CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN and I. F. BEL' SKII

1958

SovietRxiv

Abstract

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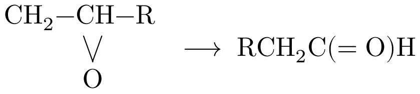
ISOMERIZATION OF γ-OXIDES (TETRAHYDROFURANS) INTO ALIPHATIC CARBONYL COMPOUNDS

The diverse chemical transformations of alkylene oxides are associated with the readily occurring opening of the α-oxide ring under the action of various agents. Among the well-studied reactions in the series of α-oxides is their isomerization into aliphatic carbonyl compounds. This reaction occurs on heating to 300-500° or at lower temperatures in the presence of catalysts (alumina, phosphoric acid, metal phosphates, silicates, etc.).

Unsymmetrical α-oxides having one or two alkyl substituents at one carbon atom of the ring (propylene oxide, isobutylene oxide) isomerize with ring opening predominantly at the bond joining the oxygen atom to the carbon atom bearing the substituents, which leads to the formation of aldehydes (^{1}):



$$\begin{array}{c} CH_2-CH-R \\ \vee \\ O \end{array} \longrightarrow RCH_2C(=O)H$$

Up to the present time an analogous isomerization reaction in the series of γ-oxides (tetrahydrofurans) has not been known. The catalysts most active in the isomerization of α-oxides cause, in the case of tetrahydrofuran and its homologs, a dehydration reaction with formation of dienic and aromatic hydrocarbons. Thus, for example, it was shown that tetrahydrosilvan, in contact with Al_2O_3, $TiO_2 \cdot Al_2O_3$, aluminum phosphate, or a mixture of phosphoric and boric acids, undergoes dehydration in the vapor phase to piperylene ($^{2-5}$). The behavior of tetrahydrofuran and some of its derivatives (tetrahydrosilvan, tetrahydrofurfuryl alcohol) has also been studied under conditions of catalytic hydrogenation in order to elucidate the mechanism of hydrogenolysis of the furan ring. It was found that, on a platinum catalyst in the liquid phase, tetrahydrofuran and tetrahydrofurfuryl alcohol undergo no changes (^{6}).

We investigated the transformations of tetrahydrofuran and its α-substituted homologs on platinized carbon in the vapor phase at 230-250° and found that under these conditions tetrahydrofuran and its homologs isomerize with ring opening at the C–O bonds into aliphatic carbonyl compounds.

Isomerization of α-alkyltetrahydrofurans with ring opening should, in the general case, lead to the formation of an aldehyde or a ketone, depending on which of the two C–O bonds undergoes cleavage:

$$\begin{array}{ll} \text{break of bond 1-2} & \longrightarrow \mathrm{R{-}CH_2CH_2CH_2C(=O)H} \\ \text{break of bond 1-5} & \longrightarrow \mathrm{R{-}C(=O){-}CH_2CH_2CH_3} \end{array}$$

The only product of isomerization of tetrahydrofuran should be *n*-butyric aldehyde. However, under the conditions used for the isomerization reaction, neither tetrahydrofuran itself nor its α-substituted homologues gave practically appreciable amounts of aldehydes. Tetrahydrofuran on platinized carbon at 250° gave a mixture of carbon monoxide and propane; from tetrahydrosilvan, α-ethyl- and α-propyltetrahydrofuran, under the same conditions, the corresponding ketones were obtained as the main reaction products, and also, in considerably smaller amounts, carbon monoxide and, respectively, *n*-butane, *n*-pentane, and *n*-hexane. The formation of carbon monoxide and paraffin hydrocarbons from tetrahydrofurans is a consequence of the secondary decarbonylation reaction of the aldehydes formed as a result of isomerization:

$$\mathrm{R{-}CH_2CH_2CH_2C(=O)H} \longrightarrow \mathrm{R{-}CH_2CH_2CH_3 + CO}.$$

Indeed, aldehydes are very readily decarbonylated on platinized carbon in the vapor phase to the corresponding hydrocarbons. Thus, we found that when heptanal-1 was passed over Pt–C at 250° in the absence of hydrogen, *n*-hexane and carbon monoxide were formed instead of the aldehyde. Under the same conditions benzaldehyde and benzyl alcohol are converted into benzene.

Thus, the relative amounts of ketones and alkanes obtained in the transformations of α-alkyltetrahydrofurans show to what extent cleavage of the C–O bonds 1–5 and 1–2, respectively, occurs in the isomerization of the γ-oxide ring. As a result of the experiments carried out, it was found that α-alkyltetrahydrofurans having methyl, ethyl, and propyl groups in the side chain are isomerized on Pt–C mainly into aliphatic ketones in yields of 90–95%, calculated on the converted α-alkyltetrahydrofuran; isomerization of the γ-oxide into an aldehyde with opening of the ring at the C–O bond 1–2, adjacent to the alkyl radical, proceeds to an insignificant extent (5–10%).

