

SOV/ 20-120-3-31/67

Isomeric Transformation of  $\gamma$ -Oxides (Tetrahydrofuranes) of Aliphatic Carbonyl Compounds

There are 2 tables and 7 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR  
(Institute of Organic Chemistry imeni N. D. Zelinskiy AS USSR)

SUBMITTED: January 11, 1958

1. Furan derivatives--Isomerism 2. Aliphatic compounds--Chemical reactions  
3. Carbonyls--Chemical reactions.

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**AUTHORS:** Shuykin, N. I., Corresponding Member, SOV/20-122-4-24/57  
Academy of Sciences, USSR, Bel'skiy, I. F.,  
Karakhanov, R. A.

**TITLE:** On the Reaction Mechanism of the Furane Cycle Catalytic  
Hydrogenolysis (O mekhanizme reaktsii kataliticheskogo  
gidrogenoliza furanovogo tsikla)

**PERIODICAL:** Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 4, pp 625 -  
628 (USSR)

**ABSTRACT:** The problem whether the reaction mentioned in the title  
passes the hydration stage of double bonds of the cycle,  
i.e. with a subsequent cleavage of the formed tetra-  
hydrofurane cycle at one of the C-O-bonds, was raised  
several times. This problem was rejected by several scien-  
tists (Refs 1 - 3). It was proved that the tetra-hydro-  
furane-cycle does not hydrogenolyze at all under the condi-  
tions of the hydration in the liquid phase, whereas the  
furane cycle hydrogenolyzes to a great extent. The authors  
proved recently (Ref 6) that the homologs of tetra-hydro-  
furane can be isomerized on Rt-coal at 250 - 300° in  
aliphatic ketones. However, this reaction passes much more

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On the Reaction Mechanism of the Furane Cycle  
Catalytic Hydrogenolysis

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slowly than an immediate hydrogenolysis of the alkyl furanes themselves under the same conditions. Therefore, the tetrahydrofuranes cannot be considered to be intermediate products in the hydrogenolysis reaction of the furane compounds. All mentioned investigations led thus to the conclusion that the hydrogenolysis of the C-O-bond may take place either in the cycle of furane itself or in the dihydrofurane cycle. The formation of the latter as an intermediate product is confirmed by the transformation of silvane into  $\gamma$ -acetone-propylalcohol in the presence of water (Ref 7). In the present paper the authors investigated the hydration of the dihydrosilvane in the gaseous phase on platinized charcoal and on nickel to zinc oxide at 250 - 260°. Thus it was proved that not the hydrogenolysis of the C-O-bond, but the hydration of the C-C-bond in the cycle is the main reaction. The formation of methyl-propylketone in the hydration of the dihydrosilvane on Pt-C may take place in consequence of a secondary isomerization reaction of tetra-hydrosilvane. Tetra-hydrosilvane is not isomerized to methyl-propylketone on Ni-ZnO. The above results are interpreted differently

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On the Reaction Mechanism of the Furane Cycle  
Catalytic Hydrogenolysis

SOV/20-122-4-24/57

by the authors. There are 13 references, 3 of which are  
Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii  
nauk SSSR (Institute of Organic Chemistry imeni  
N. D. Zelinskiy, AS USSR)

SUBMITTED: June 20, 1958

Card 3/3

AUTHORS: Shuykin, N. I., Bel'skiy, I. F. SOV/79-29-2-19/71

TITLE: Hydrogenation of Furane Compounds Over the Ni-ZnO Catalyst  
(Gidrirovaniye furanovykh soyedineniy na Ni-ZnO-katalizatore)

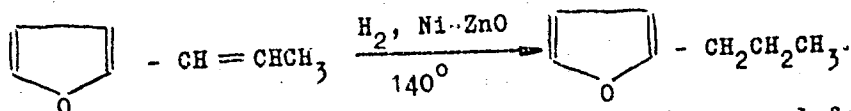
PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 442-445 (USSR)

ABSTRACT: Investigations carried out by Shuykin and other chemists (Refs 1-5) show that the properties of nickel catalysts are considerably dependent on the nature of the carrier. This is confirmed by the present investigation. The authors found that nickel stored upon ZnO hydrogenates the double bond in the side chain of  $\alpha$ -alkenyl furane under conditions of hydrogenation in the vapor phase or, at higher temperatures, it allows hydrogenolysis of the furane cycle to take place only on the bond C-O, which is not close to the alkyl radical. This catalyst does not have the function of hydrogenating the double bonds in the furane cycle in the vapor phase. Thus, for example, silvane, that had been left over the above catalyst at 140°, was not transformed. Under the same conditions,  $\alpha$ -propenyl furane was hydrated almost quantitatively into  $\alpha$ -propyl furane:

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SOV/79-29-2-19/71

## Hydrogenation of Furane Compounds Over the Ni-ZnO Catalyst



The hydrogenation of silvane, of  $\alpha$ -ethyl and  $\alpha$ -propyl furanes at  $250^\circ$  led to the complete cleavage of the cycle at the C-O bond 1-5 and, correspondingly, to the formation of pentanone-2, hexanone-3 and heptanone-4 (up to 95% yield) (Scheme 2). Thus, depending on temperature, the Ni-ZnO catalyst hydrogenates the olefin bond in the side chain of the alkenyl furanes in the selective way, or it may allow hydrogenolysis of the furane cycle at the C-O bond, which is not close to the alkyl radical. In the latter case, corresponding aliphatic ketones in yields up to 95% form at  $250^\circ$ . There are 1 table and 10 references, 5 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: November 28, 1957  
Card 2/2

5 (3)  
AUTHORS:

SOV/79-29-3-25/61  
Shuykin, N. I., Bel'skiy, I. F., Savekina, O. N.

TITLE:

Hydrogenation of Silvan on Nickel Catalysts in the Liquid Phase  
(Gidrirovaniye sil'vana na nikelevykh katalizatorakh v zhid-  
koy faze)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 869-874 (USSR)

ABSTRACT:

In the present paper the authors investigated the hydrogenation capability of the skeleton-Ni-Al- and -Ni-ZnO-catalyst in the liquid phase to determine the influence of the phase conditions in carrying out the reaction upon the hydrogenation of the furan ring. The experimental data obtained were compared with the rules which were earlier found by the authors on hydrogenation of the furan homologues on the same catalysts in the vapor phase. These data led to the conclusion that the hydrogenation of the furan ring can proceed on one and the same catalyst in different directions, according to the reaction in the liquid or vapor phase; Silvan and  $\alpha$ -propenyl furan were hydrogenated in the autoclave at 120-150° under a hydrogen pressure of 50-150 atmospheres excess pressure on the skeleton-Ni-Al-catalyst. The principal reaction products were, accord-

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SOV/79-29-3-25/61

## Hydrogenation of Silvan on Nickel Catalysts in the Liquid Phase

ingly, tetrahydrosilvan and  $\alpha$ -propyltetrahydrofuran (85-95%). On this hydrogenation of silvan in addition to tetrahydrosilvan (90%) the pentanediol-1,4 is formed, in which connection a certain part of the silvan molecule is subject to cleavage, forming  $H_2O$  and high-molecular compounds. Under the above reaction conditions, but on addition of water, about the same quantities of tetrahydrosilvan and pentanediol-1,4 are formed as well as about 7% of butanol-2 and pentanol-2 which are products of hydrogenolysis of the ring. The hydrogenolysis of the furan ring in silvan on hydrogenation on the skeleton-nickel-catalyst at 120-150° in the liquid phase proceeds similarly as in the vapor phase, i.e. on the C-O-bond 1-5 and on the bonds 1-5 and 4-5, yielding pentanol-2 and butanol-2, accordingly. The nickel on the ZnO is capable of hydrogenating the double bonds in the furan ring in the liquid phase at 200-250°, as contrasted with the vapor phase. Here, hydrogenolysis of the ring takes place only on the C-O-bond 1-5 yielding pentanone-2 as principal product which is not the case on the other catalysts. Thus the direction of the hydrogenation of the furan ring depends on the nature of the catalyst

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SOV/79-29-3-25/61

Hydrogenation of Silvan on Nickel Catalysts in the Liquid Phase

and on the phase conditions of the reaction. There are 1 table and 9 references, 7 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: December 20, 1957

Card 3/3

E, (3)

AUTHORS:

Shuykin, N. I., Bel'skiy, I. F.

SOV/79-29-3-26/61

TITLE:

Catalytic Reduction of the Phenyl Carbinols in Aromatic Hydrocarbons (Kataliticheskoye vosstanovleniye fenilkarbinolov v aromaticheskiye uglevodorody)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 875-877 (USSR)

ABSTRACT:

If R in the compounds of the R-CH- $\overset{\text{OH}}{\text{Alk}}$  type represents an

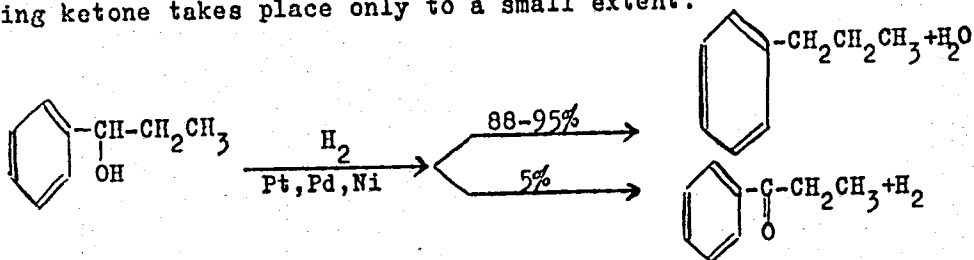
alkyl, no reduction of the hydroxyl group takes place on the catalysts Pd-C and Ni-ZnO, but more or less a dehydrogenation of the alcohol into the ketone. The question was of which chemical nature R should be, in order that an activated hydrogen could be substituted for the hydroxyl group by the catalytic method. The results of the investigations reported in the present paper show that with  $\text{R}=\text{C}_6\text{H}_5$ , using the catalysts Pt-C, Pd-C, Ni-ZnO and skeleton-Ni-Al, at 250° in the vapor phase a reduction of the hydroxyl group and a transformation of the phenyl carbinols into the aromatic hydrocarbons take place. Thus, e.g. ethyl phenyl carbinol is reduced at 250° in the vapor phase on all catalysts used to propyl benzene (yield 88-95%). On the Ni-Al-catalyst in addition to propyl

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SOV/79-29-3-26/61

## Catalytic Reduction of the Phenyl Carbinols in Aromatic Hydrocarbons

benzil benzene (3%) and toluene (3%) are formed, owing to the hydrolysis process of the C-C-bonds in the side chains. The dehydrogenation of ethyl phenyl carbinol to the corresponding ketone takes place only to a small extent:



The catalytic reduction of benzene alcohol proceeds under the same conditions yielding toluene and dehydrogenation to benzaldehyde which is readily decarbonylated into benzene at 250°. The aliphatic alcohols (pentanol-2 and heptanol-1) are not reduced on the platinum and nickel catalyst, but, accordingly, dehydrogenated to give pentanone-2 and heptanal, with the latter being decarbonylated to n.-hexane (Scheme 2). There are 1 table and 1 Soviet reference.

