Deazetation of 1,4-Dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene: Stereochemistry and the Formation of Dimethylcyclohexene

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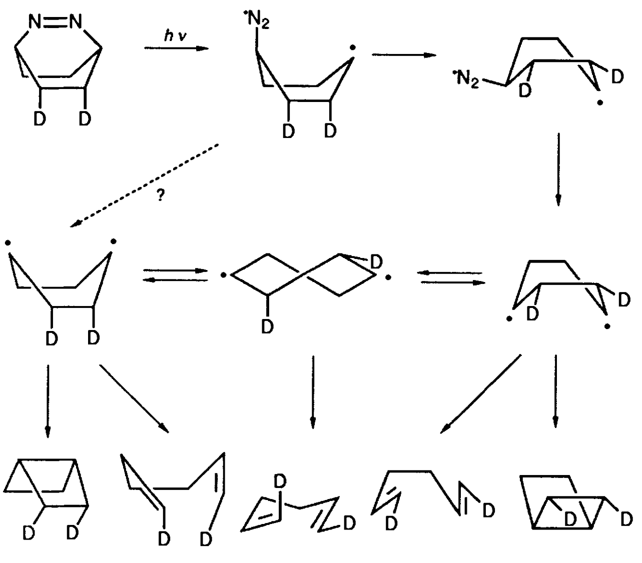
Irradiation of stereospecifically labelled [5,6-$^2H_2$]-1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene gave 1,4-dimethylbicyclo[2.2.0]hexane and 2,5-dimethylhexa-1,5-diene with the label randomly distributed between the stereochemically differentiated positions, together with 1,4-dimethylcyclohexene, which was only formed in the direct photolysis.

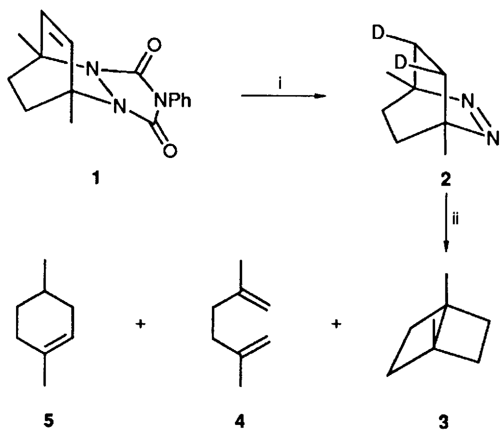
We have recently reported[1] a detailed study of the stereochemistry of deazetation of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), the results of which we explained by conformational interconversions of both a diazenyl biradical and the cyclohexanediyl (Scheme 1). In particular, the predominant inversion of configuration in the formation of bicyclohexane (BCH) appeared to require conformational inversion of a diazenyl biradical in which the diazenyl group, produced initially in the flagpole position, goes to the more stable bowsprit position. In the hope of influencing the relative energies of relevant conformations in an interpretable fashion, we carried out a similar study of dimethyl DBO (**2**). This was synthesised in unlabelled form by analogy with the published route,[2] and shown, on deazetation, to give the reported products, dimethyl BCH (**3**) and dimethylhexadiene (**4**). In addition, direct photolysis gave the previously unreported 1,4-dimethylcyclohexene (**5**) (Scheme 2).



Scheme 1

Replacement of hydrogen by deuterium in the catalytic reduction step (Scheme 2) gave results which depended on the catalyst and solvent, but the highest *anti*:*syn* ratio came from Adam's catalyst in ethyl acetate (90:10 by ^2H NMR spectroscopy). Conventional methods permitted assignment of the *syn* and *anti* methylene proton resonances in the ^1H NMR spectra of the urazole precursor **1** (2.01 and 1.70 ppm respectively) and dimethyl DBO (1.12 and 1.47 ppm respectively), and the *exo* and *endo* resonances of dimethyl BCH (1.86 and 2.02 ppm respectively).

