

A NOVEL MERCURIC ACETATE OXIDATION OF HEXAMETHYL(DEWARBENZENE).

Grant R. Krow and James Reilly

Temple University, Department of Chemistry, Philadelphia, Penna. 19122

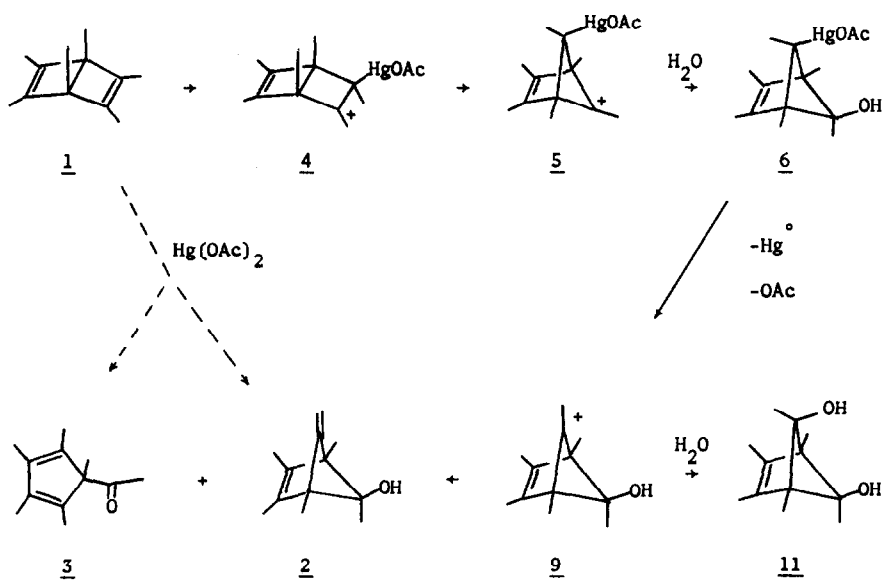
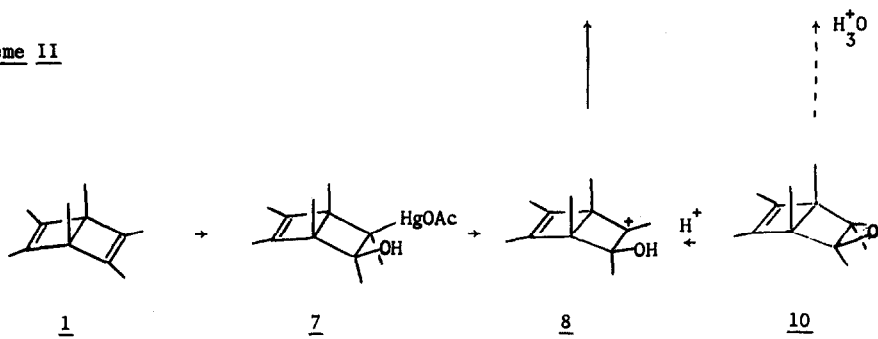
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Electrophilic additions to hexamethyl(Dewarbenzene) **1** have led to the isolation of a variety of unusual molecular structures resulting from facile cationic rearrangement of this highly strained hydrocarbon.¹ Although product studies tell us much about such rearrangements, we have yet to determine if the site of initial bonding to **1** is exo or endo for any but concerted additions, such as epoxidation,² carbene additions,^{3,4} and osmium tetroxide⁵ or phenyl azide¹ cycloadditions, which are free of rearrangements. Since mercuric acetate additions to norbornadiene^{6a} and norbornene^{6b} have been found to occur free of rearrangements, we oxymercured **1** hoping to obtain unrearranged product which would enable us to determine the stereochemistry of addition.

Addition of **1** (1.1 g) to an equimolar quantity of mercuric acetate in 40 ml of 50% aqueous tetrahydrofuran resulted in an immediate precipitate of elemental mercury. Overnight stirring at ambient temperature, filtration, and removal of solvent afforded an oily solid, shown by nmr analysis to be a 1:1 mixture of **2** and **3**. Washing of the solid with ether left a residue of alcohol **2**, mp 161-162°, ir (CCl₄) 3621 cm⁻¹, nmr (CDCl₃) δ7.8 (9) broadened, δ7.67 (6), δ5.25 (2), δ8.71 (1).

The ether soluble material contained some **2** and the known ketone **3**,² which was isolated by vpc (10% XF-1150 Chrom W, 85°, RT = 12.5 min at 150 ml/min). The stereochemistry of **2** is likely endo, as shown by the failure to observe intramolecular hydrogen bonding between hydroxyl and the π-system as expected for the exo isomer.⁷

Two variations of a mechanistic pathway to **2** and **3** are shown below. In Scheme I initial electrophilic attack on **1** by mercury(+) acetate forms cation **4**. For mechanistic simplicity we here assume attack on the exo face of **1**.⁸ Cation **4** can rearrange to **5**, and add water to

Scheme IScheme II

form oxymercurial ζ , with the overall sequence from λ to ζ also generating an equimolar quantity of acetic acid. Although oxymercurials are generally either stable to this mercuric acetate synthetic procedure or revert to olefin in the presence of acid,^{8,9} rearranged mercurial ζ behaves differently. Organomercurials can undergo acid catalyzed heterolysis of the carbon-mercury bond to generate carbenium ions.^{9,10} While heterolysis of organomercurial acetates is generally slow,¹¹ anchimeric assistance to demercuration of ζ by the neighboring π -bond, by relief of steric strain, and by the acetic acid generated in forming ζ , can facilitate formation of η . Cation η can then lose a proton from carbon or oxygen to form either ξ or ζ . In Scheme II, carbenium ion η is again formed from λ , but the timing is different. A *cis*-oxymercuration without rearrangement to give ζ may subsequently demercurate to ξ which rearranges to η .

We presently favor Scheme I since cation η , previously generated by acid catalyzed rearrangement of hexamethyl(Dewarbenzene) epoxide $\lambda\eta$, under conditions where solvation of the cation would be expected, formed exclusively diol $\lambda\lambda$.⁵ A poorly solvated transient cation η , such as would be generated via demercuration of ζ ^{11b} in Scheme I, can explain the formation of ξ and ζ rather than $\lambda\lambda$.

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Footnotes and References

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