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SOV/79-29-3-26/61

Catalytic Reduction of the Phenyl Carbinols in Aromatic Hydrocarbons

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR  
(Institute of Organic Chemistry of the Academy of Sciences,  
USSR)

SUBMITTED: December 20, 1957

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5(3)

SOV/79-29-4-10/77

AUTHORS:

Shuykin, N. I., Bel'skiy, I. F.

TITLE:

Hydrogenation of Furan Compounds on Platinum and Rhodium Catalysts (Gidrirovaniye furanovykh soyedineniy na platinovom i rodiyevom katalizatorakh)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1093-1096 (USSR)

ABSTRACT:

The hydrogenation results of furan compounds in the presence of catalysts containing metals of the group VIII of the periodic system lead to the conclusion that some of them are active predominantly in the hydrogenolysis of the double bond in the furan ring, and others develop a high activity in the hydrogenolysis of the ether bonds of the furan ring. As regards the action of the catalysts also the phases and temperatures play an important part in one and the same catalyst. Many examples are presented for this fact which underline that in general the comparison data on the properties of the catalysts can only be obtained under certain standard conditions during the reaction. For this reason the hydrogenation of silvan and  $\alpha$ -vinyl furan on rhodium deposited on active charcoal in the vapor phase at 150, 200, and 300° was investigated. For comparison purposes also the hydro-

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## Hydrogenation of Furan Compounds on the Platinum- and Rhodium Catalyst

SOV/79-29-4-10/77

genation of silvan and  $\alpha$ -propenyl furan on platinated charcoal in the vapor phase at 150° was carried out. On the rhodium catalyst at 150° the furan ring hydrogenates very slowly which makes it possible to reduce the olefin bond in the side chain, maintaining the double bonds in the ring.  $\alpha$ -vinyl furan is transformed at this temperature into  $\alpha$ -ethyl furan (90% yield) (Scheme 1). The hydrogenation of silvan on Rh-C at 200° yields a mixture of tetrahydrosilvan (40%) and pentanone-2 (60%); at 300° only pentanone-2 is found in the hydrogenation products (Scheme 2). Similar results are offered by the hydrogenation products of both compounds on Pt-C at 150°. The Pd-C catalyst is found to be a specific catalyst of the hydrogenolysis of double bonds in the furan ring during the hydrogenation in the vapor phase (140-275°). The Pt-C catalyst proved to be a specific catalyst of the hydrogenolysis of the furan ring on the C-O-bond 1-5 under the given conditions. The effect of the Rh-C catalyst is equal to that of the Pt-C catalyst at 300°; at 200° it assumes an intermediary position between Pd-C and Pt-C as far as its properties are concerned. There are 1 table and 7 references, 6 of which are Soviet.

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Hydrogenation of Furan Compounds on the Platinum- and Rhodium Catalyst

SOV/79-29-4-10/77

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: March 6, 1958

Card 3/3

5(3)

AUTHORS:

Shuykin, N. I., Bel'skiy, I. F.

SOV/79-29-4-11/77

TITLE:

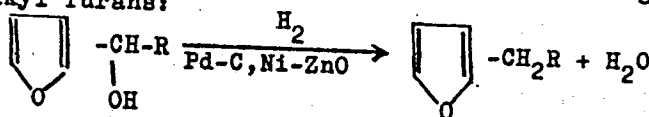
Catalytic Reduction of 2-Methyl-5-acetyl Furan  
Into 2-Methyl-5-ethyl Furan (Kataliticheskoye  
vosstanovleniye 2-metil-5-atsetilfurana v 2-metil-5-etilfuran)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1096-1099  
(USSR)

ABSTRACT:

In addition to the reports of some chemists (Refs 1 - 6) on the part played by various catalysts under different conditions in the hydrogenation of furan ketones the authors investigated in the present paper the hydrogenation of 2-methyl-5-acetyl furan in the vapor phase at 250° on the catalysts Ni-ZnO, Ni-CdO and Pd-C. As was already earlier shown by the authors (Ref 7), on the hydrogenation of alkyl furyl carbinols on Pd-C and Ni-ZnO first the reduction of the hydroxyl group takes place, under forming the corresponding alkyl furans:



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Catalytic Reduction of 2-Methyl-5-acetyl Furan  
Into 2-Methyl-5-ethyl Furan

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As was to be expected, on the hydrogenation of the 2-methyl-5-acetyl furan the resulting methyl-(5-methylfuryl)-carbinol on Ni-ZnO and Ni-CdO in the vapor phase at 250° was subject to a further reduction into the 2-methyl-5-ethyl furan (Scheme 2), in contrast with the Pd-C catalyst nearly ineffective as regards the reduction of the carbonyl group and the hydrogenolysis of the furan ring into the 2-methyl-5-acetyl furan. As side reaction on the hydrogenation of the 2-methyl-5-acetyl furan on Ni-ZnO the hydrogenolysis of the ring takes place, thus yielding heptanone-2, which is scarcely the case on Ni-CdO (Scheme 3). The definite solution of this problem requires further investigations. The direct catalytic reduction of alkyl furyl ketones into alkyl furans may be of preparative importance since it is more convenient than the method of Kizhner (Ref 8) by way of the hydrazones, with subsequent reduction of these intermediate products. There are 9 references, 4 of which are Soviet.

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Catalytic Reduction of 2-Methyl-5-acetyl Furan  
Into 2-Methyl-5-ethyl Furan

SOV/79-29-4-11/77

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR  
(Institute of Organic Chemistry of the Academy of Sciences,  
USSR)

SUBMITTED: March 6, 1958

Card 3/3

5(3)

AUTHORS:

Shuykin, N. I., Bel'skiy, I. F., Grushko, I. Ye. SOV/79-29-6-23/72

TITLE:

On the Reaction of Tetrahydrofuran With Halogen Silanes (O vzai-  
modeystvii tetragidrofurana s galoidsilanami)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 6,  
pp 1882 - 1885 (USSR)

ABSTRACT:

From among all organic oxides those chemical transformations of the ethylene oxides are investigated most thoroughly, which yield the aliphatic compounds with reactive groups by the ready opening of the  $\alpha$ -oxide ring under the influence of various agents. Far less investigated are the chemical transformations of the  $\gamma$ -oxides of tetrahydrofuran and its homologs. They possess a considerably lower reactivity and are of great importance for the organic synthesis since they can yield the 1,4-bifunctional derivatives of the aliphatic series: the dihalogen-alkanes, dinitriles, glycols, halogen-hydrins; besides the tetrahydrofuran derivatives are a sufficiently accessible and cheap material. In the present paper the reaction of tetrahydrofuran with alkyl- and aryl-chloro-silanes with two or three chlorine atoms in the molecule was investigated. It takes place only in the presence

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On the Reaction of Tetrahydrofuran With Halogen Silanes SOV/79-29-6-23/72

of anhydrous zinc (II) chloride in different directions according to the number of chlorine atoms in the chloro silane molecule. Methyl-dichloro-silane and dimethyl-dichloro-silane split up the tetrahydrofuran ring at both C-O bonds with 1,4-dichloro-butane being formed as main product (Scheme 1). In contrast to the dichloro-silanes the reaction of tetrahydrofuran with alkyl and aryl-trichloro-silanes takes place with ring opening only at one C-O-bond and yields the chlorine-substituted ester of the ortho-silicic acid (Scheme 2). In all cases the yields in mono-( $\delta$ -chloro-butoxy)-dichloro-silanes are very high (80-90%). Two chlorine atoms in the molecule of the mono ( $\delta$ -chlorobutoxy)-dichloro-silane are active, but react mainly under formation of 1,4-dichloro-butane (Scheme 3). An interpretation of this reaction is suggested. The compounds synthesized are listed in two tables. There are 2 tables and 11 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: April 18, 1958

Card 2/2

5(3)

AUTHORS:

Shuykin, N. I., Bel'skiy, I. F., Grushko, I. Ye.

