

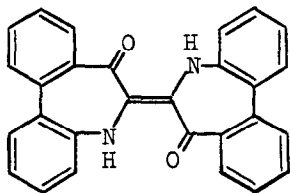
DIBENZAZEPINONES

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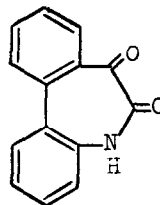
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The supposed azadibenzotropone reported by Paterson and Proctor¹ is now shown to have the structure I. The exact mass found for the molecular ion was 414.13688 ($C_{28}H_{18}N_2O_2$ requires 414.13682) and there was a peak from the doubly charged ion at m/e 207. Oxidation of I with PbO_2 produces a dehydro derivative, orange crystals, mp. 230° ; molecular ion exact mass 412.12132 ($C_{28}H_{16}N_2O_2$ requires 412.12117). Ozonolysis of I gives the dioxodihydrodibenz[bd]azepine (II), pale yellow prisms, mp. $233-4^\circ$; IR (KBr) 3195 (NH), 1685 (CO). The mass spectrum showed the molecular ion at m/e 223 and after loss of CO the remainder of the spectrum was closely similar to that of phenanthridone.



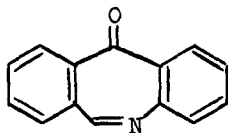
I



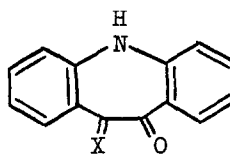
II

By Sonn-Müller reduction of the known morphanthridine-6,11-dione² we have prepared 4-oxodibenz[bel]azepine (III) pale yellow crystals, mp. $93-4^\circ$; IR (KBr) 1655, 1650, no NH or OH absorption; NMR ($CDCl_3$) 1.19τ (1H, singlet), $1.7-1.95\tau$ (2H, multiplet), $2.2-2.6\tau$ (6H, multiplet). The mass spectrum shows the molecular ion at m/e 207 and after loss of CO the remainder of the spectrum is identical with that of phenanthridine.

An isomer of II has also been prepared from the known³ oxo-dihydrodibenz[bf]azepine (IV) by acetylation, oxidation with SeO_2 and hydrolysis. The resulting dioxodihydrodibenz[bf]azepine (V) forms orange red crystals which decompose, without melting, above 360° in a sealed tube; IR (KBr) 3322, 1648, 1632, 1600, 1580; NMR (dimethyl sulphoxide- d_6) -0.92τ (1H, broad), 2.3-2.9 τ (8H, ABCD multiplet). The mass spectrum shows the molecular ion at m/e 223 and after loss of CO the remainder of the spectrum is identical with that of acridone. The compound undergoes very facile benzylic acid rearrangement and dehydration to acridine-9-carboxylic acid. By catalytic hydrogenation one carbonyl group can be reduced and the resulting product readily undergoes acid catalysed dehydration with rearrangement to 9-formylacridine. Compounds II and V are formally azadibenzotropolones but their properties do not appear to support such a formulation. However, they require further examination before excluding the possibility of tautomerism.



III

IV X = H₂

V X = O

References

1. W. Paterson and G. R. Proctor, J. Chem. Soc. 1962, 3468
2. M. M. Coombs, J. Chem. Soc. 1958, 4200
3. British Patent 943, 277 [Chem Abstracts 61, 1815 (1964)]