

PALLADIUM-CATALYZED ISOMERIZATION OF UNSATURATED ALCOHOLS

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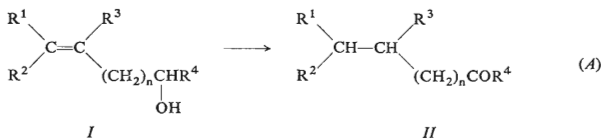
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Unsaturated primary and secondary alcohols can be isomerized to corresponding aldehydes by passing their vapours over palladium catalysts in the presence of small amounts of hydrogen. Under suitable conditions hydrogenation to saturated alcohols proceeds only to a small extent. In some cases dehydration to dienes completes with isomerization. Influence of the double bond position upon the reactivity of unsaturated alcohols was studied, and with allyl alcohol as an example, the preparative utility of this reaction was verified.

Isomerization of unsaturated alcohols to corresponding aldehydes or ketones (Equation (A)) may be effected by the action of acids¹, some oxides^{2,3}, metals⁴⁻¹⁵, and metal carbonyls^{16,17}. Of metals, much attention has been paid to copper in spite of its low catalytic activity for double bond migration which made it necessary to use the temperatures 250–400°C. At such temperatures isomerization is accompanied by dehydrogenation and, besides saturated carbonyl compounds, also unsaturated substances are usually formed^{4,6,8,11,14,15}; e.g. allyl alcohol (*Ia*) gives not only propanol (*IIa*) but also acrolein. Even worse results were obtained with nickel^{8,12}. Of metal oxides, aluminium oxide turned out to be a comparatively good catalyst^{2,3}. With sulphuric acid the reaction proceeds smoothly with majority of branched alcohols, however, allyl alcohol shows very poor reactivity¹⁸. Furthermore, some unsaturated alcohols do not isomerize but dehydrate, in others double bond migration is accompanied by migration of a methyl group¹⁸. Platinum metals, that efficiently catalyze double bond migration in hydrocarbons already under mild conditions, have attracted only scarce attention, as far as the isomerization of unsaturated alcohols is concerned. Delaby⁷ observed that when palladium black was introduced into 4-penten-3-ol (*Ij*) the liquid warmed up, 50% of the alcohol being transformed to 3-pentanone (*IIf*). Šimonik¹³ noted that in the hydrogenation of crotonaldehyde on platinum the transiently formed 2-butene-1-ol (*If*) is isomerized to 1-butanol (*IIf*). Pascal and collaborators^{14,15} used copper and also palladium to isomerize unsaturated diols; a variety of products was found in the reaction mixture in both cases. Žitný and Kraus¹⁹ have found that all platinum metals are effective catalysts for isomerization of unsaturated alcohols at mild conditions. The best results were obtained with palladium, ruthenium, and rhodium. The above authors also observed that for retaining activity of the catalyst, the presence of a small amount of hydrogen in the reaction mixture is necessary.

This work is devoted to comparison of the influence of the structure of unsaturated alcohols upon their ability to isomerize to corresponding aldehydes or ketones on palladium as the catalyst.



a, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$, $n = 0$

b, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$, $n = 1$

c, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$, $n = 2$

d, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$, $\text{R}^3 = \text{CH}_3$, $n = 0$

e, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$, $\text{R}^3 = \text{C}_2\text{H}_5$, $n = 0$

f, $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$, $n = 0$

g, $\text{R}^1 = \text{R}^2 = \text{CH}_3$, $\text{R}^3 = \text{R}^4 = \text{H}$, $n = 0$

h, $\text{R}^1 = \text{R}^3 = \text{CH}_3$, $\text{R}^2 = \text{R}^4 = \text{H}$, $n = 0$

i, $\text{R}^1 = \text{R}^4 = \text{CH}_3$, $\text{R}^2 = \text{R}^3 = \text{H}$, $n = 0$

j, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{C}_2\text{H}_5$, $n = 0$

k, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{C}_2\text{H}_5$, $n = 1$

EXPERIMENTAL

Compounds Used

Allyl alcohol (*Ia purris*) was supplied by Fa Berlin-Chemie and used without further purification. 3-Butene-1-ol (*Ib*) was prepared by Grignard synthesis from allyl chloride and gaseous formaldehyde; b.p. 110–113°C (ref.²⁰ gives 112.5–113.5°C). 4-Pentene-1-ol (*Ic*) was obtained²¹ from tetrahydrofurylmethyl chloride by the action of sodium; b.p. 136–137°C (ref.²¹ gives 134–137°C). 2-Methyl-2-propene-1-ol (*Id*) was prepared by reduction of methyl methacrylate with bis(2-methoxyethoxy)aluminium hydride in benzene-ether (1 : 9); b.p. 112–114°C (ref.¹⁸ gives 113–114°C). 2-Ethyl-2-propene-1-ol (*Ie*) was prepared by reduction of 2-ethyl-2-propanal¹⁸ with lithium hydride; b.p. 132–133°C (ref.¹⁸ gives 133–134°C). 2-Butene-1-ol (*If*) was prepared from crotonaldehyde by the same method; b.p. 120°C (ref.²² gives 118°C). 3-Methyl-2-butene-1-ol (*Ig*), too, was prepared by reduction of methyl of 3-methyl-2-butenolate^{23,24} with lithium aluminium hydride; b.p. 137–140°C (ref.²² gives 140°C). According to gas-chromatographic analysis this compound was contaminated by 3-methyl-1-butanol (about 10%), attempted separation of which has failed. 3-Pentene-2-ol (*Ii*) was obtained from crotonaldehyde and methylmagnesium chloride; b.p. 120°C (ref.²⁵ gives b.p. 119–121°C). 2-Methyl-2-butene-1-ol (*Ij*) was prepared by reduction of 2-methyl-2-butanone with lithium aluminium hydride; b.p. 135–140°C. 2-Cyclohexane-1-ol was prepared by reduction of 2-cyclohexene-1-one²⁶ with lithium aluminium hydride; b.p. 67–69°C/22 Torr (ref.²¹ gives 85°C/25 Torr). The purity of all the compounds was checked by gas chromatography.

Catalysts

Palladium on charcoal: Supersorbon charcoal of the grain size 0.2–0.4 mm was washed by boiling it with hydrochloric acid and then many times with distilled water, until the test with silver nitrate on the presence of chloride ions in the extract was negative. The carrier so prepared was not active for the isomerization of allyl alcohol. It was impregnated with palladium (II) chloride by sorption of the salt from its diluted aqueous solution (10 ml of 0.05% solution per 1 g of the charcoal). After separation from the liquid and drying at 120°C, separate portions of impregnated carrier were reduced directly in the catalyst bed at 180–200°C for 1 hour in a stream of hydrogen diluted with nitrogen (1 : 9). The catalyst so prepared contained 0.3% Pd.

Palladium on polymer: Macroreticular styrene-divinylbenzene co-polymer (Research Institute of Resins and Lacquers, Pardubice) of internal surface 100 m²/g as balls of the radius 0.2–0.3 mm,

was washed with benzene and dried. Then 2 ml of 0.5% palladium(II) chloride solution in ethanol was poured over the carrier (1 g) and the mixture was evaporated under vacuum to dryness. The impregnated balls were then poured out and, by determining the weight of the palladium salt which adhered to vessel walls, it was found that the balls contain 0.75% PdCl₂. Therefore, after reduction for one hour at 180°C with the mixture hydrogen-nitrogen (1 : 19), the catalyst contained 0.45% Pd.

Palladium black: Aqueous solution of palladium (II) chloride (1%) was reduced with 40% aqueous formaldehyde. The precipitate was filtered and dried over phosphorus pentoxide.

Procedure

Isomerization with substrates in the gaseous phase was studied in a flow apparatus of the standard type, consisting of a liquid feeder, an evaporator and a mixer of vapours with gases, a glass reactor equipped with a central thermocouple well, and a condenser cooled with solid carbon dioxide. The pressure in the reactor was atmospheric. The apparatus was provided with a control of the temperature of the electric oven, into which the reactor was inserted, and of the evaporator. Hydrogen from pressure cylinder was freed from minute amounts of oxygen by passing it over palladium catalyst and then dried over 4 Å molecular sieve. Weighted amounts of catalysts varied from 0.1 to 1.0 g. After reduction of the catalyst, a mixture of unsaturated alcohol and hydrogen (the content of which in the reaction mixture was always 10 mol %) was contacted with the catalyst. Products were analyzed by gas chromatography on an instrument equipped with a thermal-conductivity detector. Poly(ethylene glycol) (10%) on Celite and hydrogen were used as a stationary phase and a carrier gas, respectively.

RESULTS

Palladium exhibits very strong tendency to isomerize unsaturated alcohols to aldehydes, rather than to catalyze their hydrogenation to saturated alcohols. Table I shows the ratio of the 1-propanol to propanal formed on passing vapours of allyl alcohol over palladium catalysts in the presence of varying ratio of hydrogen to the substrate. At the same time, the presence of hydrogen is requisite to effect isomerization. This is demonstrated by experiment in which hydrogen was replaced by nitrogen (a partial pressure of allyl alcohol was 0.35 atm) only first drops of the

TABLE I
Influence of Partial Pressure of Hydrogen upon Yield of 1-Propanol in the Reaction of Allyl Alcohol Catalyzed by Palladium on Polymer at 180°C and with the Feeding Rate of the Alcohol 0.22 mol/h g_{cat}

