dibromo-1,2-dimethylcyclopropanes was accomplished in yields of 70–80% from either olefin. These products did not react with bromine in carbon tetrachloride. The infrared spectra of the cyclopropanes produced from either the *cis*-(II) or the *trans*-(III) olefin were distinctly different and the superposition of these spectra showed that each of these products contained no more than a trace of the other isomer (an amount consistent with the 99 mole % purity of the starting olefins). That this difference in spectra is not attributable to the presence of varying amounts of 1,1-dibromo-2,2-dimethylcyclopropane (I), (by addition of $:CBr_2$ to isobutene, resulting from the dehydration of *t*-butyl alcohol)[1t,4] is readily apparent from an examination of the spectra. Since the mechanism of this reaction apparently involves a step in which the dibromocarbene, $:CBr_2$, adds to both atoms of the double bond, and for the reasons developed below, the following structural relations are indicated.



II

III

With the experimental information cited above, it is possible to eliminate entirely or place limits on alternative mechanistic pathways.

The possibility that the products, $C_5H_8Br_2$, were produced in a free-radical chain reaction followed by dehydrohalogenation of the 1:1 adduct[5] can be rejected for (a) the products of such a process would be unsaturated and (b) an identical mixture of products would be obtained from either of the 2-butenes.[3]

A reaction sequence involving addition of $:CBr_3^-$ to the olefin, followed by ring closure, was considered unlikely by Doering and Hoffman[1t] because there seemed to be little precedent for the addition of anions to unactivated double bonds. Although there is considerable merit to this argument, it becomes necessary to reconsider this possibility, for the recent reports of the addition

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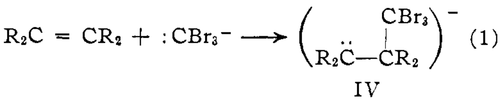
[1] For references and discussion see: (a) A. Michael, THIS JOURNAL, **42**, 817 (1920); (b) E. Bergmann and J. Hervey, *Ber.*, **62B**, 893 (1929); (c) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 708 (1930); (d) C. D. Hurd, "Organic Chemistry" (Gilman), Vol. I, 1st Ed., John Wiley and Sons, Inc., 1938, New York, N. Y., p. 468; (e) P. S. Skell and C. R. Hauser, paper presented before Organic Division of 104th Meeting of ACS, Buffalo, N. Y., Sept. 8, 1942, page 24M of Abstracts; (f) H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942); (g) L. Hellerman and R. L. Garner, THIS JOURNAL, **68**, 819 (1946); (h) R. G. W. Norrish and G. Porter, *Disc. Faraday Soc.*, **2**, 97 (1947); (i) K. J. Laidler and E. J. Casey, *J. Chem. Phys.*, **17**, 213 (1949); (j) F. C. Palazzo, *Gazz. chim. ital.*, **79**, 13 (1949); (k) J. Lennard Jones and J. A. Pople, *Disc. Faraday Soc.*, **10**, 9 (1951); (l) J. Hine, THIS JOURNAL, **72**, 2438 (1950); (m) G. F. Hennion and D. E. Maloney, *ibid.*, **73**, 4735 (1951); (n) P. Yates, *ibid.*, **74**, 5376 (1952); (o) W. H. Urry and J. R. Eiszner, *ibid.*, **74**, 5822 (1952); (p) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952); (q) J. L. Margrave and K. Weiland, *J. Chem. Phys.*, **21**, 1552 (1953); (r) M. S. Kharasch, T. Rudy, W. Nudenberg and G. Büchi, *J. Org. Chem.*, **18**, 1030 (1953); (s) W. E. Parham and W. R. Hasek, THIS JOURNAL, **76**, 935 (1954); (t) W. von E. Doering and A. K. Hoffman, *ibid.*, **76**, 6163 (1954); (u) W. E. Parham and H. E. Reiff, *ibid.*, **77**, 1177 (1955); (v) S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955).

