Selective Friedel–Crafts Reactions. I. Boron Halide Catalyzed Haloalkylation of Benzene and Alkylbenzenes with Fluorohaloalkanes

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A general new haloalkylation method has been found in the boron halide catalyzed alkylation of benzene (and other aromatics) with fluorohaloalkanes. The C–F bond reacts preferentially over the C–Cl, C–Br, or C–I bonds, allowing the chloro-, bromo-, and iodoalkylations to proceed in high yield with a minimum of dialkylation. The order of reactivity of the boron trihalide catalysts is $BI_3 > BBr_3 > BCl_3 > BF_3$, whereas the reactivity of the carbon–halogen bonds in the investigated dihalides is C–F > C–Cl > C–Br > C–I.

Although the Friedel–Crafts reactions are some of the most versatile tools of organic chemistry, there are often serious limitations in their use. One of these is encountered in reactions where more than one reactive, functional group or atom is present. Such a group can interact with catalyst and lead to unwanted reactions. This lack of "selectivity" is well demonstrated in attempted alkylations with vinyl chloride or ethylene dichloride in the presence of aluminum chloride or related catalysts. No compound containing a chloroethyl or a vinyl group is obtained. Owing to the presence of two reactive functional groups (olefinic double bond and chlorine atom in one case and two chlorine atoms in the other), the reactions proceed rapidly past the point of initial haloalkylation and lead to mixtures derived from secondary alkylation.

Di- and polyhaloalkanes are well known and easily available alkylating agents. However, apart from a few exceptions, Friedel–Crafts alkylation involving these compounds does not stop at the primary haloalkylated product. Instead, polycondensation products are obtained, mainly because the haloalkylated substances formed in the first reaction step are more reactive than the starting polyhaloalkanes.

Many investigators have studied the reaction of chloroform with benzene in the presence of aluminum chloride, but it was Boeseken[2a] who first obtained a haloalkylated product from the reaction mixture. Boeseken found that diphenylmethane, triphenylmethane, and triphenylchloromethane are formed in the reaction. Benzene also reacts with carbon tetrachloride and $AlCl_3$.[2] The main product under ordinary conditions is dichlorodiphenylmethane (90%).

The Friedel–Crafts reaction of aromatics with methylene chloride proceeds with substitution of both chlorine atoms. No simple chloromethylation of aromatics with dichloromethane according to the reaction shown has been achieved. Under the reaction conditions that have been used, the intermediately formed benzyl chloride reacts at once with a second molecule of benzene to form diphenylmethane. Weak Friedel–Crafts catalysts like $ZnCl_2$, $SnCl_4$, and BCl_3, which generally are useful in chloromethylations, do not effect alkylations with dihalomethanes.

In the aluminum chloride catalyzed reaction of benzene with 1,2-dichloroethane a small amount of ethylbenzene and triphenylethane is obtained.[3] Diphenylethane is, however, the main product.[4] With 1,2-dibromoethane and toluene in the presence of aluminum chloride, ditolylethane can be isolated. Similarly, mesitylene and 1,2-dibromoethane afford mesitylethane.[5]

No simple chloroethylation with 1,2-dichloroethane according to the equation

$$C_6H_6 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2Cl + HCl$$

is possible under used conditions, as the initially formed (2-chloroethyl)benzene immediately reacts with a second molecule of benzene to form 1,2-diphenylethane.

1,2-Dichloropropane and benzene in the presence of aluminum chloride give 1,3-diphenylpropane.[4,6]

1,4-Dihaloalkanes preferentially afford cycloalkylation products through the intermediate formation of a (4-haloalkyl)arene. The latter by an intramolecular alkylation step yields the cyclocondensation product.[7]

