3,3-Difluoro-2,4-pentanedione.—2,4-Pentanedione (89 g., 0.89 mole) in 500 ml. of absolute ethanol was treated with perchloryl fluoride while adding 102 g. (1.9 moles) of sodium methylate portionwise as described in the previous experiment. The product, isolated as before, was 94 g. (77% yield) of 3,3-difluoro-2,4-pentanedione, a colorless liquid, b.p. 114° with slow decomposition; 61° (102 mm.), $n^{27}\text{D}$ 1.3680.

Anal. Calcd. for $C_5H_6F_2O_2$: C, 44.12; H, 4.45. Found: C, 44.33; H, 4.93.

The infrared spectrum showed absorption at 5.71 μ characteristic of the carbonyl linkage. The starting material, 2,4-pentanedione, shows little or no normal carbonyl absorption because of almost complete enolization of the compound.[10] A strong band at 8.93 μ may be associated with the carbon–fluorine stretching frequency.

The 2,4-dinitrophenylhydrazone derivative was prepared in aqueous ethanol from the fluorinated pentanedione and 2,4-dinitrophenylhydrazine in dilute sulfuric acid to give yellow plates from benzene–light petroleum ether, m.p. 124–125°.

Anal. Calcd. for $C_{11}H_{10}F_2N_4O_5$: N, 17.72. Found: N, 17.92.

Diethyl 2-Fluoro-2-phenylmalonate.—Using the procedures described in the previous two experiments, diethyl 2-phenylmalonate (87 g., 0.37 mole) in 300 ml. of absolute ethanol was treated with perchloryl fluoride while adding 24 g. (0.44 mole) of sodium methylate portionwise. The product, isolated as before, was 88 g. (93% yield) of diethyl 2-fluoro-2-phenylmalonate, a colorless oil, b.p. 124° (0.3 mm.), $n\text{D}^{28}$ 1.4792. Absorption in the infrared spectrum characteristic of the carbonyl linkage appears at 5.69 μ. This compares with absorption at 5.76 μ in the starting material, diethyl phenylmalonate.

Anal. Calcd. for $C_{13}H_{15}FO_4$: C, 61.41; H, 5.95; F, 7.47. Found: C, 61.59; H, 5.88; F, 7.27.

2-Fluoro-2-phenylmalonamide was prepared by reaction of the diethyl ester with liquid ammonia containing sodium to give white needle crystals from 95% ethanol, m.p. 204–205°.

Anal. Calcd. for $C_9H_9FN_2O_2$: C, 55.10; H, 4.62; N, 14.29. Found: C, 55.42; H, 5.19; N, 14.45.

Acknowledgments.—The authors wish to express their gratitude to Miss Ruth Kossatz and Dr. R. N Haszeldine for their valuable assistance in supplying and interpreting infrared data, to Dr. H. Q Smith for contributing the fluorobarbiturate synthesis, and to Mr. Howard Francis and co-workers for the microanalysis herein reported.

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[10] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, 71, 1068 (1949).

[CONTRIBUTION NO. 4 FROM THE EXPLORATORY RESEARCH LABORATORY OF DOW CHEMICAL OF CANADA, LTD.]

Aromatic Substitution. IV.[1a] Protonated and Deuterated Alkylbenzene Tetrafluoroborate Complexes[1b]

BY G. A. OLAH AND S. J. KUHN

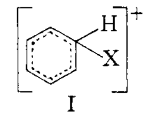
RECEIVED JULY 7, 1958

As a preparative proof of H. C. Brown's "σ-complex" theory, onium salt (or σ-complex) intermediates of alkylbenzenes with HF + BF_3 and DF + BF_3, with molecular composition of 1:1:1 were isolated. Silver tetrafluoroborate with HCl and HBr or DCl and DBr was also found to be a suitable reagent for preparing the intermediate complexes.

Theoretical Considerations.—During the study of the mechanism of the electrophilic aromatic substitutions the S_E1 reaction type was found to be objectionable by Dewar[2] for theoretical and kinetic reasons. Even if a dissociation equilibrium in benzene exists, this has to occur so slowly and to such a small extent that this cannot serve as a basis for the substitution process.

In connection with the results of the kinetic measurements a mechanism following the second order has to be taken into account.

