

ACID-CATALYZED TRANSFORMATIONS IN 1,3-DIOXACYCLANES IN LIQUID PHASE

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Abstract - Data about 1,3-dioxacyclane reactions with water, alcohols, thiols, H_2S , esters, amines, phenols are given. For the first time results obtained from reactions of reacetalization, exchange and recyclization of 1,3-dioxacyclanes have been summarized. Reaction mechanisms and kinetics have been investigated.

In recent years, there has been observed in our country and abroad a trend towards increased industrial production of 4,4-dimethyl-1,3-dioxan, which is intermediate in the synthesis of high-purity isoprene¹. Theoretical fundamentals have been developed and methods for manufacturing a whole series of other alkyl-, aryl-, halide- and polycyclic 1,3-dioxacycloalkanes²⁻⁹ have been introduced industrially. Ready availability of raw materials and easy manufacturing techniques on the one hand, and simplicity of transition to a wide spectrum of organic compound of various classes on the other hand, underlie the unremitting interest expressed by investigators in the chemistry and the technology of cyclic acetals. Generalizations of the achievements in the field of manufacture and study of the chemical and physical properties, stereochemistry and some aspects of practical utilization of 1,3-dioxacyclanes, published up to 1970, are contained in a number of reviews and monographies¹⁰⁻²².

In subsequent years, there were conducted detailed investigations of homolytical liquid-phase reactions and new heterolytical transformations of 1,3-dioxacyclanes under the action of thiols, esters, amines, phenols and other compounds leading to products of a great economical importance. The possibilities have been established of exchange reactions and recycling cyclic acetals effected under acid catalysis conditions.

The results of a study of the structure and the reactivity of 1,3-dioxacyclane

radicals and of the various transformations have been summed up in a recently published review²³.

In the present work, the authors have generalized the achievements of recent years in the field of some reactions of 1,3-dioxacyclanes with heterolytic breakdown of carbon-oxygen bonds.

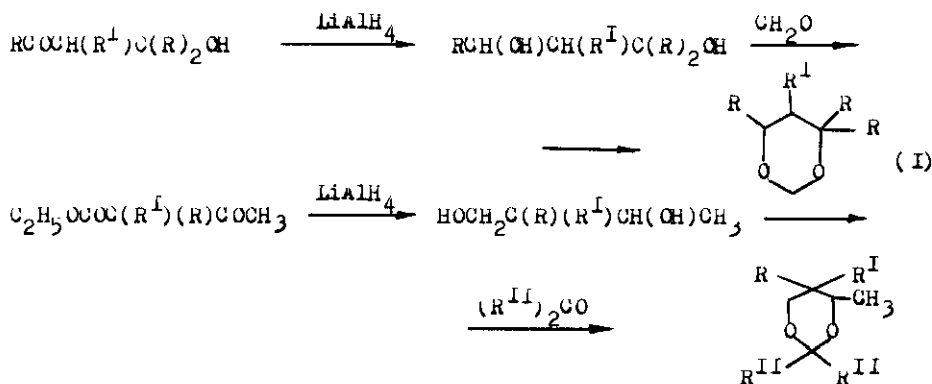
STEREOCHEMISTRY, KINETICS AND MECHANISM OF REACTIONS OF 1,3-DIOXACYCLANES WITH ALCOHOLS

Reactions of cyclic acetals with alcohols are a convenient method for obtaining glycols and another products²⁴⁻³⁷, methanolysis being very widely employed in preparative organic chemistry²⁸⁻³³.

However, the number of publications devoted to the stereochemistry, kinetics and mechanism of the reactions is very limited.