Very few examples of haloalkylations with dihaloalkanes have been reported. When 1-chloro-3-bromopropane is reacted with benzene at 6–12° in the presence of $AlCl_3$, (3-bromopropyl)benzene[8] forms (60% yield), but at a higher temperature diphenylpropane is the product. Schmerling, *et al.*,[9a] have found that certain dihaloalkanes, in which one halogen atom is attached to a tertiary and the other halogen to a primary carbon atom, react with aromatic hydrocarbons in the presence of an aluminum chloride–nitroalkane catalyst to form (haloalkyl)arenes. Schmerling, *et al.*, have also found that 1,2-dichlorobutane reacts with benzene in the presence of aluminum chloride at 0–25° to form 1-chloro-2-phenylbutane.[9b]

Results and Discussion

In previous work we have reported the Friedel–Crafts alkylation of aromatics with alkyl fluorides in

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[2] (a) J. Boeseken, *Rec. trav. chim.*, **22**, 301 (1903); (b) H. Gomberg and J. R. Jickling, *J. Am. Chem. Soc.*, **37**, 2575 (1915).

[3] R. D. Silva, *Bull. soc. chim. France*, **36**, 24 (1881).

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[7] H. A. Bruson and G. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 36 (1940).

[8] I. Tsukervanik and K. Yatsimirskii, *J. Gen. Chem. USSR*, **10**, 1075 (1940).

[9] (a) L. Schmerling, R. W. Welch, and J. P. West, *J. Am. Chem. Soc.*, **78**, 5406 (1956); (b) L. Schmerling, R. W. Welch, and J. P. Lewis, *ibid.*, **79**, 2636 (1957).

TABLE I
BORON HALIDE CATALYZED ALKYLATION OF AROMATICS WITH ALKYL FLUORIDES

Alkyl fluoride	Catalyst	% yield of alkylate C_6H_6	$C_6H_5CH_3$	1,2-$(CH_3)_2C_6H_4$	1,2,3-$(CH_3)_3C_6H_3$
CH_3F	BF_3	58	62		
C_2H_5F		77	81	83	79
n-C_3H_7F		80	77		
i-C_3H_7F		82	84	72	70
t-C_4H_9F		74	70	76	69
$C_6H_{11}F$		80	83		
CH_3F	BCl_3		60		
C_2H_5F		69	78	80	76
i-C_3H_7F		63	72	77	
t-C_4H_9F		60	73	75	
sec-C_4H_9F			68		
$C_6H_{11}F$			81		
CH_3F	BBr_3		54		
C_2H_5F			63		
i-C_3H_7F		72	79	66	70
t-C_4H_9F		65	76		
sec-C_4H_9F			71		
C_6H_{11}			89		
i-C_3H_7F	BI_3	60	64	69	
t-C_4H_9F		64	69	70	
$C_6H_{11}F$			90		

the presence of a BF_3 catalyst.[10] Extension of this investigation has now shown that alkyl fluorides, such as methyl, ethyl, isopropyl, *sec*-butyl, *t*-butyl, and cyclohexyl fluoride, are also able to alkylate aromatics in the presence of BCl_3, BBr_3, or BI_3 as the catalyst. Yields from 54–90% of alkylated product can be obtained. The alkylation results are summarized in Table I.

As a rule, if alkyl chlorides,[11] bromides,[12] or iodides are used in boron trifluoride catalyzed reactions, no alkylation takes place. This is definitely true for primary alkyl halides. With secondary and tertiary halides, some alkylation was observed in the present work using BI_3 or BBr_3 as the catalyst. The yields, however, were negligible compared with alkylations using alkyl fluorides.

The observed difference between the reactivity of alkyl fluorides and the other alkyl halides towards boron halides has enabled us to carry out Friedel–Crafts haloalkylations with dihaloalkanes in which one of the halogen atoms is fluorine.

Fluorochloro-, fluorobromo- and fluoroiodoalkanes were found to be effective chloro-, bromo- and iodoalkylating agents in the Friedel–Crafts alkylations of benzene and alkylbenzenes in the presence of a boron halide catalyst.

$$\mathrm{ArH} + \mathrm{F(CH_2)}_n\mathrm{X} \longrightarrow \mathrm{Ar(CH_2)}_n\mathrm{X}$$
$$n > 1;\ \mathrm{X} = \mathrm{Cl, Br, I}$$

Fluorohaloalkanes used in the boron halide catalyzed haloalkylations included 1-chloro-2-fluoroethane, 1-bromo-2-fluoroethane, 1-iodo-2-fluoroethane, 1-bromo-3-fluoropropane, 1-bromo-2-fluoropropane, 1-chloro-4-fluorobutane, 1-bromo-4-fluorobutane, and 1-bromo-3-fluorobutane. Data obtained are summarized in Table II.

