[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Alkylation of Naphthalene with Alcohols and Boron Fluoride. The Mechanism of the Reaction

BY CHARLES C. PRICE AND JOSEPH M. CISKOWSKI

The alkylation of benzene by alcohols in the presence of boron fluoride has been reported by McKenna and Sowa[1] to yield, in addition to monoalkylated benzene derivatives, disubstituted products in which the second alkyl group entered the ring para to the one already present. Since this orientation differed from that usually reported for Friedel–Crafts alkylation, the present investigation was undertaken to determine whether a difference in orientation might exist in the case of naphthalene as well. It was of particular interest to investigate this possibility since it might lead to a method for preparing the α-alkylnaphthalenes, in contrast to the readily available β-isomers prepared by the Friedel–Crafts reaction.

Naphthalene was alkylated smoothly and rapidly on passing boron fluoride into a suspension of the hydrocarbon in isopropyl, cyclohexyl, *t*-butyl, or benzyl alcohol. The reaction was usually quite rapid, exothermic and accompanied by the development of a color characteristic of the alcohol used. This color always faded on washing with dilute alkali to remove the catalyst. The reaction is superior to the Friedel–Crafts reaction in these instances in that a cleaner product is obtained with a larger yield, frequently in a much shorter time.

The monoalkylated material, however, consisted chiefly of the β-isomer except in the case of benzyl alcohol, in which case α-benzylnaphthalene was the chief product, accompanied by a small amount of the β-isomer. Roux[2] has reported the preparation of β-benzylnaphthalene from the hydrocarbon and benzyl chloride at 160°. Even in this case, however, the α-isomer results when the reaction is carried out at 90° for only a very short time.

Sowa[3] has proposed that the mechanism for alkylation reactions using boron fluoride as a catalyst, with esters and ethers as well as alcohols, consists primarily in the formation of an olefinic hydrocarbon to which the aromatic compound then adds under the influence of the catalyst. In support of the view is the fact that olefins may be condensed with aromatic compounds to form the corresponding alkylated product. Slanina, Sowa and Nieuwland[4] have reported this reaction but the boron fluoride was always used in conjunction with a co-catalyst, the most effective of which was sulfuric acid. This acid, of course, could readily convert the olefin to the alcohol or its sulfate.

Naphthalene was therefore treated with an olefin, cyclohexene, in the presence of boron fluoride alone. A moderately good yield of β-cyclohexylnaphthalene was obtained, indicating that direct, catalytic addition of an aromatic compound to an olefin is possible in the presence of this catalyst.

Two experimental facts, however, cannot be accounted for on the basis of the olefin mechanism. In the first place, it has been found that cyclohexanol, which reacts with naphthalene readily, can be recovered quantitatively after treatment with boron fluoride under conditions considerably more drastic than those required for alkylation. Not even traces of the olefin were detected.

Secondly, the formation of an olefin as an intermediate is impossible in the case of the benzyl group, which may be introduced as readily as any secondary or tertiary alkyl groups.

It therefore seems quite apparent that the ease of reaction is dependent not on the ease of olefin formation but on the frequently parallel activity of the alcoholic hydroxyl group. It is a well-known fact that benzyl and allyl alcohols, the only primary alcohols condensing readily with aromatic compounds, behave in a manner similar to secondary and tertiary alcohols in reactions involving replacement of the hydroxyl group.

Therefore, a much more likely mechanism for the catalytic effect of the boron fluoride may be still further weakening of the carbon–oxygen bond in the association complex formed between the catalyst and the oxygen-containing organic

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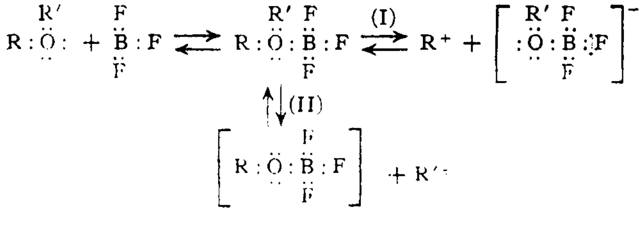
[1] McKenna and Sowa, THIS JOURNAL, **59**, 470 (1937).

