CATALYTIC TRANSFORMATIONS OF 1,6-DIOXASPIRO[4.4]NONANES

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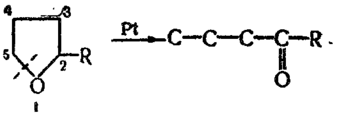
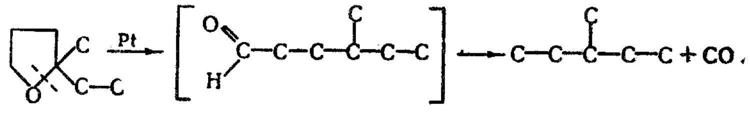
It was shown recently that γ-epoxides (tetrahydrofurans) may be isomerized into aliphatic carbonyl compounds in the vapor phase over catalysts containing Group VIII metals [1]. 2-Alkyltetrahydrofurans are isomerized with opening of the ring mainly at the 1,5 ether link that is not adjacent to the alkyl substituent, and are converted into aliphatic ketones

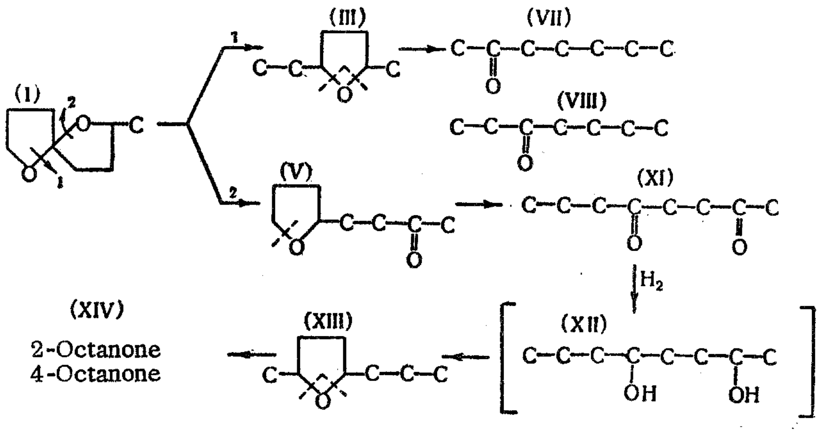


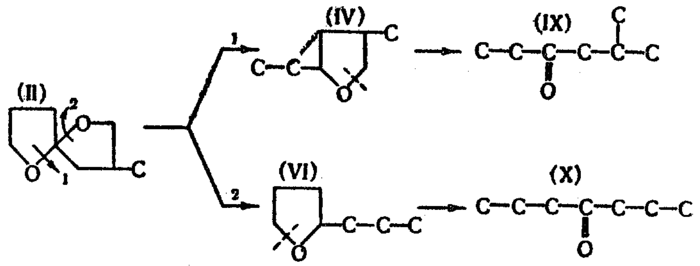
With increase in the length of the alkyl group R, and rise in the reaction temperature, there is an increased tendency for the tetrahydrofuran ring to isomerize at the 1,2-C – O link adjacent to the alkyl group [2]. 2,2-Dialkyltetrahydrofurans are isomerized in only one direction: at the C – O link adjacent to the alkyl groups [2]:



The aldehydes cannot be isolated, for they are readily decarbonylated to hydrocarbons. This case is similar to that of the transformations of 1,6-dioxaspiro[4.4]nonanes, which were studied in the present investigation.

We synthesized two 1,6-dioxaspiro[4.4]nonane homologs: 2- and 3-methyl-1,6-dioxaspiro[4.4]nonanes. The transformations of these compounds were investigated under the conditions under which the isomerization of the tetrahydrofuran ring occurs, i.e., in the vapor phase over platinized charcoal at 300-320°. The conformation conditions existing in 1,6-dioxaspiro[4.4]nonane molecules are, to a certain extent, analogous to those found in 2,2-dialkyltetrahydrofurans, so that it may be regarded as very probable that the opening of the tetrahydrofuran rings comprising the spiran molecule will proceed at C – O links formed between the spiro carbon atom and the ether oxygen. This leads to the following scheme of transformations, which was confirmed by our experiments:





The primary reaction in the scheme of the transformations of 1,6-dioxaspiro[4.4]nonanes is the isomerization of one of the tetrahydrofuran rings with formation of mono- and di-substituted tetrahydrofurans. Experiment shows that the tetrahydrofuran ring which does not contain the alkyl substituent isomerizes somewhat more readily. Thus, 2-methyl-1,6-dioxaspiro[4.4]nonane (I) gives 60-65% of the heptanones (VII) and (VIII), and 3-methyl-1,6-dioxaspiro[4.4]nonane (II) gives about the same amount of 5-methyl-3-hexanone (IX). It is readily seen that, if it is the tetrahydrofuran ring not containing an alkyl substituent which first isomerizes in 1,6-dioxaspiro[4.4]nonanes, then there will be formed tetrahydrofuran aldehydes, which after decarbonylation will give the dialkyltetrahydrofurans (III) and (IV). A more fundamental difference is found when the primary reaction in the transformations of 1,6-dioxaspiro[4.4]nonanes is the tetrahydrofuran ring containing the alkyl substituent. In this case, from 2-methyl-1,6-dioxaspiro[4.4]nonane, 4-(tetrahydro-2-furyl)-2-butanone (V) is formed, and 3-methyl-1,6-dioxaspiro[4.4]-nonane gives a tetrahydrofuran aldehyde, which is decarbonylated to give tetrahydro-2-propylfuran (VI). Since the platinum catalyst used in our experiments is extremely effective in the isomerization of the tetrahydrofuran ring, then, as would be expected, the tetrahydrofuran homologs formed are isomerized into the aliphatic ketones (VII)-(X), and 4-(tetrahydro-2-furyl)-2-butanone is converted into 2,5-octanedione (XI). To a very small extent this γ -diketone may undergo various further transformations attributable to the presence of hydrogen adsorbed by the catalysts during its reduction. From 2,5-octanedione there is successive formation of 2,5-octanediol (XII), tetrahydro-2-methyl-5-propylfuran (XIII), and the octanones (XIV). Such conversion of 2,5-octanedione into octanones becomes more appreciable when 1,6-dioxaspiro[4.4]nonanes are passed in the vapor state over the catalyst in admixture with hydrogen. The other transformations of 1,6-dioxaspiro[4.4]nonanes are not affected by the presence or absence of hydrogen.

Thus, in the vapor phase over a platinum catalyst, 2- and 3-alkyl-1,6-oxaspiro[4.4]nonanes undergo the following transformations: First one of the tetrahydrofuran rings isomerizes and, as a result, tetrahydrofuran homologs and tetrahydrofuran ketones are formed (the latter are obtained from 2-alkyl-1,6-dioxaspiro[4.4]nonanes); then the tetrahydrofuran homologs and tetrahydrofuran ketones formed are isomerized into aliphatic ketones and γ -diketones, respectively.

EXPERIMENTAL

2-Methyl-1,6-dioxaspiro[4.4]nonane was prepared in about 15% yield by the hydrogenation of 4-(2-furyl)-3-buten-2-one in an autoclave over a skeletal nickel–aluminum catalyst at 120-140°; b.p. 163-165° (758 mm); $n^{20}D$ 1.4435; d^{20}_4 0.9928. 3-Methyl-1,6-dioxaspiro[4.4]nonane was prepared in about 12% yield by the hydrogenation of α-methyl-2-furanacrolein in an autoclave over a skeletal copper–aluminum catalyst at 120-140° [3]; b.p. 58.5-60° (15 mm); $n^{20}D$ 1.4452; d^{20}_4 0.9966.

The catalyst was platinized charcoal, and was prepared by impregnation of activated birch charcoal with chloroplatinic acid solution with subsequent reduction with hydrogen in a reaction tube at 250-300°. The catalyst contained 10% of platinum.

1,6-Dioxaspiro[4.4]nonanes were passed in the vapor state over the catalyst at 300-320°. The catalyst (50 ml) was placed in a quartz tube. The temperature was measured with a chromel–alumel thermocouple placed in the middle of the catalyst layer. In the experiments we took 50 g of each 1,6-dioxaspiro[4.4]nonane homolog. This was fed to the catalyst at a space velocity of 0.1 hr^{-1}. After being dried with calcium chloride, the catalyzates were fractionated through a column. The content of mono- and di-oxo compounds in the catalyzates was 90-95%. From the catalyzate of 2-methyl-1,6-dioxaspiro[4.4]nonane we isolated a fraction of b.p. 146-150° (750 mm). The semicarbazone prepared from it had m.p. 113-114°. This fraction therefore contained mainly 2-heptanone [2]. The other product obtained from 2-methyl-1,6-dioxaspiro[4.4]nonane was 2,5-octanedione, which had the following properties: b.p. 70-72° (2 mm); $n^{20}D$ 1.4430; d^{20}_4 0.9635. From 3-methyl-1,6-

dioxaspiro[4.4]nonane we obtained: 5-Methyl-3-hexanone; b.p. 132-133° (740 mm); $n^{20}D$ 1.4070, d^{20}_4 0.8131; semicarbazone, m.p. 152°. 4-Heptanone; b.p. 142-143° (740 mm); $n^{20}D$ 1.4085, d^{20}_4 0.8180; semicarbazone, m.p. 131-132°.

SUMMARY

In the vapor phase over platinized charcoal at 300-320°, 2- and 3-alkyl-1,6-dioxaspiro[4.4]nonanes undergo the following transformations: isomerization of one of the tetrahydrofuran rings with formation of tetrahydrofuran oxo compounds, decarbonylation of tetrahydrofuran aldehydes, and isomerization of tetrahydrofuran homologs and tetrahydrofuran ketones to give aliphatic ketones and γ-diketones, respectively.

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