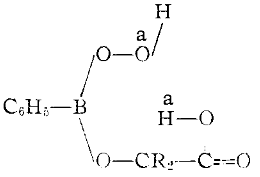
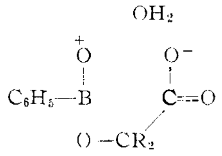
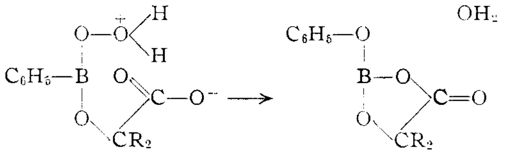
acid. The chelating tendency of the catalyst must play an important role in making it effective. One possible intermediate is represented by structure I.

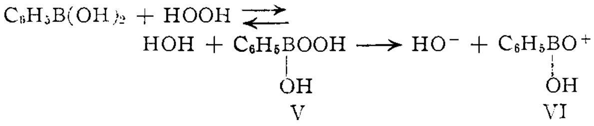

I


II

Transfer of H^a to O^a and cleavage of the peroxide bond to give II would occur in the slow step. An alternate path from the same intermediate could involve the processes I ⇄ III → IV with the last step rate determining. The conformational possibilities for I are such that the proton transfer and


III IV

boron–oxygen bond formation cannot occur simultaneously. This path is attractive in that the slow step involves the loss of opposite charges. This process should be favored by a decrease in polarity of the solvent and, being a rate process, the effect should overbalance the opposing effect on the equilibrium I ⇄ III. Changing from water to 50% methanol does in fact increase the rate of the mandelic acid-catalyzed reaction. This same solvent change has the opposite effect on the rate of the uncatalyzed reaction (compare the first three data in Table I and that in Table III, footnote *h*) for which the rate determining process V → VI appears to be reasonable.



$$C_6H_5B(OH)_2 + HOOH \rightleftarrows HOH + C_6H_5\underset{\underset{V}{OH}}{\underset{|}{B}}OOH \longrightarrow HO^- + C_6H_5\underset{\underset{VI}{OH}}{\underset{|}{B}}O^+$$

Experimental

Materials.—Benzeneboronic acid was prepared from butyl borate and phenylmagnesium bromide by the method of Bean and Johnson.[9] The samples, used as the anhydride, had neutral equivalents of 103.9 ± 0.5.

1-Hydroxycyclohexanecarboxylic acid was graciously provided by Dr. R. E. Lyle.

The α-hydroxyisobutyric acid had m.p. 78.0–79.0°.

Anhydrous pinacol was prepared from the crude hydrate.[10]

3-Hydroxypropanoic acid was prepared by warming a solution of β-propiolactone on the steam-bath. The resulting solution was assayed by titration with sodium hydroxide and used as such.

All other reagents were C.P. or reagent grade where available and used without further purification, or were prepared by conventional methods and had melting points agreeing with those given in the literature.

Rate Measurements.—These were made as described previously[3] using the colorimetric method of Eisenberg[11] for determining the concentrations of unreacted peroxide. The optical density of the pertitanate was diminished in the presence of oxalic acid so that a separate calibration curve was prepared in this case. All kinetic runs were made at 24.93 ±0.02° at ionic strength 0.50.

Titrations.—All *p*H measurements were made with a Beckman Model H-2 meter and were usually reproducible to 0.03 *p*H unit. When ionic strengths were adjusted with sodium perchlorate difficulties were encountered in the titrations after some time probably because of the formation of potassium perchlorate at the calomel electrode. When sodium nitrate was used in adjusting ionic strengths the difficulty disappeared. Sodium perchlorate was used in all the kinetic runs.

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(9) F. R. Bean and J. R. Johnson, This Journal, **54**, 4415 (1932).

(10) C. F. H. Allen and A. Bell, *Org. Syntheses*, **22**, 40 (1942).

(11) G. Eisenberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 327 (1943).

Durham, N. H.