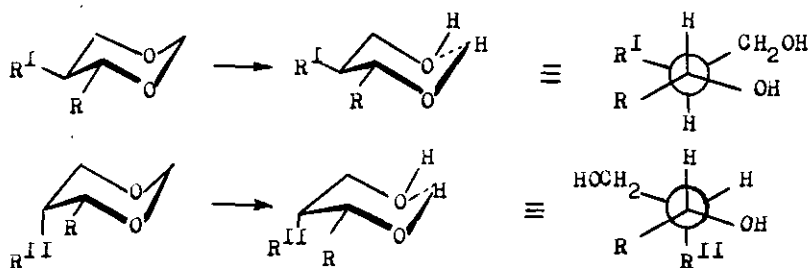
Initial data on the maintenance of the configuration of the diol part of the molecule in acetalization and alcoholysis were obtained by Garner and Lucas³⁴. It was established that 4,5-dimethyl- and 2,4,5-trimethyl-1,3-dioxolanes obtained from an optically active 2,3-butandiol exhibit an optical activity³⁴, the loss in optical activity on transition from glycol to formal and then again to glycol amounts to a mere 0.3%.

The retention of the steric centres of molecules of 1,3-dioxane in methanolysis has been noted in several works^{22,35-37}. Thus the reduction by lithium aluminium hydride of oxyketones^{35,36} or acetoacetic esters³⁷ resulted in substituted 1,3-diols whose acetalization leads to 1,3-dioxanes with a preferable content of one of the isomers:



R, R^I, R^{II} = H, ALKYL

Initial glycols were obtained by methanolysis I, trans-isomers yielding trans-1,3-diols, and from cis-erythro:



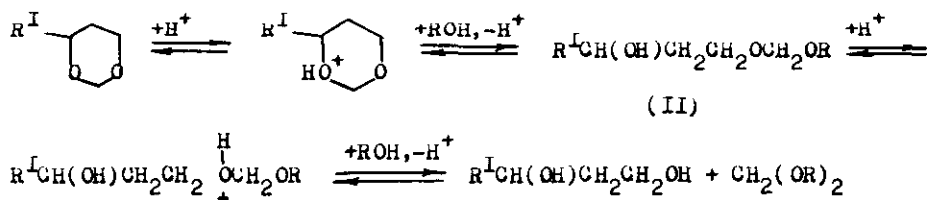
Retention of the configuration in the transition from diol to dioxycyclane and back evidences the fragmentation of the heterocycle ring on the carbon-oxygen bonds by the acetal carbon.

Five- and seven-link cyclic acetals show, during the methanolysis, a greater reactivity as compared to 1,3-dioxan³⁸. Farberov and co-workers³⁹ have found that the methanolysis of 4-alkyl-1,3-dioxan may be described by an equation of reversible reactions of the third order (first order in each of the reagents and the catalyst).

A highly negative value of S^{\ddagger} (-24 to -27 e.u.), in the view of the authors, confirms that methanolysis follows a bimolecular mechanism. The quantitative effect of the substituents on the rate of reaction is described by the Taft equation:

$$\lg \frac{k}{k_0} = -1.35 \cdot \sigma^* \quad (r = 0.985)$$

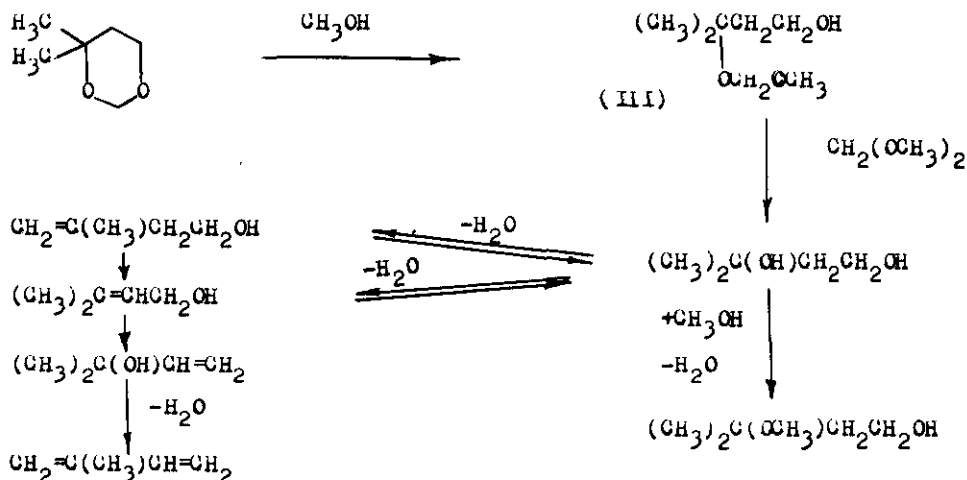
The suggested mechanism consists in a consecutive formation of oxonium and carbenium ions and fragmentation of the molecule on the O_1-C_2 and C_2-O_3 bonds:



The addition of the first molecule of alcohol is, probably, the rate determining step. The asymmetric acetal (II) reacts with the second molecule ROH rapidly, this leading to the observed products of the reaction, i.e. to diol and dialkoxy methane. The possible formation of oxonium ion as a result of attack by a proton remote from the oxygen atom substituent is not discussed.

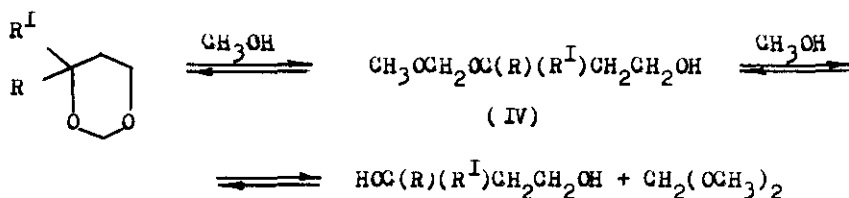
A detailed study of the products of the methanolysis of 1,3-dioxans^{40, 41} has revealed 4,6-dioxaneptan-1-ols which are very important for determining the sequence of the reaction stages. The study of the behavior of the individual compo-

nents of the reaction mixture in an acid catalysis has made possible a conclusion that the primary product in a reaction between 4,4-dimethyl-1,3-dioxan and methyl alcohol is 3,3-dimethyl-4,6-dioxo-1-heptanol (III) whose transformations lead to the following products of the reaction:



The close values of the kinetic parameters of methanolysis of 1,3-dioxans substituted at C_4 (Table 1) are probably the effect of the remoteness of the substituents from the reaction centre of the molecule^{42, 43}.

The reaction includes the formation of the first stage of the intermediate substituted 4,6-dioxoheptan-1-ol (IV) which may be obtained, under certain conditions, also as the main product of the reaction⁴⁴:



The authors explain the failure of 4-alkenyl-1,3-dioxans to conform to the rate constant vs. Taft constant correlation by a possible split of the heterocycle on O_3-O_4 bond and a formation of a stable allyl cation.

REACTIONS OF 1,3-DIOXACYCLANES WITH THIOLS AND HYDROGEN SULFIDE

The possibility of the interaction between cyclic acetals and thiols was shown for the first time by Shestakovskii and co-workers⁴⁵. Cyclic acetals, similar to linear ones^{46,47}, react with thiols in the presence of acid catalysts p-toluene-

sulfonic acid, HCl, ZnCl₂:

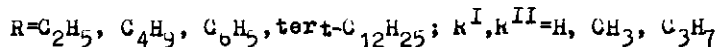
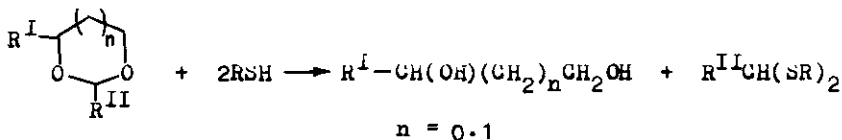
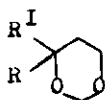


