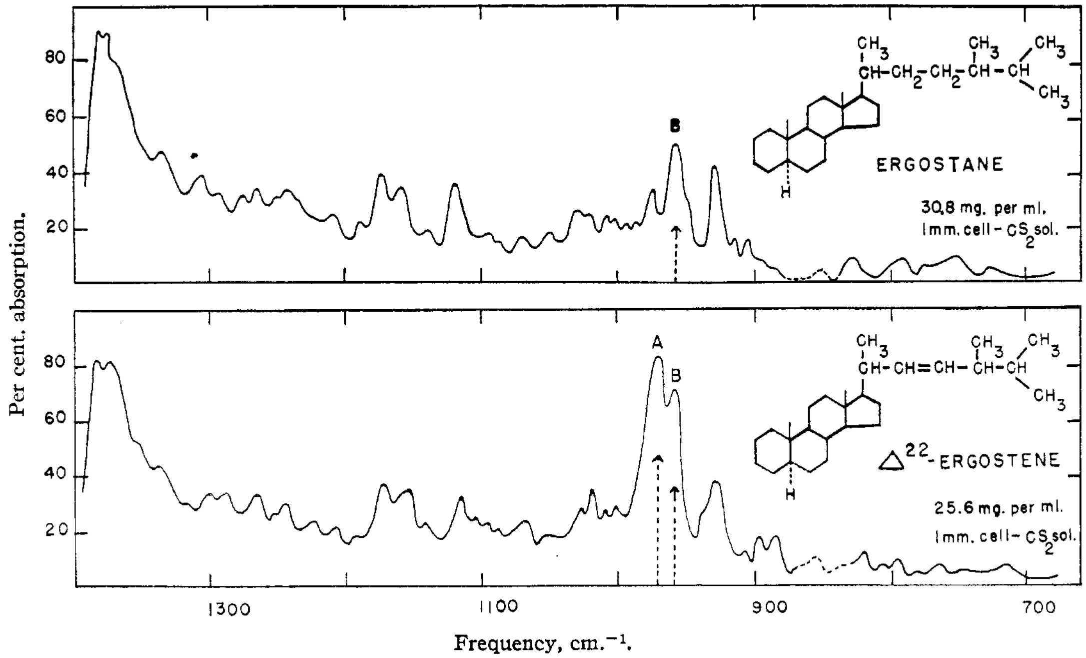

Fig. 1.

H. Jones of Manchester University. His interest in this problem was stimulated by discussion with Dr. Barton.

Division of Chemistry
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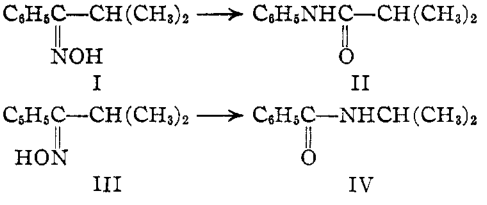
## The Geometric Isomers of Isobutyrophenone Oxime

By Henry M. Kissman and John Williams

The melting point of isobutyrophenone oxime has been reported as 58°,[1] 61–62°,[2] 75°[3] and 94°.[4] We have now found that isobutyrophenone oxime when prepared in the usual manner from isobutyrophenone, hydroxylamine hydrochloride and sodium acetate in ethanol melts at 58–60°. When this material was recrystallized slowly from pentane, there could be isolated two sets of crystals. The less soluble variety formed large prisms which melted at 96°, while the more soluble form crystallized in small plates and melted at 90°. A mixture of these two substances melted between 58–60°. Analyses showed these two compounds to be isomeric. Both substances could be cleaved with phthalic anhydride[5] to regenerate isobutyrophenone which was identified by its 2,4-dinitrophenylhydrazine derivative.[6]

It seemed probable that we were dealing with the *syn*- and *anti*-isomers of isobutyrophenone oxime. This possibility was confirmed through the application of the Beckmann rearrangement. The higher melting form rearranged easily with benzenesulfonyl chloride in pyridine[7] at room temperature into isobutyranilide (II), but the lower melting material had to be heated on the steam-bath with the same reagents in order to effect rearrangement. It yielded a compound which was identified through a mixed melting point as N-isopropylbenzamide (IV). This amide, which has not been previously reported, was prepared from isopropylamine and benzoyl chloride.