[2] Isotopic exchange experiments indicate that both steps are reversible. See J. Horiuti, K. Tanabe and K. Tanaka, *J. Research Inst. Catalysis Hokkaido Univ.*, **3**, 119 (1955). See also, J. Hine and A. M. Dowell, Jr., THIS JOURNAL, **76**, 2688 (1954).

[3] P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

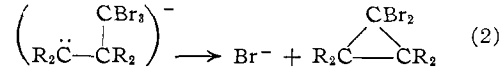
[4] J. Hine, E. L. Pollitzer and H. Wagner, *ibid.*, **75**, 5607 (1953).

[5] M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **68**, 154 (1946); **69**, 1100 (1947).



$$R_2C = CR_2 + :CBr_3^- \longrightarrow \left(\begin{array}{c} \quad CBr_3 \\ \quad | \\ R_2\ddot{C}-CR_2 \end{array}\right)^- \qquad (1)$$

IV



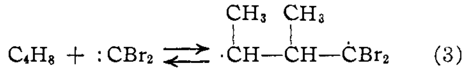
$$\left(\begin{array}{c} \quad CBr_3 \\ \quad | \\ R_2\ddot{C}-CR_2 \end{array}\right)^- \longrightarrow Br^- + R_2C\overset{CBr_2}{\triangle}CR_2 \qquad (2)$$

IV

of unactivated olefins to sodium alkyls[6] and aluminum alkyls[7] are among the reactions which offer good analogies for step 1. However, it is possible to reject a mechanism involving steps 1 and 2 on stereochemical grounds. Species IV would be expected to equilibrate between the diastereomeric carbanions at a rate comparable with the rate of racemization of optically active carbanions. Thus this reaction sequence would predict that from both *cis*- and *trans*-2-butenes an identical mixture of diastereomeric cyclopropanes would be obtained. If steps 1 and 2 are to correctly represent the mechanism, 2 must proceed at a rate of at least 10–100 times greater than the rate of equilibration of IV, thus requiring that the SN2 type ($R:^- + R'CBr_3 \rightarrow Br^- + R-CBr_2-R'$) of ring closure proceed at a highly improbable rate. As a crude approximation, the rate of equilibration of IV can be estimated by assuming: (a) that the inversion at the trivalent carbon takes place at the same rate as the ammonia inversion and (b) that the rate of rotation about the C–C bond can be estimated by using the Transition State Theory rate equation and assigning +2.38 e.u. as the entropy of activation ($S_{\text{free-rotor}} - S_{\text{hindered rotor}}$) and the barrier to rotation (8 kcal./mole from isopentane or 3 kcal./mole from ethane) as the heat of activation.[8] The rates estimated in this fashion are 5×10^{10} sec.$^{-1}$ (from the ammonia inversion) and 10^8 to 5×10^{12} sec.$^{-1}$ (for the rotations with isopentane or ethane barriers, respectively). In order to account for the observed stereospecificity of this reaction, it would be necessary to assign to reaction 2 a specific rate constant of at least 10^{10} sec.$^{-1}$ ($\Delta H^* = 4$ kcal./mole if $\Delta S^* = 0$).

Elimination of reaction mechanisms involving $\cdot CBr_3$ and $:CBr_3^-$ leads one to consider mechanisms involving $:CBr_2$ intermediates.

A mechanism involving reversible association of $:CBr_2$ and 2-butene to produce a bi-radical is precluded by the failure to observe isomerization in the recovered olefin.

