Cyclisation Reactions of 1-Aryl-3-diazoalkenes: a New Rearrangement of 3*H*-Pyrazoles to 3*H*-1,2-Benzodiazepines

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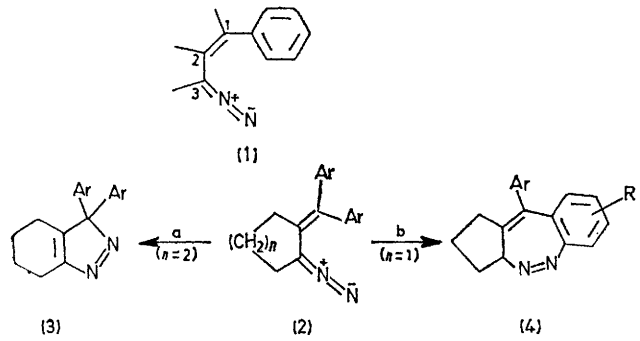
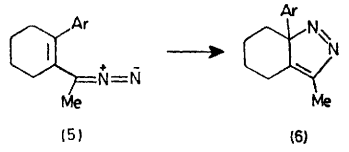
Summary 1-Aryl-2-(1-diazoethyl)cyclopentenes (**7**) are the first 1-aryl-3-diazoalkenes to undergo both 1,5- and 1,7-cyclisation to give 3*H*-pyrazoles and 3*H*-1,2-benzodiazepines; the strained pyrazoles (**8**) undergo a ring expansion to the benzodiazepines (**9**) rather than a thermal van Alphen rearrangement.

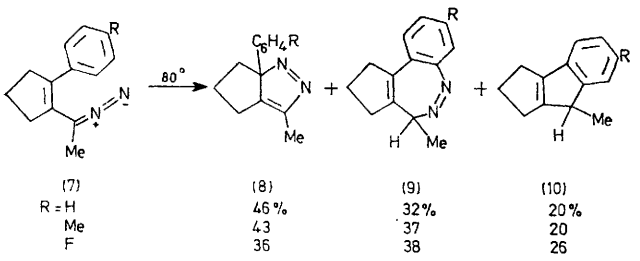
WE have recently shown[1,2] that 1-aryl-3-diazoalkenes (**1**), which normally cyclise to give pyrazoles *e.g.* (**3**) from (**2a**), can be induced to undergo 1,7 ring closure to give 3*H*-1,2-benzodiazepines *e.g.* (**4**) from (**2b**), by the fusion of a cyclopentyl ring at C(2), C(3). The change in the mode of cyclisation was attributed[2] to the inhibition of 1,5-ring

closure in (**2b**) due to steric constraints imposed by the cyclopentyl ring. In a further study of the structural factors affecting the mode of ring closure and in the hope of extending the range of the benzodiazepine synthesis we have examined the reactions of (**5**) and (**7**) which differ from (**2**) in having the carbocyclic rings annelated at C(1), C(2) rather than C(2), C(3).



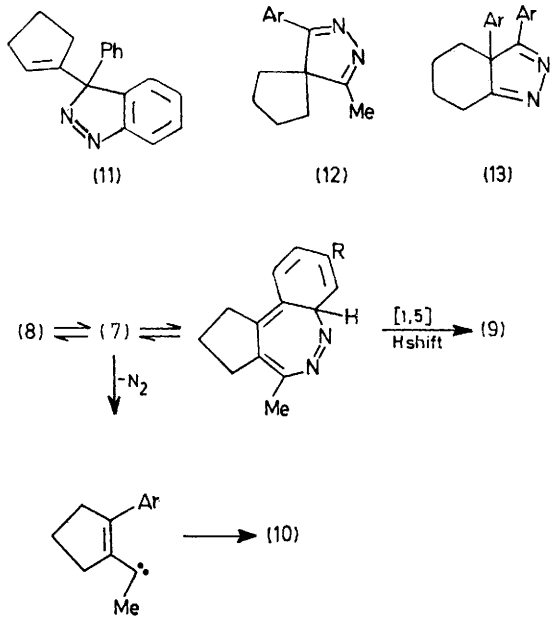
As expected the cyclohexene derivative (**5**) reacted like (**2a**) and underwent only 1,5-cyclisation to give the 3*H*-pyrazole (**6**). The products to be expected from (**7**) were less easy to predict but since models showed that the critical separation[2] between the termini of the π-system for 1,5-closure was less for (**7**) (3·7 Å) than for (**2b**) (3·85 Å) there seemed a greater likelihood of pyrazole formation in this case. In fact (**7**) gave both the 3*H*-pyrazole (**8**) and the benzodiazepine (**9**) together with much more carbene-derived product (**10**) than had been found for (**2b**). These are the first 1-aryl-3-diazoalkenes to undergo both 1,5- and 1,7- cyclisation. The yields are shown in Scheme 1 for reaction times just sufficient to decompose the tosylhydrazone salt precursors of (**7**).





SCHEME 1

After separation the 3*H*-pyrazoles (**8**) were heated again at 80° and in part rearranged to the benzodiazepines (**9**) (31—37%) but also lost nitrogen to give more of the indenes (**10**) (24—41%). The ring expansion of (**8**) to (**9**) is an unprecedented reaction of 3*H*-pyrazoles and provides the second example of rearrangement of a five- to a seven-membered cyclic azo-compound, the first being the reversible interconversion of (**4**) and (**11**).[3] In this case the rearrangement to (**9**) is irreversible but it is expected that these benzodiazepines will undergo reversible ring contraction to 3*H*-indazoles at higher temperatures.



SCHEME 2

A probable mechanism for the decomposition of (**8**) is shown in Scheme 2. The intermediacy of the diazoalkene in the formation of both products is supported by the observation that neither are formed when the decomposition of (**8**, R=H) is carried out in the presence of tributylphosphine which intercepts the diazo-intermediate to give, eventually, 1-acetyl-2-phenylcyclopentene hydrazone in high yield. Tributylphosphine does not react with (**9**) or with (**6**) under the reaction conditions.

3-Aryl-3*H*-pyrazoles normally undergo the thermal van Alphen–Huttel rearrangement[4] rather than the ring expansion observed for (**8**) and the cyclohexapyrazole (**6**) reacted in this way at 80° to give the 4*H*-pyrazole (**12**). This rearrangement of (**6**) was much slower than the decomposition of (**8**). Similarly (**3**) rearranged thermally to (**13**) and gave no benzodiazepine. The dissimilarity between the thermal reactions of (**8**) and [(**6**) and (**3**)] is probably due to the greater ring strain in (**8**) which facilitates ring opening to (**7**).

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[1] R. H. Findlay, J. T. Sharp, and P. B. Thorogood, *Chem. Comm.*, 1970, 909.
[2] R. H. Findlay, J. T. Sharp, and P. B. Thorogood, *J.C.S. Perkin I*, in press.
[3] J. N. Done, J. H. Knox, R. McEwan, and J. T. Sharp, *J.C.S. Chem. Comm.*, 1974, 532. Another example of the ring contraction of a 3*H*-benzodiazepine to an indazole has since been published, *ibid.*, p. 936.
[4] R. Baumes, J. Elguero, R. Jaquier, and G. Tarrago, *J. Heterocyclic Chem.*, 1973, **10**, 763; *Tetrahedron Letters*, 1973, 3781.