The results of these rearrangement reactions indicate that the higher melting form is the *anti*-phenyl (I) and the lower melting substance the *syn*-phenyl isomer (III) of isobutyrophenone oxime.



$$\underset{\text{I}}{C_6H_5\underset{\text{NOH}}{\underset{\|}{C}}\text{—}CH(CH_3)_2} \longrightarrow \underset{\text{II}}{C_6H_5NH\underset{\text{O}}{\underset{\|}{C}}\text{—}CH(CH_3)_2}$$

$$\underset{\text{III}}{C_6H_5\underset{\text{HON}}{\underset{\|}{C}}\text{—}CH(CH_3)_2} \longrightarrow \underset{\text{IV}}{C_6H_5\underset{\text{O}}{\underset{\|}{C}}\text{—}NHCH(CH_3)_2}$$

A few attempts toward a chromatographic separation of these isomers were made. A very low degree of separation could be obtained when a hexane solution of the oxime mixture was passed through a column of alumina. The lower melting form was adsorbed slightly less strongly than the other isomer. This method was, however, useless for actual separation since it did not give the higher melting isomer in pure form.

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(1) Claus, *J. prakt. Chem.*, **46**, 481 (1892).

(2) Magnani and McElvain, This Journal, **60**, 819 (1938).

(3) Franke and Klein, *Monatsh.*, **33**, 1139 (1912).

(4) Lapworth and Steele, *J. Chem. Soc.*, **99**, 1885 (1911).

(5) Tiemann, *Ber.*, **33**, 3721 (1900).

(6) Evans, *J. Chem. Soc.*, 788 (1936).

(7) Werner and Piguet, *Ber.*, **37**, 4295 (1904).

The ultraviolet absorption spectra of the two forms show a displacement toward the visible of the absorption maximum of the *anti*-phenyl isomer (I).

No attempt has been made to convert one isomer into the other. Both forms are stable at room temperature and can be distilled unchanged under reduced pressure.

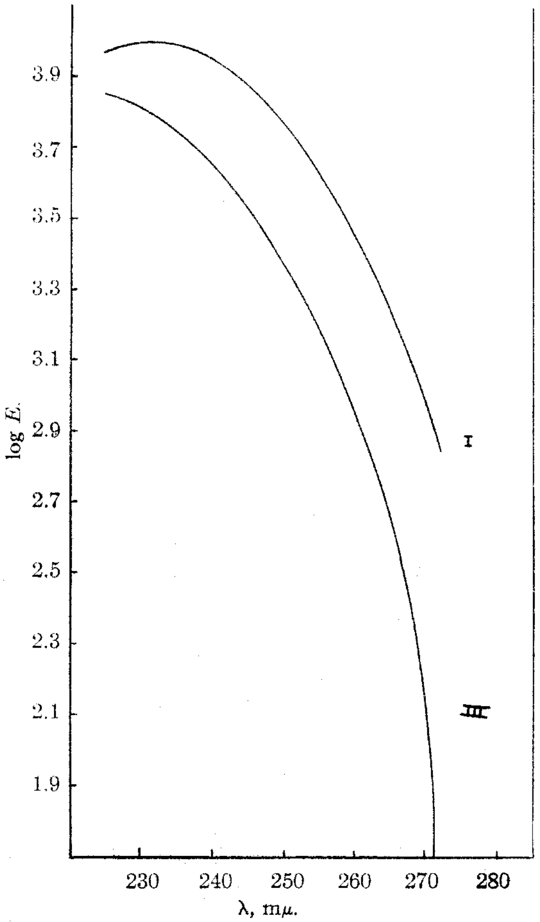

Fig. 1.—Absorption spectra of (I) *anti*-phenyl and (III) *syn*-phenyl isobutyrophenone oxime in 95% ethanol.

