STUDY OF THE TRANSFORMATION OF 1,3-DIOXACYCLOALKANES ON A PLATINUM CATALYST. EXPERIMENTAL RESULTS AND DISCUSSION

(Review article)

By

M. BARTÓK and J. APJOK
Institute of Organic Chemistry, Attila József University, Szeged

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The experimental results of the isomerization and hydrogenolysis of 1,3-dioxacycloalkanes (about 60 compounds) on a platinum catalyst are reviewed, and an account is given of new reaction directions determined by the structures of the compounds and by the experimental conditions, and of the main parameters affecting these.

Introduction

Of the 1,3-dioxacycloalkanes, we have dealt mainly with the transformation of the 1,3-dioxanes in the presence of heterogeneous catalysts [1—8], for these stand out within this family of compounds from both theoretical and practical aspects. Investigation of homologues with five, seven or eight atoms in the ring was considered as a part of our task only in so far as it was necessary to prove the general nature of new regularities revealed in the case of the 1,3-dioxanes [9]. This gave the possibility of studying the change of certain reaction types depending on the number of atoms in the ring.

The first reviews on the chemistry of the 1,3-dioxanes appeared in 1952 [10, 11]; these were supported by a considerable number of experimental results, and drew attention to this type of compounds. In recent years, interest in the chemistry of the 1,3-dioxanes has increased significantly; this is proved not only by the practical application of this family of compounds, but also by the increasing number of publications dealing with the 1,3-dioxanes. The reviews published more recently focus attention also on the theoretical aspects of the chemistry of the 1,3-dioxanes, *e.g.* on their stereochemistry and on their heterogeneous catalytic transformations [12, 13].

The practical importance of the 1,3-dioxanes has not yet attained the level which would be expected on the basis of the comparatively ready availability of these compounds. For instance, direct transformation (Prins reaction) [14] of the great amounts of olefins produced by the petrol-chemical industry is a cheap source of 1,3-dioxanes. It should be noted, however, that the use of 1,3-dioxanes is continuously increasing (solvents, antidetonators, intermediates in the organic chemical industry, starting and auxiliary materials in drug syntheses, plastics monomers, etc.). From this respect 4,4-dimethyl-1,3-dioxane should be stressed as it has acquired great importance because of its role in the manufacture of isoprene.

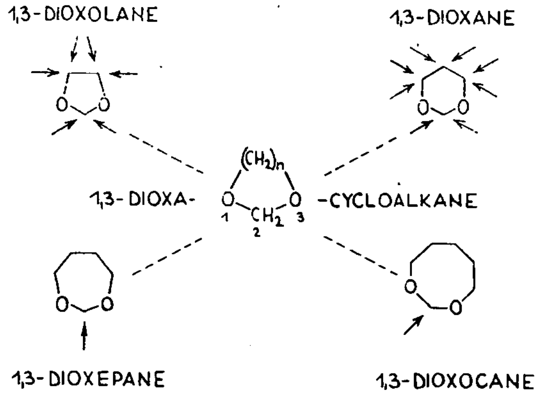
The 1,3-dioxacycloalkanes can be considered as cyclic derivatives of bifunctional diols with oxo compounds (cyclic acetals and ketals), and those can similarly be regarded as bifunctional systems. It is known that bifunctional systems undergo special chemical transformations which are not characteristic of the individual isolated functions. Thus, the new isomerization reactions observed in the heterogeneous catalytic transformations of 1,3-dioxacycloalkanes form in our view, an extremely interesting part of the chemistry of cyclic systems containing two hetero atoms.

A systematic survey of literature dealing with this family of compounds indicates that the heterogeneous catalytic transformations of the 1,3-dioxanes can be classified in three main groups [13]:

(a) transformation of 1,3-dioxanes to conjugated dienes;
(b) isomerization of 1,3-dioxanes to β-alkoxyoxo compounds;
(c) hydrogenolysis of 1,3-dioxanes to primary alcohols, 1,3-diols and 1,3-diol monoethers.

In the study of the first two processes, heterogeneous catalysts with various electrophilic characters, mainly phosphates, oxides and silicates have been used. The catalytic hydrogenolysis has been investigated in a static system, in the liquid phase, at high pressure, in the presence of various metals and copper(II)-chromium(III) oxide. The 1,3-dioxanes and their cyclic homologues with different numbers of ring atoms have not been examined in the vapour phase in the presence of metal catalysts.

Accordingly, we set out to investigate the transformations of mono-, di- and polysubstituted 1,3-dioxanes and of some 1,3-dioxolane, 1,3-dioxepane and 1,3-dioxocane derivatives on the action of metal heterogeneous catalysts.



Of the 1,3-dioxacycloalkanes presented in the scheme, a study was made of about sixty compounds from the derivatives containing a substituent (primarily an alkyl group) on the carbon atom denoted by an arrow.

A large proportion of the model compounds were prepared as described previously [15], while some stereoisomeric 1,3-dioxanes were made available by the Department of Organic Chemistry, State University, Odessa.

The isomerization and hydrogenolysis of these compounds on a platinum catalyst were examined at atmospheric pressure. Experiments were also carried out on other metal catalysts, and procedures were elaborated for the liquid-phase catalytic hydrogenolysis of certain dioxanes under pressure [16], and for their transformation to oxacyclobutanes on a catalyst of acidic character [17].

The aim of our experiments was to establish the reaction directions on platinum catalysts of the transformations of 1,3-dioxacycloalkanes containing different numbers of atoms, and to examine the variation of the reaction directions as a function of the structure of the starting material. A study was further made of the effects of the nature, number and ring-position of the substituents with regard to the stability of the ring. The changes in the extent and main directions of the transformation were determined as a function of the individual reaction parameters. A thermolite-supported catalyst containing 10% platinum (in the following Pt/T) was mainly employed [18, 19]. The experiments were performed with a microreactor built into a gas-chromatograph with impulse injection, in a carrier gas stream of hydrogen or helium [18, 19]. Examinations were also made on a Pt/C catalyst, and on ammonia-poisoned catalysts.

The chemical processes were followed qualitatively and quantitatively by analytical and preparative gas-chromatography, as well as by IR spectrophotometry, together with the other generally used methods of separation and identification. In some cases investigations of a preparative nature, too, were carried out in a continuous-operation reactor. Experiments were also performed to establish the mechanisms and stereochemical courses of the new processes discovered.

Relative stabilities of 1,3-dioxacycloalkanes in their transformations on Pt/T in the presence of hydrogen

Already the preliminary experiments drew attention to some novel changes: hitherto unobserved directions of transformation of 1,3-dioxacycloalkanes in the presence of various heterogeneous catalysts; these made the topic under examination even more interesting, and underlined its importance. On the basis of the appropriate thermodynamic data, it was possible to assume the isomerization of 1,3-dioxanes to esters. However, it was not expected to find the considerable selectivity determined by the number of atoms in the rings and by the positions and numbers of the substituents, nor the fact that in certain cases isomerization leading to the formation of esters would become the characteristic reaction direction.

