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Abstract

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HYDROGENATION OF CARBONYL-CONTAINING FURAN DERIVATIVES

CONVERSION OF 2-ALKYL-5-ACYLFURANS INTO 2,6-DIALKYLTETRAHYDROPYRANS

2-Alkyl-5-acylfurans (I), on catalytic hydrogenation in the vapor phase, can undergo transformations in two directions.

1. First, the carbonyl group can be reduced to a CH_2 group, which leads to the formation of 2,5-dialkylfurans (II). The latter may then undergo hydrogenolysis to aliphatic ketones (III). Such a course of the reaction is observed, for example, on skeletal Cu–Al catalyst (^{1}), Ni–ZnO and Ni–CdO (^{2}):

$$\text{(I)}\quad R-\text{furan ring}-C(=O)-R' \xrightarrow{H_2} \text{(II)}\quad R-\text{furan ring}-CH_2-R' \xrightarrow{H_2} R-C(=O)-(CH_2)_4-R'$$

$$R-(CH_2)_3-C(=O)-CH_2-R' \quad \text{(III)}$$

2. Before reduction of the carbonyl group, hydrogenolysis of the furan ring occurs. Platinum catalysts, for example platinum on carbon and platinum on asbestos, are capable of carrying out the reaction in this direction. We have established that, during hydrogenation over platinum, the furan ring in 2-alkyl-5-acylfurans is cleaved exclusively at the C–O bond adjacent to the carbonyl group (^{3}). The 1,5-diketones (IV) formed as a result, under the conditions of vapor-phase hydrogenation, undergo cyclization to mono- and disubstituted homologues of cyclohexanone (VI) or phenol (VII). On platinized carbon at 300°, alkylphenols are obtained in yields of 50–60% (^{4}):

$$\text{(I)}\quad R-\text{furan ring}-C(=O)-R' \xrightarrow{H_2} R'-C(=O)-CH_2-CH_2-CH_2-C(=O)-R' \underset{H_2}{\rightleftarrows}$$

$$\text{(IV)}$$

$$\begin{array}{llcl} \text{(IV)} \downarrow & \begin{array}{c}\text{cyclohexanone homologue}\\ \text{(VI)}\end{array} & \longrightarrow & \begin{array}{c}\text{phenol homologue}\\ \text{(VII)}\end{array} \end{array}$$

$$\rightleftarrows \; R{-}CH(OH){-}CH_2{-}CH_2{-}CH_2{-}CH(OH){-}R' \quad \text{(V)}$$

$$\downarrow$$

$$\begin{array}{c}\text{2,6-dialkyltetrahydropyran}\\ \text{(VIII)}\end{array}$$

We have shown that if the hydrogenation of 2-alkyl-5-acylfurans is carried out at temperatures of 200–230°, phenols are practically absent from the reaction products; instead, the catalyzate contains homologs of cyclohexanone and cyclohexanol. In the present work, the formation of 2,6-dialkyltetrahydropyrans during the hydrogenation of 2-alkyl-5-acylfurans over a platinum catalyst is reported for the first time.

The 1,5-diketones formed as primary products of the hydrogenolysis of 2-alkyl-5-acylfurans can either cyclize to six-membered carbocyclic compounds [4], or, depending on the temperature conditions, be hydrogenated to the corresponding 1,5-alkanediols (V), which, as a result of intramolecular elimination of water, give tetrahydropyrans (VIII). The diketone ⇄ diol equilibrium shifts toward the diol as the temperature is lowered, whence it follows that formation of tetrahydropyrans should be favored by a lower temperature. Indeed, as our experiments showed, tetrahydropyrans are formed in the highest yield at 200–220°; at 300–350° tetrahydropyrans are practically absent from the reaction products.

Another condition favorable for a deeper conversion of 1,5-diketones into 1,5-diols is an increase in the hydrogen pressure in the hydrogenation reaction. However, experiments carried out by us on the hydrogenation over Pt–C of 2-methyl-5-acetylfuran in a flow system at a hydrogen pressure of 50 atm showed that under these conditions the primary reaction is not hydrogenolysis of the furan ring, but reduction of the carbonyl group followed by hydrogenation and hydrogenolysis of the furan ring [5].

Conversion of 2-methyl-5-acetylfuran into 2,6-dimethyltetrahydropyran. Hydrogenation of 2-methyl-5-acetylfuran (b.p. 68–69° (VII); n_D^{20} 1.5090; d_4^{20} 1.0655) over Pt–C at 200–210° and atmospheric pressure, at a space velocity of 0.1 h^{-1}, gives 2,6-dimethyltetrahydropyran in 25–35% yield:

$$\mathrm{CH_3{-}furan\ ring{-}C({=}\,O){-}CH_3} \xrightarrow[200-210^\circ]{\mathrm{H_2,\ Pt{-}C}} \mathrm{CH_3{-}tetrahydropyran\ ring{-}CH_3}$$

