The Structure of the Benzil Monoximes

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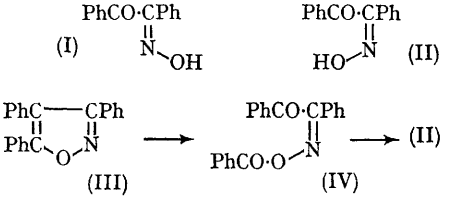
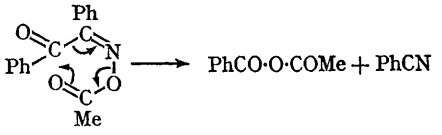
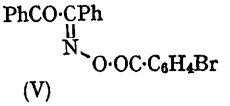
THE accepted structures for benzil α-monoxime (I), and benzil β-monoxime, (II), are based mainly on the fact that ozonization of triphenylisoxazole, (III), affords the benzoate of benzil β-monoxime, (IV).[1]



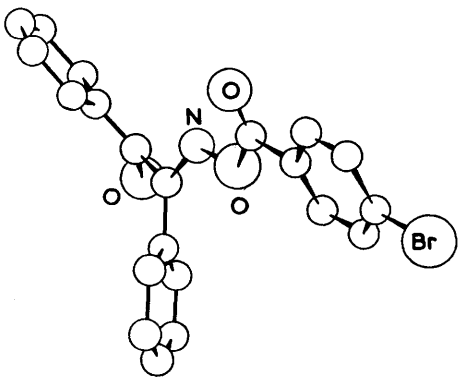
Other facts, however, could be interpreted by reversing the structures assigned to the two forms of benzil monoxime. The acetate of benzil β-monoxime is thermally stable at 190°. The acetate of benzil α-monoxime is thermally unstable at 140°, and is converted into substances which on treatment with water yield acetic acid, benzoic acid, and benzonitrile.[2] Undoubtedly benzonitrile and acetic–benzoic anhydride are the initially-formed products. Since many pyrolytic decompositions occur by intramolecular cyclic mechanisms, one might use the above facts to argue that the acetate of benzil α-monoxime has the acetoxy- and benzoyl groups in the *cis*-configuration and hence the structures for (I) and (II) should be reversed.*



With the above argument in mind, a solution to this problem was sought by a method which would not require the speculation inherent in the interpretation of chemical evidence. Accordingly we have determined the structure of the *p*-bromobenzoate of benzil α-monoxime[3] by *X*-ray crystallographic analysis. The results show clearly that the structure is (V), with the *p*-bromobenzoate group *trans* relative to the carbonyl group. Hence Meisenheimer's assignment of structure to the oximes (I) and (II) is correct.



Crystals of benzil α-monoxime *p*-bromobenzoate (V), $C_{21}H_{14}NO_3Br$, m.p. 105°, are triclinic, space group $P\bar{1}$ (C_i), with 2 molecules in a unit cell with



FIGURE

Benzil α-monoxime p-*bromobenzoate viewed along the* c *crystal axis.*

* This suggestion was originally made in an oral examination for the Ph.D. degree at Ohio State University in 1959 by the candidate, Tadamichi Fukunaga.

$a = 8{\cdot}78$, $b = 17{\cdot}01$, $c = 6{\cdot}27$ Å, $\alpha = 95{\cdot}1°$, $\beta = 91{\cdot}1°$, $\gamma = 102{\cdot}3°$. $D_m = 1{\cdot}47$ g.cm.$^{-3}$, $D_c = 1{\cdot}49$ g.cm.$^{-3}$. The crystals were twinned, but intensity data were estimated from Weissenberg photographs obtained from a specimen with one individual of the twin sufficiently larger than the other to permit accurate indexing.

About 1300 independent structure factors were evaluated, and the analysis proceeded by three-dimensional Patterson and minimum functions. The electron-density distribution revealed the positions of the 25 light atoms in the molecule. Refinement proceeded by Fourier and least squares methods, the final R-value being 16·0% over all the observed structure factors.

The configuration of the molecule obtained from the X-ray analysis is best illustrated in the view obtained in projection along the short c axis, which is shown in the Figure.

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[1] J. Meisenheimer, *Ber.*, 1921, **54**, 3206.
[2] A. H. Blatt and R. P. Barnes, *J. Amer. Chem. Soc.*, 1934, **56**, 1148.
[3] R. P. Barnes, *J. Amer. Chem. Soc.*, 1938, **60**, 1082.