the same velocity whether the reagent is dilute sodium carbonate, water or dilute sulfuric acid, although both alcohol and olefin are formed in large amount. This surely indicates that the total decomposition is unimolecular, and that the speed is independent of reagent anions. The mechanisms at work here are $S_N1$ and E1. The unimolecular character of the reaction in homogeneous solution has been confirmed by the writer.

## Experimental

The bimolecular character of the alkaline hydrolysis of methyl and ethyl halides has been previously established.[8] The point of mechanistic change in the alkyl series is illustrated by the figures in the subjoined table, selected from dynamical experiments which will be published in detail later. They refer to experiments in which the concentration of the alkyl halide does not appreciably change during the reaction. The velocity in dilute alkaline solution is then constant and is identical with that in acid solution. The first five lines are self-explanatory. The figures in lines 6 and 7 show the average changes in titer per hour; they relate to 10 cc. of the reaction mixtures and are expressed in cc. of 0.005 *N* acid and alkali, respectively.

| Halide | *i*-PrBr | *s*-BuBr | *t*-AmCl |
|---|---|---|---|
| Moles halide per mole KOH | 70 | 63 | 38 |
| Medium, % EtOH | 60 | 60 | 90 |
| Temperature, °C. | 45 | 45 | 25 |
| Range of readings alkaline *N* ⟶ acid *N* | 0.0030–.0040 | 0.0029–.0035 | 0.0043–.0030 |
| Velocity in alk. soln. | 2.60 | 2.52 | 3.00 |
| Velocity in acid soln. | 2.58 | 2.44 | 3.12 |

The author wishes to express his indebtedness to Professor C. K. Ingold, F.R.S., for his invaluable help.

## Summary

The dynamics of the hydrolysis of certain secondary and tertiary alkyl halides have been investigated and the mechanism of the reaction is discussed.

LONDON, ENGLAND RECEIVED NOVEMBER 30, 1934

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[8] Bruyn and Steger, *Rec. trav. chim.*, **18**, 311 (1899); Grant and Hinshelwood, *J. Chem. Soc.*, 258 (1933).

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

# Organic Reactions with Boron Fluoride. IX. The Alkylation of Phenol with Alcohols[1]

BY F. J. SOWA, G. F. HENNION AND J. A. NIEUWLAND

In a recent publication[2] it was shown by conductivity measurements that the system phenol-boron fluoride possessed acid properties considerably stronger than phenol. Evidence was also presented for compound formation from one mole of boron fluoride and two moles of phenol. Boron fluoride has been used as an agent in the formation of alkyl phenyl ethers from olefins and phenols,[2] from ethers and phenols[3] and as an esterifying agent.[4] These properties should make this agent particularly adaptable in the reaction between alcohols and phenols.

Altogether neither methyl nor ethyl alcohol reacted with phenol in the presence of boron fluoride by heating at atmospheric pressure, they did react quite readily when heated in a sealed tube. The products were mainly anisole and phenetole, respectively. Small quantities of substituted phenols and alkyl phenyl ethers were also formed.

Isolated cases of reactions between alcohols and phenols using various catalysts have been reported.[5,6,7,8] Some of these experimenters claim to have obtained *p*-isobutylphenol from the condensation of isobutyl alcohol with phenol. It has since been demonstrated[9] that isobutyl phenyl ether rearranges to tertiary butylphenol. In none of these investigations was there any attempt made to prove the mechanism of condensation between the alcohol and phenol.

Attempts are reported in this paper to determine, first, if the reaction between alcohols and phenols involves the removal of the elements of water, as in most esterification reactions, equation I

$$C_6H_5OH + C_nH_{2n+1}OH \longrightarrow C_6H_5OC_nH_{2n+1} + H_2O \quad (I)$$

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[1] Paper VIII. Dorris, Sowa and Nieuwland, THIS JOURNAL, **56**, 2689 (1934).

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

[3] Hennion, Hinton and Nieuwland, *ibid.*, **55**, 2857 (1933).

[4] Hinton and Nieuwland, *ibid.*, **54**, 2017 (1932).

[5] Liebmann, *Ber.*, **15**, 150 (1882).

[6] Senkowski, *ibid.*, **24**, 2974 (1891).

[7] Mazzara, *J. Chem. Soc.*, **62**, 838 (1882).

[8] Mazzara, *Gazz. chim. ital.*, **12**, 505 (1882).

[9] Smith, THIS JOURNAL, **55**, 3718 (1933).

or, second, if it took place by the removal of water from the alcohol with the formation of the olefin, followed by the condensation of this olefin with the phenol as in equations II and III.

$$C_nH_{2n+1}OH \longrightarrow C_nH_{2n} + H_2O \qquad (II)$$

$$C_6H_5OH + C_nH_{2n} \longrightarrow C_6H_5OC_nH_{2n+1} \qquad (III)$$

The use of methyl or ethyl alcohol did not answer this question, since the product would be the same regardless of the course of the reaction.

