fied by sublimation and crystallization from pentane to give *trans*-9-decalol, m.p. 51–54°. The infrared spectrum was identical with that of an authentic sample. Oxygen-18 analysis showed 0.00, 0.03 atom % oxygen-18.

Reaction of Cumene Hydroperoxide with Triphenylphosphine in the Presence of H_2O^{18}.—To a stirred solution of 15.72 g. (0.10 mole) of cumene hydroperoxide in 40 ml. of absolute ethanol and 30 ml. of H_2O^{18} (1.5 atom % oxygen-18) was added 26.23 g. (0.10 mole) of triphenylphosphine in 100 ml. of ethanol. After stirring at room temperature for two hours, the ethanol and water were removed *in vacuo*. The viscous residue was triturated with three 50-ml. portions of petroleum ether. The residue after this treatment was washed with 100 ml. of ether and then recrystallized from hexane–ether to give 10.6 g. of triphenylphosphine oxide, m.p. 154–156°, no depression on admixture with an authentic sample. Oxygen-18 analysis showed 0.00, 0.00 atom % oxygen-18.

The petroleum ether extracts were concentrated and the residue was distilled under reduced pressure. The distillation was exceedingly difficult since triphenylphosphine oxide precipitated and caused bumping. In this connection it should be pointed out that subsequent work has shown that chromatography of these reaction mixtures is the easiest way of separating them. The distillation afforded relatively pure alcohol, b.p. 74–90° (28 mm.). Some of this material (1.7 g., 0.012 mole), was treated with 2.0 g. (0.017 mole) of phenyl isocyanate and the mixture was heated at 75° for five hours. Water was added and the solid, containing the urethan and diphenylurea, was extracted with boiling carbon tetrachloride. The carbon tetrachloride extracts were evaporated to give material m.p. 103–115°. Two recrystallizations from petroleum ether gave 0.052 g. of the phenylurethan, m.p. 113–114° (lit.[11] 113°). The infrared spectrum of this material was identical with an authentic sample and there was no melting point depression on admixture with an authentic sample. The oxygen-18 analysis of the phenylurethan showed 0.00, 0.00 atom % oxygen-18.

Reaction of Cumene Hydroperoxide with Tri-*n*-butylphosphine in Methanol.—Tri-*n*-butylphosphine (56.6 g., 0.280 mole) in 25 ml. of methanol was added dropwise at 10° to 43.4 g. (0.276 mole) of cumene hydroperoxide in 100 ml. of methanol. The methanol was removed *in vacuo* and the residue distilled; total weight of distillate, 35.8 g. (92%). The major fraction, 27.1 g., b.p. 69–72° (5 mm.), appeared from its infrared spectrum to be only cumyl alcohol. A Zeisel methoxyl analysis on this fraction showed no methoxyl group was present.

---

(11) B. Schroeter, *Ber.*, **36**, 1863 (1903).

NEW BRUNSWICK, N. J.

[CONTRIBUTION NO. 521 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Syntheses by Free-radical Reactions. XI. Additive Dimerizations with Bromine Atoms

BY C. M. LANGKAMMERER, E. L. JENNER, D. D. COFFMAN AND B. W. HOWK

RECEIVED AUGUST 20, 1959

Bromine atoms have been obtained by the one-electron oxidation of bromide anions with either cerium(IV) ions or hydroxyl radicals. These atoms, generated in stoichiometric quantities, brought about the additive dimerization of butadiene to form unsaturated eight-carbon dibromides, $BrC_4H_6–C_4H_6Br$, in 46% yield.

The one-electron *reduction* of molecules containing oxygen–oxygen bonds to produce free radicals, as brought about by a variable valence metal ion, has been employed extensively in the generation of free radicals.[1] Radicals from such "oxidation–reduction systems" have been used to initiate polymerization,[2] effect oxidation[3] and bring about additive dimerization.[4,5] Systems in which the metal ion plays the opposite role, *i.e.*, functions as a one-electron *oxidizing* agent, have been postulated from results of kinetic studies. Thus, halide anions have been oxidized to free halogen, presumably *via* halogen atoms.[6] However, this mode of radical generation has not been utilized in preparative chemistry.

