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THERMAL ISOMERIZATION OF BICYCLO[4.2.2]DECA-2,4,7,9-TETRAENE[1]

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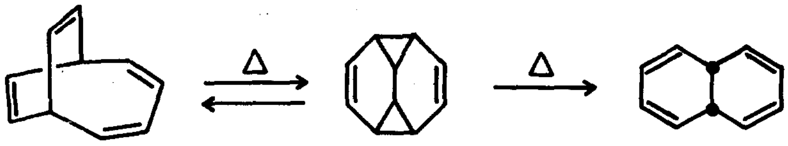
CENTRAL to the consideration of mechanism in many of the transformations of molecules of the formula $(CH)_{10}$ has been tetracyclo$[4.4.0.0^{2,10}.0^{5,7}]$deca-3,8-diene (I).[3a-g] We describe here a degenerate isomerization of bicyclo-[4.2.2]deca-2,4,7,9-tetraene (II) which most strongly implicates I as an intermediate.



II I III

When II is heated either neat or in pentane solution at temperatures greater than 170° cis-9,10-dihydronaphthalene (III) and products of its further decomposition are slowly produced. We have long thought that this rather sluggish conversion might be preceeded by a reaction invisible in the absence of a label. Accordingly, 7-deuterio-II was prepared in a sequence starting from cycloöctatetraene and deuterio ethyl diazoacetate.[3d] Consistent with our previous mechanistic views,[4] II was obtained with deuterium exclusively on the ethylene bridge.

This is easily determined from a consideration of the 100 MHz nmr spectrum in figure 1. The assignments shown in the figure are derived from decoupling experiments in which the signals at 604Hz and 546Hz were collapsed on irradiation of the signal due to the bridgehead hydrogens at 312Hz. The signal centered at 568Hz remains unchanged and thus is due to the protons on the remote or central portion of the diene.[5]

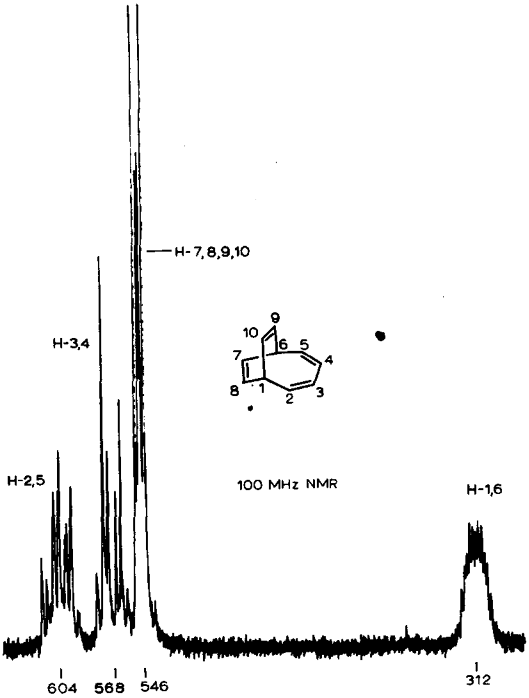


Figure 1

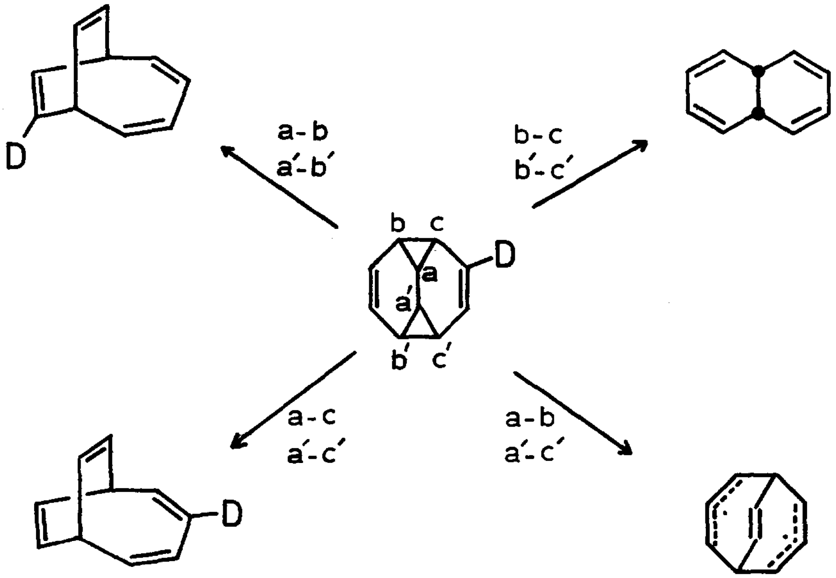
When deuterio-II is heated at 170° for 1.25 hours only *ca*. 5% is converted to III. The deuterium, however, is scrambled between the ethylene bridge and remote diene positions. No deuterium appears in either the bridgehead or other diene positions. Further heating results in no scrambling of the deuterium to the other positions in the molecule.

Table

Thermal Isomerization of 7-Deuterio-bicyclo[4.2.2]deca-2,4,7,9-tetraene

Conditions	H-7,8,9,10	H-2,5	H-3,4	H-1,6
Start	3.1	2.0	2.0	1.9
170^0/1.25hr	3.3	2.0	1.8	1.9
175^0/3.5hr	3.5	2.0	1.6	1.9
Calculated[6] full H-3,4,7,8,9,10 scramble	3.4	2.0	1.6	2.0

The intermediacy of I explains this specific scrambling of the deuterium between the 3,4,7,8,9 and 10 positions. Several paths are formally available



to I for further reaction. These include two possible reversals of the original 2+4 intramolecular Diels-Alder reaction (breaking of a-b and a'-b' or a-c and a'-c'), a reverse 4+4 cycloaddition leading to *cis*-9,10-dihydronaphthalene (breaking of b-c and b'-c') and a reverse 2+3+3 reaction leading presumably to bullvalene or tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene[7] (breaking of a-b and a'-c'). According to the formulations of Woodward and Hoffmann,[8] of these possibilities only the 2+4 reaction is permitted to be concerted in a thermal process. It was not surprising, then to find that it predominates over the detectable but relatively slow 4+4 reaction[9] and the as yet undetected 2+3+3 reaction.

REFERENCES AND NOTES

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5) The 100MHz nmr spectrometer was purchased with the help of grant CP-6803 from the National Science Foundation. The departmental instrument laboratory is in part supported by Biochemical Sciences Support Grant FR-07057.

6) All figures are corrected for 95% deuteration in the starting material.

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