SOV/79-29-8-29/81

TITLE:

On the Reaction of Tetrahydrosilvane With Silicon Tetrachloride

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 8,  
pp 2591 - 2594 (USSR)

ABSTRACT:

In the present paper, the authors investigated the reaction of tetrahydrosilvane with silicon tetrachloride. This reaction takes place only in the presence of anhydrous zinc chloride. The reaction products underwent an intense decomposition in the vacuum distillation. For this reason, they were previously subjected to a hydrolysis with water. The products of this hydrolysis had to be fractionated at reduced pressure with a column top section. In this connection, the 1,4-dichloropentane (15-20%) and the chlorine-substituted amyl alcohol (70-80%) were separated, the latter of which was likewise obtained on hydrolysis of the chlorine esters of silicic acid (Scheme 1). Depending on the cleavage of the C-O bond in position 1-2 or 1-5, the alcohol can be formed with a primarily (I) or secondarily (II) bound hydroxyl group (4-chloro-pen-

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On the Reaction of Tetrahydrosilvane With Silicon  
Tetrachloride

SOV/79-29-8-29/81

tanol-1 or 5-chloro-pentanol-2). The structure of the chlorohydrin obtained by hydrolysis was confirmed according to the transformations of scheme 2. The reducing dehalogenation of 2-chloro-5-acetoxy-pentane (III) on platinized carbon in the vapor phase proceeds smoothly and with high yields (95%) at the primary amyl acetate (IV). The chlorohydrin obtained by hydrolysis of the reaction products of tetrahydrosilvane with  $\text{SiCl}_4$  thus represents the 4-chloro-pentanol-1. This means that the ring in the tetrahydrosilvane is cleft at the C-O bond adjoining the methyl group, under the influence of  $\text{SiCl}_4$ . There are 10 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: July 4, 1958

Card 2/2

3(5)

SOV/79-29-9-34/76

AUTHORS:

Shuykin, N. I., Bel'skiy, I. F., Minachev, Kh. M.

TITLE:

Hydrogenation of the Furan Compounds by Means of Metals.  
VIII. Groups of the Periodic System

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2969-2973 (USSR)

ABSTRACT:

Owing to the results of previous investigations (Refs 1-5) the problem arose which of the metals of group VIII are like palladium, capable of bringing about the catalytic hydrogenation of the furan cycle in a wide temperature range, and which of them are the most active ones. The catalytic properties of osmium, iridium, and ruthenium, applied to carbon, were investigated in the hydrogenation of silvane and  $\alpha$ -vinyl furan in the vapor phase and at various temperatures.  $\alpha$ -Vinyl furan is hydrogenated on all these catalysts at 150° into  $\alpha$ -ethyl furan in yields of 95-100% (Scheme 1). On Ir-C and Ru-C a small portion (~5%) of  $\alpha$ -ethyl furan formed is subjected to hydrogenolysis on the C-O bond 1-5 (Scheme 2). Hydrogenation of silvane on Os-C, Ir-C, Ru-C at higher temperatures shows that these catalysts are not able to reduce the furan cycle, but are only capable of hydrogenolysis on the C-O bond 1-5 under the formation of the

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SOV/79-29-9-34/76  
Hydrogenation of the Furan Compounds by Means of Metals. VIII. Groups of the Periodic System

methylpropyl ketone (Scheme 3). The results of this paper as well as those already previously obtained permit to draw some general conclusions. All catalysts containing metals of group VIII, applied to carbon could be in hydrogenation conditionally divided in the vapor phase under comparable temperature conditions into two groups, depending on their effect upon the furan cycle: 1) The catalysts of the platinum type (Pt, Os, Ir, Ru, Rh) show either a weak or practically no capability of hydrogenation of the double bond in the furan cycle. On these catalysts only hydrogenolysis of the furan cycle on the C-O bond 1-5 occurs at 200-300°. 2) The catalysts of the palladium type are in a sufficiently wide temperature range capable of hydrogenating the double bond in the furan cycle. Hydrogenolysis of this cycle occurs only at higher temperatures. There are 7 Soviet references.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

Card 2/3



5(3)

AUTHORS:

Shuykin, N. I., Bel'skiy, I. F.

SOV/79-29-9-35/76

TITLE:

On the Reaction of Propylene Oxide With Some Compounds Containing an Active Chlorine Atom

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2973-2975 (USSR)

ABSTRACT:

The present paper describes the investigation of the reaction of propylene oxide with  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ , and  $\text{PCl}_3$ . The two first chlorides were previously (Ref 9) used in the reaction with tetrahydrosilvane so that it was possible to compare their effects upon  $\alpha$ - and  $\gamma$ -oxides. The reaction products of propylene oxide with  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ , and  $\text{PCl}_3$  decomposed in distillation already at reduced pressure; for this reason they were subjected to hydrolysis. An analysis of the products yielded the following results: 1) The reaction with  $\text{AlCl}_3$  proceeds in a similar way as the reaction of tetrahydrosilvane (Ref 9), i.e. under the formation of 1,2-dichloro propane (Scheme 2). The products of hydrolysis do not contain chlorohydrin. 2)  $\text{PCl}_3$  and  $\text{TiCl}_4$  open propylene oxide on the C-O-bond next to the methyl

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SOV/79-29-9-35/76  
On the Reaction of Propylene Oxide With Some Compounds Containing an Active Chlorine Atom

group, which leads to unstable chlorine-substituted esters of phosphorous- and titanac acid. Hydrolysis of these esters yields 70-85% 2-chloropropanol-1 (Scheme 3). In order to prove the structure of the final product (chlorohydrin), the latter was transformed into the acetate which by reducing dehalogenation in the vapor phase over Pt-C at 300° could be smoothly quantitatively transformed into propyl acetate without difficulty (Scheme 4). This method of proving the structure of halohydrin is more convenient than the usual oxidation method. Titanium tetrachloride is known to cause a splitting of the  $\gamma$ -oxide cycle under elimination of the oxygen atom and formation of 1,4-dichloropentane in the reaction with tetrahydrosilvane.  $\text{PCl}_3$  and  $\text{TiCl}_4$  therefore have the same effect upon the  $\alpha$ -oxide cycle as the other acid chlorides of inorganic acids, e.g.  $\text{ACl}_3$ ,  $\text{SiCl}_4$ , etc. There are 11 references, 8 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)  
Card 2/3

SHUYKIN, N.I.; HBL'SKIY, I.F.

Hydrogenation of furan compounds on skeletal catalysts. Dokl.  
AN SSSR 125 no.2:345-347 Mr '59. (MIRA 12:4)

1. Chlen-korrespondent AN SSSR (for Shuykin). 2. Institut  
organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.  
(Furan) (Hydrogenation)

5(3)

AUTHORS:

Shuykin, N. I., Corresponding Member, SOV/20-125-5-27/61  
AS USSR, Bel'skiy, I. F., Karakhanov, R. A.

TITLE:

Thermal Isomerization of 2-Methyl-4,5-dihydrofuran to  
Methyl-cyclopropyl Ketone (Termicheskaya izomerizatsiya  
2-metil-4,5 digidrofurana v metiltsiklopropilketon)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 5,  
pp 1051-1052 (USSR)

ABSTRACT:

According to reference 1 2,3-dihydrofuran isomerizes at 375°  
to cyclopropane aldehyde. A small quantity of croton aldehyde  
is formed therein, which is partially decarbonylated to  
propylene under the experimental conditions. The gas  
development increases with rising temperature. The first  
reaction is reversible. The inequivalence of the C-O bonds  
depends in the dihydrofuran molecule only on the presence  
of the double bond. This very fact is bound to determine  
the place of rupture of the dihydrofuran ring. Wilson (Ref 1)  
assumed that 2,3-dihydrofuran behaves in the aforesaid  
isomerization like simple vinyl ethers. According to  
formal-structural considerations it is, however, clear that

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Thermal Isomerization of 2-Methyl-4.5-dihydrofuran to Methyl-cyclopropyl Ketone SOV/20-125-5-27/61

the formation of cyclopropane aldehyde in the rupture of the dihydrofuran ring is possible at the C-O bond 1.2 as well as at the C-O bond 1.5. Therefore the results of the isomerization of the 2.3-dihydrofuran cannot indicate definitely the place of rupture of the dihydrofuran ring. In the case of the isomerization of  $\alpha$ -alkyl-dihydrofurans two different products - aldehyde or ketone - are bound to be produced according to the C-O bond which has been ruptured. The authors tried to investigate the isomerization of such  $\alpha$ -alkyl-substituted 2.3-dihydrofurans mentioned in the title, the alkyl group of which is found at the double bond. They found that 2-methyl-4.5-dihydrofuran isomerizes to methyl-cyclopropyl ketone at 475 - 500° (Reaction II, see Scheme). Thus, the C-O bond 1.5 is ruptured and a new bond is formed between the C-atoms 3 and 5 and the keto-group in the side chain. The reaction carried out here is irreversible, in contrast with the isomerization of 2.3-dihydrofuran to cyclopropane aldehyde which is reversible. There are 2 references.

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Thermal Isomerization of 2-Methyl-4,5-dihydrofuran to Methyl-cyclopropyl Ketone. SOV/20-125-5-27/61

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: February 5, 1959

Card 3/3

5(3)

AUTHORS:

Bel'skiy, I. F., Shuykin, N. I.,  
Corresponding Member, AS USSR

SOV/20-127-1-23/65

TITLE:

Catalytic Isomerization of  $\delta$ -Oxides (Tetrahydropyrans) to Aliphatic Carbonyl Compounds (Kataliticheskaya izomerizatsiya  $\delta$ -okisey (tetragidropiranov) v alifaticheskkiye karbonil'nyye soyedineniya)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 1, pp 91-92 (USSR)

ABSTRACT::

Hitherto it has been assumed that the  $\gamma$ - and  $\delta$ -oxides cannot be isomerized by the opening of the ring to the compounds mentioned in the title, in contrast to the  $\alpha$ -oxides. The authors proved, however, (Ref 1) that this is possible as well in the case of the  $\delta$ -oxides (tetrahydrofuran and its homologs) in the vapor phase on platinized charcoal at 250°. They are transformed mainly into aliphatic ketones. The reaction of the  $\delta$ -oxides mentioned in the title could be carried out as well with an alkyl substituent in an  $\alpha$ -position at 300-350°, as was expected. The corresponding aliphatic ketones (yield 70-80 %) and alkanes (20-30 %) are formed also in this case (see Scheme). This speaks in favor of the fact that the isomerization of

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Catalytic Isomerization of  $\delta$ -Oxides (Tetrahydro-  
pyrans) to Aliphatic Carbonyl Compounds

SOV/20-127-1-23/65

$\alpha$ -alkyl-tetrahydropyrans proceeds like in the case of the  $\gamma$ -oxides, mainly by the opening of the ring of the C—O bond which is farthest away from the alkyl substituent (bond 1—6). The reaction proceeds as smoothly as that of the  $\gamma$ -oxides; the reaction products are the same. An analogy with the  $\gamma$ -oxides exists with respect to the easiness of opening (raskrytiye) of the ring as well. The transformation degree of the  $\delta$ -oxides into ketone and aldehydes was higher than that of the  $\gamma$ -oxides (50-60 % per passage over the catalyst), since their isomerization was carried out at a higher temperature. There are 2 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 18, 1959

Card 2/2



5 (3)

AUTHORS:

Shuykin, N. I., Corresponding Member  
AS USSR, Bel'skiy, I. F.

