with 15 cc. of concentrated sulfuric acid and the mixture allowed to stand for forty-eight hours at room temperature, the product obtained proved to be unchanged butene, a small amount of diphenylethylene, and water-soluble sulfonated products. No triphenylmethylhydrindene could be isolated. When a similar mixture was allowed to stand for six weeks, only about 0.1 g. of the hydrindene was obtained, although Bergmann and Weiss[19] state that the hydrindene can be readily prepared from the butene by means of sulfuric acid.

## Summary

1.   The quantitative absorption spectra of the following compounds have been obtained: asymmetrical diphenylethylene, methyldiphenylcarbinol, methyldiphenylchloromethane, methyldiphenylchloromethane plus stannic chloride, and triphenylchloromethane plus stannic chloride.

2.   The preparation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and stannic chloride has been investigated and the effect of polar and non-polar solvents noted.

3.   A reaction mechanism involving quinoidation has been postulated to explain the formation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and also the formation of 4-phenyltetraphenylethylene from tetraphenylethylene dichloride and phenylmagnesium bromide.

[19] Bergmann and Weiss, *Ann.*, **480**, 49 (1930).

ANN ARBOR, MICHIGAN

---

## ORGANIC REACTIONS WITH BORON FLUORIDE. III.   THE CONDENSATION OF PROPYLENE WITH PHENOL

BY F. J. SOWA, H. D. HINTON AND J. A. NIEUWLAND

The condensation of unsaturated hydrocarbons with phenols in the presence of condensing agents has been studied by various investigators. Amylene, di-isobutylene,[1] cyclohexane,[2] styrene,[3] isoprene,[4] acetylene,[5] and propylene[6,7] have been condensed with phenol or phenolic type compounds to yield substituted phenols, phenyl ethers or substituted phenyl ethers.

In an earlier publication a study was made of the rearrangement of isopropyl phenyl and cresyl ethers[8] in an attempt to determine the position occupied by the isopropyl group after the rearrangement.   The results

[1] Niederl and Natelson, THIS JOURNAL, **53**, 272 (1931).

[2] Liebermann and Hartmann, *Ber.*, **25**, 957 (1892).

[3] König, *ibid.*, **24**, 3889 (1891).

[4] Claisen, German Patent 374,142, 1923.

[5] Wenzke and Nieuwland, THIS JOURNAL, **46**, 177 (1924).

[6] Howard and Blagden, British Patent 214,866, 1923.

[7] Sowa, Sc. M. Dissertation, University of Notre Dame, 1930.

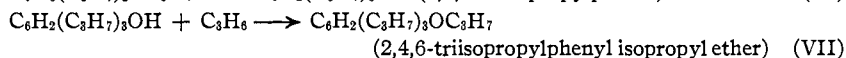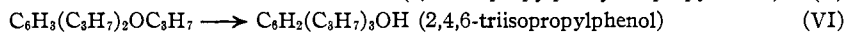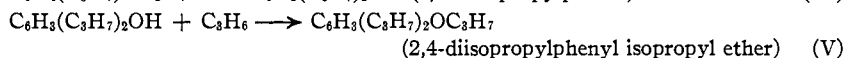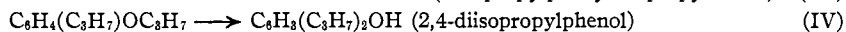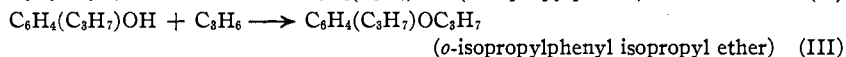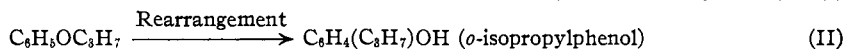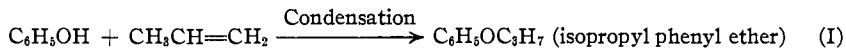[8] Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 2019 (1932).

obtained by using boron fluoride were shown to be similar to those previously reported.[9]

Gasselin[10] studied the action of boron fluoride on phenol and found that one mole of boron fluoride was absorbed by two moles of phenol. The boron fluoride was evolved quantitatively on heating, and the phenol remained unchanged.

