

3,4-Dimethyl-1-naphthyl acetate⁷ gave an nmr spectrum whose aromatic portion was substantially superimposable over those of the two methyl ethyl homologs. The three methyl singlets appeared at τ 7.50, 7.58, and 7.66 (4-CH₃, 3-CH₃, and OCOCH₃, respectively).

Registry No.—3-Methyl-3-phenyl-1-pentanol, 25594-39-2; 1-chloro-3-methyl-3-phenylpentane, 13556-52-0; 4-methyl-4-phenylhexenoic acid, 25607-04-9; 2-bromo-

4-ethyl-4-methyl-1-tetralone, 25607-05-0; 3-ethyl-4-methyl-1-naphthol, 25607-06-1; 4,4-dimethyl-1-tetralone, 2979-69-3; 2-bromo-4,4-dimethyl-1-tetralone, 17426-90-3; 4,4-dimethyl-1-keto-1,4-dihydronaphthalene, 16020-16-9; 3,4-dimethyl-1-naphthyl acetate, 25607-10-7; 2, 25607-11-8; 2 (2,4-dinitrophenylhydrazine), 25607-12-9; 4, 25607-13-0; 8, 25607-14-1; 8 (2,4-dinitrophenylhydrazine), 25607-15-2; 10, 25607-16-3; 11, 17057-93-1.

Boron Fluoride Catalyzed Ethylation of Benzene with Radioactive Ethyl Fluoride

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Received March 30, 1970

Boron fluoride catalyzed ethylation of benzene was carried out with ethyl-2-¹⁴C fluoride in homogeneous solution of nonpolar organic or basic organic solvent. The ethylbenzenes obtained were oxidized with nitric acid. Radioactivity of *p*-nitrobenzoic acid which was found in the *n*-hexane, cyclohexane, or nitromethane system was 47.9, 34.1, or 3.5% of radioactivity of ethyl-2-¹⁴C fluoride, respectively. It was confirmed that an electrophile in boron fluoride catalyzed ethylation is either an ethyl carbonium ion in the nonpolar organic solvent or a nonionized complex in the basic organic solvent.

In basic solvent the catalytic activity of Friedel-Crafts catalyst decreases in terms of a competing donor effect of the solvent. Solvated Friedel-Crafts catalyst forms with ethyl fluoride the nonionized complex which is an electrophile of Friedel-Crafts ethylation in basic solvents.¹ In nonpolar solvents a Friedel-Crafts catalyst which does not form a complex with the solvent ruptures a C-X bond of ethyl halide, and an incipient ethyl carbonium ion is an ethylating agent. This was proved by a finding that, when aluminum bromide catalyzed ethylation of benzene with ethyl-2-¹⁴C iodide was carried out in the *n*-hexane solution, oxidation of the ethylbenzene with nitric acid gave radioactive *p*-nitrobenzoic acid, indicating the migration of radioactivity from β to α carbon atom of the ethyl group.² When the ethyl carbonium ion is an ethylating agent, an anomalous substrate selectivity (a relative rate of toluene to benzene lower than 1) was found.²

In this work boron fluoride catalyzed ethylation of benzene with ethyl-2-¹⁴C fluoride in the nonpolar solvent has been carried out to obtain an additional evidence for the formation of the incipient ethyl carbonium ion as an ethylating agent.

Results and Discussion

Ethyl fluoride forms a yellow polarized complex with boron fluoride at low temperatures.³⁻⁵ The complex completely dissociates into gaseous components at room temperature. When the gaseous mixture was left for many hours, a yellow-brown oily polymer was formed. The gaseous mixture is soluble in the nonpolar solvent like *n*-hexane or cyclohexane, although the solubility of boron fluoride is low. The colorless solution is thus formed. Also, when the colorless

solution was left for many hours, the yellow-brown oily polymer was formed and deposited on the bottom of the vessel. These results suggest that the ethyl carbonium ion is formed as an intermediate.⁶ When the gaseous mixture was introduced in the nonpolar solvent with a trace of water, the polymer was immediately formed, and the solution showed a Tyndall effect. The gaseous mixture is very soluble in a basic solvent like nitromethane. Even if the solution was left for many hours, the oily polymer was not formed, indicating the impossibility of formation of the ethyl carbonium ion in the solution.