Boron halides, other than the fluoride, also effect halogen exchange of the fluorohaloalkanes as shown.

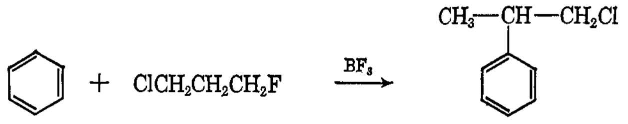
$$3\mathrm{F(CH_2)}_n\mathrm{Cl} + \mathrm{BCl_3} \rightarrow 3\mathrm{Cl(CH_2)}_n\mathrm{Cl} + \mathrm{BF_3}$$

Thus, a decreased amount of fluorohaloalkane is available for haloalkylation. Consequently, yields obtained using boron fluoride as the catalyst are generally higher than those obtained with BCl_3, BBr_3, or BI_3, although longer reaction times are needed than in reactions involving other boron halide catalysts. 1-Chloro-2-fluoroethane chloroalkylates aromatics with good yields in the presence of BI_3 or BBr_3 as the catalyst (the strongest of the boron halides), but no alkylation was achieved when weaker BCl_3 or BF_3 were employed as catalysts.

The relative order of catalyst activity thus found is $BI_3 > BBr_3 > BCl_3 > BF_3$. This sequence is in agreement with the relative Lewis acid strengths of the boron halides determined by the measurement of the heats of formation of their complexes.[13–15]

The substantially higher reactivity of the C–F bond over that of the C–Cl, C–Br, and C–I bonds in Lewis acid catalyzed reactions of fluorohaloalkanes is at first sight unexpected in view of the carbon–halogen bond energies, which show increasing strength from iodine to fluorine. However, the base strength of halide reagents in Friedel–Crafts systems is a consequence of a number of contributing factors involving both the donor base and acceptor acid. Mentioned are only the more important: (a) electronegativity of the halogen ligands (which is in the order F > Cl > Br > I), (b) bond lengths and strengths in interaction with catalyst, and (c) steric effects. The high polarity of the C–F bond to be cleaved as well as the high bond energy of the B–F bond to be formed by the interaction with the Lewis halide catalyst, together with an obviously small steric hindrance, must contribute substantially to the high reactivity of the C–F bond.

It is interesting to note that, if BF_3 is used as the catalyst in reactions of straight-chain fluorohaloalkanes, almost complete isomerization of the alkyl chain occurs,



whereas, in the case of the other boron halide catalysts, the isomerized product amounts to only 5–15%. The isomerization observed with boron trifluoride is probably due to the cocatalytic effect of HF formed in the reaction, providing the strong conjugate acid HF + BF_3. No similar conjugate acid is known with hydrogen halides and the other boron trihalides. No attempt was made, however, in the present investigation to determine the isomer distribution of the fluoroalkylmethylbenzenes obtained.

No halomethylation was obtained when halofluoromethanes were used. The deactivating effect of more than one halogen atom attached to the same carbon, renders the C–F bond unreactive.

The reactions described above for the haloalkylation (except halomethylation) of arenes seem to have gen-

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[11] W. Wohl and E. Wertyporoch, *Ber.*, **64**, 1357 (1931).
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[14] H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956).
[15] N. N. Greenwood and B. G. Perkins, *J. Chem. Soc.*, 1141 (1960).

