Synthesis of a Derivative of Cycl[3,3,3]azine (9b-Azaphenalene)

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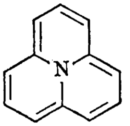
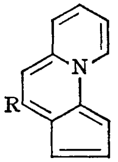
THE azaphenalene (I), also known[1] as cycl[3,3,3]-azine, is of considerable theoretical interest[1,2] and has been the object of synthetical endeavours[3] for more than a decade. Following our recently discovered synthesis[4] of cyclopenta[*c*]quinolizines (II), a convenient route to the ring system (I) appeared to be available for it seemed probable that compounds (II) would react with electrophilic acetylenes to give dihydrocyclopentacyclazines (III; R′ = electron-accepting group).

The 4-methyl compound (II; R = Me) reacted with dimethyl acetylenedicarboxylate, in dry ether at room temperature, to give, *inter al.*, an orange and a green compound, both of which gave analytical results acceptable for 1 : 1 adducts. Neither compound, however, showed n.m.r. absorptions attributable to the allylic hydrogen atoms of structure (III). The orange compound was probably the open-chain adduct (IV or the 3-substituted isomer) since it showed a low-field doublet (τ = 1·37), due to the 9-proton, and a one-proton, olefinic singlet (τ = 4·27). The green compound, however, contained a slightly lower percentage of hydrogen and its n.m.r. spectrum, which showed no α-pyridine proton absorption, indicated a ratio of methyl (O–Me plus C–Me) to aromatic hydrogen atoms of 3 : 2. It appeared, therefore, that dehydrogenation had occurred to give compound (V; R = Me, R′ = R″ = CO_2Me).

Conclusive evidence for this ring system was more easily obtained by reaction of the 4-phenyl compound (II; R = Ph) with methyl phenylpropiolate in boiling nitrobenzene. The resulting green ester (V; R = R″ = Ph, R′ = CO_2Me) was hydrolysed and decarboxylated to give compound (V; R = R″ = Ph, R′ = H), the symmetry of which was apparent from its n.m.r. spectrum. The latter showed, in addition to the phenyl group absorptions (τ 2·1–2·7), two singlets (τ = 2·78 and 3·40; two protons each), attributable to the protons at positions 1, 2, 4, and 8, and an AB_2 multiplet (τ_A = 2·94; τ_B = 3·19) attributable to the protons at positions 5, 6, and 7. The compound formed greenish-black prisms, m.p. 186–187°, and deep green solutions, $\lambda_{max.}$ (ethanol) 207, 262, 285, 342, 366, 467; (tetrahydrofuran) 602, 655, and 723 mμ (log ϵ 4·5, 4·68, 4·70, 4·14, 4·23, 4·03, 2·65, 2·71, and 2·44). Its chemical properties, and those of related compounds, are under investigation with particular emphasis towards methods of effecting fission of the 1,2-bond.


(I)



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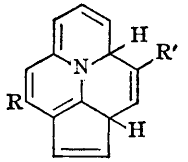

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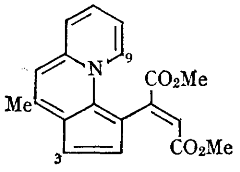

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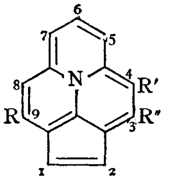

(V)

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[1] R. J. Windgassen, W. H. Saunders, and V. Boekelheide, *J. Amer. Chem. Soc.*, 1959, **81**, 1459.

[2] R. D. Brown and B. A. W. Coller, *Mol. Phys.*, 1959, **2**, 158.

[3] V. Boekelheide and W. G. Gall, *J. Org. Chem.*, 1954, **19**, 499; H. V. Hansen and E. D. Amstutz, *ibid.*, 1963, **28**, 393; V. Boekelheide, H. Fritz, J. M. Ross, and H. X. Kaempfen, *Tetrahedron*, 1964, **20**, 33; D. Leaver and J. D. R. Vass, *J.*, in press.

[4] W. K. Gibson and D. Leaver, *Proc. Chem. Soc.*, 1964, 330.