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THE AZASEMIBULLVALENE SYSTEM[1]

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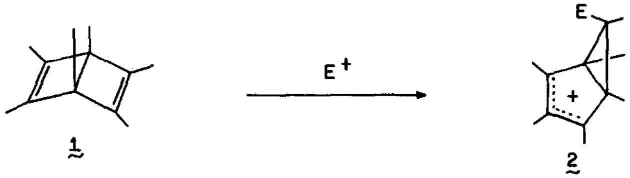
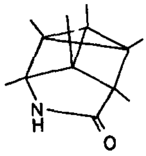
Previously, we reported the facile and rapid conversion of hexamethyldewarbenzene (**1**) into the interesting bicyclo[3.1.0]hexenyl cation **2** under electrophilic conditions.[2] This transformation is somewhat reminiscent of the manner in which electrophiles attack cyclooctatetraene to become bonded to the *endo* C-8 position of the resulting homotropylium cation.[3] The utilization of the powerfully electrophilic chlorosulfonyl isocyanate (CSI) reagent in the recent successful synthesis of an azabullvalene derivative from cyclooctatetraene[4,5] has led us to examine other CSI-polyolefin reactions. In this communication, we wish to describe the particularly interesting reaction of CSI with **1**, and the ultimate conversion of the resulting adduct into the azasemibullvalene system.



1 **2**

Addition of CSI to **1** in cold (-15°) methylene chloride solution afforded a crystalline N-(chlorosulfonyl) lactam which, without purification, was carefully hydrolyzed in aqueous acetone by titration with 4N NaOH to give the derived amide, mp 168-170°,[6] in 87% overall yield; $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}; λ_{max}^{EtOH} end absorption; $\delta_{TMS}^{CDCl_3}$ singlets at 1.62 (6H), 1.28 (6H), 1.18 (3H), and 1.05 (3H). When this amide was hydrogenated catalytically over rhodium on carbon at room temperature, the uptake of hydrogen proceeded slowly to give in 94% yield a *lone* dihydro derivative (**9**), mp 155-155.5°;[6] $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ *ca.* 2.1 (2H, complex multiplet), singlets at 1.16 (3H) and 1.07 (9H), and doublets (J = 7 Hz) at 0.90 (3H) and 0.78 (3H). A similar stereochemical result was observed when the amide was epoxidized with *m*-chloroperbenzoic acid in chloroform solution to give a single epoxide (10), mp 178-9°;[6] ν_{max}^{Nujol} 1700 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ singlets at 1.29 (6H), 1.21 (3H), 1.15 (3H), 1.04 (3H), and 0.98 (3H).

Because the above data conclusively establish that the adduct possesses only one site of unsaturation, the molecule must be tricyclic and therefore cannot be 3.[7] The carbonyl stretching frequencies similarly dismiss structures incorporating a β-lactam moiety, e.g., 4, as logical possibilities. Although 5 and 6 are mechanistically feasible candidates,[8] it remains difficult to reconcile the stereoselective nature of the reduction and oxidation reactions with structure 5. On the basis of the following evidence, the lactam in question has been formulated as 6.



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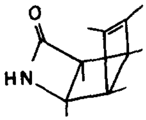

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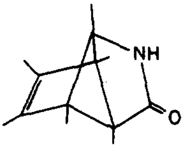

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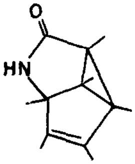

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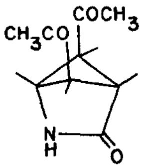

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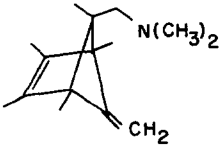