Already at the beginning of the experimental work it was found that for isomerization to the ester the combined presence of both platinum and gaseous hydrogen is necessary. Thus, the thermolite support in the presence of hydrogen, and the Pt/T in the absence of hydrogen, did not prove active under similar experimental conditions [1]. As regards the open-chain acetals, ester formation could not be observed in the transformation of acetaldehyde diethylacetal in the presence of hydrogen.

The degrees of transformation of the dioxacycloalkanes as a function of temperature are shown in Figs 1—6, which indicate the relative stability or reactivity of the above compounds under the given experimental conditions.

The experimental data ([1—4, 9], Figs 1—6) permit the following main conclusions.

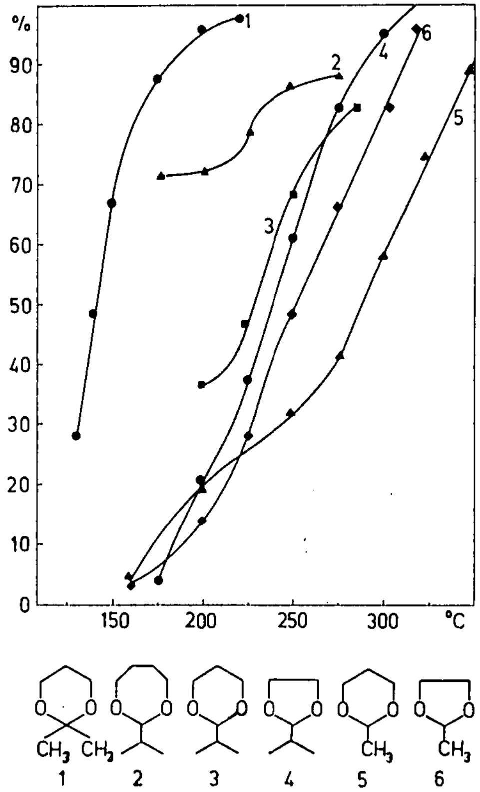


Fig. 1

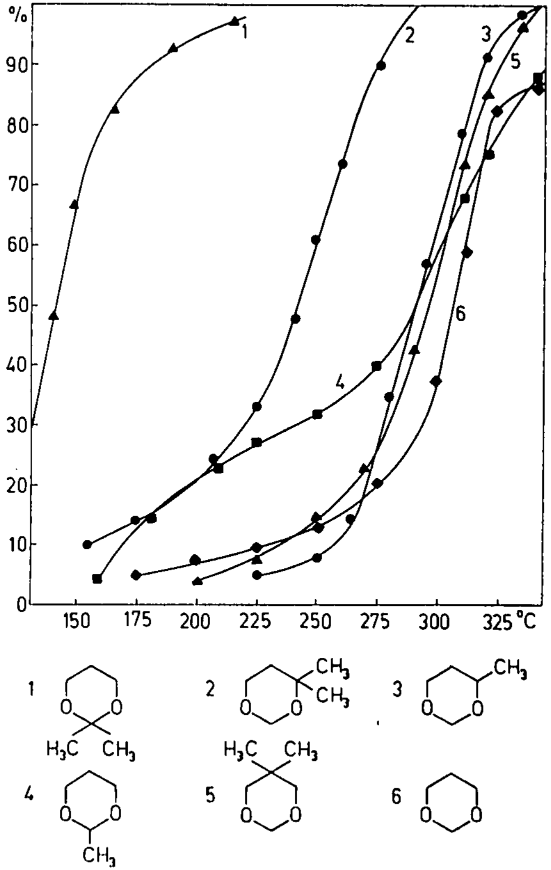


Fig. 2

Figs 1—6. Variation of the conversion in the transformations of 1,3-dioxacycloalkanes on Pt/T, as functions of the number of ring atoms, the nature, position and number of the substituents and the temperature.

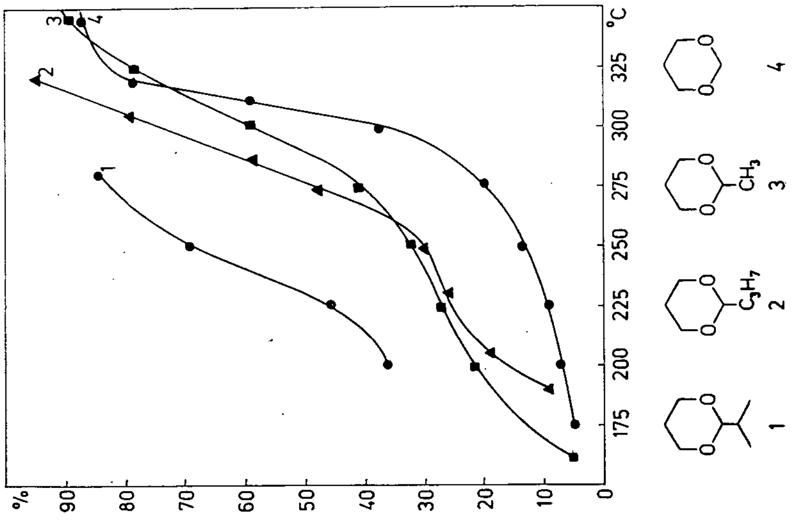

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Fig. 3

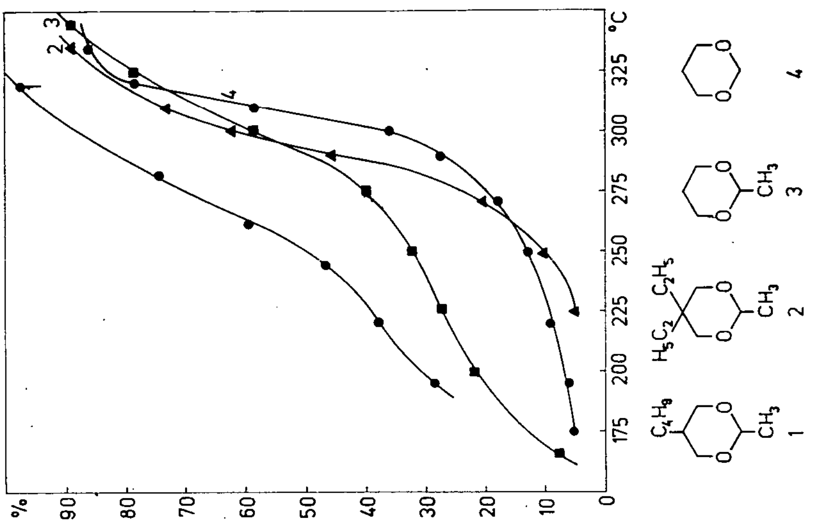
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Fig. 4

