

8.50% nitrogen (calcd., 8.31%). The benzyl ether melted at 123° and showed 8.94% nitrogen (calcd., 8.86%).

**Preparation of 4,4'-Dimethyl-2-ethoxyazobenzene.**—1-Methyl-3-hydroxy-4 nitrobenzene<sup>29</sup> was converted to the ethyl ether through the silver salt.<sup>30</sup> This was reduced by boiling with iron filings and dilute acetic acid. The amino ether after extraction with petroleum ether was coupled with *p*-nitrosotoluene<sup>31</sup> as outlined above. The product was extracted with petroleum ether and was crystallized from alcohol. Analysis showed it to contain 11.14% nitrogen; calcd., 11.02%; melting point, 76°.

Attempts to prepare the benzyl ethers of the ortho and meta hydroxy compounds and the ethyl ether of the meta compound by similar condensations led to tars.

**Examination of the Alkali-insoluble Rearrangement Compound.**—This material was crystallized from benzene, acetic acid and 75% alcohol as orange scales which melted at 208–210° with apparent decomposition. Analysis showed C, 74.66; H, 6.38; N, 12.28; calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O: C, 74.30; H, 6.24; N, 12.39. The molecular weight, observed cryoscopically in camphor, was 190 (calcd. 226). The observed value is too low, but the accuracy of the method is only 10%. At least the compound is not a polymer of a substituted azobenzene.

The benzoate of the alkali-insoluble compound melted at 121–122° and showed a nitrogen content of 8.36%; (calculated for the benzoate of a dimethyl azobenzene containing one hydroxyl group, 8.48%).

(29) Schultz, *Ber.*, **40**, 4322 (1907).

(30) Staedel and Kolb, *Ann.*, **259**, 224 (1890).

(31) Bamberger and Brady, *Ber.*, **33**, 274 (1900).

The alkali-insoluble compound was reduced by iron filings and acetic acid. The only reduction product which could be identified was *p*-toluidine, which was present in large amount.

### Summary

1. A new method of synthesizing some unsymmetrical methylazobenzenes has been developed.

2. The well-known method of preparation of nitrosobenzene from nitrobenzene through the intermediate phenylhydroxylamine has been simplified and improved.

3. Some methyl substituted azoxybenzenes have been subjected to the Wallach rearrangement and the following observations have been made. (a) If the para positions are not filled by substituents the hydroxyl group will appear in the para position. (b) In the cases of mono-ortho and mono-meta methylazoxybenzenes the hydroxyl group enters the para position of the substituted ring. (c) If both para positions are filled, two products are obtained. One of them is soluble in alkali and the other is not. They may be 3-hydroxy-4,4'-dimethylazobenzene and 4-methyl-4'-hydroxymethyl-azobenzene.

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## Organic Reactions with Boron Fluoride.<sup>1</sup> XII. The Preparation of Esters of Aromatic Acids

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In an earlier paper<sup>2</sup> the preparation of esters of aliphatic acids was described. The purpose of the present investigation is to extend the study of this process to the formation of esters of aromatic acids and to consider the effect of various factors upon the yield of the esters.

The yield of ester increases as the quantity of boron fluoride used is increased until a maximum yield of ester is reached. The quantity of boron fluoride beyond this point is ineffective and in certain cases is deleterious to the quantity of ester formed. The amount of boron fluoride necessary to give a maximum yield is dependent upon the nature of the substituent in the benzene nucleus. For example, with benzoic acid a maximum yield of 85% is obtained when 14 g. of boron fluoride is

(1) For previous paper see, Croxall, Sowa and Nieuwland, *This Journal*, **57**, 1549 (1935).

(2) Hinton and Nieuwland, *ibid.*, **54**, 2017 (1932).

used, while a maximum is reached only after 70 g. of the same agent is used for certain substituted benzoic acids, compared on a one-half mole acid basis. With *p*-aminobenzoic acid it is necessary first to add equimolar quantities of boron fluoride before any ester is formed, the maximum of 53% being reached when three moles of boron fluoride is used for each mole of acid. The reluctance of the first mole of boron fluoride to act as an esterifying agent is undoubtedly due to the formation of a stable coördinate covalent compound between the agent and the nitrogen of the amino group in the *p*-aminobenzoic acid. It is also worthy of note that methyl anthranilate can be produced in a yield of 85% by employing two moles of boron fluoride for each mole of acid. Here again the first mole of boron fluoride is ineffective toward ester formation.

