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.

NOTRE DAME, INDIANA RECEIVED MARCH 21, 1935

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

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

BY W. J. CROXALL, F. J. SOWA AND J. A. NIEUWLAND

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).

vestigation it is obvious that esters of salicylic acid rearrange only directly to the benzene nucleus; esters of *m*-hydroxybenzoic acid also rearrange in the greatest portion to the benzene nucleus while esters of *p*-hydroxybenzoic acid rearrange to the hydroxy group and then into the benzene nucleus.

The proof of the structure of the isolated compounds was determined by hydrolyzing the esters and identifying the isopropyl alcohol by the iodoform reaction; further proof that these are isopropyl esters was shown by double decomposition with hydrogen iodide and identifying the isopropyl iodide. The acids obtained from the above reactions were either decomposed to yield the corresponding isopropyl phenyl ethers or further treated with hydrogen iodide to give isopropyl iodide and a known phenolic acid which was then characterized by decomposing into the corresponding phenols.

## Experimental Part

**Condensation of Propylene with *p*-Hydroxybenzoic Acid.**—The procedure was the same as that described for the condensation of propylene[3] with salicylic acid[1] with the exception that carbon tetrachloride was used as a suspending medium instead of heptane and potassium hydroxide (10%) was used to remove any phenolic compounds.

From one experiment in which 69 g. (0.5 mole) of acid, a total of 13 g. of boron fluoride and 40 g. of propylene were used, the following products were obtained: ten grams of a white solid acid which was shown to be some unreacted *p*-hydroxybenzoic acid (m. p. 210°) and 4-isopropoxybenzoic acid[4] (m. p. 160–163°).

The carbon tetrachloride portion was saved and combined with another experiment. In a second experiment, using 69 g. (0.5 mole) of acid, 20 g. of boron fluoride, and approximately 109 g. of propylene, no acids were obtained.

The carbon tetrachloride residue on fractional distillation yielded the following fractions: 38 g., b. p. 145–150° (10 mm.); 12 g., b. p. 150–155° (10 mm.); 42 g., b. p. 155–162° (10 mm.); and a small amount of tar. These fractions and those in the first experiment were combined and carefully fractionated to give the following two fractions: b. p. 145–147° (10 mm.), $n^{25}\text{D}$ 1.5007, sp. gr. 1.0076 (25°); b. p. 160–161.5° (10 mm.), $n^{25}\text{D}$ 1.4959, sp. gr. 0.9754 (25°).

The compound of b. p. 145–147° (10 mm.) was identified as isopropyl 4-isopropoxybenzoate by saponification and identifying the isopropyl alcohol and the acid as 4-isopropoxybenzoic acid.[4]

Similarly the fraction of b. p. 160–161.5° (10 mm.) was shown to be isopropyl 3-isopropyl-4-isopropoxybenzoate. This compound gave isopropyl alcohol on saponification and an acid (m. p. 108–109°) (equivalent wt. calculated for $C_{12}H_{18}O_3$, 222; found, 224) which was identified as 3-isopropyl-4-isopropoxybenzoic acid by decomposition with sodium carbonate into *o*-isopropyl phenyl ether.[2] In neither of these two experiments were any compounds obtained soluble in potassium hydroxide.

**Condensation of Propylene with *m*-Hydroxybenzoic Acid.**—From the following condensation using 207 g. of acid, 781 g. of carbon tetrachloride, 34 g. of boron fluoride and approximately 156 g. of propylene the following compounds were obtained according to the above procedure. Three grams of an acid (m. p. 88–89°) (equivalent wt. calculated for $C_9H_{13}O_3$, 180; found, 182), which was shown to be 3-isopropoxybenzoic acid. The structure of this compound was proved by synthesis according to the method of Cohen and Dudley.[4]

The potassium hydroxide soluble portion yielded on acidification with hydrochloric acid 10 g. of isopropyl *m*-hydroxybenzoate b. p. 162–164° (15 mm.) (m. p. 59–60°).

