Formation of α-Ketols in the Reduction of 1,3-Diketones under Clemmensen Conditions

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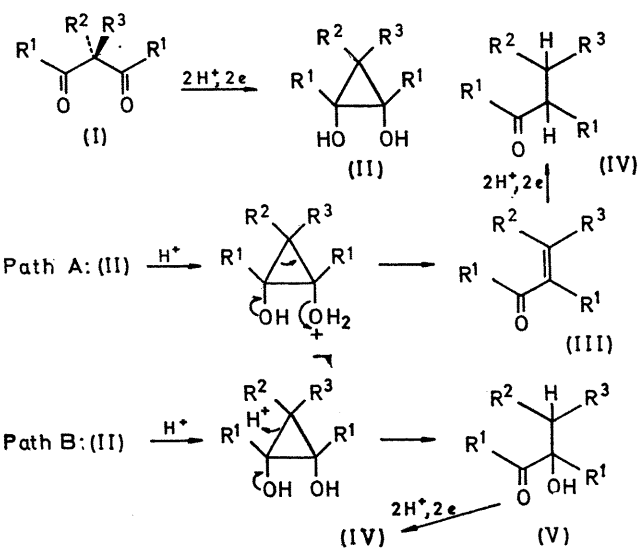
THE reduction of 1,3-diketones (I) under Clemmensen conditions yielding skeletally rearranged monoketones (IV) has for some time been believed to proceed by the sequence [path (A)] involving an $\alpha\beta$-unsaturated ketone intermediate (III).[1] Recently, another path [path (B)] has been suggested by which the acid-catalysed cleavage of the initially formed cyclopropanediol intermediate (II) leads not to an enone but to a ketol (V) as a potentially trappable intermediate which is directly reduced to (IV).[2]

We report a clear case where path (A) is blocked, by taking advantage of the incompatibility of structural requirements for an olefinic carbon atom also to be the bridgehead in the camphane system: the reduction proceeds indeed *via* path (B) to afford a ketol. Thus reduction of 6-oxocamphor[3] (VI) under Clemmensen conditions with amalgamated zinc and concentrated hydrochloric acid in the presence of tetrahydrofuran† results in the formation of an α-ketol (IX), m.p. 124–125°.

Evidence for structure (IX) is as follows: i.r. (CCl_4), 3500 (OH),[4] 1748 (C=O) cm.$^{-1}$; mass spectrum (70 ev), 168 (M^+), 153, 140, 135, 125, 111, 109, and 98, with no peak corresponding to loss of water from the molecular ion, *i.e.* 150, (indicating that the hydroxy-group is located at the bridgehead); n.m.r. ($CDCl_3$,Me_4Si), a doublet of relative area 3·0 at 0·70 p.p.m. (J 7·0 Hz.), a singlet (3) at 0·87 p.p.m., a singlet (3) at 1·16 p.p.m., and the remaining



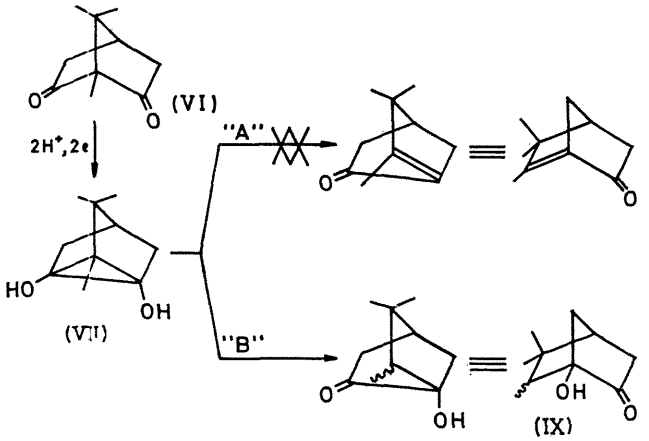
† In the presence of ethanol, (VIII) is formed in a significant amount.

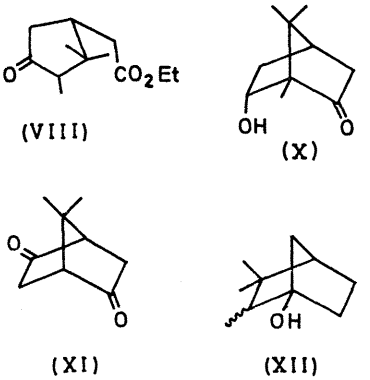
hydrogens scattered between 1 and 3 p.p.m. If the ring cleavage proceeds *via* edge-protonated tricyclenediol as in the case of cyclopropanols,[5] the 6-methyl will be *exo*.

There was no evidence for the formation of a compound of the type (IV) from reduction of the hydroxy-group in (IX), suggesting that an intermediate for (V) to proceed to (IV) is structurally prohibited in this case.

In a competitive reduction between 6-oxocamphor (VI) and 5-oxocamphor (XI) under Clemmensen conditions, (VI) was completely reduced to the α-ketol whereas (XI) remained unchanged, indicating that the formation of the tricyclenediol (VII) is an intramolecular pinacol reduction which, because of conjugative interaction of keto-groups, is easier than the reduction of a diketone in which there is much less, if any, interaction between keto-groups. The interaction of keto-groups in (VI) is consistent with the failure of (IX) to be further reduced to (XII). Further evidence for the intramolecular pinacol reduction is the failure to detect an unrearranged β-ketol (X) as a product.

It should be emphasized that while the present result confirms the path (B), it does not serve to discriminate between the two possibilities in non-bridgehead cases.





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[2] E. Wenkert and E. Kariv, *Chem. Comm.*, 1965, 570; K. M. Baker and B. R. Davis, *Chem. and Ind.*, 1966, 768.

[3] An authentic sample of this compound was prepared by a published method (K. Miyake, *Proc. Imp. Acad.* (*Tokyo*), 1935, **11**, 106. Its spectral properties (i.r. and n.m.r.) agree with the structure.

[4] This value is in good agreement with those obtained from α-ketols and therefore rules out the possibility of the product's being compound (X) (bonded OH, 3606s, free OH, 3620w cm.$^{-1}$): L. Joris and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1968, **90**, 4599.

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