The gaseous mixture of ethyl fluoride and boron fluoride was dissolved in the nonpolar solvents, in which the aromatics were dissolved. When the homogeneous colorless solution thus formed was left for many hours, the oily polymer was not formed, but the ethylation of aromatics proceeded gradually.² However, the materials should be the purest, for when a trace of water exists in the solution, the oily polymer is immediately formed, and the solution shows the Tyndall effect.

Ethylation with Radioactive Ethyl Fluoride.—Boron fluoride catalyzed ethylation of benzene was carried out at room temperature with ethyl-2-¹⁴C fluoride in the homogeneous solution of *n*-hexane, cyclohexane, or nitromethane. The ethylbenzenes obtained were oxidized with nitric acid. The *p*-nitrobenzoic acid thus obtained was dissolved in a liquid scintillator, and the radioactivity of the solution was counted.^{2,7} The results are summarized in Table I. When the ethylation was carried out in *n*-hexane solution, 47.9% of radioactivity of ethyl-2-¹⁴C fluoride was found in the *p*-nitrobenzoic acid obtained, indicating the formation of ethyl-1-¹⁴C-benzene and hence the migration of radioactivity from β to α carbon position of the ethyl

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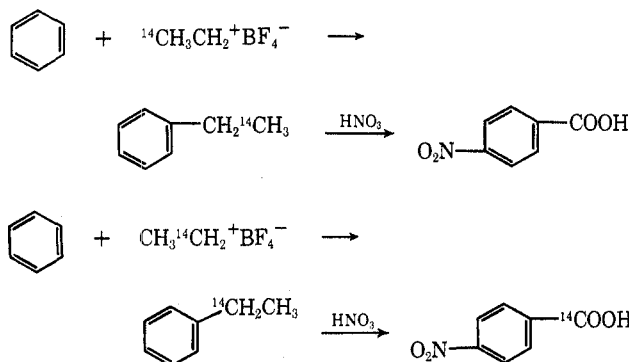
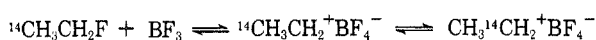
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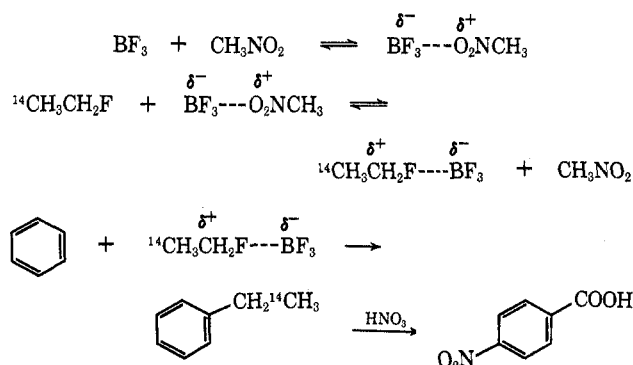
TABLE I
BORON FLUORIDE CATALYZED ETHYLATION OF
BENZENE WITH ETHYL-2-¹⁴C FLUORIDE
(206.5 μ Ci/mmol)

Solvent	Radioactivity of <i>p</i> -nitrobenzoic acid, μ Ci/mmol
<i>n</i> -Hexane	98.9
Cyclohexane	70.4
Nitromethane	7.3

group. If the ethyl carbonium ion is formed as an intermediate and an internal hydride shift occurs completely in the ethyl group before the ethyl carbonium ion combines with the benzene ring, a maximum of 50% isotope position rearrangement, corresponding to a complete equilibration of the α and β carbons of the ethyl group, should be reached. The ethylbenzene obtained, therefore, exhibits almost complete rearrangement, indicating that the ethyl carbonium ion is an electrophile in the ethylation carried out in the *n*-hexane solution. When the ethylation was carried out in the



cyclohexane solution, 34.1% of radioactivity of ethyl-2-¹⁴C fluoride was found in the *p*-nitrobenzoic acid obtained. This result also suggests that the ethyl carbonium ion is an electrophile. However, when the ethylation was carried out in the nitromethane solution, only 3.5% of radioactivity of ethyl-2-¹⁴C fluoride was found in the *p*-nitrobenzoic acid obtained. The ethylation of benzene in the basic solution gave the ethylbenzene, in which only a little isotope position rearrangement in the ethyl group was taken place. This suggests that the ethylation in the basic solution proceeds almost in terms of a displacement mechanism involving no free ethyl fragments. The electrophile in the basic solvents is the nonionized complex, $\text{C}_2\delta^+\text{H}_5\text{F} \cdots \delta^-\text{BF}_3$.



