crystallized on cooling of the solution. After the product, benzene-1,3-diboronic acid (II), had been recrystallized from water and dried in an evacuated desiccator, it did not melt up to 420°.

Anal. Calcd. for $C_6H_8B_2O_4$: C, 43.47; H, 4.87; B, 13.06. Found: C, 43.71; H, 4.99; B, 12.77.

B. **Use of 1,3-Dilithiobenzene.**—To a solution of 15.9 g. (0.068 mole) of *m*-dibromobenzene in 300 ml. of petroleum ether was added 100 ml. of a petroleum ether solution containing 0.135 mole of *n*-butyllithium. The mixture was stirred for five hours, the temperature being maintained at about 34°. To the resulting mixture, cooled in an acetone–Dry Ice-bath, was added 14.0 g. (0.135 mole) of methyl borate. The mixture was allowed to warm gradually to room temperature, hydrolyzed with dilute hydrochloric acid and extracted with ether. After distillation of the ether and petroleum ether, the residue was digested with hot water and filtered. From the filtrate there was obtained 1.1 g. (10%) of benzene-1,3-diboronic acid (II).

When the exchange mixture was caused to react with carbon dioxide, rather than with methyl borate, isophthalic acid could be isolated in 30% yield.

Proof of Structure of Benzene-1,3-diboronic Acid (II).—The method used was the same as that described for the proof of structure of benzene-1,4-diboronic acid (I). However, in this experiment *m*-bromophenylboronic acid, m.p. 169–173° (reported[11] m.p. 170°), was isolated instead of *m*-dibromobenzene. The infrared spectrum of a chloroform solution of the product was identical with that of a chloroform solution of authentic *m*-bromophenylboronic acid.

In an independent experiment it was shown that *m*-bromophenylboronic acid is not cleaved by bromine water under the conditions used for the proof of structure of benzene-1,3-diboronic acid (II).

***m*-Dibromobenzene.**—This compound was prepared in 51% yield by a modification of the method of Mathieson and Newberry.[12] A cold solution of *m*-bromobenzenediazonium bisulfate was added to a suspension of cuprous bromide in water, through which a vigorous current of steam was being passed. Mathieson and Newberry[12] obtained *m*-dibromobenzene in 25% yield by adding cuprous bromide to *m*-bromobenzenediazonium bisulfate at 75°.

***m*-Bromophenylboronic Acid.**—The acid, m.p. 161–166°, was obtained in 46% yield from *m*-dibromobenzene, the procedure being the same as that employed for the preparation of *p*-bromophenylboronic acid.

1,3-Bis-(dichloroboryl)-benzene (X).—Tetra-*n*-butyl benzene-1,3-diboronate was caused to react with phosphorus pentachloride in the same manner as described for the preparation of bis-1,4-(dichloroboryl)-benzene (IX). After distillation of the carbon tetrachloride and the by-products *n*-butyl chloride and phosphorus oxychloride at atmospheric pressure, the residue was distilled *in vacuo*. There was obtained a 58% yield of 1,3-bis-(dichloroboryl)-benzene (X), b.p. 82–84° (1.2 mm.). After two sublimations at 50 mm. pressure, the colorless sublimate had a m.p. of 54–56° in a sealed tube.

Anal. Calcd. for $C_6H_4B_2Cl_4$: C, 30.08; H, 1.68; B, 9.03; Cl, 59.20. Found: C, 29.98; H, 1.78; B, 9.23; Cl, 58.95.

Phenyldichloroborane.—Di-*n*-butyl phenylboronate was prepared by the method of Torssell.[13] To a stirred suspension of 57.0 g. (0.274 mole) of phosphorus pentachloride in 130 g. of carbon tetrachloride was added 32.1 g. (0.137 mole) of di-*n*-butyl phenylboronate. A mildly exothermic reaction occurred, but only a small amount of the phosphorus pentachloride was consumed. Distillation of the solvent was commenced and as the distillation proceeded the remainder of the phosphorus pentachloride was consumed. After removal of solvent and the by-products *n*-butyl chloride and phosphorus oxychloride, the residue was distilled *in vacuo*. There was obtained 17.2 g. (79%) of phenyldichloroborane, b.p. 65–67° (14 mm.); reported b.p. 175°[14] and 178°[15] (760 mm.).

Anal. Calcd. for $C_6H_5BCl_2$: C, 45.37; H, 3.17; B, 6.81; Cl, 44.65. Found: C, 45.61; H, 3.44; B, 6.56; Cl, 44.84.

In order to determine the yields of by-products, the reaction was repeated without a solvent. To 130 g. (0.625 mole) of phosphorus pentachloride was added 68.5 g. (0.292 mole) of di-*n*-butyl phenylboronate. Much heat was evolved as the reagents were mixed, but not all of the phosphorus pentachloride was consumed until the mixture had been heated at about 70° for an additional two hours. Fractional distillation of the liquid product gave 53.1 g. (0.574 mole, 98%) of *n*-butyl chloride, b.p. 74–78°; 73.3 g. (0.479 mole, 82%) of phosphorus oxychloride, b.p. 90–105°; and 33.1 g. (0.208 mole, 71%) of phenyldichloroborane, b.p. 63–70° (14 mm.).

The crude *n*-butyl chloride was washed with dilute sodium carbonate solution, dried over anhydrous sodium sulfate, redistilled, converted to the Grignard reagent in ether solution and added to powdered carbon dioxide. *n*-Valeric acid was obtained by acidification of the mixture and extraction with ether. A portion of the acid was converted to the *p*-bromophenacyl ester, m.p. 73.6–75.2°, and another portion to the α-naphthalide, m.p. 112.4–113.8°, by conversion to the acid chloride and reaction of the latter with 1-aminonaphthalene.

LAWRENCE, KANSAS

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[11] B. Bettman, G. E. K. Branch and D. L. Yabroff, THIS JOURNAL, **56**, 1865 (1934).

[12] D. W. Mathieson and G. Newberry, *J. Chem. Soc.*, 1133 (1949).

[13] K. Torssell, *Acta Chem. Scand.*, **8**, 1779 (1954).

[14] A. Michaelis and P. Becker, *Ber.*, **13**, 58 (1880).

