Hydrogenolysis and Hydrogenation of Some 2, 3-Unsaturated Alcohols with Platinum Oxide and with Platinized Raney Nickel

By Shigeo Nishimura and Kazuko Mori

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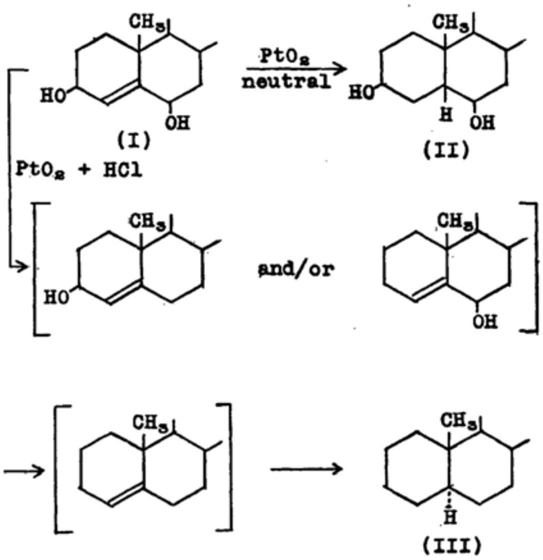
The hydrogenation of cholest-4-ene-3β, 6β-diol (I) in neutral ethanolic solution with platinum oxide as a catalyst gives 5β-cholestane-3β,6β-diol (II)[1]. The present authors carried out the same reaction in the presence of a trace of hydrochloric acid, when a little less than three moles of hydrogen were absorbed and 5α-cholestane (III) was obtained as the main product[2] (Table I). Shoppee et al.[3] obtained similar results in the hydrogenation of cholest-4-en-3-ols and related compounds, but they gave no account on the course of the hydrogenation.

Since it has been found that neither 5α-cholestane-3β, 6β-diol nor 5β-cholestane-3β, 6β-diol can be hydrogenolyzed with platinum oxide and hydrochloric acid, it can be assumed that the cholestenediol (I) underwent for the most part the hydrogenolysis before the saturation of the double bond, giving 5α-cholestane as the main product as illustrated below:



The above assumption is further supported by the fact that the product obtained by an incomplete hydrogenation of the cholestenediol (I) gave coloration with tetranitromethane in chloroform, while the cholestenediol (I) is entirely indifferent to the reagent.

The formation of 5β-cholestane from 3α-acetoxycholest-4-ene[3] can not be explained in a similar way, because, if cholest-4-ene were an intermediate product, then 5α-cholestane should be the main product as in the hydrogenation of the cholestenediol (I).

Similar results have been obtained in the hydrogenation of other 2, 3-unsaturated alcohols and phenol, as summarized in Table I.

In the presence of platinum oxide and hydrochloric acid the substances absorbed more hydrogen than is necessary to transform them into the corresponding saturated alcohols. Since none of 3-phenyl-1-propanol, tetrahydrofurfuryl alcohol and

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[1] V. Prelog and E. Tagmann, *Helv. Chim. Acta*, **27**, 1880 (1944).

[2] In ether-acetic acid solution, two moles of hydrogen are absorbed by the diacetate of the diol, and 5α-cholestane-3β,6β-diol, 5α-cholestan-3β-ol and 5α-cholestane are obtained: O. Rosenheim and W. W. Starling, *J. Chem. Soc.*, **1937**, 383.

[3] C. W. Shoppee, B. D. Agashe and G. H. R. Summers, ibid., **1957**, 3107.

TABLE I
MOLES OF HYDROGEN ABSORBED IN 95% ETHANOL AT THE ORDINARY TEMPERATURE AND PRESSURE

Compound	Catalyst		
	PtO_2	PtO_2 +HCl	Platinized Raney Ni[5]
Cholest-4-ene-3β, 6β-diol	1.0	2.7	1.1
Cinnamyl alcohol	1.0	1.5	0.98
Furfuryl alcohol[4]		3.1	2.1
Phenol		3.4	3.0

cyclohexanol could be hydrogenolyzed under the same conditions, it is concluded that the hydrogenolysis took place prior to the saturation of the double bond. On the other hand, in neutral ethanolic solution cinnamyl alcohol absorbed only 1 mole of hydrogen in the presence of either platinum oxide or platinized Raney nickel prepared in alkaline solution[5], while furfuryl alcohol gave a quantitative yield of tetrahydrofurfuryl alcohol with the latter catalyst.

It has been reported that cinnamyl alcohol gives about equal moles of 3-phenyl-1-propanol and propylbenzene with palladium-charcoal and hydrogen[6]. It is very probable that the catalyst contained a trace of hydrochloric acid.

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Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Tokyo

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[4] Furfuryl alcohol absorbs about 2.5 moles of hydrogen in the hydrogenation with platinum oxide either in the presence or in the absence of ferrous chloride or sulfate giving tetrahydrofurfuryl alcohol along with other products: W. E. Kaufmann and R. Adams, *J. Am. Chem. Soc.*, **45**, 3029 (1923); J. S. Pierce and C. Parks, ibid., **51**, 3384 (1929).

[5] S. Nishimura, This Bulletin **32**, 61, (1959).

[6] R. Baltzly and J. S. Buck, *J. Am. Chem. Soc.*, **65**, 1984 (1943). Cf. W. H. Hartung and R. Simonoff, "Org. Reactions", Vol. VII, p. 267, John Wiley & Sons (1953).