infrared spectrum and appearance of the crude salt constituted further likenesses.

Authentic Materials.—Dicyclohexyl carbonate (mp 43°, lit.[50] mp 42–42°) and diisopropyl carbonate ($n^{23}\text{D}$ 1.3999, lit.[51] $n^{15}\text{D}$ 1.3967) were prepared according to a literature procedure.[52] The aryl isopropyl carbonates[7] and tolyl cyclohexyl carbonates[49] are described elsewhere. The remaining products are commercially available.

Competitive Oxygenation.—The general procedure was followed with certain adaptations: duplicate experiments were performed with at least two different concentrations of the aromatic components in the cupric chloride[5] and ferric chloride cases. In all duplicate runs excellent reproducibility was observed.

Analytical Procedures. A. Gas Chromatography.—The instruments and glpc columns are described elsewhere.[4]

B. For Peroxides.—An iodometric method was taken from the literature.[53]

C. For Product Yields.—Glpc analysis as described elsewhere[4] was used to calculate product yields. Carbon dioxide was determined by known procedures (ref 4, method B for neat systems and method A for reactions in acetonitrile).

D. Isomer Distributions.—The majority of the aryl isopropyl carbonate isomer compositions were determined directly by glpc,[4] although in some cases a combination glpc–infrared technique[4] was used.

Registry No.—$CuCl_2$, 7447-39-4; $CuBr_2$, 7789-45-9; $Cu(SCN)_2$, 15192-76-4; $Cu(ClO_4)_2$, 13770-18-8; $Cu(BF_4)_2$, 14735-84-3; CuCl, 7758-89-6; CuBr, 7787-70-4; $FeCl_3$, 7705-08-0; $FeCl_2$, 7758-94-3; $SbCl_5$, 7647-18-9; $(C_6H_{11}OCO_2)_2$, 1561-49-5; $(i\text{-}PrOCO_2)_2$, 105-64-6; $RuCl_3$, 10049-08-8; Na_2IrCl_6, 12016-14-7; O_sCl_4, 10026-01-4; $MoCl_5$, 10241-05-1; $HgCl_2$, 7487-94-7; $AuCl_3$, 13453-07-1; O_2, 7782-44-7; I_2, 7553-56-2; Br_2, 7726-95-6; Cl_2, 7782-50-5; $Co(OCS_2Et)_3$, 15215-68-6; toluene, 108-88-3.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work. Our thanks are extended to Dr. T. A. Stephenson for informative discussions.

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[50] R. L. Frank, H. R. Davis, Jr., S. S. Drake, and J. B. McPherson, Jr., *J. Am. Chem. Soc.*, **66**, 1509 (1944).

[51] P. N. Kogerman and J. Kranig, *Acta et Commentationes Univ. Tartuensis*, 3 (1927); *Chem. Abstr.*, **21**, 1729 (1927).

[52] D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).

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Boron Fluoride Catalyzed Alkylation. III.[1] Ethylation with Ethyl Fluoride at Low Temperatures

RYOHEI NAKANE, TOSHIYUKI ŌYAMA, AND AKIKO NATSUBORI

The Institute of Physical and Chemical Research, Bunkyo-ku, Tokyo, Japan

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Additional evidence is obtained for the formation of a termolecular oriented π complex at low temperatures by measurements of infrared spectra of the isotopic toluene–ethyl fluoride–boron fluoride complexes. Ethylation proceeds at −45 to −95° on the removal of boron fluoride from the complexes. It is suggested that for boron fluoride-catalyzed alkylation with primary alkyl halides at low temperatures a transformation from the termolecular oriented π complex into a benzenonium ion complex is involved in the rate-determining step. The intermediate benzenonium ion complex is not isolated at low temperatures.

An SN2-type displacement mechanism was proposed by Brown and coworkers[2] for Friedel–Crafts alkylation with primary alkyl halides. Olah and coworkers[3] reported the isolation of an intermediate ethyl benzenonium tetrafluoroborate complex, when ethyl fluoride dissolved in toluene was saturated with boron fluoride at −80°. The complex yielded ethyltoluene when warmed above −80°. We concluded, however, from the absorption spectrum and thermodynamic isotope effect[4] that a termolecular oriented π complex is formed when the reactants are solidified in the order of toluene, ethyl fluoride, and boron fluoride at liquid nitrogen temperature and are then allowed to warm to about −100°. If both conclusions are correct, the nature of the complexes should very much depend on the way they are prepared. To ascertain this, the low temperature infrared spectra have been taken of the isotopic toluene–ethyl fluoride–boron fluoride complexes prepared under two different conditions. The infrared spectra of the isotopic methyl fluoride–boron fluoride complexes are known,[5] but those of the isotopic ethyl fluoride–boron fluoride complexes have not yet been reported.