[15] E. Pace, *Atti accad. Lincei*, **10**, 193 (1929); *C. A.*, **24**, 1360 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Mechanism of Fluorination. III.[1] Fluorine Atom Reactions. The Olefin Dimerization Reaction[2,3]

BY WILLIAM T. MILLER, JR., AND STANLEY D. KOCH, JR.

RECEIVED AUGUST 10, 1956

A general mechanism is presented for the reactions of elemental fluorine with perhalo-olefins. This mechanism accounts for the formation of dimer addition products by the diffusion-controlled combination of free radicals which are produced in pairs with the intermediate formation of fluorine atoms. This process appears to be unique with fluorine. The important new steps in the mechanism are tested by reactions of fluorine with mixtures of perhalo-olefins of different reactivities and with an olefin and chloroform. The results obtained are shown to support the proposed mechanism and to demonstrate the very great and indiscriminate reactivity of fluorine atoms.

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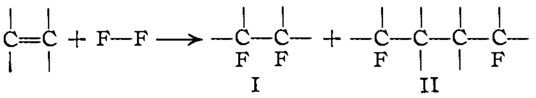
[1] Preceding paper in this series, W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty, THIS JOURNAL, **78**, 4992 (1956).

[2] Presented at the 118th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1950 (Abstracts of Papers, p. 23L).

[3] This work has been supported in part by the Office of Naval Research.

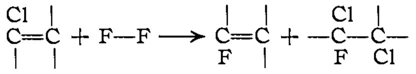
Introduction

A characteristic feature of the reactions of elemental fluorine with organic compounds is the formation of polymeric products.[4] With unsaturated compounds coupling can occur both by dehydrogenation and by reaction with olefinic bonds. As a result complicated mixtures of reaction products usually are formed. In contrast, reactions between fluorine and perhalo-olefins containing only chlorine and/or fluorine can be limited to attack at the double bond and useful yields of pure products obtained. A number of such reactions have been carried out by passing gaseous fluorine into rapidly stirred liquid olefins at 0° or below and described previously as synthetic procedures.[5,6] The principal products are the fluorine addition product I and the dimer addition product II. The yield of dimer addition product varies with olefin structure and parallels the rate of reaction with fluorine. An unreactive olefin yields little dimer while a highly reactive olefin always gives appreciable amounts.[7] Polymeric products higher than dimers are not obtained. With chlorine-containing olefins varying amounts of by-products corresponding to substitution of chlorine by fluorine III[9] and to the addition of chlorine fluoride IV are usually formed.



$$\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + \mathrm{F{-}F} \longrightarrow -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}- + -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}- \qquad (1)$$

I II



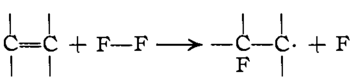
$$\overset{\mathrm{Cl}\ |}{\mathrm{C}{=}\mathrm{C}}\hspace{-1em}\underset{|\ \ |}{} + \mathrm{F{-}F} \longrightarrow \overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + -\overset{\mathrm{Cl}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{Cl}}{\mathrm{C}}}- \qquad (2)$$

III IV

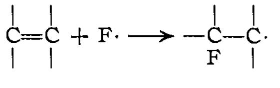
The present paper presents a general free radical mechanism that accounts for the formation of these typical reaction products, and the results of new experiments with mixtures of olefins designed especially to test the proposed mechanism for the formation of fluorine dimer addition products and to furnish information regarding the behavior of fluorine atoms.

Results and Discussion

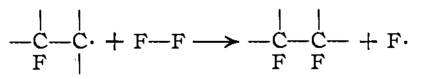
General Reaction Mechanism.—The following series of reactions has been found to be consistent with available experimental observations on the reactions of fluorine with perhalo-olefins.



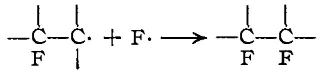
$$\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + \mathrm{F{-}F} \longrightarrow -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot + \mathrm{F}\cdot \qquad (3)$$



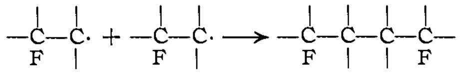
$$\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + \mathrm{F}\cdot \longrightarrow -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot \qquad (4)$$



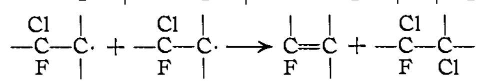
$$-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot + \mathrm{F{-}F} \longrightarrow -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}- + \mathrm{F}\cdot \qquad (5)$$



$$-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot + \mathrm{F}\cdot \longrightarrow -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}- \qquad (6)$$



$$-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot + -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot \longrightarrow -\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}- \qquad (7)$$



$$-\overset{\mathrm{Cl}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot + -\overset{\mathrm{Cl}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot \longrightarrow \overset{|}{\underset{\mathrm{F}}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + -\overset{\mathrm{Cl}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{Cl}}{\mathrm{C}}}- \qquad (8)$$

The key to the over-all mechanism is provided by the discovery that fluorine molecules react rapidly with olefinic bonds at low temperatures to produce a fluorinated free radical and a fluorine atom. This process is formulated as the rate-controlling initiation step 3. The fluorine atom can combine with an adjacent olefin molecule to yield a second free radical (4) or with the first-formed free radical (6). Combination of the radicals produced by reactions 3 and 4 yields fluorine dimer addition product (7).[10,12] Disporportionation and secondary reactions of the resulting olefin account for the principal by-products (8).[14] The occurrence of reactions 3 and 4 was shown by experiments with the addition of oxygen and of chlorine, in which fluorine served as a free-radical initiator. Products corresponding to the initial free radicals were isolated and the formation of the usual fluorination products was inhibited.[1,15] In the presence of an appreciable concentration of fluorine, reactions 5 and 4 similarly lead to the formation of fluorine addition product I. Such conditions are achieved when the rate of mixing of fluorine is fast in terms of reaction 3. However, with most of the olefins which have been investigated reaction 3 appears to occur so rapidly even at −75° (Dry Ice temperature) that it is difficult or impossible to attain an appreciable concentration of fluorine in the liquid phase. Under these conditions it is considered that the pairs of radicals formed in close proximity by reactions 3 and 4 have a relatively high probability of collision and of reaction before diffusing apart or encountering a fluorine molecule. The required very high efficiency of reaction 4 is consistent with the expected great reactivity and small steric requirement for reaction of

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[4] L. A. Bigelow, *Chem. Revs.*, **40**, 51 (1947).

