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*The Clemmensen Reduction  
of 1,4-Diketones*

**A Thesis  
presented to the University of Auckland  
for the Degree of**

**Doctor of Philosophy**

**by**

**Douglas R. Crump**

**University of Auckland  
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	(i)
ABSTRACT	(ii)
INTRODUCTION	1
Mechanism of the Clemmensen Reduction	1
Clemmensen Reduction of Difunctional Ketones	12
DISCUSSION	23
Clemmensen Reduction of Hexane-2,5-dione	23
Fragmentation Reactions	44
Synthesis of 1,4-Diketones	55
Clemmensen Reduction of 1,5-Diketones	75
Clemmensen Reduction of Formyl-Ketones	77
EXPERIMENTAL	93
REFERENCES	213
DIAGRAMS	228
ACKNOWLEDGEMENTS	235

ABSTRACT

The mechanisms proposed for the Clemmensen reduction of simple ketones are critically examined, and the Clemmensen reduction of difunctional ketones is reviewed.

The Clemmensen reduction of a number of 1,4-diketones has shown<sup>44</sup> that the products formed depend on the conformation of the carbonyl groups:

- (a) syn or ~~anti~~-periplanar alignment of the carbonyl groups with the C<sub>2</sub>-C<sub>3</sub> bond favours fragmentation e.g. cyclohexane-1,4-dione leads to hexane-2,5-dione and hex-5- $\alpha$ F.-2-one,
- (b) with 1,2-diacetyl systems formation of alcohols and furans predominates e.g. hexane-2,5-dione gives hexan-2-ol, hex-4-en-2-ol, and 2,5-dimethyltetrahydrofuran,
- (c) when both carbonyl groups are in a large ring (> C<sub>7</sub>) formation of cyclobutanediols is possible e.g. 2,6,6-trimethylcycloheptane-1,4-dione is reduced to 2,3,6-trimethylbicyclo[3,2,0]-1 $\beta$ ,5 $\beta$ -diol,
- (d) when none of these conditions is satisfied normal reduction occurs e.g. cholestane-3,6-dione yields cholestan-6-one.

A mechanism is proposed for the formation of hexan-

2-ol, hex-4-en-2-ol, and 2,5-dimethyltetrahydrofuran from the Clemmensen reduction of hexane-2,5-dione. The reduction of a number of similarly constructed 1,4-diketones and  $\gamma$ -functionalised ketones is also examined.

The synthetic viability of the fragmentation reaction, previously observed to occur under Clemmensen conditions, is investigated and it is shown that this is of limited value for the preparation of large rings. The stereochemical requirements for this reaction are verified and the mechanism is further studied.

A review of the synthesis of 1,4-diketones is given and the preparation of the compounds used in this study is discussed in detail.

The Clemmensen reduction of two 1,5-diketones is examined.

The formation of cyclopropanediols and cyclopropanols from the Clemmensen reduction of 1,3-diketones and  $\alpha\beta$ -unsaturated ketones is discussed. The Clemmensen reduction of some monocyclic formyl-ketones and  $\beta$ -hydroxy-ketones is studied. The reduction of hexane-2,5-dione and pentane-2,4-dione with different metals is investigated.