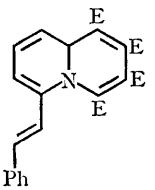
A Cycl[3,3,2]azine

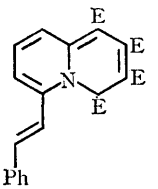
By R. M. ACHESON and R. S. FEINBERG

(*Department of Biochemistry, University of Oxford and the Department of Chemistry, University of Oregon*)

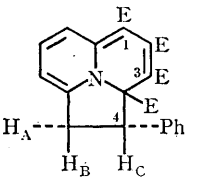
THE special interest in the adducts from *trans*-stilbazole and dimethyl acetylenedicarboxylate arises from the observation[1] that the isomerisation of the "1st labile adduct" to the "1st stable aduct," now formulated as (I) and (II) respectively by analogy[2] and on the basis of their chemical reactions, n.m.r., i.r., and u.v. spectra, by heat also gives an isomeric "2nd stable adduct" for which a satisfactory formulation could not be suggested.[1] It is now established that heating (II) also gives the "2nd stable adduct."



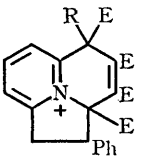
(I)



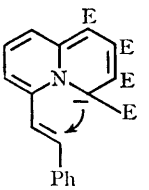
(II)



(III)



(IV)



(V)

The "2nd stable adduct" has been identified as the cycl[3,3,2]azine (III). The absence of the styryl double bond in the adduct (III) is suggested by its resistance to oxidation while both (I) and (II) yield benzoic acid readily. Five moles of hydrogen are absorbed in the catalytic reduction of (III) while both (I) and (II) absorb 6 moles. The n.m.r. spectra of both (I) and (II) show the four protons of the heterocyclic system with their expected[3] chemical shifts and coupling constants, also the two styryl protons, four ester-methyl groups and five benzene protons. The main differences in the spectrum of the adduct (III) are the replacement of the styryl and the saturated protons by a high field three spin ABX system and by the movement of one of the ester groups up-field to τ 6·8. The ABX system at 60 Mc./sec. has the parameters H_A τ 7·05, H_B 6·17, and H_C 5·54, and J_{AB} = 17·5, J_{AC} = 0·0, J_{BC} = 7·5 c./sec., and agreement between theoretical and observed spectra at both 60 and 100 Mc./sec. is excellent. Decoupling of proton B caused the collapse of both protons A and C resonances to singlets. The high field positions of the A and B protons, and their very large coupling constant shows that they must be present as a methylene group and the lack of coupling between the A and C protons is consistent with the geometry of the molecule. Rotation of the 4-phenyl group is hindered, and the high-field resonance of the 3-ester group is due to its position above the plane of this ring. The ultraviolet absorption spectrum of the cyclazine (III) is very similar to that of tetramethyl 6-methyl-4*H*-quinolizine-1,2,3,4-tetracarboxylate.[3] The cyclazine (III), with strong acids, protonated mainly at position-1 yielding the cation (IV, R = H) and with nitric acid gave the nitrate of the cation (IV, R = OH).

cis-Stilbazole with the acetylenic ester gave the *cis*-analogue of (I) which was easily isomerized by heat to *cis*-(II). Only a trace of the cyclazine (III) was isolable under conditions where it was formed in good yield from *trans*-(I). The original stereochemistry of the styryl double bond therefore remains intact until cyclization has been

[1] O. Diels and F. Möller, *Annalen*, 1935, **516**, 45.
[2] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 149.
[3] R. M. Acheson, R. S. Feinberg, and J. M. F. Gagan, *J. Chem. Soc.*, 1965, 948.

initiated, and it is suggested that the loss of a proton from the adducts (I) and (II) gives the resonance-stabilized anion (V) which attacks the styryl double bond prior to proton addition; the anion (V) may also be an intermediate in the conversion of (I) into the more conjugated (II).

The adduct (III) appears to be the first compound recognized containing the cycl[3,3,2]azine ring system.

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