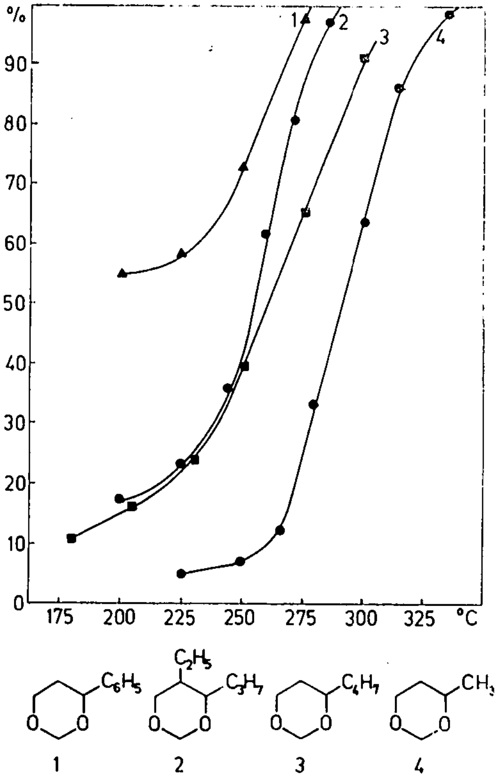
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Fig. 5

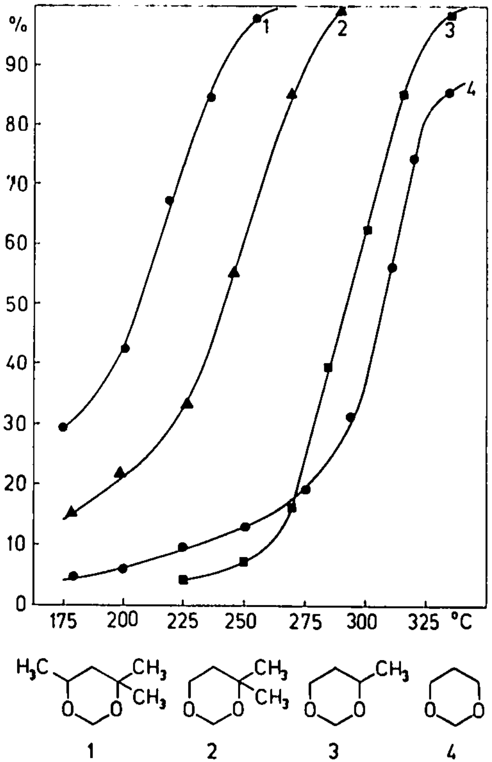
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Fig. 6

On a Pt/T catalyst the stability of the 1,3-dioxacycloalkanes as a function of the number of atoms in the ring exhibits the following sequence: $8 \sim 7 < 6 \sim 5$ (Fig. 1). As it will be seen later, the differences in the rates of decomposition of the dioxacycloalkanes are brought about primarily by the differences in reaction direction, these depending on the number of atoms in the ring and on the substituents.

The stability of the 1,3-dioxanes as a function of the number of C_2 substituents varies as follows: formal > acetal > ketal (Fig. 2). The stability series for the alkyl-substituted 1,3-dioxanes is: 2- < 4- < 5-alkyl-1,3-dioxanes.

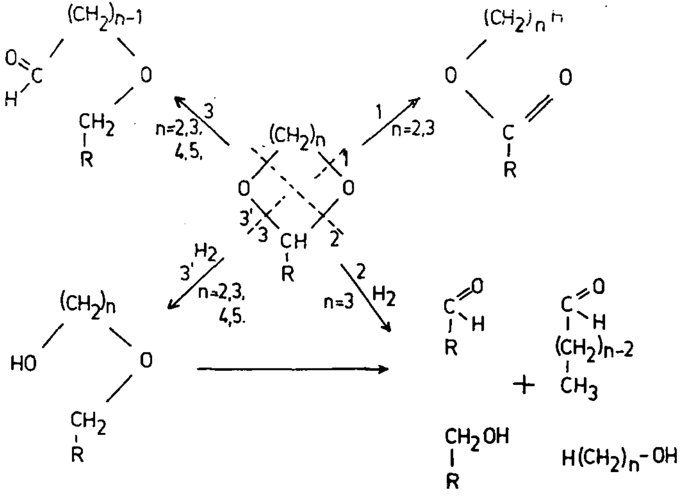
The stability of the 1,3-dioxanes depends on the number of substituents on C_5 in the following way: 5,5-dialkyl-1,3-dioxane > 5-alkyl-1,3-dioxane (Fig. 3).

Alkyl substituents at a given position in the ring affect the stability of the 1,3-dioxanes in the sequence of their +I effects (possibly on the basis of their effects on the adsorption of the substrate molecules) (Figs. 4 and 5). The reactivity of the 1,3-dioxanes increases proportionly to the number of substituents on C_4 (Fig. 6). The C_2 isopropyl group increases the reactivity of the 1,3-dioxanes more than that of the other studied members of the 1,3-dioxacycloalkanes.

As already mentioned, the differences in stability of the 1,3-dioxacycloalkanes can be explained decisively by the transformation directions; these will be reported in detail later. In the case of the acetals we shall discuss the characteristics of the transformations of five-, six-, seven-and eight-membered 1,3-dioxacycloalkanes on Pt/T. Since formals and ketals were prepared only from 1,3-diols, it can be understood that in these sub-sections only the corresponding dioxanes will be involved. A special account is given of the transformations of the derivatives of 1,3-dioxadecalin, and 5-alkoxyalkyl-1,3-dioxane stereoisomers of known structure.

Transformation of 1,3-dioxacycloalkanes of acetal type

The main transformation directions observed can be seen in the following process scheme on the example of the non-substituted cyclic acetals:



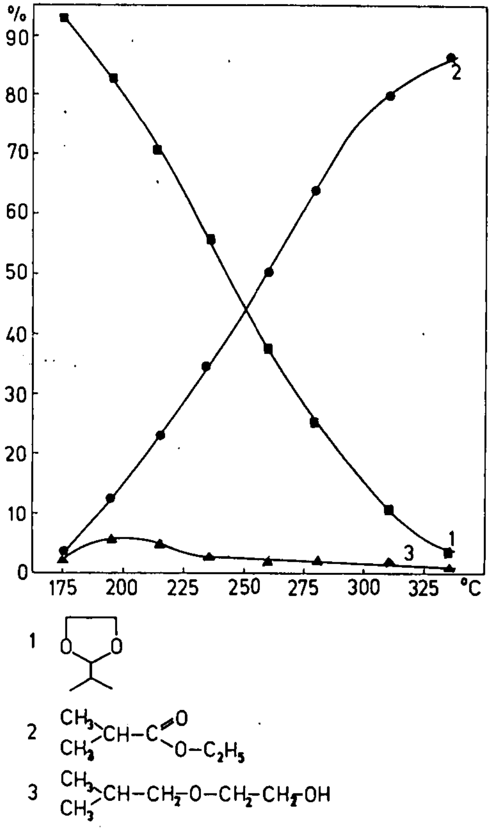


Fig. 7

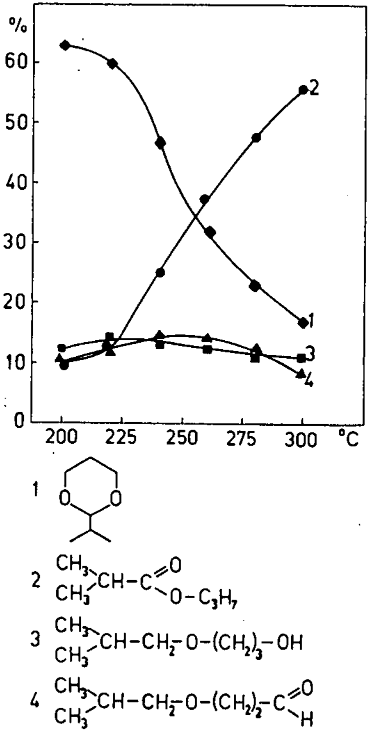


Fig. 8

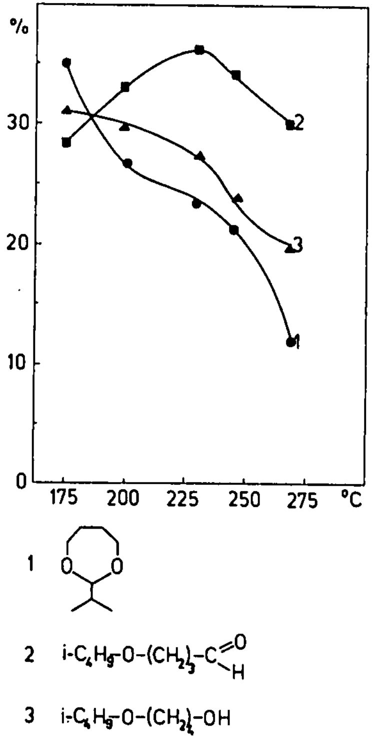


Fig. 9

Figs 7—12. Variation of the product composition as a function of temperature in the transformation of some 1,3-dioxacycloalkanes on Pt/T.

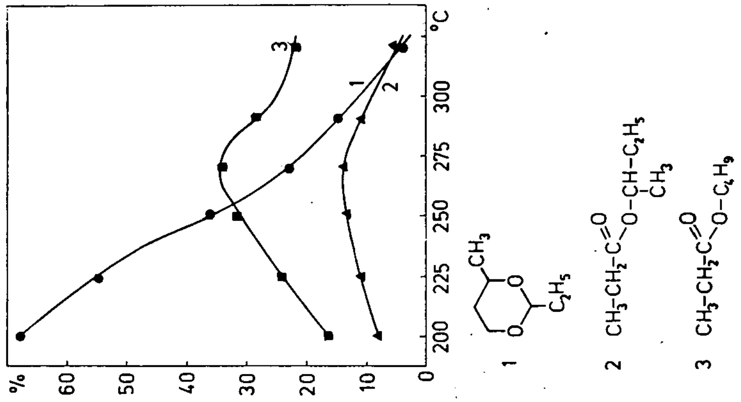


Fig. 10

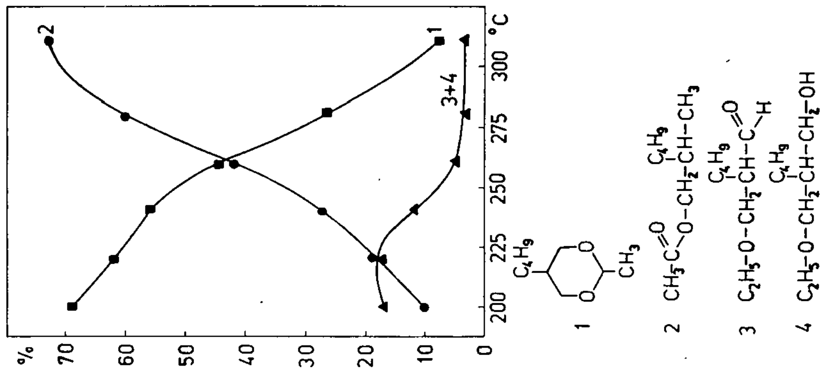


Fig. 11

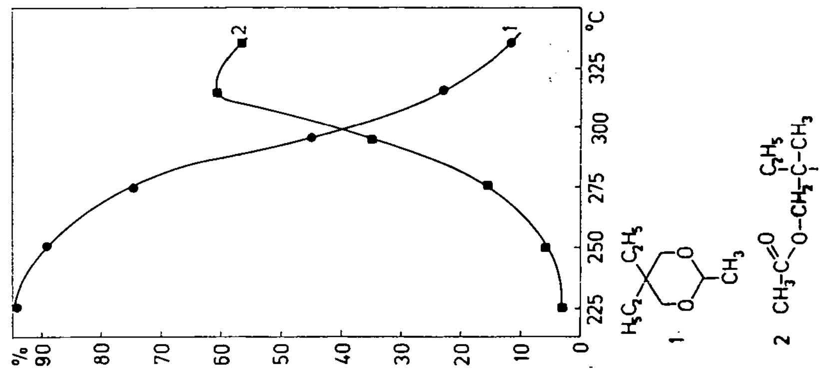


Fig. 12

Of the four main reaction directions, two are isomerizations, one is hydrogenolysis, and one is a fragmentation process. The extents of these main processes are determined decisively by the number of ring atoms, but other factors exerting an effect are the ring substituents and the reaction parameters (predominantly the surface state of the catalyst and the temperature). Before giving a more detailed treatment of the experimental results [1—4, 9], the temperature-dependent variation of the composition of the catalysate is plotted for a number of model compounds in Figs 7—12.

