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).

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.

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	2.26	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.

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).

TABLE II

POLYHALOMETHANES AND ETHANOL[a]

Compound	Milli-moles	Reacn. time, hr.	Products,[b] millimoles Acid	CH_3CHO	Others
CCl_4	258	24	0	0	...
CH_2ClBr	385	24	0	0	...
$CHBr_3$	243	24	0.45	0.20	CH_2Br_2
$CBrCl_3$	259	20.5	5.76	2.71	$CHCl_3$
CF_2Br_2	270	24	0.96	0.87	...

[a] 25 ml. of ethanol and 25 ml. of reagent allowed to stand at room temperature. [b] See footnotes *c* and *d*, Table I.

The halide ion naturally reacts with silver ion when it is present

$$HX + AgNO_3 \longrightarrow AgX + HNO_3 \tag{2}$$

Reaction 1 is not completely independent of the presence of silver nitrate, as will be pointed out later.

A free-radical reaction is indicated by several facts: (1) The reaction was inhibited by hydroquinone and similar inhibitors. (2) Compound I appeared to contain variable concentrations of an inhibitor which led to variable induction periods. The inhibitor was removed by sweeping the reagents with nitrogen before mixing. (3) Compound I was completely unreactive toward 10% aqueous silver nitrate solution over a 24-hr. period. Similarly, solutions of I in a 2% moist acetone solution of silver nitrate did not precipitate silver bromide. (4) The products point to a radical reaction.

Alkyl halides, such as methyl iodide, react with ethanolic silver nitrate to form silver halide and alkyl nitrite esters or olefins. Whitmore and his co-workers[3] have established conclusively the ionic nature of this type of reaction. On the other hand, decomposition of benzoyl peroxide in a mixture of methanol and carbon tetrachloride produced formaldehyde, hydrogen chloride and chloroform.[4] Pyrolysis of carbon tetrachloride–ethanol mixtures produced chloroform, hydrogen chloride and acetaldehyde, while photolysis of the same mixture produced acetaldehyde, hydrogen chloride and hexachloroethane.[5] Also, the thermal reaction of carbon tetrabromide with ethanol produced bromoform, acetaldehyde and hydrogen bromide.[6] Since the latter four reactions most probably involve free-radicals, the similarity of their products with those of the silver nitrate reaction lends added weight to the proposed free-radical course of reaction. In confirmation, decomposition of α,α'-azobisisobutyronitrile in ethanol–polyhalomethane mixtures produced the same products as the ethanolic silver nitrate reaction (Table III). The extent of reaction due to azonitrile decomposition is not certain in the case of I and bromotrichloromethane since these compounds react with ethanol alone.

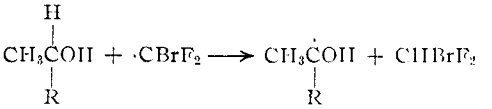
While a free-radical mechanism seems safely established in the observed reactions of polyhalomethanes with ethanol, the detailed mechanism is still obscure. Compound I was found to react with saturated isopropanolic silver nitrate, giving acetone, acid and silver bromide but not with saturated *t*-butanolic silver nitrate. This indicates that reactions 3 through 5 ($R = H$ or CH_3) are involved since when α-hydroxy radicals cannot form

TABLE III

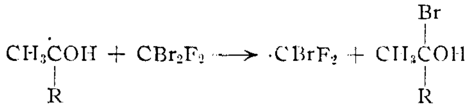
AZONITRILE-CATALYZED REACTIONS

Compound	Milli-moles	C_2H_5-OH, ml.	Mole %[a] azo-nitrile	Temp., °C.	Time, hr.	Products Acid milli-moles	Others[b]
CCl_4	590	250	2.1	60	26	61.8	$CHCl_3$ CH_3CHO
$CBrCl_3$	626	60	2.0	70	5	17.7	$CHCl_3$ C_2H_5Br CH_3CHO
CF_2Br_2	1380	125	2.0	30	37	96	CH_3CHO

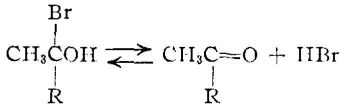
[a] Based on moles polyhalomethane. [b] See footnotes *c* and *d*, Table I.