SOV/20-127-2-34/70

TITLE:

Hydrogenolysis of Carbonyl-containing Furan Compounds. Transformation of Alkyl-acyl-furans Into Six-membered Carbocyclic Compounds

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 359-361 (USSR)

ABSTRACT:

The direction of the hydrogenolysis of the furan ring depends on various factors, in the first place on the nature of the catalyst and on the properties of the lateral substituents (Refs 1-5). Strict conclusions on the influence of the latter on the mentioned direction of the ring cleavage are possible only on the strength of the comparison of experimental results obtained under equal conditions of phase state and pressure. In a previous paper (Ref 5) the authors found a ring aperture in the  $\alpha$ -alkyl-furans on Pt-C only at the C—O-bond at normal pressure which is not adjacent to the alkyl radical. Aliphatic ketones are formed here. In the present paper the hydration reaction of pyromucic acid-methyl-ester and 2-methyl-5-acetyl-furan was investigated under conditions completely analogous to the last mentioned ones. In this case the carbonyl-containing groups influence decisively

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Hydrogenolysis of Carbonyl-containing Furan Compounds. SOV/20-127-2-34/70  
Transformation of Alkyl-acyl-furans Into Six-membered Carbocyclic Compounds

the direction of the aperture of the furan ring. The effect of these groups is opposed to that of the alkyl radical. The hydrogenolysis mentioned in the title proceeds in all substances investigated easily and only at the C—O-bond adjacent to carbonyl-containing groups. The primary products produced by this are subjected to further changes in the vapor phase under the hydration conditions. This hydration is interesting not only from the theoretical point of view, but also opens new ways of catalytic synthesis of valuable compounds on the furfural base. The mentioned ester forms methyl butyrate with a yield of 95 % in the hydration on Pt-C at 275°. This is a decarbonylization product of the esters of the corresponding aldehyde acid produced meanwhile (see Scheme). 3-methyl-cyclohexanone, 3-methyl-cyclohexanol as well as metacresol are produced as main products from 2-methyl-5-acetyl-furan under the mentioned hydration conditions. This formation of carbocyclic compounds is based upon profound structural changes in the molecule of this heterocyclic ketone (2-methyl-5-acetyl-furan) and is certainly a result of several subsequent reactions (see Scheme). Thus a hydrogenolysis of the furan ring at the C—O-bond adjacent to the

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Hydrogenolysis of Carbonyl-containing Furan Compounds. SOV/20-127-2-34/70  
Transformation of Alkyl-acyl-furans Into Six-membered Carbocyclic Compounds

carbonyl group proceeds first on Pt-C (in contrast to Ni catalysts). This leads to the formation of carbocyclic compounds. A primary reduction of the carbonyl group in 2-methyl-5-acetyl-furan takes as well place on Pt-C, however, to a much lower extent than on Ni catalysts. An immediate transformation of I into IV and V (see Scheme) has obviously a general importance and may serve as a catalytic synthesis method of the alkyl-cyclohexanones and alkyl-phenols from 2-alkyl-5-acyl-furans. Finally the hydration apparatus, the reaction conditions, and the physical constants of the obtained substances are described. There are 6 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 18, 1959

Card 3/3

SOV/20-127-4-24/60

5(3)

AUTHORS:

Shuykin, N. I., Corresponding Member, AS USSR, Bel'skiy, I. F.,  
Karakhanov, R. A.

TITLE:

Isomerization of  $\mu$ -Oxides to Aliphatic Carbonyl Compounds.  
Effect of the Temperature and Structure of These Compounds

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 4, pp 815-817 (USSR)

ABSTRACT:

Four problems are solved in this article: (1) What is the action exercised by the length of the carbon chain of the alkyl radicals placed in  $\alpha$ -position on the capacity of the tetrahydrofuran cycle to isomerize: Does this action proceed in the direction I (splitting of the 1,5-bond), or in the direction II (splitting of the 1,2-bond, Scheme)? (2) What is the effect of temperature on the relative capacity of the 1,2- and 1,5-bonds to be split by the isomerization of  $\alpha$ -alkyl tetrahydrofurans? (3) How does the isomerization of 2,5-dialkyl tetrahydrofurans develop, which possess alkyl radicals with different numbers of carbon atoms? (4) What is the direction in which the isomerization of 2,2-dialkyl tetrahydrofurans takes place? Table 1 shows experimental results. S o l u t i o n s :  
(1) The isomerization of  $\alpha$ -n-propyl-,  $\alpha$ -n-butyl-, and  $\alpha$ -n-amyl tetrahydrofuran was investigated under equal conditions in the vapor phase on platinized coal at 350°. Table 1 indicates

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Isomerization of  $\gamma$ -Oxides to Aliphatic Carbonyl  
Compounds. Effect of the Temperature and Structure of These Compounds

SOV/20-127-4-24/60

that the increasing number of carbon atoms in the side chain of  $\alpha$ -alkyl tetrahydrofurans increases the capacity of the C-O bond to be split in the cycle isomerization. On the other hand, the tendency of the C-O bond 1,5 towards splitting decreases. The yields of the isomerization products are given. In this case, a pronounced dependence of the capacity of the tetrahydrofuran cycle to isomerize on the length of the alkyl side radical is noticeable in direction I or II. (2) This problem was solved by results obtained from the isomerization of  $\alpha$ -n-propyl tetrahydrofuran at 250, 350, and 400°. The relative quantities of n-hexane and dipropyl ketone show an orientation of the isomerization of the tetrahydrofuran cycle on the C-O 1,2- and 1,5-bond in dependence on temperature. Table 1 further shows that the relative capacity to isomerize under the action of the ring splitting at the C-O bond in the vicinity of the alkyl radical increases with rising temperature. (3) In so far as the difference of the C-O bonds 1,2 and 1,5 in their capacity to be split by the isomerization of the substituted tetrahydrofuran ring depends on the length of the alkyl radical in  $\alpha$ -position, it may be expected that this difference also exists in 2,5-dialkyl tetrahydrofurans containing various numbers of C-atoms. This was

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Isomerization of  $\gamma$ -Oxides to Aliphatic Carbonyl Compounds. Effect of the Temperature and Structure of These Compounds SCV/20-127-4-24/60

twice confirmed. (4) In the isomerization of dialkyl tetrahydrofurans containing both alkyl radicals in  $\alpha$ -position on one and the same C-atom, the rings are always split at the C-O bond which is adjacent to the alkyl side radical. After the decarbonylization of the aldehyde formed in the meantime, this leads to the formation of corresponding aliphatic hydrocarbons. There are 1 table and 3 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni E. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: May 21, 1959

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66169

SOV/20-128-5-22/67

~~5(3)~~ 5.3400

AUTHORS:

Bel'skiy, I. F., Shuykin, N. I., Corresponding Member, AS USSR

TITLE:

A New Method for the Synthesis of Tetrahydrofuran Homologs

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 5, pp 945-947 (USSR)

ABSTRACT:

The authors recall the methods used so far for the above synthesis (Refs 1-3). The new method worked out by the authors is described. It is based on a direct transformation of 1-furyl-alkanols-3 into tetrahydrofurans of varying structure. This depends on intermediate formation of 1,4-diols due to hydrogenolysis of the furan cycle in the molecule of the 1-furyl-alkanols-3. In hydrogenation in the vapor phase 1,4-diols are easily cyclized. They separate water and form corresponding tetrahydrofurans. Two cases are to be discussed with regard to the possibility of synthesizing various homologs (mentioned in the title) due to furfural and aliphatic ketones: 1) Condensation of furfural with methylalkyl ketones. 2-n-propyl-5-alkyl-tetrahydrofurans (III) are formed (see Diagram). 2) Condensation of furfural with ketones of the type  $R-CH_2-\overset{\text{O}}{\underset{\text{O}}{\parallel}}-CH_2-R$ . 2-n-propyl-4,5-dialkyl-tetra-

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hydrofurans (VI) are formed ( see Diagram). The reaction ✓

66169

SOV/20-128-5-22/67

A New Method for the Synthesis of Tetrahydrofuran  
Homologs

mechanism mentioned above is proved by the structure of di- and trialkyl-tetrahydrofurans formed by hydrogenation of 1-furyl-alkanols-3 in the vapor phase. This is a peculiar case of hydrogenolysis of the furan cycle and of simultaneous closure of the new tetrahydrofuran cycle by carbon atoms, three of them having formed a side chain in the initial substance. This fact offers many possibilities of synthesizing various homologs of tetrahydrofuran since the side chain may vary in dependence on the structure of the carbonyl-containing group of the furan compound as well as the structure of the aliphatic ketone. The structure of this side chain of 1-furyl-alkanols-3 is decisive for the structure of the new substituted furan cycle being formed. Hydrogenolysis of the furan cycle readily proceeds on various catalysts containing metals of group VIII, e.g. on Pt-C and skeleton Ni-Zn, as well as on a skeleton Cu-Al catalyst. The most important side reactions on Pt-C are: a) isomerization of the homologs of tetrahydrofuran to aliphatic ketones (Ref 4). b) Formation of 1,4-dions. c) Hydrogenation of 1-furyl-alkanols-3 to 1-tetrahydrofuryl-alkanols-3. The authors obtained furfurylidene-

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NARYSHKINA, T.I.; BEL'SKIY, I.F.

Synthesis of cyclopentadiene homologs. Izv. AN SSSR. Ser. khim.  
no.3:570-571 '65. (MIRA 18:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.

ABGAFOROVA, G.Ye.; SHUYKIN, N.I.; BEL'SKIY, I.F.

