

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Chlorobenzophenone Oximes

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For some time it has been considered important to obtain the isomeric forms of the *o*-monohalogenobenzophenone oximes. An indoxazene should be obtained readily from one member of each pair of these isomers through elimination of a halogen acid. Heretofore only one member of each pair has been made. The *o*-bromobenzophenone oxime prepared by Meisenheimer and Meis reacts with an aqueous alkali yielding an indoxazene and undergoes the Beckmann rearrangement yielding an amide in which the unsubstituted benzene ring becomes attached to the nitrogen atom.¹

This result has been regarded as evidence in support of Meisenheimer's interpretation of the rearrangement but the isomeric form of the oxime, which presumably would not yield an indoxazene and in which the substituted phenyl group should migrate when subjected to the action of phosphorus pentachloride, could not be isolated.

The one form of *o*-chlorobenzophenone oxime which has been described yields an indoxazene when heated with sodium hydroxide but all earlier attempts to obtain the isomeric form of this oxime were futile. We have succeeded in isolating both forms of *o*-chlorobenzophenone oxime. One form melts at 131° and the other at 96–97°. The high-melting form yields the anilide of *o*-chlorobenzoic acid, $C_6H_4ClCONHC_6H_5$, when subjected to the Beckmann rearrangement. This anilide melts at 117–118°. The low-melting oxime under the same treatment yields the *o*-chloroanilide of benzoic acid, $C_6H_5CONHC_6H_4Cl$, melting at 99°.

Neither of these oximes yields an indoxazene when treated with a 30% solution of sodium hydroxide at room temperature. When heated with alkali of this concentration both oximes lose hydrogen chloride and yield the same indoxazene.

Instead of supplying unambiguous answers to the questions relating to the configurations of these oximes and the mechanism of the Beckmann rearrangement our work has merely invalidated some of the conclusions previously drawn from experiments in this field. The formation of an indoxazene from an *o*-halogenobenzophenone oxime does not prove that in the original form of the

oxime the hydroxyl group and the halogen substituted ring were on the same side of the molecule. A *cis-trans* isomerization may precede the elimination of the halogen acid.

Experimental Part

Preparation of the Oximes.—To a solution of 150 g. of *o*-chlorobenzophenone in 2250 cc. of methyl alcohol was added slowly and with vigorous mechanical stirring 200 g. of potassium hydroxide in 150 cc. of water. The alkaline solution was heated, under a reflux condenser, and the stirring was continued while a solution of 150 g. of hydroxylamine hydrochloride in 150 cc. of water was added through a dropping funnel. The solution was kept boiling for three and one-half hours (three hours after all the hydroxylamine had been added). After cooling the mixture the precipitate of potassium chloride was removed by filtration. The filtrate was diluted with water to a volume of 10 liters, then neutralized by the slow addition of glacial acetic acid. A voluminous precipitate of mixed oximes was formed. The crystalline product was washed with water, then dried in a vacuum desiccator. The two oximes contained in the crystalline product were separated by fractional crystallization from methyl alcohol. To accomplish this the mixed oximes were dissolved in methyl alcohol at 25° and enough water was added to produce a slight turbidity. The solution was then placed in a stoppered flask in a refrigerator until a small crop of crystals had formed. The crystals were removed and the filtrate was returned to the refrigerator for the formation of another crop. This practice was continued until crystals no longer formed in a twenty-four hour period. The solution was then warmed to 25° and more water was added to produce faint turbidity. The process of crystallization at a low temperature was carried out as before. The intermediate crops were redissolved and the process of fractionation was continued until good yields of the two pure forms were obtained. This part of the work required time and patience. Between eighty and one hundred crops of crystals were isolated in the fractionation of each preparation of these oximes.

It is possible that earlier investigators have actually isolated the two forms of this oxime and have failed to identify the low-melting form, for the low-melting oxime, when heated, changes rapidly into the high-melting form. The rate of change is much slower when a pure sample is heated than when a little of the high-melting form is present. If a sample of the *n*-oxime (m. p. 96–97°) is placed in a capillary tube and immersed in an oil-bath at 90°, then slowly heated, it does not melt until it reaches a temperature only a little below 131°, which is the melting point of the *h*-oxime. If the sample is immersed in the oil-bath at 96° it melts quickly, then resolidifies and melts again at 131°.

(1) Meisenheimer and Meis, *Ber.*, **57**, 289 (1924).

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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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.¹ 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 Lloyd² using hydrochloric acid as catalyst in the esterification of this same series of acids with isopropyl alcohol. It should be noted that Lichty³ 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 reaction⁴ 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, rearrangement⁴ 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.⁵ 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.¹ 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).