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THE EFFECT OF ALKENE CONFIGURATION ON THE PARTITIONING BETWEEN THE CARBENIC REACTIONS AND THE 1,7-ELECTROCYCLISATION OF α-(o-ALKENYLARYL)DIAZOALKANES

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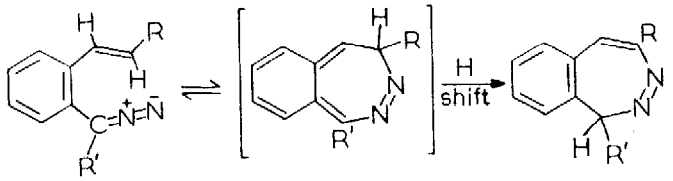
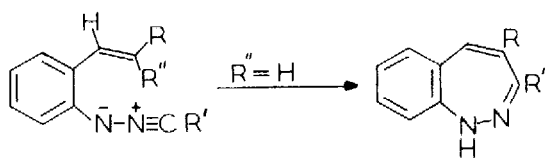
The 1,7-electrocyclisation of α-(o-alkenylaryl)diazoalkanes to 1H-2,3-benzodiazepines is blocked by the cis substituent in Z alkenyl groups and the diazo-compounds then react via alternative routes including a new intramolecular carbene reaction to give naphtho[a]cycloheptenes.

The 1,7-electrocyclisation of unsaturated diazocompounds of type (1) provides a general, high-yielding route to 1H-2,3-benzodiazepines (3).[1] We have recently extended this synthesis



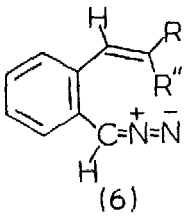
(1) (2) (3)

to the preparation of 1,2-diazepines fused to five-membered heteroaromatic rings[2] and the same synthetic principle has been applied by Garanti and Zecchi[3] to the preparation of the 1,2-benzodiazepines (5) from the nitrile imines (4).



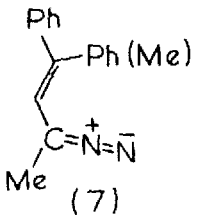
(4) (5)

The conversion of (1) to (3) is considered to take place in two steps, an 8π electrocyclic ring closure to give (2) followed by a [1,5] sigmatropic hydrogen shift which restores aromatic stability to the arene ring. We have recently been examining the effect on this reaction of replacing the terminal 'migrating' hydrogen atom with groups of differing mobility in sigmatropic shifts. Early results have shown that the cyclisation fails for diazo-compounds which are disubstituted at the ring closure site e.g.(6a-d), these compounds give only carbene-derived products as discussed below. Garanti and Zecchi have also reported that the 1,7 electrocyclisation of (4) is also strongly suppressed when R''≠H and that an alternative 1,1 mode of cyclisation of the 1,3-dipole is then favoured.[3,4] The failure of the 1,7-electrocyclisation in these cases could be due either (i) to the reluctance of groups other than hydrogen to undergo migration in the second stage of the reaction, or (ii) to inhibition of the first, ring-closure step.



(6)

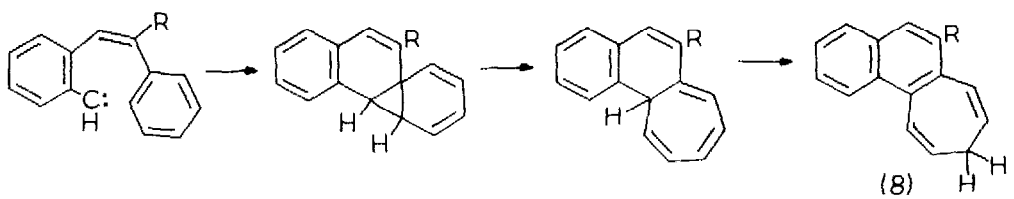
(a) R=R"=Me
(b) R=Ph, R"=Me
(c) R=Me, R"=Ph
(d) R=R"=Ph
(e) R=Me, R"=H
(f) R=Ph, R"=H
(g) R=H, R"=Me
(h) R=H, R"=Ph



(7)

We have differentiated between these alternatives by examining the reactions of the mono-substituted E and Z isomers (6e-h). The E isomers (6e) and (6f) cyclised normally to give diazepines in 78% and 75% yields respectively, but the Z isomers (6g,h) under the same reaction conditions did not produce any detectable amounts of the diazepines. Thus it is clear for (6g,h) and by inference for (6a-d) that the bulk of the cis substituent so sterically hinders the transition state for cyclisation that the diazocompounds are forced into other reaction paths. It is interesting to note that the balance between the cyclisation and carbenic alternatives in the decomposition of these diazo-compounds is much finer than for 3-diazoalkenes, e.g. (7); the 6π electron 1,5-cyclisation of the latter to give 3H-pyrazoles is not generally inhibited by cis methyl or phenyl substituents.[5,6]

The alternative reaction paths taken by the non-cyclisable diazo-compounds fall into two categories: (i) those of type (6a,6b,6g) where R"=Me showed typical intermolecular diazo-compound reactions giving carbene/solvent insertion products, carbene 'dimers' and azines in varying proportions depending on the nature of R; these will be detailed in the full report, and (ii) those of type (6c,6d,6h) where R"=Ph reacted by a new variant of intramolecular carbene attack on an aromatic ring to give naphtho[a]cycloheptenes (8) most likely via the intermediates shown.



(8)

Yield: R=H, 37%; R=Me, 76%; R=Ph, 47%

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REFERENCES

1 A.A. Reid, J.T. Sharp, H.R. Sood, and P.B. Thorogood, J.C.S.Perkin I, 1973, 2543.
2 D.P. Munro and J.T. Sharp, J.C.S.Perkin I, in press.
3 L. Garanti and G. Zecchi, J.C.S.Perkin I, 1977, 2092.
4 L. Garanti and G. Zecchi, J. Heterocyclic Chem., 1979, 16, 377.
5 J.T. Sharp, R.H. Findlay, and P.B. Thorogood, J.C.S.Perkin I, 1975, 102.
6 T. Sato and S. Watanabe, Bull.Chem.Soc.Japan, 1968, 41, 3017.

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