## Experimental

**Isobutyrophenone Oxime.**—To a solution of 41.25 g. (0.28 mole) of isobutyrophenone in 125 cc. of absolute ethanol was added 28 g. of hydroxylamine hydrochloride and 41 g. of anhydrous sodium acetate. The mixture was refluxed for two hours and then filtered while hot. The filtrate was poured into 200 cc. of water and most of the alcohol was removed by distillation. The yellow oil which had separated solidified on cooling. It was filtered off and recrystallized from aqueous ethanol to yield 38 g. (83%) of a substance melting at 58–59.6°.

**Separation of the Isomers.**—When some of the above prepared oxime was dissolved in hot pentane and allowed to stand undisturbed for three days, there was formed a mixture of crystals. The large prisms were separated from the small plates by hand and recrystallized individually several times from pentane. Evaporation of the original mother liquor yielded more of the plate-like crystals. The less soluble form (prisms) melted at 95–96°, while the more soluble substance (plates) had a melting point of 89–90°. A mixture of the two melted somewhere between 57–60°, the exact melting point depending somewhat on the proportion of the two compounds.

*Anal.* Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03. Found (prisms): C, 73.70; H, 8.01 (plates): C, 73.67; H, 8.25.

**Cleavage of the Oximes.**—Both forms of the oxime were cleaved with phthalic anhydride[5] to yield **isobutyrophenone** which was identified by its **2,4-dinitrophenylhydrazone** derivative which melted at 161–162°. The reported[6] m. p. is 163°.

**N-Isopropylbenzamide** (IV).—To a stirred mixture of 42 g. of anhydrous potassium carbonate and 11 g. (0.2 mole) of isopropylamine in 180 cc. of ether was added, dropwise, 28 g. (0.2 mole) of benzoyl chloride over a period of forty minutes. The mixture was then stirred and refluxed for an additional hour after which it was added to 200 cc. of water and allowed to stand in a slow stream of air until all of the ether had evaporated. A white solid which had precipitated was filtered off, dried in air, and recrystallized from ethanol to give 29.3 g. (89%) of a substance which melted at 103–104°. After two recrystallizations from heptane the compound formed chunky needles which melted at 104–104.5°.

*Anal.* Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03. Found: C, 73.70; H, 7.90.

**Beckmann Rearrangement.**—The method of Werner and Piguet[7] was used. A solution of 1.63 g. (0.01 mole) of the higher melting oxime in 20 cc. of dry pyridine was mixed with 1.8 g. of benzenesulfonyl chloride and was allowed to stand at room temperature for three hours. The orange solution was then poured into 125 cc. of 6 *N* $H_2SO_4$ and extracted with 250 cc. of ether. The ether extracts were dried over potassium carbonate and then evaporated to leave an oily residue which could be crystallized from hexane. After two crystallizations from that solvent, the material melted at 103–104° and weighed 0.76 g. (47%). Admixture of isobutyranilide (II) did not lower the melting point.

The rearrangement of 1.63 g. (0.01 mole) of the lower melting oxime was carried out as before with the exception that the pyridine solution was heated on the steam-bath for 30 minutes. There was obtained a solid which, after three recrystallizations from heptane weighed 0.53 g. (31%) and melted at 102–103°. When mixed with IV the substance melted at 103–104° but a mixture of the reaction product and II melted from 88–96°.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

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# Error in the Average Coefficients of Specific Volume Change from 0 to 20° in Aqueous Solutions of Hydrogen Peroxide

BY FREDERICK G. KEYES AND CHARLES E. HUCKABA

It has come to our attention through the kindness of Professor W. F. K. Wynne-Jones of King's College, Newcastle-on-Tyne, England, that in a recent publication,[1] Tables VI and VII contain an anomaly due to the failure of equation 3 to reproduce the average coefficient of volume change in the specific volume of pure water between 0 and 20°. This involves also inaccuracies in the dilute solutions of peroxide. The revisions of Tables VI and VII are given below, based on a graph of the deviation of equation 3 from the experimental values of volume change, together

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(1) Charles E. Huckaba and Frederick G. Keyes, This Journal, **70**, 2578 (1948).