[Contribution from the Department of Chemistry, University of New Hampshire]

Electrophilic Displacement Reactions. VIII.[1] Rates of Brominolysis of Substituted Benzeneboronic Acids. Correlation of Rates of Aromatic Electrophilic Displacement Reactions[2,3]

By Henry G. Kuivila and Lawrence E. Benjamin

Received March 28, 1955

The rates of brominolysis of six *meta*- and *para*-substituted benzeneboronic acids in "20%" acetic acid have been measured. Correlation of the rates by the Hammett equation and with rates of other aromatic electrophilic displacement reactions are discussed.

In a previous investigation[4] the rates of brominolysis (equation 1) of ten *meta*- and *para*-substituted

$$ArB(OH)_2 + Br_2 \xrightarrow{H_2O} ArBr + B(OH)_3 + HBr \quad (1)$$

benzeneboronic acids were reported. We are using this reaction as a starting point in the study of quantitative relationships among the rates of aromatic electrophilic displacement reactions. To make our series more representative of various electronic effects seven additional members of the series have been investigated. The substituents included are *m*-Br, *p*-F, *m*-F, *p*-I, *m*-I and *p*-C_6H_5.

Results and Discussion

Kinetic Data.—The new data on the brominolysis of substituted benzeneboronic acids in "20%" acetic acid at 25° are summarized in Table I. In Fig. 1 these, along with the previous data, are represented in a typical plot for testing applicability of

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(1) For the previous publication in this series see H. G. Kuivila and R. A. Wiles, This Journal, **77**, 4830 (1955).

(2) From the Bachelor's (1953) and Master's (1954) theses of L. E. Benjamin.

(3) Substantial support of this investigation by the Office of Naval Research is gratefully acknowledged.

(4) H. G. Kuivila and A. R. Hendrickson, This Journal, **74**, 5068 (1952).

TABLE I

RATES OF BROMINOLYSIS OF SUBSTITUTED BENZENEBORONIC ACIDS IN "20%" ACETIC ACID 0.40 M IN SODIUM BROMIDE AT 25°

Substituent	10^5k, l. mole^{-1} sec.$^{-1}$	log k/k_0	σ
m-Br	21.3	−1.36	0.391
m-I	34.6	−1.14	.352
m-F	18.7	−1.41	.337
p-I	241	−0.303	.276
p-F	1,360	+0.499	.062
p-C_6H_5	10,500	+1.34	.009
None	484	0	0

the Hammett equation.[5] The sigma values used here are taken from the recent compilation of Jaffe.[6]

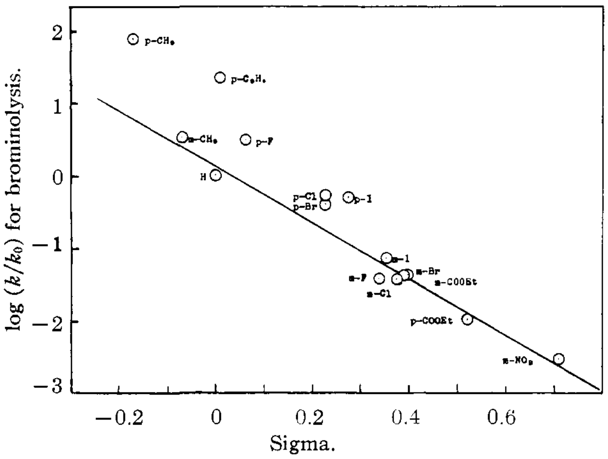
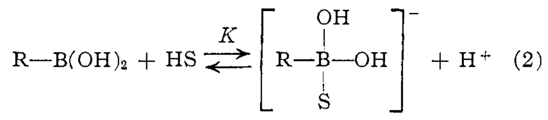


Fig. 1.—Test of Hammett equation for brominolysis of substituted benzeneboronic acids.