The pure S_E2 reaction would be expected to be the simplest mechanism when the substitution proceeds in one step, without the precipitation of the π-electrons of the benzene ring, though as a consequence of the positive charge that should be present in a polarized state. In this case the intermediate complex can be formulated[3] as (the entering electrophilic substituent is represented by X)



I

The substitution takes place on a sp²-bonded carbon atom. There is no possibility of inversion occurring as in the case of aliphatic substitutions since this causes an increase of the potential energy. After Hammett this intermediate may be considered as the most probable. since the investment of the orbit-delocalizating (resonance) energy of the aromatic system becomes superfluous for the process of the substitution.

Recently published investigations on aromatics containing hydrogen isotopes, however, excluded the possibility of the pure S_E2 mechanism, although its relative simpleness may appear convenient. Melander's[4] investigations with tritium labeled aromatics led first of all to this result. In the case of the electrophilic substitution of benzene, derivatives substituted by tritium should show a significantly different value of the substitution ratio of protium:tritium, primarily because of the differences of the zero point energies. Since kinetic investigations did not show such a difference in the case of the investigated nitration and halogenation,

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[1] (a) Part III, *J. Chem. Soc.*, 2174 (1957). (b) The work was started in the authors' earlier laboratory, the Chemical Central Research Institute of the Hungarian Academy of Sciences, Budapest (Hungary). Partly delivered as a paper at the XVI International Congress of the International Union of Pure and Applied Chemistry in Paris, July 18, 1957, and in a lecture before the Hungarian Academy of Sciences, June 15, 1956, in Budapest; preliminary communication appeared *Nature*, **178**, 694 (1956).

[2] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 162.

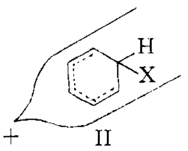
[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 309.

[4] L. Melander, *Acta Chem. Scand.*, **3**, 95 (1949); *Nature*, **163**, 599 (1949); *Arkiv. Kemi*, **2**, 213 (1950).

it is evident that the rate-determining step cannot be the expulsion of the proton or triton from the transition complex, *i.e.*, we cannot speak of a pure, simple SE2 reaction. The sulfonation reaction has to be treated separately since a measurable isotope effect is observable in this case[3] and so a divergent mechanism was taken into account.

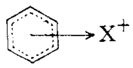
Results identical to those of Melander were obtained by Banner, Bowyer and Williams[5a] as well as by Lauer and Noland[5b] in the course of their work on deuterium labeled compounds.

On the basis of theoretical considerations, two possibilities remain for the structure of the intermediate complexes. The one arises from the deformation and use of the π-electron system of the aromatic ring and by the bonding of the substituent through a σ-complex of Brown[6]).



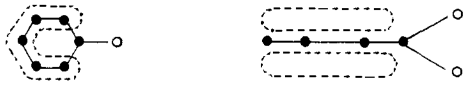
II

The other is the possibility of the complex formation between the π-electron sextet system of the aromatic ring itself (without a larger deformation) and the reagent cation (π-complex of Dewar).[7]



III

In the transition complex II the hydrogen atom to be substituted and the entering substituent are both bound to the carbon atom by complete electron pairs/*i.e.*, by σ-bonds and therefore the carbon atom itself is in a sp^3-hybrid state. Two π-electrons of the original π-electron sextet were used in the formation in the carbon atoms fourth σ-bond, while the remaining four π-electrons form a pentadienate cation system on the five available p-orbitals. Between the latter structure and the C–H bond there exists a possibility for a certain amount of hyperconjugation. The foregoing may be represented according to Melander[4] as



(plan) (side view)

Relatively little attention has been paid in the past to the structures of type II, although Robinson[8] considered them to be important and Wheland and Pauling[9] took them into account to a limited extent in considering the polarizabilities of the aromatic molecules. Ingold[10] also emphasized the role of polarizability in orientation, and in a paper which appeared in 1941, Hughes and Ingold[11] suggested explicitly that the type II structures are of paramount importance.

Wheland[12] adopted the point of view that only the type II structures need be considered at all. In a quantum mechanical discussion of orientation in aromatic molecules based on the molecular orbital method he made calculations only for activated complexes in which a covalent bond was formed between the aromatic ring and the reagent.