[5] W. T. Miller, Jr., R. L. Ehrenfeld, J. M. Phelan, M. Prober and S. K. Reed, *Ind. Eng. Chem.*, **39**, 401 (1947).

[6] W. T. Miller, Jr., Nat. Nuclear Energy Ser., Div. VII, I, "Prepn., Properties, and Technol. of Fluorine and Org. Fluorine Compds.," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, Chap. 32, p. 567.

[7] The following olefins have yielded fluorine dimer addition products as indicated[5,6]: $CCl_2{=}CCl_2$, 43% at −15°[8]; $CClF{=}CClF$, 44% at −75°; $CF_3CCl{=}CCl_2$, 15% at 0°; $CF_3CCl{=}CF_2$, 63% at −75°.

[8] W. T. Miller, Jr., and E. Rutner, unpublished work.

[9] Often separated in the form of secondary reaction products.

[10] Bockemüller early proposed that the formation of fluorine addition and dimer addition products proceeded through an unstable intermediate addition compound formed between fluorine and the olefin.[11] Aside from the nebulous formulation of such a compound for which bonding orbitals are not available, it fails to explain the free radical nature of the fluorination process and the formation of the observed by-products.

[11] W. Bockemüller, *Ann.*, **506**, 20 (1933).

[12] Bigelow has suggested that the formation of fluorine dimer addition product may occur by combination of free radicals but without accounting for how such a process could become a probable one,[4] and, more recently, the possible formation of fluorine dimer addition product by free radical addition to olefin followed by reaction with fluorine.[13] The latter explanation is inconsistent with the failure of most perhalo-olefins to undergo free radical polymerization at low temperatures and with the complete lack of formation of polymers higher than dimers by reaction with fluorine.

[13] L. A. Bigelow, "Fluorine Chemistry," Vol. I, Chap. 11, Academic Press, Inc., New York, N. Y., 1950.

[14] Other by-products that have been isolated in low yields from chlorine-containing olefins[5,6] may be attributed to the presence of oxygen, which by reaction yields chlorine atoms.[15] Chlorine fluoride addition product (IV) may also result from the oxygen reaction.

[15] W. T. Miller, Jr., and A. L. Dittman, THIS JOURNAL, **78**, 2793 (1956).

the fluorine atom and minimizes the occurrence of primary combination (6).[16,19] Reactions between free radicals which diffuse away from their original partners also become probable under conditions of sufficiently low fluorine concentration in the liquid phase, and the relative importance of the two paths, both of which lead to dimer addition product (7), will vary with olefin reactant and experimental conditions.[20] However, as shown below, considerable evidence has been obtained for the diffusion-controlled combination of original pairs under the conditions of the present work.

Low temperatures to −75° have been shown, in general, to favor the formation of fluorine dimer addition product, to reduce the formation of by-products and to a lesser extent to reduce the amount of addition product.[5,6] These observations are consistent with the expected effect of increased viscosity of the reaction medium on the coupling of free radicals produced in pairs and with a lower activation energy for radical coupling (7) as compared with disproportionation (8), which requires transfer of halogen. 2-Chloropentafluoropropene, for which reaction 8 requires shift of fluorine, gave essentially no by-products at −75°.[5,6] On the other hand, it is to be expected that at sufficiently low temperatures the rate of reaction between fluorine and olefin (3) can be reduced to the point where the yield of dimer addition product will be lowered owing to increased concentration of fluorine in the liquid phase. This effect has been observed with hexachloropropene on going from 0 to −75°.[21] The temperature, through its effect on the vapor pressure of the olefin reactant, also controls the proportion of reaction occurring in the vapor phase above the liquid surface. Increased reaction in the vapor phase would be expected to increase the amount of fluorine addition product relative to dimer addition product because of the higher concentration of fluorine present and faster separation of radical pairs.

Fluorine Dimerization of Mixed Olefins.—Experiments designed to test the fluorine–olefin dimerization process outlined above, which requires the formation of pairs of free radicals with a high probability of combination, consisted of a series of reactions between elemental fluorine and mixtures of two olefins of different reactivities. Based on the assumptions that the fluorine atom reacts with all olefinic bonds indiscriminately and that free radical pairs combine with little selectivity, unambiguous predictions could be made regarding expected reaction products. For mixtures of two (or more) olefins participation in the initiation reaction 3 should vary with olefin reactivity and occur predominantly with the more reactive olefin. On the other hand, all olefins present, regardless of their reactivity toward molecular fluorine, should be attacked by fluorine atoms (4) to form free radicals which take part in reaction 7. Consequently, appreciable amounts of mixed-type dimer addition products should be produced as well as the products formed by reaction of each olefin separately with fluorine.[22]

Reactions of fluorine with the individual olefins *sym*-dichlorodifluoroethylene, 1,2-dichlorotetrafluoropropene, hexafluorocyclobutene and 2,3-dichlorohexafluoro-2-butene and with equimolar mixtures of *sym*-dichlorodifluoroethylene and each of the three other olefins were carried out at −75° under standardized reaction conditions. These olefins cover a wide range of reactivity toward fluorine, from fast to slow, and yield dimer addition products in the same order. *sym*-Dichlorodifluoroethylene is highly reactive and readily forms a dimer addition product; 2,3-dichlorohexafluoro-2-butene is unreactive by comparison and could not be shown to yield a dimer-addition product.

$$\mathrm{CClF{=}CClF + F{-}F \longrightarrow CClF_2CClF\cdot + F\cdot} \qquad (3')$$

$$\mathrm{CClF{=}CClF + F\cdot \longrightarrow CClF_2CClF\cdot} \qquad (4')$$

$$\mathrm{CF_3CCl{=}CClCF_3 + F\cdot \longrightarrow CF_3CClFCCl(CF_3)\cdot}$$

$$\mathrm{CClF_2CClF\cdot + CClF_2CClF\cdot \longrightarrow \underset{V}{CClF_2CClFCClFCClF_2}} \qquad (7')$$

$$\mathrm{CClF_2CClF\cdot + CF_3CClFCCl(CF_3)\cdot \longrightarrow \underset{VI}{CClF_2CClFCCl(CF_3)CClFCF_3}}$$