The potassium hydroxide insoluble portion yielded on fractionation the following fractions: 102 g., b. p. 136–141° (12 mm.); 6 g., b. p. 141–155° (12 mm.); 35 g. (b. p. 155–160°) (12 mm.) and about 60 g. of the high boiling residue which could not be distilled without decomposition. Two definite compounds were isolated from the above: isopropyl 3-isopropoxybenzoate, b. p. 135–137° (10 mm.), $n^{25}\text{D}$ 1.4897, sp. gr. 0.9954 (25°); and isopropyl 3-isopropoxy-4-isopropylbenzoate, b. p. 155–156° (10 mm.), $n^{25}\text{D}$ 1.4902, sp. gr. 0.9741 (25°).

The structure of isopropyl 3-isopropoxybenzoate was proved by saponification to give isopropyl alcohol and 3-isopropoxybenzoic acid.

The proof of the structure of isopropyl 3-isopropoxy-4-isopropylbenzoate is as follows. Thirty grams of ester, on saponification, gave an oily acid which could not be crystallized. Isopropyl alcohol was identified as before. This oily residue was reacted with 50 g. of hydrogen iodide (45%) and carbon dioxide as before. Isopropyl iodide (b. p. 89–90°) was obtained and the residue yielded, on crystallization from hot water, white needle crystals (m. p. 138–140°) which was 3-hydroxy-4-isopropylbenzoic acid.[5]

**The Rearrangement of 4-Isopropoxybenzoic Acid.**—The rearrangements of the acids and esters were all carried out under similar conditions so that only one experiment will be described. Fifty-one grams of 4-isopropoxybenzoic acid, 108 g. of carbon tetrachloride, and 12 g. of boron fluoride were refluxed for one hour. The reaction product was cooled and neutralized with sodium carbonate solution and the acids precipitated with hydrochloric acid. These acids were decomposed by heating into their corresponding phenols, which on fractionation yielded 4 g. of phenol (b. p. 184°) and 12 g. of *o*-isopropylphenol (b. p. 210–214°).

**Rearrangement of 3-Isopropoxybenzoic Acid.**—Two hundred and thirty grams of 3-isopropoxybenzoic acid, 694 g. of carbon tetrachloride and 50 g. of boron fluoride gave as the main products a mixture of acids (m. p. 170–175°); these acids, on esterification with methyl alcohol using sulfuric acid and subsequent fractionation, gave as the main product 50 g. of compound of b. p. 158–165° (10 mm.). This compound was not further purified, but

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[3] The propylene (80% propylene, approximately 20% paraffins with a trace of ethylene and butylene) was obtained from Carbide and Carbon Chemicals Corp.

[4] Cohen and Dudley, *J. Chem. Soc.*, **97**, 1739 (1910).

[5] E. v. Lippmann and R. Lange, *Ber.*, **13**, 1663 (1880).

saponified and fractionally crystallized to give 3-hydroxy-4-isopropylbenzoic acid.

There also was obtained 6 g. of a compound insoluble in potassium hydroxide which on distillation was found to be 3,4-diisopropylphenyl isopropyl ether (b. p. 248–251°).

**Rearrangement of Isopropyl *m*-Hydroxybenzoate.**—One hundred and thirty grams of ester of b. p. 143–144° (5 mm.) m. p. 59–60°, 190 g. of carbon tetrachloride and 14 g. of boron fluoride were refluxed for one hour. Three grams of 3-isopropoxyisopropylbenzoate (b. p. 138–140°) (12 mm.) and 5 g. of isopropyl 3-isopropoxy-4-isopropylbenzoate b. p. 155–157° (10 mm.) were obtained from the potassium hydroxide insoluble portion. Ninety-one grams of acid was obtained which on heating practically all went into solution, leaving an oil. The oil recrystallized from methyl alcohol and was shown to be 3-isopropoxybenzoic acid (m. p. 88–89°). These acids soluble in water (m. p. 170–180°) were shown to be a mixture of *m*-hydroxybenzoic acid and 3-hydroxy-4-isopropylbenzoic acid by decomposing into phenol and *o*-isopropylphenol.