[2] Roux, *Ann. chim. phys.*, [6] **12**, 330 (1887).

[3] (a) McKenna and Sowa, THIS JOURNAL, **59**, 470 (1937); (b) McKenna and Sowa, *ibid.*, **59**, 1204 (1937); (c) O'Connor and Sowa, *ibid.*, **60**, 125 (1938).

[4] Slanina, Sowa and Nieuwland, *ibid.*, **57**, 1547 (1935).

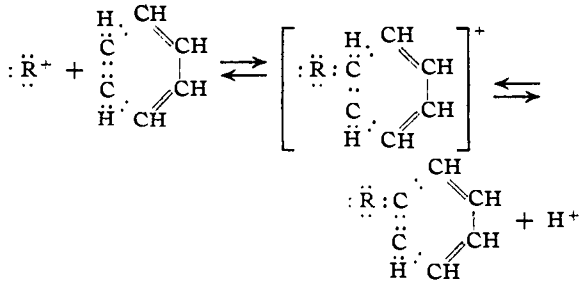
molecule. This may be represented by the following scheme in which R represents an alkyl group while R′ may be a hydrogen atom, an alkyl group or an acyl group.



That the bonds to the oxygen are actually weakened in this complex is demonstrated by the fact that the boron fluoride–alcohol complexes are strong acids, the hydrogen–oxygen bond having been weakened so as to become almost entirely ionic. Since this bond has been weakened enough to ionize it does not seem unreasonable that the carbon–oxygen bond might also ionize at least to a limited extent.

With mixed ethers the mode of ionization will depend on the two alkyl groups present. For instance, benzyl ethyl ether would be expected to ionize more readily to give the benzyl ion than the ethyl ion. In the case of esters apparently the only dissociation is according to (I) since esters in the presence of boron fluoride have been reported as alkylating agents but not acylating agents.[3h]

The positive carbonium ion thus produced may then be considered to be the active alkylating agent. Actually, of course, a free alkyl ion need exist only momentarily in the mixture just as a free hydrogen ion may have only a fleeting existence. For convenience, however, we may write the reaction using the free ion.[4a]



The reagent necessary may not be a free alkyl ion as indicated but anything capable of the donation of such an ion to the aromatic nucleus. The equations are written as reversible since, at least in the case of the Friedel–Crafts reaction, the reversibility is well known.

The ionic nature of this latter reaction seems to be a well-established fact. Dougherty[5] suggested that ionization of the alkyl halide was a portion of the catalytic effect of aluminum chloride.

$$:\ddot{\mathrm{R}}:\ddot{\mathrm{X}}: + \mathrm{AlCl_3} \rightleftharpoons :\ddot{\mathrm{R}}^+ - [\mathrm{XAlCl_3}]^-$$

Wertyporoch,[6] however, did not believe, as Dougherty had proposed, that any further activation of the aromatic nucleus was necessary. Substantiation of this modification of Dougherty's views on the reaction is obtained from the kinetic study of a Friedel–Crafts alkylation by Ulich and Heyne.[7] They found definite evidence for the formation of the complex between alkyl and metal halides and, in fact, were able to derive the equilibrium constant for its formation.

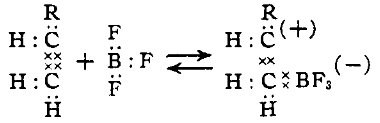
$$\mathrm{C_3H_7Cl} + \mathrm{MCl_3} \rightleftharpoons \mathrm{C_3H_7Cl{\cdot}MCl_3}$$

The rate of the alkylation was directly proportional to the concentration of this complex and of the hydrocarbon, indicating that any further function of the catalyst in activating the latter is negligible.

$$dx/dt = K'[\mathrm{C_3H_7Cl{\cdot}MCl_3}][\mathrm{C_6H_6}]$$

The rearrangements taking place in the alkyl radical during either the Friedel–Crafts reaction or alkylation with boron fluoride offer no difficulties on the basis of the reaction scheme as outlined. The products are always those predicted by Whitmore's theory of molecular rearrangements,[8] since in every case the electron deficiency in the alkyl ion has migrated from a primary to a secondary or from a secondary to a tertiary carbon atom.