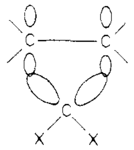


$$C_4H_8 + :CBr_2 \rightleftarrows \cdot\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-\dot{C}Br_2 \qquad (3)$$

V

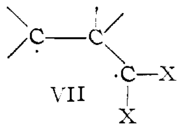
The formation of V as a relatively stable intermediate by an irreversible association of C_4H_8 and $:CBr_2$ must be considered, for Bawn and Hunter[9] have shown that $\cdot CH_2-CH_2-CH_2\cdot$ produced in the gas phase reaction of sodium with 1,3-dibromopropane must have an appreciable half-life and survive numerous collisions, since the wall-reaction which converts this di-radical to propylene is competitive with the homogeneous cyclization to cyclopropane. Here again, the stereochemical evidence precludes this possibility, for if this radical were relatively stable, it should undergo equilibration among the diastereomeric radicals through rotations and inversions, as rapidly as the radical obtained from the reaction of $\cdot CCl_3$ with the 2-butenes.[3]

Two significantly different alternatives remain to be considered. Either V is an intermediate with a half-life less than 10^{-10} to 10^{-13} sec. (see above for estimates of rates of rotation about C–C bond) or $:CBr_2$ bonds simultaneously with both carbons of the double bond. This latter possibility may be represented as



VI

The structural parameters of V are obviously quite different from those of VI, the former having the open chain configuration of propane (VII). At



VII

present it has not been possible to choose between these alternative intermediates on the basis of either experimental observations or theoretical considerations.

Although it is possible that the rate of closure of the three-membered ring in VII may be too rapid to permit a choice on phenomenological grounds between intermediates VI and VII, it is hoped that experimental work which is now in progress will either discriminate between these possibilities or place better defined limits on the half-life of VII.

Experimental

Reaction of Bromoform with an Olefin in the Presence of Potassium *t*-Butoxide.—Four-tenths of a mole of potassium *t*-butoxide was prepared by adding 16.0 g. (0.408 mole) of potassium metal to an excess of distilled *t*-butyl alcohol. The excess alcohol was distilled under vacuum on a steam-bath. The solid cake of potassium *t*-butoxide which remained was broken into flakes with a stirring rod.

The flask with the potassium *t*-butoxide in it was fitted with a mercury-sealed stirrer, a dropping funnel and a two-holed rubber stopper containing a thermocouple well and a sodium hydroxide drying tube. The flask was immersed in a Dewar flask containing Dry Ice and carbon tetrachloride at −24°. After the flask had stood in the bath for about 15 minutes, approximately 1 mole of the olefin was poured into the flask. (Olefins used were Phillips 99 mole % *cis*- and *trans*-2-butenes and Matheson isobutylene.) The olefin–potassium *t*-butoxide mixture was stirred rapidly until the thermocouple registered −24°.

At this point 75.9 g. (0.299 mole) of Dow pharmaceutical grade bromoform was added slowly over a period of about 40

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[6] H. Pines, J. A. Veseley and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955). H. Pines and V. Mark, paper presented before the Organic Division of the 127th Meeting of the American Chemical Society in Cincinnati, Ohio, March 31, 1955, page 21N of Abstracts.

[7] K. Ziegler, H. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 91 (1954); see also, *Angew. Chem.*, **64**, 323 (1952).

[8] J. G. Aston and S. C. Schuman, THIS JOURNAL, **64**, 1037 (1942).

[9] C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

TABLE I

PHYSICAL CONSTANTS OF CYCLOPROPANES, $C_5H_8Br_2$

	I	II	III
B.p., °C.	59–59.2	70–70.2	64.0
Press., mm.	20	23	23
$n^{25.1}_D$	1.5121	1.5170	1.5108
Yield, %	71.8	79.6	67.8[a]
Carbon, % found[b]	...	26.31	26.31
Hydrogen, % found[b]	...	3.61	3.57

[a] This yield is low because of small accidental loss of product. [b] Calcd. for $C_5H_8Br_2$: C, 26.34; H, 3.54.

