Photochemical Isomerisation of 3*H*-1,2-Diazepines to 4,6a-Dihydro[1,2]-diazeto[1,4-*a*]pyrroles

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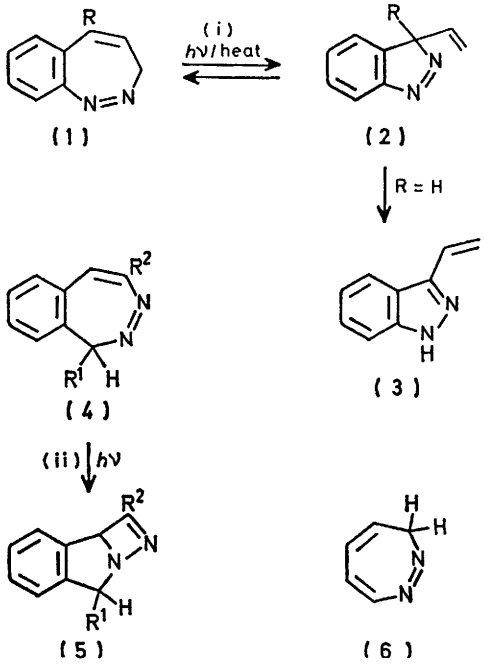
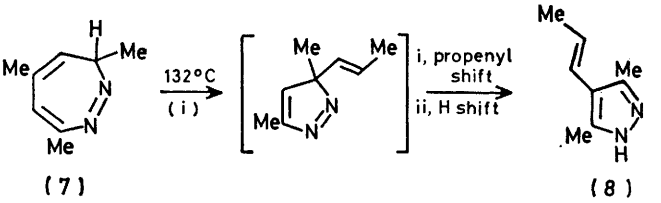
3*H*-1,2-Diazepines (9) undergo a rapid photoisomerisation to 4,6a-dihydro[1,2]diazeto[1,4-*a*]pyrroles (10).

It has recently been shown that 3*H*-1,2-diazepines annelated to aromatic rings undergo photo-induced reactions of two kinds. 1,2-Benzodiazepines (1) and analogous thienodiazepines react *via* cleavage of the bond between the azo-group and the allyl carbon atom and undergo ring contraction to 3-alkenylindazoles (2) or (3) [pathway (i)].[1-4] The mechanism of this reaction is

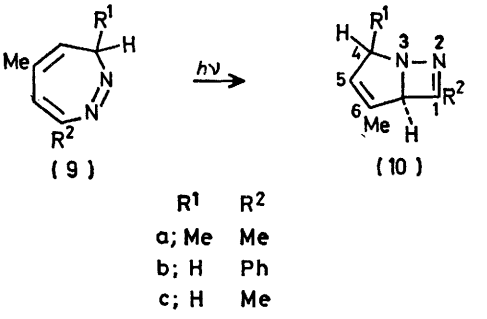


not certain, being either a two-step radical cleavage–recombination or a concerted ($\sigma_s^2 + \pi_s^2$) process. The thermal decomposition of some of these 1,2-benzodiazepines (1; R ≠ H) gives the same products (2) most likely *via* the two-step route.[1] 2,3-Benzodiazepines (4) however do not photolyse *via* a similar benzyl–azo bond cleavage but instead undergo a rapid isomerisation to (5) *via* a ($\pi_s^2 + \pi_s^2$) closure of the 1,2-diazabutadiene unit to a diazetine [pathway (ii)].[5] In these two groups of benzodiazepines the position of the benzene ring apparently has a strong influence on which reaction path is followed, *i.e.* (1) is inhibited from taking pathway (ii) because of the double bond fixation effect of the benzene ring, and (4) is inhibited from taking pathway (i) because the primary product would lose aromatic stabilisation. These constraints are lifted in the monocyclic 3*H*-1,2-diazepines (6), and it was thus of interest to determine which mode of photochemical reaction these compounds would adopt. A study of their thermal decomposition has shown that the reaction proceeds *via* pathway (i) and subsequent rearrangements to give alkenylpyrazoles, *e.g.* (7) ⟶ (8).[6]

