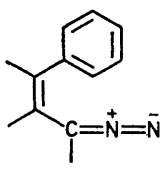
# 3*H*-1,2-Diazepines *via* 3,4-Dihydro-2-tosyl-1,2-diazepines

By Colin D. Anderson, John T. Sharp,* H. Raj Sood, and R. Stewart Strathdee
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

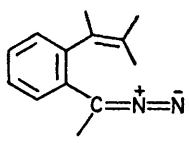
*Summary* The acid-catalysed reaction of some α,β,γ,δ-unsaturated ketones with *p*-tolylsulphonylhydrazine gives 3,4-dihydro-2-tosyl-1,2-diazepines (**5**) in good yield and the base-induced elimination of *p*-toluenesulphinic acid from these provides the first synthesis of 3*H*-1,2-diazepines (**6**).

We have recently described routes to 3*H*-1,2-benzodiazepines[1,2] and 1*H*-2,3-benzodiazepines[3] *via* the 8π-electron cyclisation of (**1**) and (**2**). It was interesting to examine the reactivity of analogous compounds with only olefinic unsaturation, *e.g.* (**3**), which could undergo ring closure to give either 3-vinyl-3*H*-pyrazoles or the virtually unknown† 3*H*-1,2-diazepines, *e.g.* (**6**). The latter formed an attractive synthetic target to compare with 5*H*-1,2-diazepines (**7**) which exist entirely as the diazanorcaradiene tautomers (**8**).[5]

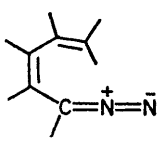
We found that the ketones (**4**, mixtures of *cis* and *trans* isomers) could not be converted into the required tosylhydrazone precursors for (**3**) but rather reacted with the *p*-tolylsulphonylhydrazine under acid conditions to give the 3,4-dihydro-2-tosyl-1,2-diazepines (**5**).‡ Base-induced elimination of *p*-toluenesulphinic acid from the latter provided an easy and high yielding route to the 3*H*-1,2-diazepines (**6**).



(1)



(2)



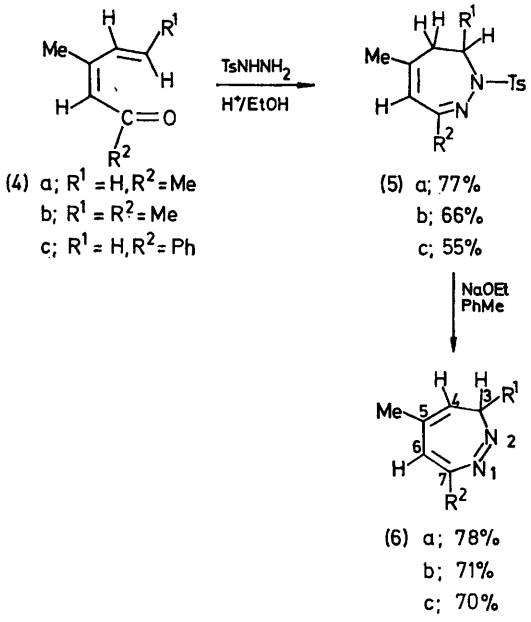
(3)

The dihydrotosyldiazepines (**5**) are colourless crystalline solids while the 3*H*-1,2-diazepines are moderately stable yellow oils which can be distilled without decomposition,

† A 3*H*-1,2-diazepine structure has been suggested as the thermal rearrangement product of a diazanorcaradiene but little information is available.[4]

‡ An alternative route to diazepines of this type has recently been published.[6]

[(**6a**) and (**6b**) at 10 mmHg] or yellow crystals [(**6c**), m.p. 63–65 °C]. The formulation of the products (**6**) as diazepines is supported by their mass spectra which show small parent ions with fragmentation by loss of $N_2$ and Me [*e.g.* (**6a**); *m/e* 122 (14), 94 (53), 79 (100), 78 (55%)] and by



