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HYDRATION OF HEXAMETHYL (DEWAR BENZENE) OXIDE. STEREOCHEMICAL ASPECTS OF THE RESULTING REARRANGEMENT

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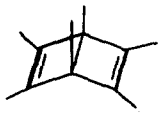
Since 1966 when hexamethyl (Dewar benzene) became readily available,[2] the chemistry of this constitutionally interesting hydrocarbon (1) has been quite intensively studied.[3] Despite the propensity of 1 for rearrangement, a consequence of its high strain energy[4] and exhaustive alkyl substitution, a significant number of its reactions do proceed without structural change. Oxidation with peracids is one of these and epoxide 2,[3a,5] recognized to be of exo stereochemistry,[6] is readily obtained. The aqueous acidic hydrolysis of 2



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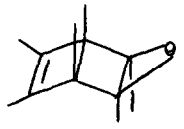

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has also been reported[3a,5] to occur with retention of structural integrity and formation of diol 3 (undefined stereochemistry). When CCl_4 solutions of this diol were treated with increasing amounts of $Eu(fod)_3$, the chemical shifts of the methyl groups were seen to increase linearly (Figure 1). Only three pairs of proton absorptions were visible in these spectra. Thus, the molecule was very likely symmetrical and trans structure 4 was considered improbable. exo, cis-Diol 5 could conceivably arise, however, because of double bond participation as in 6 or rapid capture of ion 7 from the exo direction.

Our more recent observation[3c] that exo triazoline 8 is rapidly hydrolyzed by 2 N hydrochloric acid in aqueous acetone to this same diol appeared incompatible with assignment 5. In this instance, both C-N bonds must undergo heterolytic fission with positioning of positive charge at ring carbon atoms on at least two occasions. The well established

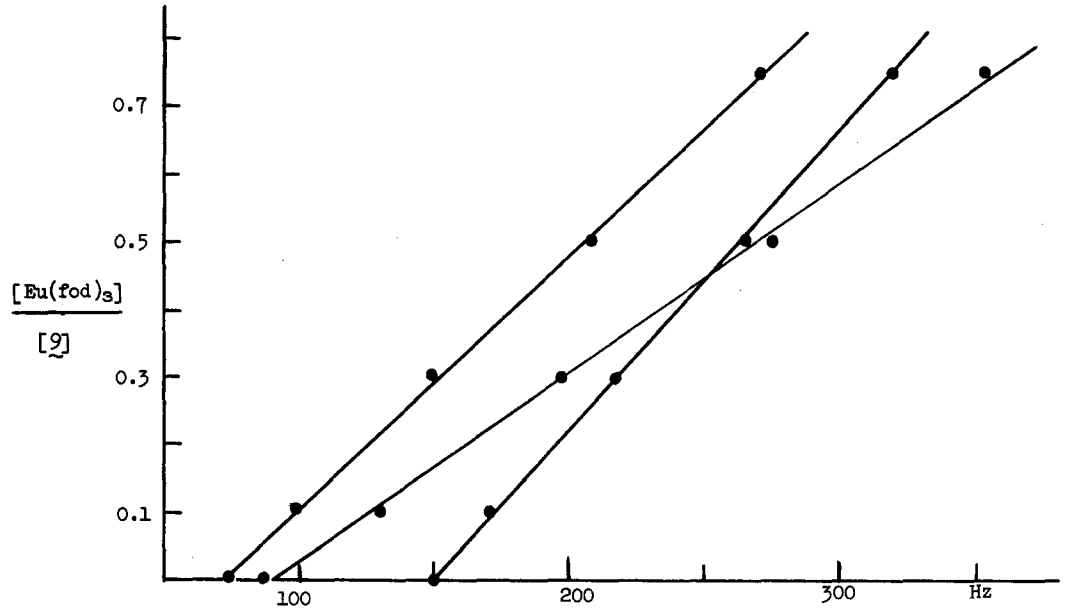
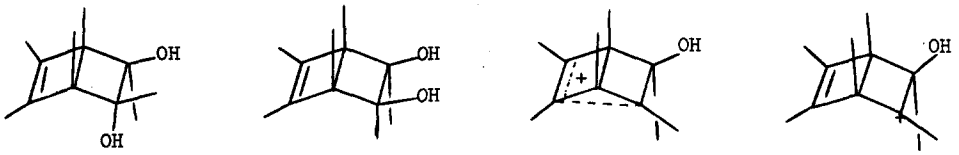


Figure 1. Field positions of the methyl resonances of the diol plotted as a function of $Eu(fod)_3$ concentration in Hz downfield from TMS (CCl_4 solution).

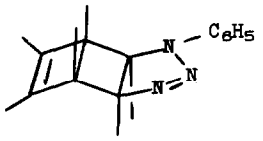


4 5 6 7

susceptibility of closely related carbonium ions for rearrangement to bicyclo[2.1.1]-hexenyl cations[7] suggested that the diol was in reality compound 9.

Three-dimensional X-ray crystal structure analysis showed the diol to belong to the orthorhombic crystal system with diffractometer measured cell constants of a = 11.65(1), b = 8.62(1), c = 12.42(1) Å. The systematic extinctions indicated space group P_{hma} or P_{hc_2a} and a calculated density indicated four molecules per unit cell. Of the 1182 unique reflections with theta less than 25° (Zr-filtered MoK_α radiation) only 465 were judged to be observed. The crystals rapidly turned yellow in the X-ray beam.

