# THE DEGENERATE THERMAL REARRANGEMENT OF BICYCLO[3.3.1]NONA-2,6-DIENE
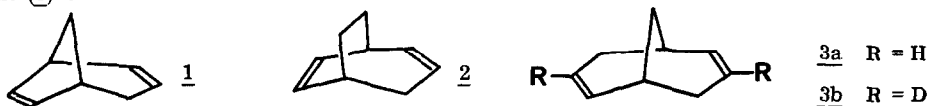
Roger Bishop[1a], William Parker[1b], and Ian Watt[*1c]

Department of Chemistry, University of Stirling, Stirling, Scotland.

A recent report by Japenga, Kool and Klumpp[2] on the thermolysis of bicyclo[3.2.1]octa-2,6-diene (1) and bicyclo[3.2.2]nona-2,6-diene (2), prompts us to report our related experiments with bicyclo[3.3.1]-nona-2,6-diene (3)[3].



3a  R = H

3b  R = D

Attempted thermolysis of 3a by heating at 300°C (sealed tube, 24hr) or by passing it through a hot silica tube at 590° in a stream of nitrogen (contact time ca. 30sec), resulted only in the recovery of un-changed 3a[4]. Use of higher temperatures (650°) in the flow system gave extensive charring and low recovery of volatile material, whose g.l.c. analysis showed at least four new compounds. The n.m.r. spectrum revealed the presence of aromatic species.

The possibility that the recovered diene had undergone a degenerate rearrangement was investigated using the specifically 3,7-deuteriated derivative 3b. This diene was prepared from the known 3,3,7,7-tetradeuteriated bicyclo[3.3.1]nonane-2,6-dione (4)[5] by the sequence of reactions indicated.



(i)  NaBH₄ in MeOH

(ii) TsCl in pyridine

DBU, Δ

DBU = 1,5-diazabicyclo[5.4.0]undec-5-ene
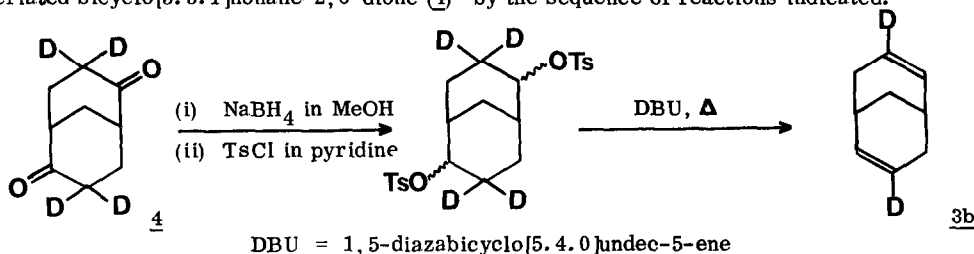
The labelled diene thus prepared, $\nu_{max.}$ (CCl₄ solution) 2250cm⁻¹ (olefinic C-D stretch), was identical in its g.l.c. behaviour to authentic unlabelled material[3]. The 220 MHz n.m.r. spectra of 3a and 3b allowed unambiguous assignment of all protons (see TABLE[6]) and confirmed the specific labelling of 3b at the 3- and 7- positions.

TABLE :   220 MHz n.m.r. spectra of 3a,b

(CCl$_4$ solution).
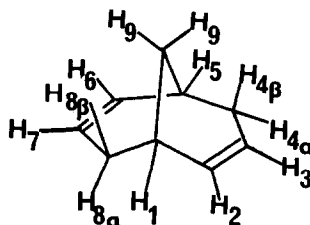
| Signal (3a) | Pattern (3a) | Protons | Integrals ($\pm$ 0.05H) | |
|---|---|---|---|---|
| | | | 3b (cold) | 3b (pyrolysed) |
| 1.65   (2H) | t; $J_{1,9}$ 3.2Hz | $H_9 \times 2$ | 2.00 | 2.00 |
| 1.80   (2H) | dd; $J_{4\alpha,4\beta}$ 17.5Hz, $J_{5,4\beta}$ 4.5Hz | $H_{4\beta}+H_{8\beta}$ | 2.00 | 2.00 |
| 2.18   (2H) | dm; $J_{4\beta,4\alpha}$ 17.5Hz ($W_{h/2}$ 10Hz) | $H_{4\alpha}+H_{8\alpha}$ | 1.97 | 1.99 |
| 2.40   (2H) | m ($W_{h/2}$ 11.5Hz) | $H_1+H_5$ | 2.00 | 1.58 |
| 5.50   (2H) | dq; $J_{2,3}$ 10.5Hz, $J_{4\alpha,3}$ 4.6Hz, $J_{1,3}$ 1.6Hz | $H_3+H_7$ | 0.18 | 0.62 |
| 5.62   (2H) | dq; $J_{3,2}$ 10.5Hz, $J_{1,2}$ 4.5Hz, $J_{4\alpha,2}$ 1.9Hz | $H_2+H_6$ | 1.90 | 1.90 |

