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Chemical Properties of 1,3-Dioxans

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A detailed description is given of the chemical properties of 1,3-dioxans. Special attention is paid to their thermal and catalytic reactions, and also to the preparation from them of various 1,3-bifunctional aliphatic compounds. Detailed consideration is given to the hydrolysis and the alcoholysis of dioxans, and their interaction with derivatives of carboxylic acids and also with certain inorganic compounds containing labile halogen atoms, etc. The mechanism of the various reactions of 1,3-dioxans are surveyed and discussed in detail on the basis of numerous examples. The bibliography contains 155 references.

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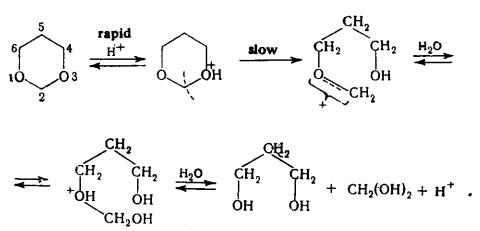
I. INTRODUCTION

The widespread application of the Prins reaction[1] has enabled alkenes[2], obtained in the petroleum-chemical industry, to be used for the single-stage synthesis of several valuable products—1,3-dioxans, diols, unsaturated alcohols, etc.—which can be employed directly as solvents, antiknock compounds, or as intermediates for the synthesis of medicinal preparations, plastics, etc. Publication of a review[2] was followed by considerable progress in the synthesis of 1,3-dioxans, connected in great measure with the use of solid electrophilic catalysts such as mineral acids on carriers (natural and synthetic aluminosilicates) and ion-exchange resins. The use of solid catalysts and flow-type apparatus in particular permitted a considerable simplification in the technology and improvement in the efficiency of the manufacture of 1,3-dioxans. The great quantity of new data which have been published on the transformations undergone by 1,3-dioxans are undoubtedly worthy of special discussion.

Most of the papers and patents which have been published recently have been concerned with the thermal and catalytic cracking of dioxans, and also their conversion into 1,3-bifunctional aliphatic compounds. Special attention will be paid to this question in the present review.

II. HYDROLYSIS OF 1,3-DIOXANS

The vapour-phase catalytic cracking of dioxans in the presence of water vapour involves chemical processes yielding products whose formation can be explained by hydrolysis of the dioxans and accompanying secondary reactions. Like the hydrolysis of acetals[3,4], that of 1,3-dioxans[5-13] is a second-order unimolecular reaction, since its rate is determined by the rate of formation of a carbon cation[12], the reaction being represented by the scheme:



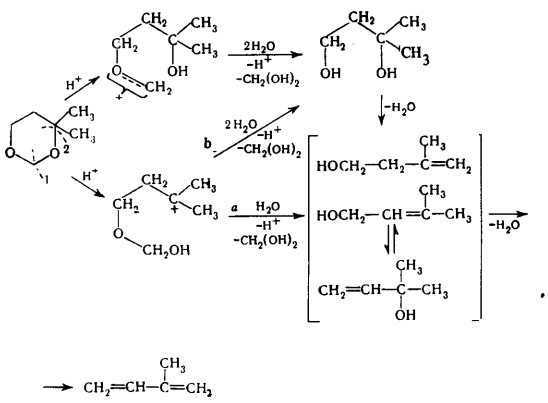
The first stage in the reaction involves addition of a proton, and is followed by slow cleavage of the 1,2- or 2,3-carbon–oxygen bond with formation of a carbon cation, which reacts with two water molecules to give an oxo-compound and a diol.

The above scheme shows that the hydrolysis of 1,3-dioxans in the presence of acid catalysts yields mainly the corresponding 1,3-diols, derivatives thereof[2,5-21], and oxo-compounds. The yield of diols varies within wide limits, since the reaction is reversible, and also because the diols undergo partial dehydration under the conditions of hydrolysis. The equilibrium can be shifted towards the diols by adding alkenes to the reaction mixture[2,14], when the formaldehyde resulting from hydrolysis reacts with the alkene to form the initial dioxan. The yield of 1,3-diol is considerably increased.

Depending on the structure of the 1,3-dioxans, under certain conditions hydrolysis leads directly to formation of conjugated 1,3-dienes[22-26]. This process occurs especially easily with 4,4-dialkyl-1,3-dioxans, hydrolysis of which involves rupture of the 3,4-carbon–oxygen bond as well as the usual cleavage of the 1,2- or 2,3-bond.

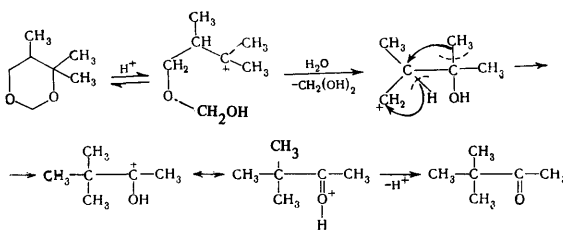
Stabilisation of the tertiary carbon cation which is formed[18,27], ultimately yielding a conjugated diene, can probably be achieved in two ways—(*a*) by loss of a proton

and formation of an unsaturated alcohol, and (*b*) by addition of two molecules of water with formation of a tertiary diol:



Alcoholysis of 4,4-dimethyl-1,3-dioxan gave a 30% yield of the corresponding tertiary ether[20,28,29], whose formation can be explained by interaction of the corresponding carbonium ion with the alcohol.

