[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

Shift in Configuration of Certain α-Benzil Monoxime Benzoates

BY R. P. BARNES

In connection with certain work on the acyl derivatives of benzil monoximes, we found that the α-benzil monoxime benzoate melted sharply at 85–86° and not at 95–96° as reported by Meisenheimer.[1] In order to establish definitely that we were dealing with the monoxime benzoate, we treated it with cold 5% sodium hydroxide and found that it cleaved, yielding the expected products.[1,2] We further attempted to hydrolyze its alcoholic solution with a small amount of concd. hydrochloric acid, and found to our amazement that instead of being hydrolyzed to any very appreciable extent, it had been rearranged to its geometric isomer, the β-benzil monoxime benzoate. Meisenheimer[1] has reported that the α-benzil monoxime benzoate when boiled for several hours with glacial acetic acid is not converted into the β-benzoate, and gives this as evidence of the stability of the benzoates of α-benzil monoximes. But it has long been known that the α-monoximes of benzils rearrange into the β-monoximes.[3,4]

The fact that the α-benzil monoxime benzoate rearranged into the β-ester seemed interesting and particularly significant in the light of the chemical evidence which Meisenheimer[1,4] and Blatt[5] have presented in relating oxime configuration to ring opening. And so we decided to make similar investigations as to the behavior of the *p*-bromobenzoate of α-benzil monoxime[5] and the benzoate of the α-monoxime of a *p*-methoxybenzil.[4] We found that these α-benzil monoxime benzoates rearrange very smoothly into the corresponding β-esters.

In view of the fact that α-benzil monoxime benzoate is unaffected by boiling glacial acetic acid, whereas it is partially hydrolyzed and partially converted into the β-ester in alcoholic solution in the presence of hydrochloric acid, it seems probable that the strength of the acid may be associated intimately with the process of conversion.

Because of the fact that in each case cited as chemical evidence relating oxime configuration to ring opening, it has been possible to effect a shift in configuration, α- to β-, the writer is skeptical as to the extent to which that evidence may be accepted as valid.

Experimental

In each case the α-benzil monoxime benzoate was prepared by mixing, in the cold, pyridine solutions of the α-benzil monoxime with the calculated quantity of the proper benzoyl chloride and allowing the mixture to stand overnight at room temperature. The pyridine solution was then decomposed by pouring with stirring over crushed ice and hydrochloric acid. In each case a practically quantitative yield of solid benzoate resulted, which was purified by recrystallization from methyl alcohol.

Cleavage of α-Benzil Monoxime Benzoate.—The material was shaken at room temperature with an excess of cold 5% sodium hydroxide. The substance liquefied producing an odor of benzonitrile. The solution was extracted with ether. The ethereal layer was concentrated and the residue hydrolyzed with alkaline hydrogen peroxide, yielding benzamide, identified by comparison with an authentic sample. The aqueous layer upon acidification gave benzoic acid.

Conversion of α-Benzil Monoxime Benzoate to β-Benzil Monoxime Benzoate.—To a solution of 5.0 g. of α-benzil monoxime benzoate, m. p. 85–86°, in 25 cc. of absolute alcohol was added 10 drops of concentrated hydrochloric acid. The solution was heated to boiling (five minutes) with the production of the odor of ethyl benzoate. Upon cooling and filtering there was obtained 1.5 g. of a beautiful colorless crystalline substance, m. p. 137°.

The m. p. of α-benzil monoxime is 137°; that of β-benzil monoxime benzoate is 137°. The mixed melting point of this conversion product with α-benzil monoxime is 108°; with β-benzil monoxime benzoate, it is 137°. The conversion product in alcoholic solution is hydrolyzed quantitatively to β-benzil monoxime by cold 5% sodium hydroxide, the oxime being identified by its melting point and mixed melting point.

Conversion of α-Benzil Monoxime *p*-Bromobenzoate to β-Benzil Monoxime *p*-Bromobenzoate.—A solution of 0.5 g. of *p*-bromobenzoate of α-benzil monoxime, m. p. 105°, in 15 cc. of absolute alcohol together with 10 drops of concd. hydrochloric acid was treated as above, producing an ethereal odor and 0.4 g. of the *p*-bromobenzoate of β-benzil monoxime, m. p. 147°, identified by a mixed melting point with a pure sample of the β-*p*-bromobenzoate prepared from β-benzil monoxime. An alcoholic solution of the conversion product is hydrolyzed quantitatively by cold 5% sodium hydroxide, to β-benzil monoxime, identified by its m. p. and mixed m. p.

Conversion of the Benzoate of the α-Monoxime of a *p*-Methoxybenzil to the Benzoate of the β-Monoxime of *p*-Methoxybenzil.—A solution of 0.5 g. of the benzoate of the α-monoxime of a *p*-methoxybenzil, m. p. 137°, in 25

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(1) Meisenheimer, *Ber.*, **54,** 3206 (1921).

