

CX.—*The Oximes of 2:4-Dinitrobenzil and the Beckmann Change.*

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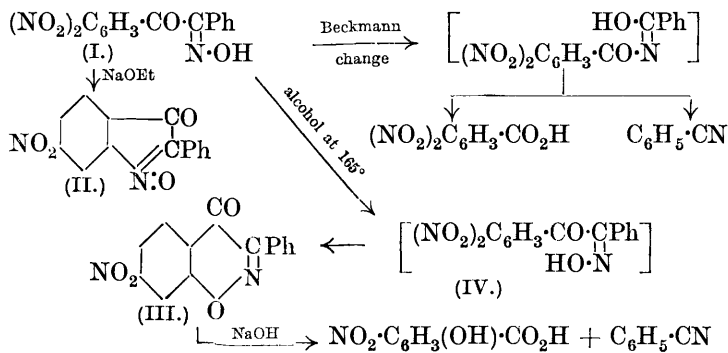
IN a previous communication (J., 1922, **121**, 2364), two substances, regarded as monoximes of 2:4-dinitrobenzil, were described to which, on account of their behaviour in the Beckmann change, the following structures were assigned:



Further investigation, however, has shown that the supposed  $\beta$ -oxime was a mixture and that its reactions were untrustworthy guides to its constitution. Consequently, our early view of the configurations of the substances requires modification. We are now of opinion that their reactions are best explained by adopting Meisenheimer's view that the Beckmann change takes place in a *trans*- and not in a *cis*-sense (*Ber.*, 1921, **54**, 3206; 1924, **57**, 276, 282, 289), ring closure being assumed to involve no change in configuration (compare, however, Kuhn and Ebel, *Ber.*, 1925, **58**, 919; Böseken, *ibid.*, p. 1470; Meisenheimer, *ibid.*, p. 1491). The  $\alpha$ -oxime has accordingly been given the configuration (I). The Beckmann change leads to benzonitrile and 2:4-dinitrobenzoic acid as previously described. By boiling with the calculated quantity of sodium dissolved in alcohol, the  $\alpha$ -oxime is converted, by elimination of nitrous acid, into a brilliant scarlet compound which, on account of its colour, we consider to be 6-nitro-3-keto-

2-phenyl- $\psi$ -indole-1-oxide (II), the  $\alpha$ -oxime, since the oxygen atom is remote from the nitro-group, reacting in the nitron form. This compound on treatment with excess of alkali gives benzaldehyde and an amorphous compound, thus behaving similarly to the  $\alpha$ -oxime itself when treated with excess of aqueous sodium hydroxide. When the  $\alpha$ -oxime is heated in alcohol to 165°, nitrous acid is eliminated and 7-nitro-4-keto-3-phenyl-1 : 2-benzoxazine (III) is formed. That this compound is not produced by the action of alkali on the  $\alpha$ -oxime suggests that at the high temperature the oxime undergoes an isomeric change analogous to that of the oximes of benzil under similar conditions; in the new oxime (IV) thus produced, the hydroxyl and nitro-groups are vicinal and consequently nitrous acid is readily eliminated. 7-Nitro-4-keto-3-phenyl-1 : 2-benzoxazine on hydrolysis gives benzonitrile and 4-nitrosalicylic acid. The benzoxazine melts, by an unfortunate coincidence, at the same temperature (169°) as 4-nitrosalicylonitrile, and we have found that the compound produced by the action of alkali on the supposed  $\beta$ -oxime and described in our previous paper as 4-nitrosalicylonitrile (*loc. cit.*, p. 2369), and for the identification of which we relied on the melting point and hydrolysis to 4-nitrosalicylic acid, was in fact this benzoxazine.

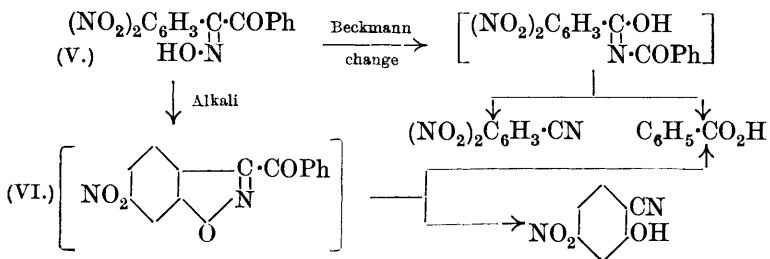
The reactions of the  $\alpha$ -oxime may be summarised thus :



The action of excess of free hydroxylamine on 2 : 4-dinitrobenzil, by which the supposed  $\beta$ -oxime was obtained, yields a complex mixture, from which 7-nitro-4-keto-3-phenyl-1 : 2-benzoxazine (III), the  $\alpha$ -oxime (I), and the pure  $\beta$ -oxime (V) have been isolated. The formation of the benzoxazine suggests that the unknown oxime (IV) is first produced and loses nitrous acid with great ease in the presence of excess of hydroxylamine.