It was observed during a study of rearrangements[10] of alkyl phenyl ethers that *n*-propyl phenyl ether did not rearrange when it was subjected to the ordinary treatment in the presence of boron fluoride. Isopropyl and *n*-propyl alcohols should then give valuable information regarding the mechanism of the condensation referred to above. For example, if equation (I) is correct, our final product should be practically all *n*-propyl phenyl ether, when employing *n*-propyl alcohol. The purpose of carrying on similar reactions with isopropyl alcohol is to prove the identity or dissimilarity of the products with those formed from *n*-propyl alcohol.

By treating *n*-propyl and isopropyl alcohols with phenol in the presence of boron fluoride identical products were obtained in each case. No *n*-propyl phenyl ether was detected. This indicates quite definitely that in the cases of the propyl alcohols at least, the reaction takes place through equations (II) and (III). Other alcohols are at present being studied.

## Experimental Part

**Reaction of Methyl Alcohol with Phenol.**—A mixture of 10 g. of methyl alcohol and 29.6 g. of a 21% boron fluoride–phenol solution was introduced into a soft glass combustion tube (61 cm. × 2 cm.). The tube was sealed and heated in a gas-fired bomb-furnace at 170° for three hours. The tube was allowed to cool to room temperature, opened, and the thick pasty product poured into a 400-cc. beaker. The tube was rinsed out with 25 cc. of water and the rinsings added to the main product. A 25% solution of sodium hydroxide was slowly added until neutralization was complete. The alkali soluble and insoluble layers were treated in the usual manner in order to isolate the phenols and anisole from the respective layers.

The alkali insoluble layer gave 14.5 g. of anisole boiling 153–155°. This corresponds to a 54% yield based on the phenol used. A small fraction boiling above 155° was also obtained. From the alkali soluble layer was recovered 5 g. of phenol boiling 180–184°.

Phenetole was formed in a similar manner in a yield of 15%.

**Reaction of Propyl Alcohols with Phenol.**—To one mole (60 g.) of propyl alcohol (*n*- or iso) and one mole (94 g.) of phenol contained in a 500-cc. round-bottomed flask, boron fluoride was passed in until an increase in weight of 24 g. was observed. The contents were refluxed. During this process the temperature rose from 115 to 160° and a water layer began to form at the bottom of the flask after ten minutes.

After heating for one hour, the lower layer which weighed 36 g. was separated. The upper layer was distilled and two fractions were collected. The first fraction which boiled up to 125° upon refractionation gave 30 g. of crude propyl alcohol. The higher boiling fraction was treated with a 15% solution of potassium hydroxide. The mixture was then shaken with 75 cc. of benzene. The alkali layer was withdrawn. The benzene layer, after washing with an equal volume of potassium hydroxide, was dried and fractionated. The results are given in Tables I and II.

The alkali layer was acidified with hydrochloric acid and extracted with 75 cc. of benzene. After removing the benzene the residue was fractionated. The fractions collected and the yields are given in Tables I and II.

TABLE I

CONDENSATION OF ALCOHOLS WITH PHENOL

| No. | Alcohol used | Product | Yield in g. per mole of phenol used |
|---|---|---|---|
| 1 | Methyl | Anisole | 58 |
| 2 | Ethyl | Phenetole | 17 |
| 3 | Isopropyl | 2,4-Diisopropylphenyl-isopropyl ether | 11 |
| 4 | | 2-Isopropylphenol | 28 |
| 5 | | 4-Isopropylphenol | 20 |
| 6 | *n*-Propyl | 2,4-Diisopropylphenyl-isopropyl ether | 13 |
| 7 | | 2-Isopropylphenol | 32 |
| 8 | | 4-Isopropylphenol | 16 |

TABLE II

PHYSICAL PROPERTIES OF PRODUCTS

| No. | B. p., °C. | $d_4^{25}$ | $n_D^{25}$ |
|---|---|---|---|
| 1 | 153 | | |
| 2 | 172 | | |
| 3 | 248 | $0.9431^a$ | $1.5096^a$ |
| 4 | 212–214 | $.9925^a$ | $1.5262^a$ |
| 5 | 228–230 | $.9824^a$ | $1.5224^a$ |
| 6 | 248 | $.9435^b$ | $1.5093^b$ |
| 7 | 212–214 | $.9930^b$ | $1.5251^b$ |
| 8 | 228–230 | $.9818^b$ | $1.5230^b$ |

[a,b] Identical with compounds reported by Sowa, Hinton and Nieuwland, Reference 1. No normal alkyl phenyl ethers were detected.