Many workers have studied the hydrolysis of polyalkylated dioxans. Thus a 50% yield of pinacoline was obtained by treating 4,4,5-trimethyl-1,3-dioxan with a 20% solution of hot hydrochloric acid[26,30], but the reaction mechanism was not discussed. The reaction can probably be represented by a double 1,2-type of rearrangement with migration of a hydride anion in the first stage and of a carbanion in the second stage:



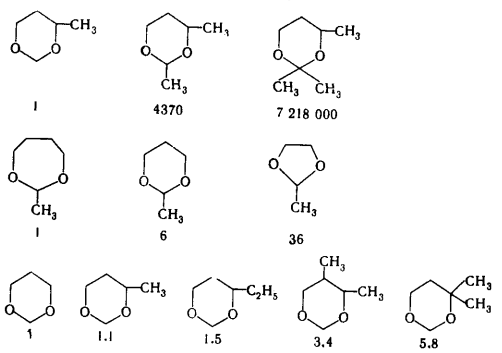
The action of dilute mineral acids (hydrochloric, sulphuric) on 4,4,5-trimethyl-1,3-dioxan gives a 50% yield of 2,3-dimethylbuta-1,3-diene[22,25,26]. The hydrolysis of 1,3-dioxans obtained from polyols leads to the formation of 1,3-dioxolans, which are in equilibrium with the initial dioxans[31]. Phenyldihydropyran has been obtained[32] by hydrolysis of 4-2'-hydroxyethyl-4-phenyl-1,3-dioxan and dehydrocyclisation of the resulting unsaturated diol.

Ion-exchange resins (Amberlite IR-120, Dowex 50-WX-4) are good catalysts for the hydrolysis of 1,3-dioxans[15,33]. Thus the latter have been used to effect the partial hydrolysis of the acetal of pentaerythritol[15]. A patent reports use of the boron trifluoride–ether complex for the hydrolysis of 4,4-dimethyl-1,3-dioxan, when isoprene was obtained as a result of hydrolysis and dehydration[24].

Skrabal[5] and Leutner[6,7] studied the kinetics of the hydrolysis of cyclic acetals in the presence of hydrochloric acid at room temperature. To obtain comparative data they examined the hydrolysis of cyclic acetals containing five-, six-, and seven-membered rings. Table 1, which we have compiled from the work of Leutner and of Gershkovich[18], enables us to compare the stability of various cyclic acetals and ketals under conditions of acid hydrolysis and to reach certain conclusions. Table 1 shows that increase in the number of alkyl radicals in position 2 of the dioxan ring produces a sharp increase in the rate of hydrolysis of the 1,3-dioxans, which enables us to trace the rule in the sequence formal–acetal–ketal (first series).

The authors showed also that the rate of hydrolysis of cyclic acetals increases as the ring becomes smaller (second series). Alkyl radicals in position 4 of the ring have a considerably smaller effect on the rate of hydrolysis (third series). The effect of aryl radicals in position 2 of the 1,3-dioxan ring was studied by Ceder[8], who showed that the rate of hydrolysis of 2-substituted 1,3-dioxans increases in the sequence—2-methyl < 2,2-diphenyl < 2-phenyl < 2-methyl-2-phenyl < 2,2-dimethyl < 2-β-styryl.

Table 1.



* The numerals below the formulae denote relative rates of hydrolysis in the given series.

Thus electron-donor substituents in position 2 increase the rate of hydrolysis of 1,3-dioxans by facilitating the formation of a carbonium ion.

Bender and Silver[10] have studied the effect of substituents in a 2-phenyl ring on the rate of hydrolysis of dioxans. They have shown that hydrolysis is accelerated by *ortho*- and *para*-hydroxyls. It is possible that direct intramolecular action of the hydroxyl on the dioxan ring takes place in the case of 2-*o*-hydroxyphenyl-1,3-dioxan. However, a high rate of hydrolysis is found also with 2-*p*-hydroxyphenyl-1,3-dioxan, where intramolecular interaction of this kind is impossible. In general these facts can obviously be explained by the strong electron-donor effect of the phenoxide ion formed under the experimental conditions[10].

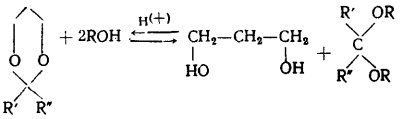
The kinetics and the mechanism of the hydrolysis of 1,3-dioxans have been discussed by Laurent et al.[9] and also by Aftalion et al.[11-13] on the basis of a large amount of experimental data. From their results they calculated several thermodynamic constants—enthalpy, activation energy, etc.—and found the hydrolysis to be endothermic, with an activation energy of approximately 26 cal mole^{-1}.

1,3-Dioxans containing electron-acceptor substituents in position 2, obtained from diols and chloral, are extremely resistant to hydrolysis, since the electron-acceptor groups prevent formation of a carbonium ion[17]. In some cases hydrolysis of the dioxans can be catalysed by traces of carbon dioxide[7]. Thus 5,5-dimethyl-1,3-dioxan-2-spirocyclopentane in an aqueous medium containing a mere trace of carbon dioxide gives 2,2-dimethylpropanediol and cyclopentanone. However, this course of reaction was not observed with the ketals of cyclohexanone and acetone.

The difference in behaviour between the dioxans was explained[33] by internal strain. Transition of a carbon atom from the tetracovalent state (ketal) to the trigonal state (cyclic ketone) is energetically more favourable in the case of cyclopentanone than with cyclohexanone[34]. The same reasons can obviously explain the hydrolysis of the acetals of 2,2-dimethylpropane-1,3-diol when they are boiled in 1,4-dioxan solution even in the absence of traces of mineral acids[15].