TABLE II

HALOALKYLATION OF BENZENE AND ALKYLBENZENES WITH FLUOROHALOALKANES

Aromatic hydrocarbon	Haloalkane	Catalyst	Reaction conditions		Product	% yield
			Temp., °C.	Time, min.		
Benzene	1-Chloro-2-fluoroethane	BBr_3	−10	30	(2-Chloroethyl)benzene	50
Benzene	1-Chloro-2-fluoroethane	BI_3	−10	30	(2-Chloroethyl)benzene	55
Toluene	1-Chloro-2-fluoroethane	BBr_3	−20	30	(2-Chloroethyl)toluenes	60
Toluene	1-Chloro-2-fluoroethane	BI_3	−20	30	(2-Chloroethyl)toluenes	63
m-Xylene	1-Chloro-2-fluoroethane	BBr_3	−20	30	(2-Chloroethyl)-*m*-xylene	62
m-Xylene	1-Chloro-2-fluoroethane	BI_3	−20	30	(2-Chloroethyl)-*m*-xylene	65
Mesitylene	1-Chloro-2-fluoroethane	BBr_3	−20	30	(2-Chloroethyl)mesitylene	70
Benzene	1-Bromo-2-fluoroethane	BF_3	20	240	(2-Bromoethyl)benzene	94
Benzene	1-Bromo-2-fluoroethane	BCl_3	−10	30	(2-Bromoethyl)benzene	61
Benzene	1-Bromo-2-fluoroethane	BBr_3	−10	30	(2-Bromoethyl)benzene	60
Benzene	1-Bromo-2-fluoroethane	BI_3	−10	30	(2-Bromoethyl)benzene	57
Toluene	1-Bromo-2-fluoroethane	BF_3	20	240	(2-Bromoethyl)toluenes	92
m-Xylene	1-Bromo-2-fluoroethane	BF_3	20	240	(2-Bromoethyl)-*m*-xylene	90
Mesitylene	1-Bromo-2-fluoroethane	BF_3	20	240	(2-Bromoethyl)mesitylene	93
Benzene	1-Iodo-2-fluoroethane	BF_3	0	15	(2-Iodoethyl)benzene	63
Benzene	1-Chloro-3-fluoropropane	BF_3	0–10	60	(1-Methyl-2-chloroethyl)benzene	90
Benzene	1-Chloro-3-fluoropropane	BCl_3 or BBr_3	0–10	30	(3-Chloropropyl)benzene (90%) and (1-methyl-2-chloroethyl)benzene (10%)	63
Benzene	1-Chloro-2-fluoropropane	BF_3	−10–+10	60	(1-Methyl-2-chloroethyl)benzene	92
Benzene	1-Bromo-3-fluoropropane	BF_3	0–20	120	(1-Methyl-2-bromoethyl)benzene	89
Benzene	1-Bromo-3-fluoropropane	BCl_3 or BBr_3	−10	30	(3-Bromopropyl)benzene	60
Benzene	1-Bromo-2-fluoropropane	BF_3	−10–+10	60	(1-Methyl-3-bromoethyl)benzene	91
Benzene	1-Chloro-4-fluorobutane	BF_3	−10	30	(1-Methyl-3-chloropropyl)benzene	84
Benzene	1-Chloro-4-fluorobutane	BCl_3 or BBr_3	−10	30	(1-Methyl-3-chloropropyl)benzene (15–30%) and (4-chlorobutyl)-benzene (70–85%)	57
Benzene	1-Bromo-4-fluorobutane	BF_3	−10–+10	30	(1-Methyl-3-bromopropyl)benzene	80
Benzene	1-Bromo-4-fluorobutane	BCl_3 or BBr_3	0–10	60	(1-Methyl-3-bromopropyl)benzene (30%) and (4-bromobutyl)benzene (70%)	61
Benzene	1-Bromo-3-fluorobutane	BF_3	−10–+10	60	(1-Methyl-3-bromopropyl)benzene	81

eral and wider application and further uses for this method can be expected by employing different fluorohaloalkanes.

Catalysts other than boron halides, which are useful in effecting haloalkylations with fluorohaloalkanes, include titanium and stannic tetrafluorides and, to a certain degree, their tetrachlorides and tetrabromides.