On Pt/T in the presence of hydrogen, the 2-alkyl-1,3-dioxolanes mainly undergo isomerization to the corresponding esters. Conversion to the ester may reach even

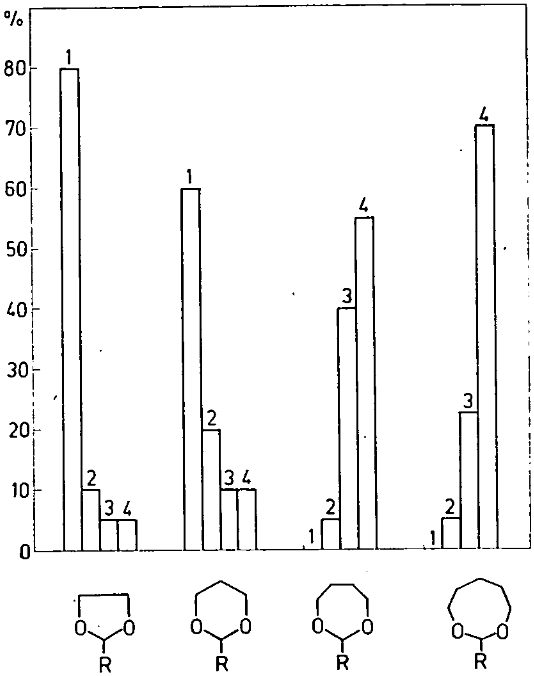


Fig. 13. Average yields of products formed in the transformations of cyclic acetals with various numbers of ring atoms on Pt/T (1: esters; 2: products of fragmentation; 3: alkoxyoxo compounds; 4: diol monoethers)

85—90%. Under the same experimental conditions the 2-alkyl-1,3-dioxanes are similarly isomerized to the corresponding esters. The selectivity of ester formation is somewhat lower, but in favourable conditions attains 80% in these systems, too. As a consequence of the splitting of the C_2-O bond under similar experimental conditions, the 2-alkyl-1,3-dioxepanes and 2-alkyl-1,3-dioxocanes are isomerized to the corresponding alkoxyaldehydes, and as a result of hydrogenolysis are transformed to the 1,4- and 1,5-diol monoethers. The two reaction directions together make up as much as 95%. Esters were not found among the reaction products, even in traces.

Thus, on the basis of the extents of the main transformation processes outlined above, the 2-alkyl-1,3-dioxacycloalkanes can be arranged in the following series (Fig. 13):

Based on the yield of ester formation: 1,3-dioxolanes > 1,3-dioxanes (1,3-dioxepanes = 1,3-dioxocanes = 0).

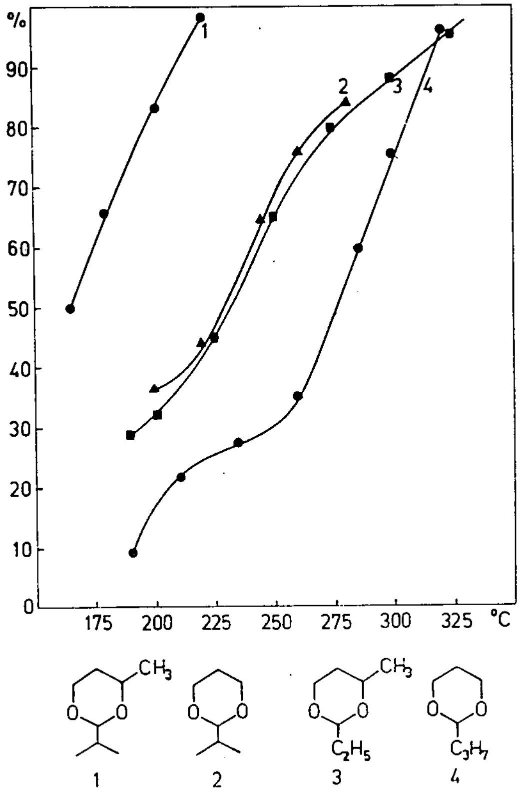


Fig. 14. Effect of the C_2-isopropyl group on the extents of transformation of 1,3-dioxanes on Pt/T.

Based on transformation to alkoxyaldehydes and diol monoethers: 1,3-dioxolanes < 1,3-dioxanes ≪ 1,3-dioxepanes ~ 1,3-dioxocanes.

Fragmentation processes occur as a consequence of the higher temperature. Of course, at higher temperature the main processes are also followed by various secondary changes due to decomposition [5].

The substituents affect the relative extent of the main reaction directions. As a function of the substituent on C_2, the degree of ester formation varies according to the following sequence: 2-isopropyl- > 2-methyl- > 2-phenyl-1,3-dioxolane; 2-isopropyl- < 2-propyl- > 2-ethyl- > 2-methyl-1,3-dioxane.

The presence of the C_2-phenyl group promotes the fragmentation processes *via* the splitting of the C_2-O bond, but it also accelerates the hydrogenolysis. The C_2-isopropyl group increases both the rate of decomposition and the extent of ester formation in the dioxolanes, but in the dioxanes it decreases the rate of ester formation in favour of the hydrogenolysis; in asymmetric dioxanes it affects the direction of ester formation [4]; in the case of dioxepanes it increases the rate of hydrogenolysis at the expense of fragmentation [9].

These experimental facts can be explained by the "shielding" effect of the isopropyl group on the C_2-H bond. Thus, owing to its spatial shielding effect, the isopropyl group inhibits the dissociative chemisorption of the substrate accompanied by the splitting of its C_2-H bond, which is very probably a condition for isomerization to the ester. Naturally, at the same time this promotes the hydrogenolysis (the competing, parallel process), as proved by the experimental data.

As a result of the asymmetry of 4-substituted 1,3-dioxanes, transformation accompanied by ring-opening leads to two series of products. The C_4 substituent promotes isomerization proceeding with splitting of the O_3-C_4 bond. Accordingly, the rate of formation of esters of primary alcohols is higher than that of the esters of secondary alcohols.

On the basis of what has been said above, it may be easily seen that the differences in the rates of decomposition of 1,3-dioxacycloalkanes can be explained by the differing reaction possibilities. The 1,3-dioxacycloalkanes decompose at the highest rate, undergoing the greatest extent of hydrogenolysis. Thus, the rate of decomposition of 1,3-dioxacycloalkanes is determined in the long run not by the number of ring atoms, but by the decomposition direction depending on the structure of the compound. This finding is well illustrated in Fig. 15. It can be seen that the highest rate of transformation is that of 2,2-dimethyl-1,3-dioxane, from which products formed by splitting of the C_2-O bond are obtained in a yield of 85%.