The reaction of the olefins themselves may also be accounted for on the basis of the electron affinity of boron fluoride or aluminum chloride.



This complex, like the alkyl cation, has a carbon atom deficient in a pair of electrons and could react with the unsaturation of the benzene ring in a similar manner, even though in this case the active intermediate has no resultant charge.

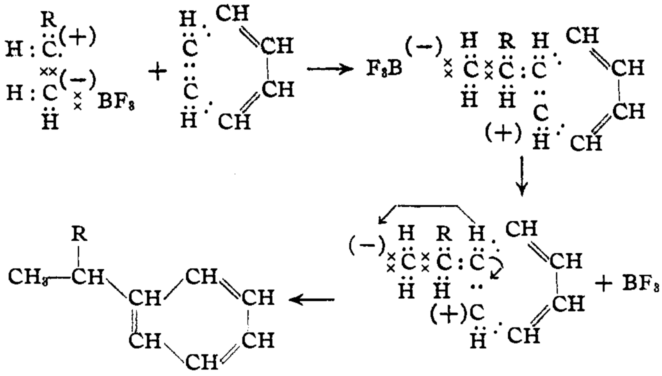
(4a) Since the preparation of this paper for publication Dilthey [*Ber.*, **71**, 1350 (1938)] has suggested this same mechanism for acylation by the Friedel-Crafts reaction.

(5) Dougherty, THIS JOURNAL, **51**, 576 (1929).

(6) Wertyporoch and Firla, *Ann.*, **500**, 287 (1933).

(7) Ulich and Heyne, *Z. Elektrochem.*, **41**, 509 (1935).

(8) Whitmore, THIS JOURNAL, **54**, 3274 (1932).

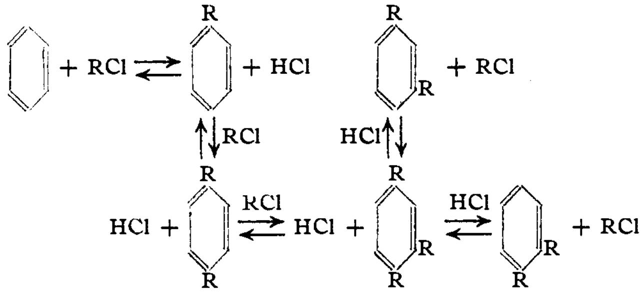


The final step, after the dissociation of the boron fluoride, is merely the α,γ-shift of a proton. Experimental confirmation of the reversible association of boron fluoride with one pair of electrons of an olefinic linkage is anticipated.

This same general mechanism may be used to account for the catalytic polymerization of olefins with boron fluoride or aluminum chloride. In this case the olefin–metal halide complex would associate with the double bond of a second olefin molecule rather than one of an aromatic ring as above.

The mechanism for alkylation and acylation of aromatic compounds is thus analogous to that for bromination[9] which also takes place through the intermediate addition of an electron deficient ion, the bromine cation, followed by elimination of a proton.