According to our former work a termolecular π complex is formed from toluene, *t*-butyl chloride, and boron fluoride in a mole ratio of 1 : 1 : 1 at low temperatures. When boron fluoride was withdrawn from the complex, the *t*-butylation proceeded at −95°.[1] This work has now been extended to the ethylation by decomposing the termolecular π complex at low temperatures.

Results

Infrared Spectrum of Ethyl Fluoride–Boron Fluoride Complex.—The infrared spectra of the liquid isotopic ethyl fluoride–boron fluoride complexes were observed in the region from 400 to 4000 cm^{-1} at −105°. They are listed in Table I. The infrared spectrum of liquid C_2H_5F was also observed at −105° and is listed in Table I. It agreed well with the spectrum observed at −45°.[6] The change in the frequencies with complex formation was observed, not in the C–F stretch, but slightly in the C–H stretches. An effect of isotopic substitution of boron was observed in the regions from 1400 to 1500 cm^{-1} and from 600 to 650 cm^{-1}, as observed on the methyl fluoride–boron fluoride complexes.[5] Thus, the 1470 and 1420-cm^{-1} frequencies can be assigned to B–F antisymmetric stretches in the $C_2H_5F\text{–}B^{10}F_3$ and $C_2H_5F\text{–}B^{11}F_3$ complexes. The 631 and 610-cm^{-1} frequencies can be assigned to

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[1] Part II: R. Nakane and A. Natsubori, *J. Am. Chem. Soc.*, **88**, 3011 (1966).

[2] H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson, and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

[3] G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6541 (1958).

[4] R. Nakane, A. Natsubori, and O. Kurihara, *ibid.*, **87**, 3597 (1965).

[5] R. Nakane and T. Ōyama, *J. Phys. Chem.*, **70**, 1146 (1966).

[6] D. C. Smith, R. A. Saunders, J. Rud Nielsen, and E. E. Ferguson, *J. Chem. Phys.*, **20**, 847 (1952).

Table I

Vibrational Frequencies of Isotopic Ethyl Fluoride–Boron Fluoride Complexes, Isotopic Toluene–Ethyl Fluoride–Boron Fluoride Complexes, Liquid Ethyl Fluoride, and Toluene[a]

C_2H_5F–BF_3[b]	$C_6H_5CH_3$–C_2H_5F–BF_3[c, d]	C_2H_5F[b]	$C_6H_5CH_3$[e]	Assignment
426 s	425 s	425 s	475 vs	C–C–F skeletal deform
	475 vs		475 vs	C–C deform
487 (B^{11}) vs	~490 (B^{11}) vs		/	BF_3 in-plane bend
~490 (B^{10}) vs	~490 (B^{10}) vs			BF_3 out-of-plane bend
610 (B^{11}) vs	612 (B^{11}) vs			
631 (B^{10}) vs	~635 (B^{10}) vs			
	700 s		701 vs	C–C stretch
	740 vs		736 vs	CH out-of-plane bend
863 vs	875 s	875 vs		C–C stretch
1027 vs	1025 vs	1037 vs		CH_3 rock
	1090 w		1087 s	CH deform
1107 s	1105 s	1105 s		CH_3 rock
1172 s	1170 s	1172 s		C–F stretch
1347 s	1345 m			Combination band ($\nu_1 + \nu_4$ of BF_3)
1371 w	sh	1371 w		CH_2 wag
1394 s	sh	1396 s		CH_2 deform
~1420 (B^{11}) vs	~1420 (B^{11}) vs			B–F stretch (antisym)
~1470 (B^{10}) vs	~1470 (B^{10}) vs			
	sh		1498 vs	C–C stretch
sh	sh	1447 s		CH_3 deform
sh	sh	1488 m		CH_2 scissor
	1605 s		1606 vs	C–C stretch
2927 s	sh	2916 s		C–H stretch
	2920 s		2917 s	C–H stretch
	sh		2948 w	C–H stretch
2999 vs	2985 vs	2990 vs		C–H stretch
	sh		3021 vs	C–H stretch

[a] Given in units of reciprocal centimeters. Abbreviations are w, weak; m, medium; s, strong; vs, very strong; sh, shoulder. [b] Observed at −105°. [c] Observed at −68°. [d] Obtained by our method. [e] Observed at −90°.