Synthesis of trialkyl derivatives of pyrrole and pyrrolidine.  
Izv. AN SSSR. Ser. khim. no.4:734-736 '65. (MIRA 18:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.

SHUKIN, N.I.; VASILEVSKAYA, G.E.; BSL'SKIY, I.F.

Hydrogenation of 2-methyl-3-acetylfuran on a platinumized carbon in a flow system under pressure. Izv. AN SSSR. Ser. khim. no.11:2029-2032 '65.  
(MIRA 18:11)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

BEL'SKIY, I.F.; KHAR'KOV, S.N.; SHUYKIN, N.I.

Synthesis of 1,4-dioxane and 1,4-dioxene homologs. Dokl. AN  
SSSR 165 no.4:821-823 D '65.

(MIRA 18:12)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shuykin).

BEL'SKIY, I.P.; KHAR'KOV, S.N.; SHUYKIN, N.I.

Synthesis of 3-oxa-1,5-ketoalcohols and study of their tautomeric transformations. Dokl. AN SSSR 165 no.5:1071-1074 D '65.  
(MIRA 19:1)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shuykin).

BEL'SKIY, I.F.; KHAR'KOV, S.N.; SHUYKIN, N.I.

Synthesis of monofurfuryl and tetrahydrofurfuryl ethers of  
1,2-glycols. *Izv. AN SSSR. Ser. khim.* no.1:170-172 '66.  
(MIRA 19:1)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
Submitted May 19, 1965.

S/079/60/030/006/033/033/XX  
B001/B055

AUTHORS: Shuykin, N. I., Bel'skiy, I. F., and Karakhanov, R. A.

TITLE: Hydrogenolysis of Tetrahydrofurans ↑

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 6,  
pp. 1933 - 1937

TEXT: Since all the investigations of Refs. 1 - 4 on the reaction mechanism of the catalytic hydrogenation of the furan ring were mainly carried out to establish only this mechanism, it sufficed to determine that the furan- and the tetrahydrofuran ring behaved differently in hydrogenolysis, without investigating possible transformations of tetrahydrofurans during hydrogenolysis in greater detail. In an investigation of the hydrogenolysis of tetrahydrofurans, however, everything indicating the difference between the furan and the tetrahydrofuran rings and their behavior in hydrogenolysis is of importance. For this reason the authors of the present work investigated the hydrogenolysis of tetrahydrofurans. They studied the hydrogenolysis of

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Hydrogenolysis of Tetrahydrofurans

S/079/60/030/006/033/033/XX  
B001/B055

2-alkyl-, 2,2-dialkyl-, and 2,5-dialkyl-tetrahydrofurans in the vapor phase at atmospheric pressure, using platinized carbon and a nickel-aluminum skeleton catalyst. The hydrogenolysis of tetrahydrofuran homologs requires higher temperatures and takes an entirely different course than the hydrogenolysis of furan compounds. Hydrogenolysis of tetrahydrofurans on platinized carbon at 350°C, besides causing isomerization to aliphatic carbonyl compounds, occurs simultaneously at both C-O bonds. This leads to paraffin hydrocarbons with the same number of carbon atoms as the initial tetrahydrofurans. On the nickel-aluminum skeleton catalyst, hydrogenolysis of 2-alkyl- and 2,2-dialkyl-tetrahydrofurans occurs at the C-O bond adjacent to the alkyl groups. Primary alcohols and aldehydes forming as intermediates react to give paraffin hydrocarbons, the carbon chains of which contain one carbon atom less than the initial tetrahydrofuran derivative. The nickel-aluminum skeleton catalyst also causes a more radical decomposition of tetrahydrofurans, thus forming water and gaseous products. The hydrogenolysis of furans has definite advantages over that of tetrahydrofurans, since in the first case aliphatic alcohols and ketones

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Oxidation of  $\beta$ -Ketoacetals by  
Means of Lead Tetraacetate

S/079/60/030/006/032/033/XX  
B001/B055

A reaction mechanism is suggested involving intermediate formation of  $\alpha$ -alkoxy vinyl ketone and subsequent acetoxylation with lead tetraacetate. A method was developed for the synthesis of  $\alpha$ -hydroxy- $\beta$ -ketoacetals by treating  $\alpha$ -acetoxy- $\beta$ -ketoacylal compounds with a methanolic solution of hydrogen chloride (Scheme 5) (yield 35 - 65%). It was shown that  $\alpha$ -acetoxy- $\beta$ -ketoacylals react with polyhydric phenols or  $\beta$ -naphthol forming 3-acetoxy substituted benzo- or naphtho-pyrylium salts. The data given show that  $\alpha$ -acetoxy- $\beta$ -ketoacylals are now accessible and may prove important for the synthesis of several hitherto inaccessible heterocyclic compounds. There are 14 references: 7 Soviet, 4 US, 3 German. ✓

ASSOCIATION: Moskovskiy gosudarstvennyy universitet and Inst. Org. Chem., AS USSR  
(Moscow State University)

SUBMITTED: June 11, 1959

Card 3/3

SHUYKIN, N.I.; BEL'SKIY, I.F.; SHOSTAKOVSKIY, V.M.

Catalytic isomerization of  $\gamma$ -oxides. Conversion of alkyl tetrahydrofuryl carbinols into aliphatic ketones. Zhur.ob.khim. 30 no.8:2757-2759 Ag '60. (MIRA 13:8)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Ketones) (Methanol)

5(3) 5.3400  
AUTHORS:

Shuykin, N. I., Corresponding Member,  
AS USSR, Bel'skiy, I. F.

68816  
S/020/60/131/01/030/060  
B011/B006

TITLE:

Hydrogenation of Furan Compounds on a Skeleton Cu-Al Catalyst

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 1, pp 109-112  
(USSR)

ABSTRACT:

The authors investigated the effects of pressure and temperature on the sequence of the reduction of unsaturated bonds in various compounds of the furan series. 1) The pressure determines the direction of hydrogenolysis of the furan ring. In the presence of skeleton Cu-Al catalyst and under normal pressure, the silvan ring is cleaved at the C-O bond not adjacent to the methyl group. Methyl propyl ketone is formed (see scheme: reference 3). Furan ring cleavage, however, is possible in both directions (C-O bonds 1,2 and 1,5) if silvan is hydrogenated in the vapor phase as before, but with pressurized hydrogen. The quantities obtained of pentanol-1 and pentanol-2 vary considerably with the pressure applied. Higher temperatures promote both the dehydration of pentanol-2 to methyl propyl ketone, and the cleavage of silvan under formation of n-pentane and

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Hydrogenation of Furan Compounds on a  
Skeleton Cu-Al Catalyst

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S/020/60/131/01/030/060  
B011/B006

water. Five to eight percent tetrahydrofuran was formed in all reactions involving pressurized hydrogen. 2) The primary reaction in the hydrogenation of alkylfurylcarbinols on skeleton Cu-Al catalyst under normal or increased hydrogen pressure is the reduction of the hydroxyl group, yielding the corresponding  $\alpha$ -alkylfurans. Under normal pressure and at 230-250° yields of up to 95% are obtained. Further hydrogenolysis of the ring (at higher temperatures) leads to aliphatic ketones. Under these conditions hydrogenolysis of the ring is much more intense in both directions. Aliphatic alcohols and small quantities of  $\alpha$ -alkyltetrahydrofurans are also contained in the reaction products. 3) In the case of alkyl- $\alpha$ -furyl ketones and alkyl- $\alpha$ -furylcarbinols selective reduction of the carbonyl group under retention of the furan ring is possible in the vapor phase. As a catalyst for this reaction, e.g., nickel, deposited on zinc- or cadmium oxide can be used (Ref 4). However, the sequence of the reactions may also be different (on platinized carbon). The effect of skeleton Cu-Al catalyst on the hydrogenation of alkylfuryl ketones at normal pressure in

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Hydrogenation of Furan Compounds on a  
Skeleton Cu-Al Catalyst

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B011/B006

the vapor phase is similar to that of nickel catalysts, but much more selective. 4) This catalyst showed high activity and selectivity in the reduction of, furfurylidene diketones and  $\alpha$ -alkyl- $\beta$ -furylacroleins to the corresponding furanols. At 120-140°, 1- $\alpha$ -furylacroleins-3, and 2-alkyl-3- $\alpha$ -furylpropanols-1 are obtained in yields of 90-95% and 75-85% respectively. 3-Methyl-1,6-dioxaspiro-(4,4)-nonane and 3-ethyl-1,6-dioxaspiro-(4,4)-nonane were obtained in yields of 12-20% from the hydrogenation products of  $\alpha$ -acryl- $\beta$ -furylacroleins. The physical constants of all these compounds are given in table 1. The authors mention A. A. Ponomarev (Ref 6). There are 1 table and 6 references, 5 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskii of the Academy of Sciences, USSR)

SUBMITTED: December 9, 1959

Card 3/3

80007

5.3400

AUTHORS: Shuykin, N. I., Corresponding Member  
AS USSR, Bel'skiy, I. F.S/020/60/131/05/037/069  
B011/B117TITLE: Catalytic Hydrogenation of Furan Compounds Under Pressure in a  
Flow System

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 5, pp 1117-1119 (USSR)

TEXT: It was established by the authors that an increased hydrogen pressure during the hydrogenation in a continuous flow system favors the hydrogenation of the multiple bonds in the furan ring at any rate. This was most obviously shown with the reaction on platinized carbon, and the least effect was found on nickel catalyst (skeleton Ni-Zn and Ni-Al catalysts). Moreover, increased pressure involves the fact that the reduction of hydroxyl and carbonyl groups on Pt-C taking place prior to hydrogenation of the furan ring becomes the most important, or even the only primary reaction when alkyl furyl carbinols and alkyl furyl ketones are hydrogenized or hydrogenolyzed. Thereby the influence of pressure on the liability of the furan ring to hydrogenation to give a tetrahydrofuran ring, or to hydrolysis has been clarified. Moreover, this influence exerted upon the order and the selectivity of the reduction of various unsaturated bonds in a furan compound has been clarified. 1) The furan ring in silvan is completely hydrolyzed at normal pressure and 275°. Methyl propyl ketone