The *meta*-substituents and *p*-carbethoxy scatter satisfactorily about a line represented by the equation

$$\log k/k_0 = 0.16 - 3.87\,\sigma$$

Studies on the mechanism of the reaction[7] have indicated that a quadricovalent boronate anion I formed rapidly and reversibly by reaction with solvent HS, is probably the species which reacts with molecular bromine in the rate-determining step. The position of this equilibrium (eq. 2) will



$$\text{R—B(OH)}_2 + \text{HS} \overset{K}{\rightleftarrows} \left[\begin{array}{c}\text{OH}\\ | \\ \text{R—B—OH}\\ | \\ \text{S}\end{array}\right]^- + \text{H}^+ \quad (2)$$

I

favor formation of I when electron withdrawing substituents are present in the benzene ring. Since this reaction involves an atom in the side chain it should be correlated by the Hammett equation as is true for the ionization constants of substituted benzeneboronic acids.[5] From eq. 2 the concentration of the intermediate will be given by eq. 3 since the concentrations of HS and H$^+$ are the same in all experiments.

$$I = \frac{K\,[\text{HS}]\,[\text{RB(OH)}_2]}{[\text{H}^+]} = aK[\text{RB(OH)}_2] \qquad (3)$$

If $\log K/K_0 = \rho'\sigma$ then the value of the rate constant obtained from the kinetic experiments will be $k = ak_{\text{I}}K_0e^{\rho'\sigma}$ where k_{I} is the specific rate constant for the reaction of I with bromine. Then

$$0.16\text{–}3.87\sigma = \log\frac{k}{k_0} = \log\frac{k_{\text{I}}}{k_{\text{I}_0}}\,e^{\rho'\sigma} = \log\frac{k_{\text{I}}}{k_{\text{I}_0}} + \rho'\sigma \qquad (4)$$

and

$$\log\frac{k_{\text{I}}}{k_{\text{I}_0}} = 0.16 - (3.87 + \rho')\sigma \qquad (5)$$

Since ρ' will be positive the value of ρ for the rate-determining step is actually a larger negative number than −3.87. If ρ' is about the same in this case as that for the ionization of benzeneboronic acids in 25% aqueous ethanol[5] then ρ will be about −6.0. This value may be compared with −7.22 observed by Roberts, *et al.*, for aromatic nitration[8] and suggests a higher degree of selectivity on the part of the electrophilic reagent in the latter reaction[9] although the nitronium ion is probably more electrophilic than the bromine molecule. In the present work, however, replacement of the boric acid group $-\text{B(OH)}_3$ rather than hydrogen is under consideration. The presence of this negatively charged group on the carbon at which electrophilic attack by the bromine molecule takes place facilitates polarization of the bromine molecule and departure of the bromide ion. As a result electron release by the substituents does not need to participate as importantly as would be expected if replacement of hydrogen were involved.

The extent to which electron release by the substituents is brought into play in the pentadienate transition state is still very large as shown by the extent of deviations of certain *para*-substituents from the line in Fig. 1. These deviations all reflect enhancements in the rate constants over those expected from a Hammett plot. The order is $C_6H_5 > CH_3 > I \sim F > Cl > Br$. Although the phenyl group has a sigma value near zero, *p*-phenylbenzeneboronic acid reacts twenty times as fast as benzeneboronic acid. With methyl the effect is nearly as large but with the halogens it is smaller. In aromatic nitration[8] *p*-iodo deviates much more than *p*-fluoro. A high degree of electrostatic polarizability in the strong electrical field of the pentadienate transition state has been invoked to account for this reversal from what would be expected on the basis of simple resonance effects alone. The latter seem to be relatively more important in the present case.

The degree of correlation between aromatic nitration and the brominolysis reaction is shown in Fig. 2. Some scatter is apparent about the least squares line which is described by eq. 6. However, there is no trend in the data so the linear relationship appears to the best one.

$$\log (k/k_0)_{\text{brominolysis}} = 0.730 \log (k/k_0)_{\text{nitration}} - 0.257 \qquad (6)$$

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[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1943, Ch. VII.

[6] H. H. Jaffe, *Chem. Revs.*, **54**, 191 (1953).

[7] H. G. Kuivila and E. K. Easterbrook, THIS JOURNAL, **73**, 4629 (1951).

[8] J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *ibid.*, **76**, 4525 (1954).

[9] *Cf.* (a) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 100 (1948); (b) P. B. D. de la Mare, *ibid.*, 2871 (1949); (c) P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, *Research*, **6**, No. 2 (1949); (d) H. C. Brown and K. LeR. Nelson, THIS JOURNAL, **75**, 6292 (1953); (e) E. Berliner and F. Berliner, *ibid.*, **76**, 6179 (1954).

