Recrystallization from acetone raised the melting point to 168–169°.

Anal. Calcd. for $C_8H_{14}N_8O_{10}$: C, 25.13; H, 3.69; N, 29.32. Found: C, 25.22; H, 3.63; N, 29.11.

1,3,5-Tris-(3′-nitrazabutyl)-hexahydro-1,3,5-triazine (XII).—To 15.6 g. (0.10 mole) of 3-nitrazabutylamine hydrochloride, 25 ml. of water and 8.1 g. (0.10 mole) of 37% formalin, a solution of 8.2 g. (0.10 mole) of sodium acetate in 15 ml. of water was added dropwise. After stirring for 30 minutes, a white solid precipitated from the solution. The product was collected, washed with water and dried; 5.9 g. (45.0%), m.p. 88–90°. Recrystallization from ethyl acetate raised the melting point to 97–97.5°.

Anal. Calcd. for $C_{12}H_{27}N_9O_6$: C, 36.63; H, 6.92; N, 32.05. Found: C, 36.98; H, 6.94; N, 31.68.

1,3-Bis-(3′-nitrazabutyl-5,5-dinitrohexahydro-1,3-diazine (XIV).—To 46.5 g. (0.30 mole) of 3-nitrazabutylamine hydrochloride, 24.9 g. (0.15 mole) of 2,2-dinitro-1,3-propanediol[10] and 100 ml. of water, was added dropwise a solution of 24.6 g. (0.30 mole) of sodium acetate in 75 ml. of water. The yellow solid which precipitated was collected, washed with water and dried; 34.6 g. (62.7%), m.p. 110–115°.

A mixture of 3.68 g. (0.01 mole) of the above yellow solid, 0.81 g. (0.01 mole) of 37% formalin and 100 ml. of water was stirred at room temperature for one hour and then at 40–45° for one hour. The tan colored solid was collected and dried; 3.2 g. (84.3%), m.p. 115–120°. Recrystallization from chloroform raised the melting point to 120–121°.

Anal. Calcd. for $C_{10}H_{20}N_8O_8$: C, 31.58; H, 5.30; N, 29.46. Found: C, 31.72; H, 5.36; N, 28.70.

AZUSA, CALIFORNIA

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[10] H. Feuer, G. B. Bachman, and J. P. Kispersky, THIS JOURNAL, **73**, 1360 (1951).

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

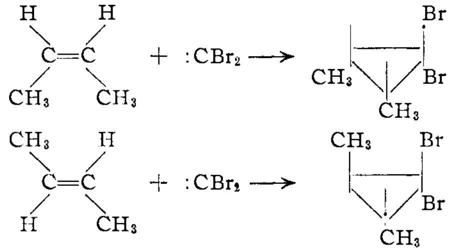
Reactions of Bivalent Carbon Compounds. Reactivities in Olefin–Dibromocarbene Reactions

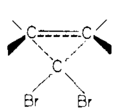
BY PHILIP S. SKELL AND ALBERT Y. GARNER

RECEIVED MAY 9, 1956

The rate of addition of dibromocarbene, :CBr_2, to olefins decreases in the order tetramethylethylene > trimethylethylene > anethole > isobutylene > *asym*-diphenylethylene > butadiene > cyclopentene > cyclohexene = styrene > 1-hexene > allylbenzene > vinyl bromide. Since essentially the same sequences of rates and stereospecificity is observed for bromination and epoxidation of olefins, a common intermediate complex is suggested for these three-center-type addition reactions. It is proposed that the intermediate complex (III) in carbene–olefin reactions is a partially-formed cyclopropane with carbonium ion character developed on one of the carbons of the double bond.

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.[1] It follows from these observations that the intermediate had either (a) a cyclopropane structure (I) in which bond formation to both carbons was established simultaneously, or (b) the structure of biradical II, with propane bond angle and bond lengths, which cyclized with a half-life less than 10^{-10} to 10^{-13} second to a cyclopropane. The limits set on the half-life of II resulted from a theoretical consideration of the rates of rotation about the single bond.





