Hydrogenation and Hydrogenolysis. IV[1]. *Catalytic Reductions of Cinnamyl Alcohols and 3-Phenylpropargyl Alcohol**

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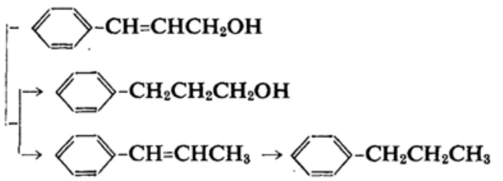
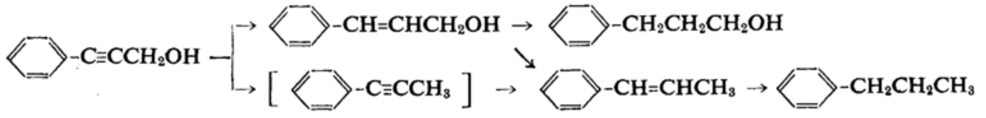
Cinnamyl alcohol may be catalytically reduced either to 3-phenyl-1-propanol, absorbing 1 mole of hydrogen, or to propylbenzene through propenylbenzene, absorbing 2 moles of hydrogen, as far as the hydrogenation is concerned with the side chain:



The reduction with nickel[2,3], cobalt[2] and copper[4] catalysts of Raney type gives phenylpropanol exclusively. Straus and Grindel[5] reduced cinnamyl alcohol with a palladium catalyst prepared by reducing palladium chloride with hydrogen in acetone, and obtained a mixture of propylbenzene (18%) and phenylpropanol (55%) with the absorption 1.38 moles of hydrogen. Baltzly and Buck[6] obtained about equal moles of the two compounds with the use of palladized charcoal in ethanol. Waser[7] obtained cyclohexylpropanol quantitatively by the reduction with a platinum black without using any solvent. Tuley and Adams[8] hydrogenated cinnamyl alcohol to phenylpropanol quantitatively in ethanol in the presence of platinum oxide and a small amount of ferrous chloride.

Different results of previous works on the hydrogenation of cinnamyl alcohol seem to be closely related to solvents and to metals and the methods of preparation of the catalysts. As reported previously[9,10], with platinum oxide as the catalyst, the hydrogenolysis of the C–O linkage with a bouble bond in β,γ- or α,β-position is much more favored than the hydrogenation of the double bond in acidic media. On the other hand, the double bond can be hydrogenated with little hydrogenolysis or none under neutral or slightly acidic conditions. In the present investigation, the influence of solvents on the hydrogenation and hydrogenolysis of cinnamyl alcohol was re-examined in detail with platinum, palladium, rhodium and rhodium-platinum catalysts.

3-Phenylpropargyl alcohol may be catalytically reduced either to 3-phenyl-1-propanol through *cis*-cinnamyl alcohol, absorbing 2 moles of hydrogen, or to propylbenzene, through *cis*-cinnamyl alcohol or through propynylbenzene, absorbing 3 moles of hydrogen:



In order to know whether the hydrogenolysis would occur or not before the reduction of the triple bond to the double bond, the catalytic reduction of 3-phenylpropargyl alcohol and of the intermediate *cis*-cinnamyl alcohol was investigated with Adams platinum oxide as a catalyst.

Experimental

Substrates.—*Cinnamyl Alcohol* (*trans*). –A commercial preparation was treated with aluminum ethoxide and absolute ethanol followed by hydrolysis with sodium hydroxide solution and extraction with ether[11], and then fractionally distilled twice under reduced pressure. B. p. 139.5~140.5°C/16 mmHg; n_D^{21} 1.5820.

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[1] Part III of this series: S. Nishimura, This Bulletin, 33, 566 (1960).

* Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

[2] B. V. Aller, *J. Appl. Chem.*, **8**, 492 (1958).

[3] Cinnamyl alcohol absorbed 0.98 mole of hydrogen in ethanol under ordinary conditions with T-4 Raney nickel (S. Nishimura, This Bulletin, 32, 61 (1959)).

[4] J. Jadot and R. Braine, *Bull. soc. roy. sci. Liége*, **25**, 62 (1956); *Chem. Abstr.*, **50**, 16651h (1956).

[5] F. Straus and H. Grindel, *Ann.*, **439**, 276 (1924).

