

$\text{RuCl}_2(\text{PPh}_3)_3$  - CATALYZED TRANSFER HYDROGENATION  
OF CYCLOHEXANE - 1,3 - DIONES

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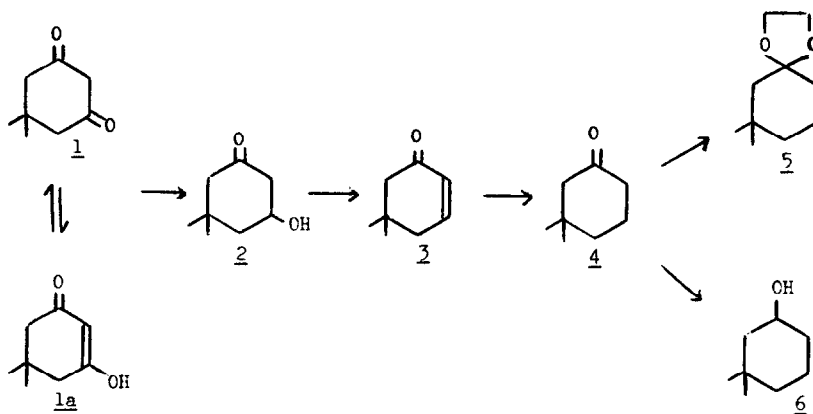
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Dichlorotris(triphenylphosphine)ruthenium has been shown to catalyze hydrogen transfer from certain carbinols, aldehydes and hydroaromatics to olefinic hydrogen acceptors<sup>1-3</sup>. We now wish to report the selective transfer hydrogenation of one carbonyl group in cyclohexane-1,3-diones using ethylene glycol as hydrogen donor<sup>4</sup> and  $\text{RuCl}_2(\text{PPh}_3)_3$  as catalyst.

When, e.g., a solution of 2.1 g (15 mmoles) 5,5-dimethylcyclohexane-1,3-dione and 30 mg  $\text{RuCl}_2(\text{PPh}_3)_3$  ( $3 \times 10^{-2}$  mmole) in 40 ml ethylene glycol was refluxed for 4 hr<sup>5</sup>, the benzene extract of the reaction mixture yielded (GLC) 42% 3,3-dimethylcyclohexanol, 30% 3,3-dimethylcyclohexanone ethylene ketal and 4% of the corresponding free ketone.

Similar results were obtained with 5-phenyl-, and 5-tert-butylcyclohexane-1,3-dione<sup>6</sup> and with the unsubstituted diketone (Table I).

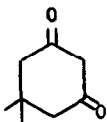
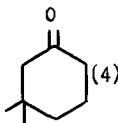
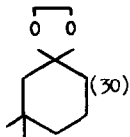
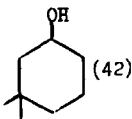
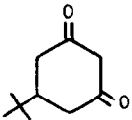
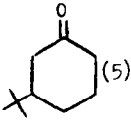
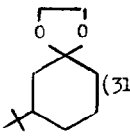
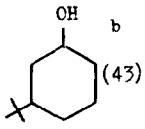
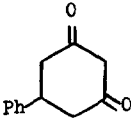
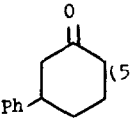
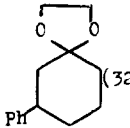
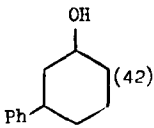
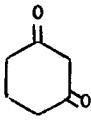
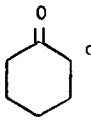
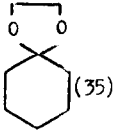
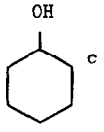
We propose that the starting diketone (e.g. 1) is converted, either directly or via the enol



form 1a, to the hydroxycyclohexanone 2. This compound is dehydrated under our experimental conditions, and the  $\alpha,\beta$ -unsaturated ketone so formed is selectively hydrogenated to the saturated ketone 4.  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyzes then both the formation of ketal 5<sup>7</sup> and the partial reduction to the cyclohexanol 6.