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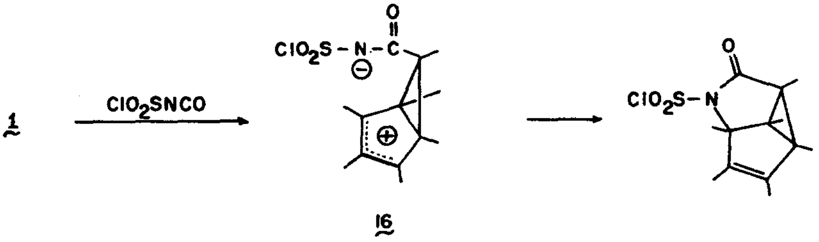
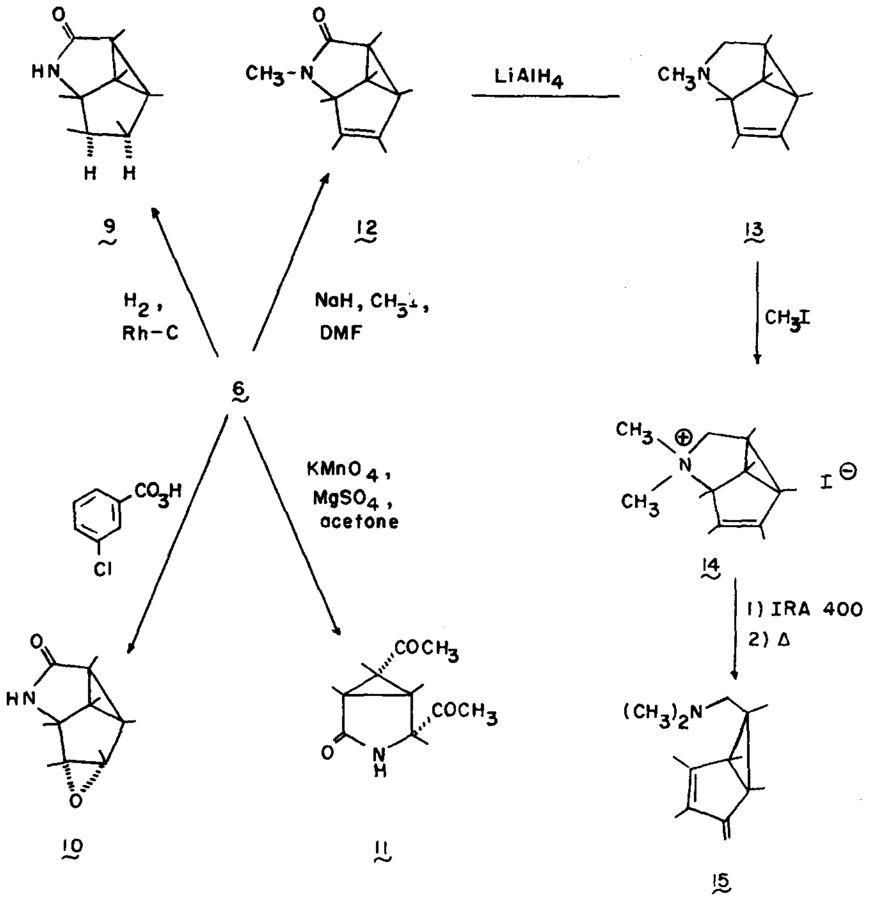
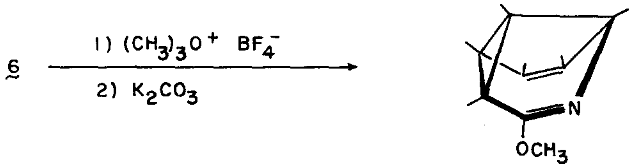
On being oxidized with buffered ($MgSO_4$) potassium permanganate in acetone solution, the lactam was converted in 65% yield to a crystalline diketone (11), mp 135-136.5°,[6] whose nmr spectrum consists, inter alia, of two sharp acetyl methyl singlets at δ 2.28 and 2.07. In another set of experiments, sequential methylation (sodium hydride-methyl iodide in DMF), lithium aluminum hydride reduction, and quaternization afforded a highly crystalline methiodide (14), mp 160-160.5°.[6] Pyrolysis of the corresponding methohydroxide gave an unsaturated tertiary amine which was characterized as its perchlorate salt, mp 148°.[6] In particular, its nmr spectrum (acetone-d_6) displays the two methylene protons as a collapsed AB doublet at δ 5.01 and 4.92. Because the planes of symmetry in 7 and 8 (derived from 5) require that both acetyl groups and the two vinyl protons be magnetically equivalent, structure 5, or any other symmetrical species, is totally inconsistent with these spectral parameters.