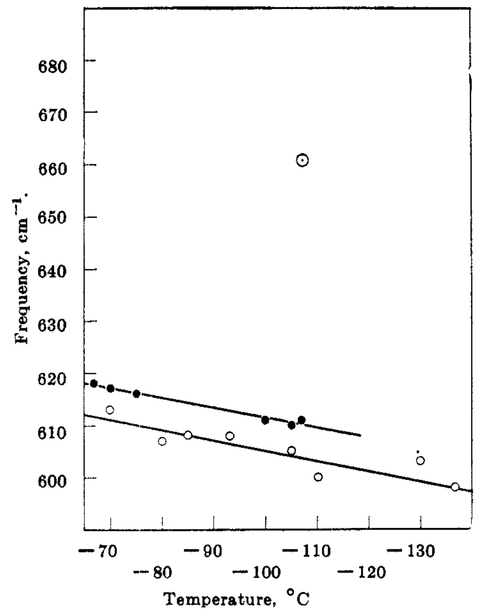

Figure 1.—Temperature dependence of BF_3 out-of-plane bending frequencies in C_2H_5F–$B^{11}F_3$ complex and $C_6H_5CH_3$–C_2H_5F–$B^{11}F_3$ complex (obtained by our method): ●, C_2H_5F–$B^{11}F_3$ complex; ○, $C_6H_5CH_3$–C_2H_5F–$B^{11}F_3$ complex; ⊙, $B^{11}F_3$ (liquid).

BF_3 out-of-plane bending bands in the isotopic complexes. The BF_3 out-of-plane bending frequency in the C_2H_5F–$B^{11}F_3$ complex was slightly lower than that in the CH_3F–$B^{11}F_3$ complex, as expected from the values of thermodynamic isotope effect.[4,5] There was no boron isotope effect on the C–H and C–F force constants in the complexes. Thus the ethyl fluoride–boron fluoride complexes, as well as the methyl fluoride–boron fluoride complexes, are the nonionized complexes, in which boron fluoride retains a planar structure.

Infrared Spectrum of Toluene–Ethyl Fluoride–Boron Fluoride Complex.—Infrared spectra of the liquid isotopic 1 : 1 : 1 complexes, formed when toluene, ethyl fluoride, and isotopic boron fluorides were solidified (in that order) in a cell cooled with liquid nitrogen and then allowed to warm, were observed at −68°. They are listed in Table I. The infrared spectrum of toluene was also observed at −90° and is listed in Table I. It agreed fairly well with published data.[7] No change in the frequencies with complex formation was observed in toluene. The C–H stretching frequency of C_2H_5F in the $C_6H_5CH_3$–C_2H_5F–$B^{11}F_3$ complex was similar to that in the nonionized C_2H_5F–$B^{11}F_3$ complex and C–F stretching bands were still observed. The boron isotope effect on the vibrational frequencies of the $C_6H_5CH_3$–C_2H_5F–BF_3 complexes closely resembled the effect on frequencies of nonionized C_2H_5F–BF_3 complexes. This was observed in the regions from 1400 to 1500 cm^{-1} and from 600 to 650 cm^{-1}, but not near 1000 cm^{-1}. The 1470 to 1420 cm^{-1} frequencies can be assigned to the B–F antisymmetric stretches in the B^{10} and B^{11} complexes. The 635- and 612-cm^{-1} frequencies can be assigned to the BF_3 out-of-plane bending bands in the B^{10} and B^{11} complexes. The shift of the BF_3 out-of-plane bending frequency with increasing temperature was followed in a solution of toluene, ethyl fluoride, and boron fluoride in a mole ratio of 1 : 1 : 0.01 in which a small amount of the $C_6H_5CH_3$–C_2H_5F–$B^{11}F_3$ complex was dissolved. The temperature dependence of the frequency is shown in

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(7) N. Fuson, C. Garrigou-Lagrange, and M. L. Josien, *Spectrochim. Acta*, **16**, 106 (1960).

TABLE II

ETHYLATION CAUSED BY WITHDRAWAL OF BORON FLUORIDE FROM TOLUENE–ETHYL FLUORIDE–BORON FLUORIDE COMPLEX AT LOW TEMPERATURES

		Reactants, %			Products, %		
Temp, °C	Time kept in cold bath, hr	Toluene	Ethyl fluoride	Boron fluoride	Toluene	Monoethyltoluene	Polyethyltoluene
−45	2[a]	33	33.5	33.5	47	28	25
−80	0[b]	33	33.5	33.5	51	26	23
−80	2[a]	33	33.5	33.5	53	24	23
−80	20[a]	33	33.5	33.5	52	25	23
−80	70[a]	33	33.5	33.5	52	24	24
−95	2[a]	5	47.5	47.5	0	25	75

[a] By evacuation of volatile material. [b] By addition of ammonia without evacuation of volatile material.