Table 1

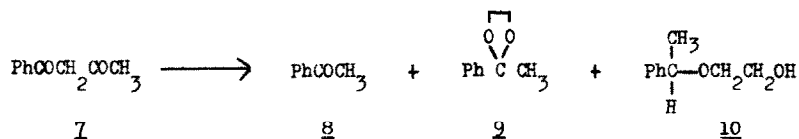
Transfer Hydrogenation of Cyclohexane-1,3-diones by  $\text{RuCl}_2(\text{PPh}_3)_3$   
(15 mmole diketone,  $3 \times 10^{-2}$  mmole catalyst, 40 ml ethylene glycol,  
4 hr of reflux).

Starting diketone	Products (yield, %) <sup>a</sup>		
			
			
			
			

(a) The products were isolated by preparative glc and identified by IR, NMR and mass spectrometric measurements. (b) As a cis and trans mixture. (c) The yield was variable and somewhat lower than in the preceding experiments due to loss of some volatile material during the catalysis.

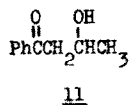
In order to confirm the proposed mechanism cyclohex-2-enone was submitted to the same reduction procedure. Three products were obtained, namely 6% cyclohexanone, 20% cyclohexanol and 38% cyclohexanone ethylene ketal. This proves the intermediate transformation of the diketones to the corresponding cyclohex-2-enones.

an acyclic 1,3-diketone, namely benzoylacetone (7) was also submitted to transfer hydrogenation at the same conditions described above. Three products were obtained: 55% acetophenone (8), 6% acetophenone ethylene ketal (9) and 20% ethylene glycol mono-(1-phenyl)-ethyl ether (10).



The first two products 8 and 9 were identified by comparison with authentic samples. The hydroxy ether 10 was identified by its NMR ( $\text{CCl}_4$ ): 7.18/bs, 5H (phenyl); 4.36/q ( $J = 7$ ) 1H ( $\alpha$ -hydroxy); 3.46/bm, 4H ( $-\text{CH}_2-\text{CH}_2-$ ); 2.10/s, 1H (OH—exchanges with  $\text{D}_2\text{O}$ ); 1.38/d ( $J = 7$ ) 3H ( $\text{CH}_3$ ); and MS,  $m/e$  166 ( $\text{M}^+$  10%); 151 (27%) 121 27% and 105 (100%).

The formation of 8, 9 and 10 can be rationalized by the following mechanism. Benzoyl acetone is preferably reduced to the hydroxyketone 11 which undergoes a fast retro-aldol reaction to yield 8 and acetaldehyde.



The acetophenone (8) formed is transformed, to some extent, into the ketal 9 and, to some extent, is reduced to 1-phenylethanol which condenses with ethylene glycol to yield 10.

These results indicate that some ketones, particularly cyclohexanones undergo transfer hydrogenation to an equilibrium mixture of the ketones and the corresponding alcohols. The conditions for such equilibrium are now under investigation.

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REFERENCES AND NOTES

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4. The advantage in using ethylene glycol as hydrogen donor in a  $\text{RuCl}_2(\text{PPh}_3)_3$ -catalyzed transfer hydrogenation reaction has recently been demonstrated. Y. Sasson, M. Cohen and J. Blum, Synthesis, in press.
5. In order to avoid undesired condensation reactions during the process, it is advisable to use an air condenser that permit the escape of glycolaldehyde as soon as it is formed.
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7. Cf., The metal-catalyzed formation of acetals, W. Voelter and C. Djerassi, Chem. Ber., 101, 1154 (1968).
8. The NMR spectrum of the ethylene-linkage in ketal 9 is an example of an AA'BB' spin system, due to two pairs of diastereotopic protons, with at least 14 lines separated.