It is obvious that the structure II and the pure SE2 structure I may be considered as two limiting configurations and between the two structures there is a possibility of continuous conjugation. This is essentially nothing else than the modern interpretation of the original idea of Pfeiffer and Wizinger[13] in 1928.

One of the most characteristic properties of the structure II is the fact that the hydrogen in the complex is not considerably loosened, which signifies that the isotopic mass of the hydrogen does not play a significant role in the velocity of the elimination.

The original π-complex theory proposed by Dewar is based on the formation of a dative bond between the whole of the aromatic ring (*i.e.*, the π-electron system of the ring) and the vacant orbitals of the cation reagent. This complex formation may then be considered as the velocity-determining step in electrophilic aromatic substitutions.

The original π-complex theory of Dewar makes allowance for only one kind of π-complex formation, a non-localized one, so that the attacking substituent may be statistically present at any point of the conjugated π-system. However, the directing effect of substituted aromatics during electrophilic substitution apparently can appear only when further reaction of the original π-complex takes place. Already Melander,[4] in 1950, has drawn attention to an essential theoretical contradiction of the original Dewar π-complex theory, concerning the nature of the intermediates of electrophilic aromatic substitutions. It is unlikely that an electrophilic substituent would attack the benzene ring at its center, with subsequent complex formation at this site, as symbolized by Dewar, because it is known that the π-electron density in the center of the benzene ring is quite small. It is rather more probable that the cation is bound on the π-electron cloud where the electron density is the highest. Thus we have to assume that the substituent, in the case of substituted benzenes, is most likely to be found statistically on the most electronegative positions, thus in the proximity of those carbon atoms where the ratio of substitution is the highest. With such an assumption, if we consider a primary π-complex type interaction between the cation and the aromatic ring as the first step of the substitution process, we can speak of a *localized π-complex* to a certain degree. This conception was actually introduced recently by Brown[14] during his investigation of the

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(5) (a) T. G. Bonner, F. Bowyer and G. Williams, *J. Chem. Soc.*, 2605 (1950); (b) W. M. Lauer and W. E. Noland, This Journal, **75**, 3689 (1953).

(6) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

(7) M. J. S. Dewar, *J. Chem. Soc.*, 406, 777 (1946); "Electronic Theory of Organic Compounds," Oxford University Press, London, 1949.

(8) R. Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London, 1932.

(9) G. W. Wheland and L. Pauling, This Journal, **57**, 2806 (1935).

(10) C. K. Ingold, *J. Chem. Soc.*, 1120 (1933); *Chem. Revs.*, **15**, 225 (1934).

(11) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 608 (1941).

(12) G. W. Wheland, This Journal, **64**, 900 (1942).

(13) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 136 (1928).

(14) H. C. Brown and H. Junk, This Journal, **77**, 5579 (1955); **78**, 2182 (1956); H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

isomerization of xylenes. From this modified conception of the π-complex, considered as the first step of the interaction, it is easy to reach the second step of the reaction, *i.e.*, the structure II in which now the substituent is bound with a σ-bond to one of the carbon atoms with the highest electron density.

If, however, the intermediate product shows only the character of a localized π-complex alone, then the exchanging hydrogen may exist in a loosened state during the substitution occurring in the intermediate complex and with the alteration in the mass of the isotopes a significant difference of velocity must appear, which, however, could not be observed during the previously reported investigations.[4-5b]

Brown[15] assumed the existence of two kinds of intermediate complexes on the basis of his investigations. He regarded the weaker complexes formed between aromatics (in his investigations alkylbenzenes) and hydrochloric or hydrobromic acid as Dewar's π-complexes, whereas the more stable complexes formed with the system aluminum chloride + hydrochloric acid or aluminum bromide + hydrobromic acid were considered to be onium salt or σ-complexes. Similarly Lien, McCaulay and Shoemaker[16] have suggested an onium ion structure for the intermediate complexes formed between alkylbenzenes HF + BF_3 in excess anhydrous hydrogen fluoride as solvent. A composition of these results with the rates of some electrophilic aromatic reactions showed that the values of complex formation (*i.e.*, the basicity values of the alkylbenzenes) with the system aromatic–HF + BF_3 agree with the experimentally established rates of aromatic substitution, whereas the order of basicity obtained in the series aromatic–HCl or aromatic–HBr do not agree with such rates. It follows that the rate of substitution of aromatic nuclei must be determined not by the stability of the π-complexes, as proposed by Dewar, but instead by the stability of the Brown σ-complexes.

