The Photolysis of 2-Chloro-2-nitrosobutane

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DURING the course of their studies on the photolysis of nitroso-compounds, Mitchell and his co-workers reported[1] that 2-chloro-2-nitrosobutane was transformed, by red light, into ethyl methyl ketoxime, biacetyl monoxime, and a compound, $C_8H_{16}O_3N_2$ to which structure (I) was assigned. Because of recent interest[2] in this area we now briefly report the results of our investigation into this reaction.

Repetition of the photolysis in a methanol–diethyl ether mixture, using a tungsten lamp, provided a hydrochloride, $C_8H_{14}O_2N_2$,HCl, transformed by treatment with triethylamine into a hygroscopic base, $C_8H_{14}O_2N_2$, molecular weight 170 (mass spectrum), best manipulated as the monohydrate, the latter being the compound originally described by Mitchell.[1] On the basis of the following evidence we now assign to the parent substance the dinitrone structure (II).

The presence of an α-dinitrone chromophore was indicated by the ultraviolet absorption, λ_{max} 347 mμ, (9,600), comparable to that of the dinitrone (III),[3] λ_{max} 331 mμ, (18,500), and also by the infrared absorption[4] at 1560—1580 cm.$^{-1}$ The n.m.r. spectrum defined the presence of two,

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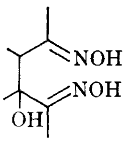
[1] S. Mitchell and J. Cameron, *J. Chem. Soc.*, 1938, 1964.
[2] J. R. Bull, Sir Ewart R. H. Jones, and G. D. Meakins, *J. Chem. Soc.*, 1965, 2601.
[3] R. F. C. Brown, V. M. Clark, M. Lamchen, and Sir Alexander Todd, *J. Chem. Soc.*, 1959, 2116.
[4] J. Harmer and A. Macaluso, *Chem. Rev.*, 1964, **64**, 673.

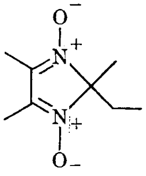
equivalent, vinyl methyl groups (τ 7·88), one quaternary methyl (τ 8·44), and one quaternary ethyl group (τ 9·37, 8·00). Reduction with sodium borohydride proceeded, initially, to a dihydro-compound (IV), whose spectral properties, $\lambda_{\max}$ 232 mμ, (8,600),[5] $\nu_{\max}$ 3200, 1620 cm.$^{-1}$, were consistent with the presence of a mononitrone residue rather than the alternative *O*-alkyl oxime group.[6] Reoxidation with mercuric oxide[7] or manganese dioxide regenerated the dinitrone thereby confirming the presence of a di-*N*-alkyl hydroxylamino-residue in the dihydro-compound. The n.m.r. spectrum of this substance demonstrated the presence of a methyl group (τ 8·70, *J* 6·5 c./sec.) adjacent to a single proton (τ 6·23, quartet); acidic hydrolysis yielded ethyl methyl ketone.

Further reduction with borohydride gave a tetrahydro-compound (V), molecular weight 174 (mass spectrum), $\lambda_{\max}$ 210 (9,000), $\nu_{\max}$ 3300 cm.$^{-1}$, giving a positive tetrazolium test for an *N*-alkyl hydroxylamine.[8,9] The newly formed *N*-s-butyl grouping was defined by the n.m.r. spectrum. Acidic hydrolysis of this compound afforded biacetyl monoxime, presumably by dehydration of the hydroxylamine and hydrolysis of the imine thus formed.

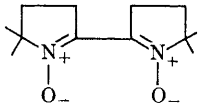
Having established the structure (II) for the photolysis product we have examined the acidic hydrolysis, which proceeded to an approximately equimolar mixture of ethyl methyl ketoxime and biacetyl monoxime. When these two compounds were treated with methanolic hydrogen chloride in the dark the same dinitrone salt was obtained as from the photochemical reaction. Thus it appears that the true photo-products of 2-chloro-2-nitrosobutane in methanol are ethyl methyl ketoxime and biacetyl monoxime, which combine in an acid-catalysed dark reaction to give dinitrone (II).



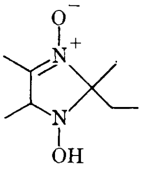
(I)



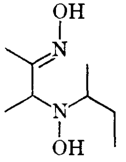
(II)



(III)



(IV)



(V)

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[5] R. Bonnett, V. M. Clark, A. Giddey, and Sir Alexander Todd, *J. Chem. Soc.*, 1959, 2094.

[6] Cholestan-3-one *O*-methyl oxime has $\lambda_{\max}$ 206 mμ, (8,300).

[7] J. Thesing and H. Mayer, *Annalen*, 1957, **609**, 46.

[8] G. A. Snow, *J. Chem. Soc.*, 1954, 2588.

[9] M. A. Thorold Rogers, *J. Chem. Soc.*, 1955, 769.