Molar ratio of hydrogen to allyl alcohol	0.1	1.5	3.0	5.5
1-Propanol, mol. % (the rest propanal)	5	20	35	55

product contained the aldehyde; after that the reaction stopped. The lack of hydrogen on the surface of the catalyst is probably the reason why all attempts to isomerize allyl alcohol in the liquid phase have failed. When allyl alcohol was boiled with the catalyst, while continuously distilling-off the formed propanal through a distillation column, the reaction ceased after several minutes, so that the aldehyde could only be detected in the first drops removed. The same behaviour was observed with all the catalysts used (palladium on charcoal or on the polymer, and palladium black). No success has been achieved even after introduction of a weak stream of hydrogen into the boiling liquid and purging the whole apparatus with hydrogen before the reduced catalyst was charged.

The influence of the double bond position and of the number of substituents at the double bond upon the reactivity of unsaturated primary alcohols is apparent from Table II. The products contained besides the aldehydes also small amounts of saturated alcohols (up to 5%) and the products of dehydration (up to 5%), the rest was the unreacted starting alcohol. Data given in Table II thus express the reactivity of alcohols on comparable basis. As the distance of the double bond from the hydroxyl group increases (the series *Ia*, *Ib*, and *Ic*), the rate of the reaction markedly decreases. Substitution by alkyl group on the α -carbon brings about only a small decrease in reactivity (the series *Ia*, *Id*, and *Ie*), while when the methyl group is attached to the β -carbon, a marked decrease in the degree of transformation is observed (the series *Ia*, *If*, and *Ih*). Similar observations have already been reported in studies of the influence of structure on the reactivity of olefins in their hydrogenation on platinum metals²⁷, where terminal olefins markedly differed in their reactivity from those having the double bond in the middle of the chain. At the same time, whether the double-bonded carbon bears one or two substituents was less important. This indicates some relation between these two reactions and allows to assume identity of some reaction steps in both reactions, most likely the adsorption on the surface of the metal *via* the double bond or *via* the double-bonded carbon atoms. This adsorbed state is obviously preceded by a π -allylic state, the presence of which as the

TABLE II

Comparison of Reactivity of Primary Unsaturated Alcohols in Their Isomerization to Corresponding Aldehydes on Palladium on Charcoal

Temperature 180°C, feeding rate 0.20 mol/h $g_{cat.}$, hydrogen partial pressure 0.1 atm. Conversions are given with accuracy of $\pm 5\%$.

Alcohol	<i>Ia</i>	<i>Ib</i>	<i>Ic</i>	<i>Id</i>	<i>Ie</i>	<i>If</i>	<i>Ih</i>
Conversion to aldehyde, %	95	40	15	90	85	40	35

intermediate in the transformation of an unsaturated alcohol into the corresponding aldehyde is highly probable, in analogy with the mechanism of these reactions catalyzed by acids and bases¹.

Apart from the alcohols given in Table II, we studied also the reaction of 3-methyl-2-butene-1-ol (*Ig*), which led, however, to the dehydration product isoprene and gave only trace of the expected aldehyde; the activity of the catalyst was rapidly decreasing during the reaction. When the carrier alone was applied extensive dehydration took place. For this reason we used the catalyst with inactive polymer carrier with which 80% isomerization and only 20% dehydration were achieved. In this connection it is noteworthy that with sulphuric acid as the catalyst¹⁸ only dehydration of this alcohol takes place.

Of secondary alcohols, 3-pentene-2-ol (*Ii*) and 2-cyclohexene-1-ol were studied in this work. Very poor results were obtained with both alcohols when using palladium on charcoal. At the temperature 180°C the alcohol *Ii* mainly dehydrated and isomerized to the corresponding ketone *IIIi* only to a very small extent. Neither lower temperatures (*e.g.* 150 and 120°C) yielded better results. The conversion did decrease, but without an improvement of the selectivity. In contrast, quantitative transformation to the ketone was achieved with the catalyst on polymer carrier at the conditions of the experiments described in Table II. The cyclic alcohol reacted on palladium on charcoal in a complex manner, besides the expected cyclohexanone also benzene, phenol, and cyclohexanol were found among the products. No marked improvement has been observed with the palladium on polymer catalyst.

We finally verified the preparative utility of the isomerization, using allyl alcohol as an example. A total of 31 g of the substrate was contacted with 3 g of 0.3% palladium catalyst (with charcoal as the carrier) at 180°C, the allyl alcohol and the hydrogen feeding rate being 6 g/h and 300 ml/h, respectively. The condensate weighed 30 g and was the pure propanal, as checked by gas chromatography. Distillation through a short column afforded 25 g (81%) of propanal, b.p. 45–47°C.

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