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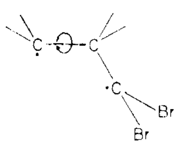
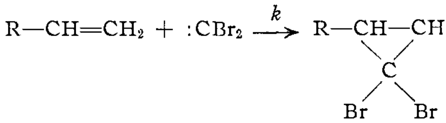


II

Relative Rates of Addition of :CBr_2 and ·CCl_3 to Olefins.

—With the hope of distinguishing between I and II on experimental grounds we sought evidence for the radical nature of the intermediate. If II has a lifetime longer than a vibration period ($\sim 10^{-13}$ sec.) the interaction of the trivalent carbons over a distance of 2.54 Å. (C_1–C_3 distance in propane) should make a minor contribution to the ground state of II. Thus if II correctly represents the structure of the intermediate in this reaction, the relative rates of reaction of olefins should be essentially the same for :CBr_2 and a radical such as ·CCl_3. Whatever structural factors operate to make one olefin more reactive than another in addition of ·CCl_3, should operate equally well in the addition of :CBr_2, if II is an intermediate.

To ascertain the necessary relative rate constants, :CBr_2 was generated in *t*-butyl alcohol solution (from bromoform and potassium *t*-butylate) in the presence of known quantities of two olefins. Preliminary experiments had demonstrated that the olefins were utilized solely in the production of dibromocyclopropanes and that these products were stable. The amounts of the two dibromocyclopropane products were determined and by difference the amounts of unreacted olefin. For two parallel bimolecular reactions (1) the ratio of rate constants is given by equation 4, C and C' being the concentrations of the respective olefins and n_i, n_f, n'_i and n'_f being the initial and final molar amounts of the respective olefins. Since the volume of the solution V increased during the reaction



(1)

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[1] P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 3409 (1956).

as a result of continual addition of potassium *t*-butylate in *t*-butyl alcohol, the expression for change in concentration of olefin must include both a kinetic and a dilution term.

$$d(C) = -k(C)(:CBr_2)\,dt - (C)(dV/V)$$

Substituting $C = n/V$

$$dn/n = -k(:CBr_2)dt \qquad (2)$$

and similarly for the other olefin

$$dn'/n' = -k'(:CBr_2)dt \qquad (3)$$

Division of 2 by 3 and integration gives

$$\frac{\log (n_f/n_i)}{\log (n_f'/n_i')} = \frac{k}{k'} \qquad (4)$$

In Table I are listed the relative rate constants for the addition to olefins of $:CBr_2$ and $\cdot CCl_3$.

Table I

Relative Rate Constants for $\cdot CCl_3$ and $:CBr_2$ Additions to Olefins

Olefin	$\cdot CCl_3$[2,3]	$:CBr_2$
Butadiene	>38	0.5
Styrene	>19	0.4
Isobutylene	1.00	1.00
$RCH{=}CH_2$	0.19[b]	0.07[a]
Trimethylethylene	.17	3.2
Cyclopentene	.15	0.5
Allylbenzene	.13	.02
Cyclohexene	.045	.4

[a] 1-Hexene. [b] 1-Octene, 1-butene.

There is no relation between the variations of rate with structure for the addition of $:CBr_2$ *and* $\cdot CCl_3$ *to olefins.* Most striking is the > 400-fold difference in the ratio $k_{\text{styrene}}/k_{\text{cyclohexene}}$ for the two series. It is difficult to avoid the conclusion that II cannot be an intermediate in the olefin–dibromocarbene reaction.

In summary, the lines of evidence which lead to the rejection of II as an intermediate in olefin–dibromocarbene reactions are (a) the failure to obtain a reactivity series characteristic of the reaction of olefins with the trichloromethyl radical, and (b) the complete stereospecificity of the reaction of the 2-butenes with dibromocarbene.

The elimination of II leaves as the most likely alternative a representation in which the dibromocarbene is bonded to both of the double bond carbon atoms simultaneously, as in I.