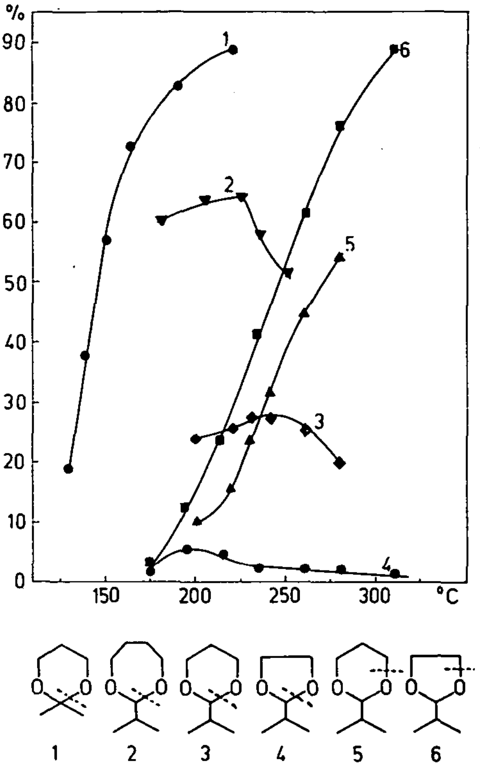
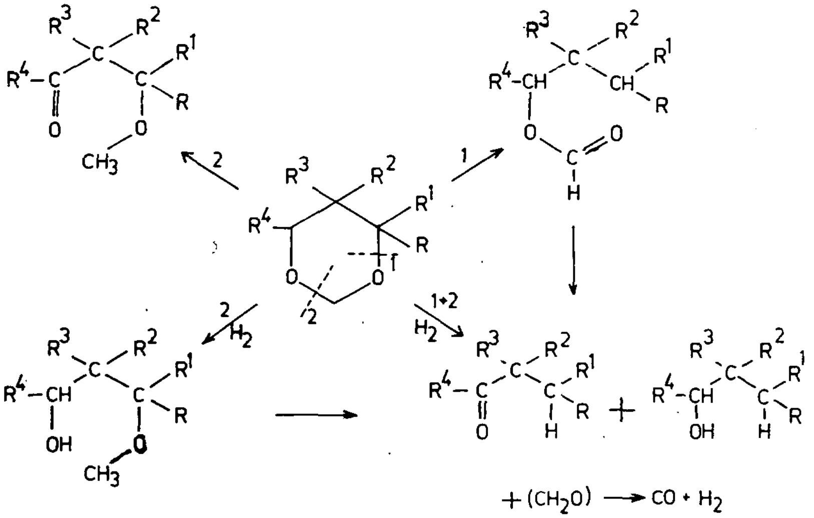


Fig. 15. Variation as a function of temperature of the yields of products formed by splitting of the C_2-O_3 and O_3-C_4 bonds in the transformation of 1,3-dioxacycloalkanes on Pt/T.

Transformation of 1,3-dioxanes of formal type

The main reaction directions observed on the basis of the experimental results [2, 3, 5, 6] can be summarized in the following reaction scheme: (For purposes of clarity the transformations accompanied by splitting of the C_6-O_1 bond have not been included in this scheme.):



Similarly as for the acetals, in the case of the cyclic formals, too, the same four main transformation directions are observed (two isomerizations, one hydrogenolysis, and one fragmentation process).

With regard to their stabilities and transformation directions under the conditions of examination, the six-membered cyclic formals can be divided into two main groups: 4-aryl-, 4,4-dialkyl-, 4,6-polysubstituted-1,3-dioxanes; and 4-alkyl-, 5-mono-, 5,5-disubstituted-1,3-dioxanes.

The cyclic formals belonging to the first group behave similarly to the acetals as regards both their stabilities and their transformations (in connection with their stabilities see Figs 5 and 6). On Pt/T they are isomerized, mainly to the corresponding formic acid esters. Since the transformation temperature is relatively low, the formates are not further converted and thus their formation can be readily followed. With the 4-aryl- and 4,4-disubstituted-1,3-dioxanes, it is only possible to observe the formation of products obtained by splitting of the C-O bond adjacent to the substituents.

The cyclic formals in the second group have higher decomposition temperatures and stabilities than those of the cyclic acetals. However, the higher temperature favours the fragmentation processes. Here we must consider not only the primary processes, but also the secondary changes following the other three primary processes; these lead to the formation of the same fragments, as shown in the Figure. The proportions of the primary and secondary processes were not investigated. For the transformation of these cyclic formals on Pt/T in the presence of hydrogen, the fragmentation processes are the more characteristic. In the course of these processes, oxo compounds and alcohols containing one carbon atom less than the starting dioxane are formed, in principle by the elimination of formaldehyde or methanol or by some other secondary processes. The combined amount of these products varies in the range 10—60%, depending on the temperature, and on the nature, position and number of the substituents in the ring. In addition to the fragmentation processes, the isomerization of these cyclic formals to esters is also appreciable (8—20%), but the secondary transformation of the formates produced considerably decreases the amount of esters observed. Under the experimental conditions applied, the formic acid esters (and particularly the esters of formic acid with secondary alcohols) are labile compounds, as can be clearly seen from the experiments with the individual formates (under the same conditions as for the 1,3-dioxanes) (Fig. 16). A comparison of Figs 2 and 16 readily reveals that the decomposition of the 2-butyl

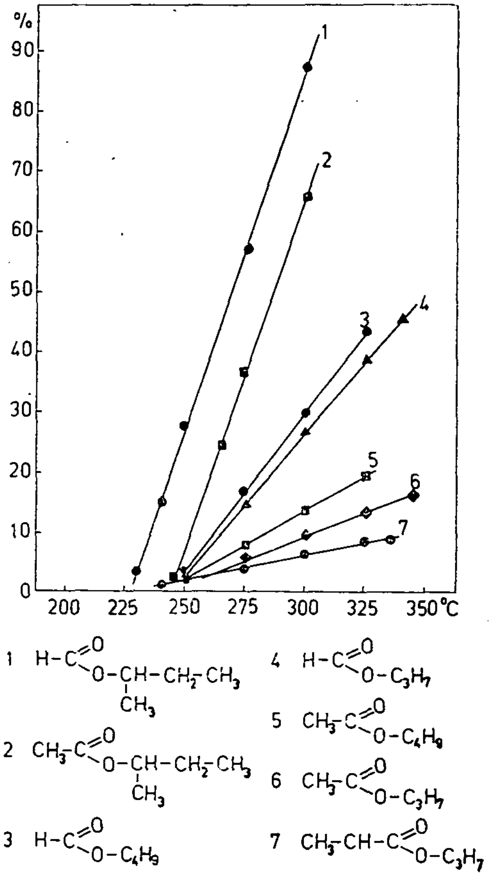
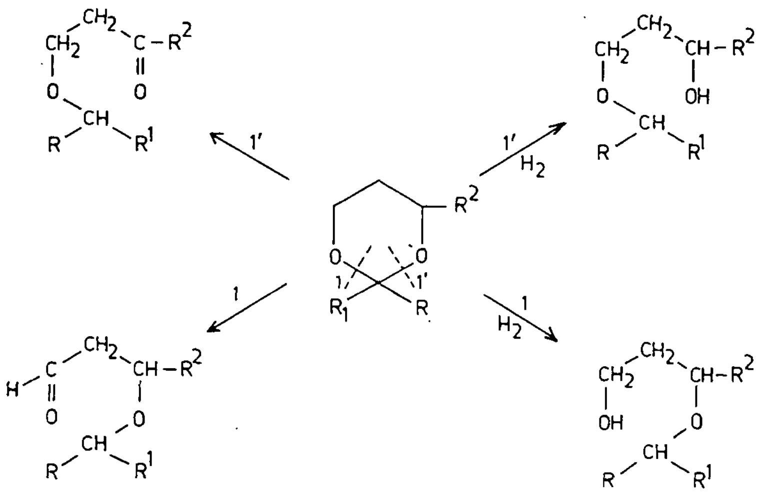


Fig. 16. Variation of the conversions of various esters on Pt/T as a function of the temperature.

formate is faster than that of 4-methyl-1,3-dioxane. The other two processes outlined in the scheme are of minor importance in the case of the formals: 1,3-diol monoethers can be found only in traces among the reaction products, and the maximum amount of β-methoxypropionaldehyde is also only ~1%.