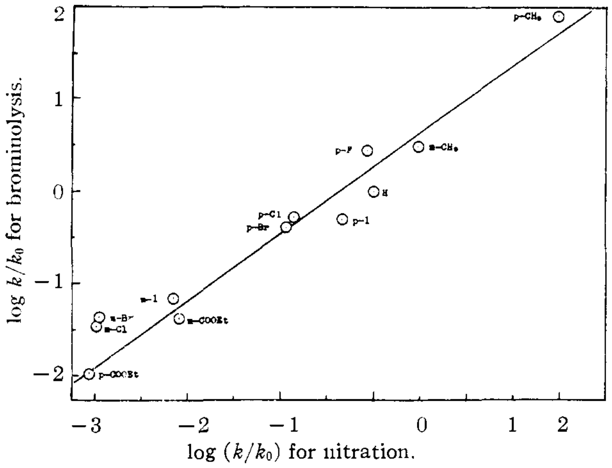
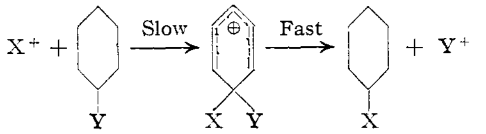


Fig. 2.—Correlation of rates of brominolysis of benzeneboronic acids and aromatic nitration.

It follows from the discussion above regarding eq. 2 that the slope for the actual substitution step in the brominolysis reaction would be greater than 0.73. We have, then, a correlation in rates between two aromatic electrophilic displacement reactions which differ both in the displacing entity and that being displaced. This suggests that such correlations may prove to be quite general for this type of reaction in which the rate-determining step involves the transfer of a pair of pi electrons from the benzene ring into an sp^3 orbital at the seat of reaction (equation 7).



(7)

The scope of such linear relationships is difficult to assess because of the nature of the data now available. Due to the extreme variation in rates among substituted benzenes comparable data for only a few substituents are usually known. As a result truly critical tests frequently cannot be made. For example, the available data for aromatic halogenation[10] correlate satisfactorily with those presented here as shown in Fig. 3, but only five items are available for comparison. Other substituents which could extend the range cause reaction with bromine to be too fast or too slow to measure.

Probably the widest range of data for comparison comes in the work of Kochi and Hammond on the solvolysis of benzyl tosylates in aqueous acetone.[11] They measured rates for substituents ranging from p-methoxy to p-nitro. As can be seen from Fig. 3 these correlate as well with the brominolysis rates as do those for nitration and bromination. This is particularly interesting because the product of the solvolysis reaction has a positive charge, not in the ring, but on a carbon atom attached to the ring. Reactions in which a cation adds to the double bond of styrene in the rate determining step would probably fall into the same category as those mentioned thus far.

To the extent that these correlations exist, new sigma constants can be set up for *para*-substituents for the formation of pentadienate cations and phenylcarbonium ions. Since data for *meta*-substituted benzenes are correlated by the original Hammett equation the old values could be used for them. Alternatively, a complete new set of sigma and rho constants with a new reference reaction could be established. In this case the reference reaction should preferably be one for which precise data covering the entire range of substituents is available. In either case it appears desirable to await the accumulation of more data so that values for the parameters, once established, will not need to be changed soon.

If the discussion of Swain and Langsdorf[12] concerning the reactions of substituted benzyl bromides with trimethylamine is valid, correlation of their data with those on aromatic substitution is not to be expected. They are dealing with true displacements rather than additions as in equation 7 or ionization as in solvolysis. Substituents may facilitate reaction either by electromeric electron withdrawal or release and therefore rho varies with substituent. Similarly in a given 1,2-shift the migrating aromatic group may provide varying amounts of driving force toward the departure of the leaving group, and hence toward the over-all rate, depending on the nature of the substituents present in the ring. When sigma values are computed for electron releasing *para*-substituents from reactions such