Relative Rates of Olefin Addition of Dibromocarbene and Other Three-center-type Associations.—Three-center-type association reactions, such as are indicated for the olefin–dibromocarbene reactions, have received little attention in the literature. As a first impression, there do not appear to be many reactions that fall into this category. The epoxidation of olefins with peracetic and perbenzoic acids[4,5] and the bromination of olefins[6] may fall within this classification. In Table II are listed, in order of decreasing olefin reactivity for the carbene series, all the reactivities determined in this work and the available relative rates of non-radical bromination in non-polar solvent and epoxidation by peracetic acid.

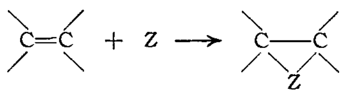

Table II

Relative Rates of Some Three-center-type Additions to Olefins

Olefin	Dibromocarbene	Bromination[6b]	Epoxidation[5]
Tetramethylethylene	3.5	2.5	V. fast
Trimethylethylene	3.2	1.9	13.5
Anethole	1.2		
Isobutylene	1.00	1.00	1.00
asym-Diphenylethylene	0.8		0.5
Butadiene	.5		
Cyclopentene	.5		2.1
Cyclohexene	.4		1.4
Styrene	.4	0.59	0.1
1-Hexene	.07	.36[a]	.05[b]
Allylbenzene	.02		.02
Vinyl bromide	V. slow	.01	

[a] Propylene. [b] 1-Pentene.

Except for the displacement of the cyclic olefins the correlation of structure with reactivity for bromination, epoxidation and dibromocarbene additions is noteworthy. The cyclic olefin displacement may be attributable to a difference in strain energy introduced in the fusion to the bicyclic system with cyclopropane and oxirane rings.

Although the data available for comparison cover a rather limited structural range, the correlation of the bromination data with the dibromocarbene data is strikingly good. A plot of the free energy of activation (log *k* *vs.* log *k*) for these two systems is a straight line with slope +2.1 (carbene/bromine).

Formation of a bromonium ion in olefin bromination,[6a] addition of an oxygen atom to an olefin in epoxide formation[5] and addition of carbenes to olefins have a feature in common, namely, the addition of a 2-electron deficient agent to the olefin. There do not appear to be further data in the literature that are suitable for extending this type of correlation. Mayo and Walling's summary of cationic copolymerization data[7] suggests the encouraging possibility of additional positive correlation since the ratio of the rates of carbonium ion additions to isobutylene and styrene are 1.0:0.1.

Structure of the Intermediate Complex and Dibromocarbene.—A knowledge of the multiplicity of the ground state of dibromocarbene would help in defining the structure of the intermediate complex in olefin additions. The results cited above favor the provisional assignment of a singlet state to di-

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(2) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949); M. S. Kharasch and M. Sage, *ibid.*, **14**, 537 (1949); M. S. Kharasch, E. Simon and W. Nudenberg, *ibid.*, **18**, 328 (1953).

(3) P. S. Skell, unpublished results.

(4) J. Stuurman, *Proc. Acad. Sci. Amsterdam*, **38**, 450 (1935).

(5) For a survey and discussion of epoxidation rates, see D. Swern, This Journal, **69**, 1692 (1947).

(6) (a) I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937); (b) C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931); S. V. Anantakrishnan and C. K. Ingold, *ibid.*, 984, 1396 (1935).

(7) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 279 (1951).