Normalized structure factors were computed and phases assigned by a symbolic



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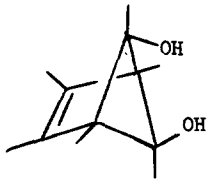

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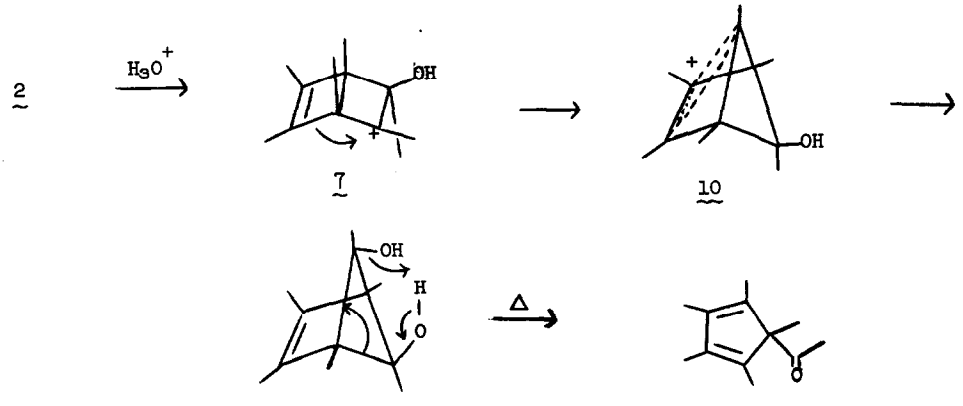
addition procedure assuming the centrosymmetry space group P_{hma}. A synthesis with the 135 largest E's clearly showed the molecular structure to be 9 (Figure 2). Full-matrix least-squares refinements converged to the present minimum of 12.7% for the observed reflections. No significant improvement was noted on lowering the symmetry to $P_{h_2,a}$. While the standard deviations are relatively high (0.02 Å and 1.5° for bond distances and angles, respectively), there exists no doubt that the oxygens are properly positioned based on (a) bond distances, (b) integrated electron density, (c) refinement with carbon and oxygen assignments switched, and (d) location of hydrogen atoms. All bond distances and angles agree well with generally accepted values.[a]

The formation of 9 from 2 is most simply rationalized in terms of the mechanistic scheme outlined below. In particular, the ultimate syn positioning of the second hydroxyl is seen to be the result of kinetically controlled solvent attack on bicyclo[2.1.1]hexenyl cation 10. The ready thermal dehydration of 9 to acetylpentamethylcyclopentadiene (11) at the melting point of the diol[3c] is now recognized to present little mechanistic novelty.



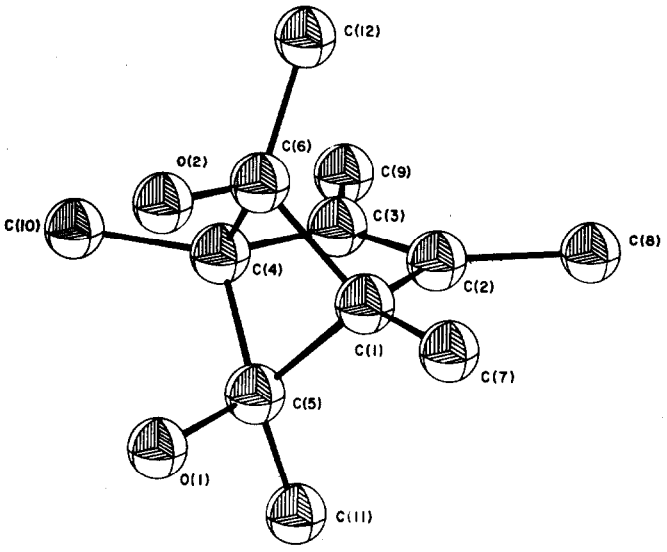


Figure 2. A structural view of 9 as determined by X-ray analysis.

FOOTNOTES AND REFERENCES

(1) Postdoctoral Fellow of the National Cancer Institute (CA-45,259) during 1971.

(2) W. Schäfer, Angew. Chem., 78, 716 (1966); Angew. Chem. Intern. Ed. Engl., 5, 669 (1966).

(3) For leading references, see: (a) W. Schäfer and H. Hellmann, Angew. Chem., 79, 566 (1967); Angew. Chem. Intern. Ed. Engl., 6, 518 (1967); (b). L.A. Paquette and G.R. Krow, J. Amer. Chem. Soc., 91, 6107 (1969); (c) L.A. Paquette, R.J. Haluska, M.R. Short, L.K. Read, and J. Clardy, ibid., 94, 529 (1972).

(4) J.F.M. Oth, Angew. Chem., 80, 633 (1968); Angew. Chem. Intern. Ed. Engl., 7, 646 (1968); Recl. Trav. Chim., 87, 1185 (1968).

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(6) L.A. Paquette, S.A. Lang, Jr., M.R. Short, B. Parkinson, and J. Clardy, accompanying paper.

(7) (a) L.A. Paquette, G.R. Krow, J.M. Bollinger, and G.A. Olah, J. Amer. Chem. Soc., 90, 7147 (1968); (b) H. Hogeveen and H.C. Volger, Rec. Trav. Chim., 87, 385 (1968).

(8) Full details of this analysis will appear elsewhere.