Transformation of 1,3-dioxanes of ketal type

The main reaction directions established on the basis of the experimental data [2, 4] are summarized in the following scheme:



The transformations of cyclic ketals on Pt/T in the presence of hydrogen are characterized by hydrogenolysis and by an isomerization process accompanied by splitting of the C_2-O bonds. These two processes lead to the β-alkoxyoxo compounds and to the corresponding 1,3-diol monoethers. A detailed study of the relative extents of the processes indicated by *1* and *1′*, and of the factors affecting these, was not dealt with. Fig. 17 shows a plot of the conversion of a model compound, 2,2-dimethyl-1,3-dioxane, to the two main products, 3-isopropoxypropionaldehyde and 3-isopropoxypropanol, as a function of temperature.

The examined representatives of the 1,3-dioxanes (cyclic ketals) exhibit considerable reactivity even at a comparatively low temperature. Being more readily deformed, compounds containing open-chain substituents at C_2 are more reactive (90% conversion at 220 °C) than those containing cyclic substituents (60% conversion at 250 °C). The cyclic ketals of cyclohexanone are more reactive than the same derivatives of cyclopentanone; this can be satisfactorily explained by the differences in stereostructural properties of the two rings. The less stable axial C-O bond is more rapidly hydrogenolyzed, and therefore under the conditions of the hydrogenolysis the cyclohexanone ketals are the more reactive. The cyclic structure of C_2 substituents on the dioxane ring has no substantial effect on the reaction directions.

The experimental fact that the cyclic ketals of the 1,3-diols exhibit considerable reactivity on a platinum catalyst in the presence of hydrogen draws attention to the preparative applications of the reaction. Thus, the literature data referring to the hydrogenolysis of dioxanes describe the use of high pressures (>100 atm).

Transformation of cis- and trans-1,3-dioxadecalin homologues

By means of the examination of the *cis*- and *trans*-1,3-dioxadecalin homologues, a possibility arose for the study of the reactivities of the geometric isomers of 1,3-diol formals, acetals and ketals, and of the stereochemistry of the chemical transformations already described [7]. At the same time, these experimental observations also provide data which help to understand the mechanisms of the processes. The transformation directions described above for the formals, acetals and ketals are also characteristic for the derivatives of 1,3-dioxadecalin, with the following

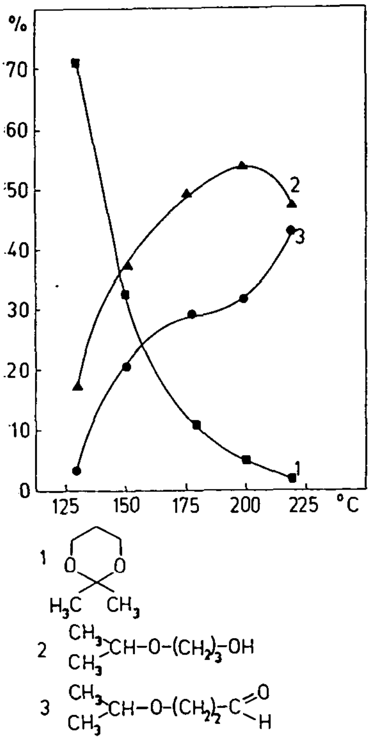


Fig. 17. Variation of the product composition in the transformation of 2,2-dimethyl-1,3-dioxane on Pt/T.

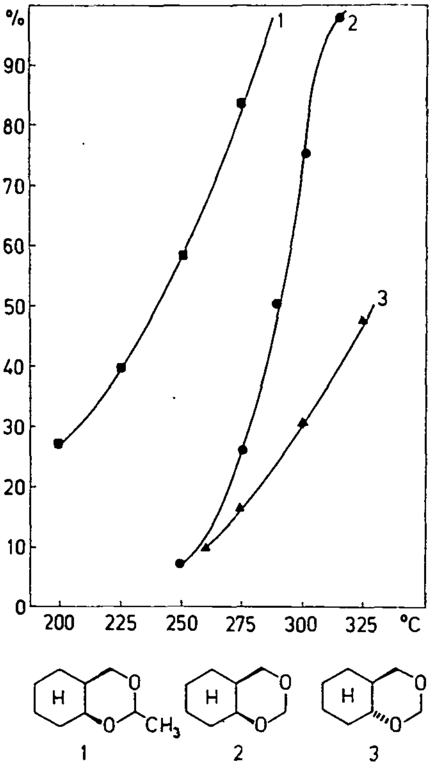
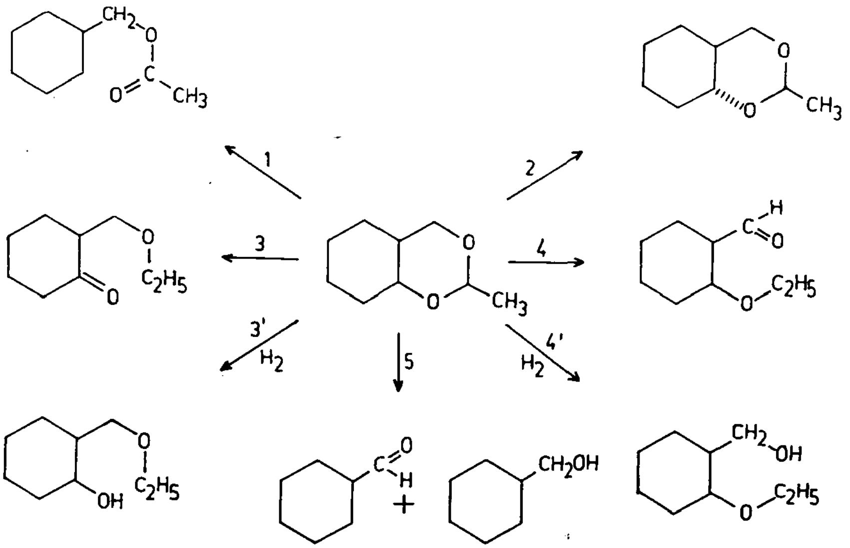


Fig. 18. Variation of the conversion of 1,3-dioxadecalins on Pt/T as a function of the temperature.

additions. The *cis*-isomers are significantly more reactive than the *trans*-isomers (Fig. 18).

