Tetrahedron Letters Vol. 22, pp 291 - 294
0040-4039/81/0122-0291$02.00/0

THREEFOLD TRANSANNULAR EPOXIDE CYCLIZATION. SYNTHESIS OF A HETEROCYCLIC C_{17}-HEXAQUINANE

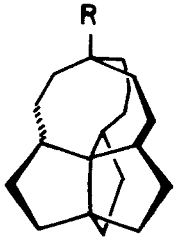
Leo A. Paquette* and Michel Vazeux

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

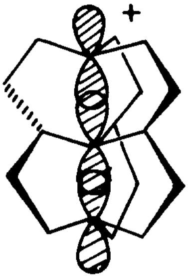
Summary: The Lewis acid-catalyzed rearrangement of two [3.3.3]propellane triepoxides to a heterocyclic C_{17}-hexaquinane derivative is described.

Although many structurally fascinating unstrained propellane structures have been synthesized in recent years,[1] none have been accorded the degree of interest recently paid to the unknown capped system 1a. Appropriate ionization of the functionalized derivative 1b would presumably lead to carbocation 2 which has been proposed on theoretical grounds to be an alluringly new nonclassical species.[2] With loss of X^-, the incipient cationic carbon is expected to move along the propellane axis toward the central carbon and set the stage for evolution of σ-allyl character. Such a symmetric combination of end-on p orbitals (pp-σ overlap), which has not been encountered previously,[3] would make 2 a doubly degenerate system incapable of retaining optical activity if 1b were resolved.

In another context, the maximally unsaturated hydrocarbon 3 known as C_{17}-hexaquinacene[4] compresses the structural elements of [3.3.3]propellatriene and triquinacene into a highly compact spherical construction having unusual connectivity.[5]



1a, R = H
b, R = X



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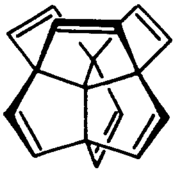

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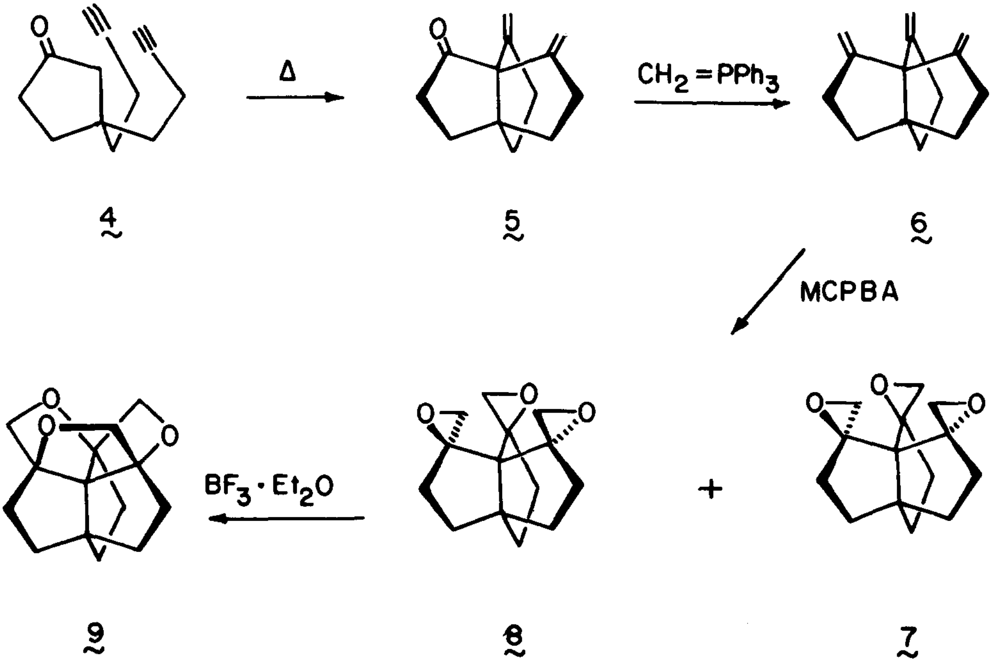
Due to the special interest in these systems, we have initiated studies aimed at their synthesis. During the early phases of the work targeted toward **1b**, a remarkable rearrangement has been encountered which provides direct access to the first known *C*$_{17}$-hexaquinane, *viz.* the *C*$_3$-symmetric trioxa derivative **9**. Our approach finds its basis in Conia's recent discovery that bispropargylic ketone **4** is subject to twofold ene reaction and closure to **5** under appropriate thermal conditions.[6] Treatment of **5** with methylenetriphenylphosphorane in benzene-diisopropyl ether (1:2) solution at the reflux temperature for 4 hr led efficiently (92%) to triene **6**:[7] ^{1}H NMR (δ, CDCl$_3$) 4.82 (t, *J* = 2 Hz, 6H), 2.30 (m, 6H), and 1.58 (m, 6H).