An essential property of the catalyst is that it should effect haloalkylations, without causing either excessive secondary alkylation, which would lead to diarylalkanes or to halogen exchange taking place. The more reactive aluminum and ferric halides are less suited, because of their lack of selectivity with regard to secondary alkylations. They are useful in haloalkylations with longer chain α,ω-fluoroalkanes, where the reactivity of the (haloalkyl)arenes produced is not too high. It is also advantageous to use the catalysts in the form of less active complexes, such as those with nitromethane. The $AlCl_3 \cdot CH_3NO_2$ or $FeCl_3 \cdot CH_3NO_2$ complexes in nitromethane solution are considerably less active catalysts than the noncomplexed halides in hydrocarbon media. Side reactions, such as the subsequent formation of diarylalkanes, can thus be very much reduced.

Experimental

The fluorohaloalkanes used have been prepared by the halogen-exchange reaction of the corresponding dichloro- or dibromoalkanes with HgF_2.[16] 1-Fluoro-2-iodoethane was prepared by the interaction of 1-fluoro-2-bromoethane and NaI in acetone.[17] The boron halides were commercial products of the highest available purity. The reactions were carried out with care to exclude moisture.

A. **Boron Halide Catalyzed Alkylation of Aromatics with Alkyl Fluoride.**—Alkyl fluoride, 0.25 mole, was dissolved in 1.0 mole of aromatic hydrocarbon cooled to −20 to −30°. Then a solution of 0.08 mole of boron halide in 0.25 mole of aromatic hydrocarbon was added dropwise to the well-stirred reaction mixture. After the addition of the boron halide, the reaction mixture was stirred for 10 min. (having been allowed to warm to room temperature). The organic layer was washed three times with water, separated, dried over $CaCl_2$. The products were separated by fractional distillation and analyzed by gas-liquid chromatography and by their n.m.r. spectra. Yields of alkylated products obtained are summarized in Table I, based on alkyl fluorides used.

B. **Haloalkylations in the Presence of BF_3 as Catalyst.**—The corresponding fluorohaloalkane, 0.5 mole, was dissolved in 2.0 moles of aromatic hydrocarbon and BF_3 gas was introduced into the mixture in a slow stream for 15 min. Depending on the reactivity of the fluorohaloalkane, the temperature of the mixtures was kept between −20 and 30°. The mixture was then worked up as in A. (For details of experimental conditions and yields of haloalkylated products see Table II.)

C. **Haloalkylations in the Presence of BCl_3, BBr_3, and BI_3 as Catalysts.**—Fluorohaloalkane, 0.5 mole, was dissolved in 2.0 moles of aromatic hydrocarbon, and 0.166 mole of boron halide dissolved in 0.5 mole of aromatic was added dropwise to the well-

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stirred reaction mixture. The reaction started immediately. The temperature of the reaction mixture was kept between −20 and 30°. After the addition of the boron halide, the reaction mixture was processed as in A.

All the haloalkylated products were known from the literature and were identified by their physical data, infrared and n.m.r. spectra, halogen analyses, and gas–liquid chromatography, using a Perkin-Elmer Model 154-C vapor fractometer.

The Hydroboration of Trialkylated Ethylenes. The Configurations of Carvomenthol and Its Geometric Isomers

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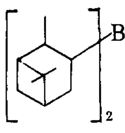
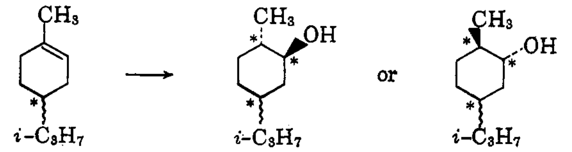
While *cis* dialkylated ethylenes undergo asymmetric, stereoselective hydroboration with optically active diisopinocampheylborane, trialkylated ethylenes undergo hydroboration stereoselectively but not asymmetrically. The results of the hydroboration of 1-*p*-menthene provide a direct chemical basis on which to make configurational assignments for the 2-*p*-menthanol geometric isomers.

A few years ago Brown and Zweifel[1] reported the conversion of *cis* dialkylated ethylenes to the corresponding optically active secondary alcohols *via* hydroboration, oxidation, and hydrolysis. The key step in the sequence involved the use of optically active diisopinocampheylborane (I) to achieve asymmetric, stereoselective hydroboration.



