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THE QUESTION OF HEXAHOMOBENZENE AUTOMERIZATION. NEW SYNTHETIC APPROACHES TO cis^3-1,4,7-CYCLONONATRIENE.

Michael R. Detty[1] and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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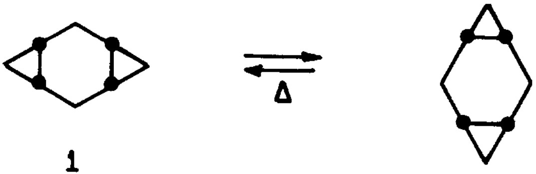
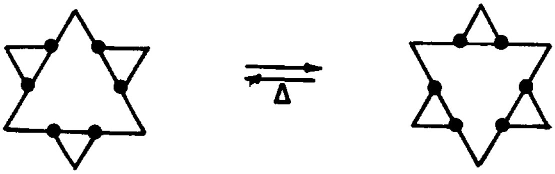
Despite the high level of interest accorded in recent years to those degenerate thermal isomerizations which involve only π electrons or a blend of σ and π electrons, automerization reactions of molecules constructed entirely of σ bonds have been given little attention. Transformations based upon the prototypical 4ε process **1** ⇄ **2** have been briefly sought, but gone undetected;[2] however, orbital symmetry can be expected to exert an untoward influence in these cases. Because the **3** ⇄ **4** isomerization (a 6ε change) is in principle not subject to comparable electronic constraints, it appeared conceivable that thermal activation might now result in observable degenerate rearrangement. Still to be reckoned with, however, was the question of mutual spatial orientation of the three inner cyclopropyl orbitals and its effect upon the energetics of the transformation. Importantly, by making recourse to a two-fold degenerate system, complicating factors arising from weighted ground state energy preferences are not present. As a result, passage of constituent isomer **3** to its isoenergetic counterpart **4** would uniquely demonstrate the feasibility of this electronic reorganization.

