Stereospecific Double Rearrangement of *anti*-1,5-Bishomocycloheptatriene. A Rebound Pathway of Thermal Rearrangement Involving Intermediate Geminal Hydrogen Interchange

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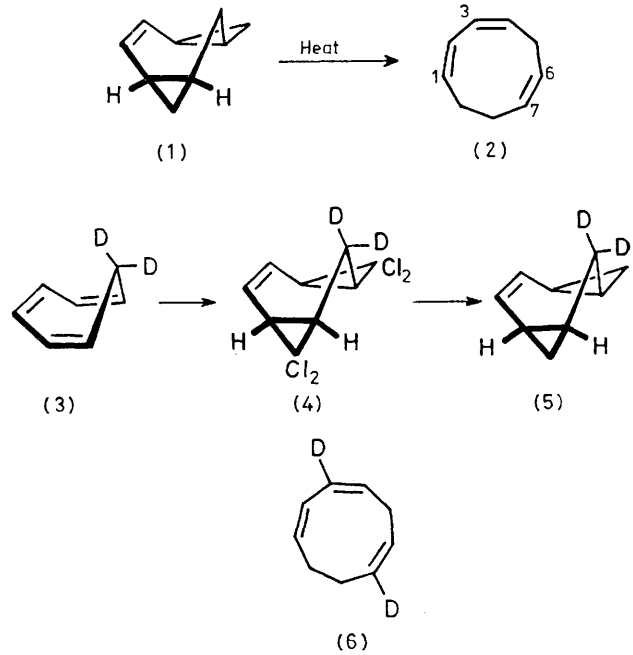
Summary Through pyrolysis of 7,7-dideuterio-*anti*-1,5-bishomocycloheptatriene, evidence has been obtained that thermal rearrangement of this ring system proceeds by twofold 1,5-homodienyl rearrangement, the second stage of which involves prior conformational ring inversion and geminal hydrogen interchange.

ALTHOUGH the seven possible bis- and tris-homocycloheptatrienes have recently become available through stereocontrolled synthesis,[1] the chemistry of these strained molecules is still largely unexplored.[2] In a transformation which is notable for its inoperability in the remaining stereoisomers of (**1**), thermolysis of *anti*-1,5-bishomocycloheptatriene (**1**) in benzene solution at > 180 °C (sealed tube) causes quantitative rearrangement to *cis*[3]-cyclonona-1,3,6-triene (**2**). This event cannot be the consequence of special stabilization of a transition state for some concerted process involving both cyclopropane rings simultaneously, since their internal bent bonds are spatially projected in opposite directions and cannot partake of overlap.[3] Rather, the two most plausible mechanisms are: (i) initial homolytic cleavage of one internal cyclopropane bond, followed by opening of the second three-membered ring and ultimate 1,2-hydrogen shift to provide (**2**); (ii) twofold 1,5-homodienyl rearrangement, where the molecule makes recourse to 'hydrogen rebounding'[4] to bypass otherwise nonconcerted reactions.

Experiments with the specifically labelled 7,7-dideuterio-derivative (**5**) permit in principle a distinction between these two mechanisms. Whereas mechanism (i) will necessarily give a product having deuterium bound to C-7 and C-8 and therefore an olefinic–paraffinic proton ratio of 1·0 : 1, the alternative pathway (ii) need not do so if stereoelectronic control is operative (see below). Thus, the labelled compound (**5**) was prepared by CuCl-promoted decomposition of CD_2N_2 in benzene,[6] dichlorocarbene addition to (**3**) under conditions of phase-transfer catalysis,[1,7] and reduction of (**4**) with lithium and Bu^{t}OH in tetrahydrofuran. The ^{1}H n.m.r. spectrum of (**5**) showed no cycloheptyl methylene absorption and a simplification of the cyclopropyl proton pattern at δ 1·40—0·50 as expected.



(1) (2) (3) (4) (5) (6)

Heating (185 °C; 10 h) samples of (**5**) in C_6H_6 afforded a cyclononatriene product having an olefinic–paraffinic proton ratio of 0·67 ± 0·04 : 1, indicating deuterium substitution at two unsaturated centres. The unchanged nature [relative to (**2**)] of the doubly allylic C-5 methylene pattern (δ 2·63, t, *J* 8·0 Hz) requires the absence of deuterium from C-4 and C-6. Additionally, the triplet nature (*J* 8·0 Hz) of both 4-H (δ 5·45) and 6-H (5·57) can be clearly seen, this lack of further sizable spin–spin coupling denoting that these protons share their respective double bonds with deuterium. This assignment conforms nicely to the remainder of the spectrum (2-H, δ 5·45, br d, *J* 10·5 Hz; 1-H, 5·48, m), especially the marked reduction in the multiplicity of the 8-H peak. The thermal isomerization of (**5**) therefore proceeds to give (**6**) and mechanism (i) can thus be excluded.