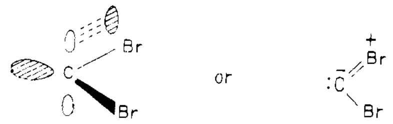
TABLE III

DATA FOR THE 1,1-DIBROMOCYCLOPROPANES

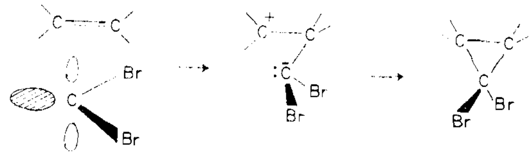
1,1-Dibromocyclopropane	Starting olefin	B.p., °C.	Mm.	$n^{25.0}$D	Yield, %	Bromine, % Calcd.	Bromine, % Found
-2-Benzyl-	Allylbenzene	104–106	1	1.5801	13.3	55.12	54.11, ...
-2-*n*-Butyl-	1-Hexene	120–122	58	1.4905	14.0[a]	62.43	63.76, 61.36
-2,2-Dimethyl-	Isobutylene	65–66	27	1.5110	65.1	70.12	69.15, 69.04
-2,2-Diphenyl-	*as*-Diphenylethylene	Solid[b]		....	66.2	45.40	44.83, ...
-2-*p*-Methoxyphenyl-3-methyl-[c]	Anethole	Dec. 155		....	~46.9	...	..., ...
-2-Phenyl-	Styrene	94	2	1.5963	36.5	57.93	56.64, ...
-2,2,3,3,-Tetramethyl-	Tetramethylethylene	93–94	22[d]	....	54.0	62.43	61.04, 58.71
-2,2,3-Trimethyl-	Trimethylethylene	83	24	1.5134	66.0	66.07	66.49, 65.84
-2-Vinyl [e]	Butadiene	70	26	1.5412	72.0	...	..., ...
7,7-Dibromobicyclo[4.1.0]heptane[13]	Cyclohexene	79–80	2	1.5560	42.7	...	..., ...
6,6-Dibromobicyclo[3.1.0]hexane	Cyclopentene	110	11	1.5744	54.2	66.62	65.42, 64.68

[a] Inverse addition. Bromoform added to solution of olefin and potassium *t*-butylate in *t*-butyl alcohol. [b] M.p. 151–152°. [c] *Trans*-. [d] M.p. 77–78°. [e] *Anal.* Calcd. for $C_5H_6Br_2$: C, 26.58; H, 2.68. Found: C, 26.61; H, 2.52.

bromocarbene,[8] for had it been in the triplet condition one would have anticipated (II) as the correct structure of the intermediate. Thus, carbenes may be described as compounds with planar carbonium ion structure in which two electrons fill one orbital, leaving one orbital unoccupied. In dibromocarbene, overlap of the vacant *p*-orbital of carbon with the filled *p*-orbitals of the bromine atoms may make substantial contributions to the ground state of this molecule.



It is generally accepted that only when two-electron-deficient species add to olefins a stereospecific addition is obtained through simultaneous bonding of the addend to both atoms of the unsaturated linkage.[9] The stereospecificity and reactivity sequence for dibromocarbene additions are consistent with the formulation of the intermediate complex (III) as a partially formed cyclopropane that has some carbonium ion character developed on one of the carbons of the double bond and which subsequently collapses to the cyclopropane.



III

As indicated in the preceding section, dibromocarbene shows a 14-fold greater olefin discriminating ability than bromine.[10] This fact is consistent with the suggestion that dibromocarbene be pictured as a resonance hybrid with considerable resonance energy and/or the intermediate complex III has more carbonium ion character than the intermediate complex of the olefin-bromination reaction (bromonium ion formation).

Three-center-type Intermediates.—As formulated above, three-center-type intermediates may be identical with the bromonium–olefin[6a] and aryl sulfenium[11]–olefin complexes that are obtained in the additions of these 2-electron-deficient species to olefins and which play a determining role in the stereochemistry of these processes. Also, many of the cyclic intermediates that occur in "neighboring-group" participations[12] may be included in this class of intermediates.

