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Hierarchy of Orbital Symmetry Allowed Pathways in the Thermal Skeletal Rearrangements of a Structurally Unconstrained Cyclooctatetraene

Sir:

Thermal activation of 1,2-disubstituted cyclooctatetraenes (1) at temperatures above 400° in the gas phase causes *initial* skeletal rearrangement to the structurally isomeric 1,4 derivatives (2) in a process which is reversible.[1] The two most plausible hypothetical mechanisms for these intriguing reactions are (i) valence isomerization to a bicyclo[4.2.0]octatriene, followed by intramolecular Diels–Alder reaction and ultimate rearrangement of the resulting cis^2-bishomobenzene intermediate, and (ii) a process again initiated by valence isomerization but now completed by [1,5] sigmatropic shift of an sp^2-hybridized cyclobutene carbon and disrotatory opening of the relocated four-membered ring.[2] Pathway i has been shown to operate in unsaturated propellanes of type 3,[3] whereas sequence
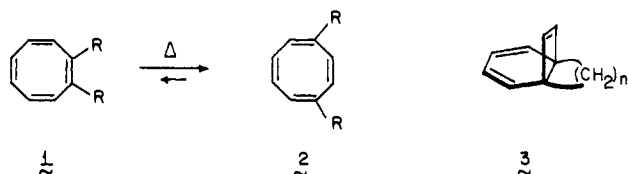
ii has been advanced as the mechanism which best explains the degenerate behavior of benzocyclooctatetraene-*3,8-d₂*.[1]

Such ancillary studies have not permitted a distinction between the two mechanistic avenues due to structural biases inherent in these systems which predispose them in opposite directions. Because knowledge of the hierarchic ordering of competitive symmetry-allowed processes such as i and ii commands special significance, we have sought to elucidate which of these thermal rearrangement pathways is most readily accessible to an *unconstrained* cyclooctatetraene derivative.

Experiments with 1,5-dimethylcyclooctatetraene (4)[4] make possible a resolution of this dichotomy. As a

(1) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, 94, 9224 (1972); M. Oku, unpublished results.

(2) A third possibility involving the intervention of bicyclo[3.3.0]-octadienediyls does not account satisfactorily for the observed translocation of substituents. Such intermediates do appear, however, to gain importance in other instances: M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, 86, 3396 (1964); M. Jones, Jr., and L. O. Schwab, *ibid.*, 90, 6549 (1968); R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, 7, 537 (1968); A. Roedig, G. Bonse, and R. Helm, *Chem. Ber.*, 106, 2156 (1973).

(3) L. A. Paquette and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, 94, 4398 (1972).

(4) L. A. Paquette, R. K. Russell, and R. E. Wingard, Jr., *Tetrahedron Lett.*, 1713 (1973).

consequence of its symmetry, 4 can give rise in preliminary isomerization only to the two bicyclo[4.2.0]-octatrienes 5 and 6. Although the values of the equilibrium constants for the 4 ⇌ 5 and 4 ⇌ 6 conversions remain as yet unknown, knowledge of these data is not necessary for the present purposes. This is due to the subtly parallel manner in which 5 and 6 can undergo further chemical change along either available reaction channel, a consequence of which is that the product mixture is independent of which triene is the reactant. As Scheme I shows, should either 5 or 6 transmute ac-

Scheme I
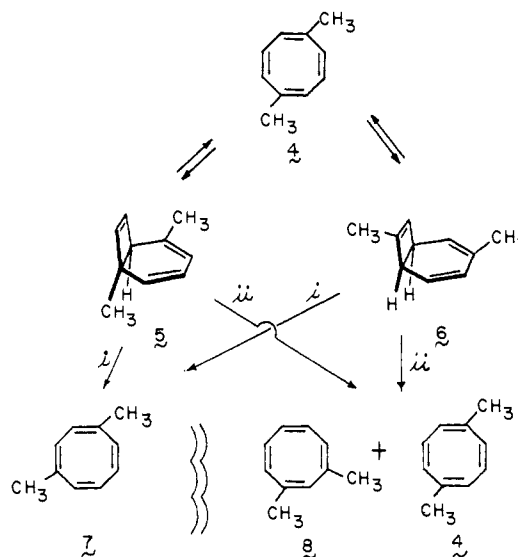
cording to mechanism i, convergence to 1,4-dimethylcyclooctatetraene (7) will result. In equally diagnostic fashion, operation of the [1,5] sigmatropic shift pathway (ii) will lead to 1,3-isomer 8 or return formally unchanged 4 depending upon which cyclobutene carbon acts as the pivot. It follows, therefore, that careful product analysis of the thermal rearrangement of 4 with increasing temperature should permit resolution of these unanswered questions. We now report such experiments which show $k_i > k_{ii}$.

