Phenanthridine 5-Oxides with Acetylenic Esters and the Preparation of Dibenzo[e,g]indolizine

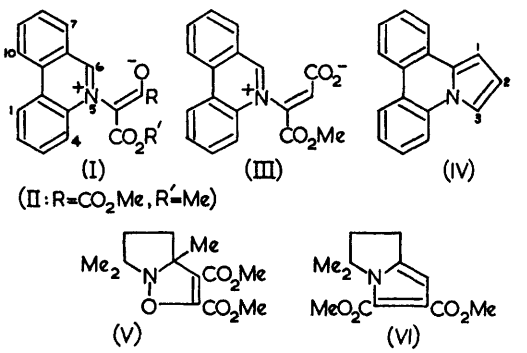
By R. M. ACHESON, A. S. BAILEY, and I. A. SELBY

(*The Department of Biochemistry and the Dyson Perrins Laboratory, University of Oxford*)

PHENANTHRIDINE 5-OXIDE, and 6-alkyl derivatives, have been shown to react with several acetylenic esters yielding 1 : 1 molar adducts of structure (I), analogous to similar products from 1,2-dimethylbenzimidazole 3-oxide.[1] Our adducts possess ultraviolet absorption spectra very similar to that of the betaine (III) and related salts,[2] and absorption at *ca.* 1550 cm.$^{-1}$ corresponding to the enolate anion.[1,3] The n.m.r. spectra of the adducts show the expected correspondence with those of the appropriate phenanthridinium salts, where a 6-methyl group appears at *ca.* τ 6·5, and the proton at position 6 when present [*e.g.*, in (I), R = H, R^1 = Me] appears as a singlet (τ 0·2) which does not exchange in deuterotrifluoroacetic acid.

While the mass spectrum of the dimethyl acetylenedicarboxylate adduct (II) showed the loss of two ester groups, and also of the whole side chain, that of its 6-methyl derivative (II, 6-Me) showed a very small molecular ion and a very large peak corresponding to the loss of water. This suggested that cyclisation to dimethyl dibenzo[*e,g*]indolizine-2,3-dicarboxylate had taken place, as was subsequently found to occur on sublimation of the adduct. Both this diester, and the original adduct (II, 6-Me) with alkali gave dibenzo[*e,g*]indolizine-2-carboxylic acid, which decarboxylated over soda-lime to dibenzo-[*e,g*]indolizine (IV). This is the first preparation of this parent heterocycle (IV) although derivatives are known.[4] The similar benzimidazole adducts do not cyclise with potassium carbonate.[1]

Dimethyl acetylenedicarboxylate with 2-methyl-Δ^1-pyrroline 1-oxides gives 1 : 1 molar adducts, described as isoxazolines [*e.g.*, (V)]. Heating caused cyclisation to pyrroles, the structure (VI) suggested in one case being supported by degradative experiments. The possibility that these pyrroline adducts are structurally analogous to the phenanthridines (I), or rearrange to such structures before pyrrole formation, does not appear to be excluded, and this interpretation leads to a simpler understanding of the facile cyclisation than that already suggested.[5]



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[1] S. Takahashi and H. Kano, *J. Org. Chem.*, 1965, **30**, 1118.
[2] R. M. Acheson and G. J. F. Bond, *J. Chem. Soc.*, 1956, 246.
[3] F. Ramirez, O. P. Madan, and S. R. Heller, *J. Amer. Chem. Soc.*, 1965, **87**, 731.
[4] N. J. Leonard and J. H. Boyer, *J. Amer. Chem. Soc.*, 1950, **72**, 2980; S. Sugasawa and S. Ohki, *J. Pharm. Soc. Japan*, 1942, **62**, 398 (*Chem. Abs.*, 1951, **45**, 5168); R. M. Acheson and A. O. Plunkett, *J. Chem. Soc.*, 1962, 3758.
[5] R. Grigg, *Chem. Comm.*, 1966, 607.