The isomerization reaction of alkyltetrahydrofurans into aliphatic carbonyl compounds is irreversible, since it is possible completely to convert the initial γ-oxide into the corresponding ketone and hydrocarbon. Thus, after tetrahydrosilvan had been passed twice over Pt–C at 250° with a space velocity of 0.1 $\mathrm{hr^{-1}}$, the liquid catalyzate contained a mixture of approximately equal amounts of pentanone-2 and unchanged tetrahydrosilvan. α-Ethyltetrahydrofuran, passed over the same catalyst at the same space velocity but four times in succession, gave 95% hexanone-3 and only about 5% *n*-pentane. If the isomerization of γ-oxides is carried out in a stream of hydrogen, then in this case on platinized carbon a secondary reaction takes place: hydrogenation of the carbonyl compounds formed to the corresponding alcohols. Thus, when tetrahydrofuran was passed over Pt—C in a mixture with hydrogen at 240°, a liquid catalyzate was obtained containing, along with unchanged tetrahydrofuran, about 20% *n*-butyl alcohol, whereas under the same conditions, but in the absence of hydrogen, tetrahydrofuran forms only a mixture of gaseous products—propane and carbon monoxide. These transformations may be expressed by the following scheme:

$$\text{tetrahydrofuran} \xrightarrow[240^\circ]{\text{Pt–C}} CH_3CH_2CH_2CHO$$

$$CH_3CH_2CH_2CHO \longrightarrow \begin{cases} CH_3CH_2CH_3 + CO, \\ CH_3CH_2CH_2CH_2OH \quad (H_2). \end{cases}$$

α-Propyltetrahydrofuran, passed in a stream of hydrogen over Pt—C at 235 —240° with a space velocity of 0.1 hr^{-1}, gave a mixture of heptanone-4 and heptanol-4 in yields of 78 and 18%, respectively, calculated on the converted α-propyltetrahydrofuran, and a little *n*-hexane.

For comparison, we carried out the isomerization of propylene oxide under the same conditions as those used for the isomerization of alkyltetrahydrofurans. The conversion per pass at a space velocity of 0.1 h^{-1} was about 30–40%. This shows that the α-oxide ring on Pt-C is isomerized to carbonyl compounds somewhat more readily than the γ-oxide ring. The formation of gaseous products was much more considerable than in the isomerization of alkyltetrahydrofurans. The liquid catalyzate, in addition to unconverted propylene oxide, contained acetone (95%) and propionaldehyde (4%), calculated on the converted α-oxide. These results show that platinized charcoal, to a greater extent than other catalysts ([1]), promotes the isomerization of unsymmetrical α-oxides into aliphatic ketones.

Experimental Part

Starting materials. Pure tetrahydrofuran was isolated from the technical product by distillation on an efficient column in the presence of sodium. α-Methyl-, α-ethyl-, and α-propyltetrahydrofurans were obtained by hydrogenation of the corresponding alkylfurans over palladized charcoal in the vapor phase at 130–150°. The properties of tetrahydrofuran and its homologs are presented in Table 1.

Table 1

Properties of tetrahydrofuran and its homologs

Tetrahydrofurans	B.p., °C/mm Hg	d_4^{20}	n_D^{20}
Tetrahydrofuran	65–66°/755	0.8886	1.4070
Tetrahydrosilvan	79–79.2°/750	0.8582	1.4060

Tetrahydrofurans	B.p., °C/mm Hg	d_4^{20}	n_D^{20}
α-Ethyltetrahydrofuran	106.5-107°/742	0.8556	1.4163
α-Propyltetrahydrofuran	131.5-132.5°/750	0.8562	1.4232

Catalyst. Platinized charcoal containing 15% platinum was prepared by impregnating activated charcoal with a solution of chloroplatinic acid and subsequently reducing it in a glass tube at 250–300°.

Table 2

Properties of the products of isomerization of γ-oxides

Isomerization products	B.p., °C/750 mm Hg	d_4^{20}	n_D^{20}
Butanol-1	116-117	0.8186	1.4004
Pentanone-2	101-102	0.8081	1.3905
Hexanone-3	123-124	0.8169	1.4006
Heptanone-4	142.5-143	0.8176	1.4085
Heptanol-4	153-155	0.8213	1.4198

Isomerization reaction of γ-oxides was carried out in the vapor phase at 235–250°. In each experiment 50 g of substance was taken and passed over the catalyst in a mixture with hydrogen, or without it, at a space velocity of 0.1 h^{-1}. The dried catalyzates were distilled on a column of efficiency 40 theoretical plates. The gaseous reaction products were analyzed in an Orsat-Lunge apparatus for their carbon monoxide content and by chromatography, where the composition and content of the saturated hydrocarbons were determined.

The properties of the products obtained in the isomerization of γ-oxides in the presence of hydrogen or without it are presented in Table 2.

Conclusions. 1. It has been established that the γ-oxide (tetrahydrofuran) ring is capable of isomerizing in the vapor phase on platinized charcoal with cleavage of the ring at the C-O bonds, as a result of which aliphatic carbonyl compounds are formed.

2. In the presence of an alkyl radical (CH_3, C_2H_5, n-C_3H_7) in the α-position of the tetrahydrofuran ring, isomerization of the γ-oxide proceeds mainly (by 90-95%) with opening of the ring at the C—O bond farthest from the side substituent, which leads to the formation of the corresponding aliphatic ketones.
3. The aldehydes formed in small amount during the isomerization of tetrahydrofuran and α-alkyltetrahydrofurans with cleavage at the C—O bond,

1–2, undergo decarbonylation under the reaction conditions to the corresponding paraffinic hydrocarbons.

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

Received
11 I 1958

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