

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

ORGANIC REACTIONS WITH BORON FLUORIDE. II. THE REARRANGEMENT OF ALKYL PHENYL ETHERS

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The rearrangement of allyl and alkyl phenyl ethers has been a subject of study before and a number of isolated cases reported. Claisen,¹ by heating certain O-allyl aryl ethers to a high temperature, transformed them into the isomeric nuclei substituted phenols (C-allyl phenols). If the alkyl group is substituted for an allyl group, isomerization does not take place under the influence of heat, the presence of inorganic substances being necessary in most cases. In order to explain the substituted phenols obtained by Koenigs² and Schrauth and Quasebarth,³ Niederl and Natelson⁴ treated *o*-cresyl di-isobutyl ether with zinc chloride and hydrochloric acid. They also studied the action of a mixture of concentrated sulfuric acid and glacial acetic acid on saturated alkyl phenyl ethers, obtaining substituted phenols.

The purpose of the following investigation is to study the action of boron fluoride as an agent in the rearrangement of alkyl aryl ethers, to demonstrate its advantages as such, and to show that the products obtained by this method follow the same rules as those products obtained by Niederl and Natelson.⁴

Experimental

Preparation of Alkyl Phenyl Ethers.—One mole of phenol or cresol was weighed in a liter flask, fitted with a reflux condenser and a dropping funnel. A sufficient amount of water was added to 59 g. (excess) of potassium hydroxide to make a thick mixture, and this was added to the phenol. The whole mass was heated until solution became complete; 125 g. (excess) of isopropyl bromide was added slowly while shaking and warming. After all of the bromide was added, the contents were refluxed for one and a half hours, then poured into 400 cc. of water to dissolve the sodium bromide formed. The oil which separated at the top was washed several times with 10% sodium hydroxide solution, and finally with water. The oil was then dried over calcium chloride and distilled; yields from 50 to 75% were obtained.

Rearrangement of Alkyl Phenyl Ethers.—The procedure for the rearrangement of alkyl phenyl ethers is very nearly uniform and may be illustrated by the rearrangement of isopropyl *m*-cresyl ether.

Ninety-eight grams of the ether was weighed into a 500-cc. flask fitted with a three-holed stopper. A thermometer and an inlet tube were inserted below the surface of the liquid. Boron fluoride gas was passed into the ether. The preparation of the boron

¹ Claisen, *Ber.*, **45**, 357 (1912); *ibid.*, **58**, 275 (1925); *ibid.*, **59**, 2344 (1926); *Z. angew. Chem.*, **36**, 478 (1923).

² Koenigs and Carl, *Ber.*, **24**, 3889 (1891).

³ Schrauth and Quasebarth, *ibid.*, **57**, 856 (1924).

⁴ Niederl and Natelson, *THIS JOURNAL*, **53**, 1928 (1931).

fluoride followed the procedure of Bowlus and Nieuwland.⁵ The temperature ranged from 27 to 43° when 3 g. of boron fluoride was added. The absorption was stopped and the mixture, which had a reddish tinge, was shaken vigorously. The temperature gradually went to 75° and the solution became dark red in color. The flask was heated to 85° and then shaken for about five minutes or allowed to stand overnight. At this point the boron fluoride gas was given off quantitatively. The solution was placed in a 500-cc. separatory funnel and washed once with 150 cc. of water and then extracted with 10% potassium hydroxide solution. The alkali insoluble layer was separated and washed with water until free from alkali. This was the reclaimed ether. The alkali-soluble layer was kept cool and neutralized with concentrated hydrochloric acid. Two layers appeared. The oily layer was separated and the other layer extracted with ether. The oily layer and the ether extract were combined. The ether was removed and the residue subjected to several fractionations.

From 98 g. of the ether, 63 g. of rearranged product was obtained, and 8 g. of the unchanged ether. This is a 64% yield based on the total quantity of ether used or 72% yield when the reclaimed ether is allowed to enter the calculations.