We have now demonstrated the formation of free radicals in a one-electron oxidation by using them in the additive dimerization of butadiene. Earlier papers in this series[4,7] described the reaction of free radicals (R·) with 1,3-dienes (M) to form additive dimers (R–M–M–R). In the current study, bromine atoms were generated by the one-electron oxidation of bromide anion by cerium(IV) ion and were captured by butadiene to give unsaturated C_8-dibromides.

$$Br^- + Ce^{4+} \longrightarrow Ce^{3+} + Br\cdot$$

$$Br\cdot + C_4H_6 \longrightarrow BrC_4H_6\cdot$$

$$2BrC_4H_6\cdot \longrightarrow BrC_4H_6C_4H_6Br$$

Alternatively, the bromine atoms were obtained by the oxidation of bromide ions by hydroxyl radicals generated from hydrogen peroxide and ferrous ion. This approach is similar to the

$$H_2O_2 + Fe^{2+} \longrightarrow HO\cdot + OH^- + Fe^{3+}$$

$$HO\cdot + Br^- \longrightarrow HO^- + Br\cdot$$

previously reported finding[7] that amino radicals, generated from hydroxylamine and titanous ion, would convert bromide ions to bromine atoms.

$$NH_2OH + Ti^{3+} \longrightarrow \cdot NH_2 + OH^- + Ti^{4+}$$

$$\cdot NH_2 + Br^- \longrightarrow NH_2^- + Br\cdot$$

In the earlier work it was noted that amino radicals would not convert chloride ions to chlorine atoms. In the present work hydroxyl radicals have been

---

(1) F. Haber and J. Weiss, *Naturwissenschaften*, **20**, 948 (1932); F. Haber and J. Weiss, *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934); Cheves Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 565–575.

(2) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946); J. H. Baxendale, M. G. Evans and G. S. Park, *ibid.*, **42**, 155 (1946); A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **4**, 377 (1949).

(3) H. J. H. Fenton, *J. Chem. Soc.*, **65**, 899 (1894); J. H. Merz and W. A. Waters, *ibid.*, S15 (1949); I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777 (1949).

(4) (a) D. D. Coffman and E. L. Jenner, *ibid.*, **80**, 2872 (1958); (b) D. D. Coffman and H. N. Cripps, *ibid.*, **80**, 2877, 2880 (1958).

(5) M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951); M. S. Kharasch and W. Nudenberg, *ibid.*, **19**, 1921 (1954).

(6) E. L. King and M. L. Pandow, THIS JOURNAL, **75**, 3063 (1953).

(7) C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner and W. E. Mochel, *ibid.*, **81**, 1489 (1959).

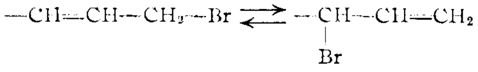
used to effect this oxidation. Thus, the previously observed inhibition of reactions of hydroxyl radicals by chloride ions[8] may be used to advantage in chemical synthesis.

The preferred method of generating bromine atoms for additive dimerization is through the action of cerium(IV) ions since the hydroxyl radical route can lead to side reactions in which hydrogen attached to carbon is abstracted by hydroxyl radical attack.[4a,9]

The present study, in which the combination of Ce^{4+} with Br^- is used to produce "bromine atoms," does not distinguish between $Br\cdot$, $\cdot Br_2^-$ and a ceric bromide complex as the actual species[6] which reacts with the diene. The hydroxyl radical–bromide ion system clearly involves cerium-free species. The similarity of the chemistry in the two cases makes it likely that either $Br\cdot$ or $\cdot Br_2^-$ is the active species in both.

The dibromoöctadienes, obtained in 40–50% yield by the additive dimerization of butadiene, boiled over a wide range and were a mixture of isomers. Although no pure isomer was isolated, it was established that approximately 75% of the butadiene was incorporated in a 1,4-fashion and thus the principal product formed was the straight-chain dibromide, $BrCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2Br$. A careful distillation of the product gave fractions which were characterized by elemental analysis, infrared spectra and determination of allylic bromine. The composition of the product was assigned on the basis of the above data interpreted in the light of previous studies of the products obtained in the additive dimerization of butadiene.[4,5,7] In the present work the number of isomers was increased and the isolation of pure compounds was hindered by the facile rearrangement of the allylic bromine.