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Catalytic Hydrogenation of Furan Compounds Under  
Pressure in a Flow SystemS/020/60/131/05/037/069  
B011/B117

(reaction II) forms. At 50 at hydrogen pressure, chiefly tetrahydrosilvan (I) results. Hydrogenolysis of the furan ring takes place to a yield of about 25%. 2) At normal pressure, hydrogenolysis of the ring at the C-O bond represents, in addition to the carbonyl group, the primary hydrogenation reaction of 2-methyl-5-acetyl-furan on Pt-C. About 20% is due to the primary reduction of the carbonyl group. With hydrogenation at 50 at pressure and 230-250°, the latter reaction practically becomes the only one to proceed. 3) Under the latter conditions, the hydroxyl group in alkyl furyl carbinols is reduced prior to the hydrogenation of the furan ring. 4) From silvan, 20% tetrahydrosilvan is formed at most when a skeleton Ni-Zn catalyst at 150° is used. By elevated pressure, the multiple bonds in the furan ring are hydrogenated, and hydrogenolysis is suppressed. This effect is less pronounced on Ni-Zn than on Pt catalysts. 5) The skeleton Ni-Al catalyst has, unlike other Ni catalysts, a specific capacity to effect the so-called "conjugated" hydrogenolysis of the furan ring when hydrogenation is performed in continuous systems and at normal pressure. The furan ring in  $\alpha$ -alkyl furans is completely split at 235-250° with three ketone series being formed: alkanones-2, -3, and -4. The elevated hydrogen pressure (50 at) used to hydrogenate silvan leads to the formation of about 50% tetrahydrosilvan, 45% aliphatic ketones and alcohols, and about 5% hepta-compounds at 270°.

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80007

Catalytic Hydrogenation of Furan Compounds Under  
Pressure in a Flow System

S/020/60/131/05/037/069  
B011/B117

There are 4 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk  
SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the  
Academy of Sciences, USSR)

SUBMITTED: November 23, 1959

Card 3/3

S/020/60/132/03/26/066  
B011/B008

5.3200

AUTHORS: Bel'skiy, I. F., Shuykin, N. I., Corresponding Member  
AS USSR; KARAKHANOV, R. A.

TITLE: Thermal Dehydrogenation of 2,5-Dihydrofurans

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 3,  
pp. 585-586

TEXT: The authors produced 2-methyl-, 2-ethyl- and 2-isopropyl-2,5-dihydrofuran under such conditions and investigated their transformations, under which 2-methyl-4,5-dihydrofuran is isomerized to methyl-cyclopropyl-ketone. The vapors of the compounds mentioned in the introduction were passed over crushed quartz or activated carbon at 470-480°. It turned out that 2-alkyl-2,5-dihydrofurans are very easily dehydrogenated to corresponding furan-homologues (see Scheme). The reaction proceeds equally easily over quartz and activated carbon. The authors conclude therefrom that this dehydrogenation is not a catalytic reaction, but is only caused by temperature which must be fairly high; 350°, for instance, are insufficient for this purpose. At 470-480° the tetra-

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Thermal Dehydrogenation of 2,5-Dihydrofurans

S/020/60/132/03/26/066  
B011/B008

hydrofuran ring is changed neither over quartz nor carbon in any way. The authors state therefore that a second (conjugated) double bond is formed more easily than the first (isolated) one. This phenomenon is also observed in other cases. Finally, the authors also point out that for the formation of a furan ring, the double bond must be shifted from the position 3,4 to the position 2,3 or 4,5. Such systems, however, would isomerize to cyclopropane-carbonyl compounds. Since this does not occur, the authors suppose that the shifting of the 3,4-double bond and the cleavage of 2 hydrogen atoms takes place simultaneously and without formation of the 2,3-dihydrofuran as an intermediate. The authors thus come to the following result: contrary to the 2,3-dihydrofurans which are isomerized to aldehydes or ketones of the cyclopropane-series, 2,5-dihydrofurans are dehydrogenated and form corresponding furan compounds. There are 5 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo  
Akademii nauk SSSR (Institute of Organic Chemistry imeni  
N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: February 22, 1960

Card 2/2

S/020/60/132/04/35/064  
B011/B003

5.0400  
AUTHORS: Shuykin, N. I., Corresponding Member of the AS USSR,  
Bel'skiy, I. F., Vasilevskaya, G. K.  
TITLE: Catalytic Conversion of 2-Alkyl-5-acylfurans Into  
.Alkylphenols ¶  
PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 4,  
pp. 861-863

TEXT: The authors investigated the catalytic hydrogenation of the following alkylacylfurans on Pt-C in a continuous system and at usual pressure: 2-acetylfuran, 2-ethyl-5-acetylfuran, 2-methyl-5-propionylfuran, and 2-n-propyl-5-acetylfuran. Hydrogenation occurred at 300 - 310°. In all cases the furan ring was hydrogenated on the C—O bond which is adjacent to the carbonyl group. The resulting intermediates (1,5-diketones) were cyclized in the vapor phase in hydrogenation. Homologs of cyclohexenone formed, which were subsequently dehydrogenated to the corresponding phenol homologs. Carbocyclization of nonsymmetrical

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Catalytic Conversion of 2-Alkyl-5-acyl-  
furans Into Alkylphenols

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S/020/60/132/04/35/064  
B011/B003

1,5-diketones generally leads to the formation of two isomeric phenols, as illustrated by the conversion of octanedione-2,6 (see Scheme). The hydrogenolysis of 2-ethyl-5-acetylfuran and 2-methyl-5-propionylfuran yields as primary product exactly the same diketone, i.e., octanedione-2,6. It yields 3-ethylphenol, whereby the ring between the C-atoms 1 and 6 is closed. 2,3-dimethylphenol is formed, however, if the ring between the C-atoms 2 and 7 is closed. 3-n-propylphenol and 2-ethyl-3-methylphenol are similarly formed from 2-n-propyl-5-acetylfuran. The following corresponding aromatic hydrocarbons were obtained by reduction of phenols resulting from 2-methyl-5-propionylfuran and 2-n-propyl-5-acetylfuran: in the first case, ethylbenzene and orthoxylene, in the second, n-propylbenzene and 1-methyl-2-ethylbenzene. Thus, the cyclization of nonsymmetrical diketones, which were obtained as intermediates of the hydrogenation of 2-alkyl-5-acylfurans, may proceed in two directions. In all cases mono- and dialkylphenols are formed. Simultaneously with the main course of the reaction the carbonyl group is primarily reduced. Subsequently, the furan ring is subjected to hydrogenolysis on one of the C—O bonds, whereby corresponding aliphatic ketones (see Scheme) are formed. 2-acetylfuran

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Catalytic Conversion of 2-Alkyl-5-acyl-  
furans Into Alkylphenols

S/020/60/132/04/35/064  
B011/B003

holds a special position among the compounds investigated. By its hydrogenolysis on the C—O bond adjacent to the carbonyl group a ketoaldehyde forms. It may not be hydrogenated like a diketone, but is completely decarbonylated to form pentanone-2. There are 4 references, 3 of which are Soviet. ✓

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SUBMITTED: February 22, 1960

Card 3/3

S/079/61/031/003/005/013  
B1:3/B207

AUTHORS: Shuykin, N. I., Bel'skiy, I. F., and Grushko, I. Ye.

TITLE: Reaction of  $\alpha$ -alkyl tetrahydrofuranes with silicon tetra-  
chloride

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 3, 1961, 815-819

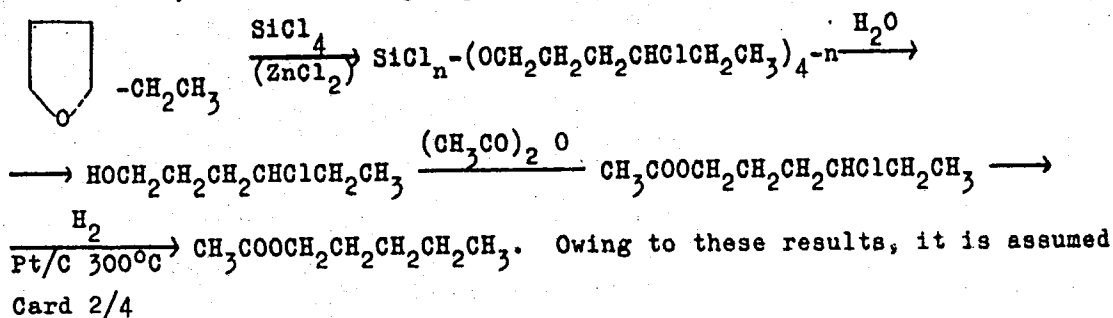
TEXT: The authors studied the reaction of  $\alpha$ -ethyl and  $\alpha$ -propyl tetrahydro-  
furane with  $\text{SiCl}_4$ , and showed that the ethyl and propyl groups exert the  
same effect upon the opening direction of the tetrahydrofurane cycle as the  
methyl radical in tetrahydro-silvane. The main reason for studying the  
hydrolysis and thermal splitting of  $\delta$ -chloro alkoxy chloro silanes thus ob-  
tained was to determine the structure of the resulting chloro hydrins and  
chloro alkenes. The above furane derivatives react with  $\text{SiCl}_4$  more dif-  
ficultly than the latter with tetrahydro-silvane. This is obviously due to  
the steric "screening effect" of the alkyl side group upon the adjacent  
C-O bond.  $\alpha$ -ethyl tetrahydrofurane splits quantitatively (at a molar ratio  
of 2:2 to  $\text{SiCl}_4$ ) after heating for 17 hr, in the presence of 2 g of anhydrous

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S/079/61/031/003/005/013  
 B1/B207

Reaction of ...