Gas-phase pyrolysis of isomerically pure 4 (diluted with nitrogen) in a flow system at 415–435° and 18 mm for short contact times (1–3 sec) proceeded to 8–14% conversion and afforded exclusively 7 (Table I). Only

Table I. Product Composition Data from the Pyrolysis of 4

Temp, °C	Pressure, mm	Recovery, %[a]	1,2-(9), %	1,3-(8), %	1,4-(7), %	1,5-(4), %
395	18	80				100
415	18	77			8	92
435	18	70			14	86
465	18	66	3	7	19	71
480	18	53	6	12	22	60
500	18	51	8	23	29	40

[a] Values relate to cyclooctatetraenes isolated upon vpc purification and do not include aromatic products.

when the temperature range was extended to 465° did minor amounts of 8[5] and 9 make their appearance.

(5) This hydrocarbon was prepared in an isomerically pure state by thermolysis of 1,3-dimethylsemibullvalene (78% yield) in the same flow apparatus at 400° and 35 mm. Full details of this synthetic sequence will appear elsewhere.

Expectedly, the proportions of these isomers increased with the input of added heat to the system. To achieve maximum sensitivity in product composition analysis, recourse was made to a combination of vpc[6] and quantitative infrared techniques.[7]

Control experiments performed under precisely identical conditions showed that rearrangement to the 1,3-dimethyl isomer occurs to a small degree from both **7** and **9** at 465° (Table II). The levels of these isomeriza-

Table II. Control Experiment Data for **7, 8,** and **9**

Hydro-carbon	Temp, °C	Pres-sure, mm	Re-covery %[a]	1,2-(9), %	1,3-(8), %	1,4-(7), %	1,5-(4), %
7	435	18	75			100	
	450	18	68	4	5	83	8
	465	18	60	6	19	61	14
8	480	18	83		100		
	525	18	49	8	27	51	14
9	395	18	71	100			
	435	18	70	95		5	
	450	18	63	91		9	
	465	18	58	84	3	11	2

[a] Values relate to purified (vpc) hydrocarbon mixture.

tions are such, however, that they could easily account for the amount of **8** which obtains during thermolysis of **4** and consequently becloud the possibility of assaying the direct **4 → 8** conversion, if operative.[8]

Notwithstanding, the thermal behavior of **4** is consistent only with an overall predominance of the Diels–Alder mechanism.[9] Detailed analysis of the reactivity patterns of **7–9** is similarly reconcilable with a marked preference of these systems for pathway i. Perhaps the concerted [1,5] migration alternative is disfavored because of the orbital symmetry requirement that the sp²-hybridized cyclobutene carbon migrate with retention rather than "opposite-face" bonding through the antisymmetric p orbitals as in **10**. This imposition

10   11

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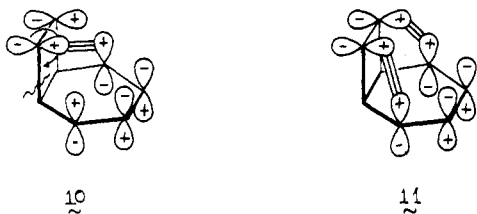
(6) Our most satisfactory vpc results were achieved with a 0.125 in. × 20 ft 5% PMPE 6-ring on Chromosorb G column operating at 40°. Under these conditions, quantitative assay of the 1,2- ($t_{ret} \approx 9.58$ hr), 1,5- ($t_{ret} = 10.66$ hr), and 1,3-/1,4- ($t_{ret} = 8.83$ hr) ratio was possible.

