The Cycloaddition of Homo-1*H*-azepine

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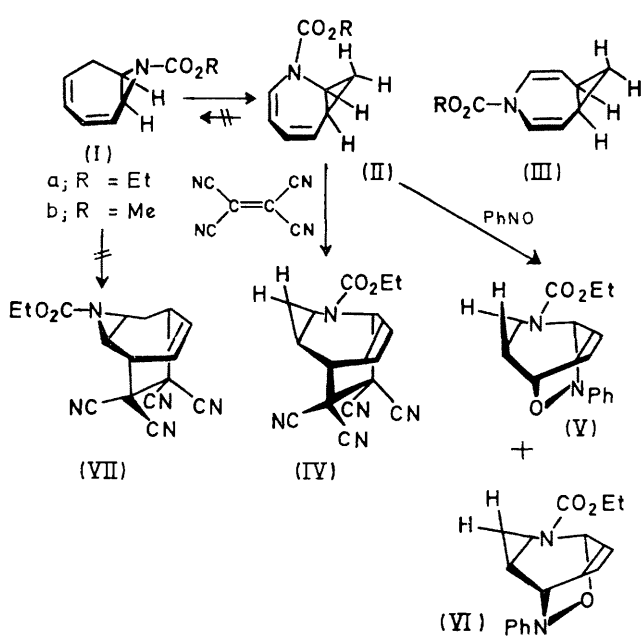
Summary Reactions of tetracyanoethylene and nitrosobenzene with 2,3-homo-1*H*-azepine (II) give the corresponding normal (4 + 2) π cycloadducts, and show that (II) reacts faster than its valence tautomer (I).

PAQUETTE[1] and OKAMURA[2] and their co-workers reported recently the synthesis of (IIa,b) and (IIIa,b) from alkyl azidoformate and cycloheptatriene. No adducts were obtained from these compounds with benzyne or diphenylisobenzofuran.[1]

We now report that we have prepared the homoazepines (IIa) and (IIIa) and that (IIa) reacts with tetracyanoethylene and with nitrosobenzene to give the adducts (IV), and (V) and (VI).

Heating ethyl azidoformate with cycloheptatriene in a sealed tube at 130° for 2 hr afforded a 2 : 1 mixture of 2,3- (IIa) and 4,5-homo-1*H*-azepines (IIIa)[3] in a combined yield of 35% (by n.m.r. and g.l.p.c. analyses). The mixture was treated with tetracyanoethylene in benzene for 2 hr at room temperature [complete disappearance of compound (IIa) on g.l.p.c.], which led to the formation of a 1 : 1 adduct (IV) as colourless crystals, m.p. 149—152°, $C_{16}H_{13}N_5O_2$, in 37% yield with complete recovery of 4,5-homo-1*H*-azepine (IIIa). The mass spectrum shows a molecular ion (M^+ *m/e* 307) and a strong peak at $M - 128$ resulting from the loss of C_6N_4 from the molecular ion, characterized as a retro-Diels–Alder type fragmentation. The n.m.r. spectrum of (IV) [$(CD_3)_2SO$ at 100 MHz] shows three triplets centred at τ 3·37 (8-H, $J_{7,8}$ 9·0, $J_{1,8}$ 7·0 Hz), 3·55 (7-H, $J_{7,8}$ 9·0, $J_{6,7}$ 7·0 Hz), and 5·58 (1-H, $J_{1,8}$ 7·0, $J_{1,2}$ 6·0, $J_{1,7}$ 1·0 Hz), double doublets centred at τ 4·49 (6-H, $J_{6,7}$ 7·0, $J_{6,8}$ 1·0 Hz), three multiplets at τ 6·85—7·15 (4-H), 8·18—8·48 (2-H) and 8·80—9·25 (2H, geminal protons at C-3), and the ethyl



protons of the ethoxycarbonyl group at τ 5·83 (2H, q, J 7·0 Hz) and 8·80 (3H, t, J 7·0 Hz). The chemical shifts of 6-H, 7-H, and 8-H closely resemble those of the (4 + 2) π cycloadducts of 1*H*-azepine[4] and 1(1*H*),2-diazepine with tetracyanoethylene.[5] The spectra show that the adduct with (IIa) is (IV) and not (VII) and that the homoazepine (IIa) reacts faster than its valence tautomer (and precursor) (Ia).

Treatment of (IIa) (isolated from the reaction mixture) with nitrosobenzene in benzene for 2 weeks at room temperature gave a 1 : 1 mixture of (V) and (VI) in 52% yield. However, similar treatment of (IIIa) with nitrosobenzene gave no adduct. Chromatography on a silica gel column using benzene as an eluant afforded compound (V) as colourless crystals, m.p. 110—112° and compound (VI) as a yellow oil. The analytical and mass spectral evidence indicate that both compounds are 1 : 1 adducts, $C_{16}H_{18}N_2O_3$, M^+ m/e 286). The n.m.r. spectra of (V) and (VI) are practically superimposable except for the signal due to 1-H; 1-H appeared at τ 5·00 (broad triplet, $J_{1,8}$ 6·0, $J_{1,2}$ 6·0, $J_{1,7}$ 1·0 Hz) in (V), and τ 5·42 (broad triplet, $J_{1,8}$ 6·0, $J_{1,2}$ 5·0, $J_{1,7}$ 1·0 Hz) in (VI). Final assignments of these signals and couplings constants were confirmed by spin-decoupling experiments at 100 MHz.

Thus, the adducts of 2,3-homo-1*H*-azepine involve a novel heterocyclic ring system (5-azatricyclo[4,2,2,$0^{2,4}$]-deca-7-ene), but 4,5-homo-1*H*-azepine did not undergo cycloaddition reactions with tetracyanoethylene and nitrosobenzene. Several attempted cycloaddition reactions of 2,3- and 4,5-homo-1*H*-azepines with dimethyl acetylenedicarboxylate were unsuccessful even in refluxing toluene.

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[1] L. A. Paquette and R. J. Haluska, *J. Org. Chem.*, 1970, **35**, 132.
[2] W. H. Okamura, W. H. Snider, and T. J. Katz, *Tetrahedron Letters*, 1968, 3367; W. H. Okamura, *ibid.*, 1969, 4717.
[3] Other minor products seem to be a mixture of cycloheptatrienylurethanes from the nitrene-insertion reaction (see ref. 1).
[4] The structures of the (4 + 2) and (6 + 2) π cycloadducts of *N*-ethoxycarbonylazepine with tetracyanoethylene and nitrosobenzene have been established; (a) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, 1965, **87**, 4819; (b) A. S. Kende, P. T. Izzo, and J. E. Lancaster, *ibid.*, p. 5044; (c) W. S. Murphy and J. P. McCarthy, *Chem. Comm.*, 1968, 1155.
[5] T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Comm.*, 1969, 432; T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, 1970, **35**, 426.