

**Summary**

The two oximes of *o*-chlorobenzophenone have been isolated. They are converted into different substituted amides when subjected to the Beck-

mann rearrangement but they yield the same indoxazene when warmed with an aqueous solution of sodium hydroxide.

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

## Organic Reactions with Boron Fluoride. VIII. The Condensation of Propylene with Acids

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Nearly all of the chemical literature on the condensation of olefins with organic acids is that of patents, the processes usually involving high temperatures and pressures. This investigation has shown that acetic, mono-, di-, trichloroacetic, and benzoic acids combine with propylene to give the corresponding isopropyl esters under such mild conditions as 25 cm. of mercury above atmospheric pressure and 70° in the presence of a small amount of boron fluoride as catalyst.

In the acetic acid series, the quantity of ester formed was found to increase as the chlorine content increased from one to three. Since the solubility of propylene in both the acids and the esters formed also increases in the same order, the relative efficiency of the catalyst could not be directly demonstrated. In order to throw further light on this subject these acids were esterified with isopropyl alcohol by an established procedure using boron fluoride as catalyst.<sup>1</sup> The same order was still found to hold true. These results are noteworthy since they are the reverse of the order found by Sudborough and Lloyd<sup>2</sup> using hydrochloric acid as catalyst in the esterification of this same series of acids with isopropyl alcohol. It should be noted that Lichty<sup>3</sup> in a study of esterification found that the quantity increased in the same order as found in this investigation. No catalyst was used in his work. This difference in catalytic activity is being carefully considered.

Benzoic acid combines with propylene to form isopropyl benzoate in practically quantitative amounts but with no substitution in the benzene ring. This is in marked contrast with salicylic acid in a similar reaction<sup>4</sup> where there result isopropyl salicylate, isopropyl substituted isopropyl

salicylate esters and salicylic acids up to and including isopropyl 2-hydroxy-3,5-diisopropylbenzoate. Likewise when isopropyl salicylate is warmed in the presence of boron fluoride, rearrangement<sup>4</sup> takes place with condensation into the nucleus to form isopropyl substituted salicylic acids. The condensation of propylene with phenol, moreover, produces not only isopropyl phenyl ether but several substituted phenols and substituted alkyl phenyl ethers in the presence of boron fluoride.<sup>5</sup> The very different behavior of benzoic acid exhibits the remarkable effect of the hydroxyl group on the benzene nucleus.

### Experimental Part

**Propylene with Acids.**—Three grams of boron fluoride was passed into one mole of the organic acid contained in a 500-cc. Florence flask fitted with an inlet tube extending to the bottom of the flask and an outlet tube extending just through the stopper. The pressure was kept between 0 and 25 cm. of mercury above atmospheric and the temperature 60–70° throughout the absorption of the propylene. After the absorption had proceeded for sixteen hours in each case the ester was purified by standard methods. The results are recorded in Table I. The yield of ester is the theoretical if the unconverted acid is taken into account, as the absorption was always stopped before completion.

The results obtained with benzoic acid must not be compared directly with those of the acetic acid series. In this experiment, 50 g. of benzoic acid was first dissolved in isopropyl benzoate and then treated as above except that the temperature was maintained between 20 and 30°, 12 g. of catalyst used, and the absorption allowed to proceed for twelve hours.

**Isopropyl Alcohol and Acids.**—The procedure is the same as that already reported.<sup>1</sup> Equimolar proportions of acid and alcohol were used, 3 g. of boron fluoride being present per mole of acid. The mixture was refluxed for three hours in each case.

Benzoic acid (61 g.) was treated with 61 g. of isopropyl alcohol and refluxed for fifty minutes. The results also are given in Table I.

(1) Hinton and Nieuwland, *THIS JOURNAL*, **54**, 2017 (1932).

(2) Sudborough and Lloyd, *Trans. Chem. Soc.*, **75**, 467 (1899).

(3) Lichty, *Am. Chem. J.*, **18**, 590 (1896).

(4) Croxall, Sowa and Nieuwland, *THIS JOURNAL*, **56**, 2054 (1934).

(5) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).