Butlerow and Goriainow[11,12] stated that boron fluoride polymerized propylene to products more complex than a trimer even at ordinary temperatures. No such action was noted throughout the present work. However, the experimental conditions are entirely different in each case.

## Theoretical Part

The action of propylene on phenol in the presence of boron fluoride may be represented by the following equations as taking place through a series of condensations and subsequent rearrangements.

$$C_6H_5OH + CH_3CH{=}CH_2 \xrightarrow{\text{Condensation}} C_6H_5OC_3H_7 \text{ (isopropyl phenyl ether)} \quad \text{(I)}$$

$$C_6H_5OC_3H_7 \xrightarrow{\text{Rearrangement}} C_6H_4(C_3H_7)OH \text{ (o-isopropylphenol)} \quad \text{(II)}$$

$$C_6H_4(C_3H_7)OH + C_3H_6 \longrightarrow C_6H_4(C_3H_7)OC_3H_7$$
$$\text{(o-isopropylphenyl isopropyl ether)} \quad \text{(III)}$$

$$C_6H_4(C_3H_7)OC_3H_7 \longrightarrow C_6H_3(C_3H_7)_2OH \text{ (2,4-diisopropylphenol)} \quad \text{(IV)}$$

$$C_6H_3(C_3H_7)_2OH + C_3H_6 \longrightarrow C_6H_3(C_3H_7)_2OC_3H_7$$
$$\text{(2,4-diisopropylphenyl isopropyl ether)} \quad \text{(V)}$$

$$C_6H_3(C_3H_7)_2OC_3H_7 \longrightarrow C_6H_2(C_3H_7)_3OH \text{ (2,4,6-triisopropylphenol)} \quad \text{(VI)}$$

$$C_6H_2(C_3H_7)_3OH + C_3H_6 \longrightarrow C_6H_2(C_3H_7)_3OC_3H_7$$
$$\text{(2,4,6-triisopropylphenyl isopropyl ether)} \quad \text{(VII)}$$

By progressive reactions of this type, substituted phenols and phenyl ethers of increasing molecular weight are gradually built up. These reactions may be controlled to a certain extent by varying the temperature, per cent. of boron fluoride, time of contact of ethers with the boron fluoride and quantity of propylene added. Temperature control is very important. For example, at 0°, reaction (I) predominates, and reaction (II) takes place to some extent. At 20°, the product of (I) is present only in a negligible quantity. The products of reactions (II) and (V) predominate at this temperature, while the products of (III), (IV), (VI) and (VII) are present in much smaller quantities. However, when the reaction took place at 40° the only products isolated were the substituted phenol and phenyl ether in reaction (VII). The latter was obtained in good yield while the former was present in only a small amount. Attempts to carry the condensation of propylene with phenol further have failed.

[9] Niederl and Natelson, This Journal, **53**, 1928 (1931).

[10] Gasselin, *Ann. chim. phys.*, [7] **3**, 67 (1894).

[11] Butlerow, *Ann.*, **189**, 44 (1877).

[12] Goriainow and Butlerow, *ibid.*, **169**, 147 (1873).

Since 2-isopropylphenyl isopropyl ether, 2,4-diisopropylphenyl iso-propyl ether and 2,4,6-triisopropylphenyl isopropyl ether have not been reported it was necessary to undertake the proof of their respective structures. The corresponding substituted phenols will be discussed in a later paper on rearrangements. The product in condensation (I) was shown to be identical with isopropyl phenyl ether by the synthesis of the latter according to the method of Williamson.[13] It has been reported[8] that iso-propyl phenyl ether rearranges to *o*-isopropylphenol in the presence of boron fluoride. In the same report it was shown that isopropyl *o*-cresyl and isopropyl *p*-cresyl ethers rearrange to 2-methyl-4-isopropylphenol and 4-methyl-2-isopropylphenol, respectively. By synthesizing 2-iso-propylphenyl isopropyl ether from *o*-isopropylphenol, it was shown to be identical with the product of reaction (III). The same procedure was carried out to prove the products in reactions (V) and (VII). It should be noted in reaction (VI) that the only active position to which the isopropyl group can rearrange is the 6-position, thereby forming the symmetrical tri-isopropylphenol. (The Zeisel reaction was used with each ether to show the nature of the alkyl group attached to the oxygen.)