TABLE IV

Competition	Olefin, init. mole	Dibromocyclopropane, g.	$CHBr_3$, mole	$KOC(CH_3)_3$, mole	k_a/k_b
a, Isobutylene	0.545	28.2	0.199	0.296	13.9
b, 1-Hexene	.500	2.2			
a, Styrene	.500	30.1	.199	.431	4.8
b, 1-Hexene	.500	6.4			
a, Isobutylene	.541	25.6	.199	.296	2.7
b, Cyclohexene	.500	10.4			
a, Isobutylene	.489	23.0	.199	.313	2.2
b, Cyclopentene	.497	11.9			
a, Tetramethylethylene	.200	13.3	.300	.221	9.4
b, Cyclohexene	.800	6.5			
a, 1-Hexene	.131	5.3	.100	.116	3.2
b, Allylbenzene	.131	2.1			
a, Isobutylene	.329	21.6	.200	.242	1.3
b, *as*-Diphenylethylene	.295	23.6			
a, Trimethylethylene	.200	15.8	.200	.226	8.6
b, Cyclohexene	1.000	11.6			
a, Anethole	0.300	23.9[a]	.200	.233	1.2
b, Isobutylene	.357	17.8			
a, Butadiene	.670	35.4	.438	.538	1.3
b, Cyclohexene	.643	29.4			

[a] By bromine content of residue after removal of unreacted anethole.

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[8] It is hoped that further work which is in progress will throw additional light on this phase of the problem.

[9] M. J. S. Dewar, *Ann. Repts. on Progr. Chem.* (Chem. Soc. London), 118 (1951). For a summary of studies relative to olefin-radical interactions, see P. S. Skell and R. C. Woodworth, THIS JOURNAL, **77**, 4638 (1955).

[10] From the slope of the log *k* vs. log *k* plot.

[11] N. Kharasch and A. J. Havlik, THIS JOURNAL, **75**, 3734 (1953); D. J. Cram, *ibid.*, **71**, 3884 (1949).

[12] For a recent summary of neighboring-group effects, see S. Winstein, *Bull. soc. chim. France*, [5] **18**, C.55 (1951).

[13] W. von E. Doering and A. K. Hoffman, THIS JOURNAL, **76**, 6162 (1954).

One is tempted to postulate that many of the reactions involving 2-electron-deficient species adding to olefins have intermediate complexes similar to III and that the olefin reactivity series for these reactions are similar.

Acknowledgment.—Financial assistance from the Penrose Fund of the American Philosophical Society is gratefully acknowledged. We wish to express our thanks to Mr. Robert C. Woodworth for supplying us with the data relative to the competition between butadiene and cyclohexene.

Experimental

All reagents were distilled before use. The *t*-butyl alcohol was distilled from potassium. The solution of potassium *t*-butylate in *t*-butyl alcohol ($\sim$1.0 *M*) was standardized by titration.

Preparation of 1,1-Dibromocyclopropanes.—Pure samples of all the 1,1-dibromocyclopropanes were prepared. A stirred solution of equimolar amounts of olefin and bromoform in *t*-butyl alcohol was maintained at temperatures between 0 and 3° while an excess of potassium *t*-butylate was added at a rate of approximately 50 millimoles of base per hour. The reaction mixture was stirred an additional hour after all the base had been added. The reaction mixture was worked up by dilution with pentane and water. The organic layer was separated, washed thoroughly with water and dried. After removal of the solvent, the crude product was distilled *in vacuo* or recrystallized from ethanol (tetramethylethylene and *asym*-diphenylethylene products). In most instances distillation residues were very small and no evidence of appreciable quantities of low boiling products was obtained. Since all attempts (including pot-molecular distillation) to purify the product from anethole (*p*-propenylanisole) resulted in decomposition at the elevated temperatures, the unreacted anethole was removed *in vacuo* and the crude product was weighed. Vinyl bromide did not react under the above conditions, the dibromocarbene being consumed in alternative reactions.

The yields, physical properties and analyses for the dibromocyclopropanes are listed in Table III. The analyses were performed by conversion to inorganic bromide with sodium and liquid ammonia.

All the cyclopropanes were thermally stable at room temperature and did not react with bromine in carbon tetrachloride or potassium *t*-butylate in *t*-butyl alcohol (no inorganic bromide after 3.5 hours at 0–10°).