$$\mathrm{CH_3\overset{H}{\underset{R}{C}}OH + \cdot CBrF_2 \longrightarrow CH_3\overset{\cdot}{\underset{R}{C}}OH + CHBrF_2} \tag{3}$$



$$\mathrm{CH_3\overset{\cdot}{\underset{R}{C}}OH + CBr_2F_2 \longrightarrow \cdot CBrF_2 + CH_3\overset{Br}{\underset{R}{C}}OH} \tag{4}$$



$$\mathrm{CH_3\overset{Br}{\underset{R}{C}}OH \rightleftharpoons CH_3\underset{R}{C}{=}O + HBr} \tag{5}$$

the reaction fails. This also eliminates another possible reaction path—*via* the alkoxy radical, *i.e.*, reactions 6 through 8 ($R = H$ or CH_3)

$$R_3COH + \cdot CBrF_2 \longrightarrow R_3CO\cdot + CHBrF_2 \tag{6}$$

$$R_3CO\cdot + CBr_2F_2 \longrightarrow R_3COBr + \cdot CBrF_2 \tag{7}$$

$$R_3COBr \longrightarrow \longrightarrow \longrightarrow R_2CO + RBr \tag{8}$$

which should occur even with *t*-butyl alcohol.

The nature of the initiation and termination steps have not been elucidated. If peroxides are involved in the initiation, they could not be detected in the ethanol with the acidic potassium iodide test.[7] Photo initiation does not appear to be involved.

Examination of the data in Tables I and II suggests that silver nitrate has an apparent catalytic effect on the over-all reaction. Thus, the three compounds which react with ethanol alone react to a greater extent when silver nitrate is present. The effect is even more striking in the case of carbon tetrachloride and chlorobromomethane, which did not react detectably with ethanol.

The apparent catalysis could be of two possible types: either one step of the reaction series is an equilibrium which is displaced by removal of halide ion as silver halide, or silver ion has a bond weakening effect, possibly of an ionic atmosphere nature.[8] Further speculation is fruitless until additional information concerning various facets of the reaction becomes available.

On the basis of a free-radical mechanism, it is readily understood why chloroform does not undergo reaction with ethanol and silver nitrate. It

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[3] F. C. Whitmore, E. L. Wittle and A. H. Popkin, THIS JOURNAL, **61**, 1586 (1939); F. C. Whitmore and G. H. Fleming, *J. Chem. Soc.*, 1269 (1934).

[4] G. A. Razuvaev, B. N. Moryganov and V. A. Stepushkiva, *J. Gen. Chem. U.S.S.R.*, **23**, 1439 (1953)(Eng. translation).

[5] G. A. Razuvaev and Y. A. Sorokin, *ibid.*, **23**, 1589 (1953).

[6] G. Ponzio, *Gazz. chim. ital.*, **36**, II, 148 (1906).

[7] L. Gattermann, "Laboratory Methods of Organic Chemistry," Macmillan and Co., Ltd., London, 1952, p. 92.

[8] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 357.

has been established[9] that the hydrogen, and not the chlorine, of this compound reacts with free-radicals in solution. The very sluggish reactivity of trichlorofluoromethane compared to carbon tetrachloride is another example of the over-all bond strengthening effect exhibited by fluorine.[10] The other observed fact that bromine, in polyhalomethanes, is more reactive than chlorine is so general to the reactions of halogen compounds that it needs no further comment.

While hydrogen–halogen exchange reactions have been known for some time,[4–6,11–13] the reactions with ethanolic silver nitrate or ethanol are believed to be the first observed under such mild conditions.

Experimental[14]

The halomethanes were all purified by distillation and gave negative tests for free halogen or hydrogen halide when shaken with 10% aqueous silver nitrate. Mass spectrometric analysis indicated that the reagents were pure. The alcohols gave negative tests for free carbonyl with 2,4-dinitrophenylhydrazine reagent.

Reaction of Polyhalomethanes with Ethanolic Silver Nitrate.—A mixture of 25 ml. (0.270 mole) of I and 25 ml. of 2% (w./w.) ethanolic silver nitrate solution was allowed to stand for 24 hr. at room temperature. The solution became opalescent almost immediately. At the end of this period, the solids were collected, dried and weighed. They were identified as silver bromide by their behavior with aqueous ammonia.[15] The filtrate was diluted to 100 ml. with ethanol and an aliquot was withdrawn and titrated for free acid with standard alkali. Another aliquot was treated with 2,4-dinitrophenylhydrazine reagent,[16] giving the 2,4-dinitrophenylhydrazone of acetaldehyde, m.p. 150–151°. A mixed melting point with an authentic specimen showed no depression. Bromodifluoromethane was isolated from the remainder of the filtrate by distillation and identified by infrared analysis. The results are shown in Table I. Light, or its absence, has no effect on the course and velocity of the reaction.