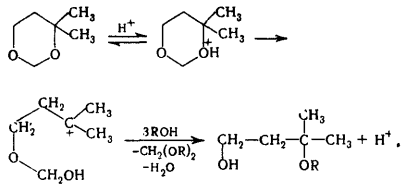
III. ALCOHOLYSIS OF 1,3-DIOXANS

1,3-Diols are obtained in good yield by the reaction between 1,3-dioxans and alcohols in the presence of acidic and electrophilic catalysts[2,27,29,35-41]:

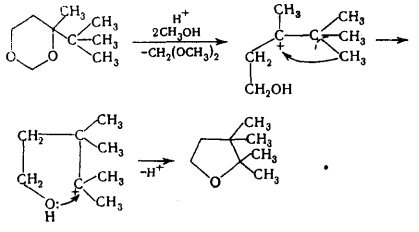


where R′, R″ = H, Alk and R = Alk. Acetals formed at the same time as the diols can be distilled from the reaction mixture, which shifts the equilibrium completely towards formation of diols. The mechanism of this reaction is analogous to that of the hydrolysis of 1,3-dioxans in the presence of acids.

Under certain conditions the alcoholysis of dioxans containing a quaternary carbon atom may lead to the formation of dienes[29,42,43], accompanied by ethers of tertiary alcohols[20,28,29]. The reaction mechanism probably includes formation of a carbonium ion[18,27]:



Korotkov et al.[27] report the formation of tetrahydrofuran compounds by the alcoholysis of 1,3-dioxan derivatives. The reaction involves cleavage of a carbon–oxygen bond adjacent to a tertiary carbon atom, followed by a retropinacoline rearrangement, leading to formation of a tetrahydrofuran ring:

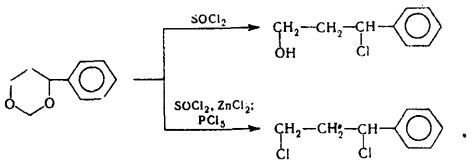


IV. INTERACTION OF 1,3-DIOXANS WITH INORGANIC COMPOUNDS CONTAINING LABILE HALOGEN ATOMS

Little work has been done on the reactions of 1,3-dioxans with inorganic halogen compounds. In 1912 the first study was made of the interaction of 1,3-dioxan with bromine, when a heavy oil, slowly decomposed by water, was formed[44]. The chlorination of 1,3-dioxans in the absence of moisture produced polychlorinated dioxans[2], whereas in aqueous solution 1,3-diols were formed in good yield.

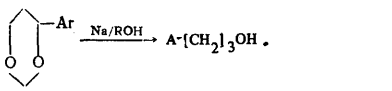
The chlorination of 4,4-dialkyl-1,3-dioxans in sodium carbonate solution produces 1,3-diols[45], one of the hydroxyls being attached to a tertiary carbon atom[46]. Compounds having this structure cannot be obtained by the hydrolysis of 1,3-dioxans, since under the conditions of the reaction the diols formed as intermediates are readily dehydrated to unsaturated alcohols and dienes.

In a large excess of thionyl chloride, as well as in the presence of concentrated hydrochloric acid, 3-phenyl-3-chloropropanol[46] is formed from 4-phenyl-1,3-dioxan, whereas in carbon tetrachloride a 50% yield of 1-phenyl-1,3-dichloropropane is obtained. Replacing the thionyl chloride by phosphorus pentachloride increases the yield to 95%:[46]

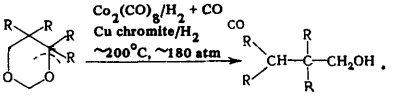


V. HYDROGENOLYSIS OF 1,3-DIOXANS

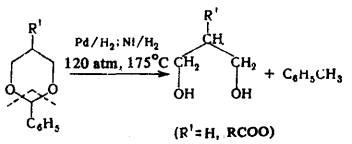
The hydrogenolysis of 1,3-dioxans leads to the formation of alcohols, the corresponding diols, or their monoethers depending on the conditions and the catalyst chosen and also on the structure of the initial compounds. This reaction has been widely studied by many investigators under various conditions in the presence of a large number of catalysts. Thus the hydrogenolysis of 1,3-dioxans has been investigated in the presence of metallic sodium in alcohol[32,47-53], Raney nickel[54,55], nickel[56], palladium[57-60], and platinum[61] catalysts, and also copper chromite[2,40,53,62-65] and octacarbonyldicobalt[66]. The changes undergone by 4-arylated dioxans have been investigated in the presence of metallic sodium and 2,6-dimethylheptan-4-ol, when the corresponding primary alcohols were obtained in yields exceeding 80%:[32,47-53]



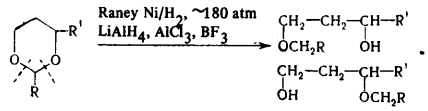
It was shown also that the hydrogenolysis of 1,3-dioxans containing mono- or poly-alkyl or -aryl substituents in positions 4 and 5 of the dioxan ring, on copper chromite or in the presence of octacarbonyldicobalt, leads to the formation of primary alcohols having an iso-structure[2,40,53,62-66]:



However, the use of metallic catalysts—nickel, palladium—for the hydrogenolysis of dioxans makes it possible to obtain 1,3-diols in good yield[56-60], whereas on platinum under analogous conditions the dioxan ring remains unchanged[61]:

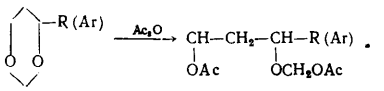


The hydrogenolysis of 1,3-dioxans in the presence of a Raney nickel–aluminium catalyst at high pressures leads to the formation of 1,3-alkoxyalkanols [54,55]. Similar results have been obtained with lithium tetrahydroaluminate and aluminium chloride, or the boron trifluoride–ether complex, as catalyst [67–70]:



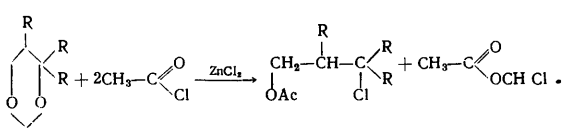
VI. REACTIONS OF 1,3-DIOXANS WITH DERIVATIVES OF CARBOXYLIC ACIDS

Many papers have been published on the reaction between 1,3-dioxans and acetic anhydride. This usually results in ester derivatives of a 1,3-diol in yields reaching 80%:[40,71–77]



Ness et al.[71] showed that, after the dioxan ring has been opened, the acetoxymethoxy-group adds to a secondary carbon atom. Results obtained by other workers[40,72–77] show that the dioxan ring is opened in only one way, whereas according to Shorygina[46,78] the esterification of 4-phenyl-1,3-dioxan may involve cleavage of the acetal ring at two bonds.

In the presence of electrophilic catalysts the chlorides of carboxylic acids open the dioxan ring to form 3-chloroacetoxyalkanes[79,80]:



These reactions are of industrial value, since the products can be used as plasticisers, solvents, etc.[79,80].

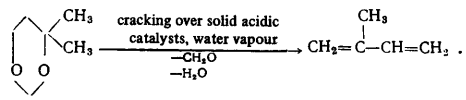
VII. THERMAL AND CONTACT–CATALYTIC REACTIONS OF 1,3-DIOXANS

Several scientific papers and patents have recently appeared on the thermal and catalytic transformations of 1,3-dioxans. These reactions of dioxans are not only of theoretical interest (in connection with the mechanism of the reaction, and the effect of the structure of 1,3-dioxans on the mechanism of catalysis) but also of great practical value. It has been found that good yields of extremely valuable conjugated dienes can be obtained by cracking 4- or 5-mono- or -di-alkyl-1,3-dioxans, synthesised by the Prins method from cheap industrial starting materials (alkenes and formaldehyde), over solid dehydration catalysts of acidic type[27,39,82–124]. The practical value of this reaction stimulated enhanced interest in the changes undergone by 1,3-dioxans, and led to the appearance of numerous publications and patents.

A systematic study of the conditions under which the process could be carried out and also the choice of catalysts was of primary importance for investigating the catalytic cracking of 1,3-dioxans. The pyrolysis of a cyclic acetal, 2-propyl-1,3-dioxan, was first reported by Bilger and Hibbert[81], who showed that, under the conditions of pyrolysis, cyclic acetals are more stable than the isomeric esters. These workers assumed that the reaction takes place by a radical mechanism.

Hamamoto and Mitsutani[122] investigated metal oxides and sulphates as catalysts. As the active component of the catalyst for the preparation of dienes from 1,3-dioxans many workers have used phosphoric acid, its acid salts, organic and inorganic phosphates on carriers and in their absence[27,39,82–112,114–124]. The carriers used have been graphite[82], coke[118], silica gel[84,90,104,114], silica–alumina[115,116], neutral silicates[101,105,108], kaolin[98], zeolite[114], kieselguhr[90,97,121], pumice[90], titanium dioxide[102,107–110], quartz[103,108–112], glass wool[105,108–110], aluminium oxide[84,90,114], silicon carbide[100,106,108–110], diatomite[99], and also mixed carriers[97].

An extremely interesting report has appeared on the transformation of 4,4-dimethyldioxan when passed together with triethyl phosphate through a tube containing silica gel heated to 400°C.[120] 4-Alkyl, 4,4-dialkyl-, and 4,5-polyalkyl-1,3-dioxans form dienes in yields which reach 90% depending on the reaction conditions[27,39,82–124]:



Water vapour is most often used as "diluent" in these processes, and plays an important part in maintaining the equilibrium of the acid phosphates in the catalytic decomposition of dioxans[94,115]. Nitrogen and the vapours of organic solvents are also employed as diluents[84,102,121]. The pyrolysis of 1,3-dioxans has been investigated over a wide range of temperatures of 150° to 450°C. The best results have been obtained at 200–350°C. There are indications that the relative proportion of side and secondary reactions increases as the period of contact becomes longer, the process shifting towards formation of isobutene or leading to the production of polymers of dienes and formaldehyde[94,117]. The pyrolysis of 1,3-dioxans has been investigated at atmospheric or nearly atmospheric pressures, but in several cases in which diluents were used the partial pressure of dioxan was 50–100 mmHg.

The effect of the nature of the catalyst and of the conditions of cracking has been investigated in detail for the conversion of 4,4-dimethyl-1,3-dioxan into isoprene[94,115,116,122,123]. The course of the reaction was shown to be greatly influenced by the nature of the carrier, its composition, and its structure, and also by the quantity of active component and the conditions under which the catalyst had been prepared (e.g. the temperature of ignition), as well as by the reaction temperature, the space velocity, etc.

In the cracking of 4,4-dimethyl-1,3-dioxan acidic carriers exhibit catalytic activity even in the absence of an active phase. In this case, however, the process exhibits poor selectivity towards formation of isoprene, the main product being isobutene[94,115]. Aluminium silicate, $B_2O_3 \cdot Al_2O_3$, Al_2O_3, SiO_2, $ZnO–SiO_2$, $Cr_2O_3 \cdot Al_2O_3$, and metal sulphates also catalyse the cracking of dimethyldioxan[94,113,115,122], the yield of isoprene being small.