zinc chloride and under the formation of chloro alkyl esters of orthosilicic acid, while, under the same conditions, 35% of the d-propyl tetrahydrofurane remains unchanged. These two compounds are split by  $\text{SiCl}_4$  only at the C-O bond which is adjacent to the alkyl group. This was confirmed by hydrolysis of the chloro alkyl esters of orthosilicic acid, ( $\delta$ -chloro alkoxy chloro silane) with water, which gives rise to the formation of  $\delta$ -chlorine-substituted hexyl or heptyl alcohol, from which acetates were obtained. Subsequently, these acetates were reduced to n-hexyl and n-heptyl acetates on Pt-C at  $300^\circ\text{C}$  in the vapor phase:





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B118/B207

Reaction of ...

that in the reaction of  $\alpha$ -alkyl tetrahydrofuranes with  $\text{SiCl}_4$  in the presence of  $\text{ZnO}_2$ , the former open their cycles only at the C-O bond which is adjacent to the alkyl radical. The  $\delta$ -chloro alkoxy chloro silanes obtained in the above reaction are thermally extremely unstable and decompose when distilled. Chloro alkenes (40-50% yield) are one of the decomposition products. The chloro pentenes obtained by thermal decomposition of  $\delta$ -chloro pentoxy chloro silanes were subjected to structural analysis; the latter result from the reaction of  $\text{SiCl}_4$  with tetrahydrofuran. The position of the chlorine atom and the double bond was studied: a Grignard compound was obtained from the chloro pentenes, which, after oxidation and treatment with dilute hydrochloric acid, yielded a mixture of unsaturated primary amyl alcohols when cooled. These were converted into primary amyl alcohols when hydrogenated. The position of the double bond was determined by studying the hydrolysis products of the organo-magnesium compound resulting from the mixture of chloro pentenes; analysis showed that the pentenes thus obtained consisted of 85% pentene-2 and 15% pentene-1. Thus, the chloro pentenes obtained from tetrahydrofuran and  $\text{SiCl}_4$  contain an initially bound chlorine atom in

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B118/B207

Reaction of ...

position 5, and two double bonds in positions 1 and 2. There are 6 refer-  
ences: 2 Soviet-bloc and 4 non-Soviet-bloc. The 2 references to English-  
language publications read as follows: Faraday's Encyclopedia of Hydro-  
carbon compounds. C<sub>7</sub>. Manchester (1953); US Patent 2, 424, 184 (1947).

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Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: April 23, 1960

Card 4/4

BEL'SKIY, I.F.; SHUYKIN, N.I.; VASILEVSKAYA, G.K.

Hydrogenation of carbonyl-containing furan derivatives.  
Conversion of 2-alkyl-5-acylfurans into 2,6-dialkyltetrahydropyrans.  
Dokl. AN SSSR 136 no. 3:591-594 Ja '61. (MIRA 14:2)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shuykin).  
(Furan) (Pyran)

S/020/61/136/005/020/032  
B103/B208

AUTHORS: Shuykin, N. I., Corresponding Member AS USSR, Kovach, E.,  
Bel'skiy, I. P., and Bartok, M.

TITLE: Catalytic hydrogenation of organic oxides in the flow  
system at increased hydrogen pressure

PERIODICAL: Doklady Akademii nauk SSSR, v. 136, no. 5, 1961, 1120-1122

TEXT: The authors wanted to obtain systematic experimental data on the hydrogenation of organic oxides, in order to elucidate the following problems: 1) Determination of the relative stability of various oxide rings to rupture by catalyzed hydrogen; 2) determination of the direction in which the oxide ring is ruptured in the hydrogenation of asymmetric organic oxides. The data available are not sufficient to solve these problems. For this purpose, the authors extended their studies of the hydrogenation of  $\gamma$ -oxides (homologs of tetrahydrofuran, Ref. 3) to other oxides. They hydrogenated the simplest representatives of asymmetric  $\alpha$ -,  $\beta$ -, and  $\gamma$ -oxides, i.e., A) propylene oxide, B)  $\alpha$ -methyl-trimethylene oxide, and C)  $\alpha$ -methyl tetrahydrofuran oxide at

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Catalytic hydrogenation of organic ...

S/020/61/136/005/020/032 ✓  
B103/B208

50 atm hydrogen pressure on skeleton catalysts such as Cu - Al, and Ni - Al catalysts. Furthermore, B) was hydrogenated on Ni - Zn catalyst, and D)  $\alpha$ -n-propyl tetrahydrofuran oxide on Ni - Al. I) Hydrogenation on Cu - Al. ad A): About 80% of A) was converted to primary propyl alcohol at 190-200°C. The rest of the catalyzate were high-boiling substances. ad B): 90-95% of primary butyl alcohol was formed at 230-250°C. ad C): The stability of the tetrahydrofuran ring was found to be much higher on the Cu - Al catalyst, since the conversion did not exceed 10% even at 300°C. The following products of hydrogenation were obtained: n-pentane (30% calculated for the converted quantity of C)), pentanol-1 (35%), and pentanol-2 (35%). II) Hydrogenation on Ni - Al catalyst: C) was converted to pentanol-2 only (about 15%) at 250°C. D) was hydrogenated to heptanol-4 (60%) at 250°C. The authors conclude from the latter reaction that the stability of the tetrahydrofuran ring to hydrogenolysis is determined by the length of the alkyl radical in the  $\alpha$ -position. Summing up: A) and B) behave in an analogous manner in the hydrogenation of asymmetric  $\alpha$ - and  $\beta$ -oxides both on Cu - Al, and on Ni - Al catalysts with respect to the rupture of the oxide ring.

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Catalytic hydrogenation of organic ...

S/020/61/136/005/020/032  
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On Cu - Al, they are ruptured with sufficient selectivity on the C-O bond adjacent to the alkyl substituent. A) and B), on the other hand, undergo hydrogenolysis in both directions on Ni - Al, i.e., also on the C-O bond not adjacent to the alkyl substituent, with about equal intensity. The asymmetric  $\gamma$ -oxides are selectively hydrogenated on Ni - Al in that their ring is ruptured only on the C-O bond not adjacent to the alkyl radical. Hydrogenolysis of  $\gamma$ -oxides occurs in both directions on the Cu - Al catalyst. At atmospheric pressure, D) is also ruptured on Ni - Al on the C-O bond adjacent to the alkyl side group (Ref. 3). The same rupture occurs in B) on Ni - Zn catalyst. There are 4 references: 2 Soviet-bloc and 2 non-Soviet-bloc.

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N. D. Zelinskiy, Academy of Sciences, USSR)

SUBMITTED: October 21, 1960

Card 3/3

BEL'SKIY, I.F.; SHUYKIN, N.I.

Conversion of amines of the furan series to pyrrolidine homologues.  
Dokl. AN SSSR 137 no.2:331-332 Apr '61. (MIRA 14:2)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shuykin).  
(Amines) (Pyrrolidine)

BEL'SKIY, I.F.; SHUYKIN, N.I.; KARAKHANOV, R.A.

Isomerization and dehydrogenation reactions of the tetrahydrofuran  
cycle. Dokl. AN SSSR 138 no.4:829-830 Je '61. (MIRA 14:5)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shuykin).  
(Furan)



SHUYKIN, N.I.; BEL'SKIY, I.F.; KARAKHANOV, R.A.

Catalytic dehydrogenation of dihydrofurans. Dokl.AN SSSR 138  
no.5:1136-1138 Je '61. (MIRA 14:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shuykin).  
(Furan) (Dehydrogenation)

S-3700 2209

30722

S/020/61/141/003/010/021  
B103/B101

AUTHORS: Shuykin, N. I., Corresponding Member AS USSR, Grushko, I. Ye,  
and Bel'skiy, I. F.

TITLE: Interaction of  $\alpha$ -methyl trimethylene oxide with chloro  
silane derivatives, aluminum chloride and titanium tetra-  
chloride

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 3, 1961, 649-651

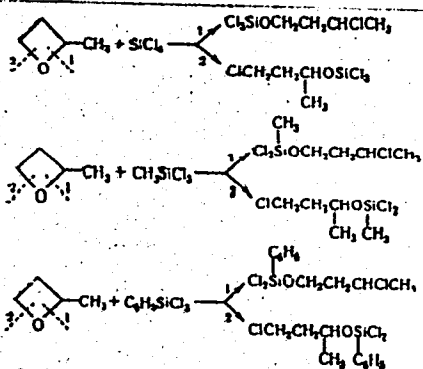
TEXT: The present work studies the interaction of  $\alpha$ -methyl-trimethylene  
oxide (MTMO) with (1)  $\text{SiCl}_4$ , (2)  $\text{CH}_3\text{SiCl}_3$ , (3)  $\text{C}_6\text{H}_5\text{SiCl}_3$ , (4)  $\text{AlCl}_3$ ,  
(5)  $\text{TiCl}_4$ , and (6)  $\text{HCl}$ . The position of the cleavage of the  $\beta$ -oxide ring  
containing an alkyl group in  $\alpha$ -position was to be established. (1), (2),  
and (3) react vigorously with MTMO at room temperature without a catalyst.  
Distillation under reduced pressure yielded chlorine-substituted esters  
of ortho-silicic acid. The reaction therefore proceeds according to the  
following processes:

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Interaction of  $\alpha$ -methyl ...

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B103/B101



These esters,  $\text{Cl}_2\text{SiOC}_4\text{H}_8\text{Cl}$  (b.p.  $56^\circ\text{C}/5$  mm Hg),  $\text{CH}_3\text{SiCl}_2\text{OC}_4\text{H}_8\text{Cl}$  (b.p.  $39^\circ\text{--}42^\circ\text{C}/5$  mm Hg), and  $\text{C}_6\text{H}_5\text{SiCl}_2\text{OC}_4\text{H}_8\text{Cl}$  (b.p.  $132^\circ\text{--}136^\circ\text{C}/8$  mm Hg), yielded the chlorohydrins on hydrolysis. To (6): Dry HCl was passed thru a layer of pure MTMO at the boiling point of the latter. By the

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Interaction of  $\alpha$ -methyl ...