Pyrolysis of 3b as before (sealed tube, 350$^o$, 24hr) gave only unchanged starting material, but the diene recovered from pyrolysis in the flow system at 590-600$^o$ showed evidence of degenerate rearrangement. The 220 MHz n.m.r. spectrum of the recovered diene showed over 300% enhancement of the signals from the 3- and 7- positions, with a corresponding decrease in signal from the bridgehead 1- and 5- positions. The other signals were unchanged in strength (see TABLE). The i.r. spectrum (CCl$_4$ solution) of the recovered diene showed a new band at 2140 cm$^{-1}$ (aliphatic C-D stretch) and mass spectral analysis showed that there was no loss of deuterium from the sample during pyrolysis.

These observations are consistent with specific exchange of label between the olefinic 3- and 7- positions and the bridgehead 1- and 5- positions. Although there are other possibilities[7], the most likely explanation is that this process is a further example of a thermal 1,3 carbon shift reaction[8]. Thus, cleavage of a 1,8 (or 4,5) bond and formation of a new bond between C$_3$ and C$_8$ (or between C$_4$ and C$_7$) would regenerate the diene framework (see FIGURE). In the absence of any isotopic preference[9], such shifts would be expected to distribute the deuterium label equally between the olefinic (3 and 7) positions and the bridgehead (1 and 5) sites.

FIGURE : Degenerate rearrangement of Bicyclo[3.3.1]nona-2,6-diene.
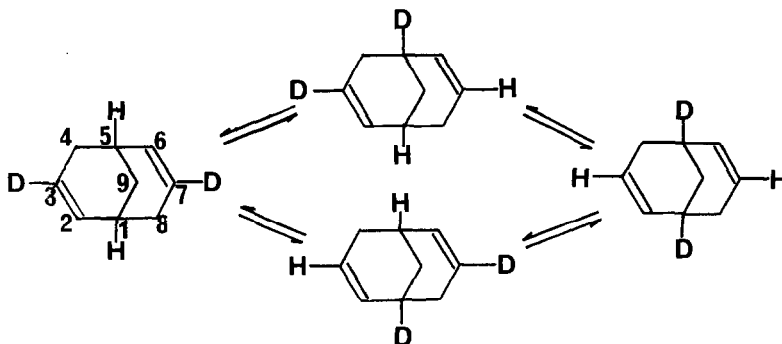


It is evident (see TABLE) that full equilibration of the label has not taken place under the reaction conditions[10]. The observed distribution corresponds to only 47% equilibration, giving a rate constant for the exchange process of ca. $10^{-2} sec^{-1}$. The activation energy must lie between 60 and 65 kcal. $mol^{-1}$. This value would be consistent with a mechanism involving homolysis of a 1,8-bond to generate a diradical species 5.



Both radical centres are formally allylic, but the stereochemical constraints imposed by the molecular framework of 3 are such that, while the cyclohexenyl centre can benefit from allylic stabilisation (ca. 13 kcal. $mol^{-1}$)[12], the migrating centre would be formed as a 'perpendicular' allyl radical in the transition state and would not be stabilised. An estimation using Benson's group increments[13], predicts that the conversion of 3 to 5 should be endothermic by 66 kcal. $mol^{-1}$.

Further discussion of the mechanism requires determination of accurate activation parameters, and of the stereochemical fate of the migrating centre.

REFERENCES AND NOTES.

1 (a)    Present address: School of Chemistry, University of New South Wales, Kensington, N.S.W.
         2033, Australia.

  (b)    Deceased 9 May 1977.

  (c)    Address correspondence to this author at present address: Department of Chemistry, University
         of Manchester, Manchester M 13 9PL, England.

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