Photolysis of 1*H*- and 5*H*-2,3-Benzodiazepines

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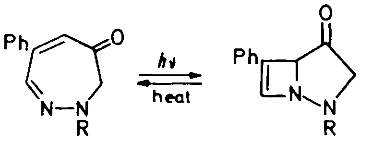
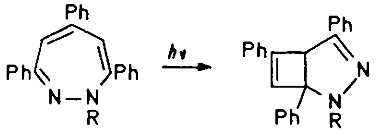
Summary 1*H*-2,3-Benzodiazepines are isomerised to benzo[*c*]-1,7-diazabicyclo[3,2,0]hepta-3,6-dienes on irradiation and do not react *via* extrusion of nitrogen; the 5*H*-isomers undergo a similar reaction followed by loss of nitrogen to give indenes.

Photochemical [$_{\pi}2_s$ + $_{\pi}2_s$] reactions of the butadiene unit in cycloheptatriene[1] and its heterocyclic analogues[2,3] are well known, and a similar azabutadiene (**1**) into 3-azetine (**2**) conversion has been reported.[4] Snieckus[5,6] has shown that highly substituted 1*H*-1,2-diazepines (**3**) photoisomerise *via* reaction of the butadiene rather than the azabutadiene unit. We have recently[7] reported the first general synthesis of 1*H*-2,3-benzodiazepines (**5**) and it was of interest to examine the photochemical reactivity of these compounds to see whether the 1,2-diazabutadiene unit would undergo an isomerisation analogous to the above or would react *via* extrusion of nitrogen as do 1,2-benzodiazepines[8] and 3*H*-pyrazoles.[9] In connection with the latter it is of interest to note that irradiation of some 3*H*-pyrazoles at very low temperatures (−60°) does give a highly unstable valence tautomer (**4**) which readily undergoes thermal reversion.[9]



(1) (2)



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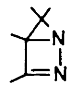
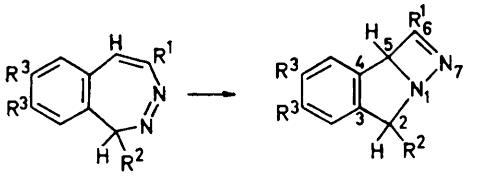


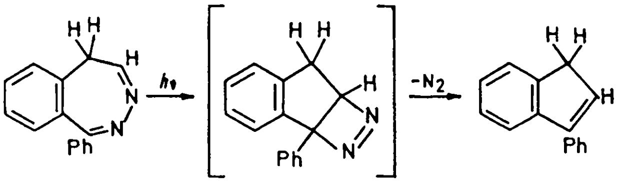
(4)

In fact no nitrogen extrusion was observed in the irradiation of a series of 1*H*-2,3-benzodiazepines (**5**) at 0°; the diazepines were converted quantitatively in 1—10 min into the novel tricyclic compounds (**6**). The products were isolated usually in an analytically pure state by the freeze drying or low temperature evaporation of the reaction solution. Prolonged irradiation gave complex mixtures of products. The formulation of the products (**6**) is supported by spectral data; all products gave mass spectra with the (M^+ − R^1CN) ion as the base peak. ^{1}H n.m.r. spectra showed no coupling between 5-H and 6-H in (**6a—d**) (*cf.* the zero coupling in related systems[2,10]) and in (**6b**) $J_{2,5}$ (*trans*) is *ca.* 2 Hz and $J_{2,5}$ (*cis*) is *ca.* 1 Hz. In (**6b**), the hydrogens at C-2 gave a broad singlet in $CDCl_3$ and a well defined AB system (J_{AB} 15 Hz) in aromatic solvents, the separation and shape of which was unaffected by temperature up to *ca.* 180° when decomposition was rapid. The n.m.r. spectra of (**6a,c,d,e**) showed the presence of only the least hindered isomer indicating steric control over the mode of disrotatory cyclisation. The products (**6**) decompose thermally by two competing paths (i) the formation of indenes, probably *via* thermal reversion to the diazepine and subsequent loss of nitrogen [this is the general mode of thermal decomposition of diazepines (**5**)[11]], and (ii) the extrusion of R^1CN which presumably also gives an unstable isoindole although the latter has so far proved impossible to trap or isolate.



(5) (6)

		M.p. (decomp.)
(a)	R^1 = H, R^2 = Me, R^3 = OMe	116—119°
(b)	R^1 = H, R^2 = H, R^3 = OMe	119—122°
(c)	R^1 = H, R^2 = Ph, R^3 = H	94—97°
(d)	R^1 = H, R^2 = Me, R^3 = H	77—81°
(e)	R^1 = Ph, R^2 = Me, R^3 = H	97—100°
(f)	R^1 = Ph, R^2 = H, R^3 = H	77—83°



(7) (8) (9)

The photolysis of the 5*H*-2,3-benzodiazepine (**7**), formed by base-catalysed isomerisation of (**5**), gave the indene (**9**) in high yield probably *via* an intermediate (**8**) analogous to (**6**).

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