A catalyst obtained by impregnating aluminium silicate with acid phosphates and then igniting possesses quite different properties. Both the yield and the selectivity are increased.

The properties of a catalyst depend substantially on the composition of the carrier. Thus increasing from 5% to 10% the alumina content of the carrier leads to a diminution in the selectivity and the stability of the catalyst[115].

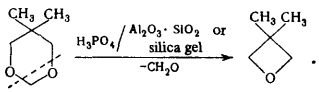
The explanation is that increase in the basicity of the carrier is accompanied by a change in the composition of the phosphate polymers formed on the catalyst surface during its ignition.

Another factor determining the activity and the selectivity of a catalyst is the concentration of active phase on the surface of the carrier and the associated proton acidity of the catalyst[116]. With increase in concentration of the active phase up to 4% a slow linear increase in proton acidity is observed; but with further increase in concentration the slope of the curve becomes greater. On the other hand, the activity and the selectivity of the catalyst with respect to isoprene increase rapidly over the section corresponding to saturation of the catalyst surface by phosphate polymers, i.e. up to 4–5% of the active phase; with further increase in concentration of the active phase and the associated acidity of the catalyst, the increase in activity and selectivity slows down, and constant values are reached[116].

1,3-Dioxans are regarded[116] as undergoing conversion both on Brønsted and on Lewis acid centres. However, the roles of the two types are different[115]. The formation of isoprene is attributed to the action of Brønsted acid centres, while the conversion of dioxan into isobutene and carbon is ascribed mainly to reaction on Lewis acid centres. Reversible adsorption of dioxans on the Brønsted centres is effected by oxygen atoms of basic character, and as a result intermediate ionic complexes are formed on the surface. These complexes break down to form dienes.

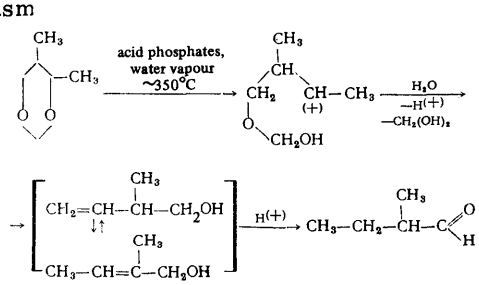
Cleavage of a carbon–carbon bond, with formation of carbon and isobutene, takes place independently of the formation of isoprene[14,115,116]. It is catalysed by both Brønsted and Lewis acid centres, but the chemisorption of dioxans on the Brønsted centres prevents this reaction[116]. Therefore variation in the number of Brønsted acid centres has a great effect on selectivity, whereas the total conversion is little affected by this factor.

In the cracking of alkyl-1,3-dioxans good yields of oxetans are obtained as well as dienes[89,124,125]. Under certain conditions oxetans can be prepared practically exclusively by means of this reaction[124]:



Little study has been made of the effect of the structure of the initial 1,3-dioxan on the course of reactions leading to the formation of oxetans. However, there are grounds for supposing that an important part is played by the symmetry of the dioxan molecule and the peculiar stability of the 3,3-dialkyloxetans formed in the series of alkyl-substituted oxetans[124].

The cracking of 4-methyl- and 4,5-dimethyl-1,3-dioxans on solid acid catalysts yields an alkylcarbinol[91,126] and isovaleraldehyde[127] depending on the space velocity, by the mechanism



VIII. CATALYTIC ISOMERISATION OF 1,3-DIOXANS

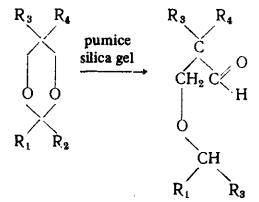
1. Heterogeneous Catalytic Isomerisation

The literature contains a large amount of experimental information on the heterogeneous catalytic isomerisation of 1,3-dioxans[125,128–131]. The isomerisation takes place by an ionic mechanism on weakly acid catalysts[125,128,129], and by a radical mechanism under thermal conditions[130,131].

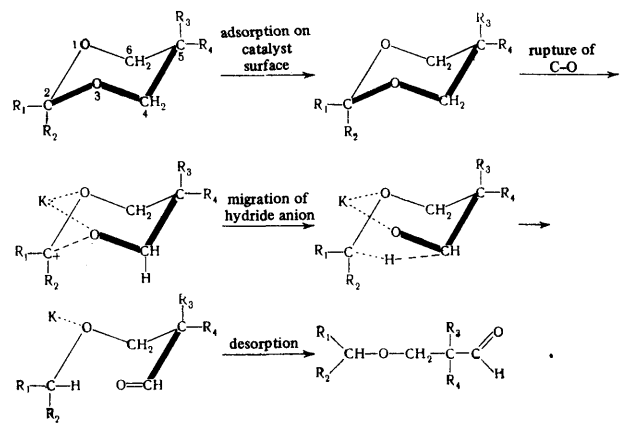
(*a*) Isomerisation by an ionic mechanism

Acid catalysts accomplish the cleavage of open-chain acetals with the formation of vinyl ethers and alcohols[132–139].