## Summary

Methyl and ethyl alcohols have been condensed with phenol, in a sealed tube, using boron fluoride as catalyst, to give small yields of anisole and phenetole.

Isopropyl and *n*-propyl alcohols have been condensed with phenol in the presence of boron

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(10) Sowa, Doctor's Dissertation, Notre Dame, Indiana, 1933.

fluoride to yield isopropyl derivatives of phenol in both cases.

Evidence has been presented which indicates that the condensation of alcohols with phenol, especially propyl (*n*- and iso), takes place through the formation of an olefin as an intermediate and subsequent condensation with phenol.

NOTRE DAME, INDIANA RECEIVED DECEMBER 10, 1934

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

# The Polymerization of Styrene, Citral and Heptaldehyde

BY HOWARD E. THOMPSON AND ROBERT E. BURK

This paper represents some observations on highly purified samples of styrene, citral and heptaldehyde in the presence and absence of oxygen.

## Experimental

The chemicals used were Eastman C. P. grade. They were dried, distilled, fractionated and the middle third subjected to two or more distillations at a pressure of $<10^{-4}$ mm. of mercury. In the case of citral, purification, according to Dodge,[1] was carried out before the above treatment was given it. The styrene was always distilled over sodium just prior to its high vacuum distillation, and the mesitylene was repeatedly distilled over metallic sodium.

Heptaldehyde was studied first.[2] We sought to investigate in particular the relation between its oxidation and polymerization reactions. Two gas burets were connected by separate tubes to the inner curvature of a reniform reaction vessel of 10-ml. capacity. The latter was immersed in a thermostat and was mechanically shaken. The arrangement allowed a charge of oxygen in the burets to be passed back and forth through the sample in a uniform manner and without loss of the latter. The oxygen circulation was automatic.

The progress of the reaction was followed by diminution in the oxygen charge, and by analysis.

The high vacuum purification apparatus was of more or less conventional design. It contained no ground glass or rubber joints and was made of Pyrex and quartz. It was provided with a very efficient two-stage mercury condensation pump, McLeod gage, etc.

In experiments on the polymerization of styrene, this substance after purification was distilled into viscometers, dilatometers, etc., which were sealed to the high vacuum system during the filling and sealed off from it after filling. The capillary viscometers had a symmetrical shape and were as nearly alike as we could make them. All of these experiments were carried out at 44 ± 0.1°.

When mesitylene was used as a diluent for styrene, it was purified and sealed in weighed bulbs of various sizes. These were then sealed together with a heavy glass slug in an appendage to the vacuum viscometers, otherwise of the usual design. After filling the viscometer with styrene and sealing it off, the mesitylene bulb was broken, and the contents passed into the viscometer. The appendage was then sealed off.

Water was introduced by sealing pure hydrates (sodium sulfate decahydrate) in appendages of vacuum viscometers otherwise of the usual design. After filling the viscometer with styrene the requisite amount of water was obtained from the hydrate by warming and the appendage containing the residue sealed off.

Non-volatile catalysts were introduced directly into the vacuum viscometers and "degassed" before introducing styrene. Volatile catalysts were sublimed into the vacuum viscometers from an appendage.

Samples of heptaldehyde which were prepared by the high vacuum technique underwent no apparent change in sealed tubes over periods of some months. Samples of this material were investigated in the oxygen apparatus by Miss E. Jamison and H. P. Lankelma. They found that the drastic purification caused no observed deviation in the behavior of the heptaldehyde. No induction period was observed and the total amount of oxygen absorbed was one mole per mole of compound. This required twenty-four hours at 42°.

Citral polymerized in the same apparatus at 98° with the absorption of one-half mole of oxygen in twenty hours, which represented substantial completion of the reaction and a marked thickening of the citral. No induction period was observed.

Styrene at 118° in the same apparatus polymerized with the absorption of one-third mole of oxygen. The reaction was substantially complete in fifty-two hours, after which time the styrene had thickened markedly. An induction period of thirty minutes was observed.

It was thus found that in the case of citral and styrene polymerization dominated oxidation, whereas the contrary was true in the case of heptaldehyde.

Citral and styrene were then drastically purified in the high vacuum apparatus. The thus purified citral in a sealed tube of Corex glass was stable for more than three years. It survived a twenty-minute treatment with the full radiation from a new 220-volt, 1.5-amp. mercury arc at 30 cm. without visible change. Nor did heating for one hour at the temperature of boiling water produce a visible effect.[3]

The vacuum purified styrene, however, continued to polymerize, though at a somewhat diminished rate. While the dependence of the polymerization of citral upon

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(1) Dodge, *Am. Chem. J.*, **11**, 456 (1889).

(2) For greater detail, see H. E. Thompson's dissertation, Western Reserve University, June, 1934.

(3) Citral in the presence of oxygen at room temperature undergoes polymerization to a thick yellow liquid.