Photolysis and Thermolysis of Highly Substituted 1*H*-1,2-Diazepines

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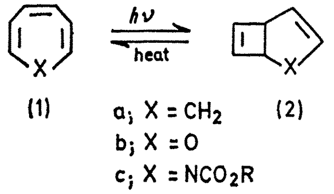
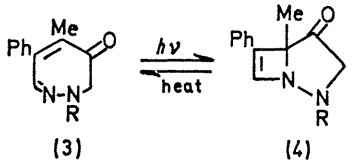
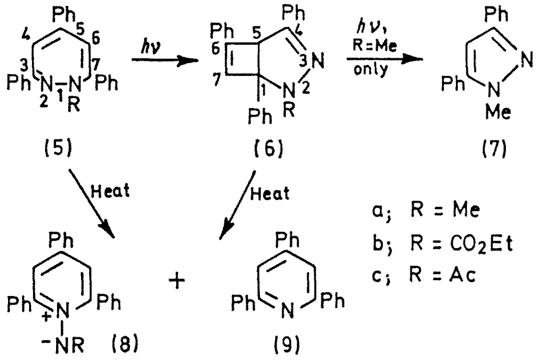
Summary Photolysis of the methyldiazepine (5a) led directly to the pyrazole (7) whereas the ethoxycarbonyl- and acetyl-diazepines (5b) and (5c) gave cycloadducts (6b) and (6c); thermolysis of the diazepines (5) or the diaza[3,2,0]bicycloheptadienes (6) produced mainly ylides (8) and small amounts of 2,4,6-triphenylpyridine (9), except for (5a) which yielded (9) only.

THE symmetry-allowed photochemical cycloaddition of butadiene units within the framework of 7-membered ring systems (1) → (2) has been reported for cycloheptatrienes,[1] oxepines,[2] and azepines,[3] and the unallowed thermal cycloreversion in two of these systems [(2a) → (1a)[4] and (2c) → (1c)[2b]] has been observed. Furthermore, an analogous azabutadiene ⇌ 3-azetine interconversion (3) ⇌ (4) has been discovered.[5] The accessibility of highly substituted 1*H*-1,2-diazepine derivatives (5a—c) and the current interest in 7-membered ring heterocycles[6] gave impetus to a similar study with these compounds.† We report the photochemical and thermal reactions of the diazepines (5a—c) and compare the behaviour of 1*H*-1,2-diazepines with that of the closely related derivatives (1b),[2] (1c),[2b,3c] and (3).[5]





Photolysis of (5a)[8] gave, after chromatography, 1-methyl-3,5-diphenylpyrazole (7)[9] in 82% yield presumably *via* the intermediate (6a) which undergoes nonconcerted loss of phenylacetylene. In the hope that replacement of the *N*-methyl group in (5a) by a neutral function would stabilize this type of intermediate, irradiation of the diazepines (5b) and (5c) was undertaken.‡ Indeed, photolysis of (5b) and (5c), gave the bicyclic compounds (6b) (89%) and (6c) (80%) respectively. Spectral data unambiguously support these formulations (*e.g.* *m/e*§ (6b) 394 (M^+) (58%), 349 (10), 321 (23), 220 (100), and 219 (77);(6c) 364 (M^+) (28%), 322 (28), 321 (14) 307 (18), 220 (94), and 219 (100); τ ($CDCl_3$) (6b): 2·20 and 2·70 (m, 15H, Ar*H*), 3·10 (s, 1H, 7-H), 5·30 (s, 1H, 5-H), 5·85 (q, 2H, *J* 7 Hz, CH_2), and 8·90 (t, 3H, *J* 7 Hz, Me); (6c) 2·10 and 2·60 (m, 15H, Ar*H*),2·90 (s, 1H, 7-H) 5·30 (s, 1H, 5-H), and 7·55 (s, 3H, Me). Pyrolysis (neat; 165—170°) of (6b) and (6c) did not yield the diazepines (5b) and (5c) as expected on the basis of previous observations[2b,5] but gave directly the corresponding ylides (8b) (70%) and (8c) (75%), and the pyridine derivative (9) (15%) in each case. Both (5b) and (5c) also produced the ylides (8b) and (8c) respectively in higher yields under identical conditions indicating that the diazepine derivatives are potential intermediates in the thermal reaction of (6b) and (6c). However, at lower temperatures (140°), (6b) decomposed very slowly to (8b) and no evidence for the presence of (5b) could be obtained. Therefore, the intermediacy of diazepines in the overall thermal rearrangement was not established.



Streith reported[7] that the thermolysis of 1-ethoxycarbonyl-1*H*-1,2-diazepine (5; R = CO_2Et, H replaces Ph) produced low yields of two isomeric open chain cyanobutadiene derivatives and a trace of the ylide (8; R = CO_2Et, H replaces Ph) but that the 1-benzoyl-1*H*-1,2-diazepine (5; R = COPh, H replaces Ph) gave the corresponding ylide (8; R = COPh, H replaces Ph) in 72% yield. Thermolysis of (5a) (benzene; sealed tube; 120—160°) gives the pyridine (9) as the only isolable product (63% yield).[8] This may be a consequence of the predictable[8,11] instability of the presumed intermediate ylide (8a). Thus the thermolysis of (5b) and (5c) under similar conditions gave mainly the ylides (8b) (84%) and (8c) (62%) together with minor amounts of (9). Confirmation of the structure of compounds (8b) and (8c) was obtained by catalytic (Pd–C) hydrogenation to (9). Photolysis of (8b) and (8c) led to the diazepines (5b) and (5c) respectively and the pyridine (9) in each case. In the thermolysis of the compounds (5a—c), the 3-phenyl substituent directs the formation of ylides (8a—c) presumably *via* a diaziridine intermediate[8] to the exclusion of the ring scission products observed with unsubstituted diazepines.[7]

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† 1-Ethoxycarbonyl-1*H*-1,2-diazepine (5b; H replaces Ph) was reported to be stable to photolysis.[7] However, recently it has been converted into the analogous system (6b; H replaces Ph) (J. Streith, personal communication).

‡ (5b) and (5c) were prepared by treatment of 3,5,7-triphenyl-4*H*-1,2-diazepine[10] with ethyl chloroformate and acetyl chloride, respectively.

§ *Cf.* analogous fragmentations for related systems: (2b)[2b], (2c)[3c].

All new compounds showed satisfactory analytical data.

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