Photochemical Deazetation of 2,3-Diazabicyclo[2.2.2]oct-2-ene; Unexpected Inversion of Stereochemistry

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Irradiation of *cis-anti*-[5,6-$^2H_2$]-2,3-diazabicyclo[2.2.2]oct-2-ene leads to bicyclo[2.2.0]hexane in which the deuterium is predominantly *exo, i.e.*, with inversion of configuration, and hexa-1,6-diene in which the 1,6-positions show equal amounts of *cis* and *trans* deuterium; the inversion is explained in terms of one-bond cleavage and conformational changes in a diazenyl biradical.

Stereochemical studies have given considerable insight into the deazetation of cyclic and bicyclic azo compounds.[1,2] In particular, 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) (**1**), and analogues show unique behaviour in that thermal and photochemical decompositions have been shown[3] to proceed with predominant inversion of configuration, an observation for which several rationales have been proposed.[3,4] For the next higher homologue, 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), formation of bicyclohexane (BCH) appeared to be stereorandom[5] since both *cis*-isomers of dimethyl-DBO (**2**) gave almost the same ratio of stereoisomeric bicyclohexanes.† However, it is not certain that this is the kinetic ratio since the high temperature needed to deazetise DBO is known to cause *exo–endo* isomerisation in bicyclohexanes. In the case of certain tricyclic azo compounds containing the DBO skeleton,

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† Calculated from data in ref. 5.

Table 1. ^1H and ^2H n.m.r. data (δ, p.p.m.) for deuteriated compounds.

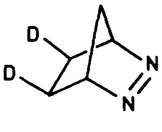
Deuteriated compound	^1H N.m.r. shifts and assignments: Deuteriated position	Geminal partner	^2H N.m.r.: Signals	Ratio (*anti* : *syn*)
(**5d**)	1.84(*anti*)	2.10(*syn*)	1.85, 2.09	68 : 32
(**3d**) from (**5d**)	1.55(*anti*)	1.27(*syn*)	1.52, 1.23	68 : 32
(**4d**)[a]	1.34 1.78 (*anti*)	1.78 2.09 (*syn*)	1.39 1.78 only	>99 : 1
(**3d**) from (**4d**)	1.55(*anti*)	1.27(*syn*)	1.52, 1.23	>99 : 1

[a] Restricted rotation about the amide bonds doubles the number of signals.

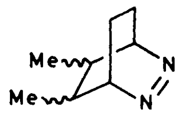
Table 2. ^2H n.m.r. analysis (δ, p.p.m.) of products from (**3d**).[a]

Compound	Source	Signals and assignments		Ratio
(**6**)	Direct photolysis	2.42(*exo*)[b]	2.03(*endo*)[b]	83 : 17
(**7**)[c]	Direct photolysis	4.99(*cis*)[b]	4.93(*trans*)[b]	50 : 50
(**6**)	Sensitised photolysis	2.42	2.03	58 : 42
(**7**)[c]	Sensitised photolysis	4.99	4.93	50 : 50

[a] (**3d**) (>99% *anti* deuterium) was irradiated at λ > 290 nm (direct photolysis), λ = 300 nm (sensitised photolysis). [b] Ref. 7. [c] Signal at δ 2.09 also present assigned to the allylic positions.



(1)



