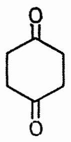
The Clemmensen Reduction of 1,4-Diketones

By D. R. CRUMP and B. R DAVIS*

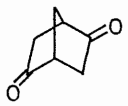
(*Department of Chemistry, The University, Auckland, New Zealand*)

Summary The Clemmensen reduction of some 1,4-diketones gives alcohols possessing unchanged carbon skeletons the necessary structural features for this reaction are discussed and a mechanism is suggested.

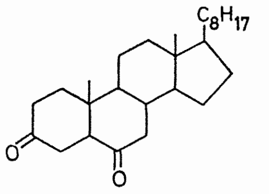
ALCOHOLS are not normally produced by the action of amalgamated zinc and concentrated hydrochloric acid on monoketones, yet the reduction of 1,4-diketones may produce alcohols as one of the many products[1,2] Our studies on a variety of structures lead us to the hypothesis that these alcohols are only produced when conformational mobility allows the carbonyl groups to approach one another Thus cyclohexane-1,4-dione (I), norbornane-2,5-dione (II), and cholestane-3,6-dione (III) give no cyclic alcohols, but hexane-2,5-dione (IV) gives hexan-2-ol, as well as *cis*- and *trans*-hex-4-en-2-ol Similarly, the diketones (V) and (VI) are also reduced to give alcohols The reduction of 1,4-diketones is rapid, being complete in 15—30 min in 6M-HCl (*cf* reduction times of several hours for similar monoketones).



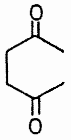
(I)



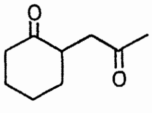
(II)



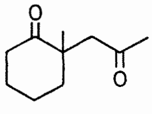
(III)



(IV)

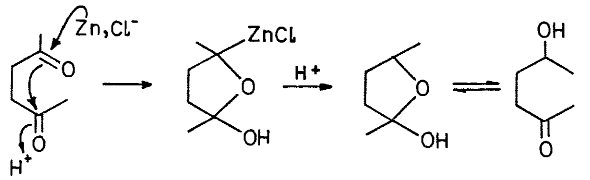


(V)



(VI)

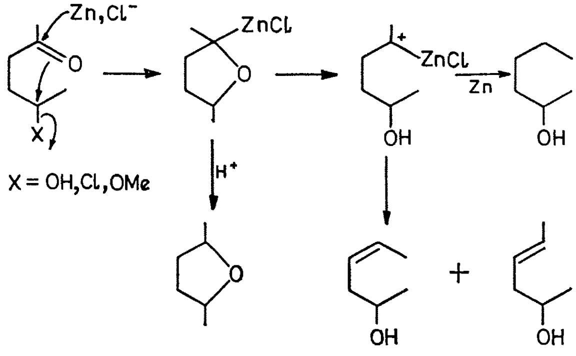
Participation of carbonyl oxygen in solvolytic reactions of halides and sulphonates has been the subject of a number of recent papers,[3] and in particular, it has been shown that a γ-keto-group greatly facilitates the removal of a halogen atom. Employing this principle and the general mechanism suggested for the Clemmensen reduction by Nakabayashi[4] the first steps in the reduction of (IV) are represented in Scheme 1.



SCHEME 1

The intermediacy of hexan-5-ol-2-one was indicated in a separate experiment when this ketol was rapidly reduced (*ca.* 5 min. in 6M-HCl) to a mixture of alcohols having the same percentage composition as that formed from hexane-2,5-dione on reduction. Two other γ- substituted ketones, 5-chloro- and 5-methoxy-hexan-2-one were similarly reduced to mixtures of the same three alcohols, although here the relative proportions were different. These subsequent steps are illustrated in Scheme 2.

Consistent with this Scheme is the fact that 3-methylhexan-5-ol-2-one is reduced to 4-methylhexan-2-ol.[5] The Scheme also provides a rationale for the formation of tetrahydrofurans in this reduction.



SCHEME 2

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[4] T. Nakabayashi, *J. Amer. Chem. Soc.*, 1960, **82**, 3900, 3906, 3909.
[5] J. G. St. C. Buchanan and B. R. Davis, unpublished work.