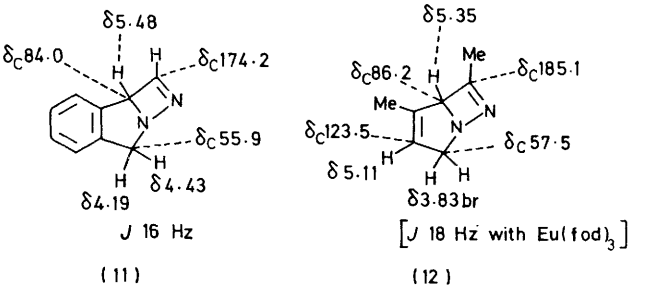


RESULTS AND DISCUSSION

It was found that the 3*H*-1,2-diazepines react exclusively by pathway (ii) to give the rather unstable 4,6a-dihydro[1,2]diazeto[1,4-*a*]pyrroles (10) in high yield. This formulation for the products is strongly supported



by the similarity of their mass and ^1H and ^{13}C n.m.r. spectra to those of the benzo-annelated analogues (5). Some comparative n.m.r. data are shown for (11) and (12). The ^{13}C assignments are supported by single frequency



off-resonance proton decoupling (SFORD) studies and this technique was also used to unambiguously assign the protons at positions 4 and 6a which both absorb in

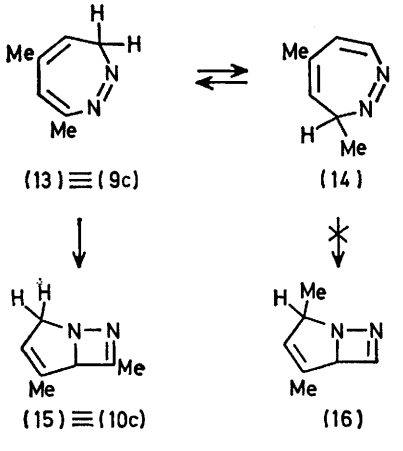
the range δ 5.1—5.6. In the diazetoisoindole (11) and related compounds the methylene protons had the same chemical shift in deuteriochloroform but were separated when run in perdeuteriobenzene (J 16 Hz). However the analogous methylene group in (10b) and (10c) gave a broad multiplet in both these solvents but this was shifted to higher frequency and separated into a pair of doublets (J 18 Hz) by the addition of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium [Eu(fod)$_3$]. The mass spectra of (10) (Table) like those

Mass spectra of 4,6a-dihydro[1,2]diazeto[1,4-*a*]pyrroles (10)

Compound	*m/e* (relative abundance %)
(10a)	39 (44), 40 (41), 41 (88), 42 (23), 43 (29), 53 (35), 54 (29), 59 (21), 67 (29), 80 (41), 94 (100), 95 (97), 136 (52), 137 (2)
(10b)	39 (46), 41 (13), 51 (36), 53 (27), 54 (54), 76 (25), 77 (20), 80 (100), 81 (98), 103 (23), 115 (23), 128 (12), 141 (11), 156 (8), 169 (4), 184 (3)
(10c)	39 (21), 40 (26), 41 (73), 53 (25), 54 (18), 80 (100), 81 (70), 95 (14), 122 (28)

of (5) show small parent-ion peaks and major fragmentation *via* loss of R^2CN.

Some of the reactions of 3*H*-1,2-diazepines are complicated by the rapid interconvertibility between the isomers *e.g.* (13) and (14) at room temperature by [1,5] sigmatropic hydrogen shifts. For (13) and (14) the equilibrium at room temperature favours (13) by *ca.* 6 : 1. It is therefore notable that in the photolysis of this mixture, although h.p.l.c. monitoring showed that the (13) : (14) ratio stayed at 6 : 1 throughout as the diazepines were consumed, only one product (15 ≡ 10c) could be detected (h.p.l.c. and n.m.r.) thus indicating a much higher rate of photochemical ring closure in (13) than (14).



These results therefore show that in 3*H*-1,2-diazepines the ($\pi_s^2 + \pi_s^2$) photochemical ring closure of the diazabutadiene unit is such a favoured reaction path that there is no effective competition from possible alternatives such as the analogous closure of the butadiene unit; or allyl–azo bond cleavage and ring contraction to a pyrazole as in the thermal decomposition; or 1,7-hydrogen migration which is the favoured path for the analogous cycloheptatrienes.[7]

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on a Varian HA 100 spectrometer and ^{13}C n.m.r. spectra on a Varian XL 100 or CFT 20 spectrometer. Chemical shifts are recorded as p.p.m. downfield from internal tetramethylsilane. Mass spectra were obtained with an A.E.I. MS902 instrument (70 eV). The photochemical reactions were carried out with a Hanovia 100 W medium-pressure lamp.

3H-1,2-*Diazepines* (9).—These were prepared as previously described.[8]

Photolysis of 3H-1,2-*Diazepines*.—Dilute solutions (*ca.* 0.01—0.02M) in dry redistilled acetonitrile were irradiated through Pyrex at room temperature under nitrogen until the yellow colour was discharged and t.l.c. (alumina; benzene–ether 1 : 1) showed that all the diazepine had been consumed. The solvent was then removed on a rotary evaporator at room temperature to give a virtually pure product (t.l.c. and n.m.r.). The final purification by distillation to remove the last traces of solvent usually entailed substantial loss of the product by polymerisation.