Figure 1. At −68°, the frequency in the solution was equal to the frequency in the liquid 1 : 1 : 1 complex, but was lower than the frequency in the C_2H_5F–$B^{11}F_3$ complex, as might be expected from the thermodynamic isotope effect.[4] The frequencies in the complexes became lower as the temperature decreased.

Similarly, the infrared spectrum of the $C_6H_5CH_3$–C_2H_5F–$B^{11}F_3$ complex obtained by adding boron fluoride gas to the equimolar solution of toluene and ethyl fluoride at −80° was measured at −68°. The spectrum was observed with difficulty, because of immediate corrosion of the cell window. However, under our conditions, the cell window was less clouded during measurements of the complexes. The observed spectrum is similar to the infrared spectrum of the $C_6H_5CH_3$–C_2H_5F–$B^{11}F_3$ complex obtained by our method. The B–F antisymmetric band was observed from 1400 to 1500 cm^{-1}, but weakly near 1000 cm^{-1}.

Ethylation by Decomposition of Toluene–Ethyl Fluoride–Boron Fluoride Complex.—The vapor pressure of toluene–ethyl fluoride–boron fluoride complex prepared by our method is 30 mm at −80°. A volatile material had been withdrawn from the liquid complex kept in a Dry Ice bath under vacuum, till no more was obtained. The remaining yellow liquid separated into two phases:[8] an upper, light yellow phase and a lower, deep yellow or orange phase. Ammonia was then added to the heterogeneous solution in order to quench any remaining boron fluoride. A white solid deposited. The liquid, which became homogeneous and colorless, was allowed to warm to room temperature and was then analyzed by gas–liquid partition chromatography. About 50% of the toluene was found to be ethylated. The volatile material was analyzed by a mass spectrometer; boron fluoride and a small amount of ethyl fluoride were detected together with silicon fluoride, which had formed mainly by reaction of hydrogen fluoride with the glass at room temperature. When a gas obtained by evaporation of the nonionized ethyl fluoride–boron fluoride complex at −80° was analyzed, silicon fluoride was not detected, because the nonionized complex dissociates reversibly into only ethyl fluoride and boron fluoride in gaseous phase at −80°.

If the termolecular complex was kept for several hours in the cold bath, ethylation did not increase appreciably.

When boron fluoride and ethyl fluoride were added to the heterogeneous solution before ammonia quenching, the upper phase decreased in volume and eventually disappeared.

If solid ammonia was immediately added to the termolecular complex without evacuation of volatile material at −80°, ethylation proceeded and yields of the ethylates were nearly equal to those obtained when the volatile material was removed.

When the volatile material was withdrawn at −45°, the yellow liquid still separated into the two phases. As the amount of the withdrawn volatile material became larger, the volume of the lower, deep yellow or orange phase decreased. Finally the lower phase disappeared and the remaining light yellow colored liquid became colorless. Ammonia was added to this colorless liquid, but no white solid deposited. If boron fluoride and hydrogen fluoride were completely withdrawn from the solution by evacuation at −45°, yields of the ethylates increased. The melting point of the complex is −80°.[3] When the volatile material was withdrawn from the termolecular complex dissolved in the nonionized ethyl fluoride–boron fluoride complex at −95°, complete ethylation occurred. Results are summarized in Table II.

An *ortho* isomer yield of monoethyltoluenes was *ca.* 30% at −45° and *ca.* 35% at −80°. The *ortho* isomer was not found when complete ethylation occurred. The *meta* and *para* isomers could not be separated sufficiently with gas–liquid partition chromatography. However, we will not discuss the isomer distribution here, since the di- and higher ethylates, which composed more than 80% of those of the monoethyltoluenes, were obtained in all cases.

If the volatile material was removed from the complex obtained by Olah's method, ethylation proceeded similarly at low temperatures.

Olah and coworkers[3] concluded that the intermediate ethyl benzenonium ion complex is isolated at low temperatures and the ethylation proceeds when the complex is allowed to warm above its decomposition point, but it appears that the ethylation proceeds even at temperatures low enough to isolate the stable complex, if boron fluoride is distilled under vacuum from the termolecular complex or if ammonia is added.

Discussion

Perkampus and Baumgarten[9] found that the infrared spectra of methylbenzene–$AlBr_3$, –$GaCl_3$, and –$GaBr_3$ complexes and of the protonated complexes are

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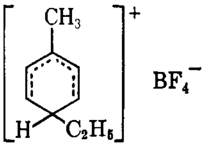
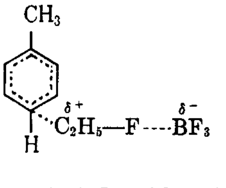
[8] In all cases when 1 mole of toluene, 0.7 to 1 mole of ethyl fluoride, and 0.05 to 0.3 mole of boron fluoride were solidified at liquid nitrogen temperature and allowed to warm gradually to Dry Ice temperature, a homogeneous solution formed.