It is necessary, however, to account for the fact that aluminum chloride leads to the formation of predominantly meta as well as ortho and para dialkylated material from benzene whereas with boron fluoride the para isomer is formed almost exclusively. This difference may be due to the fact that the Friedel–Crafts reaction is reversible. When alcohols rather than alkyl halides are used, however, the water formed may hydrolyze the catalyst and thus prevent reversibility. The formation of a meta-dialkylbenzene in spite of the ortho-para-directing influence of the first group to enter may then be accounted for by the reaction scheme shown.[10]



Actually the reversal of the alkylation may be considered to be the substitution of hydrogen in place of an alkyl group. In 1,3,4-trialkylbenzene the 1- and 3-groups both orient the incoming hydrogen to the 4-position so this is the alkyl group which would most easily be replaced, thus forming, of course, the meta-dialkylbenzene. Replacement of the 1-alkyl group, taking place to a lesser extent, would be the source of the ortho-isomer, which is not reported in the case of the boron fluoride–alcohol reaction.

Experimental

Alkylation of Naphthalene.—Since the procedures used were quite similar, the results for the various alcohols have been summarized in Table I. In each instance naphthalene (50 g.) was suspended in the alcohol and boron fluoride gas[11] was passed in until two layers separated (fifteen to thirty minutes). The reaction mixture was allowed to stand for periods varying from five minutes to two days and then washed with dilute alkali, filtered from any starting material which may crystallize (5–10 g.), dried and fractionally distilled. The reaction mixtures always developed a color dependent on the alcohol used. With cyclohexyl the color was red, with tertiary butyl purple, with isopropyl green, and with benzyl blue. It always faded on addition of alkali to hydrolyze the catalyst.

That the triisopropylnaphthalene should have the same boiling point as the β-isopropyl derivative seems quite astonishing but this point was checked several times.

Attempted Dehydration of Cyclohexanol.—Cyclohexanol was saturated with boron fluoride and kept at 100° for an hour and a half but no cyclohexene was formed although the temperature was above that required for the alkylation of naphthalene in one-third this time. The alcohol–boron fluoride complex was decomposed with dilute alkali and the alcohol recovered quantitatively. Its identity was checked by the preparation of the phenylurethan deriva-

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[9] (a) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928); (b) Price and Arntzen, THIS JOURNAL, **60**, in press (1938).

[10] Baddeley and Kenner [*J. Chem. Soc.*, 303 (1935)], have suggested this mechanism but claimed their experimental work was not in agreement. From 1,2,4-tri-*n*-propylbenzene, on treatment with aluminum chloride, they obtained a considerable quantity (35–40%) of *m*-di-*n*-propylbenzene as well as the symmetrical trisubstituted derivative. The results were interpreted against the mechanism, however, since the authors claimed (apparently with little experimental evidence) that the migrating alkyl group had undergone no isomerization. Nightingale and Smith (96th Meeting of the American Chemical Society, Milwaukee, Sept. 5, 1938) have reported that such isomerization does occur during the migration of the butyl groups in rearrangements of 1,3-dimethyl-4-butylbenzenes. *m*-Xylene was one of the products in each case. The experimental evidence, therefore, seems entirely in agreement with this mechanism.

[11] The compressed gas was obtained from the Harshaw Chemical Co., Cleveland, Ohio, and found most convenient and satisfactory.

TABLE I

ALKYLATION OF NAPHTHALENE WITH BORON FLUORIDE AND ALCOHOLS

Alcohol	Product (yield[a])	B. p. °C.	B. p. Mm.	n^{20}_D	d^{25}_{25}	M_D Calcd.	M_D Found	Picrate, m. p., °C.
Cyclohexyl	β-Cyclohexyl- (63%)	190–195	15	1.5973[d]	1.020[d]	69.95	69.7	100[d]
(1.2 moles)	Dicyclohexyl-[b] (9%)	215–225	7					
Tertiary butyl	β-*t*-Butyl- (62%)	140–145	13	1.5685	0.979	60.1	58.3	99[e]
(2.3 moles)	Di-*t*-butyl- (5%)	180–185	13					154[g]
Isopropyl	β-Isopropyl- (35%)	265–270	760	1.5775	.974	55.5	57.5	..
(1.5 moles)								
Isopropyl (4 moles)	Triisopropyl-[c] (57%)	265–270	760	1.5566	.946	87.15	86.6	..
Benzyl	α-Benzyl- (28%)	200–205	9	(m. p. 58°)[f]				100[f]
(1.1 moles)	β-Benzyl- (2%)							93[f]
	Dibenzyl- (15%)	265–275	9					
	Tribenzyl- (20%)	320–330	9					

