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Abstract

Full Text

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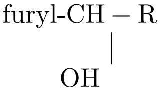
SELECTIVE REDUCTION OF ALKYLFURYLCARBINOLS TO ALKYLFURANS ON A PALLADIUM CATALYST

The hydrogenation reaction of compounds of the type



$$\text{furyl-}\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{R}$$

where R may be a hydrogen atom or an alkyl or aryl radical, has been studied in sufficient detail both with respect to the diversity of compounds and with respect to the number of catalysts employed. Depending on the nature of the catalyst and the structure of the compounds, hydrogenation of the latter may proceed in three directions: 1) only the double bonds in the furan ring may undergo hydrogenation, as a result of which alcohols of the tetrahydrofuran series are obtained; 2) hydrogenolysis of the ring may occur at one or both C—O bonds, with formation, respectively, of alkanediols and alkanols; 3) complete reduction of the side group may occur, with replacement of the hydroxyl by a hydrogen atom; 4) finally, all or some of the indicated reactions, under certain conditions, may proceed simultaneously.

Nickel catalysts, especially Raney nickel, proved to be very active in carrying out the hydrogenation reaction of multiple bonds in the furan ring. Thus, Paul (1), by hydrogenating furyl alcohol, as well as methyl-, ethyl-, propyl-, and phenylfurylcarbinols over Raney nickel at 50–80°, obtained the corresponding tetrahydrofuran derivatives in yields of 90–100%. On a platinum catalyst promoted with iron salts, hydrogenation of furyl alcohol (2) and alkylfurylcarbinols (3) also proceeded mainly toward formation of the corresponding tetrahydro derivatives. However, this catalyst, even at low temperatures, promotes hydrogenolysis of the furan ring at one or both ether bonds, as a result of which alkanediols and alkanols are formed. This latter reaction proceeds especially readily on copper catalysts, in particular on copper chromite. As a result of hydrogenation of furyl alcohol over copper chromite at 200–250° in the liquid phase, Connor and Adkins (4) obtained sylvan, pentanol-1, and pentanediols-1,2 and -1,5. Copper catalysts in various forms also proved to be the most effective in the reaction of reduction of the hydroxyl group in furyl alcohol without hydrogenation of the double bonds in the ring (^{5}). This reaction found industrial application in the preparation of sylvan from furfurol.

As is well known, palladium is an excellent catalyst for hydrogenation of double bonds in the furan ring both in the liquid (^{6}) and in the vapor phase (^{7}). However, our attempt to hydrogenate the furan ring in alkylfurylcarbinols in the vapor phase over palladized carbon led to unexpected and interesting results. Instead of hydrogenation of the double bonds in the furan ring, hydrogenolysis of the C—OH bond and replacement of the hydroxyl group by a hydrogen atom occurred. This led to the conversion of methyl- and ethylfurylcarbinols, respectively, into α-ethyl- and α-propylfurans in yields of 70–80% of theory:

$$\text{furyl-CH(OH)-R} \xrightarrow[\text{H}_2]{\text{Pd-charcoal}} \text{furyl-CH}_2\text{R} + \text{H}_2\text{O}$$

The ability of the bond between the carbon atom and the hydroxyl group in alkylfurylcarbinols to be cleaved readily under the action of hydrogen on catalysts is a specific property of this type of compound. Thus, the hydroxyl group in pentanol-2, even at higher temperatures, is not replaced by hydrogen in any appreciable amounts. Also very noteworthy is the fact that the hydroxyl group in alkyltetrahydrofurylcarbinols has absolutely no tendency toward reduction under the conditions under which this reaction takes place in alkylfurylcarbinols. Methyltetrahydrofurylcarbinol, passed by us over palladized charcoal under the same conditions under which hydrogenation of methylfurylcarbinol occurred, remained unchanged. Thus, of the three types of compounds

$$\underset{\text{I}}{\text{R}'\text{—CH(OH)—R}} \quad \underset{\text{II}}{\text{tetrahydrofuryl-CH(OH)—R}} \quad \underset{\text{III}}{\text{furyl-CH(OH)—R}}$$

only in alkylfurylcarbinols (III) is the C—O bond in the side chain so weakened that it is readily cleaved under the action of hydrogen on palladized charcoal. The reason for this fact should apparently be sought in the conjugation effect of the C—O bond in the side chain with the double bond in the furan ring.

Methyl- and ethylfurylcarbinols were synthesized according to the scheme:

$$\text{furfural} \xrightarrow{\text{RMgX}} \text{furyl-CH(OH)-R}$$

Methylfurylcarbinol had the following properties: b.p. 76-77° (23 mm), d_4^{20} 1.0780 and n_D^{20} 1.4800.

Ethylfurylcarbinol boiled at 73-75° (8 mm) and had d_4^{20} 1.0492 and n_D^{20} 1.4786.

Methyltetrahydrofurylcarbinol, obtained by hydrogenation of methylfurylcarbinol in the liquid phase on a skeletal Ni—Al catalyst at 130–150°, had the following constants: b.p. 92–93°/40 mm, d_4^{20} 1.0150, n_D^{20} 1.4485.

Palladized charcoal containing 10% palladium was prepared according to Zelinsky (8)—by impregnating activated birch charcoal with a solution of H_2PdCl_4, followed by deposition of finely dispersed palladium on the charcoal with formalin and a solution of caustic potash. The difference between the method for preparing our catalyst and that of N. D. Zelinsky consisted in the fact that, in carrying out the deposition of palladium black on the support in the presence of formalin, we used not caustic soda but caustic potash, which, according to the observations of one of us, is a promoter of metallic catalysts. In addition, after deposition of palladium black on the charcoal we removed the excess not with acetic acid, but with dilute hydrochloric acid. This procedure eliminates the formation of a colloidal film and ensures the production of a catalyst with reproducible properties.

The hydrogenation of alkylfurylcarbinols was carried out in the vapor phase at 200–230°, with a space velocity of 0.1 hr^{-1}, in 50-g portions. The catalyzates, dried with calcium chloride, were distilled on a column with an efficiency of 40 theoretical plates.

α-Ethylfuran and α-propylfuran, obtained in yields of 80 and 70% of theory, respectively, had the following properties:

α-Ethylfuran, b.p. 91–91.5°/750 mm, d_4^{20} 0.9018 and n_D^{20} 1.4402.

α-Propylfuran, b.p. 114–115°/750 mm, d_4^{20} 0.8876 and n_D^{20} 1.4395.

The reaction of reductive dehydroxylation of alkylfurylcarbinols to alkylfurans represents a very interesting case of selective action by a palladium catalyst. In addition to its theoretical interest, it may also be of great importance from the preparative standpoint, since it makes it possible to avoid, in the synthesis of alkylfurans, the stage of dehydration of alkylfurylcarbinols, which usually does not proceed very smoothly.

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Note: Figure translations are in progress. See original paper for figures.