[9] H. H. Perkampus and E. Baumgarten, *Z. Phys. Chem. (Frankfurt)*, **40**, 144 (1964); H. H. Perkampus and E. Baumgarten, *Ber. Bunsenges. Physik Chem.*, **68**, 70 (1964).

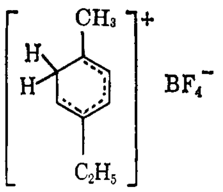
quite different from those of methylbenzenes. They explained the changes of the infrared spectra by assuming that benzenonium ions are formed. The B–F antisymmetric stretching frequencies in $NaB^{10}F_4$ and $NaB^{11}F_4$ were observed at 1016 and 984 cm^{-1}.[10] The B–F antisymmetric stretching frequencies in $CH_3COB^{11}F_4$[11] and $NO_2B^{11}F_4$[12] were observed at 1052 and 1035 cm^{-1}. If the toluene–ethyl fluoride–boron fluoride complex is an intermediate ethyl benzenonium tetrafluoroborate complex such as



the observed infrared spectra of the complex should be quite different from that of free toluene, the C–F stretching band should not be observed, and the effect of isotopic substitution of boron should be observed near 1000 cm^{-1}, but they are not. Hence, in the solution obtained by our method the complex containing both benzenonium and tetrafluoroborate ions is absent. However, some toluene complex must be formed when toluene is dissolved in the nonionized ethyl fluoride–boron fluoride complex, because the ultraviolet spectrum of the solution[4] closely resembles spectra of the protonated benzenonium ion complexes,[13] and does not resemble toluene. In this complex, toluene retains its original structure; the C–F bond is not broken; the ethyl and tetrafluoroborate ions are absent; boron fluoride retains its planar structure, and the BF_3 out-of-plane bending frequency is lower than that in the nonionized complex. Thus, from the infrared spectra of the isotopic complexes and from the previous results[4] we can assume that the complex is not the ethyl benzenonium tetrafluoroborate complex but an oriented termolecular π complex such as



The ionization of ethyl fluoride with boron fluoride at low temperatures is negligible. Under our conditions the nonionized ethyl fluoride–boron fluoride complex is formed first and then begins to gradually dissolve solid toluene at its melting point (−105°),[14] forming the yellow termolecular π complex. The termolecular π complex appears to be stable at a constant low temperature, since ethylation does not increase with time at −80°. Withdrawal of boron fluoride from the complex allows formation of toluene and the ethylates. When boron fluoride remains in the solution, hydrogen fluoride and the ethylates can form such protonated benzenonium tetrafluoroborate complexes[15] as



The protonated complexes may be involved in the observed lower, deep yellow or orange phase. These protonated complexes are not appreciably soluble in alkylbenzenes.[15] The upper phase may be composed mainly of alkylbenzenes.[16] As the amount of boron fluoride dissolved in the solution decreases, the protonated complexes dissociate reversibly into hydrogen fluoride and alkylbenzenes, resulting in volume decrease of the lower phase. When boron fluoride and ethyl fluoride are added to the heterogeneous solution, they form the termolecular π complexes with free alkybenzenes. Thus, the protonated complexes dissolve in the termolecular π complexes, resulting in reformation of the homogeneous solution.

When boron fluoride is withdrawn from the termolecular π complex dissolved in excess nonionized ethyl fluoride–boron fluoride complex, both the irreversible decomposition and the reversible dissociation of the termolecular π complex occur, together with the reversible dissociation of the nonionized complex. As long as the nonionized complex remains in the solution, the termolecular π complex is reformed from dissociated toluene and the nonionized complex and then the irreversible decomposition proceeds further. Hence the yields of ethylates increase.

Olah and coworkers reported[3] that "Alkyl fluoride (0.5 mole) was dissolved in 0.5 mole of alkylbenzene. The solution was cooled in a Dry Ice bath and 0.5 mole of boron fluoride was introduced. Boron fluoride was absorbed and the solution became brightly colored. Excess volatile material was pumped off at Dry Ice temperature and introduction of boron fluoride was discontinued after no more weight increase was observed after twice pumping the system." They concluded that in this way the ethyl benzenonium tetrafluoroborate complex is obtained which is a stable reaction intermediate capable of being isolated under such specific conditions as low temperatures and not necessarily reached in the course of usual Friedel–Crafts alkylations (by some sort of "tunneling").[17] However, the infrared spectrum of the yellow solution which is prepared by introduction of boron fluoride gas without pumping, is similar to that of the termolecular π complex obtained by our method. Boron fluoride gas is readily soluble in the equimolar solution of toluene and ethyl fluoride at −80°. When more boron fluoride is added, the temperature in some areas of the solutions may become substantially higher, facilitating evaporation of a small part of dissolved boron fluoride and then formation of small amounts of

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(10) J. Goubeau and W. Bues, *Z. Anorg. Allgem. Chem.*, **268**, 211 (1952).

