CATALYTIC HYDROGENATION OF DEHYDROLINALOOL AND DEHYDROLINALYL ACETATE

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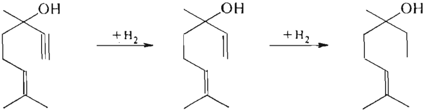
Catalytic hydrogenation of dehydrolinalool and of dehydrolinalyl acetate has been studied in the liquid phase under atmospheric pressure at 20°C with the aim to obtain selectively linalool and linalyl acetate. High selectivities have been obtained with the palladium on $CaCO_3$ catalyst which was partially poisoned by lead.

Linalool and linalyl acetate find use in perfume and pharmaceutical industry. They are synthesized by the selective catalytic hydrogenation of dehydrolinalool and dehydrolinalyl acetate which is most frequently carried out at ambient temperature under normal hydrogen pressure. For practical purposes the catalyst is nearly exclusively palladium, frequently modified in a number of ways[1-12]. Catalytic hydrogenation of dehydrolinalool can be described by Eq. (*1*). Hydrogenation of dehydrolinalyl acetate proceeds analogously. Linalool is the intermediate product in the above scheme of consecutive reactions. The final product, dihydrolinalool, is undesirable in most cases. The problem of catalytic hydrogenation of dehydrolinalool and dehydrolinalyl acetate involves the selective hydrogenation of the triple C—C bond to the double bond.



(*1*)

The present work deals with the study of solvent effects on the selectivity of hydrogenation of both compounds on two commercial palladium catalysts.

EXPERIMENTAL

Compounds used. Dehydrolinalool, dehydrolinalyl acetate, both freshly distilled (Astrid Prague — import), 96% ethanol, distilled (Spojené lihovary, Prague), octane, analytical purity grade (Jenapharm, Labor Chemie, Apolda, GDR), acetic acid, analytical purity grade (Lachema, Brno) catalysts: 0·5% $Pd/CaCO_3$-desactivated by lead (1·325 g Pb/g Pd) (Farmakon, Olomouc), 2·8% Pd/C (Chemické závody ČSSP, Záluží), particles ≦0·063 mm, electrolytic hydrogen (Technoplyn, Kyje).

Apparatus and procedure. All the measurements were carried out under atmospheric hydrogen pressure at 20°C in a standard apparatus[13]. In all runs, 10 ml of a solvent and 1 ml of the corresponding substrate were used. The weight amounts of the catalysts were changed within 0·027 to 0·180 g. The reaction course was followed by measuring time dependence of hydrogen consumption and by chromatographic analysis of the samples withdrawn from the reaction mixture at appropriate time intervals.

Analytical methods. Analyses were made on Chrom 4 instrument equipped with a flame ionisation detector, using glass columns (2·5 and 3·7 m long, 2·5 mm i.d.) packed with 15% Carbowax 20 M on Chromaton NAW-DMCS, 0·16—0·20 mm particles, temperature 140°C.

RESULTS AND DISCUSSION

All the measurements were made under conditions which excluded the effect of mass transport on the course of hydrogenation[14]. The effect of external diffusion was avoided by efficient stirring, the eventual effect of internal diffusion was limited by using small granulation of the catalysts. Hydrogenation of dehydrolinalool and of dehydrolinalyl acetate was carried out in the presence of the following catalysts:

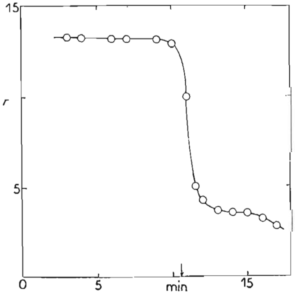


FIG. 1

Time Dependence of Rate of Hydrogenation, r (ml H_2 . min^{-1}) of Dehydrolinalyl Acetate on $Pd/CaCO_3$ + Pb Catalyst in Ethanol

Initial mixture: 1 ml of dehydrolinalyl acetate, 0·027 g of the catalyst and 10 ml of ethanol.

