416. *Aromatic Substitution. Part III.** *Alkylation of Aromatic Compounds by the Boron Trifluoride-catalysed Reaction of Alkyl Fluorides.*

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The alkylation of aromatic compounds by boron trifluoride-catalysed reaction with alkyl fluorides has been examined. Alkyl fluoride–boron trifluoride complexes have been isolated.

WOHL and WERTYPOROCH [1] attempted to alkylate benzene with alkyl chlorides in the presence of boron trifluoride as catalyst. Burwell and Archer [2] failed to alkylate toluene similarly with *cyclo*hexyl bromide or chloride, but showed that benzene is readily alkylated by *cyclo*hexyl fluoride in the presence of boron trifluoride. They assumed that the BF_4^- anion, formed in this case by co-ordination with BF_3, is much more stable than the BF_3Cl^- or the BF_3Br^- anion. Hennion and Kurz [3] observed that, in the presence of water or alcohol, benzene or toluene could be alkylated by means of alkyl chlorides or bromides and boron trifluoride; they assumed that the reaction is assisted by the water–boron trifluoride and alcohol–boron trifluoride complexes.

In our studies, we examined the alkylation of aromatic compounds, chiefly alkylbenzenes, by boron trifluoride-catalysed reaction with alkyl fluorides.

The alkyl fluorides required were prepared partly by halogen exchange of silver fluoride with alkyl iodides [4] and partly by our modification [5] of the method by Nakanishi, Myers, and Jensen [6] for the decarboxylation of fluoroformic esters.

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* Part II, *J.*, 1956, 4257.

[1] Wohl and Wertyporoch, *Ber.*, 1931, **64**, 1360.

[2] Burwell and Archer, *J. Amer. Chem. Soc.*, 1942, **64**, 1032.

[3] Hennion and Kurz, *ibid.*, 1943, **65**, 1001.

[4] Moisson, *Compt. rend.*, 1888, **107**, 99, 260.

[5] Oláh and Kuhn, *J. Org. Chem.*, in the press.

[6] Nakanishi, Myers, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 3099, 5033.

We found that methyl, ethyl, propyl, *iso*propyl, *tert.*-butyl, or *cyclo*hexyl fluoride in the presence of boron trifluoride alkylates aromatic compounds in good yields, usually without resin formation. Yields (%) are shown in the Table.

RF	PhMe	*m*-$C_6H_4Me_2$	*s*-$C_6H_3Me_3$	RF	PhMe	C_6H_6
MeF	62	—	—	Pr^iF	84	—
EtF	81	83	79	Bu^tF	68	—
Pr^nF	77	—	—	$C_6H_{11}F$	79	85

The Lewis-acid complexes formed by the alkyl halides and catalysts have been examined by numerous authors. According to the generally accepted older ideas about the mechanism of the Friedel–Crafts alkylation, the alkyl halides are directly ionised by the Lewis-acid catalysts:[7] $RX + MX_3 \rightleftharpoons R^+MX_4^-$. The pure carbonium-ionic mechanism is supported primarily by the conductivity of solutions of aluminium chloride, aluminium bromide, and ferric chloride in various alkyl halides,[8, 9] and by isotopic studies.[10]

H. C. Brown and his co-workers, on the basis of their experiments on the gallium chloride, aluminium chloride, aluminium bromide, and aluminium iodide complexes of methyl and ethyl halides, concluded that in these cases only a polar alkyl halide–metal halide complex is formed. However, they assume the formation of a different carbonium-ion complex for tertiary alkyl halides, which are easily ionised.[11] The existence of the ionic Lewis-acid complexes of alkyl halides was similarly shown by studies which proved primarily the isomerisation of alkyl halides under the influence of aluminium halides.[12]

Schneider and his co-workers [13] examined the isomerisation of *iso*alkyl compounds in the presence of alkyl fluoride and boron trifluoride, first with *iso*propyl and *tert.*-butyl fluoride; although (according to Ipatieff and Grosse [14]) the *iso*alkanes do not react with boron trifluoride and no isomerisation occurs, adding a little alkyl fluoride in the *iso*alkane causes boron trifluoride to dissolve in amount equivalent to the alkyl fluoride and isomerisation then takes place. Schneider *et al.*[13] did not examine these intermediate complexes, and no complex between alkyl halide and Lewis-acid type catalyst was obtained isolated pure.

By analogy with our earlier work on nitronium [15] and acylfluoroborates,[16] we attempted to isolate the alkyl fluoride–boron trifluoride complexes at low temperatures. Between $-50°$ and $-110°$ saturating the alkyl fluorides with boron trifluoride gave a 1 : 1 molar complex (calculated from the amount of boron trifluoride absorbed). The Table contains the melting points or decomposition points of the complexes isolated, and their specific

R in $R^+BF_4^-$	M. p.	κ (10^{-2} ohm^{-1} cm.$^{-1}$)	Colour	R in $R^+BF_4^-$	M. p.	κ (10^{-2} ohm^{-1} cm.$^{-1}$)	Colour
Me	$-110°$	0·0002	None	Pr^i	$-95°$	0·4	Yellow
Et	-105	0·0005	,,	Bu^t	-80	0·4	,,
Pr^n	-95	0·4	Yellow	C_6H_{11}	-54 to -52	0·5	,,

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[7] Hammett, "Physical Organic Chemistry," New York, McGraw-Hill Book Co., 1940; Price, "Organic Reactions," Vol. III, New York, John Wiley and Sons, 1946.

