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Abstract

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ON THE SYNTHESIS OF TETRAHYDROFURAN KETONES

AND THEIR ISOMERIZATION INTO γ-DIKETONES

Kaufmann and Adams (1), in the hydrogenation of furfurylideneacetone over a platinum catalyst, observed the following sequence in the reduction of unsaturated bonds: first the olefinic bond in the side chain is hydrogenated, then the furan ring, and finally the carbonyl group. By stopping the reaction after the absorption of three moles of hydrogen, it was possible to obtain the tetrahydrofuran ketone, 1-tetrahydrofurylbutanone-3. Later investigations (2,3) led to the conclusion that with other catalysts (Ni, Cu) a different reaction sequence takes place, in which first the olefinic bond and the carbonyl group are hydrogenated, and then the furan ring undergoes either hydrogenation to a tetrahydrofuran ring or hydrogenolysis at the ether bond.

The results of the investigation carried out by us establish the possibility of hydrogenating the furan ring before reduction of the carbonyl group in the presence of a skeletal palladium-aluminum catalyst with a fairly high degree of selectivity. From furfurylideneacetone the corresponding tetrahydrofuran ketone—1-tetrahydrofurylbutanone-3—is obtained in 70% yield:

$$\text{furyl}-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow[\text{H}_2]{\text{Pd}-\text{Al}} \text{tetrahydrofuryl}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$$

Tetrahydrofuran ketones of this structure are of special importance in the synthesis of γ-diketones. As is known, the latter are obtained by isomerization of tetrahydrofuran alcohols in yields not exceeding 50%, since one of the carbonyl groups is formed as a result of dehydrogenation of the side-chain hydroxyl group, and the hydrogen evolved in this process causes a number of side reactions leading to the formation of tetrahydrofuran homologs and aliphatic ketones (5). In the case of tetrahydrofuran ketones this complication is absent, and therefore γ-diketones are obtained in high yields (90%):

$$\text{tetrahydrofuryl}{-}CH_2{-}CH_2{-}C(=O){-}CH_3 \xrightarrow[300^\circ]{Pt{-}C} CH_3{-}CH_2{-}CH_2{-}C(=O){-}CH_2{-}CH_2{-}C(=O){-}CH_3$$

Experimental Part

The synthesis of furfurylideneacetone was carried out according to the procedure described by Hinze and co-workers ([3]). In a 5-liter round-bottomed flask equipped with a mechanical stirrer and a thermometer, 385 g (335 ml) of furfural was mixed with 3 liters of water and 500 g (630 ml) of acetone was added. The mixture, with stirring, was cooled to 10°, after which 75 ml of a 33% solution of caustic soda was added, which was accompanied by heating of the reaction mass. Then, without cooling, stirring was continued for 4 hours. Next, 10% sulfuric acid was added until an acid reaction to litmus was obtained (about 350 ml). The layers that formed were separated, and the upper aqueous layer was distilled at atmospheric pressure until the distillate no longer separated into layers. The lower layer of the distillate was combined with the original lower layer, and the liquid-

distilled from a Claisen flask with an air condenser. Furfurylideneacetone with b.p. 114–118° at 10 mm, m.p. 37–39°, was obtained in a yield of about 65%.

Preparation of catalysts. The skeletal Pd—Al catalyst was prepared by fusing aluminum (95%) with palladium (5%) and subsequently leaching about 30% of the aluminum from the crushed alloy by treatment with a 10% sodium hydroxide solution. The leached catalyst was washed with water until neutral to phenolphthalein.

Platinized charcoal was prepared by impregnating activated birch charcoal, under ice cooling, with the calculated amount of chloroplatinic acid, followed by reduction with 30% formalin in an alkaline medium. Dilute hydrochloric acid (1 : 2) was then added until a weakly acid reaction to Congo red was obtained; the material was washed with distilled water and dried. The resulting catalyst contained 10% finely dispersed platinum.

Preparation of 1-(α-tetrahydrofuryl)-butan-3-one. A mixture of furfurylideneacetone with an equal amount of alcohol was hydrogenated in an autoclave, first at room temperature and then at 100°, over a skeletal Pd—Al catalyst taken in an amount of 10% of the weight of the substance being hydrogenated. Hydrogenation at room temperature leads mainly to reduction of the double bond in the side chain; as the temperature is raised, the furan ring begins to be hydrogenated. The reaction was stopped after the uptake of hydrogen had become insignificant (2–3 atm over 5 h). As a result of fractionation, 1-(α-tetrahydrofuryl)-butan-3-one was obtained in 70% yield; it had the following properties: b.p. 90–91° (12 mm), n_D^{20} 1.4485, d_4^{20} 0.9861, MR_D found 38.63; calculated for $C_8H_{14}O_2$ 38.60.

2,4-Dinitrophenylhydrazone, m.p. 78–78.5°; on chromatography on a plate with an unfixed layer of Al_2O_3 (activity II–III, 0.5 mm) in the ethyl acetate—hexane system (3 : 1), R_f 0.89.

Isomerization of 1-(α-tetrahydrofuryl)-butan-3-one. 1-(α-Tetrahydrofuryl)-butan-3-one was passed through a layer of platinized charcoal at 300° with a space velocity of 0.1 h^{-1}. The liquid catalyzate, obtained in 95% yield, was fractionated on an efficient column under reduced pressure. Octanedione-2,5 was obtained in a yield of more than 90%: b.p. 70–71° (2 mm), n_D^{20} 1.4430, d_4^{20} 0.9638.

Found, %: C 67.69; 67.75; H 10.06; 10.12
Calculated, %: C 67.57; H 9.96

In the hydrogenation of furfurylideneacetone in the liquid phase over a skeletal Pd—Al catalyst, the double bond in the side chain is first reduced, and then the furan ring; as a result, the corresponding tetrahydrofuran ketone, 1-tetrahydrofurylbutan-3-one, is formed. Isomerization of 1-tetrahydrofurylbutan-3-one in the vapor phase over Pt—C at 300° gives octanedione-2,5 in 90% yield.

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

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