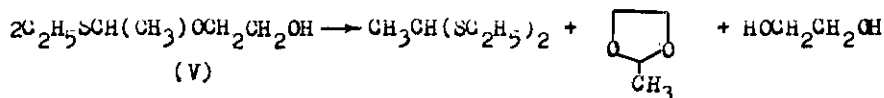
Table 1

KINETIC PARAMETERS OF METHANOLYSIS OF SUBSTITUTED 1,3-DIOXANS

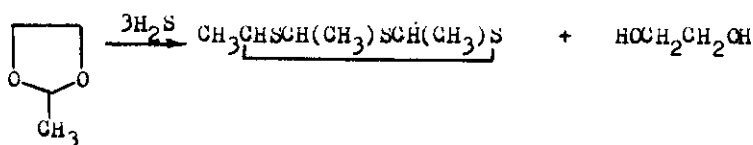


R	R ^I	K _p · 10 ³ , l/mole	H, kcal mole	K _r · 10 ⁵ , l/mole s	Δ _r , kcal mole	Referen- ces
H	C ₆ H ₅	8.40	8.1	0.39	22.7	42, 43
CH ₃	CH ₂ Cl	1.84	3.2	0.41	24.8	42, 43
H	H	10.83	5.8	1.68	26.7	42, 43
H	CH ₂ =CH	7.16	3.7	0.69	24.4	42, 43
H	CH ₃ CH=CH	14.70	3.1	1.35	21.4	42, 43
CH ₃	C ₆ H ₅	11.73	7.0	0.82	21.8	42, 43
H	CH ₃	5.40	6.1	1.20	27.0	42, 43
CH ₃	CH ₂ =CH	4.93	4.7	0.87	21.4	42, 43
CH ₃	CH ₃	7.30	4.4	2.79	23.8	42, 43
H	CH ₃				18.6	39
H	C ₂ H ₅				19.0	39
H	C ₃ H ₇				19.0	39
H	C ₃ H ₇				19.2	39

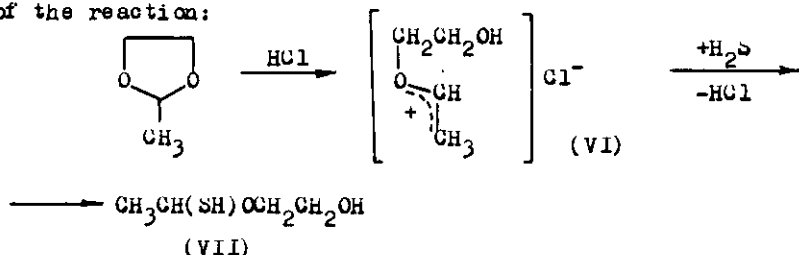
The authors have advanced a suggestion on the primary formation of intermediate product (V). However, the authors failed to isolate this compound because of its decomposition in distillation⁴⁵:



After treatment of 2-methyl-1,3-dioxolane by hydrogen sulfide the product was 2,4,6-trimethyl-1,3,5-trithiane and glycol⁴⁸.



It is assumed that an unstable α -chloro ester (VI) is formed on the first stage of the reaction:

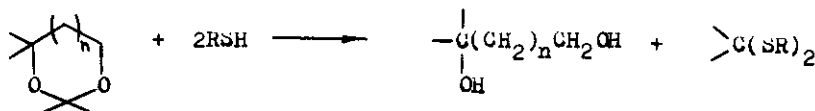


However, no VI and VII were found in reaction products. The cationite KY-2⁴⁹ may serve as a splitting catalyst.

Unsubstituted trithiane is formed from cyclic formals in a good yield⁵⁰.

The information thiolysis carries as regards the ascertainment of the stage mechanism of acid-catalysed transformations of 1,3-dioxacyclanes, and the possibility of obtaining glycols and dithioacetals having a practical significance, were the reasons for investigating the thiolysis of 1,3-dioxacyclanes in detail.

It was shown by way of numerous examples that the main products of the reaction are dithioacetals and glycols⁵¹⁻⁵⁶:

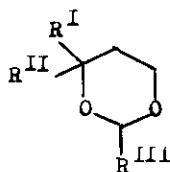


It was established that the structures of the 1,3-dioxacyclane tells, in the first place, on the selectivity of formation of glycol. Dithioacetals are formed mostly at a yield close on 90%⁵⁷ (Table 2).

The factor having a most substantial effect upon the activity of 1,3-dioxacyclane in a thiolysis is the size of the substituent by the acetal carbon of a heterocyclic compound. In a homogeneous catalysis, the reactivity of 1,3-dioxan is symbatic with the size of the substituent⁵³. In a catalysis by the KY-2 cationite^{56,58}, the rate of the reaction for 2-hexyl and 2-octyl-1,3-dioxan is probably determined by the rate of diffusion of substrates toward the active centres of the catalyst.

