Cyclisation of *trans*-Stilbene-2-carbaldehyde Tosylhydrazone

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Summary Three new 2,3-benzodiazepines have been isolated by treatment of *trans*-stilbene-2-carbaldehyde tosylhydrazone with base in protic and aprotic solvents at moderate temperature; at a higher temperature, 2-phenylindene was recovered.

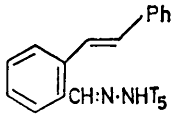
In attempts to prepare a stable derivative of 2,3-benzobicyclo[2,1,0]pentane (Pseudoindene)[1,2] the decomposition products of *o*-styrylphenylcarbene have been investigated. The present communication reports the novel results of one approach to that carbene.

trans-Stilbene-2-carboxaldehyde[3] was converted to its tosylhydrazone (I)† and the latter compound was transformed into the sodium salt. The dried salt was heated, under reflux, in 1,2-dimethoxyethane. Yellow crystals of 4-phenyl-4*H*-2,3-benzodiazepine (II) were isolated (54%), m.p. 132—133°. The same product was isolated in lower yields by the reaction of (I) with sodium methoxide in pyridine and with sodium hydride in 1,2-dimethoxyethane.

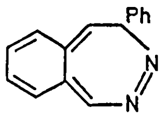
In diglyme, under reflux, using sodium hydride as base, the product from (I) was a black tar from which 8—32% of 2-phenylindene was recovered. In the higher boiling solvent, nitrogen must be lost from the intermediate diazo-compound (III) faster than cyclisation can occur. Only tar resulted when (II) was heated in diglyme alone.

The yellow colour of (II) in dilute methanol solution faded over two days. Evaporation gave 4-phenyl-1*H*-2,3-benzodiazepine (IV), m.p. 82—83°‡. This same diazepine was obtained after heating (II) in absolute methanol for several days and from the irradiation of crude (III) for 45 min in ether.

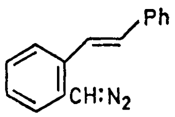
Treatment of (I) with sodium methoxide in methanol gave 4-phenyl-5*H*-2,3-benzodiazepine (V), (92%), m.p. 108—110°. The same product was obtained on treatment of (I) with sodium in refluxing ethylene glycol, or by heating (II) with sodium methoxide in methanol; it was recovered unchanged after being heated in methanol for one week. It is possible that the structures of (IV) and (V) are reversed but it should be noted that benzaldehyde azine shows a singlet at τ 1·48[4] which is clearly absent in the spectrum of (IV).



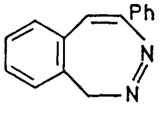
(I)



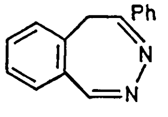
(II)



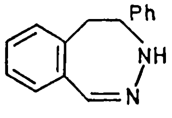
(III)



(IV)



(V)



(VI)

Catalytic hydrogenation (5% Pd–C) of diazepine (V) has given uncharacterised oils which rapidly darken upon exposure to air. Partial reduction yielded colourless crystals of 4-phenyl-3,4-dihydro-5*H*-2,3-benzodiazepine (VI), m.p. 113—115°. This reduced diazepine was the only one

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† Satisfactory elemental analyses and i.r. and n.m.r. spectra were obtained for all new compounds.

‡ This compound was not 1-benzylphthalazine as shown by comparison with authentic material.

which gave an absorption above 3100 cm^{-1} in the i.r. spectrum. No diazepine with a hydrogen atom on nitrogen, has been recovered from the reactions of (I) with base.

These ring closures are reminiscent of the formation of pyrazoles from benzenesulphonylhydrazones of α,β-unsaturated aldehydes and ketones upon treatment with sodium methoxide in refluxing acetonitrile.[5] In the present study, a quantitative yield of crude 3-phenylpyrazole was obtained from cinnamaldehyde tosylhydrazone after reaction with sodium methoxide in refluxing methanol.

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