A reaction sequence that accounts for the products can be visualized in which the bromine atoms attacked butadiene to form bromobutenyl radicals, $BrCH_2\dot{C}HCH{=}CH_2 \longleftrightarrow BrCH_2CH{=}CHCH_2\cdot$, which dimerized. Thus straight- or branched-chain products were formed depending on whether the butadiene incorporation was in a 1,4- or 1,2-fashion, *i.e.*, whether the combination of the radicals occurred in the terminal (4-) position or in the central (2-) position. Furthermore, the products in which the butadiene was incorporated in a 1,4-fashion contained allylic bromine which could isomerize



$$-CH{=}CH-CH_2-Br \rightleftarrows -\underset{\displaystyle Br}{\underset{|}{C}H}-CH{=}CH_2$$

The fractions obtained by distillation appeared to contain isomerized dibromoöctadienes as well as the primary reaction products. The low-boiling fractions contained mainly $-CH{=}CH_2$ unsaturation and a moderate amount of allylic bromine whereas the highest-boiling fractions contained mainly $-CH{=}CH-$ unsaturation and allylic bromine.

Allylic bromine was determined by a new method in which it undergoes selective hydrogenolysis to give hydrogen bromide. In the mixture of dibromoöctadienes, the C_4-units derived from 1,4-incorporation of the butadiene contain allylic bromine, even if allylic rearrangement occurs, and those from the 1,2-incorporation of the butadiene do not. Therefore this analysis will serve as a reliable index of how the butadiene units were incorporated and, therefore, of the carbon skeletons of the additive dimers. It was found that *ca.* 75% of the bromine in the dibromoöctadienes was allylic, demonstrating that 75% of the butadiene was incorporated in a 1,4-fashion. The ratio of straight- to branched-chain isomers obtained in this work is in the range reported in earlier studies.[4,5,7]

In addition to the additive dimers, an appreciable portion (18%) of monomeric (*i.e.*, C_4) products was obtained. These products may have resulted from the dimerization of bromine atoms to form bromine molecules which added to butadiene to form the 1,2- and 1,4-dibromobutenes. Alternatively, reaction of the bromobutenyl radicals with bromine molecules or atoms would lead to C_4-dibromides. The formation of monomeric products had not been observed previously in additive dimerizations employing radicals formed by reductive cleavage[4,5,7] but was an important process in additive dimerization with radicals generated by electrolysis.[10]

Chlorine atoms and butadiene were shown to form a mixture of dichloroöctadienes but in smaller yields than were obtained in the analogous bromine reactions. Chlorine atoms were best obtained by reaction of chloride ion with hydroxyl radicals derived from hydrogen peroxide and ferrous ion. Generation of chlorine atoms using cerium(IV) salt as an oxidizing agent proceeded with difficulty.

The additive dimerizations were accomplished by adding a solution of a cerium(IV) salt or solutions of hydrogen peroxide and ferrous sulfate to an acidic aqueous solution containing halide ion, butadiene and an organic solvent to promote the solubility of the butadiene. When cerium(IV) salts were employed, a dark red color appeared in the solution at the point where the cerium(IV) entered although the bulk of the solution remained colorless. This deep color is attributed to a halide complex of cerium(IV) which decomposes to cerium(III) and halogen atoms.[6]

Experimental

Additive Dimerization Using Bromine Atoms Generated by Ceric Sulfate.—In a four-necked, indented, 5-liter flask fitted with a dropping funnel and a high-speed stirrer were placed 1014 g. (6 moles) of 46% hydrobromic acid, 1750 g. of water and 580 g. of *t*-butyl alcohol. This solution was cooled and held at a temperature of 1–4° by means of an ice-bath. After butadiene had been passed into the vigorously stirred solution for several minutes, 420 g. (0.5 mole) of ceric hydrogen sulfate, $Ce(HSO_4)_4$, dissolved in 1 liter of water was added over a period of 40 minutes. Butadiene was passed into the solution throughout this period, the total amount added being about 200 g. (4 moles). The reaction mixture was stirred for another 20 minutes, and the cerous sulfate, $Ce_2(SO_4)_3 \cdot 8H_2O$, which had precipitated was removed by filtration. The filter cake was washed with chloroform, and the wash was added to the dense layer which had been separated from the filtrate. Distillation of the chloro-

---

[8] N. Uri, *Chem. Revs.*, **50**, 388 (1952).

[9] D. D. Coffman, E. L. Jenner and R. D. Lipscomb, THIS JOURNAL, **80**, 2864 (1958).