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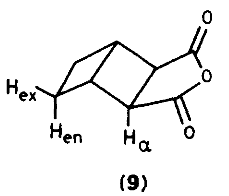
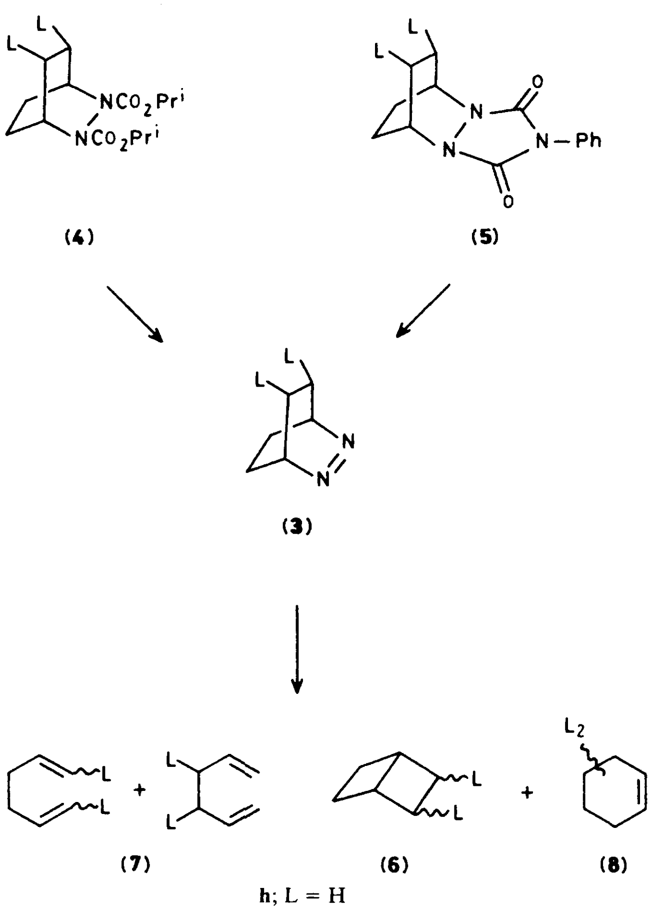


(9)



h; L = H
d; L = D

Scheme 1

inversion has been observed[6] but these were sterically biased and gave the more thermodynamically stable isomer.

We report here that photochemical deazetation of stereospecifically deuteriated DBO gives BCH with predominant inversion of configuration and hexadiene in which the 1,6-positions show equal amounts of *cis*- and *trans*-deuterium. We also discuss the relationship of these results to the known stereochemistry of deazetation of (**1**)[3] and the pyrolysis of bicyclohexanes.[7,8]

Photolysis of (**3h**) led to (**6h**) and (**7h**)[9] together with a trace of (**8h**).[10] Replacement of H_2 by D_2 in the synthesis of (**3h**) led to (**3d**) (Scheme 1). Table 1 shows n.m.r. data for (**3d**) and its precursors, together with assignments based on lanthanide induced shift (L.I.S.) studies of (**3h**) and (**5h**). Table 2 shows the data locating deuterium in the products of deazetation, (**6d**) and (**7d**).

Thus, the hexadiene is formed with a *cis* : *trans* ratio of 1, which is expected by analogy with the pyrolysis of stereospecifically deuteriated (**6**).[7] More surprisingly, *anti*-(**3d**) gives predominantly *exo*-(**6d**), *i.e.* inversion of configuration. This unexpected result caused us to look for confirmation of our assignments. Firstly, a $^{15}N\{^1H\}$ nuclear Overhauser effect (n.O.e) study of (**5h**)‡ showed a negative n.O.e. on irradiation at δ 2.10 but none on irradiation at δ 1.84, confirming that the latter is, indeed, the signal for the *anti*-protons. Secondly, we confirmed Goldstein and Benzon's assignment of the spectrum of BCH[7] by synthesising their precursor (**9**) and performing L.I.S. and $^1H\{^1H\}$ n.O.e. difference studies. In particular, irradiation at δ 3.55 (H_α) led to enhancement of the signal at δ 2.27 (H_{en}), but not the signal at δ 2.74 (H_{ex}), in full accord with their assignment.

