Synthesis of Cycl [3,3,2]azinones and Benz[*cd*]azulenones

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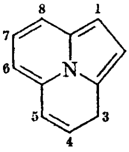
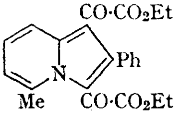
THE "second stable adduct"[1] of 2-styrylpyridine and dimethyl acetylenedicarboxylate was recently recognised[2] as the first known derivative of cycl[3,3, 2]azine (pyrrolo[2,1,5-*de*]quinolizine). This ring system is potentially capable of becoming aromatic[3] but no derivatives with uninterrupted peripheral conjugation have hitherto been available for study. We now report the synthesis of derivatives which are related to the parent compound (I; 3*H*-isomer shown) in the same way as tropolone is related to cycloheptatriene.

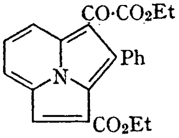
5-Methyl-2-phenylindolizine reacted with three molar proportions of ethoxalyl chloride, in dichloromethane, to give the 1,3-diethoxalyl derivaive (II). Heating this compound with sodium ethoxide in dry ethanol converted it partly into the ethanol-soluble cycl[3,2,2]azine (III) and partly into the insoluble sodium salt of the hydroxycycl[3,3,2]-azinone (IV or V; R = CO·CO_2Et). Standard procedures of hydrolysis, decarbonylation, and decarboxylation were then used to convert the former product into 2-phenylcycl[3,2,2]azine, identical with an authentic specimen,[3] and the latter into 4(or 3)-hydroxy-2-phenyl-3(or 4)-*H*-cycl[3,3,2]azin-3(or 4)-one (IV or V; R = H). The cyclazinone was a bright yellow, crystalline compound which showed infrared absorptions (in $CHCl_3$) characteristic of a hydrogen-bonded hydroxyl group (3280 cm.$^{-1}$) and of a highly polarised carbonyl group (1590 cm.$^{-1}$). Its n.m.r. spectrum (in $CDCl_3$) showed a complex but well-resolved multiplet in the region τ 1·8—2·8 (intensity 10) and a singlet near τ 1·4 (intensity 1; OH proton) which disappeared when the solution was shaken with deuterium oxide.



(I)



(II)



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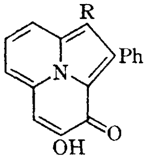
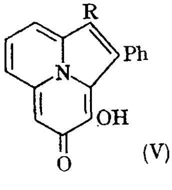
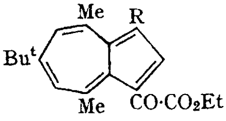


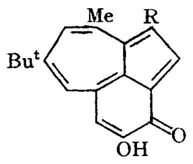
(IV)



(V)



(VI)



(VII)

By making use of the well-known[4] chemical relationship between indolizines and azulenes, we were able to carry out analogous reactions leading to derivatives of benz[*cd*]azulene, a ring system which has been the subject of recent theoretical[5] and experimental[6] investigations. For example, treatment of the 1-ethoxalylazulene (VI; R=H) with sodium methoxide in boiling methanol gave an insoluble sodium salt from which the dark green 4-hydroxy-3*H*-benz[*cd*]azulen-3-one (VII; R=H) was obtained. This compound showed infrared absorptions at 3360 and 1603 cm.$^{-1}$ and its n.m.r. spectrum was fully consistent with the assigned structure.

The monoethoxalyl compound (VI; R=H) resisted further attack by ethoxalyl chloride but it reacted with ethyl cyanoformate, in the presence of dry hydrogen chloride (Hoesch reaction), to give the 1,3-diethoxalylazulene (VI; R=CO·CO$_2$Et). This compound gave the corresponding benzazulenone (VII; R=CO·CO$_2$Et) with exceptional ease (heating in neutral ethanol) but all attempts to bring about a double cyclisation yielded a deeply coloured, amorphous material which appeared to be polymeric. It is perhaps significant that the expected product of double cyclisation could be regarded as a quinone of cyclohepta[*def*]fluorene, a hypothetical hydrocarbon for which a triplet ground state or a low-lying triplet excited state has been predicted.[7]

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[1] O. Diels and F. Möller, *Annalen*, 1935, **516**, 45.

[2] R. M. Acheson and R. S. Feinberg, *Chem. Comm.*, 1965, 342.

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

[4] M. Fraser and D. H. Reid, *J. Chem. Soc.*, 1963, 1421.

[5] R. Zahradník and J. Michl, *Coll. Czech. Chem. Comm.*, 1965, **30**, 3529; R. Zahradník, *Angew. Chem. Internat. Edn.*, 1965, **4**, 1048.

[6] K. Hafner and H. Schaum, *Angew. Chem. Internat. Edn.*, 1963, **2**, 95; 1964, **3**, 165; E. Galantay, H. Agahigian, and N. Paolella, *J. Amer. Chem. Soc.*, 1966, **88**, 3875; V. Boekelheide and C. D. Smith, *ibid.*, p. 3950.

[7] P. Baumgartner, E. Weltin, G. Wagnière, and E. Heilbronner, *Helv. Chim. Acta*, 1965, **48**, 751.