The reaction between fluorine and *sym*-dichlorodifluoroethylene and 2,3-dichlorohexafluoro-2-butene yielded especially clean-cut results which were in agreement with predictions. The highly reactive ethylene monopolizes the initiation step (3′); the ethylene and butene both participate in reaction 4′ and the resulting ethyl–ethyl and ethyl–butyl radical pairs combine as shown by the dimer addition products isolated (7′). The higher yield of mixed dimer addition product (VI) compared with the dimer addition product of the ethylene (V), 0.13/0.061 mole, can be attributed to a concentration effect on reaction 4 since the ethylene disappears from the reaction faster than the butene. Very little dimer addition product of the ethylene was formed by reaction of a 1 to 8 molar mixture of the ethylene and butene with fluorine. The low yield of fluorine addition product of the butene relative to that of the ethylene, 0.011/0.12 mole, and the lack of fluorine dimer addition product of the butene provide support for the above interpretation and suggest that most of the butyl radicals react with the *corresponding* ethyl radicals of step 3. Other factors such as steric hindrance may conceivably prevent the formation of dimer addition product from the dichloro-2-butene and favor cross combination of the perhalo-radicals. However, no evidence for the importance of such effects has been obtained. Each

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[16] Analogous to "primary recombination"[17] of pairs of radicals, produced by a dissociation, within the "cage" in which they are formed. Reaction 7 corresponds to diffusive[18] or "secondary recombination."[17]

[17] R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

[18] J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **76**, 3274 (1954).

[19] Experimental evidence for the occurrence of reaction 6 as a primary combination process is provided by the isolation of CCl_2FCCl_2F from the fluorine-sensitized oxidation[15] and chlorination[1] of $CCl_2{=}CCl_2$.

[20] Polymeric products have been obtained in relatively low yields by reaction of perfluoro-olefins with fluorine in the vapor phase due presumably to the production of high radical populations by very rapid reaction of the olefins with fluorine.[5]

[21] W. T. Miller, Jr., and G. Gavlin, unpublished work.

[22] At least one olefin must be sufficiently reactive with fluorine to form a dimer addition product when reacting alone and also to maintain a low concentration of fluorine in the liquid phase of the mixture.

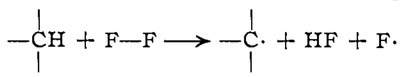
of the three possible dimer addition products was isolated from the reactions described below with hexafluorocyclobutene and 1,2-dichlorotetrafluoropropene. Further, 1,4-dichlorohexafluoro-2-butene, which is more reactive toward fluorine than the 2,3-dichloro isomer and is considered to be subject to a similar steric effect, has been shown to yield dimer addition product at 0°.[6]

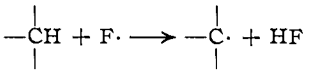
Unlike 2,3-dichlorohexafluoro-2-butene, hexafluorocyclobutene and to a greater extent 1,2-dichlorotetrafluoropropene, are sufficiently reactive to take part in the initiation reaction 3 in competition with *sym*-dichlorodifluoroethylene. In all cases each of the three possible dimer addition products was isolated in an amount proportional to the relative reactivity of the olefins involved. These observations support the postulated non-selective combination of free radical pairs. The effect of fluorine concentration was also shown more clearly. Only a trace of fluorine dimer addition product, C_8F_{14}, was formed from hexafluorocyclobutene with incomplete absorption of fluorine under the standard reaction conditions. However, reaction of the butene mixed with *sym*-dichlorodifluoroethylene gave a higher yield of C_8F_{14}, 0.025 mole, with complete absorption of fluorine, as well as the dimer addition and mixed dimer addition products derived from the ethylene. The increased yield of butene dimer addition product is consistent with a reduced fluorine concentration in the liquid phase as a result of more rapid reaction with the ethylene.

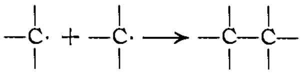
Order of Olefin Reactivity with Fluorine.—The order of olefin reactivity toward molecular fluorine as shown both by amount of dimer addition product formed and by conversion under standard conditions is: $CClF{=}CClF > CF_3CCl{=}CClF >$ $\overline{CF_2CF_2CF{=}CF} > CF_3CCl{=}CClCF_3 > [(CF_3)_2C{=}C(CF_3)_2]$.[5] This order can be rationalized in terms of electron withdrawal and steric effects. The same reactivity sequence toward chlorine atoms is indicated by qualitative observations on the relative ease of photochemical chlorination.

Application of the Olefin Dimerization Reaction to Synthesis.—The mixed-type fluorine dimer addition products prepared in this work illustrate synthetic procedures of general application to symmetrically substituted perhalo-olefins.[23] Although yields of individual products are usually small, a wide range of compounds may be prepared by a one-step process for which alternative methods are not now available.

Reaction of Fluorine Atoms with Carbon–Hydrogen Bonds.—It has been shown previously that the formation of condensation products from saturated hydrogen-containing compounds by dehydrogenation with fluorine is most satisfactorily explained by combination of free radicals (9, 10, 11).[1] This mechanism, analogous to that for the formation of dimer addition products from olefins, was tested further by treating a mixture of chloroform and *sym*-dichlorodifluoroethylene with fluorine at −75°. At this temperature chloroform is unreactive with fluorine[24] but *sym*-dichlorodifluoroethylene reacts rapidly to produce a free radical and a fluorine atom (3′). It was of interest to determine whether or not a fluorine atom thus produced


$$-\overset{|}{\underset{|}{C}}H + F{-}F \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + HF + F\cdot \qquad (9)$$


$$-\overset{|}{\underset{|}{C}}H + F\cdot \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + HF \qquad (10)$$


$$-\overset{|}{\underset{|}{C}}\cdot + -\overset{|}{\underset{|}{C}}\cdot \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \qquad (11)$$

would react with high enough efficiency with the carbon–hydrogen bond of chloroform to produce trichloromethyl radicals, in addition to fluoroethyl radicals formed from the olefin, and thus yield the mixed type condensation product $CClF_2CClFCCl_3$.

