Thermolysis of 3*H*-1,2-Benzodiazepines

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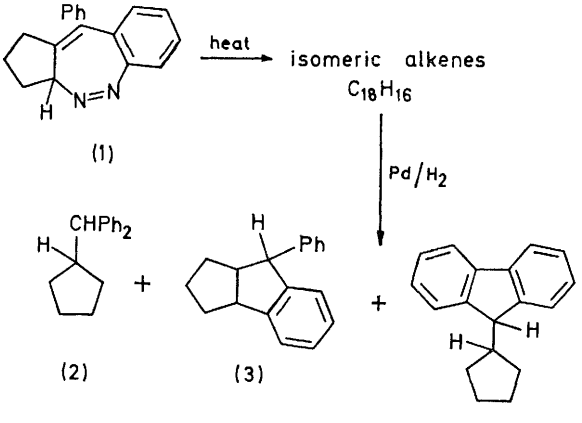
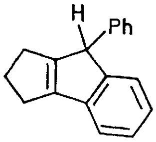
Summary The title compounds thermally eliminate nitrogen both in the gas phase and in solution but by different reaction paths involving diradical and carbene intermediates respectively.

We have recently shown that a new group of 1,2-benzodiazepines [*e.g.* (**1**)] can be readily synthesised *via* the cyclisation of certain α-diarylmethylenediazoalkanes.[1] In view of the current interest[2] in the decomposition of azo-compounds it was of interest to examine the thermolysis and photolysis of these products.



(1) (2) (3) (4)



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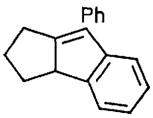

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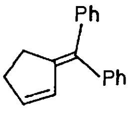
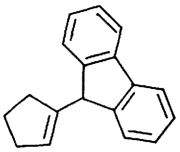


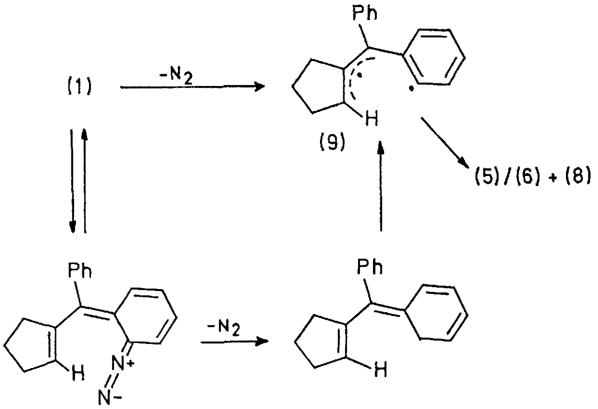
(7)



(8)

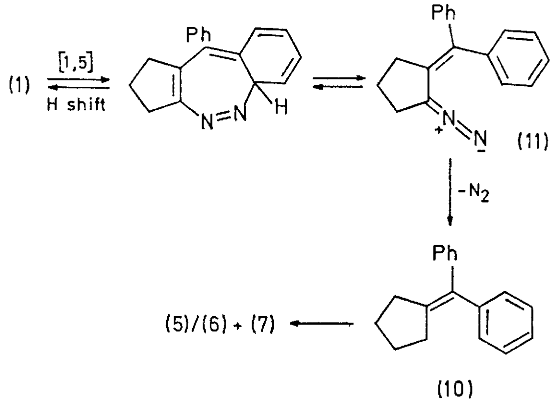
Thermolysis of (**1**) at 400° in the gas phase and at 110—220° in various solvents generally produced mixtures of alkene isomers of molecular weight 232 which on hydrogenation gave compounds (**2**)—(**4**) which were identified by comparison with authentic samples. The alkene isomers have not yet been analysed fully; however, (**7**) has been isolated and the presence of (**5**) and (**8**) inferred from the n.m.r. spectra of crude pyrolysis products.

Markedly different product distributions were observed for the gas- and liquid-phase decompositions, *e.g.* in the gas phase [flash vacuum pyrolysis (f.v.p.) at 400°] the major products after hydrogenation were (**3**) (32%), (**4**) (45%), and only *ca.* 2% of (**2**). The very low yield of (**7**) as a primary product, from which (**2**) is derived, was confirmed from the n.m.r. spectrum of the product mixture. A control experiment showed that although (**7**) was partially polymerised by f.v.p. at 400° it was not converted into the other pyrolysis products. The major products can most readily be rationalised by Scheme 1 in which (**1**) loses nitrogen either *via* direct extrusion or *via* an electrocyclic ring opening to give the diradical intermediate (**9**) which undergoes coupling to give the olefinic precursors to (**3**), *e.g.* (**6**), or aromatic substitution to give (**8**).[3]



Scheme 1

In the liquid-phase decomposition of (**1**) however, the diene (**7**) is a major product together with (**5**) and possibly (**6**), with (**8**) formed only in low yield and only in the higher-temperature reactions. For example, after hydrogenation the products from the decomposition of (**1**) in boiling chlorobenzene were (**2**) (36%) and (**3**) (42%); and in boiling dodecane (**2**) (38%), (**3**) (31%), and (**4**) (10%). The formation of (**7**) and the low conversion into (**8**) are not readily interpreted on the basis of intermediate (**9**) and it is suggested that the major reaction path in the solution decomposition involves the generation of the carbene (**10**) (Scheme 2). There is ample precedent for hydrogen-transfer in (**10**) to give (**7**) and carbene/1,3-diradical substitutions analogous to the formation of (**5**) and/or (**6**) have recently been reported.[4] The possibility that (**7**) could be derived from (**9**) by an abstraction–disproportionation sequence with the solvent has been ruled out by decomposing (**1**) in perdeuteriotoluene when no incorporation of deuterium into (**7**) was observed. A probable mode of formation of (**10**) involving a sigmatropic hydrogen shift which precedes ring cleavage is shown in Scheme 2; however, its genesis *via* hydrogen-transfer in (**9**) is also a possibility which cannot be excluded.



SCHEME 2

The suggestion that (**7**) and (**8**) are formed from different reactive intermediates, *i.e.* (**10**) and (**9**), respectively, and that (**5**)/(**6**) are formed from both intermediates is supported by results from the photolysis of (**1**). After hydrogenation the products were (**3**) and (**4**) only, suggesting the intermediacy of (**9**), whereas the generation of (**10**) by the photolysis of the tosylhydrazone salt precursor to (**11**) gave a product which on hydrogenation contained (**2**) and (**3**) and not (**4**).

(*Received, 27th November* 1972; *Com.* 1976.)

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[3] G. Baum, R. Bernard, and H. Schecter, *J. Amer. Chem. Soc.*, 1967, **89**, 5307.

[4] M. E. Hendrick, W. J. Baron, and M. Jones, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 1554.