The experimental technique used by Brown and Lien for establishing the order of basicity and the verification of the intermediate complexes rested on the determination of the solubility of hydrochloric or hydrobromic acid in aromatic hydrocarbons or BF_3 in the aromatic hydrocarbon–HF systems. This was thus essentially a method based on pressure measurement. Determinations carried out at different temperatures showed that the intermediate complex can only be formed at low temperatures.

No direct experimental evidence is available at the present time with respect to the intermediate complexes of electrophilic aromatic substitution on the basis of the original Dewar π-complex theory[17] as the rate-determining intermediates.

Little information is available in the literature about the direct chemical investigation and isolation of the intermediate complexes of the electrophilic aromatic substitutions. Norris and co-workers,[18] investigating the aluminum bromide–hydrogen bromide complexes of the alkylbenzenes, were able to isolate some crystalline complexes of mesitylene (Mes) and 1,2,5-triethylbenzene (TEB) with the brutto formulas: $3Mes{\cdot}Al_2Br_6{\cdot}HBr$; $2\ TEB{\cdot}Al_2Br_6{\cdot}HBr$; $Mes{\cdot}Al_2Br_6HBr$; $TEB{\cdot}Al_2Br{\cdot}HBr$. During investigations on the isomerization of xylenes, Baddeley, Holt and Voss[19] isolated complexes with the brutto formula of $(ArH)_x{\cdot}Al_2Br_6{\cdot}HBr$.

Discussion of Results.—In the course of our own investigations we have tried to prove the existence of the postulated intermediate complexes in the electrophilic aromatic substitution by preparative methods. Since in our previous work[20] we were able to prove the existence of some of the cation reagents of electrophilic substitution reactions by the isolation and characterization of the stable tetrafluoroborate complexes, we attempted to employ the same methods for the isolation of the intermediate complexes of the reaction occurring between a reagent cation and the aromatic nuclei.

The investigations were carried out first of all with alkyl benzenes. The methylbenzenes, such as toluene, *m*-xylene, mesitylene and isodurene, are soluble in anhydrous hydrogen fluoride to the extent of less than 1% (at −20° and lower temperatures). These results are in good agreement with Klatt's[21] earlier observations on the solubility of aromatics in anhydrous HF between +15 and −50°.

Methylbenzenes absorb only traces of boron trifluoride under anhydrous conditions.

McCauley, Shoemaker and Lien[16] observed that aromatic hydrocarbons which themselves are not soluble in hydrogen fluoride are completely miscible with the latter in the presence of boron trifluoride.

In our investigations we have found that if boron trifluoride is introduced into a two-phase heterogeneous system consisting of 1 mole of methylbenzene and 1 mole of anhydrous hydrogen fluoride (between −25 and −80°), it is absorbed vigorously (although the components separately are not able to absorb boron trifluoride). After absorbing 1 mole of boron trifluoride the system becomes completely homogeneous and brightly colored. Lien and co-workers previously have assumed that a 1:1:1 complex is formed from the aromatic hydrocarbon and HF and BF_3 at low temperature by measuring the vapor pressure of boron trifluoride. While, however, the investigations of Lien were performed with an excess of hydrogen fluoride as solvent, in our own experiments an attempt was made to isolate the intermediate complexes. This purpose was successfully attained. By treating one mole of alkylbenzene with one mole of anhydrous HF and one mole of boron trifluoride the alkylbenzene:HF:BF_3 complexes with molar ratios of 1:1:1 were isolated at low temperature. They showed a bright color (from yellow-green to

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(15) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

(16) D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950); D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951); **74**, 6246 (1952).

(17) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3580 (1952).

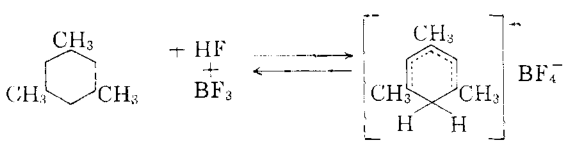
(18) J. F. Norris and N. J. Ingraham, *ibid.*, **62**, 1298 (1940); J. F. Norris and J. E. Wood, *ibid.*, **62**, 1428 (1940).