$$CHCl_3 + F\cdot \longrightarrow CCl_3\cdot + HF \qquad (12)$$

$$CClF_2CClF\cdot + CCl_3\cdot \longrightarrow \underset{\text{VII}}{CClF_2CClFCCl_3} \qquad (13)$$

Utilizing *sym*-dichlorodifluoroethylene and chloroform in the molar ratio of 1 to 2.6 for reaction, it was found possible to isolate the expected mixed condensation product VII, in addition to a larger quantity of the dimer addition product of the olefin.[25] These observations indicate a very low activation energy for reaction 12 and support the free-radical fluorine dehydrogenation mechanism presented previously. Although the fluorine atom reacted preferentially with the olefin, the selectivity is small and furnishes a striking demonstration of the high order of reactivity of the fluorine atom.

Acknowledgment.—The basic mechanism here presented for the reactions of elemental fluorine with perhalo-olefins has been developed gradually in this Laboratory over a period of years. We wish especially to acknowledge significant unpublished work by R. L. Ehrenfeld, H. F. Furber, G. Gavlin, J. M. Phelan, Maurice Prober and S. K. Reed.

Experimental Results

General Method.—Reactions were carried out with Dry Ice cooling under closely comparable conditions in a nickel U-shaped reaction vessel of the type previously described.[5] The reaction vessel was provided with a thermocouple well on the inlet side. For most of the reactions it was charged with either 0.8 mole of olefin and 1.2 moles of trichlorofluoromethane solvent or 0.8 mole of each of two olefins and 0.4 mole of trichlorofluoromethane. A 1.0-to-1.1 fluorine–nitrogen mixture was then passed in during approximately 7 hr. The fluorine–nitrogen mixture was prepared in a small brass storage tank of known volume and metered by pressure measurement.[1] Commercial tank fluorine was utilized as supplied by the Pennsylvania Salt Manufacturing Co. This was found to contain from 1.1 to 2.6% oxygen.[26] Nitrogen was utilized to exclude air during reaction and during separation of products. Reactions occurred smoothly in all cases but with an easily observable heat effect. For Dry Ice-cooled reactions internal temperatures

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[23] From a symmetrical olefin and an unsymmetrical olefin two isomeric mixed-type dimer addition products are possible. However, one product may be formed preferentially. For example, $CF_3CCl{=}CF_2 + F_2$ or $F\cdot \rightarrow (CF_3)_2CCl\cdot$ as evidenced by the formation of $(CF_3)_2CClCCl(CF_3)_2$ in high yield.[5,6]

[24] W. T. Miller, This Journal, **62**, 341 (1940).

[25] Evidence for the presence of a small quantity of hexachloroethane (*ca.* 0.005 mole) pointed to the diffusive escape of some trichloromethyl radicals from the corresponding reaction 3 ethyl radicals.

[26] Analyses were carried out by the method previously described[27] but using apparatus equipped with glass stopcocks lubricated with Kel-F type chlorofluorocarbon grease in place of mercury cut-off valves.

[27] W. T. Miller, Jr., and L. A. Bigelow, This Journal, **58**, 1585 (1936)

were maintained within the range −77 to −64° and largely below −70° (*ca.* −75°).

The reaction products were colorless and after transfer for distillation corresponded closely in weight to 95% of the combined weight of all reactants. They were separated by repeated distillations using glass and nickel wire helix packed columns. The composition of fractions containing closely boiling saturated and unsaturated compounds was determined by chlorination followed by redistillation. The weights of the more significant fractions isolated together with evidence for the identity of the new dimer-type products which are of primary importance to the present work are reported below. In all cases the characteristics of the intermediate fractions were consistent with those expected on the basis of the new products identified for the first time and with the results of previous reactions between fluorine and the same and other olefins. Boiling points are uncorrected but were determined within the range of 722 to 744 mm. pressure, unless otherwise noted. Molecular weights were determined cryoscopically in benzene. Chlorine was determined gravimetrically after sample decomposition in Parr bombs.

***sym*-Dichlorodifluoroethylene.**—Reactants: 107 g. $CClF{=}CClF$, b.p. 20.8–21.1°, prepared from CCl_3CCl_3,[28] dissolved in 165 g. of CCl_3F, b.p. 23.6–24.6°, Freon 11, Kinetic Chemicals, Inc., and 18.6 g. of fluorine. The fluorine was added with nitrogen as described above and was completely absorbed. The following fractions were separated from the 277.4 g. of colorless liquid product.

$CClF_2CClF_2$: A saturated fraction, 14.2 g., 0.083 mole, b.p. 2.0–10.3°, was indicated as largely $CClF_2CClF_2$; previously reported[28] b.p. 3.8°.

$CClF{=}CClF$: Recovered as the dichloride, CCl_2FCCl_2F, 10.3 g., b.p. 90.7–91.2°, corresponding to 6.7 g., 0.051 mole, $CClF{=}CClF$; previously reported[28] for CCl_2FCCl_2F, b.p. 92.8°.

CCl_2FCClF_2: 5.3 g., 0.027 mole, b.p. 46–47°; previously reported[29] b.p. 46.5°.

$CClF_2CClFCClFCClF_2$: 22.4 g., b.p. 70.8–71.5° (100 mm.); 21.6 g., b.p. 71.0–71.6° (100 mm.), $n^{20}\mathrm{D}$ 1.3849; total 44 g., 0.145 mole; previously reported[6] b.p. 134.1° $n^{20}\mathrm{D}$ 1.3853.

2,3-Dichlorohexafluoro-2-butene (I).—Reactants: 188 g. of $CF_3CCl{=}CClCF_3$, b.p. 66.8–67.0°, Hooker Electrochemical Co., dissolved in 165 g. of CCl_3F and 19.4 g. of fluorine. Unreacted fluorine was present in the exit gases throughout the reaction. The following fractions were separated from 353.8 g. of colorless reaction product.