TABLE I

Acid	Moles	Alcohol	Moles	BF <sub>3</sub> , G.	Time of reflux, hours	Yield of Ester G.	%	Ester B. p., °C.
Benzoic	0.5	Methyl	1.0	14.0	0.5	58.0	85.3	196
Benzoic	.5	Isopropyl	1.0	9.6	.83	49.2	60.0	208
Benzoic	.5	<i>n</i> -Butyl	1.2	18.6	.83	77.3	86.8	248
Benzoic	.5	Isobutyl	1.0	13.0	.83	72.2	81.1	235
Benzoic	.5	<i>s</i> -Butyl	1.0	14.0	.83	30.0	26.5	232
Benzoic	.5	<i>t</i> -Butyl	1.0	14.0	.83	Trace	0.0	
<i>p</i> -Nitrobenzoic	.125	Methyl	2.19	17.5 <sup>a</sup>	3.0	22.4	100.0	M. 93
<i>p</i> -Nitrobenzoic	.125	Methyl	2.19	3.4 <sup>a</sup>	5.0	21.1	93.2	
<i>p</i> -Aminobenzoic	.25	Methyl	4.38	56.6 <sup>a</sup>	3.0	20.0	53.0	
<i>p</i> -Aminobenzoic	.25	Methyl	4.38	68.0 <sup>a</sup>	3.0	15.2	40.3	
<i>o</i> -Aminobenzoic	.5	Methyl	1.6	68.0	4.5	64.5	85.4	139 (19 mm.)
<i>o</i> -Chlorobenzoic	.125	Methyl	2.19	9.5 <sup>a</sup>	3.0	15.0	70.6	119 (19 mm.)
<i>o</i> -Hydroxybenzoic	.5	Methyl	2.1	66.0	1.25	42.0	55.0	224
<i>o</i> -Hydroxybenzoic	.5	Isobutyl	1.0	17.0	2.0	72.0	74.2	135 (17 mm.)
<i>p</i> -Nitrobenzoic	.125	Methyl	2.19	3.4 <sup>a</sup>	6.0	20.0	88.3	

<sup>a</sup> Boron fluoride added as ether-boron fluoride compound.

The time of reflux shows similar effects upon the yield of ester to that just described. The time required to give a maximum yield varied from fifteen minutes for benzoic acid to five hours for some of the substituted benzoic acids.

In general it is considerably more difficult to form esters of substituted benzoic acids than of aliphatic<sup>2</sup> acids by the use of boron fluoride. Greater quantities of boron fluoride and larger time of reflux are necessary for aromatic acids.

### Experimental Part

**Materials Used.**—The boron fluoride was prepared by either the reaction of calcium fluoride (200 g.), boric oxide (100 g.), and sulfuric acid (650 cc.), or by the reaction of sodium fluoborate (327 g.), boric oxide (35 g.) and sulfuric acid (300 cc.). The latter is definitely better than the former method in at least two ways, namely, no caking and a more readily controllable gas flow.

The melting points of benzoic, *o*-chlorobenzoic (136°), *o*-hydroxybenzoic (156°), *o*-aminobenzoic (143°), *p*-aminobenzoic (185°) and *p*-nitrobenzoic (233°), checked well with those reported in the literature. The alcohols used were dried with calcium oxide.

**Procedure.**—One quarter mole of the acid to be esterified was weighed in a 500-cc. round-bottomed flask equipped with an inlet and outlet tube. To this acid various quantities of alcohol and boron fluoride were added (see Table I). The boron fluoride was passed directly into the alcohol-acid solution or added in the form of the ether-boron fluoride compound. The flask was

then connected with a reflux condenser and warmed for various periods as indicated in Table I.

The unreacted acid and boron fluoride were removed by neutralizing the contents with a 10% solution of sodium carbonate. It was found convenient in a few cases to remove the excess alcohol by distillation before the sodium carbonate treatment. The ester was either removed directly or extracted with ether or carbon tetrachloride. The solvent was removed by distillation and the ester fractionated. When the ester was a solid it was recrystallized.

The results of a series of experiments are given above in Table I. In most cases the highest yields obtained are reported and the conditions represent the optimum conditions to give a maximum yield.

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### Summary

The process for the formation of esters of aromatic acids using boron fluoride as the agent has been described.

The effects of various substituents and of per cent. boron fluoride and time of reaction have been discussed.

Yields of 100 and 85% have been reported for the methyl ester of *p*-nitro- and *o*-aminobenzoic acids, respectively.

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