

Reactions of Cycloalkanones in the Presence of Platinum-metal Catalysts and Hydrogen

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DURING a study on the stereochemistry of hydrogenation of Δ^4 -3-oxo-steroids with palladium catalysts, it was found that in ethanol solutions the resulting saturated ketones are liable to undergo further hydrogenation to give 3-ethoxy-compounds, along with small amounts of saturated alcohols.¹ Studies on this reaction have been made with cholestanones and cyclohexanone derivatives, using palladium as well as other platinum metals as catalysts. The hydrogenation was carried out at room temperature and at atmospheric pressure of hydrogen. All products were analysed by gas chromatography.

The hydrogenation of 5 α -cholestan-3-one in methanol with pre-reduced palladium hydroxide catalyst¹ gave 3 β -methoxy-5 α -cholestane (91%), 3 α -methoxy-5 α -cholestane (7%), and a small amount of 5 α - and 5 β -cholestane. The products from 5 β -cholestan-3-one under the same condition were 3 β -methoxy-5 β -cholestane (92%), 3 α -methoxy-5 β -cholestane (4%), 5 β -cholestan-3-ol (4%), and a small amount of hydrocarbons. The hydrogenations in ethanol gave similar results, although in this solvent the yields of ethoxy-compounds decreased with increase in the yields of alcohols.

The hydrogenation of cyclohexanone in ethanol with pre-reduced palladium hydroxide afforded 96% of ethoxycyclohexane and 4% of cyclohexanol. The product obtained in methanol was of similar composition, but the rate of hydrogenation was slower than in ethanol.

This reaction was investigated further with

4-methylcyclohexanone in ethanol solution, using pre-reduced palladium, ruthenium, and rhodium hydroxides,² and pre-reduced Adams platinum oxide³ as catalysts. The catalysts were washed with water and then with ethanol before use to remove alkaline substances remaining in them. The reaction products are listed in the Table. The hydrogenation with palladium catalyst yielded 1-ethoxy-4-methylcyclohexane as the predominant product, the most part of which was the *cis*-isomer. With platinum catalyst, the ethoxy-compound was also formed to some extent, but in this case the main products were 4-methylcyclohexanol and methylcyclohexane. The hydrogenation with rhodium catalyst was very slow and gave mainly 4-methylcyclohexanol of a high *cis/trans* ratio, together with a small amount of ethoxymethylcyclohexane. The hydrogenation over ruthenium catalyst led to exclusive formation of 4-methylcyclohexanol.

The analysis of the products during the reaction by gas chromatography shows that hydrogenations with washed palladium and platinum catalysts are accompanied by a rapid formation of 4-methylcyclohexanone diethyl ketal and a small amount of another compound, the retention time of which is the same with that of 1-ethoxy-4-methylcyclohexene. The ketal was also formed over rhodium and ruthenium catalysts, but at somewhat slower rates. It is noteworthy that, while the ketal formation occurs rather rapidly even with unwashed palladium catalyst, this is not the case with the other catalysts.

TABLE

Reaction products of 4-methylcyclohexanone in ethanol in the presence of platinum-metal catalysts and hydrogen^a

Catalyst	% Hydro- genation	Composition of reaction mixture ^b (mol. %)						Ketal	Ketone
		<i>cis</i> -(I)	<i>trans</i> -(I)	<i>cis</i> -(II)	<i>trans</i> -(II)	(III)	(IV)		
Palladium	100	86.9	9.7	2.3	1.1	0	0	0	0
Platinum	100	9.2	3.9	40.2	34.5	12.2	0	0	0
Rhodium	64.5	4.0	0.8	48.9	9.9	0.9	6.8	12.3	16.4
Ruthenium	100	0	0	69.0	31.0	0	0	0	0

^a 4-Methylcyclohexanone (0.2 ml.) was hydrogenated using 40 mg. of hydroxide (Pd, Rh, Ru) or oxide (Pt) catalysts in 10 ml. of ethanol at 25° and atmospheric pressure of hydrogen. The catalysts were pre-reduced in water, washed with water and then with ethanol before use.

^b (I): 1-ethoxy-4-methylcyclohexane; (II): 4-methylcyclohexanol; (III): methylcyclohexane; (IV): the compound which has the same retention time as 1-ethoxy-4-methylcyclohexene in the analysis by gas chromatography.

Presence of adsorbed hydrogen seems to be required for the ketal formation, since the reaction was greatly depressed under the atmosphere of argon. It is suggested that the adsorbed hydrogen

plays an important role in this reaction probably in an ionised state which depends on the nature of catalyst metals.⁴

(Received, March 10th, 1967; Com. 232.)

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