(19) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952).

(20) G. Olah, S. Kuhn and A. Mlinko, *ibid.*, 4257 (1956); G. Olah, S. Kuhn and J. Olah, *ibid.*, 2174 (1957); G. Olah and S. Kuhn, *Naturwissenschaften*, **43**, 59 (1956); G. Olah and S. Kuhn, *Chem. Ber.*, **89**, 856 (1956); G. Olah, A. Pavlath, S. Kuhn and G. Varsanyi, "Electronen Theorie der Homeopolaren Bindung," Akademie Verlag, Berlin, 1955, pp. 79–94.

(21) K. Klatt, *Z. anorg. allgem. Chem.*, **234**, 189 (1937).

orange), a fairly definite dissociation point and a very considerable specific electric conductivity. Their solubility in organic solvents is very poor. On heating, by thermal decomposition a vigorous evolution of BF_3 occurs while the homogeneous solution separates again into two phases, the lower layer containing HF and the upper layer containing the methylbenzenes



Some properties of the isolated alkylbenzene:HF:BF_3 complexes are summarized in Table I.

TABLE I

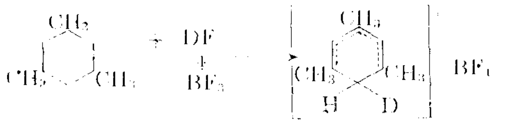
$ArH^+BF_4^-$ COMPLEXES

Ar	M.p., °C. (with some dissociation)	($\kappa\Omega^{-1}$ cm.$^{-1}$ × 10^3)	Color	Brutto formula	BF4, %, Calcd.	BF4, %, Found
$(CH_3)C_6H_5$	−65	0.8	Yell.-green	$C_7H_9BF_4$	48.3	47.5
m-$(CH_3)_2C_6H_4$	−55	2.0	Yellow	$C_8H_{11}BF_4$	41.8	43.2
sym-$(CH_3)_3C_6H_3$	−15	1.6	Yellow	$C_9H_{13}BF_4$	41.8	40.9
usym-$(CH_3)_4C_6H_2$	−10	0.6	Orange	$C_{10}H_{15}BF_4$	39.1	38.6

We formulate the complexes as stable, salt-like derivatives of the hypothetical HBF_4 complex acid, (the free HBF_4 acid under anhydrous conditions does not exist according to the investigations of McCauley and Lien; and to our own tests down to a temperature of −100°) on protonated methylbenzene tetrafluoroborates. The onium-salt (or according to Brown, σ-complex) structure is supported by the considerable value of the specific conductivities (measured at the melting point), their very poor solubility in organic solvents, their bright color and the presence of the analytically detectable BF_4^- group.

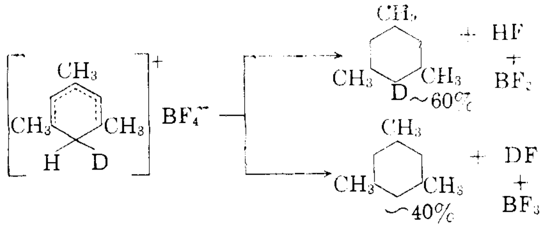
In our previous work[22] it has been proved that a pure electrophilic aromatic deuteration can be carried out in the course of a reaction with $DF + BF_3$.

The 1:1:1 molar complexes of methylbenzenes + $DF + BF_3$ were isolated in a similar way to those already described for HF. (The anhydrous DF was prepared by a method recently described.[23]) The complex formation in the case of mesitylene, for example, takes place as



The complex formation is not reversible in this case. On heating, about 60% of deuterated methylbenzenes are formed (the deuterium methylbenzenes were determined on the basis of their absorption spectra). In the case of the toluene the monodeuterium products were *para* and *ortho* deuterium toluenes.[22])

In these reactions a smaller amount of dideuterium toluenes was always formed (amount up to 10% or less). Apparently this may be due to the fact that during the fission of the intermediate complexes deuterium is also split off and the deuteron may be produced for further deuterium substitution.

