Unusual Stereochemistry in the Thermal Deazetation of a Bicyclic Azo Compound

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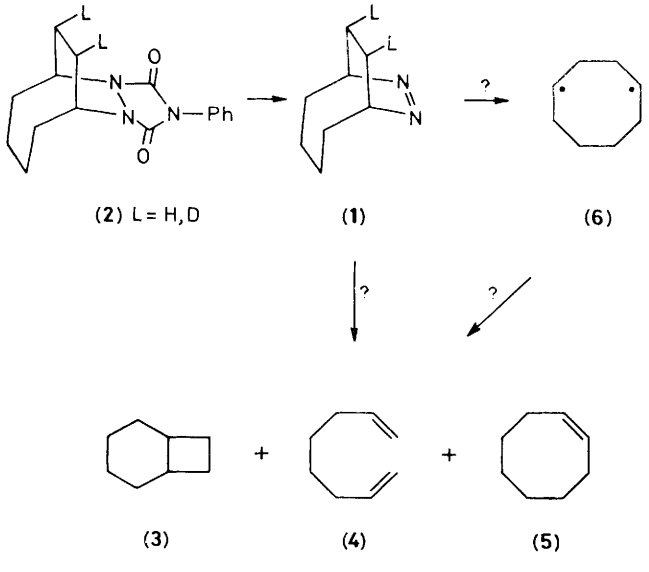
Thermolysis of the stereospecifically deuteriated azo-compound (**1D**) led to bicyclo-octane (**3**) with complete retention and octadiene (**4**) with partial loss of stereochemistry.

Since the original report by Roth and Martin[1] that deazetation of diazabicycloheptene led to bicyclopentane with predominant inversion of configuration, this has proved to be a general observation for most bicyclic and even monocyclic pyrazolines[2] with very few exceptions.[3] The interpretation of stereochemical studies[4] of the next higher homologue, diazabicyclo-octene, in which the azo-group is not part of a five-membered ring, is complicated by the thermal lability of the bicyclohexane products, but it appears to involve stereochemically equilibrated boat and chair conformers of cyclohexane-1,4-diyl.[4] As part of a detailed study of 7,8-diazabicyclo[4.2.2]dec-7-ene (**1**)[5] this communication describes the stereochemistry of its thermal deazetation.

Thermolysis of (**1H**) [170 °C, 1% in light petroleum (b.p. 30—40 °C), sealed tube] afforded three C_8H_{14} products, *cis*-bicyclo[4.2.0]octane (**3**), octa-1,7-diene (**4**), and *cis*-cyclo-octene (**5**) (Scheme 1). These were isolated by preparative gas chromatography, were spectroscopically and chromatographically identical to authentic material, and were shown to be stable under the reaction conditions. G.c. analysis showed that *trans*-bicyclo[4.2.0]octane (independently synthesised *via trans*-1,2-bisiodomethylcyclohexane, by analogy with ref. 6) was absent (< 1% of the *cis*-isomer) and a control experiment showed that, if formed, it would have survived the reaction conditions.



Scheme 1

Replacement of hydrogen by deuterium in the synthesis[5] of (**1**) led to (**2D**) and (**1D**); deuteriodi-imide reduction of bicyclo[4.2.0]oct-6-ene led to (**3D**);[7] hydroboration of octa-1,7-diyne followed by deuterionolysis[8] led to (**4D**). In each case, comparison of the ^1H n.m.r. spectrum of the protio- and deuterio-compounds, and the use of $Eu(fod)_3$ shift reagent, where appropriate, permitted the assignments shown in Table 1, which also gives the results of quantitative analysis for deuterium by ^2H n.m.r. spectroscopy.

Thermolysis of (**1D**) and ^2H n.m.r. analysis of the products gave the results shown in Table 2. The lower stereospecificity of the cleavage reaction was shown not to be due to secondary isomerisation of the olefinic bonds by pyrolysis of (**4D**) in the presence of (**1H**). ^2H N.m.r. analysis of (**4**) from this reaction

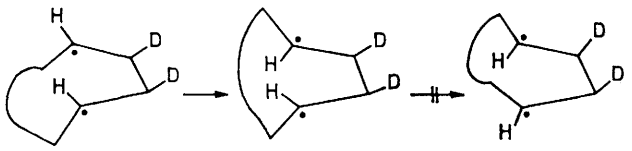
Table 1. ^1H and ^2H N.m.r. data for deuteriated compounds.

	^1H N.m.r. shifts and assignments		^2H N.m.r.	
Compound	Deuteriated position	Geminal partner	Signals	Ratio
(**1D**)	1.70 (*syn*)[a]	1.60 (*anti*)[a]	—	
(**2D**)	2.24 (*syn*)[a]	1.92 (*anti*)[a]	2.18 only	> 99:1
(**3D**)	1.84 (*exo*)[b]	1.67 (*endo*)[b]	1.84, 1.68	82:18
(**4D**)	4.92 (*E*)[c] *J* 10 Hz	4.97 (*Z*)[c] *J* 17 Hz	5.07, 5.13	> 99:1

[a] Based on $Eu(fod)_3$ induced shifts (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato). [b] Presumed preferential *exo*-attack. [c] Based on coupling constants and method of synthesis.

Table 2. ^{2}H N.m.r. analysis of products.

Compound	Source	^{2}H N.m.r. Signals	^{2}H N.m.r. Ratio
(3)	Pyrolysis of (1D)	1.83 only	> 98 : 2
(4)	Pyrolysis of (1D)	4.97, 5.03	87 : 13
(4)	Pyrolysis of (4D) + (1H)	5.07, 5.13	> 99 : 1



(6a) (6b) (6c)

Scheme 2

was unaffected by the formation of (4H) from (1H) and showed that *cis-trans* isomerisation had not occurred (Table 2).

The results in Table 2 contrast with other related studies. First, the double inversion characteristic of pyrazolines is not observed, so neither the recoil mechanism[9] nor backside attack in a diazenyl biradical[1] is involved. Secondly, the extensive stereorandomisation in the cleavage product (4) expected by analogy with the results of Roth and Martin,[4] in which they postulate almost complete stereochemical equilibration of the biradical, is not observed. Thirdly, in their studies of monocyclic six-membered ring azo-compounds, Dervan *et al.*[10] found that the cleavage reaction was more stereospecific than the coupling, the reverse of the results presented here. They explained this in terms of a competition between a concerted $\sigma 2s + \sigma 2s + \sigma 2s$ cleavage and a stepwise process leading to both cleavage and coupling *via* a partially stereorandomised biradical. If there were such a concerted component to the cleavage reaction (1) → (4), then the stereospecificity of the stepwise cleavage (1) → (6) → (4) would be even lower than Table 2 suggests and the difference from the coupling (1) → (6) → (5) even greater.

While these results may be a consequence of some intrinsic property of tetramethylene biradicals, or the involvement of a diazenyl biradical, the most economical explanation is in terms of the conformations of cyclo-octane-1,4-diyl (6) (Scheme 2). The biradical is formed in conformation (6a) which leads to products with complete retention of configuration or is converted to conformation (6b). This can only cleave, with loss of stereochemistry, since coupling would lead to the highly strained *trans*-bicyclo-octane, which is absent. Conformational equilibration is not complete, since inverted *cis*-bicyclo-octane is not formed, so (6c), which would lead to it, is not involved.

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