[10] R. V. Lindsey, Jr., and M. L. Peterson, *ibid.*, **81**, 2073 (1959).

form left 62 g. of crude product. This was dried and distilled to obtain the fractions listed in Table I.

TABLE I

DISTILLATION OF C_4- AND C_8-DIBROMIDES

Fraction	Quantity, g.	B.p.		$n^{25}D$
		°C.	Mm.	
1	7.0	64–94	25	1.5502
2	3.0	To 55	0.15	1.5510
3	23.2	60–88	.1–0.25	1.5400
4	7.4	92–132	.28–0.6	1.5394
Residue	4.6			

The product in fraction 1 and 2 (10 g., 18% yield based on oxidizing agent) was chiefly a mixture of dibromobutenes. The refractive indices are intermediate between those reported for *cis*-1,4-dibromo-2-butene, $n^{15}D$ 1.574 (b.p. 82° (14 mm.)[11]), and for 3,4-dibromo-1-butene, $n^{20}D$ 1.5302 (b.p. 56–58° (14 mm.)[12]). Upon standing, *trans*-1,4-dibromo-2-butene crystallized from the mixture, m.p. 50–54°, reported[12] m.p. 53°. The product in fractions 3 and 4 (30.6 g., 46% yield) was a mixture of C_8-dibromides.

Anal. Calcd. for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.64; mol. wt., 268. Found: C, 35.66; H, 4.58; Br, 59.92; mol. wt., 272.

Characterization of C_8-Dibromides.—The C_8-dibromide fractions obtained from four similar experiments were combined and fractionated through a 24″ distillation column packed with glass helices. The 131 g. of crude product was separated into nine fractions, as shown in Table II.

TABLE II

DISTILLATION OF C_8-DIBROMIDES

Fraction	Quantity, g.	B.p.		$n^{25}D$
		°C.	Mm.	
1	6.9	Up to 93	25	1.5460
2	5.8	52–62	0.25	1.5402
3	14.4	62–67	.25–0.5	1.5280
4	29.1	64–70	.1–0.16	1.5364
5	6.0	71	.18	1.5375
6	19.2	71–74	.13	1.5388
7	18.1	77–81	.25–0.29	1.5418
8	4.3	84	.32	1.5434
9	15.1	86–88	.45	1.5456
Residue	5.2			
Total	124.1			

Analyses of each of the fractions for carbon, hydrogen and bromine gave values corresponding to the additive dimer, $C_8H_{12}Br_2$. Fractions 3, 5 and 8, taken as representative of the three principal components of the mixture, were characterized by their infrared spectra. The vinyl group, $CH_2{=}CH{-}$, exhibits absorption at 6.06 and 10.05 μ. In compounds containing internal double bonds, $-CH{=}CH-$, the corresponding absorptions are shifted to 6.00 μ and either 10.35 (*trans*) or 14.5 μ (*cis*). Examination of these regions of the spectra indicated that the low-boiling fraction 3 contained mainly terminal unsaturation with only a small amount of internal unsaturation. The intermediate fraction 5 contained roughly equal amounts of terminal and internal unsaturation, and the high-boiling fraction 8 contained mainly internal unsaturation.

The proportion of bromine which was allylic was determined (see below for method) in each of these fractions to give a further insight into compositions. In fraction 3, 41% of the bromine was allylic. Thus, less than half of the butenyl units in this fraction were incorporated 1,4. In fraction 8, 86% of the bromine was allylic. This material therefore consists chiefly of the straight-chain isomers. Fraction 5 was intermediate and 64% of the bromine was allylic. One difficulty arising in the separation of these isomers appeared to have been that allylic rearrangement occurred during distillation making it impossible to get pure fractions.

In two separate experiments the total distilled dibromooctadiene fraction was found to contain 75.7 and 77.5% allylic bromine. This indicates that three-quarters of the butadiene molecules are incorporated in the 1,4-fashion.