Table 2

YIELD OF GLYCOL AND DIALKYLTHIOACETALS IN THIOLYSIS OF 1,3-DIOXACYCLANES IN THE PRESENCE OF KY-2 CATIONITE



n	R ^I	R ^{II}	R ^{III}	Temperature, °C	Reaction time, h	Yield of glycol	Yield of thioacetal
0	H	H	H	100	1.5	32.3	99.5
1	H	H	H	100	1.0	67.6	95.5
2	H	H	H	80	1.5	37.8	80.2
1	H	H	CH ₂	60	3.5	61.2	98.5
1	H	H	C ₆ H ₅	60	3.5	92.5	96.5
1	H	CH ₃	H	80	1.5	85.8	98.0
1	CH ₃	CH ₃	H	80	0.8	34.4	69.2
1	C ₆ H ₅	H	H	80	3.0	-	98.1
1	H	CH ₃	CH ₃	60	2.0	82.6	95.1
1	H	H	C ₄ H ₉	60	4.0	-	78.2
1	H	H	C ₃ H ₇	80	3.0	71.2	82.5
1	H	H	C ₈ H ₁₇	60	4.0	68.8	84.0
1	H	H	C ₆ H ₁₃	60	3.5	70.5	88.7
1	H	H	C ₅ H ₁₀	100	2.0	-	63.5

In a homogeneous catalysis, the activities of thioalcohols up to butanethiol differ but negligibly⁵⁶. In a heterogeneous catalysis, there is observed an appreciable difference in the activity of the primary thiols differing by one methylene group, this being linked to a drop in the rate of diffusion of the reagent toward the active centres of the catalyst. Beginning with hexanethiol, the reaction practically stops⁵⁶.

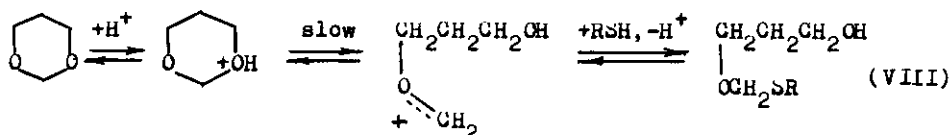
The reaction products of the thiolysis of 4,4-dimethyl-1,3-dioxane contained a compound with a structure of 4-thio-2,3-dimethylhex-1-ene⁵⁹. Tetrahydrofuran is

Table 3

 RELATIVE REACTIVITY AND ENERGY OF ACTIVATION OF THIOLYSIS OF
 1,3-DIOXACYCLANES

1,3-Dioxacyclane	Relative reactivity	Energy of activation, kcal/mole
1,3-Dioxan	1.00	14.5
1,3-Dioxolane	3.04	11.9
1,3-Dioxepane	2.69	13.6
2,4-Dimethyl-1,3-dioxan	1.19	16.3
4-Methyl-1,3-dioxan	0.51	14.3
4,4-Dimethyl-1,3-dioxan	0.49	15.9
2-Octyl-1,3-dioxan	0.31	16.7

Thus, protonation is not, in all probability, the slow stage, and the process is limited by the rate of the splitting of the cyclic compound:

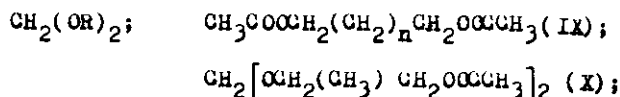


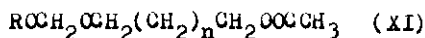
The second stage - fragmentation (VIII) to thioacetal and glycol - proceeds similarly to the first one.

REACTIONS OF 1,3-DIOXACYCLANES WITH ESTERS (ESTEROLYSIS)

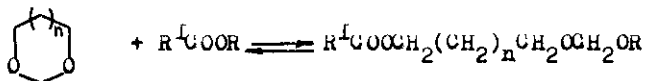
The data on reactions of 1,3-dioxacyclanes with such an abundant class of organic compound as esters have appeared in the literature but recently. Esterolysis expands substantially the potentialities of the synthesis of some very valuable compounds and the understanding of the acid-catalyzed transformations of 1,3-dioxacyclanes⁶⁶.