Particularly revealing is the ultraviolet spectrum of the Hofmann product (15) [λ_{max}^{EtOH} 257 mμ (ε 7,540)] which is characteristic of the 2,3-homofulvene chromophore.[2,9] The above sequence of reactions is reformulated in Chart I.



These results provide conclusive evidence for the intervention of cations such as 2.[2] As in the case of the homotropylium example,[4] the dipolar nature of intermediate 16 provides an effective means of trapping the reactive cation at the appropriate point along the potential energy surface.[2] This general type of ground-state transformation is under further study.



17

The azasemibullvalene 17 was prepared by treating 6 with trimethyloxonium fluoroborate in dry methylene chloride at room temperature; mp 50-51°, perchlorate, mp 192-3° dec;[6] $\delta_{TMS}^{CDCl_3}$ singlets at 3.66 (3H), 1.32 (3H), 1.22 (6H), and 0.96 (3H); singlets with additional small long range coupling at 1.67 (3H) and 1.56 (3H); λ_{max}^{EtOH} shoulder at ca. 220 mμ (ε 4,000).[10] Not too unexpectedly, the nmr spectrum of 17 was found to be unaltered from -40 to 150°; the restrictions imposed by the imino ether grouping in 17 on the possible Cope rearrangement presumably parallel those observed with methoxyazabullvalene.[4,5] Unfortunately, however, total substitution by methyl groups does not lend itself to a simple nmr analysis and refined studies on this question must await the synthesis of demethylated congeners.

Further aspects of this problem as well as logical extensions to bicyclo[2.2.0]hexa-2,5-diene are under active investigation in this laboratory.

Acknowledgment. We are indebted to the National Institutes of Health for support of this work.

FOOTNOTES AND REFERENCES

(1) Unsaturated Heterocyclic Systems. XXXVII. For paper XXXVI, see L. A. Paquette and N. Horton, Tetrahedron Letters, in press.

(2) L. A. Paquette and G. Krow, accompanying communication.

(3) J. L. Rosenberg, J. E. Mahler, and R. Pettit, J. Am. Chem. Soc., 84, 2842 (1962); S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, ibid., 87, 3267 (1965); S. Winstein, C. G. Kreiter, and J. I. Brauman, ibid., 88, 2047 (1966); G. Boche, W. Hechtl, H. Huber, and R. Huisgen, ibid., 89, 3344 (1967); R. Huisgen, C. Boche, and H. Huber, ibid., 89, 3345 (1967).

(4) L. A. Paquette and T. J. Barton, ibid., 89, 5480 (1967).

(5) L. A. Paquette, T. J. Barton, and E. B. Whipple, ibid., 89, 5481 (1967).

(6) Satisfactory elemental analyses were obtained for all new compounds.

(7) Such a structure has been proposed for the hexamethyldewarbenzene-tetracyanoethylene adduct: W. Schäfer and H. Hellmann, *Angew Chem. Intern. Ed., Engl.*, **6**, 518 (1967).

(8) Hexamethyldewarbenzene has been reported to react with 4-phenyl-1,2,4-triazoline-3,5-dione to give an adduct of type **5**: D. M. Lemal and J. P. Lokensgard, *J. Am. Chem. Soc.*, **88**, 5934 (1966).

(9) For examples, refer to D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958).

(10) This absorption maximum is roughly comparable to that [λ_{max} shoulder at *ca.* 225 mμ (ε 2,000)] observed for methoxyazabullvalene and 1-azatricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene [D. S. Wulfman and J. J. Ward, *Chem. Comm.*, 276 (1967)]. The UV spectra of dihydrobullvalene [shoulder at 230 mμ (ε 3,400)][11] and semibullvalene [shoulder at 225-235 mμ (ε 2,450)][12] also provide satisfying parallel comparisons.

(11) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

(12) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966).