Reaction Mechanism of Boron Fluoride Catalyzed Ethylation.—When the competitive boron fluoride catalyzed ethylations of benzene and toluene were carried out with ethyl fluoride at 25° in the homogeneous solutions, the relative rates of toluene to benzene, k_T/k_B , were 0.56 in the *n*-hexane solution and 0.57 in the cyclohexane solution, respectively, but 2.66 in the nitromethane solution, as observed in the previous work.² That benzene is more reactive than toluene in the nonpolar solvents was also observed in the ethylations carried out in the separate runs, but there was a question whether the competitive ethylation in the nonpolar solvents proceeded in kinetically controlled electrophilic substitutions or not. Therefore, we carried out the following control experiments in a glass flask. Boron fluoride and isopropyl fluoride were introduced in the *n*-hexane solution of *o*-ethyltoluene in presence of benzene. When a part of *o*-ethyltoluene and benzene were isopropylated, the solution was quenched in water. Unchanged *o*-ethyltoluene and benzene were found, but ethylbenzene was not formed. Next, boron fluoride and ethyl fluoride were introduced in the *n*-hexane solution of *p*-cymene in presence of benzene. Ethylation proceeded, but even a trace of cumene could not be found in presence of unchanged benzene. These results show that the transalkylations between *o*-ethyltoluene and benzene and between *p*-cymene and benzene do not take place in the *n*-hexane solution. The transalkylations between isopropylmesitylene and benzene⁸ and between *p*-*t*-butyltoluene and benzene⁹ with aluminum chloride catalyst were observed to take place under the conditions employed in the alkylations. However, since the experiments were carried out in the glass flask, hydrogen fluoride produced could be immediately captured by the wall of the flask and a protonated alkylbenzene tetrafluoroborate complex could not be formed. Consequently, the thermodynamically controlled consecutive transalkylations do not take place.¹⁰ The competitive boron fluoride catalyzed ethylations of benzene and toluene with ethyl fluoride were carried out under the similar conditions. Thus, when boron fluoride catalyzed ethylation with ethyl fluoride is carried out in the nonpolar solvent contained in the glass or stainless steel flask, the ethylation proceeds in kinetically controlled substitutions, for the hydrogen fluoride as a product is captured by the wall of the flask, and the protonated alkylbenzene tetrafluoroborate complex is not formed and then the thermodynamically controlled consecutive transethylations do not take place.

The results obtained in this work support our previous conclusions² that the electrophile of Friedel-Crafts ethylation is either the ethyl carbonium ion in the nonpolar solvents or the nonionized complex in the basic solvents, and that the substrate and positional selectivities in all Friedel-Crafts alkylations are determined by the activation energy of formation of the σ complex.

Experimental Section

Material.—Benzene, toluene, ethyl fluoride, isopropyl fluoride, boron fluoride, *n*-hexane, cyclohexane, and nitromethane were

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prepared and purified by the previously described methods.^{2,11} Ethyl-2-¹⁴C fluoride was prepared from ethyl-2-¹⁴C iodide (The Radiochemical Centre, Amersham, England) by reaction with mercuric fluoride¹² and purified by distillation at low temperatures; 330 mg of the ethyl-2-¹⁴C fluoride obtained was dissolved in a liquid scintillator (10 ml); and the radioactivity of the solution was counted. The solution had a radioactivity of 206.5 $\mu\text{Ci}/\text{mmol}$. Mercuric fluoride was prepared from mercuric chloride (Junsei Pure Chemical Co., Tokyo, Japan) by the reaction with elemental fluorine¹³ (Daikin Kogyo Co., Osaka, Japan). *o*-Ethyltoluene and *p*-cymene were obtained from Tokyo Kagaku Seiki Co. (Tokyo, Japan). Their purities were more than 99% by gas chromatographic analyses. They were used without further purification.