[a] Yield calculated on the basis of naphthalene consumed. [b] Mol. wt. calcd. 292; mol. wt. found (ebullioscopically in benzene), 291. [c] Mol. wt. calcd. 254; mol. wt. found 255, 246. *Anal.* Calcd. for $C_{19}H_{26}$: C, 89.76; H, 10.24. Found: C, 89.93; H, 10.62. [d] Bodroux, *Ann. chim. phys.*, [10] **11,** 536 (1927). [e] Barbot, *Bull. soc. chim.*, [4] **47,** 1314 (1930). [f] Roux, *Ann. chim. phys.*, [6] **12,** 330 (1887). [g] Fieser and Price, THIS JOURNAL, **58,** 1842 (1936).

tive, m. p. 82°. This seems to prove that under conditions of rapid and easy alkylation no olefin formation occurred.

Cyclohexylnaphthalene from Cyclohexene.—That olefins will react with naphthalene in the presence of boron fluoride alone, however, was demonstrated by bubbling this catalyst through 50 g. of naphthalene in 48 cc. of cyclohexene for an hour and a half. No layers separated in this case. After standing for a day the mixture was washed with water and alkali, 15 g. of naphthalene was recovered and the mixture dried and distilled. A yield of 20 g. (35%) of β-cyclohexylnaphthalene was obtained. It was identified by its physical constants and the melting point of its picrate.

Summary

The alkylation of naphthalene with alcohols using boron fluoride as a catalyst leads to the formation of the β-alkyl derivatives, with the exception of benzyl alcohol which yields largely α-benzylnaphthalene.

A mechanism for the catalytic effect of boron fluoride in aromatic alkylation is proposed involving the formation of alkyl cations which may then react with the aromatic nucleus.

A mechanism is suggested for the formation of meta-dialkylbenzene from the alkylation of benzene by the Friedel–Crafts reaction.

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[CONTRIBUTION FROM RÖHM & HAAS COMPANY, INC.]

Friedel-Crafts Condensation with Arylalkylene Ether Chlorides

BY HERMAN ALEXANDER BRUSON AND JOHN W. EASTES

While attempting to treat β-phenoxy-β'-chlorodiethyl ether with anhydrous aluminum chloride so as to form a possible chain condensation product by the elimination of hydrogen chloride from a plurality of molecules according to equation (A)

$$C_6H_5—O—C_2H_4—O—C_2H_4Cl— \xrightarrow{AlCl_3}$$
$$C_6H_5—O—C_2H_4—O—C_2H_4(—C_6H_4—O—C_2H_4—O—$$
$$C_2H_4)_x—C_6H_4—O—C_2H_4—O—C_2H_4\ldots + HCl \quad (A)$$

it was observed that practically no reaction occurred at temperatures as high as 70°, and that the starting material could be recovered substantially unchanged.

The unusual resistance of the ether linkages to splitting by the aluminum chloride, and the failure of the terminal aliphatically bound chlorine atom to react with the phenyl nucleus at temperatures of about 50–60°, where Friedel–Crafts reactions ordinarily take place with ease, suggested the possibility that other typical alkylating or acylating agents would condense probably with the benzene ring according to the customary synthesis, so as to alkylate or acylate the phenyl nucleus without affecting the ether linkages or the terminal chlorine atom.

Such compounds, where the alkyl group is of sufficient chain length and of the proper configuration, are intermediates for the synthesis of newer detergents and wetting agents, and are of interest also in other fields of organic research.[1]

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(1) Bruson, U. S. Patents (a) 2,097,441; (b) 2,098,203; (c) 2,107,366; (d) 2,107,367; (e) 2,115,250; (f) 2,115,192.