Under conditions identical to the experiment described above, carbon tetrachloride, chloroform, methylene chloride, fluorotrichloromethane, difluorodichloromethane, chlorobromomethane, bromoform and bromotrichloromethane were allowed to react separately with 2% ethanolic silver nitrate. The halogen-containing products were isolated by drowning the alcoholic solutions with water and were identified by analysis with the mass spectrometer. The other products were isolated and identified as before. The results are given in Table I.

Reaction of I with Silver Nitrate in Isopropyl Alcohol and *t*-Butyl Alcohol.—A mixture of 25 ml. of I and 25 ml. of saturated isopropanolic silver nitrate, which became opalescent in 15 minutes, was allowed to stand for 23 hr. at room temperature. The reaction mixture then contained 0.264 g. (1.40 millimoles) of silver bromide and 1.60 millimoles of acid and gave 0.205 g. (0.863 millimole) of acetone 2,4-dinitrophenylhydrazone, m.p. 124–126°, which showed no depression of melting point with an authentic specimen.

A mixture of 25 ml. of I and 25 ml. of saturated *t*-butanolic silver nitrate remained clear after standing for 4 hr. at room temperature.

Attempted Reaction of I with Silver Nitrate in Acetone and in Water.—A mixture of 25 ml. of I and 25 ml. of 2% (w./w.) solution of silver nitrate in acetone (containing a trace of water to increase the solubility of silver nitrate) remained clear after standing for 6 hr. at room temperature.

A mixture of 31 g. of I and 250 g. of 10% (w./w.) aqueous silver nitrate remained clear after stirring rapidly under a condenser cooled with Dry Ice–acetone mixture for 23 hr.

Reaction of Polyhalomethanes with Ethanol.—A mixture of 25 ml. of 95% ethanol and 25 ml. of polyhalomethane was allowed to stand at room temperature for approximately 24 hr. The polyhalomethanes used were carbon tetrachloride, chlorobromomethane, bromoform, bromotrichloromethane and difluorodibromomethane. The products were then isolated and identified in the same manner as previously described. The results are reported in Table II.

Azonitrile-catalyzed Reaction of Polyhalomethanes with Ethanol.—A solution of the halogen compound, α,α'-azobisisobutyronitrile (2 mole % based on the halogen compound) and ethanol was heated for a number of hours. The products were determined as described previously. The results are given in Table III.

WILMINGTON 39, DELAWARE

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(9) M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945); see also F. A. Raal and E. W. R. Steacie, *J. Chem. Phys.*, **20**, 578 (1952), and W. E. Hanford and R. M. Joyce, U. S. Patent 2,440,800.

(10) For example, see L. O. Brockway, *J. Phys. Chem.*, **41**, 158 (1937).

(11) J. P. West and L. Schmerling, U. S. Patents 2,553,799, 2,553,800.

(12) P. Savary and P. Desnuelle, *Bull. soc. chim. France*, 213 (1952).

(13) J. Banus, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 3041 (1950).

(14) All temperatures reported are uncorrected.

(15) J. H. Reedy, "Theoretical Qualitative Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 322, 325 and 326.

(16) G. D. Johnson, THIS JOURNAL, **73**, 5888 (1951).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reactions of Triphenylgermane with Some Organometallic Compounds. A New Method for the Preparation of Triphenylgermyllithium

BY HENRY GILMAN AND CLARE W. GEROW

RECEIVED MAY 18, 1956

Triphenylgermane has been found to react with organolithium reagents to give triphenylgermyllithium in good yields together with some of the tetrasubstituted germane. The reaction of *n*-butyllithium with triphenylgermane has been found to be of value in the preparation of triphenylgermyllithium. These reactions are compatible with the concept of a higher electronegativity for germanium as compared with silicon. The reaction of triphenylgermyllithium with triphenylgermane was found to give hexaphenyldigermane in small yield. Triphenylgermane gave no reaction with certain Grignard reagents under comparable conditions.

Generally speaking, organogermanium compounds undergo the same reactions as the analogous organosilicon compounds. There have been reported some exceptions to this generality, such as the difference in reactions of triphenylsilylpotassium[1] and triphenylgermyllithium[2] with benzophenone, and the difference in the reductions of triphenylhalogermanes and triphenylhalosilanes with tin and hydrochloric acid.[3] Perhaps one of the most pronounced differences has been found in the reactions of Si–H and Ge–H compounds with organolithium compounds. It has been reported

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(1) H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2935 (1953).

(2) H. Gilman and C. W. Gerow, *ibid.*, **77**, 5740 (1955).

(3) R. West, *ibid.*, **75**, 6080 (1953).