(11) B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **40**, 722 (1957).

(12) D. Cook, S. J. Kuhn, and G.A. Olah, *J. Chem. Phys.*, **33**, 1669 (1960).

(13) G. Dallinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

(14) G. Olah, S. Kuhn, and J. Olah, *J. Chem. Soc.*, 2174 (1957).

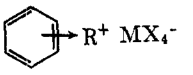
(15) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6535 (1958).

(16) The termolecular π complex appears to be very soluble in alkylbenzenes, because the homogeneous, light yellow solution is obtained when ethyl fluoride and boron fluoride are dissolved in excess toluene at low temperatures, as shown in ref 8. Hence in the light yellow upper phase the termolecular π complex may coexist with alkylbenzenes.

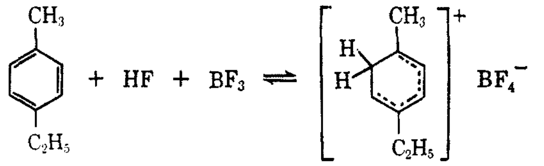
(17) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).

ethylates and hydrogen fluoride.[8,18] Moreover, it is evident that the ethylates and hydrogen fluoride are formed at Dry Ice temperature by removing excess volatile material. Hence the yellow solution obtained by Olah's method seems to be composed, not of an intermediate ethyl benzenonium tetrafluoroborate complex such as $ArHR^+BF_4^-$, but of a termolecular π complex which dissolves protonated complexes such as $Ar'H_2^+BF_4^-$. The specific conductivity of the termolecular π complex is lower than those of the protonated complexes. This is due to the coexistence of the protonated complexes which results in an increase in conductivity. However, this is not sufficient proof that the intermediate ethyl benzenonium ion complex has been isolated. The ultraviolet spectrum of the termolecular π complex[4] closely resembles those of the protonated complexes.[13] But this coloring of the solution is also not sufficient proof that the intermediate ethyl benzenonium ion complex has been isolated.

Brown and coworkers[2] suggested that Friedel-Crafts alkylation with primary alkyl halides can be described in terms of a nucleophilic attack by the aromatic on the nonionized complex. They[19] assumed that first a transfer of the alkyl group from the nonionized complex may occur to form a high energy oriented π complex such as

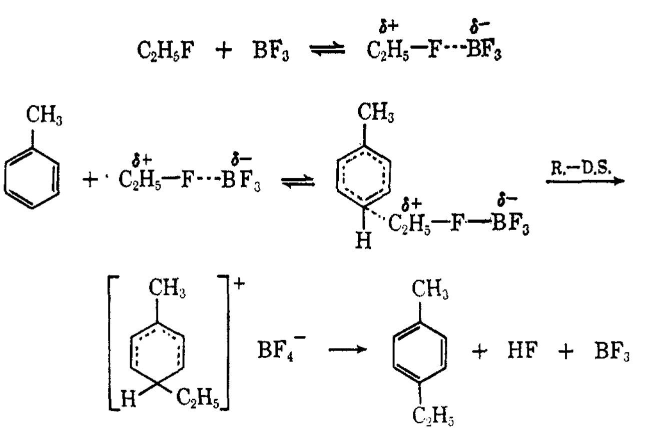


which then isomerizes to the more stable benzenonium ion complex. Olah and coworkers[14,20] suggested that the rate-determining step is not formation of the benzenonium ion complex but the formation of the π complex shown above. However, we found that the termolecular oriented π complex can be isolated when toluene is dissolved in the nonionized ethyl fluoride-boron fluoride complex, and that the ethylation proceeds by decomposition of the termolecular π complex at low temperatures. Therefore, as suggested previously[4] it seems unnecessary to assume that another π complex forms in the decomposition process. The termolecular oriented π complex may transform directly into the intermediate ethyl benzenonium ion complex, the formation of which is the rate-determining step. Thus, the boron fluoride-catalyzed alkylation with primary alkyl halides at low temperatures seems to proceed as illustrated in Scheme I. Hydrogen fluoride produced by the reaction and remaining boron fluoride form the protonated complexes with the ethylates (see eq 1). The yellow complex, which is isolated at low temperatures, is not the intermediate ethyl benzenonium ion complex, but the termolecular oriented π complex or the protonated benzenonium ion complex.