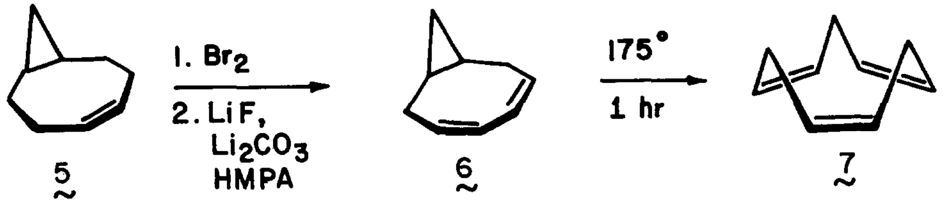


1 **2**



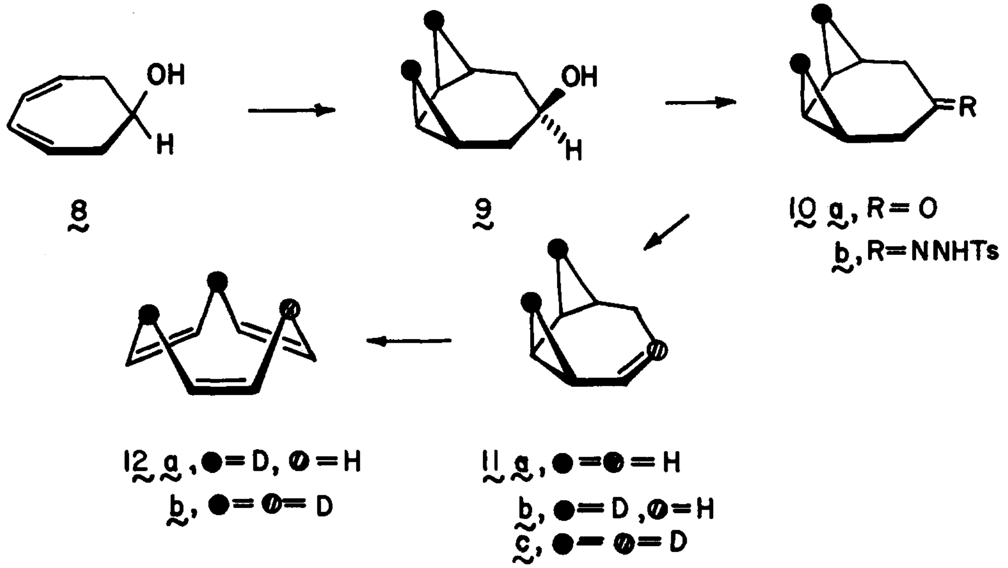
3 **4**

This study first required access to cis^3-1,4,7-cyclononatriene derivatives specifically labeled with deuterium at the methylene positions. Because the preexisting methods for gaining entry to the parent triene suffer from low overall yields and difficulties in purification,[2,3] efficient alternative synthetic approaches were sought. To this end, the readily available cis-bicyclo[6.1.0]non-4-ene (**5**)[4] was brominated (CCl_4, 0°) and dehydrobrominated (LiF, Li_2CO_3, powdered glass, HMPA, 100°) to give pure **6** in 72% yield. This diene was subsequently sealed in a glass ampoule and heated in an oil bath at 175° for 1 hr to promote sequential 1,5-dienyl



and 1,5-homodienyl shifting.[5] Direct sublimation of the crude reaction mixture gave 7 (98% purity) in 85% yield. Although this sequence represents the most efficient synthesis of 7 currently available, it is clearly not amenable to the preparation of specifically deuterated forms of the triene beyond the 3,3-$\underline{d}_2$ derivative.[6]

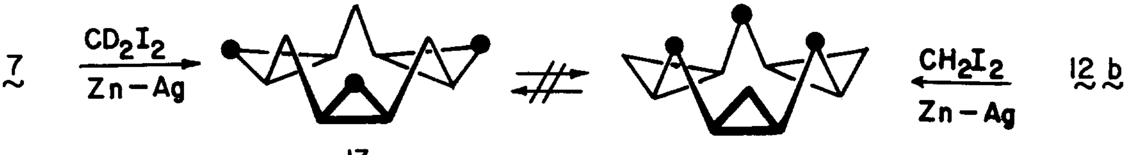
In principle, more extensive specific deuterium substitution of 7 should be realized if two of the three constituent methylene groups were present in a precursor molecule where control of H/D labeling was possible and elaboration of the third $-CH_2-$ ($-CD_2-$) moiety was reserved for the final step. Guided by this rationale and the previously explored solvolytic behavior of anti,anti-3,5-bishomocycloheptadienyl tosylate,[7a] we treated 11a[7b] with catalytic quantities of 70% perchloric acid in chloroform (reflux, 20 min) and observed conversion to



an isomeric mixture of hydrocarbons dominated by 7 (70%). Since tricyclic alcohol 9 is the major product formed upon exhaustive cyclopropylation of 8[8] with CD_2I_2 and zinc-silver couple, and 9 is readily oxidized (95%) by Collins' reagent to 10a, the tosylhydrazone of which (10b) suffers elimination to give 11b (72%) when treated with lithium 2,2,6,6-tetramethylpiperidide, this tetradeuterio hydrocarbon is conveniently accessible. Comparable acid-catalyzed rearrangement of 11b afforded 12a, its 90 MHz ^1H NMR spectrum (in $CDCl_3$, -30°) being characterized by a series of three multiplets centered at δ 5.5 (6H), 3.7 (1H), and 2.1 (1H).

Synthesized by sequential sodium borodeuteride reduction of 10a (95%), reaction of this alcohol with sulfene (93%), and KO$\underline{tert}$-Bu-induced elimination of methanesulfonic acid from the resulting mesylate (83%), bishomocycloheptatriene 11c was rearranged in chloroform solution with a catalytic quantity of perchloric acid dissolved in a 100-fold excess of D_2O. As anticipated, the ^1H NMR spectrum ($CDCl_3$ solution, -30°C) of the nicely crystalline 12b produced in this manner displays only a slightly broadened singlet at δ 5.48. A plausible mechanism for the 11 → 12 transformation involves initial protonation (deuteration) of the bishomotropilidene to form a cyclopropylcarbinyl cation, deprotonation of which with twofold cyclopropane ring cleavage ultimately delivering cyclononatriene product.

Treatment of 7 with CD_2I_2 and zinc-silver couple in ether (reflux, 12 hr), followed by preparative vpc purification, afforded colorless crystalline 13 (mp 58-62°; m/e 168.1788; 57%

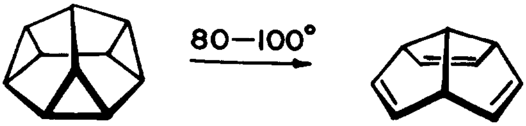


13 14

conversion). In agreement with the structural assignment, the ^1H NMR spectrum of this tetracyclic hydrocarbon (in CCl_4) lacks the upfield cyclopropyl methylene absorptions which are characteristic of the unlabeled molecule.[2,3] When 12b was exhaustively cyclopropanated as before but with CH_2I_2, the white crystalline 14 (mp 55-60°; m/e 168.1788) so produced exhibited a contrasting ^1H NMR spectrum consisting of two multiplets centered at δ 0.70 (9H) and -0.27 (3H).