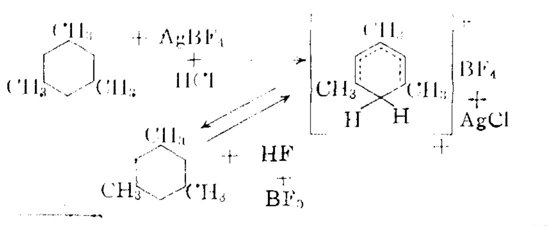


The physical properties of the deuterated methylbenzene tetrafluoroborate complexes are in general very similar to those of the protonated ones (the differences in decomposition points and specific conductivities are less than 2% and are in the order of magnitude of the error of the determination).

The preparation of the previously described protonated and deuterated alkyl tetrafluoroborate complexes involved the use of hydrofluoric acid and deuterium fluoride, respectively. In many cases, however, it is inconvenient to use hydrofluoric acid as a starting material. To overcome this difficulty, we have found silver tetrafluoroborate, previously suggested by us[24] as a new complex-forming agent, to be a very suitable reagent for preparing the intermediate tetrafluoroborate complexes from hydrogen chloride and hydrogen bromide.

Anhydrous silver tetrafluoroborate, first prepared and investigated by Sharpe[25] and now available through two other simple methods,[26,27] is significantly soluble in aromatic hydrocarbons, although the nature of the possible complex between silver tetrafluoroborate and an aromatic compound is not yet known. It seems very closely related to the earlier well known silver perchlorate complexes.[28]

To prepare the intermediate complexes with silver tetrafluoroborate, the silver salt is added to the aromatic compound and then the cold solution is allowed to react with hydrogen chloride or bromide. (It is also possible to work with only partly dissolved material by stirring the suspension of silver tetrafluoroborate in the aromatic compound.) Silver halide is split off and the corresponding protonated alkylbenzene tetrafluoroborate complexes are formed



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(22) G. Olah, A. Pavlath, S. Kuhn, J. Olah and L. Noszko, unpublished results.

(23) G. Olah and S. Kuhn, *Z. anorg. allgem. Chem.*, **287**, 282 (1956).

(24) G. Olah, A. Pavlath and S. Kuhn, *Chemistry & Industry*, 50 (1957).

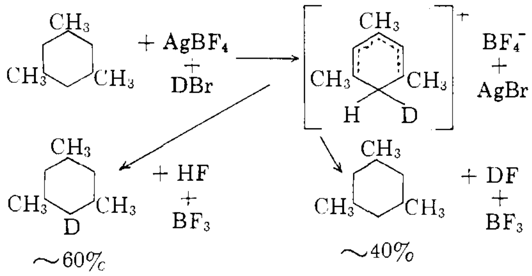
(25) A. G. Sharpe, *J. Chem. Soc.*, 4538 (1952).

(26) H. Meerwein and K. Wunderlich, *Angew. Chem.*, **69**, 481 (1957).

(27) A. F. Clifford and S. Kongpricha, *J. Inorg. Nucl. Chem.*, **5**, 76 (1957).

(28) R. E. Rundle and J. H. Goring, THIS JOURNAL, **72**, 5337 (1950).

In a similar way, performing the reaction with anhydrous DCl or DBr, it is possible to prepare the corresponding deuterated complexes.



Both chemical and spectroscopical investigation of the protonated (deuterated) aryl tetrafluoroborate complexes will be continued.

Experimental

Materials.—The alkylbenzenes were the purest available commercial products. They were fractionated in a column rated at 55 theoretical plates. Center fractions which exhibited constant boiling point and refractive index were utilized. They were stored over calcium hydride and redistilled before use. The following constants were obtained: toluene, b.p. 110°, n^{20}_D 1.4966; *m*-xylene, b.p. 139°, n^{20}_D 1.4972; mesitylene, b.p. 164°, n^{20}_D 1.4990; isodurene, b.p. (18 mm.) 85–87°, n^{20}_D 1.5130. Anhydrous hydrogen fluoride (minimum purity 99.5%) was redistilled in a silver distillation apparatus and then electrolyzed in a fluorine cell till elementary fluorine was generated to make it absolutely anhydrous. Boron trifluoride (minimum purity 99%) was redistilled from sodium in a low temperature column.

