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Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN, E. KOVÁCS, I. F. BELSKY

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Abstract

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E. KOVÁCS, I. F. BELSKY
and M. BARTÓK

CATALYTIC HYDROGENATION OF ORGANIC OXIDES IN A FLOW SYSTEM AT ELEVATED HYDROGEN PRESSURE

The process of catalytic hydrogenation of organic oxides may be of interest from two points of view: first, it may make it possible to establish the relative resistance of various oxide rings to cleavage under the action of catalytically activated hydrogen; and, second, in the case of hydrogenation of unsymmetrical organic oxides, the problem arises of determining the direction in which opening of the oxide ring occurs. Both of these questions presuppose a comparative study of the catalytic hydrogenation reaction of various organic oxides. The literature data available are far from sufficient for any general conclusions. With respect to α-oxides it is known that, on hydrogenation over reduced nickel or copper, monoalkyl- and monophenyl-substituted homologs undergo ring opening at the bond connecting the oxygen atom with the carbon atom bearing the substituent, as a result of which primary alcohols are formed (1).

Various β-oxide-2-alkyl-, 2,2-dialkyl-, and 2-phenyl derivatives have been reduced with lithium aluminum hydride. It was found that in all cases the β-oxide ring is cleaved at the bond between the oxygen atom and the carbon atom free of substituent (2).

Recently we investigated the hydrogenation of various γ-oxides (homologs of tetrahydrofuran) in a flow system at ordinary pressure over platinized charcoal and a skeletal nickel-aluminum catalyst. Over platinized charcoal at 350° tetrahydrofurans undergo hydrogenolysis simultaneously at both C–O bonds, as a result of which alkanes and water are formed. Over the skeletal nickel-aluminum catalyst, 2-alkyl- and 2,2-dialkyltetrahydrofurans undergo hydrogenolysis at the C–O bond adjacent to the side alkyl groups, and the primary alcohols or aldehydes formed undergo further reactions leading to the formation of alkanes whose carbon chain contains one carbon atom fewer than in the molecule of the starting tetrahydrofuran (3).

The aim of the present investigation was to obtain systematic experimental material that could be used for comparative conclusions. We carried out the hydrogenation of the simplest representatives of unsymmetrical α-, β-, and γ-oxides, namely propylene oxide, α-methyltrimethylene oxide, and

α-methyltetrahydrofuran, in a flow system at a hydrogen pressure of 50 atm over two skeletal catalysts, Cu—Al and Ni—Al. Under the same conditions, hydrogenation of α-methyltrimethylene oxide was carried out over skeletal Ni—Zn catalyst, and that of α-n-propyltetrahydrofuran over skeletal Ni—Al catalyst.

Hydrogenation of organic oxides over skeletal Cu—Al catalyst. Propylene oxide during hydro-

on a skeletal Cu—Al catalyst at 190-200° was converted into primary propyl alcohol with a yield of about 80%. This indicates that the α-oxide ring opened at the C—O bond adjacent to the methyl group:

$$\text{(methyl oxetane ring oxide)} \xrightarrow[\text{Cu-Al}]{H_2,\,50\text{ atm}} CH_3CH_2CH_2CH_2OH$$

About 20% of the catalyst consisted of substances with a high boiling point.

Hydrogenation of α-methyltrimethylene oxide over skeletal Cu—Al at 230-250° gave primary butyl alcohol in 90-95% yield. This indicates the following course of the reaction:

$$\text{(}\alpha\text{-methyltrimethylene oxide ring oxide)} \xrightarrow[\text{Cu-Al}]{H_2,\,50\text{ atm}} CH_3CH_2CH_2OH$$

The degree of conversion of propylene oxide and α-methyltrimethylene oxide into propyl and butyl alcohols, respectively, under the above conditions was 80-95%. The tetrahydrofuran ring proved to be considerably more resistant to hydrogenolysis on skeletal Cu—Al catalyst. Even at 300° the conversion of α-methyltetrahydrofuran did not exceed 10%. At the same time, a sharp qualitative difference was observed in the direction of opening of the γ-oxide ring as compared with α- and β-oxides. The products of hydrogenolysis of α-methyltetrahydrofuran (b.p. 79-79.5°; n_D^{20} 1.4060; d_4^{20} 0.8582) are n-pentane (30%*), pentanol-1 (35%), and pentanol-2 (35%). Thus, hydrogenolysis of the tetrahydrofuran ring on skeletal Cu—Al proceeds in both possible directions:

$$\text{(}\alpha\text{-methyltetrahydrofuran ring oxide)} \xrightarrow[\text{Cu-Al, }300^\circ]{H_2,\,50\text{ atm}} \begin{cases} CH_3CH_2CH_2CH_2CH_3 \\ CH_3CH_2CH_2CH_2CH_2OH \\ CH_3CH_2CH_2CH(OH)CH_3 \end{cases}$$

n-Pentane may be formed either as a result of hydrogenolysis of the tetrahydrofuran ring simultaneously at both C—O bonds, or as a result of reduction of the amyl alcohols initially formed. Resolution of this question requires further investigation.