2,6-Dimethyltetrahydropyran was contained in the fraction with b.p. 111–113°. The refractive index of this fraction varied from n_D^{20} 1.4195 in the experiment carried out at 200° to n_D^{20} 1.4220 in the experiment at 220°. This indicated the presence in the fraction of some other substances besides 2,6-dimethyltetrahydropyran. Spectral analysis of the fraction boiling within 111-113° revealed toluene. As we had shown earlier [4], the latter is obtained by reduction of *m*-cresol, which in turn is formed by cyclization of heptanedione-1,5, the primary product of hydrogenolysis of 2-methyl-5-acetylfuran. To obtain 2,6-dimethyltetrahydropyran in a purer state, the fraction with b.p. 111-113° was subjected to hydrogenation over Pd—C at 180° in a flow system, with the aim of converting the toluene contained in it into methylcyclohexane. After distillation of the catalyzate on an efficient column over sodium, the isolated 2,6-dimethyltetrahydropyran had the following properties: b.p. 112-113° (750), d_4^{20} 0.8384; n_D^{20} 1.4180.

2,6-Dimethyltetrahydropyran was then subjected to isomerization over Pt—C in the vapor phase at 350° to 2-heptanone:

$$2,6\text{-dimethyltetrahydropyran} \xrightarrow{\text{Pt—C, }350^\circ} \mathrm{CH_3{-}C({=}O){-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}\ (98\%)$$

The 2-heptanone obtained had the following properties: b.p. 148-150° (745), n_D^{20} 1.4096; d_4^{20} 0.8160; semicarbazone, m.p. 121°.

Conversion of 2-methyl-5-propionylfuran into 2-methyl-6-ethyltetrahydropyran. 2-Methyl-5-propionylfuran (b.p. 68-70° (3); n_D^{20} 1.5032; d_4^{20} 1.0394) was subjected to hydrogenation by the flow method over Pt—C at 200-210°:

$$\mathrm{CH_3}\text{—furan—}\mathrm{C({=}O){-}CH_2{-}CH_3} \xrightarrow[200\text{–}210^\circ]{\mathrm{H_2},\ \text{Pt—C}} \mathrm{CH_3}\text{—tetrahydropyran—}\mathrm{CH_2{-}CH_3}$$

The 2-methyl-6-ethyltetrahydropyran, obtained in a yield of about 20%, was contained in the fraction with b.p. 133-136°; d_4^{20} 0.8485 and n_D^{20} 1.4300. Spectral analysis revealed traces of ethylbenzene and *o*-xylene in this fraction. Undoubtedly, these hydrocarbons were formed by the same route as was indicated above for the formation of toluene during the hydrogenation of 2-methyl-5-acetylfuran.

Isomerization of 2-methyl-6-ethyltetrahydropyran in the vapor phase over Pt—C at 320° gave a mixture of 2-octanone and 3-octanone:

$$\mathrm{CH_3}\text{—tetrahydropyran—}\mathrm{CH_2{-}CH_3} \xrightarrow[320^\circ]{\text{Pt—C}} \mathrm{CH_3{-}C({=}O){-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C({=}O){-}CH_2{-}CH_3}$$

Conversion of 2-ethyl-5-propionylfuran into 2,6-diethyltetrahydropyran. 2,6-Diethyltetrahydropyran was obtained by us in a yield of about 20% upon hydrogenation of 2-ethyl-5-propionylfuran (b.p. 107-108° (16); n_D^{20} 1.5000; d_4^{20} 1.0152) in a flow system over Pt–C at 200-210°:

$$\mathrm{CH_3{-}CH_2{-}furan{-}C(=O){-}CH_2{-}CH_3} \xrightarrow[200-210^\circ]{\mathrm{H_2,\ Pt{-}C}} \mathrm{CH_3{-}CH_2{-}tetrahydropyran{-}CH_2{-}CH_3}$$

2,6-Diethyltetrahydropyran was contained in the fraction with b.p. 155-158°; d_4^{20} 0.8489; n_D^{20} 1.4353.

As a result of isomerization of this fraction in the vapor phase over Pt–C at 320°, 3-nonanone was obtained in 90% yield, b.p. 190-191° (755), d_4^{20} 0.8230; n_D^{20} 1.4210:

$$\mathrm{CH_3{-}CH_2{-}tetrahydropyran{-}CH_2{-}CH_3} \xrightarrow[320^\circ]{\mathrm{Pt{-}C}} \mathrm{CH_3{-}CH_2{-}C(=O){-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

It is not excluded that the tetrahydropyrans obtained by us contained an admixture of a small amount of hydrocarbons of the cyclohexane series, corresponding to the aromatic hydrocarbons formed as by-products during the hydrogenolysis of 2-alkyl-5-acylfurans over Pt–C (see above). This is all the more probable since the temperature at which the formation of tetrahydropyrans takes place is also favorable for the conversion of the benzene ring into a cyclohexane ring.

In conclusion, it should be emphasized that further study of the hydrogenation reaction of ketones of the furan series may provide a new general method for the synthesis of difficultly accessible homologs of tetrahydropyran.

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