Rondestvedt and Mantell[125,128,129] note that 2,5,5-trialkyl-1,3-dioxans undergo isomerisation on pumice and silica gel into good yields of β-alkoxy-aldehydes:



The dioxan is assumed to be adsorbed on the acid centres of the catalyst in the chair conformation, and the resulting ionic compound is stabilised by migration of a hydride ion. The reaction mechanism can probably be represented by the scheme:



(i) Adsorption. Increasing the bulk of substituents prevents two-point adsorption of 1,3-dioxans. The size of the substituents R_1 and R_2 plays an especially important part. If R_1 in a dioxan ring in the chair conformation is considerably larger than R_2, it will occupy an equatorial position, which will prevent two-point adsorption of the dioxan on a catalyst surface, owing to repulsion of R_1 from the surface. The repulsion is eliminated on the migration of R_1 to the axial position. The energy required for such migration (1–4 kcal mole^{-1}) will depend on the difference in size between R_1 and R_2, and can be balanced by the difference in energy of repulsion between the substituents R_1, R_2 and the surface. If R_1 is an aromatic substituent, the attraction of its π-electrons to the acid centres of the surface will facilitate two-point adsorption. Electron-acceptor substituents in the aromatic ring, by diminishing the

electron density of the ring, prevent formation of a complex on the catalyst surface, whereas electron-donor substituents facilitate adsorption. Substituents containing unhindered oxygen and nitrogen atoms of basic character, located in the acetal ring, diminish the probability of oriented adsorption and thereby prevent isomerisation.

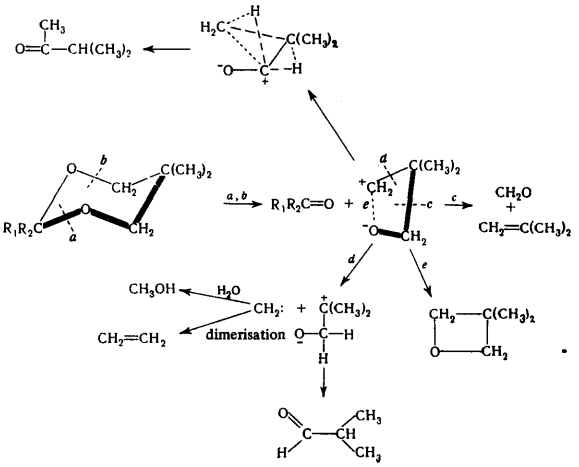
(ii) Rupture of carbon–oxygen bond and stabilisation of carbonium cation. The second stage of the reaction involves heterolytic rupture of the 2–3 carbon–oxygen bond with formation of a carbonium ion having the positive charge on the $C_{(2)}$ atom. The ability to form a cation depends on the size and the nature of the substituents attached to the $C_{(2)}$ atom. The diminution in the tendency of cyclic acetals to isomerise in the sequence—ketal > alkylacetal > formal—is associated with the formation and stabilisation of the carbonium cation, and serves to confirm the above hypotheses (see Sections II and III). The ease of isomerisation of 2-phenyl-1,3-dioxans depends on the nature of the *para*-substituent in the benzene ring. Electron-donor and electron-acceptor substituents respectively promote and impede isomerisation of 2-phenyl-1,3-dioxans, which in the absence of such substituents are extremely reactive.

The similarity in the first stages in the mechanisms of hydrolysis and isomerisation on weakly acidic catalysts (formation of a carbonium cation) explains the absence of isomerisation in 4,4-dialkyl-1,3-dioxans. Apart from obvious stereochemical considerations, it must be borne in mind that published data indicate[18,27] that 4-alkyl substituents facilitate cleavage of the 3–4 carbon–oxygen bond by diminishing the possibility of rupture of the 2–3 carbon–oxygen bond, which excludes the possibility of isomerisation. It must also be noted that the literature contains data on the successful isomerisation only of symmetrical 1,3-dioxans, for which cleavage of the 1–2 and 2–3 carbon–oxygen bonds is equally likely.

(iii) Migration of hydride anion from $C_{(4)}$ to $C_{(2)}$. Such migration accompanying cleavage of the 2–3 carbon–oxygen bond can be explained from the fact that aliphatic acetals form vinyl ethers on stabilisation of the carbonium cation formed during rupture of the carbon–oxygen bonds[132–139]. The cracking of six-membered cyclic acetals on weakly acidic catalysts yields alkoxy-aldehydes. In the latter case the catalyst ensures transfer of a hydride ion from $C_{(4)}$ to $C_{(2)}$, which is favoured also by the geometry of the intermediate complex. The constriction of the 1,3-dioxan ring at the oxygen atoms in the chair conformation brings the $C_{(2)}$ atom closer to the axial hydrogen atom attached to the $C_{(4)}$ atom, as a result of which the hydride ion migrates from $C_{(4)}$ to $C_{(2)}$ with cleavage of the 2–3 carbon–oxygen bond.

(iv) Desorption. The character of the transformation is greatly affected by the rate of desorption. A high rate at this stage favours smooth isomerisation, whereas slow desorption leads to resinification and deactivation of the catalyst. Thus the lone pairs of electrons in the case of 2-*p*-dimethylaminophenyl-1,3-dioxan or the presence of unhindered oxygen atoms in substituents in the dioxan ring prevent the isomerisation of these compounds owing to their strong adsorption.

Study of the secondary products enables conclusions to be drawn on the mechanism of the side-reactions. A detailed investigation of the products from 5,5-dimethyl-1,3-dioxan has shown that, besides the expected alkene and oxo-compound, catalysis yields substances whose formation can be explained by the scheme:

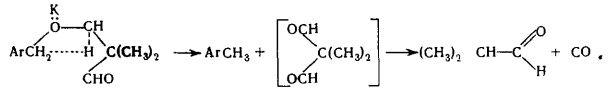


The main reaction via the zwitterion is (*d*), leading to the formation of isobutyraldehyde instead of the formaldehyde and isobutene expected according to reaction (*c*).