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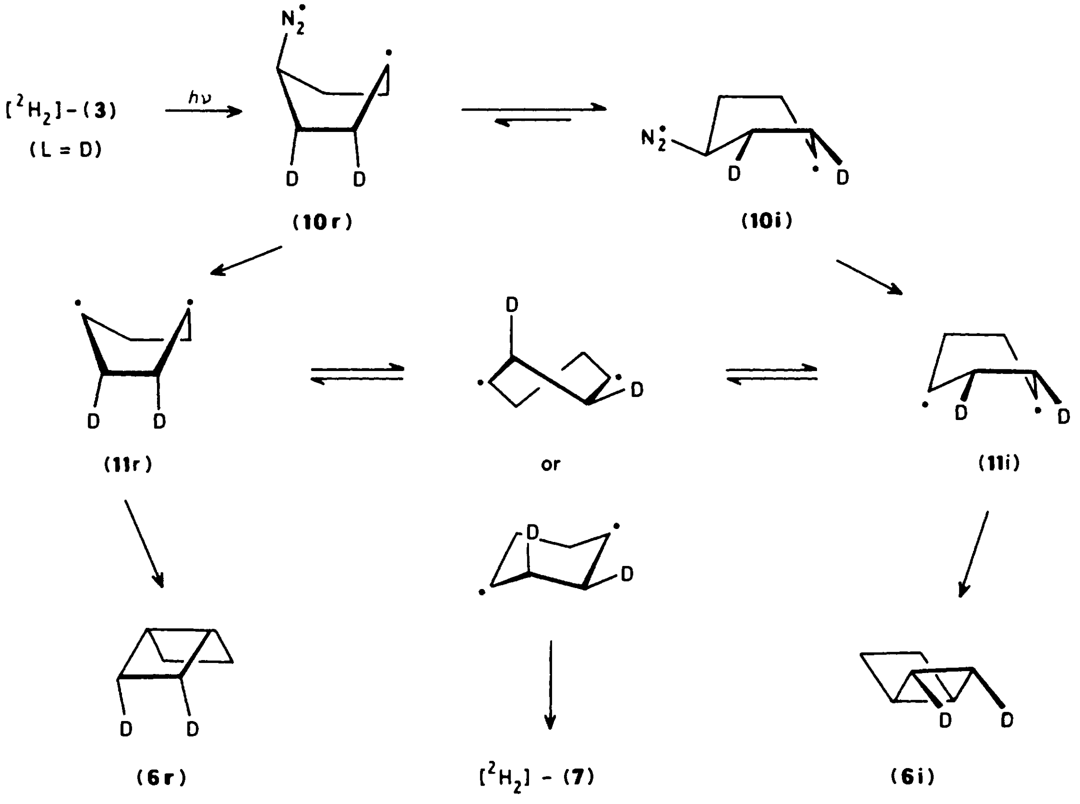
‡ To our knowledge, this is the first time this particular combination has been used to aid a stereochemical assignment.



Scheme 2

Comparing our system with the discussions on DBH,[3,4] our preferred explanation for our results is given in Scheme 2. Cleavage of one C–N bond leads to diazenyl biradical (**10r**), or the nearby twist conformer, in which the diazenyl substituent is in the flagpole position. Conformational inversion leads to the more stable (**10i**) in which the diazenyl group is in the bowsprit position. Loss of nitrogen and ring closure (or possibly S_Hi) leads to the preferred inverted BCH (**6i**). The alternative (**6r**) might arise by loss of nitrogen from (**10r**) or back-equilibration of (**11i**) to (**11r**). By analogy with BCH pyrolysis, cleavage of a chair[7] or twist[8] biradical would lead to *cis–trans*-[$^2H_2$]hexadiene.

The sensitised photolysis shows qualitatively similar results, suggesting a similar mechanism, while the quantitatively lower stereospecificity can be attributed to a spin-correlation effect.[2]

The question of one-bond or two-bond C–N cleavage has long been a contentious issue,[2,11] but alternatives such as a 'recoil mechanism'[3] or a concerted $_\sigma2_a + {}_\sigma2_a$ loss of nitrogen and C–C bond formation, both of which require the six-membered ring to be almost planar, seem less probable than the stepwise cleavage.

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