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Abstract

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HYDROGENOLYSIS OF α-METHYL-α'-ETHYLFURAN ON PLATINIZED CARBON

Our investigation of the comparative hydrogenolysis of sylvan on various catalysts (1) made it possible to obtain results of importance both theoretically and practically, concerning the dependence of the character of hydrogenolysis of the furan ring on the nature of the catalyst. On platinum, palladium, and copper-chromium catalysts in the vapor phase at 275°, the furan ring in sylvan was cleaved at the ether bond not adjacent to the side group, which led to the formation of methyl propyl ketone. However, only the platinum catalyst showed the ability to carry out selective hydrogenolysis of the furan ring at the C—O bond 1–5 without any side processes.

$$\text{[furan ring with } CH_3 \text{ substituent]} \xrightarrow[\text{Pt/C}]{H_2} CH_3 \cdot CH_2 \cdot CH_2 \cdot C(=O){-}CH_3$$

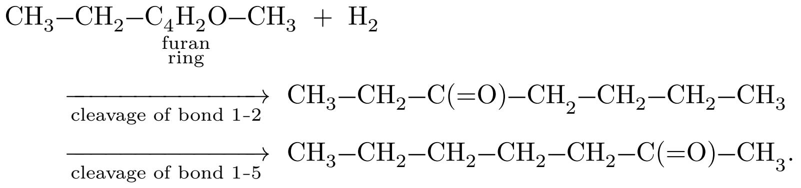
On a palladium catalyst, even at this comparatively high temperature, the principal hydrogenation product of sylvan was tetrahydrosylvan, while the yield of ketone was no more than 25–30%. The copper-chromium catalyst proved to be only slightly active in the hydrogenation of sylvan in the vapor phase. In addition to unchanged sylvan and methyl propyl ketone, the catalyzate contained considerable amounts of substances with a high boiling point.

In contrast to all these catalysts, a skeletal Ni—Al catalyst possesses the specific property of effecting hydrogenolysis of the furan ring both in the direction of cleavage of the ether bond 1–5 and in the direction of the conjugated cleavage of bonds 1–5 and 4–5, as well as 1–5 and 3–4. In the latter case ketones are formed which contain in the molecule one or two carbon atoms fewer than the initial alkylfuran. Platinum and skeletal nickel-aluminum catalysts are of the greatest preparative importance, since the former possesses the selective ability to carry out hydrogenolysis of the furan ring only in the direction of the C—O bond not adjacent to the side alkyl group, while the latter exhibits a remarkable ability to carry out so-called "conjugated" hydrogenolysis (2).

In all cases the influence of the side alkyl substituent causes an almost complete absence, in the C—O bond 1—2, of the ability to undergo hydrogenolysis. It was therefore of interest to investigate the comparative capacity for hydrogenolysis of C—O bonds under the influence of two alkyl groups with different carbon-chain lengths.

As the object of our investigation we chose α-methyl-α'-ethylfuran.

Hydrogenolysis of this compound at ether bonds 1-2 or 1-5 should give, respectively, heptan-3-one and heptan-2-one, as is seen from the following scheme:

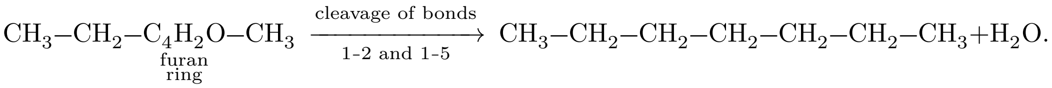


$$CH_3{-}CH_2{-}\underset{\text{furan ring}}{C_4H_2O}{-}CH_3 \ + \ H_2$$

$$\xrightarrow[\text{cleavage of bond 1-2}]{} CH_3{-}CH_2{-}C({=}O){-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

$$\xrightarrow[\text{cleavage of bond 1-5}]{} CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C({=}O){-}CH_3.$$

Indeed, hydrogenation of α-methyl-α'-ethylfuran, carried out in the vapor phase over platinized charcoal at 235°, led to the formation of heptan-2-one (yield 36%) and heptan-3-one (yield 54%). In considerably smaller amount the catalyzate contained *n*-heptane (~7%), whose formation is possible as a result of simultaneous hydrogenolysis of the furan ring at the C—O bonds 1-2 and 1-5:



$$CH_3{-}CH_2{-}\underset{\text{furan ring}}{C_4H_2O}{-}CH_3 \xrightarrow[\text{1-2 and 1-5}]{\text{cleavage of bonds}} CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3{+}H_2O.$$

The relative content of the ketones (heptan-2-one and heptan-3-one) in the products of hydrogenolysis leads to the conclusion that the ethyl group exerts a more significant stabilizing effect on the neighboring C—O bond than does the methyl group.