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heat of reaction, the temperature of reaction mixture finally rose to 105°-110°C. To (4) and (5): The reaction with MTMO is so vigorous, that it can only be carried out satisfactorily at -50° and -60°C. Hydrolysis of the reaction products by water in etheric medium yields alcohols containing primary or secondary chlorine atoms. All the Raman spectra of these chlorohydrins exhibited an extremely intense band at 660 cm<sup>-1</sup> characteristic for primary chlorine atoms. The band indicating secondary Cl atoms was weaker. From this it is assumed that the chlorohydrin mixture contains mainly 4-chloro 2-butanol. It is concluded that the treatment of  $\alpha$ -MTMO with (1)-(6) primarily leads to cleavage at the ether bond not adjoining a methyl group. In this connection it is pointed out that unsymmetric  $\gamma$ -oxides, e.g. tetrahydrosilvan, are cleaved at the C-O bond next to a methyl group under the influence of chloro silanes. The authors thank G. K. Gayvoronskaya for taking the spectra. There are 1 table and 6 references: 1 Soviet and 5 non-Soviet. The four references to English-language publications read as follows: C. G. Derrick, D. W. Bissel, J. Am. Chem. Soc., 38, 2483 (1916); S. Searles et al. J. Am. Chem. Soc., 79, 952 (1957); R. J. Meltzer, J. A. King, J. Am. Chem. Soc., 75, 1356 (1953); F. Sondheimer, R. B. Woodward, J. Am. Chem. Soc., 75,  
Card 3/4

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Interaction of  $\alpha$ -methyl ...

S/020/61/141/003/010/021  
B103/B101

5438 (1953).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii  
nauk SSSR (Institute of Organic Chemistry imeni N. D.  
Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: July 13, 1961

Card 4/4

SHUYKIN, N.I.; BEL'SKIY, I.F.; VASILEVSKAYA, G.K.

Catalytic synthesis of 1,5-diketones. Izv. AN SSSR. Otd. khim. nauk  
no.2:363-364 F '61. (MIRA 14:2)

1. Institut organicheskoy khimii im.N.D.Zelinskogo AN SSSR.  
(Ketones)

SHUYKIN, N.I.; BEL'SKIY, I.F.; GRUSHKO, I. Ye.

Reactions of  $\alpha$ -alkyltetrahydrofurans with silicon tetrachloride.  
Zhur. ob. khim. 31 no.3:815-819 Mr '61. (MIRA 14:3)

1. Institut organicheskoy khimii imeni N. D. Zelinskogo AN SSSR.  
(Silicon chloride)  
(Furan)

SHUYKIN, N.I.; BEL'SKIY, I.F.

Catalytic synthesis of 2-n-propyl-4-alkyltetrahydrofurans. Dokl.  
AN SSSR 137 no.3:622-623 Mr '61. (MIRA 14:2)

1. Institut organicheskoy khimii im. N.D.Zelinskogo. 2.Chlen-korres-  
pondent AN SSSR (for Shuykin).  
(Furan)



SHUYKIN, N.I.; BEL'SKIY, I.F.; SHOSTAKOVSKIY, V.M.

Catalytic hydrogenation of esters. Dokl. AN SSSR 139 no.3:634-636  
Jl '61. (MIRA 14-7)

1. Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk  
SSSR. 2. Chlen-korrespondent AN SSSR (for Shuykin).  
(Esters) (Hydrogenation)

SHUYKIN, N.I.; GRUSHKO, I.Ye.; BEL'SKIY, I.F.

Interaction of  $\alpha$ -methyltrimethylene oxide with chlorosilanes,  
aluminum chloride and titanium tetrachloride. Dokl. AN SSSR  
141 no.3:649-651 N '61. (MIRA 14:11)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
2. Chlen-korrespondent AN SSSR (for Shuykin).  
(Oxides) (Halides)  
(Silicon organic compounds)

KOVACH, E.; SHUYKIN, N.I.; BARTOK, M.; BEL'SKIY, I.F.

Thermal conversions of  $\alpha$ -substituted  $\beta$ -oxides. Izv. AN SSSR Otd.-  
khim.nauk no.1:124-130 Ja '62. (MIRA 15:1)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR i  
Kafedra organicheskoy khimii Segedskogo universiteta, Seged,  
Vengriya.

(Oxides) (Substitution (Chemistry))

SHUYKIN, N.I.; BEL'SKIY, I.F.; KARAKHANOV, R.A.

Catalytic dehydrogenation of dihydrofurans. Izv. AN SSSR Otd.khim.-  
nauk no.1:138-142 Ja '62. (MIRA 15:1)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Furan) (Dehydrogenation)

BEL'SKIY, I.F.

Conjugated hydrogenolysis in the synthesis of tetrahydrofuran homologs. Izv. AN SSSR Otd.khim.nauk no.1:142-146 Ja '62.

(MIRA 15:1)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Furan) (Hydrogenation) (Hydrolysis)

BEL'SKIY, I.F.

Catalytic conversions of 1,6-dioxaspiro[4,4]nonanes. Izv.  
AN SSSR Otd.khim.nauk no.2:333-336 F '62. (MIRA 15:2)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Dioxaspiro[4,4]nonane)

SHUYKIN, N.I.; BEL'SKIY, I.F.; BALABAN, A.T.; NENITSESKU, K.D.

Catalytic transformation of homologs of 2-acetylfuran to  
trialkyltetrahydropyrans. Izv. AN SSSR. Otd. khim. nauk no. 3:  
491-493 Mr '62. (MIRA 15:3)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR i  
Akademiya Rumynskoy Narodnoy respubliki.  
(Furan) (Pyran)

BEL'SKIY, I.F.

Catalytic synthesis of pyrrolidine homologs from furan amines.  
Izv. AN SSSR. Otd. khim. nauk no. 3:493-496 Mr '62. (MIRA 15:3)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.  
(Pyrrolidine) (Furan)



BEL'SKIY, I.F.; KARAKHANOV, R.A.

New method of synthesizing  $\gamma$ -diketones. Report No.1: Catalytic transformation of furan and tetrahydrofuran alcohols into  $\gamma$ -diketones. Izv. AN SSSR. Otd.khim.nauk no.5:905-907 My '62. (MIRA 15:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Furan) (Ketones)

BEL'SKIY, I.F.

Catalytic conversion of furanamines into pyrrole and pyrrolidine  
homologs. Izv.AN SSSR.Otd.khim.nauk no.6:1077-1080 '62.  
(MIRA 15:8)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Furanamine) (Pyrrole) (Pyrrolidine)

SHUYKIN, N.I.; BEL'SKIY, I.F.; BARKOVSKAYA, L.Ya.; DRONOV, V.I.;  
ALALYKINA, L.A.

Synthesis of 2,4- and 2,5- dialkylthiophanes. Izv.AN SSSR.-  
Otd.khim.nauk no.6:1093-1098 '62. (MIRA 15:8)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR i  
Institut organicheskoy khimii Bashkirskogo filiala AN SSSR.  
(Thiophene)

SHUYKIN, N.I.; BEL'SKIY, I.F.; GRUSHKO, I.Ye.

Interaction of  $\alpha$ -methyltetrahydropyran with some compounds  
containing an active chlorine atom. Izv.AN SSSR.Otd.khim.nauk  
no.8:1486-1488 Ag '62. (MIRA 15:8)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Pyran) (Chlorine compounds)

BEL'SKIY, I.F.; SHUYKIN, N.I.; SHOSTAKOVSKIY, V.M.; KHAR'KOV, S.N.

New method of synthesizing esters of  $\gamma$ -ketocarboxylic acids.

Part 1: Catalytic transformation of esters of  $\beta$ -furylacrylic acids  
to esters of  $\gamma$ -ketoenanthic acids. Zhur.ob.khim. 32 no.4:1030-  
1034 Ap '62. (MIRA 15'4)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.  
(Furanacrylic acid) (Heptanoic acid)

SHUYKIN, N.I.; HEL'SKIY, I.F.; KARAKHANOV, R.A.

Catalytic dehydrogenation of dihydrofurans. Synthesis of  
2,4-dialkyl furans. Dokl. AN SSSR 147 no.1:119-122 N '62.  
(MIRA 15:11)

1. Institut organicheskoy khimii im. N.D. Zelinskogo  
AN SSSR. 2. Chlen-korrespondent AN SSSR (for Shuykin).  
(Furan)  
(Dehydrogenation)

BEL'SKIY, I.F.; SHUYKIN, N.I.; VASILEVSKAYA, G.K.; GAYVORONSKAYA, G.K.

Catalyzed synthesis of 2,6-dialkyltetrahydropyrans. *Izv. AN SSSR. Otd. khim. nauk* 1650-1653 S '62. (MIRA 15:10)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.  
(Pyran)

SHUYKIN, N.I.; BARTOK, M.; KOVACH, E.; BEL'SKIY, I.F.

Catalytic isomerization of  $\beta$ -oxides. Izv. AN SSSR, Otd. khim. nauk no. 9:  
1653-1656 S '62. (MIRA 15:10)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.  
(Oxides) (Isomerization)



BEL'SKIY , I.F.; SHUYKIN, N.I.

Catalytic synthesis of trialkyl tetrahydrofurans. Izv. AN SSSR. Otd.  
khim.nauk no.9:1656-1660 S '62. (MIRA 15:10)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Furan)

BEL'SKIY, I.F.; SHUKIN, N.I.; SHOSTAKOVSKIY, V.M.

Effect of carbonyl and carbalkoxy groups on the direction of hydrogenolysis of furan cycle under conditions of vapor phase hydrogenation.  
Izv. AN SSSR.Otd.khim.nauk no.10:1821-1825 0 '62. (MIRA 15:10)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.  
(Furan) (Hydrogenation)

SMIRNOV, L. D.; DYUMAYEV, K. M.; SHUYKIN, N. I.; BEL'SKIY, I. P.

Synthesis of 2,4,6-trialkyl-3-hydroxypyridines. Izv. AN SSSR  
Otd. khim. nauk no.12:2246-2247 D '62. (MIRA 16:1)

1. Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR  
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(Pyridine)

BEL'SKIY, I.F.

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