Anhydrous deuterium fluoride was prepared by a method previously described.[28] Deuterium chloride and deuterium bromide were prepared according to Brown and Groot,[29] using heavy water of 99.75% purity. Anhydrous silver tetrafluoroborate was prepared according to Sharpe.[25]

Procedure for the Preparation of $ArH^+BF^-_4$ Complexes. (A) Hydrogen Fluoride Method.—Into a stirred heterogeneous mixture of 0.5 mole of alkylbenzene (toluene, *m*-xylene, mesitylene, isodurene) and 0.5 mole of anhydrous HF, contained at -20 to $-80°$ (depending on the freezing point of the hydrocarbon), 0.5 mole dry BF$_3$ was introduced under conditions precluding the entrance of atmospheric moisture. The apparatus was made of silica, Teflon and polyethylene. The amount of BF$_3$ introduced was measured by weight increase; BF$_3$ was absorbed and the solution became homogeneous and brightly colored. (Excess of volatile material was pumped off at Dry Ice temperature and introduction of BF$_3$ was discontinued after no more weight increase was observed after twice pumping the system.) Freezing and decomposition points of the resulting homogeneous complexes were determined with a calibrated Pt thermocouple. Electric conductivities were measured in a silica conductivity cell with platinized platinum electrodes, with a vigorous exclusion of moisture by transferring the complexes in a sealed system in a dry inert gas atmosphere. The conductivity was measured in a Wheatstone bridge. As source of current an audiofrequency generator was used and measurements were taken at 2 v. and a frequency of 1000–1200. For sharpening the maximum a condenser with a variable capacity from 1 to 10,000 F. was coupled in parallel with the decade resistances of the bridge. As a zero device a cathode ray-oscilloscope in conjunction with an amplifier was used. The maximum error of the determination was 0.5%.

The tetrafluoroborate determinations were carried out according to the method of Lange[30] in the form of the nitron tetrafluoroborate $C_{20}H_{16}HBF_4$.

By sealing off the purified complexes in alkaline-free glass ampoules under dry nitrogen, they could be stored without decomposition for a few weeks in a refrigerator.

(B) **Silver Tetrafluoroborate Method.**—Two-tenths mole of anhydrous silver tetrafluoroborate was added to an excess of alkylbenzene (toluene, *m*-xylene, mesitylene, isodurene) with efficient stirring. The stirred mixture was then cooled (-20 to $-80°$) and saturated with anhydrous pure HCl or HBr. The amount of hydrogen halide taken up was equivalent to the quantity of silver tetrafluoroborate present in the system. Silver halide was precipitated and a colored complex layer formed. The complex layer was separated after removing the silver halide. It was found to be identical with the protonated alkylbenzene tetrafluoroborate complexes prepared previously from alkylbenzenes with HF/BF$_3$. Thermal decomposition regenerated the corresponding hydrocarbon with equimolar quantities of HF and BF$_3$.

Procedure for the Preparation of $ArD^+BF_4^-$ Complexes. (A) Deuterium Fluoride Method.—Into a stirred mixture of 0.5 mole of alkylbenzene (toluene, *m*-xylene, mesitylene and isodurene) and 0.5 mole of anhydrous deuterium fluoride, at -20 to $-80°$, dry boron trifluoride was introduced, with exclusion of atmospheric moisture, till the saturation point was reached (0.5 mole, measured by weight increase). Boron trifluoride was absorbed whilst the heterogeneous system became homogeneous and brightly colored. (Excess of volatile materials was pumped off in vacuum at Dry Ice temperature.) Freezing and decomposition points, electric conductivities and the BF$_4$ content were determined by similar methods to those used for the $ArH^+BF_4^-$ complexes.

(B) **Silver Tetrafluoroborate Method.**—Two-tenths mole of anhydrous silver tetrafluoroborate was added to an excess of alkylbenzene (toluene, *m*-xylene, mesitylene and isodurene) with efficient stirring. The stirred mixture was then cooled (-20 to $-80°$) and saturated with anhydrous deuterium chloride or deuterium bromide. The amount of deuterium halide taken up was equivalent to the amount of silver tetrafluoroborate present in the system. Silver halide was precipitated and a colored complex layer formed. The complex layer was separated after removing the silver halide. It was found to be identical with the deuterated alkylbenzene tetrafluoroborate complexes prepared previously from alkylbenzenes with DF + BF$_3$. On heating, about 60% of ring deuterated alkylbenzenes together with about 40% of the starting hydrocarbons were formed and equimolar quantities of HF and DF and BF$_3$ evolved.

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