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ELECTROPHILIC ADDITIONS TO HEXAMETHYLDEWARBENZENE

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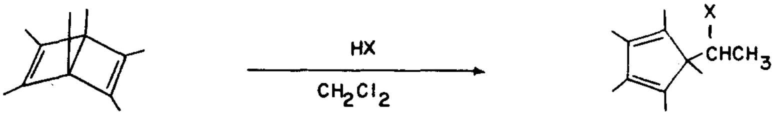
The commercial availability of hexamethyldewarbenzene (1) now provides a convenient source of the formerly elusive, but still esoteric, bicyclo[2.2.0]hexa-2,5-diene system for chemical investigation. We have examined the behavior of 1 toward a number of electrophilic reagents and wish now to describe our independent results, some of which are significantly at variance with those reported in a recent review of the subject.[1]

Exposure of methylene chloride solutions of 1 to a stream of dry gaseous hydrogen chloride or hydrogen bromide led to the almost immediate generation of a deep purple color. After several hours at room temperature, the solutions were carefully evaporated and distilled to give 2a, bp 115-117° (23 mm), and 2b, bp 68-70° (1.2 mm), respectively, in good yields (65-85%). A solution of 1 in methanol containing 1-2 drops of 60% perchloric acid likewise became highly colored after standing for 48 hr at 30°. The methoxy derivative 2c, bp 100-102° (23 mm), could subsequently be isolated in 45% yield.



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2a, X = Cl; b, X = Br; c, X = OCH_3

Evidence for the structural assignments includes their UV and NMR spectra (Table I). Similar variations in the ultraviolet maxima of permethylated cyclopentadienes have previously been noted.[2] These manifestations, as well as those clearly apparent in the nmr spectra, are very likely attributable to the preferred orientation of the ethylidene side-

Table I. Spectral Parameters for Compounds of Structure 2.

Compound	UV Maximum[a]	NMR Absorptions[b]	
		Methyl Groups	Proton
2a	264 mμ	2.24 (s, 3H), *ca* 2.08 (os, 6H), 1.97 (s, 3H), 1.33 (s, 3H), 1.23 (d, 3H, J = 6.5 Hz)	4.90 (q, 1H, J = 6.5 Hz)
2b	260 mμ	1.86 (s, 3H), *ca* 1.73 (os, 9H), 1.25 (d, 3H, J = 7 Hz), 1.12 (s, 3H)	4.10 (q, 1H, J = 7 Hz)
2c	252 mμ	*ca* 2.08 (os, 9H), 1.96 (s, 3H), 1.22 (s, 3H), 0.73 (d, 3H, J = 6.5 Hz)[c]	3.78 (q, 1H, J = 6.5 Hz)

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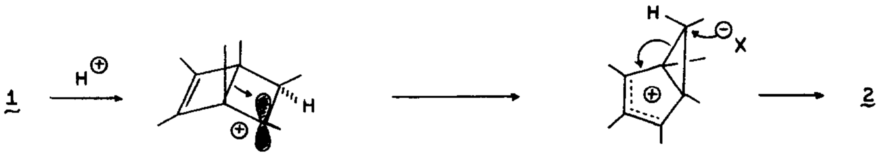
[a] Methanol solutions. [b] Spectra were obtained on dilute $CDCl_3$ solutions and values are in δ units; s = singlet, os = overlapping singlets, d = doublets, q = quartet. [c] Methoxyl absorption appears at 3.96 (s, 3H).

chain in each instance (in turn controlled by steric, dipole, and solvation effects), although full interpretation requires more experimental data. Further evidence was provided by the catalytic reduction of 2c to a tetrahydro derivative whose nmr spectrum[3] clearly establishes the fact that 2c contains four allylic methyl groups and a 1-(methoxy)ethyl side-chain.

To account for the striking, and perhaps unique, fact that these ionic transformations eventuate in *bonding of both moieties of the electrophilic reagent to the same carbon atom*, protonation of 1 from its *endo* surface[4] and subsequent or concomitant migration of the central bond in 3 is proposed. To bypass a fundamental energetic objection,[5] the central bond in 3 must become attached to the upper lobe of the vacant p orbital at C-2, this geometric



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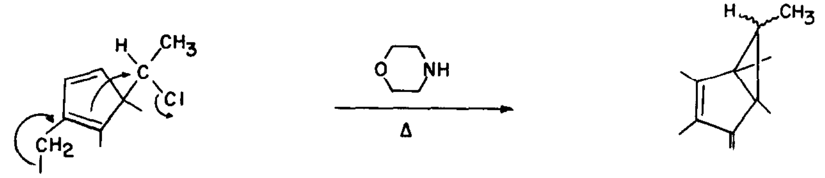
4

requirement providing access to the cis-fused bicyclo[3.1.0]cyclohexenyl carbonium ion 4 in which the cyclopropyl proton possesses the endo configuration.