TABLE I
ETHERS AND REARRANGED PRODUCTS

	Ether	B. p., °C.,	d_4^{20}	n_D^{20}	Taken, g.
1	Isopropylphenyl	178	0.975	1.4992	34
2	Isopropyl <i>o</i> -cresyl	193	.953	1.5040	97
3	Isopropyl <i>m</i> -cresyl	194	.931	1.4959	98
4	Isopropyl <i>p</i> -cresyl	194	.927	1.4952	69

REARRANGED PRODUCTS						
	Rearranged product	Yield, g.	%	B. p., °C.,	d_4^{25}	n_D^{25}
1	<i>o</i> -Isopropylphenol	22	64.7	212-214	1.004	1.5310
2	2-Methyl-4-isopropylphenol	51	52.5	231-235	0.975	1.5230
3	3-Methyl- <i>x</i> -isopropylphenol	63	64.2	230-236	.989	1.5275
4	4-Methyl-2-isopropylphenol	36	52.2	233-236	.982	1.5270

Discussion

The compounds which appear in this article have been reported previously and the structures established, with the exception of the rearranged product from isopropyl *m*-cresyl ether. The position of the isopropyl group in the ring is at present being studied at New York University.⁴

The method described in this investigation should be rather desirable: first, because never more than thirty-five minutes was required to complete a rearrangement studied. Second, the boron fluoride gas was easily recovered by merely heating the mixture. The temperature at which the gas was evolved varied from 85 to 150° for the different phenols. The amount of boron fluoride required for these rearrangements varied from one to five grams. When the minimum amount was used, warming and shaking were necessary.

The above ethers could be rearranged spontaneously by simply adding an excess of boron fluoride and allowing the temperature to rise.

⁵ Bowlus and Nieuwland, THIS JOURNAL, 53, 3835 (1931).

Solvents are not necessary but in certain cases they increase the yield. At present, an investigation regarding solvent action and the preparation of a series of new compounds of various phenolic ethers is being studied in this Laboratory.

Summary

1. The rearrangement of a series of alkyl phenyl ethers has been accomplished by the use of boron fluoride.
2. The boron fluoride can be recovered quantitatively.
3. The time required for the rearrangement of alkyl phenyl ethers has been materially shortened by this process.

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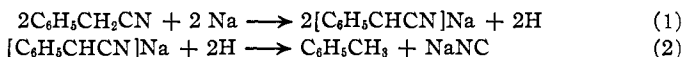
THE BEHAVIOR OF PHENYLACETONITRILE AND ALPHA-PHENYLBUTYRONITRILE WITH SODIUM ETHYLATE¹

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The isolation of the pure alkali salts of phenylacetonitrile and α -phenylbutyronitrile by Rising in collaboration with Zee,^{2a} Muskat and Lowe^{2b} and Braun,^{2c} and of the former nitrile by Upson,³ involved the treatment of the nitriles with the alkali metals or amides. As observed by E. von Meyer⁴ and his co-workers, and by Upson, and shown quantitatively for phenylacetonitrile by Braun, the reaction of the nitriles with sodium takes the course



The use of sodamide instead of sodium incurs no reduction of the salts.

It was suggested earlier^{2a} that sodium ethylate might prove to be a useful reagent for obtaining the salts of these and other nitriles. The present paper describes the behavior of phenylacetonitrile and α -phenylbutyronitrile with solid sodium ethylate in dry boiling ether in an atmosphere of nitrogen. The ethylate has been used successfully in a great number of condensation reactions of nitriles⁵ and the intermediate formation of sodium salts of the nitriles used is ordinarily assumed. We planned to

¹ The work here described forms part of the dissertation of K. T. Swartz, presented in partial fulfilment of requirements for the doctorate degree at the University of Chicago.

² (a) Rising and Zee, *THIS JOURNAL*, **49**, 541 (1927); **50**, 1699 (1928); (b) Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929); (c) Rising and Braun, *ibid.*, **52**, 1069 (1930).

³ Upson, Maxwell and Parmelee, *ibid.*, **52**, 1971 (1930).

⁴ Wache, *J. prakt. Chem.*, **39**, 245 (1889); von Meyer, *ibid.*, **52**, 114 (1895), etc.

⁵ Higson and Thorpe, *J. Chem. Soc.*, **89**, 1455 (1906); Avery and Upson, *THIS JOURNAL*, **30**, 600 (1908); Daughters, *ibid.*, **39**, 1927 (1917), and others.