Determination of Allylic Bromine.—A method previously developed in these laboratories for the determination of allylic chlorine[13] was tested to see if it could be used for allylic bromine as follows. A mixture of equal parts of *trans*-1,4-dibromo-2-butene and 1,4-dibromobutane was hydrogenated in the apparatus described by Dunlop.[14] The hydrogenation was carried out at 33° and atmospheric pressure in ethanol solution with a platinum oxide catalyst. The uptake of hydrogen was about 96% of the three moles required by the equation

$$BrCH_2CH{=}CHCH_2Br + 3H_2 \longrightarrow CH_3CH_2CH_2CH_3 + 2HBr$$

Upon completion of the hydrogenation the mixture was filtered, and the filtrate was titrated with 0.1 *N* sodium hydroxide using methyl red indicator. Calculation of the acid as allylic bromine gave values of 36.71 and 36.53% (theoretical 37.36%). From this it appears that the method can be used to determine allylic bromine in the presence of non-allylic bromine.

Additive Dimerization Using Bromine Atoms Generated by Hydroxyl Radicals.—The reaction vessel described above was charged with 103 g. of sodium bromide, 1500 g. water and 1000 ml. of *t*-butyl alcohol. The solution was held at 5° while 108 g. of butadiene, a solution of 34 g. of hydrogen peroxide in 130 g. of water and a solution of 278 g. of ferrous sulfate heptahydrate and 98 g. of sulfuric acid in 575 g. of water were added simultaneously at equivalent rates. There was obtained 10.5 g. (8% yield) of C_8-dibromides, b.p. 62–82° (2 mm.), $n^{25}D$ 1.5270.

Anal. Calcd. for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.64. Found: C, 34.61; H, 4.82; Br, 58.11.

Additive Dimerization Using Chlorine Atoms Generated by Hydroxyl Radicals.[15]—The reaction vessel described above was charged with a solution of 234 g. of sodium chloride, 390 g. of *t*-butyl alcohol and 2 liters of water. Butadiene was passed into the rapidly stirred solution at 0° while a solution of 278 g. of ferrous sulfate heptahydrate and 98 g. of sulfuric acid in 575 g. of water and a solution of 34 parts of hydrogen peroxide in 130 parts of water were added simultaneously and equivalently. The additions required 14 minutes, during which time 116 g. of butadiene was added. The mixture was extracted three times with ether, and the combined ether extracts were dried over magnesium sulfate. After removal of the ether and the *t*-butyl alcohol, the fractions listed in Table III were obtained.

TABLE III

DISTILLATION OF UNSATURATED CHLORIDES

Fraction	Weight, g.	B.p.		$n^{25}D$
		°C.	Mm.	
1	31	31–32	11	1.4025
2	10	34–36	11	1.4438
3	6	44–62	1	1.4798
4	6	63–72	1	1.4828
Residue	6			

Fractions 3 and 4 (13% yield) were chiefly C_8-dichlorides.

Anal. Calcd. for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.60. Found: C, 53.25; H, 7.61; Cl, 33.47.

The low chlorine content of this product is believed to have been caused by participation of the *t*-butyl alcohol to give products containing tertiary alcohol groups.[4a]

Additive Dimerizations Using Chlorine Atoms Generated by Cerium (IV) Salts.—In a similar experiment in which sodium chloride in aqueous *t*-butyl alcohol was treated with butadiene, ceric perchlorate and perchloric acid at 0°, the

---

(11) C. Prevost and A. Valette, *Compt. rend.*, **222**, 326 (1946).

(12) A. L. Klebanskii, R. M. Sorokina and Z. Ya. Khavin, *J. Gen. Chem. (U.S.S.R.)*, **17**, 235 (1947); *C. A.*, **42**, 516 (1948).

(13) Private communication of E. C. Dunlop and W. H. Taylor.

(14) E. C. Dunlop, *Ann. N. Y. Acad. Sci.*, **53**, 1087–1092 (1951).

(15) Since the completion of this work, a patent has appeared in which this reaction is described; C. E. Frank and I. L. Mador, U. S. Patent 2,832,809, April 29, 1958.

red color of cerium(IV) persisted, and no C_8-dichlorooctadienes were formed. At 65°, however, the red color of the cerium(IV) ion was discharged rapidly, and a 5% yield of C_8-dichlorides, b.p. 61–75° (1 mm.), was obtained.