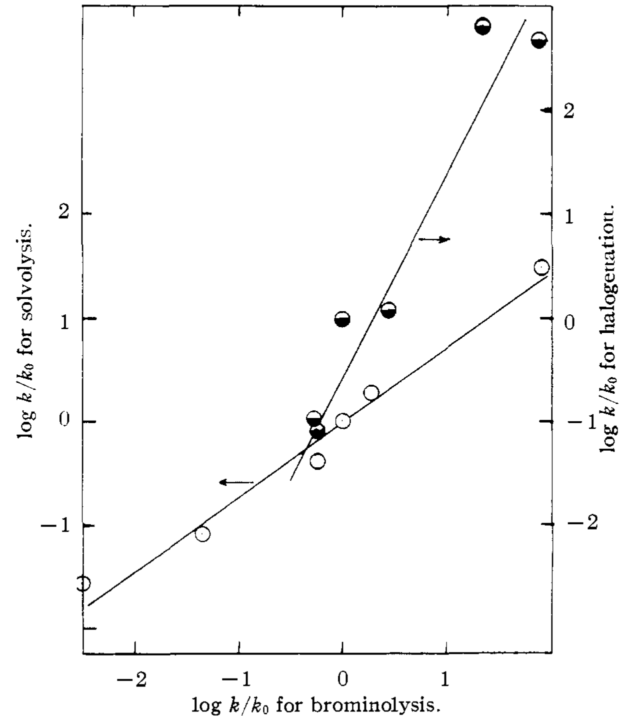


Fig. 3.—Correlation of rates of brominolysis of substituted benzeneboronic acids and solvolysis of benzyl toluenesulfonates (open circles) and aromatic halogenation (half-closed circles). The solvolysis rate for m-nitrobenzyl tosylate was obtained by interpolation from the data of Kochi and Hammond.

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(10) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

(11) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

(12) C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951).

as these, a whole spectrum of values will be found. Their magnitudes will depend on which part of the Hammett plot is used in estimating rho. Thus the tentative values for electrophilic reactions proposed by Pearson, *et al.*,[13] on the basis of data on the Beckmann rearrangement of acetophenone are not applicable to nitration or brominolysis of areneboronic acids, nor are they entirely satisfactory for the pinacol rearrangement.

Experimental

All melting points are uncorrected.

Analyses were performed by Dr. Carl Tiedcke and by the Galbraith Laboratories.

***p*-Iodobenzeneboronic Acid.**—The preparation of the *p*-iodo acid has not been described in the literature. *p*-Diiodobenzene was prepared by iodination of iodobenzene.[14] This compound was converted to the monomagnesium iodide and added to butyl borate; the product was hydrolyzed to give the acid.

To 5.4 g. (0.22 mole) of magnesium turnings in 50 ml. of dry anisole was added dropwise a solution of 73.2 g. (0.22 mole) of *p*-diiodobenzene in 175 ml. of dry anisole. This solution was kept warm to prevent separation of the diiodobenzene. Ethyl iodide was added to start the reaction. As the reaction proceeded the reaction mixture became dark brown. After the diiodobenzene had all been added and evolution of heat had ceased, stirring was continued for a half hour whence only a small amount of magnesium remained.

This solution was added dropwise to 75 ml. (0.28 mole) of butyl borate in 175 ml. of dry ether cooled in a Dry Ice–acetone bath. After warming to room temperature overnight the reaction mixture was poured on 135 g. of ice and 7 ml. of concd. sulfuric acid. The resulting layers were separated and the water layer extracted with three 50-ml. portions of ether. These were combined with the original extract and extracted with four 50-ml. portions of 10% sodium hydroxide. These latter were combined and acidified with sulfuric acid, yielding a brown resinous material and white solid which were filtered off and extracted with portions of hot dilute sulfuric acid until a precipitate no longer appeared in the extract on cooling. The combined precipitates were tan in color, 9.8 g. Crystallization from benzene and twice from water (treated with Norite) yielded white needles of the acid which after drying at 110° for three hours yielded the anhydride, 3.2 g., 6.3% yield, m.p. 314–318°.

Anal. Calcd. for C_6H_4BIO: C, 31.36; H, 1.75; I, 55.26; neut. equiv., 229.8. Found: C, 31.27, 31.41; H, 1.74, 1.78; I, 55.19, 55.31; neut. equiv., 229.4.