The crude hydrocarbon products from both direct and sensitised deazetation† of the labelled (90:10) dimethyl DBO were analysed by ^1H and ^2H NMR spectroscopy, then separated by preparative GC. The deuterium was located by ^2H NMR spectroscopy for dimethyl BCH and by ^1H NMR spectroscopy for dimethylhexadiene, and in all cases it was distributed equally between the stereochemically differentiated sites. This stereorandom behaviour contrasted with the parent DBO[1] for which direct photolysis gave >80:20 inversion of configuration, while even the sensitised deazetation, which would be expected to show a lower stereospecificity, if a spin correlation effect operates, was far from stereorandom.



Scheme 2 *Reagents:* i, H_2 or D_2, PtO_2; KOH; Cu^{II}; ii, *hν* or heat

One possibility is that the methyl and diazenyl groups are similar in size and that the conformational equilibrium between the diazenyl biradicals is evenly balanced, leading to equal inversion and retention. Alternatively, since it is likely that the methyl groups stabilise the radical centres and hinder coupling, they will extend the lifetime of the cyclohexanediyl,[3] thereby permitting complete equilibration on the twist-boat pseudorotation cycle of the nitrogen-free biradical.

An extra feature arising from this work is the formation of dimethylcyclohexene. While we have reported[1] that cyclohexene was formed from DBO, but only on direct photolysis, our main evidence for its formation was a comparison of minor resonances in the ^2H NMR spectra of product mixtures with the ^1H NMR spectrum of authentic cyclohexene. We thus considered it unwise to draw firm mechanistic conclusions from the observation. However, 1,4-dimethylcyclohexene was formed on direct irradiation of dimethyl DBO (> 10% by GC), was

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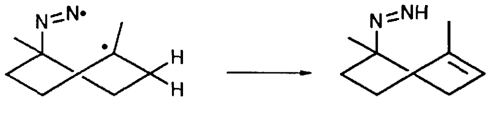
† Photolysis conditions: 1% solutions in pentane. Direct: medium pressure mercury lamp through pyrex. Sensitised: 3-methoxyacetophenone (0.02 mol dm^{-3}), Rayonet-type reactor, fitted with '300 nm' lamps.

isolated by preparative GC, was characterised spectroscopically, and was found to be identical to material prepared independently from 4-methylcyclohexanone.[4] It was shown to be absent (< 1%) both from the sensitised photolysis, and also from pyrolysis of either dimethyl DBO or dimethyl BCH.* Under all these conditions, it was shown to be stable.

We thus have here a clear case where a hydrocarbon product is formed only from the singlet excited state of an azo compound and not from the ground or triplet state. Nitrogen-containing products are known to show this multiplicity dependence,[5] but it is rare for nitrogen-free products to be so selective.[6]

An attractive mechanism for the formation of dimethylcyclohexene is that the terminal nitrogen in the diazenyl biradical **6** abstracts a hydrogen atom from C-3, and this is followed by loss of nitrogen from the resulting cyclohexenyldiazene **7** [eqn. (1)].



6 **7** (1)

This, however, would require that the hydrogen which migrated was initially *syn* to the azo group and is ruled out by the stereochemical results we reported for DBO.[1] A hydrogen migration in the nitrogen-free cyclohexanediyl seems to be required.

The fact that the cyclohexenes only occur on direct irradiation is intriguing and may be an experimental example of a phenomenon implicit in a theoretical discussion of Dannenberg.[7] His calculations showed that the occurrence of disproportionation or coupling of two ethyl radicals should depend on the initial phase relationship between the two SOMOs (singly occupied molecular orbitals) of the radicals, and he generalised this to suggest that the fate of relatively uncoupled biradicals might depend upon whether the radical sites are in-phase or out-of-phase in their most stable conformation. In the work discussed here, the phase relationship between the two SOMOs of the biradical might be expected to depend on the orbital character of the electronic state of the azo compound from which it is formed, and thus on whether the deazetation is thermal or photochemical.

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* Pyrolysis conditions: 1% solutions in pentane, in sealed pyrex tubes. Dimethyl DBO: 513 K; 2.5 h. Dimethyl BCH: 443 K; 8 h.