[6] R. Baltzly and J. S. Buck, *J. Am. Chem. Soc.*, **65**, 1984 (1943).

[7] E. Waser, *Helv. Chim. Acta*, **8**, 117 (1925).

[8] W. F. Tuley and R. Adams, *J. Am. Chem. Soc.*, **47**, 3061 (1925).

[9] S. Nishimura and K. Mori, This Bulletin, **32**, 103 (1959). Also cf. C. W. Shoppee et al., *J. Chem. Soc.*, **1957**, 3107.

[10] S. Nishimura, This Bulletin, **32**, 1155 (1959).

TABLE I. MOLES OF HYDROGEN ABSORBED BY CINNAMYL ALCOHOL AT ORDINARY TEMPERATURE AND PRESSURE[a]

Catalyst*	Solvent			
	EtOH, 20 cc.	AcOH, 20 cc.	EtOH, 20 cc. + 3N HCl, 0.1 cc.	AcOH, 20 cc. + 3N HCl, 0.1 cc.
Pt oxide	1.03	1.31	1.60	1.79
Pd oxide	1.02	1.10	1.21	1.63
Rh-Pt (1 : 1) oxide		1.10		1.73**
Rh-Pt (2 : 1) oxide		1.07		1.71**
Rh-Pt (3 : 1) oxide	0.94	1.04	1.25	1.66**
Pd-on-carbon (I)	0.99		1.22	
Pd-on-carbon (II)	1.10	1.07	1.23	1.57
Rh-on-carbon (II)	1.24	1.14	1.33	1.45

a) 1.342 g. (0.01 mol.) of cinnamyl alcohol was hydrogenated with 50 mg. of the oxide or 600 mg. of the supported catalysts each time.

* For the notations attached to the catalysts, see the experimental part.

** These are approximate values, because the further hydrogenation of the benzene nucleus made obscure the completion of the reduction of the side chain.

Cinnamyl Acetate (*trans*).—Cinnamyl alcohol was refluxed with acetic anhydride and the product was fractionated twice under reduced pressure. B. p. 140∼141°C/16 mmHg ; n_D^{21} 1.5439.

3-Phenylpropargyl Alcohol.—This compound was prepared by passing mixed nitrogen and formaldehyde gases into an ethereal solution of phenylethynylmagnesium bromide prepared from phenylacetylene and ethylmagnesium bromide[12]. The product was distilled twice under reduced pressure. B. p. 150°C/30 mmHg ; n_D^{20} 1.5845.

cis-Cinnamyl Alcohol.—3-Phenylpropargyl alcohol was partially hydrogenated in ethyl acetate with 5% palladium-on-barium sulfate[13] poisoned with a few drops of quinoline. The rate of the hydrogenation became markedly slow after the absorption of 0.97 mole of hydrogen. The product was distilled twice under reduced pressure. B. p. 125°C/14 mmHg (lit.[13] 125.5°C/13 mmHg); n_D^{16} 1.5745 (lit.[13] n_D^{14} 1.573). It was confirmed by the infrared adsorption that the alcohol thus prepared contained, if any, less than 10% of its trans isomer and less than 3% of 3-phenylpropargyl alcohol*.

Catalysts. — Platinum oxide was prepared by fusion of ammonium chloroplatinate with sodium nitrate according to the method of Bruce[14].

Palladous oxide was prepared by the fusion of palladium chloride with sodium nitrate according to the method of Shriner and Adams[15].

Rhodium-platinum oxide catalysts were prepared by fusion of the mixtures of rhodium chloride and chloroplatinic acid or ammonium chloroplatinate with sodium nitrate as reported previously[1]. The figures in parentheses in Table I indicate the ratios of rhodium to platinum by the weights of the metals.

Palladium-on-carbon (I) (5% Pd) was prepared by reducing a palladium chloride solution with aqueous formaldehyde and sodium hydroxide[16].

Palladium-on-carbon (II) and rhodium-on-carbon (II) (5% Pd or Rh) were prepared by reducing palladium and rhodium chloride solutions with hydrogen with the addition of sodium acetate[17].

Solvents.—*Acetic Acid*. — Glacial acetic acid of Wakō Pure Chemical Industries G. R. grade was used without further purification.

Ethanol.—Commercial 95% ethanol was used after distillation.