$CF_3CClFCClFCF_3$: 4.7 g., b.p. 50–57°; 22.6 g., b.p. 56.8–57.0°; 24.8 g., b.p. 57.5–60.5°; total 52.1 g., 0.19 mole; previously reported[30] b.p. 62.9°.

$CF_3CCl{=}CClCF_3$: Recovered as the dichloride $CF_3CCl_2CCl_2CF_3$, 106.0 g., b.p. 130.5–132.5°, corresponding to 81.2 g., 0.35 mole, $CF_3CCl{=}CClCF_3$; previously reported[31] for $CF_3CCl_2CCl_2CF_3$, b.p. 131°.

$CF_3CCl_2CClFCF_3$: 1.2 g., b.p. 102–106° (micro-distillation), $n^{20}\mathrm{D}$ 1.3529; previously reported[30] b.p. 97.5°, $n^{20}\mathrm{D}$ 1.3530. Approximately 1 g. of higher boiling material was found.

2,3-Dichlorohexafluoro-2-butene (II).—A duplicate reaction was carried out with ice-bath cooling, internal temperature 0 to 2.3°. The fluorine was incompletely absorbed throughout.

$CF_3CClFCClFCF_3$: 62.5 g., 0.23 mole, b.p. 62.6–62.8°.

$CF_3CCl{=}CClCF_3$: Recovered as $CF_3CCl_2CCl_2CF_3$: 7.8 g., b.p. 128.0–131.1°; 78.6 g., b.p. 131.5–131.9°; corresponding to 66.2 g., 0.28 mole of $CF_3CCl{=}CClCF_3$.

$CF_3CCl_2CClFCF_3$: 10.2 g., 0.036 mole, b.p. 95.0–97.0°. Approximately 1 g. of higher boiling material was found.

***sym*-Dichlorodifluoroethylene and 2,3-Dichlorohexafluoro-2-butene** (I).—Reactants: 107 g. of $CClF{=}CClF$ and 187 g. of $CF_3CCl{=}CClCF_3$ dissolved in 107 g. of CCl_3F and 19 g. of fluorine. A trace of unabsorbed fluorine was detected in the exit gases.

$CClF_2CClF_2$: 20.7 g., 0.12 mole, b.p. *3–11*°.

$CClF{=}CClF$: Recovered as the dichloride CCl_2FCCl_2F: 12.8 g., b.p. 85.0–89.5°; 23.6 g., b.p. 85.9–90.0°; corresponding to 25.4 g., 0.19 mole, $CClF{=}CClF$.

CCl_2FCClF_2: 5.0 g., 0.027 mole, b.p. 49–51°.

$CF_3CClFCClFCF_3$: 3.0 g., 0.011 mole, b.p. 56.0–56.5°.

$CF_3CCl{=}CClCF_3$: Recovered as $CF_3CCl_2CCl_2CF_3$, 154.9 g., b.p. 128.5–131.5°, corresponding to 119 g., 0.51 mole, $CF_3CCl{=}CClCF_3$.

$CF_3CCl_2CClFCF_3$: 1.6 g., 0.0056 mole, b.p. 96–100°.

$CClF_2CClFCClFCClF_2$: 18.4 g., 0.061 mole, b.p. 132–136°.

$CF_3CClFCCl(CF_3)CClFCClF_2$: 27.5 g., b.p. 171.2–*176.6*–176.8°; 19.8 g., b.p. 176.8–177.0°; 3.8 g., b.p. 175.0–175.5°; total 51.1 g., 0.13 mole. Redistillation yielded a center cut of 30.5 g., b.p. 107.7–*108.0–108.2*°–108.4° (100 mm.), formed glass between −75° and −100°, $n^{20}\mathrm{D}$ 1.3861, d^{20}_4 1.9016. Calcd. for $C_6Cl_4F_{10}$: $MR^{20}\mathrm{D}$, 50.1[32]; mol. wt., 404; Cl, 35.1. Found: $MR^{20}\mathrm{D}$, 49.9; mol. wt., 415, 427, 421; Cl, 35.2, 35.2.

***sym*-Dichlorodifluoroethylene and 2,3-Dichlorohexafluoro-2-butene** (II).—Reactants: 13.3 g., 0.10 mole, of $CClF{=}CClF$, and 186 g. of $CF_3CCl{=}CClCF_3$ dissolved in 151 g. of CCl_3F and 19.0 g. of fluorine. Small amounts of unabsorbed fluorine were detected throughout the reaction.

$CClF_2CClF_2$: 4.1 g., 0.024 mole, b.p. 5.0–6.5°.

$CF_3CClFCClFCF_3$: 44.7 g., 0.16 mole, b.p. 59.0–63.0°.

$CF_3CCl{=}CClCF_3$: Recovered as the dichloride $CF_3CCl_2CCl_2CF_3$: 4.0 g., b.p. 125–132.0°; 127.1 g., b.p. 130.0–132.2°; corresponding to 100.2 g., 0.43 mole, of $CF_3CCl{=}CClCF_3$.

$CF_3CCl_2CClFCF_3$: 2.7 g., 0.0094 mole, b.p. 94.0–107.0°.

$CF_3CClFCCl(CF_3)CClFCClF_2$: 4.7 g., b.p. 102.0–107.8° (100 mm.); 4.3 g., b.p. 107.8–109° (100 mm.); 8.2 g., b.p. 108.8–110.0° (100 mm.), $n^{20}\mathrm{D}$ 1.3861, mol. wt. 402, 408; 1.6 g., b.p. 110.0–110.5°; total 18.8 g., 0.047 mole.

Hexafluorocyclobutene.—Reactants: 125 g. of $CF_2CF_2CF{=}CF$, b.p. 0.0–0.2°, prepared by dechlorinating $CF_2CF_2CClFCClF$,[34] dissolved in 165 g. of CCl_3F and 18.6 g. of fluorine. About 10% of the fluorine was unabsorbed as determined iodometrically. A 61.3-g. loss was incurred in working up the fraction b.p. 2–19° obtained by initial distillation.

$CF_2CF_2CF_2CF_2$: 26.6 g., 0.13 mole, b.p. −1.0 to 0.0°; previously reported[6] b.p. −4.0°.