Experimental Part

Hydrogenation of α-methyl-α'-ethylfuran was carried out in the vapor phase at 235° over platinized charcoal containing 15% finely dispersed platinum. The starting substance was fed into the reaction zone at a space velocity of 0.1 hr^{-1}. α-Methyl-α'-ethylfuran was synthesized according to the scheme:

$$\text{methylfuran} \xrightarrow[(H_3PO_4)]{(CH_3CO)_2O} \alpha\text{-methyl-}\alpha'\text{-acetylfuran} \xrightarrow{NH_2NH_2} \text{hydrazone}$$

$$\xrightarrow[\text{KOH}]{\text{N}} \alpha\text{-methyl-}\alpha'\text{-ethylfuran} + N_2.$$

Acetylation of sylvan with acetic anhydride in the presence of iodine or hydroiodic acid did not lead to positive results, although in the case of furan this method proved quite satisfactory. Of the two other catalysts examined by us ($SnCl_4$ and orthophosphoric acid), the latter gave higher and steadier yields (up to 50% of theory).

Into a flask equipped with a mechanical stirrer and a reflux condenser were placed 2 gram-moles of sylvan and 3 gram-moles of acetic anhydride. The flask was cooled to 0°, and 10–15 g of orthophosphoric acid was introduced into it, after which the reaction mixture was stirred for 30 min while cooled with ice. The flask was then heated for 3 hr on a water bath. The reaction mixture was washed with a soda solution to neutral reaction, the product obtained was extracted with ether and distilled under reduced pressure. The isolated α-methyl-α'-acetylfuran had the following properties: b.p. 68–69°/7 mm, d_4^{20} 1.0655 and n_D^{20} 1.5090.

The hydrazone, obtained by boiling on a water bath a solution of α-methyl-α'-acetylfuran and hydrazine hydrate in ethyl alcohol, thoroughly

was dried with calcium chloride and subjected to decomposition in the presence of anhydrous KOH and Ni/Al_2O_3 (^{3}). The products of decomposition of the hydrazone were washed with a weak solution of acetic acid and, after drying with calcium chloride, were fractionated on a column with an efficiency of about 40 theoretical plates. The average yield of α-methyl-α'-ethylfuran, having b.p. 116–117°/750 mm, d_4^{20} 0.8937 and n_D^{20} 1.4468, from several experiments was 55%.

In the experiment, 50 g of α-methyl-α'-ethylfuran was taken. This gave 48 g of catalyzate, which, after drying with potassium, was fractionated on a column. The following compounds were isolated from the catalyzate:

I. *n*-Heptane, b.p. 97–98°/750 mm, d_4^{20} 0.6852, n_D^{20} 1.3894.

II. Heptanone-3, b.p. 145–146.2°/755 mm, d_4^{20} 0.8212, n_D^{20} 1.4112. Semicarbazone, m.p. 101°.

III. Heptanone-2, b.p. 150–150.2°/755 mm, d_4^{20} 0.8148, n_D^{20} 1.4095. Semicarbazone, m.p. 120°.

The residue with b.p. above 150.2°, amounting to 3% of the weight of the catalyzate, had n_D^{20} 1.4200 and apparently consisted of a mixture of 2- and 3-heptanols.

Thus, as a result of the investigation carried out, it was established that on platinized carbon in the vapor phase at 235° the ring in α-methyl-α'-ethylfuran is completely cleaved at the C—O bonds 1–2 and 1–5, with the formation, respectively, of heptanone-3 (yield 54%) and heptanone-2 (yield 36%), as well as a small amount of *n*-heptane owing to simultaneous rupture of both ether bonds.

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CITED LITERATURE

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

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