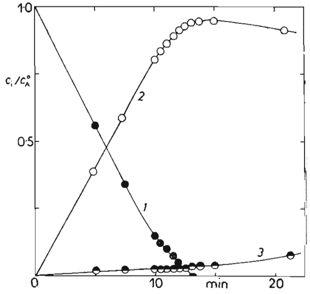


FIG. 2

Time Dependence of Concentrations of Substances in Hydrogenation of Dehydrolinalyl Acetate on $Pd/CaCO_3$ + Pb Catalyst in Ethanol

c_i/c_A^0 the actual concentration of the component i related to the initial concentration of dehydrolinalyl acetate, *1* dehydrolinalyl acetate, *2* linalyl acetate, *3* dihydrolinalyl acetate.

0·5% $Pd/CaCO_3$ + Pb and 2·8% Pd/C and that always in ethanol, octane and in acetic acid (the acid was not used in the case of the catalyst containing $CaCO_3$).

Typical experimental dependences are shown in Figs 1 and 2. From Fig. 1 it is obvious that the hydrogenation of dehydrolinalyl acetate proceeds at practically constant rate up to theoretical consumption of hydrogen necessary for hydrogenation of the triple to double C—C bond (designated by arrow). After disappearance of the triple bond, the reaction rate substantially slows down (several times) and the undesirable hydrogenation of the double bond of linalyl acetate proceeds to greater or smaller extent in all cases, producing dihydrolinalyl acetate. Time dependence of the concentrations of individual reaction components for the hydrogenation of dehydrolinalyl acetate is shown in Fig. 2. Analogous dependences were obtained also in all the other experiments.

From practical point of view, the most important factor is the selectivity of hydrogenation defined as the percentage amount of linalyl acetate (resp. linalool) in the

TABLE I

Selectivity of Hydrogenation of Dehydrolinalyl Acetate and Dehydrolinalool (%)

Solvent	Dehydrolinalyl acetate		Dehydrolinalool	
	0·5% $Pd/CaCO_3$-Pb	2·8% Pd/C	0·5% $Pd/CaCO_3$-Pb	2·8% Pd/C
Ethanol	95·0	83·0	99·0	80·0
Octane	96·0	86·0	99·5	nonselective
Acetic acid		nonselective		nonselective

TABLE II

Initial Rate of Hydrogenation of Dehydrolinalyl Acetate and Dehydrolinalool (ml H_2 min^{-1} g_{cat}^{-1})

Solvent	Dehydrolinalyl acetate		Dehydrolinalool	
	0·5% $Pd/CaCO_3$-Pb	2·8% Pd/C	0·5% $Pd/CaCO_3$-Pb	2·8% Pd/C
Ethanol	481	100	324	163
Octane	500	229	150	159
Acetic acid	—	67	—	114

moment of the disappearance of dehydrolinalyl acetate (resp. dehydrolinalool) from the reaction mixture. The difference from 100% represents the amount of dihydrolinalyl acetate and dihydrolinalool, respectively. The selectivities so calculated are presented in Table I. In those cases in which at 50% conversion of the starting compound the reaction mixture contained more than 10% of dihydrolinalyl acetate or of dihydrolinalool were regarded as nonselective and were not followed up to the total conversion of the starting compound.

Of the two catalysts used, 0·5% Pd/$CaCO_3$ desactivated by lead turned out to be more suitable in all respects. Acetic acid was found to be unsuitable solvent. In nonpolar octane, the selectivity of hydrogenation was higher than in polar methanol. In both cases the hydrogenation of dehydrolinalool was somewhat more selective than that of dehydrolinalyl acetate. With respect to the synthesis of linalyl acetate, the esterification of the already hydrogenated dehydrolinalool to linalool has not to be generally more advantageous compared to the esterification of dehydrolinalool followed by its hydrogenation, since one can expect that the esterification of the dienic substance will be accompanied by its polymerisation to the greater extent than in the case of the esterification of the substance of the acetylene-ethylenic type.

In Table II are presented the initial rates of hydrogenation of dehydrolinalyl acetate and of dehydrolinalool. Also from this aspect 0·5% Pd/$CaCO_3$ + Pb catalyst is more advantageous compared to the unmodified catalyst. The rate of hydrogenation of both substrates can be regarded as comparable, with the exception of the low rate of hydrogenation of dehydrolinalool in octane on Pd/$CaCO_3$ + Pb catalyst. The results obtained in this work are comparable with the most selective hydrogenations of the same substrates so far reported.

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