Anal. Calcd. for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.60. Found: C, 54.98; H, 7.33; Cl, 37.39.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Methylene Derivatives as Intermediates in Polar Reactions. XIX. The Reaction of Potassium Isopropoxide with Chloroform, Bromoform and Dichlorofluoromethane[1]

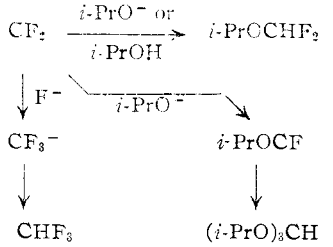
BY JACK HINE, ARTHUR D. KETLEY AND KOZO TANABE

RECEIVED JULY 30, 1959

On reaction with potassium isopropoxide in isopropyl alcohol, dichlorofluoromethane gives triisopropyl orthoformate as the only product detected, while chloroform and bromoform give, in addition, propylene, diisopropyl ether, acetone, carbon monoxide, a methylene halide, and under some conditions dark-colored products of higher molecular weight. Mechanistic interpretations are given for some of these and related observations.

Introduction

In the reaction of potassium isopropoxide with chlorodifluoromethane[2] it appears that the intermediate, difluoromethylene, is formed first and this either combines (1) with a fluoride ion to give fluoroform, (2) with isopropyl alcohol to give isopropyl difluoromethyl ether or (3) with an isopropoxide ion to give isopropyl difluoromethyl ether or, *via* the intermediate isopropoxyfluoromethylene, triisopropyl orthoformate.



Since no compounds of the type $ROCHX_2$ have ever been isolated from the reaction of non-fluorine-containing haloforms with alcohols in alkaline solution, although the orthoesters[3] and olefins[4] corresponding to the alcohols have been, we decided to study the reaction of potassium isopropoxide with some fluorine-free haloforms and also with a monofluoro compound.

Results

The reaction of dichlorofluoromethane with potassium isopropoxide gave triisopropyl orthoformate as the only organic product detected (isolated in 71% yield). The corresponding reaction of chloroform followed a considerably different course. In all cases carbon monoxide, propylene and diisopropyl ether were formed in addition to the orthoformate; and with the more concentrated potassium isopropoxide solutions methylene chloride, acetone and dark-colored by-products were formed as well. With bromoform considerable amounts of dark-colored materials were formed in addition to the observed products, methylene bromide, acetone, triisopropyl orthoformate, carbon monoxide, diisopropyl ether and propylene.

Discussion

Since the isopropoxide ion is an even stronger base than the hydroxide ion, which is known to bring about almost exclusive α-dehydrohalogenation of haloforms, it seems quite probable that in every case the first steps of the reaction are those transforming the haloform to a trihalomethyl carbanion and then to a dihalomethylene.

Methylene Halide Formation.—The methylene halides observed probably are formed by the electrophilic dihalomethylenes'[5] abstraction of a hydride ion from the α-carbon atom of the isopropoxide ion, or isopropyl alcohol[6] (see reaction scheme I). From the higher yields of methylene chloride obtained in the presence of higher concentrations of base it seems that the alkoxide ions are the principal hydride-donating reagents. The absence of methylene halides in the reactions of difluorochloromethane[2] and dichlorofluoromethane with potassium isopropoxide may be rationalized by consideration of several points. Studies of the effect of structure on the rates of dihalomethylene formation[7] seem to show that fluorine atoms donate their unshared electron pairs to the electron-deficient divalent carbon atom better than other halogen atoms do. Thus fluorine-containing dihalomethylenes should be less electrophilic and hence less capable of hydride-ion abstraction than dichloro- and dibromomethylene. A further argument relies on the fact that a dihalomethyl carbanion, or at least a transition state that probably has considerable carbanion character, is being formed by the hydride-ion abstraction. As α-substituents, fluorine atoms are known to facilitate carbanion formation least of all the halogens.[8] This factor, too, would discourage hydride-ion abstraction by difluoro- and chlorofluoromethylene. A third factor may be found in the tendency of α-

---

(1) For part XVIII see J. Hine and J. M. van der Veen, THIS JOURNAL, **81**, 6446 (1959).

(2) J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957); **80**, 3002 (1958).

(3) A. W. Williamson, *Ann.*, **92**, 346 (1855).

(4) J. Hine, E. L. Pollitzer and H. Wagner, THIS JOURNAL, **75**, 5607 (1953).

(5) (a) J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(6) For discussion of hydride transfers see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, sec. 11-4.

(7) J. Hine and S. J. Ehrenson, THIS JOURNAL, **80**, 824 (1958).

(8) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1046 (1957).