1,6-Cycloaddition to *N*-Ethoxycarbonylazepine

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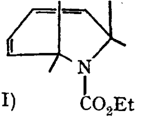
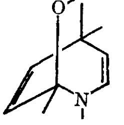
IT has been suggested[1d] that 1,6-cycloaddition occurs between tetracyanoethylene and *N*-ethoxycarbonylazepine.[2,3] However, it was shown later[3] that a 1,4-cycloaddition product was formed exclusively. The recent examples[4] of the unusual 1,6-cycloaddition reaction led us to examine further the cycloadditions to azepines.

Nitrosobenzene[5] reacted with *N*-ethoxycarbonylazepine[6] within 24 hr. under nitrogen, in benzene. Light yellow crystals (55%), $C_{15}H_{16}N_2O_3$,† m.p. 109—110°, separated. The same yield was obtained when light was excluded. The compound appears to be a 1,6-adduct (I) rather than a 1,4- (II) or a 1,2-adduct (III).‡

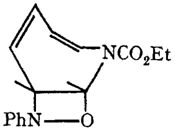
The i.r. spectrum (KBr disc) showed no absorptions due to OH or NH stretching vibrations. The u.v. spectrum [λ_{max} (hexane) 2350 Å, ϵ 14,600; λ_{max} 2550 sh Å, ϵ 9800, λ_{max} 2610 Å, ϵ 9400] was similar to related systems.[4a-d,7] To confirm the conjugation, the adduct was hydrogenated in methanol with Pt catalyst at 50 lb. pressure for 48 hr. A tetrahydro-adduct $C_{15}H_{20}N_2O_3$,† m.p. 50—51°, was obtained in 73% yield. The i.r. spectrum confirmed that no N–O cleavage had occurred. The u.v. difference curve between the adduct (I) and the tetrahydro-adduct effectively removed the aniline chromophore absorption. This



(I)



(II)



(III)

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† Elemental analysis was satisfactory. Molecular weight of the adduct was determined from the mass spectrum, since it appears to dimerize in benzene even at 37°. Molecular weight of the tetrahydro-adduct was determined cryoscopically.

‡ The other isomers from 1,4- and 1,2-addition were considered and excluded by the spectroscopic evidence outlined.

curve [λ_{max} (hexane) 2570 Å, ϵ 8700; λ_{max} 2800 Å, sh ϵ 5400] was consistent with a conjugated *cis*-diene chromophore.[4a–d,7] A similar u.v. difference curve was obtained from adduct (I) and phenylhydroxylamine. Structure (II) was thereby discounted. Differentiation between structures (I) and (III) was based on the n.m.r. spectrum (60 Mc./sec., in $CDCl_3$) which showed a poorly resolved multiplet due to five benzenoid protons (τ 2·85), a five proton singlet due to the four vinylic protons and a methine proton (τ 3·79), the signal of the second methine proton as a one proton singlet (τ 4·02), a two proton quartet due to the ester methylene (τ 6·08), and a three proton triplet due to the ester methyl (τ 9·02). The assignments are based on the comparison with the n.m.r. of the tetrahydro-adduct which differed only in that there were two one proton singlets, methine protons (τ 4·00 and 4·32), and an eight proton, poorly resolved multiplet (τ 8·12). The simplicity of the vinylic region in the n.m.r. spectrum of adduct (I) strongly indicates a symmetrical molecule such as structure (I). Moreover, it resembles the n.m.r. spectra of related systems.[4a–d,7] Structure (III) would have splitting patterns due to 1,2 and 1,3 coupling of the vinylic protons.[3b,c,8] This point has been discussed elsewhere.[3b] Structure (III) is therefore rejected. The mass spectrum of adduct (I) showed a molecular ion *m/e* 272, and a peak at *m/e* 185 indicated the loss of NCO_2Et from the molecular ion, whereas strong peaks at *m/e* 256, 243, and 156 suggested that graded loss of O, CH, and NCO_2Et from the molecular ion led to the stable *N*-phenylpyridium ion (*m/e* 156). Peaks were found also at *m/e* 165 $(C_9H_{11}NO_2)^+$ and *m/e* 107 $(PPhNO)^+$. This spectrum is consistent with structure (I).

A thermally induced [6 + 2] cycloaddition is not permissable according to the Hoffmann–Woodward correlations.[9] The probability of a non-concerted reaction[4c,d] is being studied.

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