[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride.[1] X. Condensation of Propylene with Aromatic Hydrocarbons

BY S. J. SLANINA, F. J. SOWA AND J. A. NIEUWLAND

Boron fluoride recently has been shown to function quite favorably as a catalytic agent in the condensation of olefins with phenols[2] and acids.[3,4] It was noted during this condensation with propylene that, whenever benzene was used as a solvent, appreciable quantities of a product boiling around 152° were isolated. This product proved to be cumene and can best be accounted for by considering the over-all reaction as a direct condensation of propylene with benzene, catalyzed by boron fluoride.

The purpose of this investigation was to study the catalytic effect of a number of inorganic or organic oxygen compounds which had been treated with boron fluoride, in alkylating several aromatic hydrocarbons. Although this study will be chiefly concerned with the use of propylene as the olefin and benzene as the aromatic hydrocarbon, other olefins and hydrocarbons will be considered.

Gustavson[5] prepared isopropylbenzene in a 34% yield by the reaction of isopropyl bromide with benzene in the presence of aluminum chloride. He also prepared higher derivatives by the same method.

By treating benzene with isopropyl alcohol and 80% sulfuric acid Meyer and Bernhauer[6] obtained mono-, di-, and triisopropylbenzene. A method directly related to the present work was that carried out by Berry and Reid.[7] They prepared isopropylbenzenes, up to and including the tetraisopropyl derivative, from propylene and benzene in the presence of aluminum chloride and with stirring at eight thousand revolutions per minute. In their runs the rate of absorption increased as propylation progressed. With monoisopropylbenzene it was double and with the tri- it was ten times what it was with benzene; 250 g. of triisopropylbenzene absorbed about 106 g. in twelve hours.

In this investigation ethyl acetate, ether, *p*-toluenesulfonic acid, sulfuric acid, the mono- and the trichloroacetic acids, salicylic acid, and phenol have been tried as condensation accelerators in conjunction with boron fluoride. In the runs with boron fluoride compounds of ether and of ethyl acetate no apparent condensation of propylene with benzene took place; while acetic acid, mono- and the trichloroacetic acids, each treated with boron fluoride, gave small but increasing yields of monoisopropylbenzene in the order given. These facts indicated that acidity had played an important part in these condensations. Consequently concentrated sulfuric acid with boron fluoride was tried as a catalyst and the result was surprising in that propylene was absorbed by the benzene with considerable evolution of heat, at the rate of over 45 g. of gas per mole of benzene per hour in the first hour under a pressure of 23 cm. of mercury above atmospheric. At that rate absorption is complete when the mixture is stirred at 950 revolutions per minute. It was found that the ratio by weight of mono- to diisopropylbenzene varies with the ratio by weight of boron fluoride to concentrated sulfuric acid. The absorption rate is little affected during the first hour by changes in temperature within the range zero to the boiling point of benzene. It was noted that deactivation of the catalyst slowly occurs. For a certain weight of acid the absorption during the second hour is approximately one-fourth that of the first. The previously used catalyst does not cause condensation of propylene with benzene. In these absorptions only traces of the triisopropyl derivative were present even when 90% of the benzene was converted to diisopropylbenzene. Very interesting is the fact that diisopropylbenzene propylates readily to the tri and tetra derivatives. Benzene in the presence of sulfuric acid–boron fluoride does not react with diisopropylbenzene even on warming with stirring.

Condensation of propylene with benzene occurs in the presence of phenol–boron fluoride. There is no destruction of the catalyst during the absorption period. In every run all isopropyl derivatives including the tetra were isolated.

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(1) For previous papers see Sowa, Hennion and Nieuwland, THIS JOURNAL, **57**, 709 (1935).

(2) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).

(3) Croxall, Sowa and Nieuwland, *ibid.*, **56**, 2054 (1934).

(4) Dorris, Sowa and Nieuwland, *ibid.*, **56**, 2689 (1934).

(5) Gustavson, *Ber.*, **11**, 1251 (1878).

(6) Meyer and Bernhauer, *Monatsh.*, **53-54**, 721 (1929).

(7) Berry and Reid, THIS JOURNAL, **49**, 3142 (1927).

Berry and Reid,[7] using aluminum chloride, report that of the diisopropylbenzenes in their condensations the meta compound seems to predominate, as does the symmetrical among the tri compounds. Although aluminum chloride and boron fluoride catalyze similarly in many reactions, in this condensation practically no meta compound is formed: approximately 98% of the diisopropylbenzene is the para and the remainder the ortho compound.