Hydrogenation.—Hydrogenation was carried out at room temperature (20∼25°C) and atmospheric pressure. After the catalyst was shaken with hydrogen in 15 cc. of the solvent until no more hydrogen was absorbed, the substance, dissolved in 5 cc. of the solvent, was added. The mixture was shaken with hydrogen at about 350∼400 oscillations per minute. In using rhodium-platinum oxide catalysts, hydrochloric acid was added after the oxide was reduced to the metal, since the presence of hydrochloric acid greatly retarded the reduction of the oxide.

Results and Discussion

Catalytic Reduction of Cinnamyl Alcohol (trans).—The effects of solvents on the hydrogenation of cinnamyl alcohol are summarized in Table I in the moles of hydrogen absorbed per mole of cinnamyl alcohol. As expected from previous results, little hydrogenolysis or none occurred in neutral ethanolic solution[18]

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[11] H. Meerwein and R. Schmidt, *Ann.*, **444**, 221 (1925).

[12] H. H. Guest, *J. Am. Chem. Soc.*, **47**, 860 (1925).

[13] Cf. M. Bourguel, *Bull. soc. chim. France*, [4], **45**, 1083 (1929).

* The authors wish to thank Dr. H. Iwamura of this laboratory for his kind help in the measurement of infrared spectra.

[14] W. F. Bruce, *J. Am. Chem. Soc.*, **58**, 687 (1936); R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses", Col. Vol. 1, 2nd Ed., John Wiley & Sons, Inc., New York (1941), p. 463.

[15] R. L. Shriner and R. Adams, *J. Am. Chem. Soc.*, **46**, 1683 (1924).

[16] R. Mozingo, "Organic Syntheses", Col. Vol. 3, John Wiley & Sons, Inc., New York (1955), p. 685 (Method B).

[17] Method D in Ref. 16.

[18] The hydrogen uptake less than 1 mole with rhodium-platium (3 : 1) oxide in ethanol may be due to dimerization though it has not been investigated further.

TABLE II. EFFECT OF VARYING AMOUNTS OF ADDED HYDROCHLORIC ACID ON THE HYDROGEN UPTAKE BY CINNAMYL ALCOHOL[a]

Solvent	Hydrogen uptake mol./mol.
AcOH, 20 cc. + 3N HCl, 0.025 cc.	1.72
〃 , 0.05 cc.	1.78
〃 , 0.10 cc.	1.78
〃 , 0.15 cc.	1.79
〃 , 0.20 cc.	1.79

a) 1.342 g. (0.01 mol.) of cinnamyl alcohol was hydrogenated with 50 mg. of platinum oxide each time.

TABLE III. CATALYTIC REDUCTIONS OF CINNAMYL ACETATE AND CINNAMYL ALCOHOL[a]

Solvent	Hydrogen uptake mol./mol.	
	Cinnamyl acetate	Cinnamyl alcohol
AcOH, 20 cc.	1.30	1.31
EtOH, 20 cc. + 3N HCl, 0.1 cc.	1.50	1.60
AcOH, 20 cc. + 3N HCl, 0.1 cc.	1.80	1.79

a) 0.01 mol. of the substrate was hydrogenated with 50 mg. of platinum oxide each time.

except in hydrogenation with palladium-on-carbon (II) and rhodium-on-carbon (II), which were prepared from acidic media though washed with water many times and dried before use. Generally, the absorption of hydrogen increased in the following order with respect to the solvents; ethanol, acetic acid, ethanol with hydrochloric acid, and acetic acid with hydrochloric acid. This may be interpreted as the order of the abilities of the solvents as proton donors, which may become clearer by considering their conjugate acids, namely, $EtOH < AcOH < EtOH_2^+ < AcOH_2^+$[19], indicating that the hydrogenolysis is acid-catalyzed[20]. With respect to the catalysts, platinum oxide causes the greatest absorption of hydrogen[21], and rhodium added to platinum decreases the hydrogenolysis markedly. For instance, in acetic acid with hydrochloric acid, as much as 79% of cinnamyl alcohol is reduced to propylbenzene with platinum oxide. On the other hand, with rhodium-platinum (3 : 1) oxide only 4% is hydrogenolyzed in acetic acid, compared with 31% with platinum oxide in the same solvent.