In an acid catalysis, the main products of esterolysis (at temperatures of up to 150°C) of unsubstituted 1,3-dioxans are four products, linear acetal, glycol diacetate (IX), oxy ester formal (X) and unsymmetric oxy ester and aliphatic alcohol formal (XI)^{66, 67};





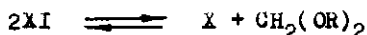
A separate study of the behaviour of (XI) in an esterolysis is indicative of its formation in the first stage of the reaction⁶⁶:



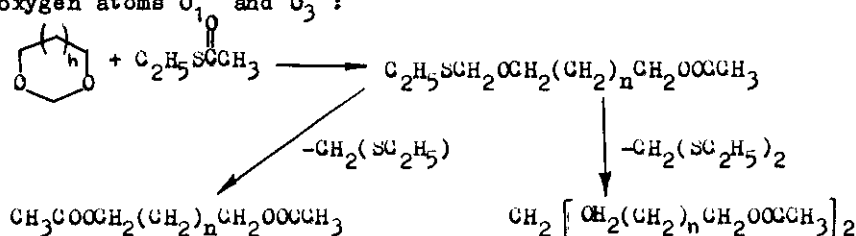
Interacting with the second molecule of ester, (X) turns to a diester (IX) and acetal:



Symmetrization of (XI) leads to acetal and (X):

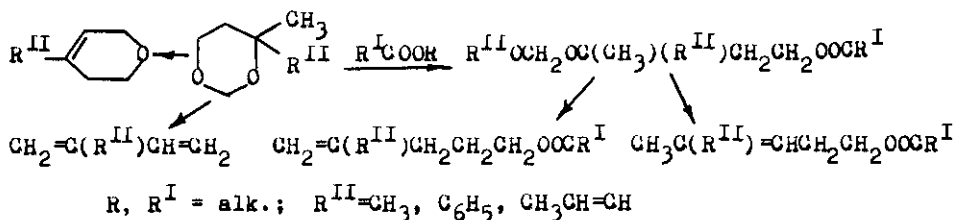


Products, similar to compounds (IX), (X) and (XI), are formed in esterolysis by thioesters⁶⁸. As the sulphur atom is always with acetal carbon, it may be assumed that the heterocyclic compound is fragmented on the bonds between acetal carbon and oxygen atoms O₁ and O₃:

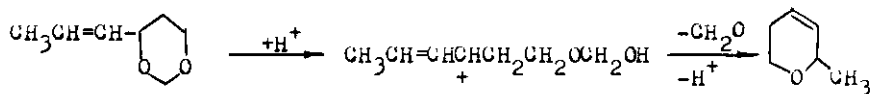


It should be noted that active and selective esterolysis catalysts are proton-donor acids^{69, 70}. Polymers are mainly formed in catalysis by Lewis acids. The selectivity of formation of diacetates increases by a factor of 1.5-2 in a heterogeneous catalysis by cation-exchange resins⁶⁸.

The introduction of the propenyl, methyl or phenyl substituent in the fourth position of the ring results in cracking products⁶⁸:



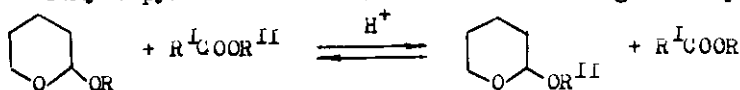
The formation of 2-methyl-5,6-dihydro-2H-pyran is the result of the elimination of the formaldehyde molecule from 4-propenyl-1,3-dioxan:



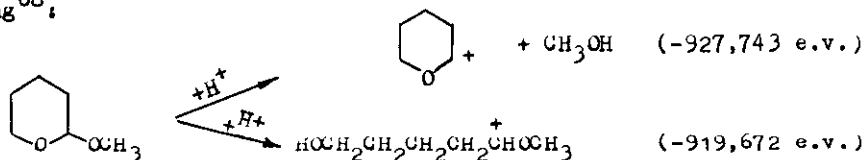
As the molecular weight of the ester increases, its activity in the esterolysis falls off⁶⁸.