Butylene condenses very rapidly with benzene to yield various butylbenzenes. Ethylene does not work as well as does propylene with these catalysts. Further work will be carried on with addition of various olefins, and substituted olefins such as ethylene, vinyl chloride, crotonic acid, etc., to benzene.

Toluene propylates rather easily in the presence of sulfuric acid–boron fluoride to para-cymene as the first product of the reaction. Propylene absorption was not given sufficient time to obtain higher substituted derivatives of toluene.

Naphthalene condenses with propylene when sulfuric acid–boron fluoride is used as a catalyst.

Data for the various runs are given in Table I. In Table II are listed the physical constants of the isopropylbenzenes.

Experimental Part

A one-liter three-necked flask was equipped with an inlet tube extending to the bottom, a reflux condenser, and a mechanical stirrer geared to 950 revolutions per minute. A connection was made by means of a glass tube from the condenser to an apparatus by the aid of which a pressure in the system could be maintained. After sulfuric acid containing the catalyst was added to the flask, in order to avoid the expulsion of boron fluoride, the benzene which had been dried over calcium chloride was added by pouring carefully down the side of the flask. The stirrer was started, then propylene gas was passed through the mixture at such a rate that the pressure in the system was maintained at 23 cm. of mercury above atmospheric. Commercial propylene contains propane so consequently the system was allowed to blow off about every ten minutes in order to expel the accumulated propane. After sufficient time was allowed for the absorption, the contents of the flask was transferred to a separatory funnel. The acidl ayer was run off and the product was refluxed for one-half hour with 200 cc. of 20% sodium hydroxide solution. The cool mixture was separated, the product washed twice with water, dried over calcium chloride and distilled. Some compound of sulfuric acid which is not destroyed by refluxing with alkali, is present in the mixture for in almost every run on distillation of the mixture the compound decomposes with evolution of heat; some charring sets in and a little sulfur dioxide goes over. Except for the factors such as time, concentration of catalyst, temperature, and pressure all other runs were made in a manner similar to that described above. All mixtures were refluxed with excess alkali.

TABLE I

Moles of benzene	Compound	Grams	BF_3, g.	Temp., °C.	Propylene absorbed	Absorption time, hrs.	Benzene recov., g.	Mono, g.	Di, g.	Tri, g.	Residue, g.
1.93	$CH_3CO_2C_2H_5$	9.6	7.4	25		3.5	148	Trace			
1.93	$C_2H_5OC_2H_5$	8.8	8.2	25		5	146	None			
1.93	CH_3CO_2H	8	9	25		3.5	145	2			
1.93	CH_2ClCO_2H	16	1.5	25		3.5	175	9			
1.93	CCl_3CO_2H	29	1.5	25		3.5	171	17			
1.93	H_2SO_4	17	2.4	^{a}	66	1	46	109	34		7
1.93	H_2SO_4	17	2.6	^{a}	67	1	53	103	40		5
1.93	H_2SO_4	17	5.1	^{a}	68	1	45	100	52		5
1.93	H_2SO_4	34	10.1	^{a}	66	1	47	90	48		4
1.93	H_2SO_4	17	2.5	^{a}	88	9.5	36	102	80		4
1.93	H_2SO_4	49.5	8.5	^{a}	140	1.5	10	34	190		10
1.93	H_2SO_4	50.3	9.7	^{a}	188	4	0	20	237	Trace	6
1.93	H_2SO_4	17	1	1	54.4	1	87	53	41		4
1.93	H_2SO_4	41.8	9.7	1	115	3	0	0	128	Trace	10
1.93	H_2SO_4	17.7	2.4	35	52	7.5	67	92	21		5
1.93	Oleum (15%)	21	1.5	^{a}	77	1	27	76	105		9
2.3	Phenol	17	3	^{a}	43	1.2	180	36	8	15	4
6.2	Phenol	6	4	^{a}	451	...	175	173	221	126 Tetra 88	

[a] Temperature allowed to rise to maximum in the exothermic reaction.

TABLE II

Isopropyl derivative of benzene	B. p., °C.	d^{25}_{25}	$n^{25}D$
Mono	151 (742 mm.)	0.8574	1.4879
Di	204.5 (736 mm.)	.8580	1.4881
Tri	237.0 (736 mm.)	.8599	1.4896
Tetra	M. p. 119		

The propylene used in this investigation was obtained from the Carbide and Carbon Chemicals Corporation and is very well suited for this purpose.