$CF_2CF_2CF{=}CF_2$: Recovered as the dichloride $CF_2CF_2CClFCClF$, 54.0 g., b.p. 57.2–57.7°, corresponding to 37.5 g., 0.23 mole, $CF_2CF_2CF{=}CF$; previously reported[35] for $CF_2CF_2CClFCClF$, b.p. 59.87°.

$[CF_2CF_2CF_2CF{-}]_2$: The presence of this compound was indicated by the isolation of 0.8 g., micro b.p. 85–93°, f.p. near 0° (see below for properties). Evidence for the formation of C_8F_{14}, b.p. within the range 85–102°, by reaction of fluorine with $CF_2CF_2CF{=}CF$ had been obtained previously.[36]

***sym*-Dichlorodifluoroethylene and Hexafluorocyclobutene.**—Reactants: 107 g. of $CClF{=}CClF$ and 130 g. of $CF_2CF_2CF{=}CF$ in 55 g. of CCl_3F, and 19.4 g. of fluorine. Complete absorption of fluorine was observed. An 81-g. loss was incurred from the initial fraction, b.p. 2.5–24.0°.

$CF_2CF_2CF_2CF_2$ and $CClF_2CClF_2$: 2.5 g., b.p. −6.9 to −5.9°; 3.6 g., b.p. −5.9° to −1.0°; 7.2 g., b.p. −1.0 to 5.3°, largely b.p. 1.3–3.2°.

$CF_2CF_2CF{=}CF$: Recovered as dichloride CF_2CF_2CClFC-

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(28) E. G. Locke, W. R. Brode and A. L. Henne, This Journal, **56**, 1726 (1934).

(29) H. S. Booth, W. L. Mong and P. E. Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).

(30) A. L. Henne and T. H. Newby, This Journal, **70**, 130 (1948).

(31) A. L. Henne, J. B. Hinkamp and W. L. Zimmerschied, *ibid.*, **76**, 1907 (1945).

(32) Molecular refractivities were calculated using the following values for $R^{20}\mathrm{D}$; C, 2.584; Cl in CX_2, 5.69; Cl in CX_1, 5.85; F, 1.165; C_4 ring increment (+0.1).[33]

(33) A. H. Fainberg and W. T. Miller, Jr., unpublished work.

(34) Prepared by A. H. Fainberg.

(35) A. L. Henne and R. P. Ruh, This Journal, **69**, 279 (1947).

(36) W. T. Miller, Jr., and S. K. Reed, unpublished work.

ClF, 77.2 g., b.p. 51.7–75.0°, largely b.p. 58.0°; corresponding to 53.5 g., 0.33 mole, $\overline{CF_2CF_2CF=C}F$.

$CClF=CClF$: Recovered as the dichloride, CCl_2FCCl_2F, 17.3 g., b.p. 89.5–90.0°; corresponding to 11.3 g., 0.085 mole, $CClF=CClF$.

$CClF_2CClFCClFCClF_2$: 21.2 g., 0.070 mole, b.p. 67.0–68.3° (100 mm.).

$[\overline{CF_2CF_2CF_2C}F-]_2$: 6.1 g., b.p. 83.4–86.8°; 2.8 g., b.p. 87.4–92.7°, total 8.9 g., 0.025 mole. Redistillation yielded a center cut of 3.8 g., b.p. 85.2–86.3° (737 mm.), f.p. −6.8°, n^{20}_{D} 1.295[37]; d^{20}_4 1.7511. Calcd. for C_8F_{14}: MR^{20}_{D} 37.2; mol. wt., 362; Cl, 0.00. Found: MR^{20}_{D} 38.0; mol. wt., 368, 364; Cl, 0.7, 0.5.

$\overline{CF_2CF_2CF_2C}FCClFCClF_2$: 6.9 g., b.p. 100.0–103.9°; 18.1 g., b.p. 103.7–104.1° (738 mm.), formed glass between −84 and −100°, n^{20}_{D} 1.3294, d^{20}_4 1.7410; total 25.0 g., 0.075 mole. Calcd. for $C_6Cl_2F_{10}$: MR^{20}_{D} 38.8; mol. wt., 333; Cl, 21.3. Found: MR^{20}_{D} 38.9; mol. wt. 343, Cl, 21.4, 21.0.

1,2-Dichlorotetrafluoropropene.—Reactants: 146.4 g. of $CF_3CCl=CClF$, b.p. 46.5° (742 mm.), dissolved in 164 g. of CCl_3F and 19.0 g. of fluorine. The $CF_3CCl=CClF$ was prepared by the following reaction sequence: $CF_3CCl=CCl_2 \rightarrow CF_3CCl_2CCl_3$[38] $\rightarrow CF_3CCl_2CCl_2F$[39] $\rightarrow CF_3CCl=CClF$.[40] Approximately 3% of the fluorine was not absorbed.

$CF_3CClFCClF_2$: 23.0 g., 0.10 mole, b.p. 32.7–35.2°; previously reported b.p. 34.7°.

$CF_3CCl=CClF$: 32.8 g., b.p. 43.4–46.5°; 4.9 g., b.p. 47–53°; total wt. 37.7 g., 0.21 mole.

$C_6Cl_4F_{10}$: 34.5 g., 0.09 mole, b.p. 107.5–110.0°, largely b.p. 108.0–109.1° (100 mm.), n^{20}_{D} 1.3883; previously found[41] b.p. 170.5–176.7° (732 mm.).

The fluorine dimer addition product $C_6Cl_4F_{10}$ may be composed of a mixture of three possible isomers. However, the symmetrical structure $CClF_2CCl(CF_3)CCl(CF_3)CClF_2$ is favored by analogy with the structure of the corresponding product obtained from $CF_3CCl=CF_2$.[23]

***sym*-Dichlorodifluoroethylene and 1,2-Dichlorotetrafluoropropene.**—Reactants: 106.3 g. of $CClF=CClF$ and 146 g. of $CF_3CCl=CClF$ dissolved in 54.9 g. of CCl_3F and 19.2 g. of fluorine. The fluorine was absorbed completely.