Pure samples of 13 and 14 were next individually subjected to conditions of flash vacuum pyrolysis in a quartz reactor packed with quartz chips (N_2 extrainment). At temperatures up to and including 485° (contact time ~ 3 sec), the two hexahomobenzenes were recovered totally unchanged. Progression to 500° caused the onset of low level decomposition, but no automerization. Clearly, there exists insufficient interaction among the three constituent rings in 13 and 14 to allow for bond shifting, a result in agreement with the recently reported noninterconvertibility of two "trioxa-hexa-σ/π-homobenzenes" (a related nondegenerate valence isomer pair)[9] and the unresponsiveness of the three stereoisomeric trishomotropilidenes to thermal activation (500°).[7b]

The demonstrated lack of interconversion of 13 and 14 does not appear attributable to adverse electronic effects if the facile 6ϵ reversion of diademane (15) to triquinacene (16) serves as suitable analogy.[10] Rather, it is more likely that the geometric conditions prevailing in these hexahomobenzenes preclude the possibility of attaining interactomic distances sufficiently proximate to permit interaction. Given the well characterized three-dimensional structure of 7,[11] we see the crucial nonbonded 1,3 sp^2C-sp^2C distances (2.46 Å) to be such as to deny the possibility for meaningful homoaromatic delocalization.[12] Since cyclopropanation



15 16

17

of the *cis*^{3}-1,4,7-cyclononatriene system inflexibly fixes the 9-membered ring[13] while simultaneously compounding compression energies within the molecular crown, we view an improved juxtapositioning of the key reactive centers as unlikely. In this context, the still less favorable three-dimensional features of **16**[14] which lead to a further decrease in overall π orbital interaction relative to **7**[15] augur poorly for the capacity of **17**[16] to experience concerted $({}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s)$ bond reorganization.[17]

FOOTNOTES AND REFERENCES

(1) University Graduate Fellow, 1974-1975; Dissertation Fellow, 1976-1977.

(2) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963); K. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963).

(3) W. Roth, *Ann.*, **671**, 10 (1964).

(4) Prepared by treatment of *cis*^{2}-1,5-cyclooctadiene with dichlorocarbene [G. I. Fray, *J. Chem. Soc.*, 4284 (1963)] and reduction of the monoadduct with sodium in liquid ammonia [compare P. G. Gassman, J. Seter, and F. J. Williams, *J. Am. Chem. Soc.*, **93**, 1673 (1971)].

(5) D. S. Glass, R. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).

(6) Attempts to promote H/D allylic exchange in **7** with a strong base have seemingly failed: J. W. H. Watthey and S. Winstein, *J. Am. Chem. Soc.*, **85**, 3715 (1963).

(7) (a) L. A. Paquette and M. R. Detty, *J. Am. Chem. Soc.*, in press; (b) M. R. Detty and L. A. Paquette, *ibid.*, in press.

(8) D. I. Schuster, J. M. Palmer, and S. C. Dickerman, *J. Org. Chem.*, **31**, 4281 (1966).

(9) H. Prinzbach, V. Wessely, and H. Fritz, *Tetrahedron Lett.*, 2765 (1976).

(10) A. de Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem. Intern. Ed. Engl.*, **10**, 417 (1971).

(11) W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yü, *J. Am. Chem. Soc.*, **86**, 3178 (1964).

(12) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).

(13) R. S. Boikess and S. Winstein, *J. Am. Chem. Soc.*, **85**, 343 (1963).

(14) E. D. Stevens, J. D. Kramer, and L. A. Paquette, *J. Org. Chem.*, **41**, 2266 (1976).

(15) J. C. Bunzli, D. C Frost, and L. Weiler, *Tetrahedron Lett.*, 1159 (1973); P. Bischof, D. Bosse, R. Gleiter, M. J. Kukla, A. de Meijere, and L. A. Paquette, *Chem. Ber.*, **108**, 1218 (1975).

(16) D. Bosse and A. de Meijere, *Tetrahedron Lett.*, 871 (1975).

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