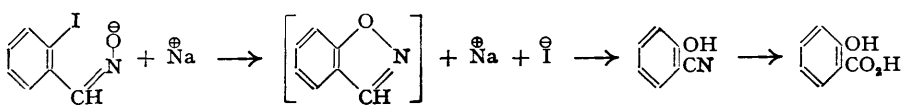
251. *The Isomerism of the Oximes. Part XLI. The Action of Alkali on α- and β-o-Iodobenzaldoximes.*

By O. L. Brady and S. G. Jarrett.

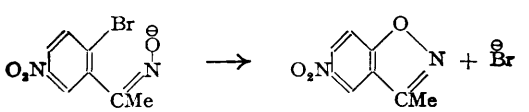
The relative rates of decomposition of α- and β-*o*-iodobenzaldoximes by alkali to salicylonitrile are approximately 1 : 10. This confirms the results obtained by Brady and Bishop with the α- and β-2-chloro-5-nitrobenzaldoximes, from which these authors adduced the *anti*-configuration for the β-benzaldoximes.

In the case of β-*o*-iodobenzaldoxime only, a secondary reaction takes place involving the transformation of about 50% of the oxime into *o*-iodobenzamide.

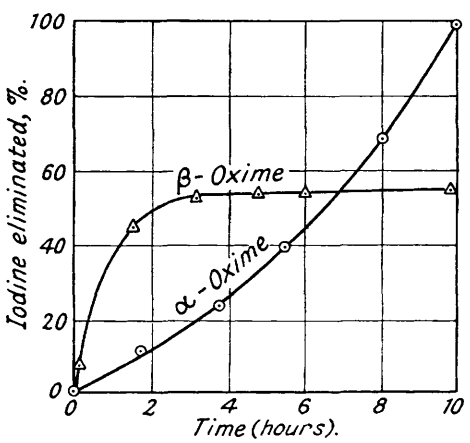
Brady, Cosson, and Roper (*J.*, 1925, **127**, 2427) observed that α-*o*-iodobenzaldoxime, when boiled with excess of 30% sodium hydroxide solution, lost iodine with the formation of salicylic acid. The reaction was supposed to involve the formation of an unstable *iso*oxazole:



With 2-bromo-5-nitroacetophenone oxime the *iso*oxazole, being incapable of tautomeric change, can be isolated (Meisenheimer, Zimmermann, and Kummer, *Annalen*, 1926, **446**, 207).



Rates of elimination of iodine by the o-*iodobenzaldoximes in* 2N-*sodium hydroxide at* 64°.

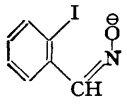


These authors proposed to investigate the rates of elimination of iodine from the α- and β-isomerides to confirm the results obtained with α- and β-2-chloro-5-nitrobenzaldoximes by Brady and Bishop (*J.*, 1925, **127**, 1357), but they were unable to prepare β-*o*-iodobenzaldoxime. We have now prepared this isomeride.

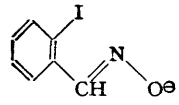
When the α- and β-*o*-iodobenzaldoximes were heated at 65° with 2N-sodium hydroxide the α-isomeride slowly eliminated iodine completely; the β-isomeride lost iodine more rapidly but the liquid soon became turbid and crystals of *o*-iodobenzamide slowly formed. The rates of elimination are shown in the figure; only a little more than 50% of the theoretical amount of iodine

was eliminated from the β-isomeride. Elimination of iodine was about ten times as fast from the β- as from the α-isomeride.

These results confirm those of Brady and Bishop that, if *iso*oxazole formation occurs most easily when the anionic oxygen is nearest to the halogen, the β-oxime must have the *anti*-configuration.

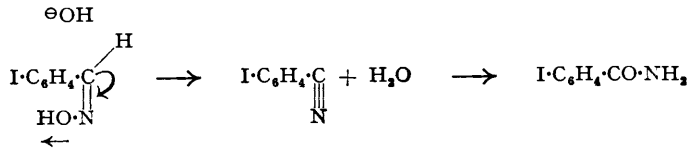


β-Oxime anion.



α-Oxime anion.

With the β-aldoxime two simultaneous reactions occur : attack by the oximino-anion on the nuclear carbon atom bearing iodine, leading to *iso*oxazole formation; and attack by a hydroxyl ion on the methine-hydrogen atom, with simultaneous elimination of the hydroxyl group attached to nitrogen :



As in the case of the acetyl derivatives the methine-hydrogen atom is more readily removed from the β- than from the α-isomeride, so that the second reaction is observed only in this case. *o*-Iodobenzaldoxime, therefore, supplies another example of nitrile formation direct from the oxime under the influence of hydroxyl ions, but, unlike the previous one, *o*-nitrobenzaldoxime (Reissert, *Ber.*, 1908, **41**, 3815; Brady and Goldstein, *J.*, 1926, 1918), only the β-isomeride undergoes this reaction. This is understandable since iodine will be less effective than the nitro-group in facilitating the attack by hydroxyl ions on the methine-hydrogen atom.

Experimental.

α-*o*-Iodobenzaldoxime (m. p. 107—108°) was prepared by the method of Patterson (*J.*, 1896, **69**, 1006) from *o*-iodobenzaldehyde prepared from *o*-aminobenzaldehyde (Weitzenbock, *Monatsh.*, 1913, **34**, 206). β-*o*-Iodobenzaldoxime (m. p. 135°) was obtained by using hydrogen bromide in place of hydrogen chloride in the usual conversion (Brady and Jarrett, *J.*, 1950, 1227).

Action of Sodium Hydroxide.—The α- and β-oximes (2·47 g. = M/10) were each dissolved in 2N-sodium hydroxide (100 c.c.) and heated at 65° (thermostat). At intervals samples (10 c.c.) were removed, added to ice-cold N-nitric acid (25 c.c.), N/10-silver nitrate (10 c.c.) was added, and the excess titrated with N/10-ammonium thiocyanate.

In the case of the β-isomeride a turbidity soon appeared in the solution, and later long crystals formed which were identified as *o*-iodobenzamide by the usual means (Found : C, 34·1; H, 2·7. Calc. for C_7H_6ONI : C, 34·0; H, 2·4%).

If the reaction is of the first order, the rate constant for the formation of iodide from the α-aldoxime was *k* (after 100 min.) 0·00121, (after 335 min.) 0·00146, and (after 480 min.) 0·0025, and for the β-aldoxime (after 10 min.) 0·0106, (after 25 min.) 0·0233, and (after 90 min.) 0·0084. As might be expected the results for the β-aldoxime are poor but the figures indicate the relative speeds of the two reactions. With the β-aldoxime between 90 and 285 min. the amount of iodine eliminated increased only from 53·0 to 55·0%, and then ceased.

The other product of the reaction with both isomerides was salicylonitrile, which was isolated from the alkaline solutions by the addition of dilute sulphuric acid and extraction with ether. Attempts to avoid amide formation by varying the concentration of the alkali and the temperature of the solution were unsuccessful.

Sir William Ramsay and Ralph Forster Laboratories.
University College, London, W.C.1.

[*Received, October 7th*, 1949.]