$CClF_2CClF_2$: 19.8 g., 0.12 mole, b.p. 1.5–3.7°.

$CClF=CClF$: Recovered as CCl_2FCCl_2F, 32.7 g., b.p. 90.0–92.0°, corresponding to 21.3 g., 0.16 mole, of $CClF=CClF$.

$CF_3CCl=CClF$: Recovered as $CF_3CCl_2CCl_2F$, 105.4 g., b.p. 110.2–111.2°, corresponding to 77.0 g., 0.42 mole, of $CF_3CCl=CClF$.

$CClF_2CCl_2F$: 2.5 g., 0.013 mole, b.p. 47.2–48.5°.

$CClF_2CClFCClFCClF_2$: 8.3 g., b.p. 130.1–135.9°; 6.1 g., b.p. 134.0–135.9°; 4.4 g., b.p. 135.9–146.1°; total 18.8 g., 0.062 mole.

$C_5Cl_4F_8$: 9.7 g., b.p. 146.1–153.0°; 5.5 g., b.p. 152.4–153.0° (738 mm.), forms glass between −111 and −126°, n^{20}_{D} 1.3885, d^{20}_4 1.8335; 10.1 g., b.p. 153.1–154.7°; total 25.3 g., 0.072 mole. Calcd. for $C_5Cl_4F_8$: MR^{20}_{D} 45.3; mol. wt., 354; Cl, 40.1. Found for fraction b.p. 152.4–153.0°: MR^{20}_{D} 45.5; mol. wt., 342, 353; Cl, 38.6, 39.4.

Two structures are possible for $C_5Cl_4F_8$ without rearrangement of groups initially present. Of these $CClF_2CCl(CF_3)$-$CClFCClF_2$ is preferred by analogy with the reaction of CF_3-$CCl=CF_2$ with fluorine.[23]

$C_6Cl_4F_{10}$: 6.1 g., b.p. 96.0–102.5° (100 mm.); 1.2 g., b.p. 103.0° (100 mm.), n^{20}_{D} 1.3859; total wt. 7.3 g., 0.018 mole.

***sym*-Dichlorodifluoroethylene and Chloroform.**—Reactants: 83 g., 0.62 mole, of $CClF=CClF$; 195 g., 1.63 moles, of chloroform; and 19.0 g. of fluorine. The fluorine was almost completely absorbed. Two duplicate reactions were carried out and the products combined for separation.

CF_3CClF_2: 3.2 g., 0.021 mole, b.p. −40.2 to −38.8°; previously reported[28] b.p. −38°.

$CClF_2CClF_2$: 5.6 g., b.p. −1.1 to 1.3°; 33.8 g., b.p. 1.3–2.7°; 7.7 g., b.p. 2.7–3.7°; total 47.1 g., 0.28 mole.

$CClF=CClF$: 20.7 g., 0.16 mole, b.p. 19.2–23.7°.

$CClF_2CCl_2F$: 19.6 g. of material, b.p. 37.9–50.1°, was collected.

$CClF_2CClFCClFCClF_2$: 7.5 g., b.p. 69.5–72.2° (100 mm.); 45.2 g., b.p. 72.0–72.2° (100 mm.); total 52.7 g., 0.17 mole.

$CCl_3CClFCClF_2$: 4.7 g., b.p. 87.2–87.3° (100 mm.); 3.7 g., b.p. 87.5–88.0° (100 mm.), estimated b.p. 153° (760 mm.), formed glass between −109° and −117°, n^{20}_{D} 1.4384, d^{20}_4 1.7603; 2.2 g., b.p. 88.3–88.8° (100 mm.); 5.1 g., b.p. 89.0–94.0° (100 mm.); total 15.7 g., 0.058 mole. Calcd. for $C_3Cl_5F_3$: MR^{20}_{D} 40.3; mol. wt., 270; Cl, 65.6. Found for fraction b.p. 87.5–88.0° (100 mm.): MR^{20}_{D} 40.3; mol. wt., 261, 261; Cl, 66.0, 66.1.

The following properties have been reported for CCl_3-$CClFCClF_2$: b.p. 153.3°, f.p. −14.8°, n^{20}_{D} 1.43919, d^{20}_4 1.7702, MR^{20}_{D} 40.18.[43] However, the evidence for the assigned structure is not entirely conclusive[44] and would now appear to require re-examination.

The residue from the above separation contained 1.2 g. of sublimable white solid which appeared to be hexachloroethane.

ITHACA, NEW YORK

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[37] Estimated using an Abbe refractometer equipped with a scale reading to n_{D} 1.3000.

[38] A. L. Henne and A. M. Whaley, THIS JOURNAL, **63**, 3478 (1941).

[39] A. L. Henne and A. M. Whaley, *ibid.*, **64**, 1157 (1942).

[40] A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946).

[41] A reaction carried out on a larger scale with 1 part $CF_3CCl=CClF$ dissolved in 2 parts CCl_2FCClF_2 and fluorine at Dry Ice temperature yielded 41% $CF_3CClFCClF_2$, b.p. 33.0–34.1°, and 28% $C_6Cl_4F_{10}$, b.p. 170.5–176.7° (732 mm.).[42]

[42] W. T. Miller, Jr., and M. D. Hurwitz, unpublished work.

[43] A. L. Henne and M. W. Renoll, THIS JOURNAL, **61**, 2489 (1939).

[44] We are indebted to A. H. Fainberg for drawing our attention to this point.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyalkylene Disulfides

BY C. S. MARVEL AND L. ELMER OLSON[1]

RECEIVED FEBRUARY 20, 1957

The oxidation of alkylene dimercaptans by air in soap emulsion has been found to be a useful method of producing polyalkylene disulfides.

The oxidation of a dimercaptan by air to a polydisulfide has been patented as a polymer-forming reaction by Patrick,[2] but it has never been very widely used in scientific work.

In the distillation of some dimercaptans which were being purified for other uses, it was noted that a polymeric material built up in the flask apparently

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[1] Some of the preliminary experiments which led to the work discussed in this manuscript were performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the government synthetic rubber program.

[2] J. C. Patrick, U. S. Patent 2,363,614 (November 28, 1944).