

A Cyclopropanol Intermediate in the Clemmensen Reduction

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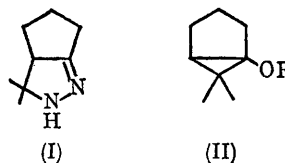
In a recent paper¹ we suggested that Clemmensen reduction of a cyclohex-2-enone to give the corresponding cyclohexanone and a 2-substituted cyclopentanone, proceeded, at least in part, through an intermediate cyclopropanol, in this case the previously unknown bicyclo[3,1,0]hexan-1-ol. We now present evidence to confirm this view.

Brief treatment (5 min., reflux) of 4-methylpent-3-en-2-one with amalgamated zinc and 6M-hydrochloric acid gave, in 76% yield, a mixture of monoketones separated by gas-liquid chromatography and identified by comparison of their i.r. and n.m.r. spectra with those of authentic samples, as 3,3-dimethylbutan-2-one and 4-methylpentan-2-one. The two ketones were formed in the ratio 72:28.

1,2,2-Trimethylcyclopropanol² was similarly treated with 6M-hydrochloric acid, the same two monoketones being produced in the same relative proportions (73:27) as found in the above reduction.

This work was then extended to the synthesis of a bicyclo[3,1,0]hexan-1-ol. The pyrazoline (I) obtained from 2-isopropylidencyclopentanone was treated with lead tetra-acetate to give the acetoxy-pyrazoline (81%) which was thermally decomposed at ca. 170° to give the cyclopropyl acetate (II, R = Ac) in 45% yield (based on crude acetoxy-pyrazoline), b.p. 76—78°/20 mm. Lithium aluminium hydride reduction then gave the unstable

alcohol (II, R = H) in 57% yield, b.p. 84—86°/19 mm. Treatment of this alcohol with hydrochloric acid, as before, gave a mixture of two ketones. These were identified as 2-isopropylcyclopentanone and 2,2-dimethylcyclohexanone by comparison of their i.r. and n.m.r. spectra, and g.l.c. retention volumes, with those of authentic samples. The product ratio was 25:75.



Hence, it is very likely that both the five- and six-membered ring ketones produced in the Clemmensen reduction of cyclohexenones arise from a cyclopropanol intermediate. Comparison of the ratio of the ketones formed in the reduction with the ratio from acidolysis of the cyclopropanol supports this view. Since, in the acid-catalysed cleavage of cyclopropanols, bond fission takes place predominantly towards the less alkylated group, it can be predicted that the ratio cyclopentanone:cyclohexanone should increase in the order 2-methylcyclohex-2-enone < cyclohex-2-enone = 5,5-dimethylcyclohex-2-enone < 3-methylcyclohex-2-enone. Yields of cycloalkanones

obtained from the Clemmensen reduction of these enones did in fact follow this order.

Hence, taken together, our findings provide strong support for the hypothesis that Clemmensen reduction of both cyclic and acyclic $\alpha\beta$ -unsaturated

ketones, to yield both rearranged and unrearranged monoketones, proceeds through the intermediacy of a cyclopropanol.

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¹ B. R. Davis and P. D. Woodgate, *J. Chem. Soc.*, 1965, 5943.

² J. P. Freeman, *J. Org. Chem.*, 1964, **29**, 1379.