Table II shows the effect of varying amounts of added hydrochloric acid on the hydrogen uptake by cinnamyl alcohol in acetic acid with platinum oxide as a catalyst. It is seen that a very small amount of hydrochloric acid is sufficient for the maximum absorption of hydrogen and further addition has little effect. It seems improbable that the greater absorption of hydrogen would result from the intermediate formation of cinnamyl acetate, because cinnamyl acetate absorbed no more hydrogen than cinnamyl alcohol in hydrogenation with platinum oxide as shown in Table III.

With respect to the activities of the three oxide catalysts, it may be said that the order was as follows; rhodium-platinum (3 : 1) oxide > palladous oxide > platinum oxide, though an accurate comparison was not possible because of the different amounts of hydrogen absorbed. For example, with 50 mg. of each catalyst, 1.342 g. (0.01 mol.) of cinnamyl alcohol was reduced in 11 min. with rhodium-platinum (3:1) oxide, in 14 min. with palladous oxide, and in 26 min. with platinum oxide, in 20 cc. of acetic acid at 25°C and under atmospheric pressure.

Catalytic Reduction of 3-Phenylpropargyl Alcohol and *cis*-Cinnamyl Alcohol.—Table IV summarizes the results of the hydrogenation of 3-phenylpropargyl alcohol and *cis*-cinnamyl alcohol in various solvents with the use of platinum oxide as a catalyst together with those of the trans isomer. It is seen from the table that 3-phenylpropargyl alcohol absorbs nearly one mole of hydrogen more than *cis*-cinnamyl alcohol in any solvent used. This means that little hydrogenolysis or none occurred before the reduction of the triple bond to the double bond. The result may be explained by the strong affinity of the triple bond for the catalyst surface, which may prevent the C–O linkage from being adsorbed

TABLE IV. CATALYTIC REDUCTIONS OF 3-PHENYLPROPARGYL ALCOHOL AND CINNAMYL ALCOHOL[a]

Solvent	Hydrogen uptake mol./mol.		
	3-Phenylpropargyl alcohol	Cinnamyl alcohol *cis*-	Cinnamyl alcohol *trans*-
EtOH, 20 cc.	2.01	1.04	1.03
AcOH, 20 cc.	2.29	1.24	1.31
EtOH, 20 cc. + 3N HCl, 0.1 cc.	2.64	1.64	1.60
AcOH, 20 cc. + 3N HCl, 0.1 cc.	2.79	1.77	1.79

a) 0.01 mol. of the substrate was hydrogenated with 50 mg. of platinum oxide each time.

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[19] For the superacidic character of hydrochloric acid in acetic acid, see for instance; G. Schwarzenbach and P. Stensby, *Helv. Chim. Acta*, 42, 2342 (1959).

[20] This does not mean that the hydrogenation of the double bond is unaffected by acid, but does mean that the hydrogenolysis is much more promoted by acid than the hydrogenation.

[21] This does not mean necessarily that platinum oxide has the highest activity for the hydrogenolysis. The lower values for palladous oxide may probably result from its greater activity for the hydrogenation of the double bond.

on the surface of the catalyst, just as the triple bond is more tightly adsorbed than the double bond. Though the fact that *cis*-cinnamyl alcohol absorbed almost as much hydrogen as its trans isomer seems to suggest isomerization to a large extent in the course of the reduction, it will be difficult to say whether or not this is the case from the data now available[22].

Summary

1. The hydrogenation and hydrogenolysis of cinnamyl alcohol was studied with platinum, palladium, rhodium, and rhodium-platinum catalysts. The following results were obtained:

(i) The absorption of hydrogen increases with respect to the solvents in the following order; ethanol, acetic acid, ethanol with hydrochloric acid, and acetic acid with hydrochloric acid. The order was interpreted as that of the abilities of the solvents as proton donors.

(ii) With respect to the catalysts, platinum oxide causes the maximum absorption of hydrogen, and rhodium added to platinum decreases the hydrogenolysis markedly.

(iii) With respect to the activities of the three oxide catalysts in acetic acid, the order was; rhodium-platinum (3 : 1) oxide> palladous oxide> platinum oxide.

2. From the comparison of the hydrogen uptakes by 3-phenylpropargyl alcohol and by *cis*-cinnamyl alcohol, it was shown that little hydrogenolysis or none occurs before the reduction of the triple bond of the phenylpropargyl alcohol to the double bond.

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[22] Cf. R. L. Burwell, Jr., *Chem. Revs.*, 57, 895 (1957).