Cyclisation Reactions of Diazoalkenes: 2,3-Benzodiazepines from α-(*o*-Alkenylaryl)diazoalkanes

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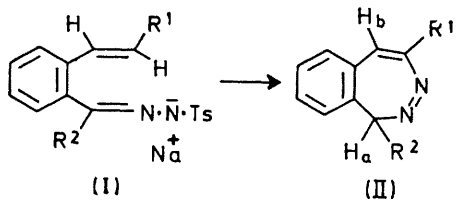
Summary The sodium salts of the tosylhydrazones of *o*-alkenyl aryl ketones decompose thermally with retention of nitrogen to give 2,3-benzodiazepines, rather than by a carbenic route.

αβ-UNSATURATED diazoalkanes generated by the thermal decomposition of tosylhydrazone sodium salts react by two main pathways (i) *via* loss of nitrogen to give carbene- or carbonium-ion-derived products,[1,2] depending on solvent protonicity, and (ii) with retention of nitrogen *via* electrocyclic reactions to give heterocyclic products, such as 1H- and 3*H*-pyrazoles,[1-4] and 1,2-benzodiazepines[2] in cases where there is steric constraint on pyrazole formation. The more stable α-aryldiazoalkanes, generated by the same method, have been reported to react principally by route (i) to give azines and/or stilbenes;[5] although in cases where the aromatic 'double bonds' are more localised *e.g.* in (1-naphthyl)- and (9-phenanthryl)-diazomethanes, cyclisation on to the *ortho*-position of the aromatic ring competes more successfully with loss of nitrogen to give benzindazoles in useful yields.[6]

Suschitzky and Mobbs[7] have recently reported their work on the thermal, base-induced decomposition of the tosylhydrazones of benzaldehydes with various saturated *ortho*-substituents (*e.g.* alkyl, alkoxy-, and dialkylamino-) and like the earlier workers[5] have found that reaction occurs mainly *via* (i) and the subsequent intramolecular cyclisation of the arylcarbene intermediate. In contrast to this, we

now report that in similar compounds where the *ortho*-substituent is unsaturated, such as a vinyl or styryl group, the tosylhydrazone sodium salts decompose with retention of nitrogen to give 2,3-benzodiazepines in good yield (Scheme 1). This reaction takes place at 80—120° in



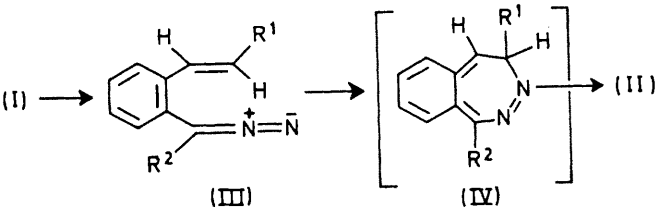
(I) (II)

(a) R^1 = H, R^2 = Me; yield 64%
(b) R^1 = Ph, R^2 = Me; yield 70%
(c) R^1 = Ph, R^2 = *p*-Tolyl; yield 67%

SCHEME 1

dilute suspension in aprotic solvents such as cyclohexane or toluene, and provides a straightforward route to a previously unknown class of 2,3-benzodiazepines.[8] The products are yellow crystalline solids, unstable to light and very readily isomerised by u.v. irradiation.[6]

The structures of the products were deduced from analytical and spectroscopic data. All gave mass spectra with a small peak due to the parent ion and a larger (P − 28) peak corresponding to the ready loss of N_2 from the molecular ion. The i.r. spectra showed no peak due to an N–H stretching vibration. The n.m.r. spectrum of (IIa) showed absorptions at τ 7·75 (d, J 6 Hz, R^2); 732 (q, J 6 Hz, H_a); 2·0 (d, J 9 Hz, H_b); 3·35 (d, J 9 Hz, R^1) and 2·4—2·8 (m, aromatic 4H); and that of (IIb) was similar except that H_b gave a singlet at τ 3·23 and in that of (IIc) both H_b and H_a gave singlets at τ 2·90 and 6·05, respectively.



SCHEME 2

It seems probable that the product is formed *via* an electrocyclic ring closure of the diazoalkene (III) (Scheme 2), whose presence is indicated by a transient red in the reaction mixture, to give (IV) which aromatises by a [1,5] sigmatropic hydrogen migration—a similar mechanism to that recently suggested for the formation of 1,2-benzodiazepines.[2]

(*Received, July 28th*, 1970; *Com.* 1243.)

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