[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. II. The Alkylation of Benzene by Olefins

BY J. H. SIMONS AND S. ARCHER

In a previous communication[1] we announced the successful alkylation of benzene using hydrogen fluoride as the condensing agent. The first successful alkylation of aromatic compounds by olefins was reported by Balsohn in 1879.[2] Since that time acidic substances such as sulfuric acid,[3] phosphoric acid,[4] and phosphorus pentoxide[5] have been used to effect such condensations. Hydrogen fluoride has been used as a promoter with boron fluoride in the alkylation of paraffins by olefins.[6]

Ipatieff[3] stated that in the case of the condensation reaction catalyzed by sulfuric acid, there were three competing reactions. These were, first, alkylation of the aromatic hydrocarbon, second, polymerization of the olefin, and, third, the reaction of the unsaturated compound with the acid to form an ester. Since it has been shown that hydrogen fluoride polymerizes olefins,[7] and also adds to double bonds,[8] we believe that similar side reactions also can take place in the case of alkylation catalyzed by hydrogen fluoride. However, under the conditions employed, no evidence was found for any reaction except alkylation. If polymerization or addition of hydrogen fluoride occurred, they were in relatively small amounts.

The reaction mixture after removal of the acid and subsequent drying, was always clear and almost colorless. Fractionation proceeded smoothly and efficiently in all cases, and no compounds boiling at temperatures between those of benzene and the alkylbenzenes were found. The olefins used were propylene, isobutene, pentene-2, trimethylethylene, and cyclohexene. All, except propylene, were prepared by dehydration of the proper alcohol. The alkylbenzenes formed were characterized by means of physical constants and by conversion to the monoacetamino derivative as described by Ipatieff and Schmerling.[9]

Experimental

General Method.—One to five mols of relatively dry hydrogen fluoride was distilled from the container through a water-cooled copper coil into a copper flask in an ice-bath. Two to five mols of benzene was then added and a rubber stopper inserted. This stopper carried an inlet and an outlet tube of copper and a copper stirrer provided with a mercury seal. One-half to one mol of olefin was then added slowly with stirring. The stirring was continued for three to five hours usually at 0°, but sometimes the reaction was allowed to warm to room temperature. The mixture was poured onto ice and neutralized with sodium carbonate. After washing the benzene layer with sodium carbonate solution, it was separated, dried with potassium carbonate or magnesium sulfate, and distilled. The product was then redistilled and a portion converted into the acetamino derivative. The yields and certain physical properties of the products are given in Table I.

Conclusions.—As indicated in a previous communication, hydrogen fluoride has been found to be useful as an agent for the alkylation of benzene by olefins. Although the reactions were performed using sufficient hydrogen fluoride to give two liquid layers, the reaction probably takes place in the hydrocarbon layer. The amount of hydrogen fluoride could be varied within wide limits without affecting the results, and other experiments which have been performed in this laboratory indicate that the reactions proceed rapidly with only sufficient hydrogen fluoride to form a saturated solution in the hydrocarbon.

As no great care was taken to ensure high yields and as the reactions were not studied to find the conditions for maximum yield, the yields obtained were surprisingly high. These probably could be increased to practically the theoretical by using greater care and larger reaction mixtures.

Extreme precautions to ensure anhydrous conditions were not taken. In some cases the reaction mixtures were exposed to moist laboratory air for considerable periods of time without affecting the results. Aqueous solutions of hy-

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[1] Simons and Archer, THIS JOURNAL, **60**, 986 (1938).

[2] Balsohn, *Bull. soc. chim.*, [2] **31**, 539 (1879).

[3] Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).

[4] Ipatieff, Pines and Komarewsky, *Ind. Eng. Chem.*, **28**, 222 (1936).

[5] Truffault, *Compt. rend.*, **202**, 1286 (1936).

[6] Ipatieff and Grosse, THIS JOURNAL, **57**, 1616 (1935).

[7] Fredenhagen, *Z. physik. Chem.*, **A164**, 176 (1933).

[8] Grosse and Linn, *J. Org. Chem.*, **3**, 26 (1938).

[9] Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

TABLE I

ALKYLATION OF BENZENE BY OLEFINS USING HYDROGEN FLUORIDE

Olefin	Product	Yield, %	B. p., °C.	Press., mm.	n^{20}	M. p., acetamino deriv., °C.
Propylene	Monoisopropylbenzene	84	149–150	730	1.4913–6	105–105.5
Isobutene	Mono-*t*-butylbenzene	44	166.5–168	728	1.4921	168–169.5
	Di-*t*-butylbenzene	41	77–78[a]			
Pentene-2[b]	Phenylpentane[c]	47	79–80	17	1.4883	119–120
Trimethylethylene	Mono-*t*-amylbenzene	21	71–72	12	...	140–142
	Di-*t*-amylbenzene	60	262–265	740	...	
Cyclohexene	Cyclohexylbenzene	62	234.5 7–8[a]	737	...	129–131

[a] Melting point. [b] Prepared from redistilled *s*-amyl alcohol: b. p. 117° (742 mm.), n^{20} 1.4083. The olefin boiled at 35.4° (742 mm.), n^{20} 1.3809. [c] This is probably a mixture of beta and gamma phenylpentanes. (n. b.) Propylene also reacted with naphthalene to give monoisopropylnaphthalene and probably a di- and triisopropylnaphthalene in good yields.

drofluoric acid undoubtedly can be used for some reactions.

Summary

Hydrogen fluoride has been found to be a very useful agent for the alkylation of benzene by olefins. Propylene, isobutane, pentene-2, trimethylethylene, and cyclohexene were used. Very good yields were obtained.

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Hydrogen Fluoride as a Condensing Agent. III. Alkylation of Aromatics with Aliphatic Halides

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In a previous communication[1] we have indicated the use of hydrogen fluoride to promote the reaction between benzene and alkyl halides. A more detailed account of reactions between aromatic compounds and alkyl halides can now be reported.

The use of aluminum chloride and other metallic halides to catalyze condensations between alkyl halides and aromatic compounds is very well known.[2] However, a search of the literature failed to reveal any instance wherein sulfuric or other acidic catalysts have effected such a condensation. It is worthy of note, therefore, that hydrogen fluoride can promote such a condensation.

When tertiary chlorides are used, only extremely mild conditions are required. The reaction proceeds smoothly at 0° and at atmospheric pressure. When secondary halides are employed, higher temperatures are necessary to bring about a reaction. At 25° a small amount of propylated benzenes was formed from the reaction between isopropyl chloride and benzene. Primary halides did not react detectably at either 0 or 25°. At higher temperatures, however, *n*-propyl bromide does react readily with benzene.

In addition to alkylation two other reactions might be expected. When metallic halides are used in reactions involving aromatic compounds, condensation of the rings occurs and resins and tars are formed. In these reactions using hydrogen fluoride no such residues were found. In another experiment reported from this Laboratory,[3] it was found that either *t*-butyl chloride or *t*-amyl chloride, when treated with hydrogen fluoride, produced a complicated mixture of higher boiling compounds. Fortunately in the presence of the aromatic compound in excess these reactions took place to a negligible extent if at all.

The halides used were isopropyl chloride, *t*-butyl chloride, *t*-amyl chloride and *n*-propyl bromide.

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(1) Simons and Archer, THIS JOURNAL, **60**, 986 (1938).

(2) N. O. Calloway, *Chem. Rev.*, **17**, 327 (1935).

(3) Simons, Fleming, Whitmore and Bissinger, THIS JOURNAL, **60**, 2267 (1938).