TABLE II

MAJOR ABSORPTION BANDS OF THE ISOMERIC CYCLOPROPANES[a]

I	II	III
2.31V.W.	2.31V.W.	2.31V.W.
3.34S.	3.37S.	3.36S.
3.38S.	3.42S.	3.41S.
3.43S.	3.48M.	3.48M.
3.48M.	3.64V.W.	3.64V.W.
3.65V.W.	5.40V.W.	4.62V.W.
4.82V.W.	6.00V.W.	5.77V.W.
5.18V.W.	6.38V.W.	6.25V.W.
6.81S.	6.83S.	6.38V.W.
6.91S.	6.89S.	6.89V.S.
6.97S.	7.20S.	7.23M.S.
7.20M.	8.08M.	8.21M.
7.26M.S.	8.66M.	8.53V.S.
7.95M.	8.90V.S.	9.27S.
9.11S.	9.23M.	9.97M.S.
9.57V.S.	9.57W.	10.42V.S.
10.01M.S.	10.03W.	10.60V.S.
10.39M.	10.32M.S.	11.05W.
11.22W.	10.75V.S.	12.04W.
11.96M.	12.13S.	12.29M.
14.35V.S.	13.67V.S.	12.75W.
15.05M.		13.50V.S.
		15.20W.

[a] Infrared spectra were taken neat in a 0.0235-mm. cell using a Perkin–Elmer model 21 spectrophotometer with NaCl optics.

minutes. The complete reaction took place between −24 and −10°. The mixture was stirred for 2 hr. after all of the bromoform had been added. The reaction flask was removed from the cooling bath and was allowed to come to room temperature. An outlet tube was connected to a trap to catch the unreacted olefin. When the olefin was *cis*- or *trans*-2-butene, a sample of the unreacted olefin was admitted into a 10.0-cm. gas cell (NaCl optics) at 200 mm. pressure and 28° for infrared analysis. The spectra of these olefins showed no evidence of contamination by its isomer.

After all of the olefin had evaporated, 250 ml. of pentane was added with stirring and then was followed by a similar volume of water. Stirring was continued until all of the solid had dissolved. The pentane and water layers were separated, and the water layer was extracted several times with pentane. The pentane extracts were combined and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled in vacuum through a 6″ Vigreux column. The main body of the product was collected in six successive fractions to aid in the detection of any nonhomogeneity of the products.

The physical properties of 1,1-dibromo-2,2-dimethylcyclopropane (I, from isobutylene), *cis*-1,1-dibromo-2,3-dimethylcyclopropane (II, from *cis*-2-butene) and *trans*-1,1-dibromo-2,3-dimethylcyclopropane (III, from *trans*-2-butene) are listed in Table I.

For each run, comparison by superposition of the infrared spectra which were obtained for an early and a late fraction failed to demonstrate any heterogeneity in these samples or contamination by the isomeric products. The major absorption bands of these cyclopropanes are shown in Table II and absorption from 7.75 to 8.5 μ in Fig. 1.

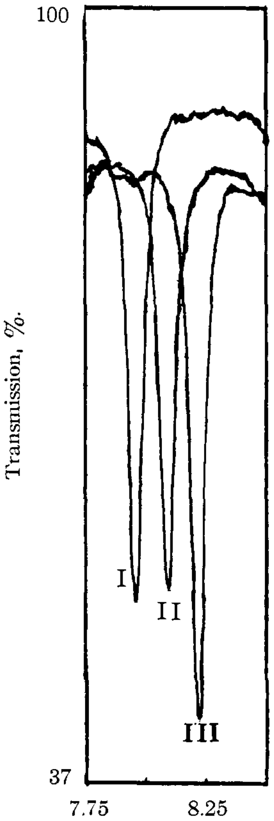

Fig. 1.—Absorption spectra of the isomeric cyclopropanes from 7.75 to 8.50 μ.

All samples reacted when warmed with alcoholic $AgNO_3$ and failed to react with bromine in carbon tetrachloride.

The dibromocyclopropanes were dehalogenated rapidly with a slurry of Raney nickel catalyst in 95% ethanol to produce hydrocarbons. The infrared spectra, freezing points and vapor pressures indicated that neopentane and 1,1-dimethylcyclopropane (latter probable) were obtained from I and isopentane from (III).

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