

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- <i>t</i> -butylbenzene	44	166.5-168	728	1.4921	168-169.5
	Di- <i>t</i> -butylbenzene	41	77-78 ^a			
Pentene-2 ^b	Phenylpentane ^c	47	79-80	17	1.4883	119-120
Trimethylethylene	Mono- <i>t</i> -amylbenzene	21	71-72	12	...	140-142
	Di- <i>t</i> -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 monoisopropyl-naphthalene and probably a di- and triisopropyl-naphthalene 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.

STATE COLLEGE, PENNA. RECEIVED SEPTEMBER 1, 1938

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

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

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In a previous communication¹ 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.

(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).

TABLE I
 ALKYLATION OF AROMATICS BY ALIPHATIC HALIDES USING HYDROGEN FLUORIDE

Halide	Product	Yield, %	B. p., °C.	Press., mm.	n_D^{20}	M. p. of acetamino deriv., °C.
<i>n</i> -Propyl ^a bromide	Propylbenzene ^b	48	150-153	740
Isopropyl chloride	Polyisopropylbenzene ^c	..	155-175	740	166
<i>t</i> -Butyl chloride	Mono- <i>t</i> -butylbenzene	10	167-170	740	1.4908	169-170
	Di- <i>t</i> -butylbenzene	60	77-78 ^d			
<i>t</i> -Amyl chloride	Mono- <i>t</i> -amylbenzene	41.5	71-74	12		139-140.5
	Di- <i>t</i> -amylbenzene	21.5	127-130	12		
<i>t</i> -Butyl chloride	<i>p</i> - <i>t</i> -Butyltoluene ^e	75	72-72.5	12	1.4919	163.5-164.5 ^f
			188	740		
<i>t</i> -Butyl chloride	Mono- <i>t</i> -butylnaphthalene ^g	46	142-143	14		
	Di- <i>t</i> -butylnaphthalene ^h	8	148 ^d			
	Di- <i>t</i> -butylnaphthalene	28	80-81 ^d			

^a This reaction was run in a copper bomb at 80°. ^b This was a mixture of 88% isopropylbenzene and 12% normal propylbenzene determined from the melting point 80-92° of a sulfonamide derivative. The technique of this identification is given in the following paper of this series. ^c This reaction proceeded very slowly at 25°; only a small amount of product was obtained, which distilled over a considerable range. The acetamino derivative was made of the highest boiling portion which is probably a polysubstituted benzene. ^d Melting point. ^e The aromatic used was toluene. ^f This is the melting point of *p*-*t*-butylbenzoic acid made from the product by oxidation with (1:2) nitric acid. Its determined neutral equivalent was 179, calcd. 178. ^g The aromatic used was naphthalene. It was dissolved in carbon tetrachloride for the reaction. ^h Two isomeric di-*t*-butylnaphthalenes were obtained. See Gump, *THIS JOURNAL*, **53**, 380 (1931).

The aromatic compounds employed were benzene, toluene and naphthalene.

Experimental

General Method.—The method used was similar to that reported in the second paper of this series.⁴ The reactions, however, usually required two to three times as long. Hydrogen chloride was evolved in the reactions using chlorides and this was tested for in the escaping gases with a bead of silver nitrate solution. The reactions were stopped when this test was negative. Table I gives the collected results of the experiments.

Conclusion.—Hydrogen fluoride has been found to be an unusually effective agent to promote the reaction between alkyl halides and aromatic compounds. The reaction has been found to be most rapid with tertiary halides and least rapid with primary halides. The yields are relatively high although no effort has been made to obtain high yields and no study has been made of the best conditions for the reactions. The yields probably could be greatly improved. The amount of hydrogen fluoride necessary is probably greater than when olefins are used but only because some

of it is lost in the escaping gas. Great care for the exclusion of moisture was not taken and small amounts of water apparently do not prevent the reaction.

Hydrogen fluoride has several advantages over the use of metallic halides for these reactions. Polymerization of the aromatic compounds is avoided and this results not only in higher yield but also in greater ease of separation and purification of the products. For aromatic compounds such as naphthalene that are solid at temperatures at which most of the reactions take place, a very convenient solvent (carbon tetrachloride) can be used with no apparent reaction between it and the other reagents. This solvent cannot be employed when aluminum chloride is used instead of hydrogen fluoride.

Summary

Hydrogen fluoride has been found to be an effective agent to promote the reaction between alkyl halides and aromatic compounds. The halides used were *n*-propyl bromide, isopropyl chloride, *t*-butyl chloride and *t*-amyl chloride, and the aromatic compounds were benzene, toluene and naphthalene.

(4) Simons and Archer, *THIS JOURNAL*, **60**, 2952 (1938).