[8] Wohl and Wertyporoch, *Ber.*, 1931, **64**, 1357; Wertyporoch, *ibid.*, p. 1369; Wertyporoch and Firla, *Z. phys. Chem.*, 1932, **162**, *A*, 398; Wertyporoch, Kowalski, and Roeske, *Ber.*, 1933, **66**, 1232; Wertyporoch and Kowalski, *Z. phys. Chem.*, 1933, **166**, *A*, 205.

[9] Fairbrother, *Trans. Faraday Soc.*, 1941, **37**, 763.

[10] *Idem, J.*, 1937, 503.

[11] Brown, Pearsall, Eddy, Wallace, Grayson, and Nelson, *Ind. Eng. Chem.*, 1953, **45**, 1462.

[12] Kekulé and Schrotter, *Ber.*, 1879, **12**, 2279; Gustavson, *J. prakt. Chem.*, 1886, **34**, 161; *Ber.*, 1883, **16**, 958; Wibaut and Brouwer, *Rec. Trav. chim.*, 1934, **53**, 1001; Mayo and Dolmick, *J. Amer. Chem. Soc.*, 1944, **66**, 985; Nash, Taylor, and Doering, *ibid.*, 1949, **71**, 1516; Roberts, Ropp, and Neville, *ibid.*, 1955, **77**, 1764; Sixma and Hendriks, *Rec. Trav. chim.* 1956, **75**, 169.

[13] Schneider and Kennedy, *ibid.*, 1951, **73**, 5013, 5017, 5024; Donnell and Kennedy, *ibid.*, 1952, **74**, 4162.

[14] Ipatieff and Grosse, *ibid.*, 1935, **57**, 1617.

[15] Oláh and Kuhn, *Chem and Ind.*, 1956, 98; Oláh, Kuhn, and Mlinko, *J.*, 1956, 4257.

[16] Oláh and Kuhn, *Chem. Ber.*, 1956, **89**, 866.

conductivities in the molten state. The specific conductivities of methyl and ethyl fluoroborate are less by three powers of ten than that of the propyl and butyl compounds. Thus the former have an only slightly dissociated polar covalent bond, while the propyl and *tert.*-butyl complexes have a much more dissociated ionic character owing to the greater possibility of stabilisation. (The boron trifluoride-assisted isomerisation of propyl and butyl fluoride will be discussed in another paper.)

The complexes isolated, when allowed to react at low temperatures with alkylbenzenes, gave the corresponding alkylated derivatives directly, in good yields.

Our experiments gave a direct experimental proof of the H. C. Brown's results [11] in a different field. According to these, the intermediate complexes formed with catalysts of Lewis-acid type during alkylations with alkyl halides fall into two classes: 1 : 1 addition complexes, containing a polarised covalent bond (in our experiments the methyl and ethyl complexes); and the considerably ionised complexes of ionic character (in our experiments, the propyl and *tert.*-butyl complexes).

EXPERIMENTAL

Alkylations with Alkyl Fluorides in the Presence of Boron Trifluoride.—Alkyl fluoride (0·5 mol.) was dissolved in alkylbenzene (1 mol.) at −20° to −80°. Boron trifluoride was passed into the solution till it became saturated (0·5 mol. absorbed), during which a coloured lower phase separated. The mixture was allowed to warm to above the decomposition point of the complex; there was copious evolution of boron trifluoride. The organic layer was separated, washed free from acid, dried, and fractionated. After removal of the excess of the original alkylbenzene, the fraction containing the monoalkylated isomers was separated without trying to separate the isomers by distillation. In the alkylation of benzene with *cyclo*hexyl fluoride the solution was saturated with boron trifluoride with ice-cooling.

Separation of the Boron Trifluoride Complexes of Alkyl Fluorides.—Boron trifluoride was passed into alkyl fluoride (0·5 mol.) at −50° to −110°. 0·5 mol. was absorbed, giving a colourless product with methyl and ethyl fluoride, and a coloured product with propyl, *tert.*-butyl, and *cyclo*hexyl fluoride. The complexes were frozen with liquid air and were then allowed to warm slowly, in order to determine their m. p.s or decomp. points.

The preparations were carried out in silica apparatus under anhydrous conditions.

The molar composition of the complexes was proved in part by measuring the amount of boron trifluoride taken up, and in part by determination of the BF_4^- content as nitron fluoroborate.

Determination of Conductivity.—This was generally done with 30 ml. of material (molten), in a silica vessel; an immersed silica conductivity vessel with platinised platinum electrodes (conductivity constant 0·71; 0·1N-HCl), a Wheatstone-bridge apparatus, and an audiofrequency generator with a variable voltage and frequency as sources were used; measurements were carried out at 2 v with a frequency of 1000—2000. To make maximum sharpness, a condenser whose capacity could be varied between 1 pF and 10,000 pF, was connected in parallel to the resistance. The zero-instrument was a CRO, connected through an amplifier. The error of the determination was 0·5%.

Reaction of the Alkyl Fluoroborate with Toluene.—To the previously prepared ethyl, propyl, and *tert.*-butyl fluoroborate, an equimolar amount of toluene, cooled to −80°, was added, with vigorous stirring. The mixture became homogeneous, and on warming above the decomposition point of the complexes evolved boron trifluoride. After separation of the organic layer and washing of it acid-free, the monoalkylated products were isolated in 80—85% yield, with a little dialkylated product.

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