***m*-Iodobenzeneboronic Acid.**—Direct iodination of benzeneboronic acid in sulfuric acid with silver sulfate as a promoter[15] could not be used because of hydrolytic cleavage to yield benzene and boric acid. A procedure involving the reaction of the diazonium salt from *m*-aminobenzeneboronic acid with iodide also proved to be unsuccessful.

The method which was successful[16] started with *m*-phenylenediamine which was tetrazotized and converted to *m*-diiodobenzene in 75% yield. A 40% excess of potassium iodide over that necessary for the formation of *m*-diiodobenzene was used in order to ensure destruction of any excess nitrite. When urea or stannous chloride was used excessive foaming occurred and yields were negligible. Using the same procedure as for *p*-iodobenzeneboronic acid a yield of 5.1% of the *m*-iodo acid was obtained; m.p. 186.5–187.5° (anhydride).

Anal. Calcd. for C_6H_4BOI: neut. equiv., 229.8; I, 55.24. Found: neut. equiv., 227.9; I, 54.84.

The other boronic acids used have been prepared previously and characteristics of the samples in this investigation are listed in Table II.

TABLE II

SUBSTITUTED BENZENEBORONIC ANHYDRIDES[a]

Substituent	M.p., °C. This paper	M.p., °C. Lit.[c]	Neut. equiv. Obsd.	Neut. equiv. Calcd.
p-F	265–266	289–290[d]	121.1	121.9
p-C_6H_5	231–232	232–234[e]	180.6	182.6
m-Br	172.5–175.5	170[d]	182.6	182.6
m-F	211.5–213.5	220–221[d]	121.8	121.9
m-OCH_3	158.5–159.5	147[f]	134.4	134.0

[a] Acids dried to constant weight at 110°. [b] Uncorrected. [c] Corrected. [d] B. Bettman, G. E. K. Branch and D. L. Yabroff, THIS JOURNAL, **56**, 1865 (1934). [e] D. L. Yabroff and G. E. K. Branch, *ibid.*, **56**, 1850 (1934). [f] W. Konig and W. Scharrnbeck, *J. prakt. Chem.*, **128**, 153 (1930); *C. A.*, **25**, 927 (1931).

The kinetic procedure was as previously described.[4]

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(13) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

(14) R. L. Datta and N. R. Chatterjee, THIS JOURNAL, **41**, 293 (1919).

(15) D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 3694 (1950).

(16) K. H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications," Edward Arnold and Co., London, 1949, p. 25.

DURHAM, N. H.

[CONTRIBUTION NO. 97 FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING CO.]

The Chemistry of Perfluoro Ethers. I. Substitution of α-Fluorine by Chlorine: The α,α,α'-Trichloro Perfluoro Ethers[1]

BY GEORGE VAN DYKE TIERS

RECEIVED FEBRUARY 23, 1955

The first chemical reaction of perfluoro ethers is reported. Selective substitution of the α-fluorine atoms by chlorine has been achieved, using aluminum chloride as the exchange agent. Perfluorotetrahydrofurans and tetrahydropyrans bearing a single perfluoroalkyl substituent in the α-position are converted to their α,α,α'-trichloro analogs in good yield. Physical properties are reported for the compounds prepared. Synthesis of a perhalo lactone is described.

Perfluoro ethers are thermally and chemically very stable; indeed, chemical reactions have not hitherto been reported.[2] However, researches carried out in this Laboratory have indicated slight but definite activation of the α-fluorine atoms. This communication describes the reaction of aluminum chloride with members of a class of cyclic perfluoro ethers bearing a single perfluoroalkyl substituent in the α-position.[3,4]

The use of aluminum chloride to replace fluorine

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(1) Presented at the 126th Annual Meeting of the American Chemical Society, New York, 1954; Abstracts, p. 27M.

(2) (a) W. H. Pearlson in J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, p. 489; (b) R. N. Haszeldine and A. G. Sharpe. "Fluorine and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 144.

(3) T. J. Brice and R. I. Coon, THIS JOURNAL, **75**, 2912 (1953).

(4) E. A. Kauck and J. H. Simons, U. S. Patent 2,644,823, July 7, 1953.