Ethylation with Ethyl-2-¹⁴C Fluoride.—When the boron fluoride catalyzed ethylation of benzene was carried out with ethyl-2-¹⁴C fluoride in the *n*-hexane solution, benzene (0.15 mol), and *n*-hexane (1.5 mol) were first charged in the glass flask. From gas reservoirs gaseous ethyl-2-¹⁴C fluoride (0.09 mol) and gaseous boron fluoride (0.01 mol) were introduced in the flask and dissolved in the solution. Then a magnetic stirrer was started. After the reaction which continued for 120 hr, the solution was quenched in water. When the ethylation was carried out in the cyclohexane solution, benzene (0.1 mol), cyclohexane (1 mol), ethyl-2-¹⁴C fluoride (0.026 mol), and boron fluoride (0.014 mol) were charged in the flask and the solution was quenched in water after the reaction which continued for 17 hr. When the ethylation was carried out in the nitromethane solution, benzene (0.15 mol), nitromethane (0.45 mol), ethyl-2-¹⁴C fluoride (0.015 mol), and boron fluoride (0.03 mol) were charged in the flask, and the solution was quenched in water after the reaction which continued for 1 hr. In the preliminary experiments with nonradioactive ethyl fluoride by the similar procedure it was confirmed that about 5% of benzene was ethylated in each case. The organic layer was washed with 4% NaOH solution and then five times with water. The organic solution was dried over calcium chloride and subjected to fractional distillation. A large amount of solvents was removed. Oxidation of the remaining solution was carried out by the previously described methods.^{2,7} The *p*-nitrobenzoic acid obtained (5 mg) was dissolved in a liquid scintillator (10 ml), and the radioactivity of the solution was counted.

Radiochemical purity of the ethyl-2-¹⁴C iodide obtained from the Radiochemical Centre was 99%. Radiochemical purity of the ethyl-2-¹⁴C fluoride prepared was not measured. When the

ethylation was carried out in the nitromethane solution, 3.5% of radioactivity of ethyl-2-¹⁴C fluoride was found in the *p*-nitrobenzoic acid. This result suggests the following two possibilities: the one is that the radiochemical purity of ethyl-2-¹⁴C fluoride was 96.5%, because a little isotope position rearrangement in the ethyl group was taken place when ethyl-2-¹⁴C fluoride was prepared from ethyl-2-¹⁴C iodide by the reaction with mercuric fluoride; the other is that the radiochemical purity of ethyl-2-¹⁴C fluoride was 99%, but a little rearrangement proceeded in the ethylation. At any rate, the radiochemical purity of ethyl-2-¹⁴C fluoride was equal to or higher than 96.5%.

Isopropylation of Benzene and *o*-Ethyltoluene with Isopropyl Fluoride in *n*-Hexane Solution.—Isopropyl fluoride (0.0025 mol) and boron fluoride (0.0015 mol) were introduced in the glass flask, in which benzene (0.0125), *o*-ethyltoluene (0.0125 mol), and *n*-hexane (0.25 mol) were charged. After the reaction which continued for 20 min, the solution was quenched in water, extracted with ether, dried over calcium chloride, and analyzed by gas chromatography.

Ethylation of Benzene and *p*-Cymene with Ethyl Fluoride in *n*-Hexane solution.—Ethyl fluoride (0.0025 mol) and boron fluoride (0.0025 mol) were introduced in the glass flask, in which benzene (0.0125 mol), *p*-cymene (0.0125 mol), and *n*-hexane (0.25 mol) were charged. After the reaction, which continued from 24 hr, the solution was quenched in water, extracted with ether, dried over calcium chloride, and analyzed by gas chromatography.

Radioactivity Measurements.—Radioactivity measurements were carried out with a Beckman LS-150 liquid scintillation system at room temperatures by an external channel ratio method. Dioxane containing the usual scintillators was used as a solvent. A counting efficiency of about 85% with a background of about 50 cpm was obtained.

Gas Chromatographic Analyses.—Analyses were carried out with a Hitachi Perkin-Elmer gas chromatograph Model F6D using a hydrogen flame ionization detector. Golay column HB-2000 (1, 45 m, i.d. 0.25 mm) coated with polypropylene glycol (Ucon oil 50-HB-2000 Poly) was used. The column temperature was 120° with dry nitrogen gas flow rate at approximately 1.1 at ml/min atmospheric pressure.

Registry No.—Boron fluoride, 7637-07-2; benzene, 71-43-2; ethyl-2-¹⁴C fluoride, 25636-50-4.

Acknowledgment.—The authors wish to thank Dr. Osamu Kurihara for his valuable advice on many of the experimental details.

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