Besides compounds of the type $R_1R_2C:O$ (*a*–*b*) the reaction products were found to include formaldehyde, isobutene, isobutyraldehyde, isopropyl methyl ketone, $\alpha\alpha$-dimethylpropionaldehyde, methanol, 3,3-dimethyloxetan, ethylene, propene, and also hydrocarbons having a longer carbon chain than in the initial dioxan, with in rare cases vinyl ethers. Reaction (*e*) corresponds to closure of the zwitterion. Thus the ketal of cyclohexanone gives a 10% yield of the dimethyloxetan, whereas in the case of the initial ketal of cyclopentanone only traces of the dimethyloxetan were detected in the catalyst.

Under analogous conditions the seven-membered dioxetans are converted mainly into tetrahydrofuran derivatives, this reaction probably also involving the intermediate formation and closure of zwitterions. The detachment of a methylene radical by reaction (*d*) is confirmed by the presence of C_6 hydrocarbons among the products.

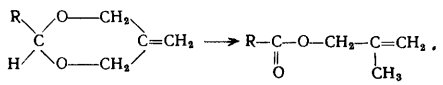
The by-products of the cracking of 2-aryl-1,3-dioxans include also toluene. The formation of toluene is probably accompanied by that of dimethylmalonaldehyde, which is decarbonylated to isobutyraldehyde:



It is very probable that benzaldehyde also is formed.

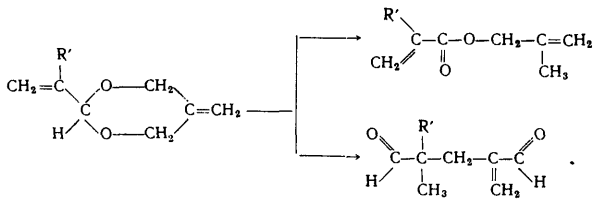
(*b*) Thermal isomerisation of 1,3-dioxans

An interesting case of the isomerisation of 1,3-dioxans on glass beads was observed by Weiss et al.[130,131], who found that with 5-methylene-1,3-dioxans the principal final products were methylallyl esters. Isomerisation into such esters is possible only with dioxans that contain a 2-hydrogen atom:



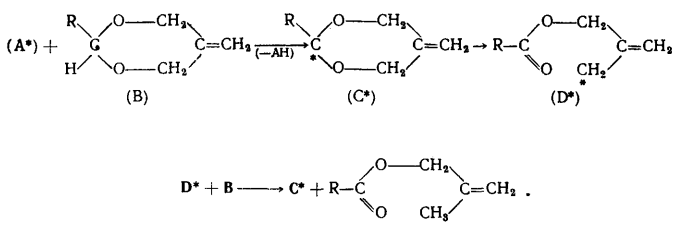
The nature of the 2-substituent has a fundamental effect on the character of the transformation of dioxans, but methylallyl esters are formed in all cases. If the substituent R

is a vinyl group, parallel formation of a dialdehyde takes place:

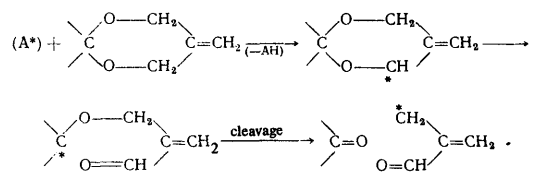


The presence of two 2-alkyl substituents stabilises the dioxan molecule. It must be noted that a radical mechanism has been suggested[140-146] for the conversion of acetals into esters. There appears to be no need[130] to introduce a free radical into the reaction medium to initiate the reaction, for the structure of the initial dioxan and diacetyl, containing double bonds of allyl type[130,131,140,141], creates favourable conditions for the occurrence of a radical reaction under the thermal conditions described.

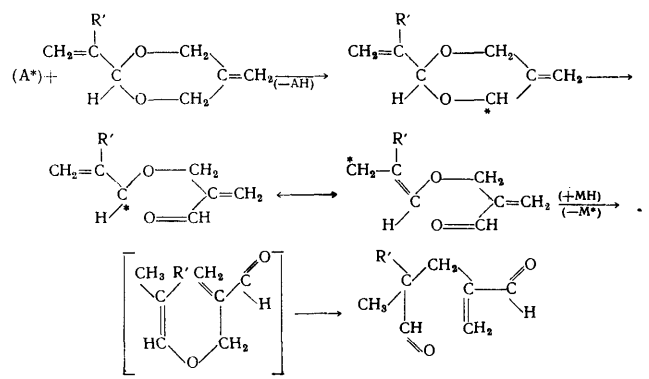
The reaction proceeds according to the scheme



The dioxan molecule undergoes cleavage if the primary act is attack on the quaternary carbon atom:

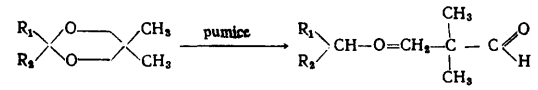


With 5-methylene-2-vinyl-1,3-dioxan as initial compound, however, analogous attack on the quaternary carbon atom leads to the formation of a dialdehyde:



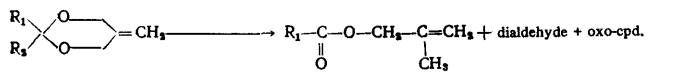
The possibility of the existence of an allyl vinyl ether—the hypothetical intermediate compound—represents a new concept in the field of radical reactions. Analogous views have been expressed earlier in the case of ionic reaction[147,148]. It is interesting to compare the results obtained by Rondestvedt[125,128,129] with those of Weiss et al.[130]. The tendency of 5,5-dimethyl-1,3-dioxans to isomerise increases with the structure of the initial oxo-component of the dioxans in the sequence—$\alpha\beta$-unsaturated aldehydes < aliphatic aldehydes < aromatic aldehydes < ketones—whereas 5-methylene-1,3-dioxans show an increase in activity in the reverse sequence—ketones < aliphatic aldehydes < aromatic aldehydes < $\alpha\beta$-unsaturated aldehydes[130]—see Tables 2 and 3. This is explained by differences in the structure of the 1,3-dioxans and in the mechanism of isomerisation.