(1)

Scheme I



Experimental Section

Materials.—Toluene, ethyl fluoride, enriched $B^{10}F_3$ (95 at. % B^{10}) and normal boron fluoride, which was used in place of enriched $B^{11}F_3$, were prepared and purified by previously published methods.[4,5]

Measurement of Infrared Spectra.—The infrared spectra of the toluene-ethyl fluoride-boron fluoride complex, etc., were measured with a Perkin-Elmer Model 521 grating infrared spectrometer. A cell made specifically for measurements of infrared spectra of the isotopic methyl fluoride-boron fluoride complexes at low temperatures[5] was used. The experimental precedures were usually those used in previous work. In the observations of infrared spectra of the isotopic toluene-ethyl fluoride-boron fluoride complex obtained by our method, toluene, ethyl fluoride, and boron fluoride (in that order) were introduced into the cell, which was cooled with liquid nitrogen, and were solidified between two cell windows. The cell was then allowed to warm in melting trichloroethylene (−87°) which was also used as a coolant during observations. A thermocouple attached near the cell window indicated −68 ± 1°. The solid specimen in the cell melted and the yellow solution was formed. The cell window was directly placed in the radiation path of the infrared spectrometer. During the observations liquid nitrogen was continuously added to the coolant, and the temperature of the cell was kept constant. After the addition of liquid nitrogen was stopped and the solid had melted completely, the temperature of the cell was gradually raised. Even when no solid existed in the coolant, the temperature of the cell could be kept at any constant value by controlling the addition of liquid nitrogen to the liquid coolant. With liquid isopentane as the coolant, the BF_3 out-of-plane bending frequency in a solution composed of toluene, ethyl fluoride, and boron fluoride in a mole ratio of 1:1:0.01 was measured in the region from −65 to −140° using the above method for temperature control.

Similar procedures were used to observe infrared spectra of the isotopic ethyl fluoride-boron fluoride complexes, liquid ethyl fluoride, and toluene using melting *n*-pentane (−130°) and carbon disulfide (−112°) as coolants. The thermocouple indicated −105 and −90 ± 1°.

The infrared spectrum of the toluene-ethyl fluoride-boron fluoride complex obtained under Olah's preparative conditions was obtained by the following procedure. Boron fluoride gas was introduced into the equimolar solution of toluene and ethyl fluoride, which was contained in another vessel at Dry Ice temperature. The vessel was connected to the cell by a thermally insulated valve and pipe. The cell was cooled with melting trichloroethylene. After the liquid yellow solution was formed in the vessel, the valve was opened and the solution introduced into the cell through the pipe. The spectrum was then observed. The KRS-5 plate windows were corroded during the measurement.

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[18] Initially boron fluoride gas gave a homogeneous solution with equimolar toluene-ethyl fluoride at −80°, but after a while vapor pressure suddenly increased and the solution separated into two phases.[3] When excess toluene was added to the liquid ethyl fluoride-boron fluoride complex at −80°, the vapor pressure immediately increased and a heterogeneous solution which resembled that obtained by evaporating volatile material from the 1:1:1 complex, was formed.

[19] H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **78**, 2182 (1956).

[20] G. A. Olah, in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 926.

Ethylation at Low Temperatures.—The apparatus used for ethylation was similar to that used for *t*-butylation.[1] A glass flask was charged with 0.022 mole of toluene and the toluene frozen with liquid nitrogen. The glass flask was then evacuated and 0.022 or 0.21 mole of ethyl fluoride and 0.022 or 0.21 mole of boron fluoride condensed onto the frozen toluene. The flask was then immersed in a Dry Ice bath or a low temperature bath at the melting point of chlorobenzene (−45°) or toluene (−95°). The vapor pressure was measured by a manometer. The yellow solution formed in the flask. After the solution had been kept for several hours in the cold bath, a valve which connected the flask to an evacuated glass vessel cooled with liquid nitrogen was opened. Any volatile material was thus withdrawn and condensed in the vessel. This procedure was continued for about 2 hr and the valve then closed. The withdrawn volatile material in the vessel was allowed to warm and was then transferred to another glass gas reservoir. A small amount of colorless liquid which had a high vapor pressure, remained in the vessel at room temperature. The liquid, which might be hydrogen fluoride, was completely evaporated. The gas was introduced into the gas reservoir and a white deposit was found in the vessel which had corroded. The gas introduced into the reservoir was analyzed with a 15-cm, 60°-sector-type mass spectrometer made in our laboratory. The boron fluoride and ethyl fluoride peaks were observed at *m/e* 68, 67, 49, 48, 30, 29, etc. and at *m/e* 47, 46, 45, 33, 28, 27, 26, etc. Silicon fluoride peaks were observed at *m/e* 85, 66, 47, 28, etc. For comparison, commercial hydrogen fluoride was evaporated in the above glass vessel at room temperature and the resulting gas was analyzed. Peaks were observed at *m/e* 85, 66, 47, 28, etc. Analysis of the gas withdrawn from the 1:1:1 complex at −45 or −80° gave a spectrum in which the peak intensities for ethyl fluoride were much lower than those for boron fluoride and silicon fluoride.