**Rearrangement of Isopropyl *p*-Hydroxybenzoate.**—Fifty-six grams of ester, b. p. 158–160° (5 mm.), 108 g. of carbon tetrachloride and 9 g. of boron fluoride were refluxed for one hour. From 23 g. of an acid (m. p. 155–160°) obtained from above, 4 g. of methyl-4-isopropoxybenzoate[4] (from acid and methyl alcohol using sulfuric acid) were obtained.

ANALYSIS OF COMPOUNDS

| Name | Calcd., % C | Calcd., % H | Found, % C | Found, % H |
|---|---|---|---|---|
| 4-Isopropoxybenzoic acid[a] | 66.68 | | 65.98 | |
| 3-Isopropoxybenzoic acid[a] | 66.68 | | 66.01 | |
| 3-Isopropyl-4-isopropoxybenzoic acid[a] | 70.23 | | 71.06 | |
| Isopropyl 3-isopropoxybenzoate | 70.23 | 8.14 | 70.19 | 8.10 |
| Isopropyl 4-isopropoxybenzoate | 70.23 | 8.14 | 70.00 | 8.00 |
| Isopropyl 3-isopropoxy-4-isopropyl benzoate | 72.90 | 9.35 | 72.46 | 9.18 |
| Isopropyl 4-isopropoxy-3-isopropyl benzoate | 72.90 | 9.35 | 72.38 | 7.13 |

[a] Rowan, "Wet Combustion," Thesis, University of Notre Dame, 1935.

## Summary

Propylene has been condensed with *m*- and *p*-hydroxybenzoic acids in the presence of boron fluoride.

The course of the condensation and rearrangement has been determined.

Six new compounds have been reported.

NOTRE DAME, INDIANA RECEIVED APRIL 17, 1935

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

# The Compressions and Specific Volumes of Aqueous Solutions of Resorcinol and Methanol at 25° and the Behavior of Water in these Solutions

BY R. E. GIBSON

The results obtained in a systematic study of the compressions and volumes of aqueous salt solutions show regularities which we have already discussed.[1] In particular they give experimental confirmation of the generalization that the apparent volumes and the apparent specific compressions of salts in aqueous solutions are linear functions of the square root of the volume concentration[2] or in many cases of the square root of the weight or mole ratio.[3] We have also found that from pure water to 40% acid the apparent specific compression of acetic acid in aqueous solutions varies linearly with the square root of the volume concentration. There are, however, notable exceptions to these rules. Examination of the data available has shown,[4] moreover, that it is probable that such relations also hold in solutions of non-electrolytes such as urea and sucrose. The case of sucrose is doubtful, however, as the deviations from the linear relation are outside the estimated experimental error. The data of Perman and Urry[5] at pressures up to 100 atm. for glucose and raffinose show that except in the highest concentrations the apparent compression of the solute is zero. Evidently solutions of weak or non-electrolytes require further investigation.

With the object of looking into these regularities we have examined solutions of methanol and resorcinol in water. Methanol is a highly compressible liquid infinitely miscible with water, while resorcinol is a solid melting at 110° and very soluble in water. Both solutes are non-electrolytes. The results will be discussed in this paper.

## Experimental

The densities and the compressions of the solutions under an increase of pressure from 1 to 1000

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[1] Gibson, (a) THIS JOURNAL, **56**, 4 (1934); (b) **56**, 865 (1934); (c) **57**, 284 (1935). These papers may be consulted for explicit definitions of the terms used here.

[2] See Gucker, *ibid.*, **55**, 2709 (1933). In this article reference to the earlier work will be found.

[3] Adams, *ibid.*, **54**, 2229 (1932).

[4] Gucker, *Chem. Reviews*, **13**, 128 (1933). See, however, Redlich and Klinger, *Monatsh.*, **65**, 137 (1934).

[5] See Thomas and Perman, *Proc. Roy. Soc.* (London), **A146**, 640 (1934).