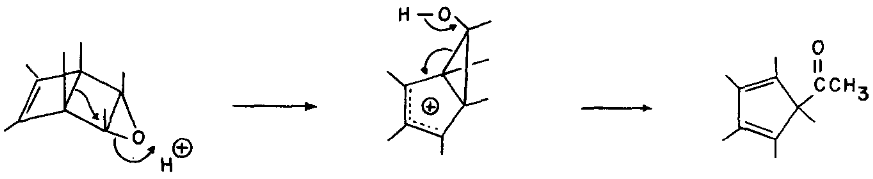
On being heated in excess morpholine, 2a afforded the diene 5, bp 84-86° (15 mm), $\lambda_{max}^{CH_3OH}$ 255 mμ (ε 10,600). Although a single isomer of 5 appears to have been isolated, its stereochemistry has not been established unequivocally.



2a

5

Oxidation of 1 with one molar equivalent of perbenzoic acid in benzene at 0° afforded the endo[4] 2,3-oxide 6, bp 68-70° (18 mm). Exposure of 6 to traces of acid resulted in facile rearrangement to 8, bp 95-96° (16 mm).[6] This result is consistent with a mechanism in which 6 is converted to the hydroxyl substituted bicyclo[3.1.0]hexenyl cation 7 which collapses to give ketone 8.



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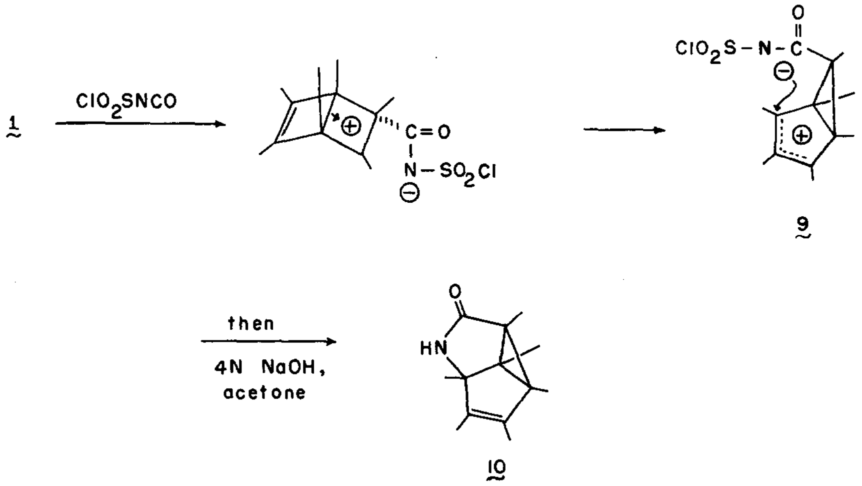
7

8

To test the assumption that cyclopropylcarbinyl cations such as 4 and 7 are intermediates in these rearrangements, 1 was treated with chlorosulfonyl isocyanate (CSI) in cold methylene chloride solution. CSI has already been shown to be an effective trap for the homotropylium cation formed upon its addition to cyclooctatetraene.[4] Direct hydrolysis of the resulting N-(chlorosulfonyl) lactam afforded 10, mp 168-170°, in 87% yield.[7] The formation of this tricyclic lactam (10) obviously provides strong evidence for the intervention of cations such as 4, 7, and 9 in electrophilic additions to 1. The driving force behind these interesting skeletal rearrangements is no doubt attributable to the strain of the system and the stability associated with the resulting cycloalkenyl cations.[8]



Acknowledgment. We wish to thank the National Institutes of Health and the Alfred P. Sloan Foundation for generous support of this work.

FOOTNOTES AND REFERENCES

(1) W. Schäfer and H. Hellmann, Angew. Chem. Intern. Ed. (Engl.), 6, 518 (1967).

(2) L. DeVries, J. Org. Chem., 25, 1838 (1960); see also S. McLean and P. Haynes, Tetrahedron, 21, 2313 (1965).

(3) $\delta^{CDCl_3}_{TMS}$ 3.38 (q, 1H, CH_3O-$\overset{|}{\underset{|}{C}}H$), 3.27 (s, 3H, $-OCH_3$), 0.98 (s, 3H, tertiary CH_3), and five doublets in the 0.73-1.18 region.

(4) Electronic and steric considerations agree with this assumption. Thus, because of the bent nature of 1, the point of highest electron density is to be found on its endo surface; furthermore, the presence of two methyl groups on the top surface of the hydrocarbon should effectively deter approach from that direction. Electronic factors appear to control the direction of electrophilic additions to cyclooctatetraene: L. A. Paquette and T. J. Barton, J. Am. Chem. Soc., 89, 5480 (1967), and reference 16 of this paper.

(5) The strained nature of the alternative type of transition state, i.e., bonding to the lower lobe, has been recognized in two previous situations: K. B. Wiberg and A. J. Ashe, Tetrahedron Letters, 1553 (1965); R. N. McDonald and E. C. Reinecke, J. Org. Chem., 32, 1878 (1967).

(6) H.-N. Junker, W. Schäfer, and H. Niedenbrück, Chem. Ber., 100, 2509 (1967).

(7) Proof for the structure of 10 and its conversion to an azasemibullvalene derivative is discussed in the accompanying communication.

(8) N. C. Deno, Progr. Phys. Org. Chem., 2, 129 (1964), and subsequent papers by Professor Deno; see also, D. W. Swatton and H. Hart, J. Am. Chem. Soc., 89, 5075 (1967).