A portion of the fraction boiling at 204.5° was oxidized with hot nitric acid (1:3). The solid product, which sublimes above 300° without melting, was warmed with methyl alcohol in the presence of hydrogen chloride gas.

The resulting ester crystallized in flat plates melting at 140°, which is the melting point of the dimethyl ester of terephthalic acid.

The tri- and tetra-isopropylbenzenes were made from the di-isopropylbenzene. The tri compound is the 1,3,4-tri-isopropylbenzene. The distillation was carried up to 240°. On cooling the residue a white solid appeared. It was recrystallized from alcohol and the needles melted at 119°.

Anal. Calcd.: C, 87.72; H, 12.27; mol. wt., 246. Found: C, 86.48; H, 12.38; mol. wt., 244.

This compound seems to be identical with the 1,2,4,5-tetraisopropylbenzene prepared by Berry and Reid.[7]

The fraction of propylated toluene boiling at 175° was heated with nitric acid (1:3). Toluic acid was separated from the phthalic acid by means of ether. The ether extract yielded crystals which melted at 177°; *p*-toluic acid melts at 177°.

With the sulfuric acid–boron fluoride catalyst naphthalene dissolved in carbon tetrachloride reacted with propylene to give a compound boiling at 260–270°. β-Isopropylnaphthalene boils at 265°.

Summary

Mono-, di-, tri-, and tetraisopropyl derivatives of benzene have been prepared by the condensation of propylene with benzene.

The yields of the mono- and various poly-isopropyl derivatives of benzene can be controlled.

It has been found that acidity has a great influence upon the rate of condensation and is directly proportional to the acidity of the catalyst carrier.

Aluminum chloride promotes the formation of *m*-diisopropylbenzene by the condensation of propylene with benzene while boron fluoride gives the *p*-diisopropylbenzene.

Other olefins and cyclic compounds can be used.

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Organic Reactions with Boron Fluoride. XI. The Condensation of Propylene with *m*- and *p*-Hydroxybenzoic Acids

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In a previous article[1] it was shown that propylene condenses with salicylic acid in the presence of boron fluoride to form isopropyl salicylate and nuclear alkylated esters of salicylic acid.

The purpose of this work was to investigate the condensation of propylene with *m*- and *p*-hydroxybenzoic acids.

The condensation of propylene with *p*-hydroxybenzoic acid gave the following products: 4-isopropoxybenzoic acid, isopropyl 4-isopropoxybenzoate, and isopropyl 3-isopropyl-4-isopropoxybenzoate. The course of this condensation can be considered to take place as follows. First, the etherification of the hydroxyl group and, second, the esterification of the carboxyl group. This is supported by the fact that during the condensation 4-isopropoxybenzoic acid is isolated but no isopropyl *p*-hydroxybenzoate. To account for the nuclear alkylated product there are three possibilities: (1) the rearrangement of the oxy isopropyl group to the benzene nucleus, (2) the rearrangement of the carboxy isopropyl group to the benzene nucleus, and (3) direct nuclear condensation of propylene. Reaction one is supported by the fact that the main part of the rearrangement product of *p*-isopropoxybenzoic acid is 4-hydroxy-3-isopropylbenzoic acid, which seems to indicate that reaction two takes place mostly from oxygen to oxygen. The oxygen to carbon rearrangement as outlined in reaction two is undoubtedly the minor part. Reaction three is also possible as is indicated by the condensation of propylene with anisole.[2]

The condensation of propylene with *m*-hydroxybenzoic acid gave the following products: 3-isopropoxybenzoic acid, isopropyl 3-isopropoxybenzoate, isopropyl 4-isopropyl-3-isopropoxybenzoate and a small amount of isopropyl *m*-hydroxybenzoate. The course of the condensation from the above products probably results in etherification and esterification simultaneously. The alkylation can occur by the rearrangement of either the oxy isopropyl group or the carboxy isopropyl group, as is shown by the fact that both 3-isopropoxybenzoic acid and isopropyl *m*-hydroxybenzoic acid rearrange to give as the main product 3-hydroxy-4-isopropylbenzoic acid. This also does not eliminate the direct nuclear condensation of propylene with *m*-hydroxybenzoic acid.

From a previous article[1] and the present in-

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[1] Croxall, Sowa and Nieuwland, THIS JOURNAL, **56**, 2054 (1934).

[2] Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).