Hydrogenation of organic oxides on skeletal Ni—Al catalyst. Skeletal Ni—Al catalyst, in the hydrogenation of organic oxides, exhibits properties substantially different from those of skeletal Cu—Al catalyst. Propylene oxide and α-methyltrimethylene oxide, which selectively open the ring on skeletal Cu—Al, are cleaved on skeletal Ni—Al catalyst in both directions:

$$\text{(propylene oxide ring oxide)} \xrightarrow[\text{Ni-Al, }200^\circ]{H_2,\text{ 50 atm}} \begin{cases} CH_3CH_2CH_2OH & 45\% \\ CH_3CH(OH)CH_3 & 55\% \end{cases}$$

$$(\alpha\text{-methyltrimethylene oxide ring oxide}) \xrightarrow[\text{Ni-Al, }200^\circ]{H_2,\text{ 50 atm}} \begin{cases} CH_3CH_2CH_2CH_2OH & 50\% \\ CH_3CH_2CH(OH)CH_3 & 50\% \end{cases}$$

In exactly the same way, with respect to the γ-oxide ring, skeletal Cu—Al and skeletal Ni—Al display different properties. α-Methyltetrahydrofuran on skeletal Ni—Al at 250° was converted only into pentanol-2, and the degree of conversion was only about 15%. Thus, on this catalyst the γ-oxide ring undergoes hydrogenolysis by a different route,

* The yield is given calculated on the converted α-methyltetrahydrofuran.

than the α- and β-oxides, opening only in one direction—at the C—O bond not adjacent to the side alkyl radical:

$$[\text{tetrahydrofuran ring bearing } CH_3] \xrightarrow[\text{Ni—Al, }250^\circ]{H_2,\text{ 50 atm}} CH_3CH_2CH_2CH(OH)CH_3 \quad 15\%$$

It is interesting to note that under these same conditions α-n-propyltetrahydrofuran (b.p. 131-132°; n_D^{20} 1.4232; d_4^{20} 0.8562) was converted into heptanol-4 (b.p. 153-155°; n_D^{20} 1.4710; d_4^{20} 0.8178) with a yield of the latter of $\sim$ 60%, which, evidently, indicates the influence of the length of the alkyl radical in the α-position on the stability of the tetrahydrofuran ring toward the hydrogenolysis reaction:

$$[\text{tetrahydrofuran ring bearing } CH_2CH_2CH_3] \xrightarrow[\text{Ni—Al, }250^\circ]{H_2,\text{ 50 atm}} CH_3CH_2CH_2CH(OH)CH_2CH_2CH_3 \quad 60\%$$

In connection with these results, it is necessary to point out an experimental fact concerning the influence of pressure on the hydrogenolysis reaction of the tetrahydrofuran ring.

Previously, while studying the hydrogenation reaction of α-n-propyltetrahydrofuran over a skeletal Ni—Al catalyst at ordinary pressure, we found that ring cleavage in this case proceeds at the C—O bond adjacent to the side alkyl group (3). These results quite definitely establish the role of pressure with respect to the direction of opening of the unsymmetrical γ-oxide ring.

In the present study we made one further observation concerning the influence of the second component on the properties of skeletal nickel catalysts: we found that α-methyltrimethylene oxide, when hydrogenated over skeletal Ni—Zn under conditions completely analogous to those for its hydrogenation over skeletal Ni—Al, is converted only into primary butyl alcohol; i.e., opening of the β-oxide ring over skeletal Ni—Zn, in contrast to skeletal Ni—Al, occurs only in one direction —at the C—O bond adjacent to the methyl group:

$$[\alpha\text{-methyltrimethylene oxide}] \xrightarrow[\text{Ni—Zn, } 200^\circ]{\text{H}_2\text{, 50 atm}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \quad 90\%$$

As we established earlier ( ), the difference in the properties of skeletal Ni—Al and skeletal Ni—Zn catalysts is also manifested in the hydrogenation of furan compounds.

In summary, one may arrive at the following main conclusion: unsymmetrical α- and β-oxides, when hydrogenated over skeletal Cu—Al and Ni—Al catalysts in a flow system under elevated hydrogen pressure, behave analogously with respect to the direction of opening of the oxide ring. Over a skeletal Cu—Al catalyst these oxides, with a sufficiently high degree of selectivity, are cleaved at the C—O bond adjacent to the alkyl substituent, whereas over a skeletal Ni—Al catalyst they undergo hydrogenolysis in both directions, to approximately an equal extent. Conversely, unsymmetrical γ-oxides (α-alkyltetrahydrofurans) are selectively hydrogenated over a skeletal Ni—Al catalyst, with ring opening at the C—O bond remote from the alkyl radical, while over a skeletal Cu—Al catalyst hydrogenolysis of γ-oxides proceeds in both directions.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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