## Experimental Part

Isopropyl Phenyl Ether.[14]—One mole of phenol was weighed in a three-necked round-bottomed flask; 5 g. of boron fluoride (prepared as previously described[15]), and 100 g. of benzene were added to the phenol. The flask was fitted with a mechanical stirrer and immersed in an ice brine bath, so as to keep the temperature between $-2°$ and $2°$. Propylene was passed in at the rate of 10 g. per hour of propylene. The absorption was carried out under a pressure of 7.6–10.2 cm. of mercury. When 21 g. (0.5 mole) of propylene had been added the flow of the gas was stopped. The mixture was transferred to a separatory funnel and 100 cc. of cold 10% potassium hydroxide solution was added. Two layers separated. The upper layer was washed with 20-cc. portions of the 10% potassium hydroxide solution until a portion of the alkali extract, upon acidifying with hydrochloric acid, gave no evidence of phenol separating. The benzene extract of the upper layer was dried over calcium chloride or anhydrous potassium carbonate. The benzene was removed by distillation. The second fraction was shown to be isopropyl phenyl ether; 37 g. of the product was isolated. This corresponds to a 54% yield based on the propylene used; b. p. 178°; sp. gr. 0.975 (20°); $n_D^{20}$ 1.4992.

*o*-Isopropylphenol.[16]—The alkali extracts obtained from the above mixture, under isopropyl phenyl ether, were combined and acidified either by passing a stream of carbon dioxide into it until no more phenol separated or by the addition of hydrochloric acid. Two layers appeared. The phenol layer was separated and the aqueous portion extracted once with ether. The latter was added to the phenol layer and washed with 100 cc. of cold water. After separating and drying the ether layer over anhydrous potassium carbonate it was fractionated; 28 g. of *o*-isopropylphenol was obtained, a

13 Williamson, *J. Chem. Soc.*, **4**, 106 (1851).

14 Perkin, *ibid.*, **69**, 1187, 1250 (1896).

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

16 Spica, *Gazz. chim. ital.*, **9**, 442 (1879).

yield of 41% based on the propylene used; 66 g. of phenol was recovered, b. p. 212–214°; sp. gr. 1.0140 (20°); $n_D^{20}$ 1.5310.

*o*-**Isopropylphenyl Isopropyl Ether.**—The method used in the preparation of this compound was the same as in the preparation of isopropyl phenyl ether with two exceptions. The temperature was maintained between 13 and 17° and two moles of propylene was added for one mole of phenol used.

| Fraction | I | II | III |
|---|---|---|---|
| B. p., °C. | 177–180 | 222–230 | 238–250 |
| Grams | 6 | 74 | 20 |

Fraction (I) was identified as isopropyl phenyl ether. It was shown in an earlier paper[17] that isopropyl phenyl ether is rearranged to *o*-isopropylphenol by means of boron fluoride. *o*-Isopropylphenol was treated with potassium hydroxide, then with isopropyl bromide. The compound thereby obtained appears to be identical with fraction (II). Fraction (III) appears to be 2,4-di-isopropylphenyl isopropyl ether and will be discussed under the preparation of that compound. The 74 g. of fraction (II) corresponds to a 41% yield based on the propylene used; b. p. 225–227°; sp. gr. 0.9192 (25°); $n_D^{25}$ 1.4948; calcd. mol. wt. 178.1; found, 176.0.

**2,4-Di-isopropylphenyl Isopropyl Ether.**—Since the product of the reaction served as an excellent solvent and at the reaction temperature the phenol–boron fluoride mixture was liquefied at the start of the absorption, no solvent was added; 3.5 g. of boron fluoride was passed into each mole of phenol. The temperature of the mixture did not rise above 22° at any time during the reaction. The absorption of propylene took place under a pressure of 20 cm. of mercury. After one mole of propylene had been added the mixture was treated as described under isopropyl phenyl ether. The fractions isolated were

| | Alkali Soluble | | | Alkali Insoluble | |
|---|---|---|---|---|---|
| Fraction | B. p., °C. | G. | Fraction | B. p., °C. | G. |
| I | 213–220 | 44 | I | 220–230 | 5 |
| II | 230–240 | 12 | II | 240–250 | 41 |
| III | 240–256 | 10 | III | 258–265 | 18 |