TABLE I

Isopropyl ester of . . .	CH <sub>3</sub> -COOH	ClCH <sub>2</sub> -COOH	Cl <sub>2</sub> CH-COOH	Cl <sub>3</sub> C-COOH	C <sub>6</sub> H <sub>5</sub> -COOH
Yield of ester from alcohol and acid, %	16.8	38.8	48.6	57.8	60.0
Yield of ester from propylene and acid, %	7.0	34.2	39.5	48.8	88.0
B. p., °C. (747 mm.)	87-89	149.5	164.0	173.5	215.5
$n_D^{25}$	1.3745	1.4175	1.4306	1.4409	1.4890
MR <sub>D</sub> (obs.)	27.240	31.791	36.884	42.010	46.741
MR <sub>D</sub> (calcd.)	26.823	31.770	36.717	41.664	46.551
$d_4^{25}$	0.8570	1.0812	1.1989	1.2911	1.0102

The results in Table I may be varied greatly by changing somewhat the conditions of the experiment. If carbon tetrachloride, for example, is used in conjunction with chloroacetic acid as a solvent or suspension medium and the mixture agitated, one mole of the acid can be practically converted to the ester in one hour.

**Solubility of Propylene in Acids and Esters.**—Propylene was passed into the flask containing the liquid compound with shaking at a pressure of 25 cm. of mercury above atmospheric. The flask was then brought to 64° and a weight taken. This process was repeated until there was no further gain in weight. The flask, containing a weighed amount of the compound, was fitted with a stopcock for weighing at this pressure. The results are recorded in Table II.

The propylene used in this study was obtained from the Carbon and Carbide Chemicals Corporation. Similar reactions are being investigated with other olefins and acids.

TABLE II

SOLUBILITY OF PROPYLENE IN GRAMS PER MOLE OF COMPOUND				
No. of Cl sub.	0	1	2	3
Acetic acids	0.96	1.71	2.41	2.69
Isopropyl acetates	1.40	1.90	2.99	3.76

### Summary

A method has been described by which propylene can be condensed with acids to form the corresponding esters.

The methods of esterification by condensation and by double decomposition have been compared, the order of ester formation being found the same when boron fluoride is the catalyst used.

The solubility of propylene in the acids and esters of the acetic acid series has been determined. The effect of this factor in determining the yields when condensing propylene with the various acetic acids has been noted.

A difference in the catalytic activity of boron fluoride and hydrochloric acid has been observed.

The effect of the hydroxyl and the carboxyl on the benzene nucleus has been noted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## A Study of the Addition Reactions of Certain Alkylated Naphthoquinones<sup>1</sup>

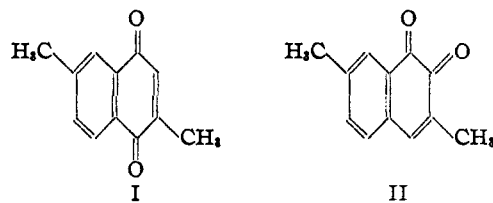
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Although the unsubstituted quinones derived from benzene and naphthalene are known to combine with a great variety of different reagents by way of an addition to the double bond, the carbonyl group or the system of conjugated linkages, there has been little systematic investigation of the possible hindrance to such additions exerted by substituent groups since the classical work of Kehrman on oxime formation, although two papers bearing on the problem have appeared during the course of the present study.<sup>2</sup> It occurred to us that particularly promising compounds for investigation would be found in the quinones I and II, which were prepared several years ago by Weissgerber and Kruber<sup>3</sup> from 2,6-dimethylnaphthalene.

(1) The greater part of the work here reported was described in a thesis presented by the junior author in candidacy for the A.B. degree with honors.

(2) (a) Erdtmann, *Proc. Roy. Soc. (London)*, **A148**, 177 (1933); (b) Madinaveita, *Anales soc. españ. fis. quim.*, **31**, 750 (1933).

(3) Weissgerber and Kruber, *Ber.*, **52**, 346 (1919).



As an example of a carbonyl addition it was of interest to establish the course of the oximation of 2,6-dimethyl-3,4-naphthoquinone, II. Like  $\beta$ -naphthoquinone itself, this was found to form a  $\beta$ - rather than an  $\alpha$ -oxime, for there was obtained on reduction not the known 2,6-dimethyl-4,3-aminonaphthol<sup>3</sup> but an unstable substance which probably is the 3,4-isomer. The methyl group retards somewhat the oximation of the carbonyl group to which it is adjacent, but it does not alter the direction of the reaction.

Toward reagents which attack ordinary quinones by way of a 1,4-addition, the isomers I and II showed a marked difference in behavior. The