

A CONFIRMED ENDO ADDITION TO HEXAMETHYL(DEWARBENZENE).

HEXAMETHYL(DEWARBENZENE) DIOLS

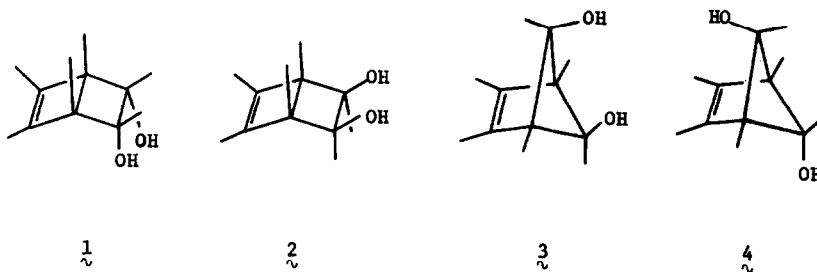
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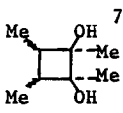
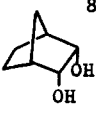
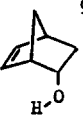
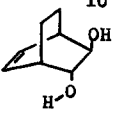
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Analysis of electronic, steric and torsional effects upon stereochemical preferences for electrophilic additions to hexamethyl(Dewarbenzene) suggest that under suitable conditions either exo or endo addition might occur.^{1,2} Heretofore, however, only exo stereochemistry has been confirmed for unrearranged addition products, and unfortunately, because of facile cationic isomerizations, rearranged products can be rationalized mechanistically from either initial exo or endo electrophilic attack.²⁻⁶

We here report an example of endo attack on hexamethyl(Dewarbenzene) by osmium tetroxide in a pyridine solution to afford after sodium bisulfite workup the crystalline diol 1, mp 97-98°. The structure of 1 follows from its nmr (CDCl₃), τ 8.48 (3), τ 8.82 (3), τ 9.12 (3), τ 8.46 (1), and ir (CCl₄, c = 1 mg/ml) 3618 cm⁻¹ (OH)_f, 3594 cm⁻¹ (OH)_{b π} , 3530 cm⁻¹ (OH)_b. On the basis of intramolecular hydrogen bonding to both oxygen and the π -system, the endo-cis stereochemistry of 1 is indicated and structures 2-4 are ruled out.



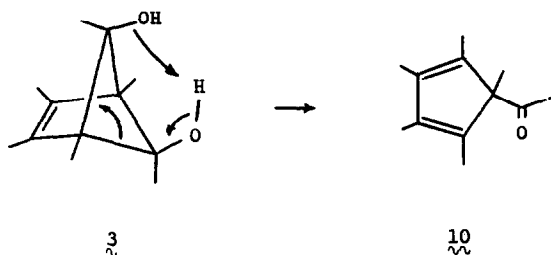
In Table I there is a tabulation of $\Delta\nu(\text{OH})$ for structurally rigid alcohols with properties comparable to 1. The increasing magnitude of $\Delta\nu$ in going from cis-cyclobutene diol to cis-cyclobutane diol to 1 to cis-bicyclo[2.2.1]heptane-2,3-diol is consistent with the stretched central bond (1.61 \AA^0) found in a similar disubstituted hexamethyl(Dewarbenzene) moiety.² The stretched central bond results in less spreading of the substituent groups than in a normal cyclobutane, but there is more spreading than in the bridged system 7. The strength

Table I.	Compound	$\nu(\text{OH})_f$	$\nu(\text{OH})_b$	$\Delta\nu$
	<u>1</u>	3618	3530	88
			3594	24
	<u>3</u>	3610	3474	136
	<u>cis</u> -1,2,3,4-tetramethylcyclobut-3-ene-1,2-diol ⁷	ξ 3601	3546	55
ξ		3623	3558	65
ζ		3633	3531	102
ξ		3622	3592	30
η		3627	3606	21

of the hydrogen bond to the π system in 1 is comparable in magnitude to that in the bicyclic alkenols 8 and 9.

A diol, mp 155-157°, whose nmr is consistent with 1-4, has been reported as 1 or 2,^{2,4,11} the cis-diols which would result from acid catalyzed reactions of hexamethyl bicyclo[2.2.0]-hexane precursors without rearrangement.

We now assign rearranged structure 3 to this diol (Table I) on the basis of a $\Delta\nu(\text{OH}) = 136\text{cm}^{-1}$. This value is too large for a hydrogen bond to a π -system,¹² which eliminates 4, and is too large a value for 2, for which molecular models indicate a hydrogen bond similar to that found for 1. Structure 3 is consistent with the facile formation of the bicyclo[2.1.1]-hexane system from hexamethyl(Dewarbenzene)⁶ in the presence of acid, with our inability to epoxidize or hydrogenate the double bond because of the methyl groups above and below the π system, and with the facile formation of 10 when 3 is raised to its melting point.^{6e}



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FOOTNOTES AND REFERENCES

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