Upon treatment with *m*-chloroperbenzoic acid in dichloromethane solution at 0°C, **6** was transformed during 24 hr into an *ca* 1:1 mixture of the stereoisomeric triepoxides **7** and **8** which could be efficiently separated by medium pressure liquid chromatography on silica gel (elution with 4:1 hexane:ethyl acetate). The more rapidly eluted colorless solid was easily discerned to be the highly symmetric **7** on the basis of its NMR spectra (CDCl$_3$ solutions). Thus, while the epoxidic methylene protons of **7** are seen as a well separated AB pattern (δ 2.65, $\Delta\nu_{AB}$ = 0.23, *J* = 3.5 Hz), those of **8** appear as a series of multiplets in the region 2.9-2.42. Furthermore, whereas the broad-band decoupled ^{13}C spectrum of **7** is characterized by



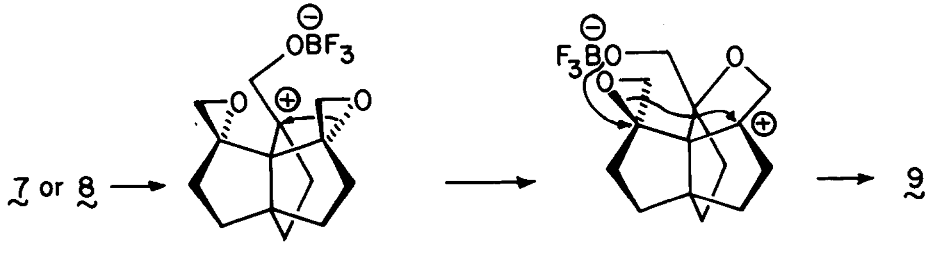
4 **5** **6**

9 **8** **7**

merely six lines (65.74, 64.57, 61.71, 46.80, 35.97, and 34.91 ppm), that of 8 shows the full complement of 14 peaks.[8,9]

Exposure of cold (near 0^{o}C) benzene solutions of 7 to catalytic quantities of boron trifluoride etherate or aluminum chloride for 1 min followed by addition of water resulted in complete conversion to an isomeric crystalline substance.[9] Since 8 reacted analogously, the rearrangement was clearly independent of epoxide stereochemistry. The ^{1}H NMR spectrum (in $CDCl_3$) of the new compound was extraordinarily simple, consisting only of a downfield AB quartet (δ 4.10, $\Delta\nu_{AB}$ = 0.46, $\underline{J}$ = 11 Hz, 6H) and a narrow upfield multiplet (2.2-1.65, $\omega_{\frac{1}{2}}$ = 2.5 Hz at 60 MHz) of area 12. That a highly symmetric material had been produced was clearly apparent from the six-line ^{13}C NMR spectrum [103.70(s), 77.73(t), 65.88(s), 55.78(s), 37.04(t), and 33.06(t)]. Structural assignment as the $\underline{C}_3$-trioxa-$\underline{C}_{17}$-hexaquinane 9 follows directly from these spectral properties. The topology of 9 is such that the endo and exo protons of the three identical methylene groups adjacent to oxygen are projected into quite different chemical environments, while the methylene protons of the [3.3.3]propellane subunit are not.

The unusually facile conversion of 7 and 8 to 9, which requires the unprecedented rupture of an equivalent bond in three different epoxide rings, is undoubtedly made possible by the unique proximity factors contained within these systems. As illustrated in 10 and 11, Lewis acid-promoted opening of one epoxide ring so as to induce cationic character at a more highly substituted cyclopentyl carbon induces neighboring group participation by a second oxygen atom. This process continues intramolecularly until the trioxatriquinane part structure is fully knitted.[10]



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Attempts are currently being made to foster a similar rearrangement in the triscyclopropane analogue of 7 and 8, a much less reactive substance.

Acknowledgment. The authors thank the National Science Foundation for their financial support and Dr. Charles Cottrell for recording the ^{13}C NMR spectra.

References and Notes

(1) Ginsburg, D. "Propellanes. Structure and Reactions," Verlag Chemie 1975.

(2) Lipkowitz, K. B.; Larter, R. M.; Boyd, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 85.

(3) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.

(4) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600.

(5) Dr. Howard Simmons (duPont) has informed us of the unusual graph-theoretical properties of **3**.

(6) Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron* **1980**, *36*, 1203.

(7) Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron Lett.* **1975**, 4053.

(8) All new compounds were fully characterized by infrared, ^{1}H and ^{13}C NMR, accurate mass spectral and/or combustion data.

(9) Compounds **7**-**9** are easily sublimed white solids which have indefinite melting points when placed in sealed tubes. Upon being heated briefly at 230-240°C, **7** was observed to undergo simultaneous isomerization to **9** and polymerization.

(10) We have recently been informed by Dr. Howard Simmons, III and coworkers that similar findings have been uncovered by them at Harvard University (*J. Am. Chem. Soc.*, submitted for publication).

(Received in USA 21 November 1980)