5,7-*Dimethyl- and* 3,5-*dimethyl*-3H-1,2-*diazepine* (13) *and* (14) (with C. Argo). The diazepines (0.50 g, 4.1 mmol) in acetonitrile (175 ml) were irradiated for 30 min to give 4,6a-*dihydro*-1,6-*dimethyl*[1,2]*diazeto*[1,4-a]*pyrrole* (10c) (0.466 g, 93%) after removal of solvent. Distillation gave the product as a pale yellow oil (0.25 g, 50%), b.p. 85 °C at 50 mmHg (Found: *m/e*, 122.084 136; 81.057 520. $C_7H_{10}N_2$ requires M^+, 122.084 394; C_6H_9 requires $M^+ - 41$, 81.057 846); δ(CDCl$_3$) 1.82 (m, 6-Me), 2.00 (s, 1-Me), 3.83br (s, 4-CH$_2$), 5.11 (m, 5-H), and 5.35 (m, 6a-H); δ_C(CDCl$_3$) 185.1 (C-1), 135.1 (C-6), 123.5 (C-5), 86.2 (C-6a), 57.5 (C-4), and 16.2 and 13.6 (1- and 6-Me).

Monitoring of the reaction by h.p.l.c. [15 × 0.5 cm, Spherisorb S5Y silica at 0 °C using a mixture (1 : 9 v/v) of dry ether and 50% v/v water–saturated hexane as eluant at a flow rate of 2.5 ml min^{-1}] showed that the ratio (13) : (14) remained at *ca.* 6 : 1 throughout as they were consumed but only a single product peak was detected although a variety of solvent combinations were used as eluant (*e.g.* 100% ether and mixtures of hexane and dioxan ranging from 1 : 3 to 1 : 1).

3,5,7-*Trimethyl*-3H-1,2-*diazepine* (9a). The diazepine (0.454 g, 3.34 mmol) in acetonitrile (175 ml) was irradiated for 30 min to give 4,6a-*dihydro*-1,4,6-*trimethyl*[1,2]*diazeto*-[1,4-a]*pyrrole* (10a) (0.40 g, 88%). Distillation gave the product as a pale yellow liquid b.p. 101 °C at 32 mmHg (Found: *m/e*, 136.100 043; 95.073 281. $C_8H_{12}N_2$ requires M^+ 136.100 043; C_7H_{11} requires $M^+ - 41$, 95.073 496); δ(CDCl$_3$) 1.13 (d, J 7 Hz, 4-Me), 1.80 (m, 6-Me), 2.00 (s, 1-Me), 3.95 (m, 4-H), 5.13br (d, J 4 Hz, 5-H), and 5.34 (m, 6a-H); δ_C(CDCl$_3$) 184.4 (C-1), 134.7 (C-6), 129.0 (C-5), 85.7 (C-6a), 63.4 (C-4), and 22.2, 16.2, and 13.6 (1-, 4-, and 6-Me).

5-*Methyl*-7-*phenyl*-3H-1,2-*diazepine* (9b). The diazepine (0.24 g, 1.3 mmol) in acetonitrile (175 ml) was irradiated for 15 min. Evaporation of the solvent left a red oil which was distilled (Kugelrohr) under high vacuum and then recrystallised at −30 °C from light petroleum (b.p. 40—60 °C) to give 4,6a-*dihydro*-6-*methyl*-1-*phenyl*[1,2]*diazeto*[1,4-a]-*pyrrole* (10b) (0.16 g, 67%) as colourless crystals, m.p. 67—68 °C (Found: C, 78.1; H, 6.7; N, 15.0. $C_{12}H_{12}N$ requires C, 78.2; H, 6.6; N, 15.2%); δ(CDCl$_3$) 1.90 (m, 6-Me), 3.98 (m, $J_{2a,5}$ 3.5, $J_{4,5}$ 2 Hz, 4-CH$_2$), 5.42 (m, $J_{2a,4}$ 1.5, $J_{4,5}$ 2 Hz, 5-H), 5.58 (m, 6a-H), and 7.2—7.7 (5 H, m, ArH); δ_C(CDCl$_3$) 182.2 (C-1), 135.4 (C-6), 124.4 (C-5), 84.5 (C-6a), 57.8 (C-4),

130.0 (tert.), 130.6, 128.8, and 124.4 (aromatic), and 14.1 (Me).

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