(7) The four isomerically pure cyclooctatetraenes exhibit selected fingerprint infrared absorptions which are mutually exclusive of each other; 1,2-, 646, 710, and 857 cm⁻¹; 1,3-, 600, 708, and 828 cm⁻¹; 1,4-, 655, 701, and 844 cm⁻¹; 1,5-, 627, 722, and 891 cm⁻¹. To obtain the ratio of 1,3- to 1,4-dimethyl compounds in the pyrolysate, the relative intensities of the 708 (ϵ 210) and 701 cm⁻¹ (ϵ 182) bands were determined.

(8) In contrast to the data of Table II, the original product composition ratios for pyrolysis of 7 and 9[1] are now considered of low accuracy because of too great reliance on pmr spectroscopy as the method of analysis. We have since found pmr methods to be quantitatively unreliable for this series of hydrocarbons.

(9) We have considered, and subsequently discounted, the possibility that the pair of 1,5-sigmatropic rearrangements available to 5 and 6 are so energetically imbalanced as to give only 4 (degenerate reaction and consequently unobservable) to the exclusion of 8. Rather, the transition states of the processes in question are assumed to bear a close quantitative resemblance.

forces the potential migratory carbon to maintain an ungainly spatial relationship to the migration terminus, a factor not present in the competing $[_\pi4_s + _\pi2_s]$ transition state **(11)**.[10]

(10) Nonconcerted diradical alternatives to these mechanisms are less attractive explanations of our findings since they lack electronic allowedness and a maximum of contiguous bonding.

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Kinetic Evidence Attesting to the Absence of Enhanced Anchimeric Assistance during Solvolytic Generation of Unsymmetrical (2 + 2 + 0) Laticyclic Cations

Sir:

Remarkably little attention has been given to ionic systems endowed with laticyclic topologies comprised of more than two ribbons[1] despite the extensive structural variations possible and inherent novelty of such species. In the first and only example known to us, Allred and Hinshaw examined the solvolysis of *p*-nitrobenzoate **1** and concluded on the basis of rate constant comparisons that this π-orbital arrangement furnished perhaps the largest driving force to ionization yet discovered.[2] Enhanced ionic stabilization was presumed and attributed to extended charge delocalization epitomized by nonclassical ion **2**. However, the dearth of experimental data on relevant model compounds other than *anti*-7-norbornenyl derivative **3** re-

1   2   3
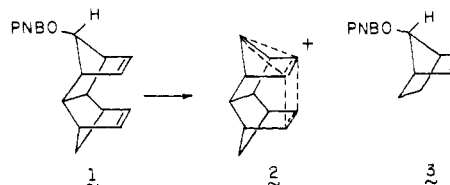
quires this theoretical interpretation to be less than unambiguous. Because π participation seems to be a sensitive function of puckering of the 5-ring in the bicyclo-[x.2.1] series, e.g., **4–6**,[3,4] comparable effects by more

4	5	6
(k_{rel}[5a]) 2 × 10⁸	10¹¹	5 × 10¹⁴
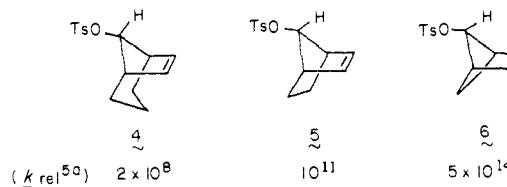
subtle strain influences could be anticipated but remained untested. We now wish to report convincing evidence which shows that the enhanced solvolytic reactivity of **1** need not be attributed to laticyclic stabilization arising from involvement of the more remote

(1) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(2) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 1293 (1968).

(3) B. A. Hess, Jr., *J. Amer. Chem. Soc.*, **91**, 5657 (1969).

(4) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969).

(5) (a) 7-Norbornyl tosylate, $k_{rel} \approx 1$; (b) *anti*-7-norbornenyl brosylate, $k_{rel} = 10^{11.1}$.