Given that the rearrangement begins with a 1,5-homodienyl shift, then deuterium would be required to migrate in (**5**) and an isotope effect should be observed if this first-stage conversion into (**7**) is rate-determining. Kinetic data obtained on (**1**) at 151—174 °C (flame ionization v.p.c. analysis) have revealed this bishomocycloheptatriene to undergo conversion into (**2**) with an energy and enthalpy of activation (Table) quite similar to those found earlier by

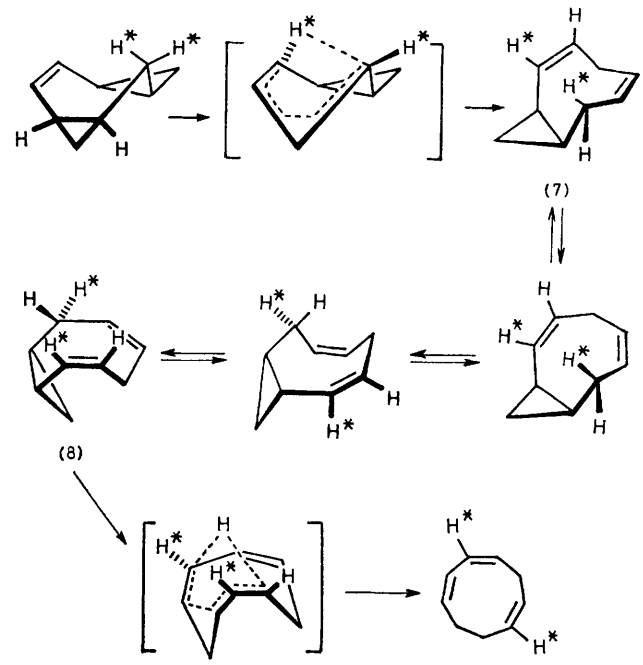
TABLE. Kinetic and thermodynamic data for thermal rearrangement of (**1**) and (**5**)

Compd.	T/°C	$k \times 10^5$/s^{-1}	Activation parameters[a]
(**1**)	151·0	2·44, 2·53	$\Delta H^{\ddagger}$ 34·1, $\Delta S^{\ddagger}$ 0·3
	162·6	7·16, 7·20	$\Delta G^{\ddagger}$ 34·0
	173·8	18·9 19·1	E_a 34·7 ± 0·3
(**5**)	173	2·8, 2·81	$\Delta H^{\ddagger}$ 38·4
	183	7·37, 7·37	E_a 39·0

[a] 298 K; $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and E_a in kcal mol^{-1}; $\Delta S^{\ddagger}$ in cal K^{-1} mol^{-1} (1 cal = 4·184 J).

Winstein for other 1,5-homodienyl transformations.[8] However, while the half-life for the disappearance of (**1**) at 150 °C is *ca.* 10 h, that involved in the second homodienyl shift which transforms bicyclo[6.1.0]nona-2,5-diene to (**2**) (see Scheme) is known to be complete within 1 h at 130 °C. Consequently, the rate-determining step must be the first hydrogen migration. In line with this analysis, there is observed at 173 °C an intermolecular isotopic fractionation factor (k_H/k_D) of 6·7.

Considering the topologies of (**1**) and (**5**),[1] we see that the *endo* cycloheptyl hydrogen is both ideally aligned with, and in adequate proximity to, the π bond for concerted homo-1,5-dienyl shifting. However, because of the strict stereoelectronic demands placed upon such migrations,[8b,10] the conformation of the bicyclo[6·1·0]nona-2,5-diene initially produced in this rearrangement, *viz.* (**7**), lacks the capability for hydrogen (or deuterium) 'rebound.' However, such can be realized by ring inversion of (**7**) to its saddle form (**8**). Importantly, this conformational flexing of the medium ring results in simultaneous exchange of the relative positioning of hydrogen and deuterium at C-7 (when starting from (**5**) such that only the hydrogen is now stereodisposed for migration. At this level of mechanistic detail, (**5**) should *not* be transformed to nine-membered ring product isotopically substituted at vicinal carbon atoms. Rather, adherence to those isomerization pathways which are facilitated energetically by favourable orbital overlap must deliver (**6**) as is observed.



SCHEME

Berson and his co-workers have earlier established that the pyrolytic transformation of bicyclo[4.2.1]nona-2,4,7-triene to *cis*-8,9-dihydroindene proceeds by way of an initial transannular shift followed by rebound of the *same* hydrogen to its ultimate position.[4] The intermediates in their sequence were not of adequate flexibility to allow for conformational biases to appear. The greater mobility of the medium ring contained within (**7**) and (**8**) does allow for this possibility and the present study clearly establishes that rearranging systems having increased conformational freedom may experience ring flipping in advance of product formation to permit electronically preferred processes to occur. That the first hydrogen to migrate within (**1**) is subsequently bypassed during the rebound in favour of its geminal counterpart is a fascinating observation. However, we do expect that other flexible rearranging systems will be found which adopt this convenient device to maximize concertedness.

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