Apart from the four main transformation directions discussed earlier, *cis-trans* isomerization, too, is observed with 1,3-dioxadecalin and 2-methyl-1,3-dioxadecalin. This phenomenon was also observed in the course of the investigation of the transformation of decalin on Pt/T in the presence of hydrogen.

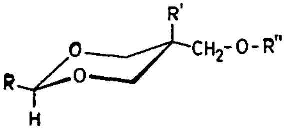
The transformation directions in the case of *cis*-2-methyl-1,3-dioxadecalin are presented in the following scheme:

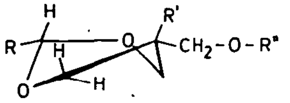


The relative extents of the reaction directions outlined in the scheme at *e.g.* 254 °C (60% conversion) are as follows: reaction direction *1* 40%; reaction direction *5* 25%; reaction directions *3*+*3'*+*4*+*4'* 25%; reaction direction *2* 10%. Other theoretically possible ester-formation was not observed. The fact that *trans*-1,3-dioxadecalin and *trans*-2-methyl-1,3-dioxadecalin are of significantly lower reactivity than the *cis*-isomers is shown by the decrease of the ester-formation reaction being minimal. In the case of 2,2-dimethyl-1,3-dioxadecalins only the reaction directions *3*, *3'* and *4*, *4'* can be observed. Processes beginning with the splitting of the C_2-O bond take place at very high rate. There is no substantial difference between the reaction rates of the *cis*- and *trans*-stereoisomers.

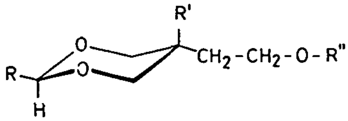
Transformation of stereoisomeric 5-alkoxyalkyl-1,3-dioxanes

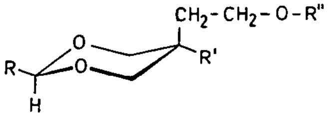
According to structural examinations to date, some of the 5-alkoxyalkyl-1,3-dioxanes are stereoisomers with different conformations, while in another group the isomers are compounds with the same conformation, *viz.* stereoisomers in the symmetric chair conformation:





R	CH_3	$i\text{-}C_3H_7$
R'	C_2H_5	C_2H_5
R"	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$





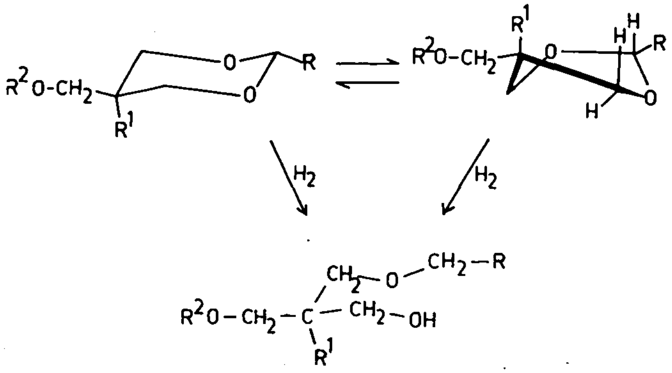
R	CH_3	$i\text{-}C_3H_7$	CH_3
R'	CH_3	C_2H_5	$i\text{-}C_3H_7$
R"	CH_3	CH_3	C_2H_5

The stereostructures of the compounds examined were established by measurement of the dipole moments and by study of the IR and NMR spectra (described in [20]).

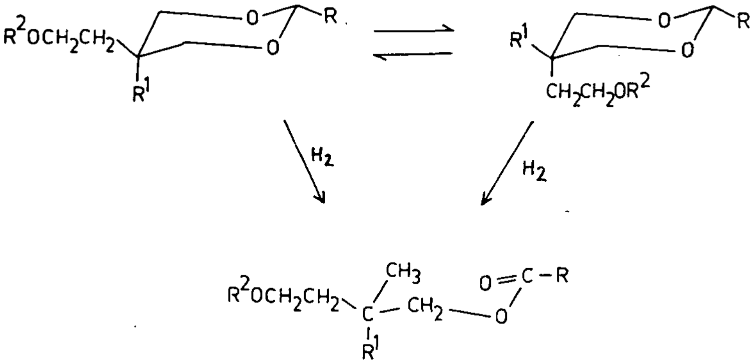
As regards the rates of transformation of the compounds, it can be stated that the *trans*-isomers are more stable than the *cis*-isomers. This finding refers mainly to the stereoisomers in different conformations; clearly, this difference in stability is less significant in the case of stereoisomers with the same conformation.

The main directions of transformation of 5-alkoxyalkyl-1,3-dioxanes on Pt/T in the presence of hydrogen are [8]: isomerization accompanied by the formation of esters; interconversion of the isomers (configurational isomerization); hydrogenolysis to the corresponding triol diethers; fragmentation.

The characteristic reaction directions for the transformations of stereoisomer pairs with different conformations are hydrogenolysis and isomerization. Ester formation is not observed:



In the case of stereoisomer pairs in the same (*i.e.* chair) conformation, the main process is isomerization accompanied by ester formation. It should be noted that, here too, isomerization of the stereoisomers takes place:



At higher temperature, or in the case of a longer contact time, the primary process resulting in the formation of the alkoxy esters in these compounds is accompanied by the hydrogenolysis of the ether bonds as a secondary process. The formation of products involving hydrogenolysis of the β-alkoxy group could also be observed.

During the study of the transformations of these compound types, therefore, interesting stereoselective catalytic processes were discerned, which at the same time also provide valuable data for the investigation of the mechanisms of transformation of dioxanes.

The substantial difference between the retention times of stereoisomers with different conformations draws attention to the applicability of gas-liquid chromatography in the conformational analysis.

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ИЗУЧЕНИЕ ПРЕВРАЩЕНИЙ 1,3-ДИОКСАЦИКЛОАЛКАНОВ ВПРИСУТСТВИИ ПЛАТИНОВОГО КАТАЛИЗАТОРА. ЭКСПЕРИМЕНТАЛЬНЫЕ РЕЗУЛЬТАТЫ И ДИСКУССИЯ. ОБЗОР

М. Барток, Й. Апьок

В настоящем обзоре обсуждаются и обобщаются экспериментальные результаты изомеризации и гидрогенолиза 1,3-диоксациклоалканов (60 соединений), выявляются новые направления превращений, определяющиеся структурой исходных соединений и другими параметрами реакций.