Thermal *E*- to *Z*-Isomerisation of *E,Z*-Cyclo-octa-1,3-Diene

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Deuterium labelling has shown that the isomerisation of *E,Z*-cyclo-octadiene to the *Z,Z*-isomer does not occur by a 1,5-hydrogen shift as previously supposed, and thus must occur by a *trans-cis* rotation.

A number of groups have contributed to our understanding of the thermal and photochemical interconversions of *Z,Z*-cyclo-octa-1,3-diene (**1**), *E,Z*-cyclo-octadiene (**2**), and bicyclo[4.2.0]oct-7-ene (**3**),[1—7] summarised in Scheme 1.

It has generally been considered that the isomerisation of (**2**) to (**1**) occurs at such low temperatures (< 150 °C) that it is unlikely to involve simple rotation about the double bond, and a 1,5-hydrogen shift, as shown in Scheme 1, has been postulated.[4] We present here a deuterium labelling study which rules out any hydrogen shift mechanism, and thus shows that it must indeed occur by a simple *trans*-to *cis*-rotation.

Thermolysis of (**2**) is reported to give 'essentially quantitatively'[1] or 'quantitatively'[4] only (**3**), but in another study,[7] formation of (**1**) is reported to compete with the cyclisation, suggesting the feasibility of the experiment described here.

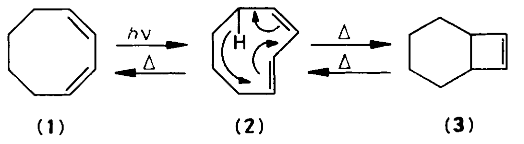
Scheme 2 shows the consequences of the alternative mechanisms when applied to (**2D**) produced photochemically from 5-[$^{2}H_{1}$]-*Z,Z*-cyclo-octadiene (**1D**), noting that either of the double bonds can isomerise in the formation of (**2**), leading to (**2D′**) and (**2D″**). *Trans*-to *cis*-rotation leads back to (**1D**) with deuterium exclusively in the allylic position, whereas a 1,5-shift would give deuterium in the homoallylic position from (**2D′**) and in the vinylic and allylic positions from (**2D″**). The distinction can thus be made by the presence or absence of vinylic and homoallylic deuterium in (**1**) recovered from the reaction.

The synthesis of (**2D**) is also outlined in Scheme 2. Allylic bromination of (**1**) using *N*-bromosuccinimide followed by reduction with lithium triethylborodeuteride afforded (**1D**). Photochemical isomerisation[6] of (**1D**) and extraction with aqueous silver nitrate[8] led to (**2D**) which showed only allylic deuterium in the ^{2}H n.m.r. spectrum. A sample of (**2D**) was heated under reflux under nitrogen in dilute solution in carbon tetrachloride and examined by ^{2}H n.m.r., which showed the formation of (**3D**) as the major product (76%), together with (**1D**) (24%). This was confirmed by g.c. analysis. The only significant signals were at δ 1.45 and 1.62 [the *exo*- and *endo*-2-positions of (**3D**)] and at δ 2.11 [the allylic-position of (**1D**)]. In particular, there is no signal $>1\%$ in the vinyl region. Thus the isomerisation of (**2D**) to (**1D**) gives deuterium exclusively in the allylic position.

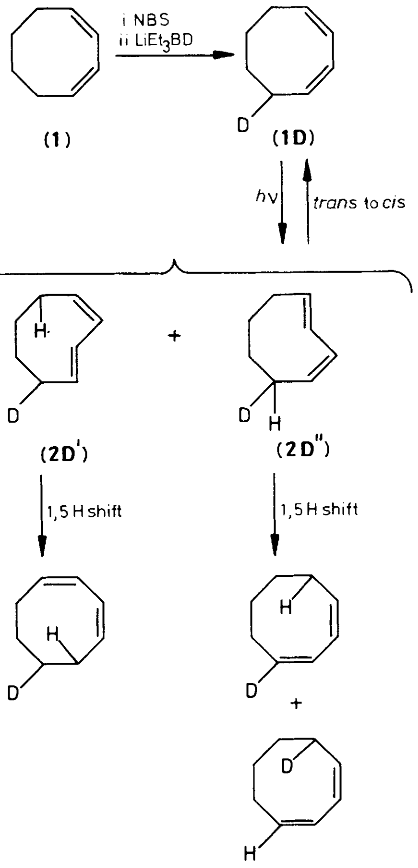
This rules out any mechanism involving a hydrogen shift, whether the concerted 1,5-process shown in Scheme 1, or an acid catalysed process *via* a cyclo-octenyl cation or a radical induced process *via* a cyclo-octadienyl radical, and leaves only the simple *trans*- to *cis*-rotation, which must thus occur at a remarkably low temperature (77 °C).

The activation energy for *cis*- to *trans*-isomerisation of penta-1,3-diene is 222 kJ mol^{-1},[9] and this must be lowered by about 80 kJ mol^{-1} to account for the facility of the present reaction. A molecular mechanics[10] study of cyclo-octa-1,3-diene[11] shows two factors which together might account for this. Firstly, (**2**) is strained relative to (**1**) by 75 kJ mol^{-1}, and a substantial part of this may be released in the transition state. Secondly both (**1**) and (**2**) have dihedral angles > 50° between the double bonds in their lowest energy conformations and thus lose much of the butadiene resonance energy which is estimated to be 16 kJ mol^{-1}.[12] A 'transition state' was calculated using the dihedral driver option in MMX and, while it could not be characterised as a transition state and its energy is unlikely to be quantitatively significant, two features are relevant. Its structure approximates the expected allyl-alkyl biradical with a *ca.* 90° dihedral angle at the isomerising double bond and with very small dihedrals in the allyl part. There is no butadiene resonance energy in either ground state to be lost, and allylic resonance energy is gained in the transition state. Furthermore the 'transition state' shows no large destabilising terms in its energy except for that associated with the isomerising double bond.

Baldwin and Reddy[13] have recently reported another low temperature *cis*- to *trans*-isomerisation. *Cis,cis,cis*- and *cis*,-



Scheme 1



Scheme 2

cis,trans-octa-2,4,6-triene were known to interconvert at 110 °C, and a reversible 1,7-hydrogen shift mechanism had been postulated.[14] The more recent study established that the major pathway was the hydrogen shift, but also revealed a direct pathway involving *cis* to *trans* isomerisation about the terminal double bond. They 'supposed that the triene reactants have substantially higher heats of formation than related isomers . . .,' so they, too, are postulating an explanation in terms of ground state destabilisation, rather than stabilisation of the transition state, though they were not able to be more specific.

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