The gas obtained by evaporation of the nonionized ethyl fluoride–boron fluoride complex at −80° was analyzed. The intensities of the peaks due to boron fluoride and ethyl fluoride were high, but no peaks due to silicon fluoride were detected at *m/e* = 85, etc.

Ammonia was added to the liquid and the mixture allowed to warm to room temperature. The flask was slightly corroded. The liquid was separated from the white solid and directly analyzed with a Hitachi Perkin-Elmer Programmed Temperature Gas Chromatograph Model F 6 D using a Golay column HB-2000 (length, 45 m; i.d., 0.5 mm) coated with polypropylene glycol (UCON oil 50-HB-2000 Poly) and a hydrogen flame ionization detector. The column temperature was 120° with a dry nitrogen gas flow rate of approximately 4.5 cc/min. The accuracy of measurements of *ortho*, *meta*, and *para* isomers in monoethyltoluenes was checked by analyses of standard samples of isomers obtained from Tokyo Kagaku Sieki Co. The *meta* and *para* isomers were not separated sufficiently well on the above capillary column, although it was possible to separate the *ortho* isomer from the combined *meta* and *para* isomers.

Registry No.—Boron fluoride, 7637-07-2; ethyl fluoride, 353-36-6; $C_2H_5F\text{–}BF_3$ complex, 373-60-4; $C_6H_5CH_3\text{–}C_2H_5F\text{–}BF_3$, 4601-90-5; $C_6H_5CH_3$, 108-88-3.

The Preparation and Reactions of Lithium Derivatives of Trifluoropropene and Trifluoropropyne

F. G. DRAKESMITH, O. J. STEWART, AND PAUL TARRANT

Department of Chemistry of the University of Florida, Gainesville, Florida

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3,3,3-Trifluoroisopropenyllithium has been prepared by exchange metallation between 3,3,3-trifluoroisopropenyl bromide and an alkyllithium reagent. The unsaturated fluoroorganic lithium compound is unstable even below −90° decomposing by elimination of lithium fluoride to produce 1,1-difluoroallene. Reaction of butyllithium with 1,1,1-trifluoropropyne has given 3,3,3-trifluoropropynyllithium which is stable up to 0°. Good yields of unsaturated alcohols have been obtained on reaction of each of the above lithium compounds with carbonyl compounds. Some of the alcohols have been dehydrated to give high yields of fluorine-containing substituted butadienes, which may give useful polymeric products. Reactions with triethylchlorosilane and the synthetic limitations of the lithium reagents are also discussed.

Many fluoroorganic lithium and Grignard reagents have been prepared by exchange metallation between alkyllithium and Grignard reagents and fluoroorganic compounds containing bromine,[1] iodine,[2] or "acidic" hydrogen[3,4] atoms.

Here we report the preparation of 3,3,3-trifluoroisopropenyllithium and 3,3,3-trifluoropropynyllithium.

The former reagent was prepared by reaction of trifluoroisopropenyl bromide with butyllithium (eq 1).

$$CF_3CBr{=}CH_2 + C_4H_9Li \longrightarrow CF_3CLi{=}CH_2 + C_4H_9Br \quad (1)$$

Trifluoroisopropenyl bromide was prepared by quantitative bromination of trifluoropropene, followed by dehydrobromination by potassium hydroxide in the absence of solvent (eq 2). This method proved more suitable than that reported in the literature[5] and gave the product in quantitative yield. The extent of exchange was determined by the amount of butyl bromide produced. When the exchange reaction was conducted at temperatures higher than −90°, the yield of useful products obtained by reaction of trifluoroisopropenyllithium and a carbonyl compound was low compared with the actual amount of lithium reagent produced as indicated by the butyl bromide formed. Apparently, the lithium reagent underwent decomposition before the desired reaction could occur.

$$CF_3CH{=}CH_2 \xrightarrow{Br_2} \underset{100\%}{CF_3CHBrCH_2Br} \xrightarrow[\text{no solvent}]{KOH} \underset{100\%}{CF_3CBr{=}CH_2} \quad (2)$$

Thus, the problem became an experimental one of preparing the fluoroorganic lithium compound and preventing its decomposition before the carbonyl compound was added.

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