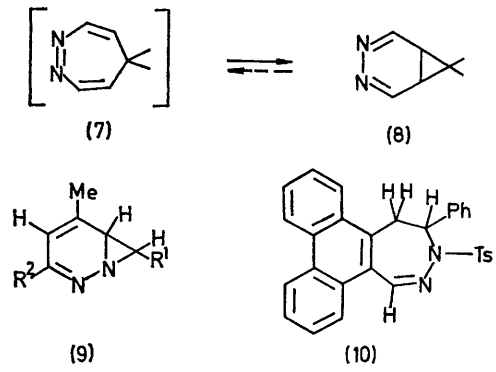

(4) a; $R^1$ = H, $R^2$ = Me
b; $R^1$ = $R^2$ = Me
c; $R^1$ = H, $R^2$ = Ph

(5) a; 77%
b; 66%
c; 55%

(6) a; 78%
b; 71%
c; 70%

comparison of their $^1$H and $^{13}$C n.m.r. spectra with those of 1*H*-2,3- and 3*H*-1,2-benzo-diazepines. For example, the saturated carbons attached to the azo-group have characteristic[1] chemical shifts (66, 67, 71 p.p.m.) for such carbons in seven-membered rings. The geminal protons on C-3 [(**6a**) $\tau$ 4·2 and 8·0; (**6c**) $\tau$ 4·1 and 8·0] have similar chemical shifts (with characteristically wide separation) to analogous methylene groups in both 1*H*-2,3-[3] and 3*H*-1,2-benzodiazepines.[7] Remarkably (**6a**) and (**6c**) are more resistant to ring inversion than the unsubstituted benzo-analogues which have coalescence temperatures of *ca.* 60 °C[3] and −20 °C[7] respectively while for (**6a**) coalescence is not observed up to 130 °C (decomp.) although peak broadening is visible at 70 °C.

The 3*H*-1,2-diazepines make an interesting addition to the "chemical playground"[5] of the cycloheptatrienes and their hetero-analogues in that they exist as diazepines while their 5*H*-counterparts favour the bicyclic form (**8**). Both (**6**) and (**7**) suffer the energetic disadvantage of an azo-group but in contrast to (**7**) which is much stabilised[5] by tautomerisation to (**8**), rough bond energy calculations§ show that (**6**) is marginally favoured over (**9**). It will be interesting to find out if the position of equilibrium can be controlled by the nature of the substituents on C-3 as it can in the cycloheptatriene–norcaradiene case.[8]



(7) (8)

(9) (10)

So far it appears that a substituent on the $\beta$-C of the unsaturated ketone (**4**) is necessary for tosyldiazepine formation; several compounds with a hydrogen at this point have given only tosylhydrazones which were cyclised under basic conditions to give vinylpyrazoles. The reactions of *o*-acyl-stilbenes and -styrenes, 9-formyl-10-styryl-phenanthrene, and (**4**) with *p*-tolylsulphonylhydrazine form an interesting gradation. Whereas the first group invariably gave tosylhydrazones,[3] the analogous acyl phenanthrene, in which the double bond character of the $\alpha,\beta$-double bond is increased, reacted like (**4**) to give (**10**) which was similarly converted to the 3*H*-1,2-diazepine with base.

(*Received*, 15*th May* 1975; *Com.* 555.)

§ Using the bond energy values and estimated cycloheptatriene/norcaradiene energy difference quoted in ref. 5 and assuming the same changes in ring strain in the carbocyclic and heterocyclic species.

[1] J. T. Sharp, R. H. Findlay, and P. B. Thorogood, *J.C.S. Perkin I*, 1975, 102.
[2] J. Dingwall and J. T. Sharp, *J.C.S. Chem. Comm.*, 1975, 128.
[3] A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J.C.S. Perkin I*, 1973, 2543.
[4] J. Sauer and G. Heinrichs, *Tetrahedron Letters*, 1966, 4979.
[5] A. Steigel, J. Sauer, D. A. Kleier, and G. Binsch, *J. Amer. Chem. Soc.*, 1972, **94**, 2770.
[6] T. Tsuchiya and V. Snieckus, *Canad. J. Chem.*, 1975, **53**, 519.
[7] J. Kurita and T. Tsuchiya, *J.C.S. Chem. Comm.*, 1974, 936.
[8] R. Hoffmann, *Tetrahedron Letters*, 1970, 2907; H. Günther, *ibid.*, 1970, 5173.