(2) R. P. Barnes and A. H. Blatt, THIS JOURNAL, **57,** 1330 (1935).

(3) Karl Auwers and Victor Meyer, *Ber.*, **22,** 537 (1889).

(4) Meisenheimer and Lange, *ibid.*, **57,** 282 (1924).

(5) A. H. Blatt, *Chem. Rev.*, **12,** 215 (1933).

cc. of absolute alcohol was treated as above with 10 drops of concd. hydrochloric acid. A strong odor of ethyl benzoate developed. The solution turned faintly yellow. Upon chilling there was obtained a solid mixture which upon fractional recrystallization was separated into two fractions which melted at 95 and 131°. Mixed melting points with authentic samples proved that these two fractions were the benzoate of the β-monoxime of the *p*-methoxybenzil and the β-*p*-methoxybenzil monoxime, respectively.

In order to establish the fact that these experiments did not involve hydrolysis to the oxime with subsequent rearrangement and esterification, the following experiment was carried out:

A solution of 1.0 g. of α-benzil monoxime and 0.6 g. of benzoic acid in 15 cc. of absolute alcohol was treated as above with 10 drops of concd. hydrochloric acid. There developed a strong odor of ethyl benzoate, but there was no trace of an oximino ester produced.

Summary

In this paper we have first established that a shift in the configuration of certain benzoyl derivatives of α-benzil monoxime does occur, and, second, we have pointed out the possible bearing which these findings may have upon the relation of oxime configuration to ring opening.

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Contact Potentials of Stearate Films on Metal Surfaces

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1. Introduction

Blodgett[1] and Blodgett and Langmuir[2] recently have described the building up of multilayer films of stearates on metal slides by successive dippings of the slides into aqueous solutions covered with a monomolecular layer of the stearate. These films are of two types, called *X* and *Y*, determined by the composition of the aqueous substrate from which they are obtained. Langmuir has suggested on the basis of the way in which they are deposited that in *X* films the molecules in successive layers are oriented in the same way, whereas in *Y* films the molecules in successive layers are oriented oppositely.

We have pointed out that if this hypothesis is correct the two kinds of film should produce quite different effects on the contact potentials of the slides, and have shown that this is in fact the case. A change of contact potential of 8.6 v. was obtained with 170 layers of an *X* film while the change remained constant at 0.12 v. from 10 to 220 layers of a *Y* film.[3]

On the other hand, recent X-ray studies by Holley and Bernstein[4] of the spacing of the Ca and Ba ions in built-up *X* and *Y* films provided by Langmuir and Blodgett seem to indicate that the orientation of the stearate molecules is the same in both, for they obtained the same spacing (48 Å.) for Ca in *X* films as for Ba in *Y* films. Clearly our results suggest that even though this spacing is the same, either the orientation of the molecules or the arrangement of the loci of the positive or negative charges is different in the two types of film. In order to throw more light on the whole problem, we have performed a series of experiments on the contact potentials of mixed *X* and *Y* films and on the effect of heat, X-rays, and ionic discharge on such potentials of *X* and *Y* films.

2. Materials and Methods.—The built-up *X* films were formed by the method of Blodgett[1] by depositing from a solution 10^{-3} molar in potassium bicarbonate, 10^{-4} molar in Ca ions, and adjusted with sodium or potassium hydroxide to a *p*H of about 9.4. Built-up *Y* films were formed (a) by depositing from a solution like that used for the *X* films but adjusted with carbon dioxide gas to a *p*H of 6.0–6.2 and (b) from solutions containing barium and copper as follows:

Solution 1 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 2×10^{-6} *m* $CuCl_2$ *p*H 7.4

Solution 2 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 2×10^{-6} *m* $CuCl_2$, 1 *m* KOH to *p*H 9.4

Solution 3 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 4×10^{-6} *m* $CuCl_2$, CO_2 gas to *p*H 6.2

Solution 4 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 4×10^{-6} *m* $CuCl_2$, 1 *m* HCl to *p*H 5.8

Solution 2 differs from Solution 1 only in *p*H and potassium concentration. Solution 3 contains twice the copper concentration of Solution 1 and the *p*H is lower due to increased carbonic acid concentration. Solution 4 is the same as Solu-

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(1) Blodgett, THIS JOURNAL, **57**, 1007 (1935).

(2) Blodgett and Langmuir, *Phys. Rev.*, **51**, 664 (1937).

(3) Porter and Wyman, THIS JOURNAL, **59**, 2746 (1937).

(4) Holley and Bernstein, *Phys. Rev.*, **52**, 525 (1937).