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THE HYDROLYTIC CLEAVAGE OF α-ACYLOXY AZOXY COMPOUNDS

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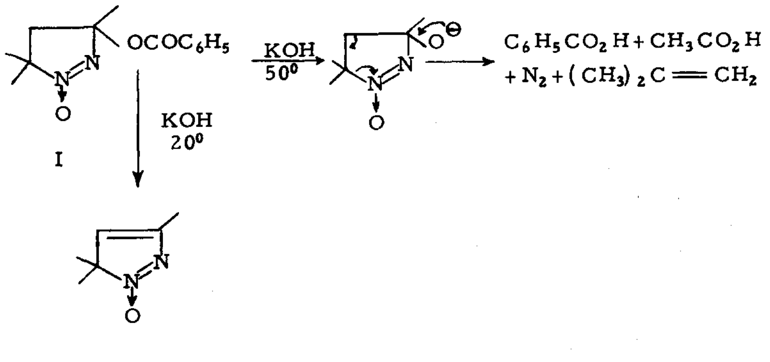
AN interesting and structurally specific hydrolytic cleavage of a pair of α-acyloxy azoxy compounds has been observed. Treatment of 3-benzoyloxy-3,5,5-trimethyl-Δ^1-pyrazoline 1-oxide (I) with 10% ethanolic potassium hydroxide at 50° produced equimolar quantities of benzoic acid, nitrogen, and isobutylene; based on the cleavage scheme (a), acetic acid is presumed to be the other product. This cleavage accounts for about 70% of the starting material. A second concurrent reaction which is favored at lower temperatures produces 3,5,5-trimethylisopyrazole 1-oxide (II).[2]

(a)



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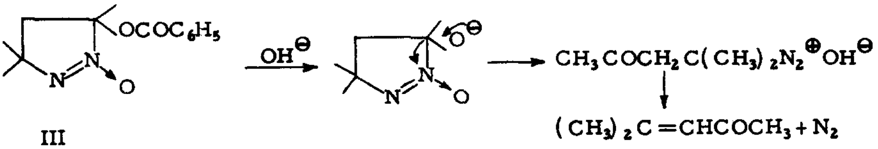
[1] This research was carried out under Army Ordnance Contract D-01-021-ORD-11878.

Treatment of 3-benzoyloxy-3,5,5-trimethyl-Δ^1-pyrazoline 2-oxide (III) with ethanolic potassium hydroxide at 50° produced benzoic acid, nitrogen, and mesityl oxide (b).

(b)



III

The direction of cleavage (path a versus path b) of the alkoxide ion produced on hydrolysis is thus controlled by its position in relation to the quaternary nitrogen of the azoxy group. This reaction may be of use in determining the position of the oxygen in saturated aliphatic azoxy compounds, a particularly difficult problem.[4]

The cleavage of I is another example of the fragmentation reactions discussed by Grob[5] and is similar to the fragmentation of γ-hydroxypropylammonium salts recently reported.[6] The cleavage of III is the first well-documented example of a reaction which has been suggested to account for the decomposition products of α-hydroxy azoxy compounds.[7]

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[2] The characterization of II is completely described in a forthcoming publication. Its structure is based on its elementary analysis, infra-red and NMR spectrum, and absorption at 305 mμ in the ultraviolet indicating an extended rather than crossed conjugated system. Unsaturated azoxy compounds of the alternate configuration absorb at 240 mμ.[3]

[3] C.L. Stevens, B.T. Gillis, J.C. French and T.H. Haskell, J.Amer. Chem.Soc. **80**, 6088 (1958).

[4] See B. Witkop and H.M. Kissman, J.Amer.Chem.Soc. **75**, 1975 (1953) for a discussion of this point.

[5] C.A. Grob, Kekule Symposium on Theoretical Organic Chemistry p. 114. Butterworths, London (1959).

[6] V.J. Traynelis and J.G. Dadura, J.Org.Chem. **26**, 686 (1961).

[7] G.M. Robinson and R. Robinson, J.Chem.Soc. **125** 834 (1924); B.W. Langley, B. Lythgoe and N.V. Riggs, Ibid. 2309 (1951).

Compounds I and III were obtained from a common intermediate, 3-benzoyloxy-3,5,5-trimethyl-Δ^1-pyrazoline (IV) m.p. 70-71° (aq. ethanol) (Found: N, 11.9 $C_{13}H_{16}N_2O_2$ requires: N, 12.1%) prepared by the action of lead tetrabenzoate on 3,5,5-trimethylpyrazoline.[8] Interestingly enough oxidation with peracetic acid gave exclusively III, m.p. 147-148°, (hexane), (Found: C, 63.0; H, 6.7 $C_{13}H_{16}N_2O_3$ requires: C, 62.9, H, 6.5%) while oxidation with perbenzoic acid gave predominantly I along with small amounts of III. The structure of I, m.p. 89-90° (hexane), is based on its conversion to the known isopyrazole oxide II;[2] the structure of III is based on its being isomeric with I and on the similarity of their infra-red and NMR spectra. Compound I could be prepared directly from 3,5,5-trimethylpyrazoline by treatment with perbenzoic acid.[2]

The corresponding acetates appear to give the same reaction. Further details concerning the characterization of these compounds including rather striking NMR effects and other reactions will be forthcoming.

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[8] D.C. Iffland, L. Salisbury and W R. Schafer, J.Amer.Chem.Soc. **83**, 747 (1961).