Competition Reactions.—Pairs of olefins were chosen for the competition reactions on the basis of suitable reactivity and convenience in isolation of the pure cyclopropanes by distillation. The reactions were carried out essentially as described above. Potassium *t*-butylate solution was added slowly to the cooled solutions of the two olefins and bromoform in *t*-butyl alcohol ($\sim$ 100 ml.) (containing some pentane ($\sim$ 100 ml.) to prevent solidification of the solvent). When volatile olefins were reactants, a Dry Ice condenser was used to prevent loss. Separation of the products was achieved by vacuum distillation. Purity was indicated by boiling point and refractive index. The relatively small middle cuts were partitioned between the higher and lower boiling materials on the basis of refractive index.

The data obtained in the competition reactions are summarized in Table IV.

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[CONTRIBUTION NO. 193 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

A Reaction of Some Perhalomethanes and Alcohol[1]

BY J. W. HEBERLING, JR., AND W. B. MCCORMACK

RECEIVED SEPTEMBER 26, 1955

The reaction of certain polyhalomethanes with ethanolic silver nitrate was found to give acetaldehyde, silver halide, an acid and the partially reduced polyhalomethane as products. Evidence suggests that a free-radical exchange of halogen and hydrogen between the polyhalomethane and ethanol is involved.

During the course of other work in this Laboratory, a reaction was observed when equal volumes of dibromodifluoromethane (I) and 2% ethanolic silver nitrate solution were mixed at room temperature. Tchakirian[2] has reported that bromoform, methylene bromide and methylene iodide react in dilute solution, at the boiling point, with ethanolic silver nitrate (0.1 g. in 50 ml. of 1% solution) but that carbon tetrachloride, chloroform and methylene chloride do not. As he did not investigate the nature of the products, the reaction of I and several other polyhalomethanes with 2% silver nitrate reagent has been investigated. The results of the study are given in Table I.

The reaction of carbon tetrachloride observed here is in contrast to the lack of reaction reported by Tchakirian.[2] This difference probably is due to the more concentrated solutions used here since it was found that Compound I gave no reaction in a more dilute solution (1 ml. in 25 ml. of silver nitrate reagent).

TABLE I

POLYHALOMETHANES AND ETHANOLIC SILVER NITRATE[a]

Compound	Millimoles	PPt.[b] time, min.	Reacn. time, hr.	Products,[c] millimoles AgX	Acid	CH_3CHO	Others[d]
CBr_2F_2	270	<1	24	2.36	3.21	2.05	$CHBrF_2$
CCl_4	258	15	19	2.55	3.08	1.29	$CHCl_3$
$CHCl_3$	311	..	24	0	0	0	...
CH_2Cl_2	393	..	24	0	0	0	...
$CFCl_3$	266	[e]	24	0	0	0	...
CF_2Cl_2	289	..	24	0	0	0	...
CH_2ClBr	385	2	24	1.50	1.54	1.50	...
$CHBr_3$	243	<1	24	2.33	3.21	1.14	CH_2Br_2
$CBrCl_3$	259	<1	20	2.26	7.39	2.65	$CHCl_3$

[a] 25 ml. of 2% ethanolic silver nitrate and 25 ml. of reagent allowed to stand at room temperature. [b] First appearance of opalescence. [c] Methods of determination described in Experimental section. [d] The low concentration of the halomethanes prevented other than qualitative determination. [e] $CFCl_3$ reacts during longer periods.

Several of the polyhalomethanes also reacted with ethanol itself when equal volumes of the two materials were mixed at room temperature. The results of several such experiments are given in Table II.

The stoichiometric equation for these reactions all appear to be of the same type

$$RX + C_2H_5OH \longrightarrow RH + CH_3CHO + HX \quad (1)$$

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[1] Presented, in part, before the Fluorine Symposium at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 15–16, 1955.

[2] A. Tchakirian, *Compt. rend.*, **196**, 1026 (1933).