Fraction (I) under alkali soluble was identified as *o*-isopropylphenol. Further work is being done on Fractions (II) and (III). Fraction (I) under alkali insoluble is *o*-isopropylphenyl isopropyl ether. Fraction (II) was proved by synthesis to be 2,4-di-isopropylphenyl isopropyl ether (see theoretical part). Fraction (III) appears to be 2,4,6-tri-isopropylphenyl isopropyl ether and will be discussed under the preparation of that compound. A yield of 30% of 2,4-di-isopropylphenyl isopropyl ether was obtained; b. p. 248° (uncorr.); sp. gr. 0.9432 (25°); $n_D^{25}$ 1.5087; calcd. mol. wt. 220.1; found, 217.5.

**2,4,6-Tri-isopropylphenyl Isopropyl Ether.**—The method used in the preparation of this compound was the same as the procedure in the preparation of 2,4-di-isopropylphenyl isopropyl ether except that the temperature of the reaction was maintained between 30 and 40° and propylene was passed into the mixture until practically no more absorption took place. A product weighing 241 g., insoluble in alkali and boiling between 258 and 265° was isolated. The structure of this compound was discussed in the theoretical part of this paper. A 92% yield based on the phenol used was obtained; b. p. 263° (uncorr.); sp. gr. 0.9132 (25°); $n_D^{25}$ 1.4982; calcd. mol. wt. 262.2; found, 258.8.

[17] Sowa, Hinton and Nieuwland, THIS JOURNAL, **54,** 2019 (1932).

Further work is being carried out in this Laboratory in an effort to study the condensation of a number of different unsaturated compounds with phenols in the presence of boron fluoride.

The authors wish to express their appreciation to the E. I. du Pont de Nemours Company for supplying the propylene used in this investigation.

## Summary

A procedure has been outlined by which propylene may be condensed with phenol using boron fluoride as a catalyst.

The catalyst used serves two purposes, namely, as condensing agent and rearranging agent. This affords a method for the formation of a series of condensations and subsequent rearrangements to form phenyl ethers, substituted phenols and substituted phenyl ethers in one operation.

The synthesis of isopropyl phenyl ether and its homologs has been described.

NOTRE DAME, INDIANA

---

## REDUCTION STUDIES OF SCHIFF BASES. II. THE POLYMERIC STATES AND THE STRUCTURES OF METHYLENE-ANILINE AND METHYLENE-PARA-TOLUIDINE. THE CONDENSATION OF ANILINE AND ACETALDEHYDE[1]

BY JOHN G. MILLER AND E. C. WAGNER

N-Methylene-aniline and N-methylene-$p$-toluidine are Schiff bases which have been obtained only in polymerized forms.[2] Published evidence as to their polymeric states is in part conflicting,[2d,3] and that as to their structures is scanty and unconvincing.[2a,b,3,4]

Methylene-aniline has long been recognized as trimeric. Methylene-$p$-toluidine, stated by Bischoff[2d] to be trimeric, was later reported by Ingold and Piggott[3] to be dimeric at ordinary temperature, a finding shown below to be incorrect. Though the degree of polymerization is affected by conditions such as temperature and presence of the bases in hot solvents, the

[1] From the thesis presented by John G. Miller in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Pennsylvania, June, 1932.

[2] (a) Wellington and Tollens, Ber., 18, 3298 (1885); (b) Miller and Plöchl, ibid., 25, 2020 (1892); (c) Pulvermacher, ibid., 25, 2762 (1892); (d) Bischoff, ibid., 31, 3248 (1898).

[3] Ingold and Piggott, J. Chem. Soc., 123, 2745 (1923).

[4] (a) Pratesi, Gazz. chim. ital., 14, 351 (1884); (b) Tröger, J. prakt. Chem., [2] 35, 225 (1887); (c) Grünhagen, Ann., 256, 285 (1890); (d) Eibner, ibid., 302, 349 (1898); (e) Löb, Z. Elektrochem., 4, 428 (1898); (f) Goecke, ibid., 9, 470 (1903).