Table 2. Ionic heterogeneous catalytic isomerisation.



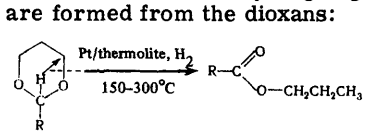
R_1	R_2	Unchanged dioxan, %	Yield based on dioxan converted, mole %		Isomerisation temp., °C
				$R_1-\underset{\underset{O}{\|}}{C}-R_2$	
$CH_2=CH-$	H	100	0	0	480
H	H	37	60	—	400—440
$(CH_3)_2CH-$	H	16	82	—	410
CH_3-	CH_3-	12	51	31	360
	H	0	>80	—	400
	H	0	75—80	5	400
	$-(CH_2)_5-$ O	0	80	10	390

Table 3. Radical heterogeneous catalytic isomerisation at 450°C.



R_1	R_2	Unchanged dioxan, %	Yield based on dioxan converted, mole %		
			methylallyl ester	dialdehyde	$R_1-\underset{\underset{O}{\|}}{C}-R_2$
$CH_2=C(CH_3)-$	H	8	39	13	47
$CH_2=CH-$	H	26.5	26	46	18
	H	41.5	79	—	17
$(CH_3)_2CH-$	H	58	97.5	—	1
	H	67	88	—	1.5
H	H	74	62	—	—
CH_3-	CH_3-	78.5	—	—	
	$-(CH_2)_5-$	100	—	—	0

An interesting possibility of isomerisation has been observed[149] with 2-alkyl-1,3-dioxans on platinum deposited on thermolite (1). In a stream of hydrogen good yields of propyl esters are formed from the dioxans:



2. Homogeneous Catalytic Isomerisation of 1,3-Dioxans

Esters are formed by the transformation of 1,3-dioxans in the presence of organic peroxides or by the action of ultraviolet radiation on these acetals[144,146]. The first stage in the reaction is regarded as involving detachment of hydrogen from the $C_{(2)}$ atom of the dioxan ring, this being followed by cleavage of a carbon–oxygen bond and formation of an ester molecule. 4-Methyl-2-phenyl-1,3-dioxan yields mainly n-butyl benzoate, the isobutyl ester being formed in smaller amount[144]:

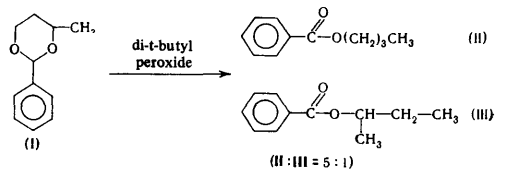
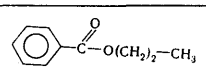
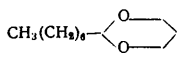
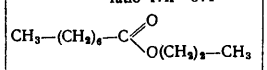
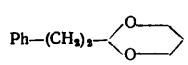
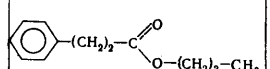


Table 4. Homogeneous catalytic isomerisation.

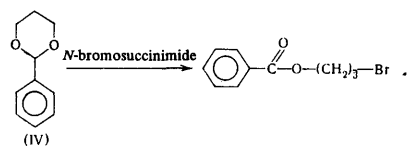
Dioxan	Catalyst	Reaction conditions	Reaction products	Ref.
IV	di-t-butyl peroxide	132°C 18 h		144
I	ditto	135°C 18 h	II III ratio I:II=5:1	144
	ultraviolet + acetone + t-butyl alcohol	20—40 h		146
	ditto	ditto		146

A similar distribution of products is observed in the isomerisation of mixed open-chain acetals in the presence of d-t-butyl peroxide, the course of the reaction being determined by the ability of the intermediate radicals formed to be stabilised by hyperconjugation[145]. Table 4 gives comparative data obtained for the isomerisation of 1,3-dioxans.

IX. POLYMERISATION AND OXIDATION OF 1,3-DIOXANS

The polymerisation, the copolymerisation, and also the oxidation of 1,3-dioxans have been very little studied. Strepikheev and Volokhina[150] investigated the possibility of their polymerisation in the presence of camphorsulphonic acid and obtained negative results. However, five-, seven-, and eight-membered cyclic acetals are in considerable measure polymerised under analogous conditions, the stability of the acetal ring increasing—and the tendency to polymerisation decreasing—with rise in temperature. These workers also found that the tendency to polymerise diminishes with decrease in the size of the ring in series of cyclic acetals, in the sequence—8 > 7 > 5 > 6—little difference in capacity for polymerisation being found between the five- and seven-membered rings. The enthalpy of cyclisation of acetals[151] also diminishes with the size of the ring, in the sequence 8 > 5 > 7 > 6. These results enable an assessment to be made of the relative tendency of cyclic acetals to polymerise.

The patent literature contains reports of the polymerisation and copolymerisation of 1,3-dioxans[79,152,153]. Peroxides, $\alpha\beta$-unsaturated esters, and their polymers have been obtained by the oxidation of 2-alkylene-1,3-dioxans in the presence of oxygen and cobalt(II) ions[154]. A good yield (~ 95%) of a benzoic ester has been obtained[155] by the reaction between *N*-bromosuccinimide and 2-phenyl-1,3-dioxan:



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