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MUTUAL CATALYTIC CONVERSIONS OF UNSUBSTITUTED FURAN AND PYRAN SYSTEMS

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The conversions of furan, di- and tetrahydrofuran, and di- and tetrahydropyran on a molybdenum catalyst in a hydrogen atmosphere have been investigated. The studied cyclic systems readily undergo mutual conversions at 125-215°C and also undergo a hydrogenation-dehydrogenation reaction. Expansion of the unsubstituted furan rings to pyran without the introduction into the reaction medium of components capable of generating methyl radicals are described by us for the first time.

The chemistry of the simplest oxygen containing five- [1, 2] and six- [1, 3] membered heterocyclic systems have been quite widely studied. These compounds find broad usage in fine organic synthesis and also (in particular tetrahydrofuran) in other branches of the chemical industry. Exceptions are the unsubstituted pyrans [4, 5]; 4-H pyran being obtained only in 1962 [6, 7] and 2H-pyran not obtained at all. The mutual interconversions of these heterocyclic systems have been quite inadequately studied. If the reactions leading to ring contraction (pyran—furan) are more or less known then for ring expansion (furan—pyran) there are relatively few examples. Such reactions are observed if 2-methyl derivatives [8, 9] are used as starting materials or there are present in the reaction medium components able to generate methyl radicals (the synthesis of tetrahydropyran from tetrahydrofuran over a ruthenium catalyst in the presence of CO and H_2 is reported in [10]).

We have shown that five- and six-membered oxygen containing heterocycles are readily mutually interconverted without any other components in the reaction medium by passage over a molybdenum catalyst in a stream of hydrogen.

The results of the conversion of furans and pyrans at 200°C are given in Table 1.

As shown in the data obtained, the investigated 5- and 6-membered heterocycles are readily interconverted by reduction with the molybdenum catalyst; in all cases the reaction mixture contained all five compounds. There are also formed small amounts of low-molecular-weight decomposition products. The highest reactivity on the molybdenum catalyst is shown by furan and dihydrofuran and the lowest by tetrahydrofuran. The saturated heterocyclic

TABLE 1. Catalyzate Composition for the Conversion of Furan and Pyran Compounds over 1% MoO_3 on Corundum at 200°C

Starting product	Catalyzate composition, mass %						
	Furan	Dihydrofuran	Tetrahydrofuran	Dihydropyran	Tetrahydropyran	Decomposition products	Unidentified products
Furan	5,2	20,4	28,4	25,1	19,4	1,5	—
Dihydrofuran	9,4	4,4	38,1	33,6	14,2	0,3	—
Tetrahydrofuran	26,2	19,0	39,0	6,4	8,1	0,4	0,9
2,3-Dihydropyran	26,5	9,5	25,6	18,2	18,3	0,6	1,4
Tetrahydropyran	2,9	4,0	5,8	66,7	18,3	2,3	—

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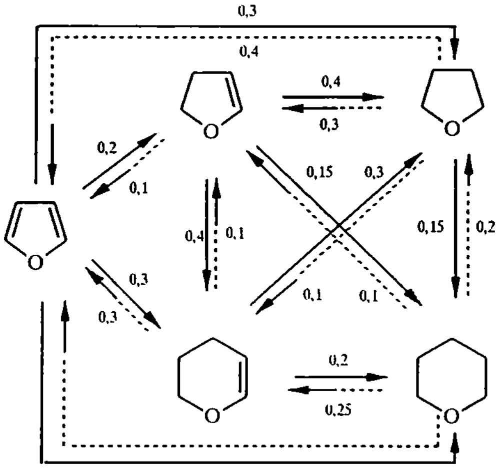
compounds basically undergo a dehydrogenation reaction but the unsaturated heterocycles react via hydrogenation and ring transformation. Moreover, in the case of furan the products of hydrogenation and of homologation to the pyran series occur in approximately equal amounts but, by contrast, for dihydrofuran and dihydropyran the transformation products of the five- to the six-membered ring and the inverse predominate. Comparison of the amounts of the furan—pyran and pyran—furan products formed suggests that the ring contraction reaction occurs more readily. The yield of products of the conversion of 2,3-dihydropyran to furan compounds is around 62% whereas that of the reaction of furan heterocycles to pyrans is 45-49%.

Even though the qualitative composition of the reaction mixture is comparatively simple (in all cases only four basic compounds are formed), quite a complex process is taking place. There occur simultaneously hydrogenation and dehydrogenation; molecular fission and condensation of the fragments formed; and ring contraction and expansion. Hence a smooth change in the composition of the catalyzate when increasing the reaction temperature from 125-215°C is not observed. There was noted only a tendency for an increase in the mutual transformation of the five-membered to six-membered rings and the inverse with increase in temperature.

As a result of what has been said, we propose the following scheme for the furan—pyran transformations (the relative partial degrees of conversion to the corresponding products are indicated by arrows).



It was interesting to find that expansion of the ring from five- to six-membered occurred without the introduction into the reaction mixture of any kind of carbon containing material. We propose that this reaction can occur through the insertion into the cyclic system of the furan of carbon radicals formed by fission of part of a molecule of a starting material.

The discussed reaction has been observed by us for the first time and its study, in particular an investigation of the mechanism of ring expansion, is of particular interest.

EXPERIMENTAL

The molybdenum catalyst used for the experiments was prepared by application of molybdenum trioxide at a 1% level to corundum with subsequent reduction using hydrogen at 350°C. The reaction was carried out in a catalytic, continuous flow micro reactor in a stream of hydrogen (80 cm^3/min) at 125-215°C. Analysis of the reaction products was performed using gas liquid chromatography on a Biochrom-1 instrument. The columns used (2 m × 0.25 cm) contained Apiezon M (20% on Celite 545) or polyethyleneglycol 2000 (20% on Celite 545).

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