The  $\beta$ -oxime, in the Beckmann change, gives benzoic acid and 2 : 4-dinitrobenzonitrile. On heating with alkali, it gives benzoic

acid and 4-nitrosalicylonitrile through the unstable *isooxazole* (VI). Its reactions may be represented thus :



There was also evidence that the crude oximation mixture contained the fourth oxime,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\underset{\text{N}\cdot\text{OH}}{\underset{|}{\text{C}}}\cdot\text{COPh}$ . The presence of

this would account for the isolation, in the previously described experiments, of 2:4-dinitroaniline after the supposed  $\beta$ -oxime had undergone the Beckmann change. In a subsequent similar experiment with the crude oximation mixture, we were unable to separate the dinitroaniline from the other products, but isolated 2:4-dinitrophenol by heating with concentrated alkali, acidifying, and distilling in steam.

#### EXPERIMENTAL.

$\alpha$ -2:4-Dinitrobenzilmonoxime.—The preparation is described in our previous paper. The  $\alpha$ -monoxime (3 g.) was heated for 5 hours with absolute alcohol (5 c.c.) in a sealed tube at 165°. On cooling, a colourless, crystalline compound separated which after crystallisation from alcohol gave 7-nitro-4-keto-3-phenyl-1:2-benzoxazine (III), m. p. 169° (Found: N, 10.4.  $\text{C}_{14}\text{H}_8\text{O}_4\text{N}_2$  requires N, 10.4%). This compound was identical in properties with the supposed 4-nitrosalicylonitrile previously obtained by the action of alkali on the impure  $\beta$ -oxime (Bishop and Brady, *loc. cit.*) and on admixture did not depress its melting point. 7-Nitro-4-keto-3-phenyl-1:2-benzoxazine was boiled for a short time with 10% sodium hydroxide; the odour of benzonitrile was observed and on distilling in steam this nitrile was obtained in the distillate; the residue, on being acidified, gave a precipitate from which 4-nitrosalicylic acid was obtained by crystallisation.

The action of alkali in excess on the  $\alpha$ -oxime was described in the previous paper. When, however, the oxime (5 g.), dissolved in absolute alcohol (20 c.c.) containing the calculated quantity of sodium to give the sodium salt (0.36 g.), was boiled for 15 minutes, a brilliant scarlet precipitate of 6-nitro-3-keto-2-phenyl- $\psi$ -indole 1-oxide formed which crystallised from alcohol as a red, crystalline

powder, m. p. 198° (Found : C, 62·5; H, 3·1; N, 10·5.  $C_{14}H_8O_4N_2$  requires C, 62·7; H, 3·0; N, 10·4%). Nitrite was detected in the mother-liquor from the preparation. Boiled with excess of aqueous alkali, the compound behaves in a similar manner to the  $\alpha$ -oxime, giving benzaldehyde and an amorphous product.

$\beta$ -2 : 4-Dinitrobenzilmonoxime.—A solution of 2 : 4-dinitrobenzil in alcohol cooled in ice was treated with an alcoholic solution of 3 equivalents of hydroxylamine. After a few moments, crystals of 7-nitro-4-keto-3-phenyl-1 : 2-benzoxazine began to separate and after 12 hours these were collected and the filtrate from them was diluted with water ( $\frac{1}{4}$  vol.); a small quantity of impure  $\alpha$ -monoxime was then precipitated. The filtrate from the  $\alpha$ -oxime was poured into excess of water, kept over-night, and the precipitate repeatedly crystallised from dilute alcohol until its melting point was constant;  $\beta$ -2 : 4-dinitrobenzilmonoxime, m. p. 168°, was thus obtained (Found : N, 13·4. Calc., N, 13·3%).

A solution of the  $\beta$ -oxime in ether was cooled in ice, and the calculated quantity of phosphorus pentachloride added. After 12 hours, ice-water was added, and the mixture then kept for 3 hours. The ether layer was shaken several times with 2*N*-sodium carbonate and evaporated; 2 : 4-dinitrobenzotrile, identified by comparison with an authentic specimen, was thus obtained. The alkaline extracts on acidification and re-extraction with ether gave benzoic acid.

The  $\beta$ -oxime was boiled under reflux for an hour with 2*N*-sodium hydroxide; no darkening or evolution of ammonia occurred as with the  $\alpha$ -oxime, and on cooling and saturating with carbon dioxide 4-nitrosalicylonitrile crystallised. This was identified by comparison with a specimen prepared from 2 : 4-dinitrobenzaldoxime (Borsche and Oppenheimer, *Annalen*, 1912, **390**, 10). The carbonate solution, after removal of dissolved nitrosalicylonitrile with ether, gave benzoic acid on being acidified and extracted with ether.

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