I

This paper reports the results of our attempts to prepare optically pure secondary alcohols from trialkylated ethylenes *via* the same reaction sequence. The objective was to prepare any one of the 2-*p*-menthanol optical isomers free of its enantiomer and diastereoisomers. Hydroboration of the readily available (+)-1-*p*-menthene[2] with I seemed to offer an efficient, direct route free of troublesome isomer separation problems. The over-all reaction (hydroboration, oxidation, and hydrolysis) was visualized as taking place as shown.



II III IV

Thus, (+)-1-*p*-menthene would provide the optical purity required in position 4 of the product, and efficient, asymmetric, stereoselective hydroboration would provide the optical purity required at positions 1 and 2 of the product.

Before experimenting with diisopinocampheylborane (I) of high optical purity, a more readily obtainable material, containing about 75% of one optical isomer and about 25% of the other, was used. The anticipated end product would be a mixture of diastereoisomers III and IV in the same ratio as that of the enantiomers in the hydroborating agent, *i.e.*, 3 to 1, or 1 to 3. Such a result would justify the hydroboration of II with less plentiful diisopinocampheylborane (I) of high optical purity to obtain a single 2-*p*-menthanol optical isomer. After the steps of hydroboration, oxidation, and hydrolysis, (−)-carvomenthol, $[\alpha]^{25}\text{D}$ −25.40°, and (+)-isocarvomenthol, $[\alpha]^{25}\text{D}$ +16.30°, were isolated in a *1.3 to 1.0 ratio.* Based on these specific rotations, both compounds are at least 90% optically pure.[3]

Hydroboration of the same olefin with diborane also gave carvomenthol and isocarvomenthol in the same ratio. Thus, the optical activity of the diisopinocampheylborane (I) played no special role in controlling the optical purity of positions 1 and 2 of the product, and asymmetric hydroboration did not take place.

In order to determine the structural features of 1-*p*-menthene which preclude asymmetric, stereoselective hydroboration, the hydroboration of two simple olefins, *cis*-2-butene and 3-methyl-2-butene, with the hydroborating agent I of high optical purity was studied. *cis*-2-Butene, the simplest *cis* dialkylated ethylene, has been converted with this hydroborating agent by Brown and Zweifel[1] to 2-butanol of 87% optical purity. In our hands, *cis*-2-butene yielded 2-butanol, $[\alpha]^{25}\text{D}$ −12.0°. Leroux and Lucas[4] report $[\alpha]^{25}\text{D}$ −13.51° for L(−)-2-butanol. Hence our product is about 89% optically pure and the experiment confirms the work of Brown and Zweifel.[1] On the other hand, 3-methyl-2-butene, the simplest trialkylated ethylene, yielded 3-methyl-2-butanol, $[\alpha]^{25}\text{D}$ +0.4°. Pickard and Kenyon[5] report $[\alpha]^{20}\text{D}$ +4.85° for (+)-3-methyl-2-butanol. Hence our product is only about 8% optically pure.

These experiments show that, while *cis* dialkylated ethylenes undergo asymmetric, stereoselective hydroboration with I, trialkylated ethylenes do not. Thus, branching on one carbon atom of an olefinic bond precludes asymmetric addition of optically active diisopinocampheylborane. It should be remembered that α-pinene (a trialkylated ethylene) reacts asymmetrically with diborane but does not react with diisopinocampheylborane.[1]

Zweifel, *et al.*,[6] have pointed out the importance of the asymmetric bulk of optically active diisopinocampheylborane in the asymmetric, stereoselective hydro-

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[2] W. F. Newhall, *J. Org. Chem.*, **23**, 1274 (1958).

[3] J. L. Simonsen ["The Terpenes," Vol. 1, Cambridge University Press, Cambridge, 1947, p. 252] lists the following specific rotations at 16° for 2-*p*-menthanol isomers: *d*-carvomenthol, +26°; *l*-isocarvomenthol, −18°; *l*-neocarvomenthol, −42°; *l*-neoisocarvomenthol, −35°.

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