The rate of the reaction of 1,3-dioxolane, 1,3-dioxan and 1,3-dioxepane with amyl acetate is proportional to the concentration of each of the reagents and the catalyst, which is sulfuric acid⁷¹. The energy of activation, determined on the interval of temperatures between 40 and 80°C by the beginning rate of consumption of 1,3-dioxacyclanes, amount to 8.0, 13.2, 10.8 kcal/mole for 1,3-dioxolane, 1,3-dioxan and 1,3-dioxepane respectively. The character of the value of concentration as a function of time is typical of reversible reactions, and the results evidence a possibility of describing esterolysis by the reversible reaction equations^{71, 73}.

2-Alkoxytetrahydropyrans react with esters to exchange alkoxy groups⁷²:



It was shown by quantum-chemical calculations that the splitting of exo-cyclic acetal bond is energetically more favourable (by 100 kcal/mol) than the opening of the ring⁶⁸:



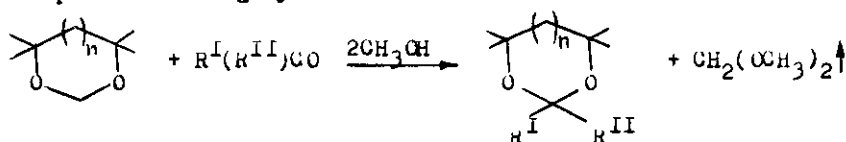
The esterolysis of 2-alkoxytetrahydropyrans is described by an equation for reversible third-order reactions⁶⁸.

The dependences of rate constants and reaction equilibrium upon the temperature (Table 4) have yielded the energies of activation of the forward and the reverse reaction (12.3 and 9.1 kcal/mole respectively).

Based on the consideration of the structure of the reaction products and the kinetic regularities, the mechanism of esterolysis may be represented as the splitting of the cyclic compound along the C-O-C bond of the acetal carbon by the action of the acyl cation:

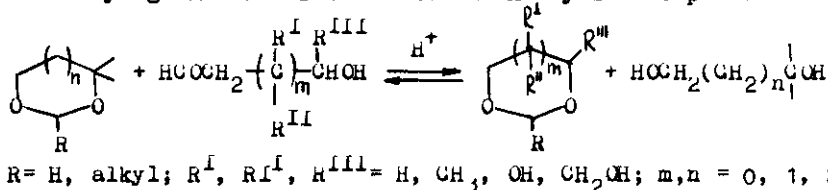


are used, a convenient method for shifting the equilibrium is to conduct the reaction in methanol. The removal of methylal from the reaction zone ensures obtaining the end product in high yield⁷⁷:



When ketones are employed, the formation of 1,3-dioxacyclanes proceeds smoothly for both 1,3-dioxacyclanes unsubstituted and substituted at C₄⁷⁸.

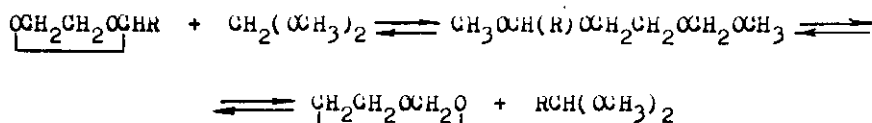
The reacetalization of 1,3-dioxacyclanes by di-, tri- and tetraols is the method for introducing various substitutes into the fourth, fifth, sixth position of the ring and varying the number of links in the cyclic compound^{78, 79}:



It becomes possible to shift the equilibrium by removing the low-boiling 1,3-dioxacyclane from the reaction zone. For said purpose, it is good practice to employ as starting compounds ethylene glycol and 1,3-dioxacyclane, free from substitutes at C₂. Because of a high yield of 1,3-dioxalane, said method may be recommended as means for analyzing high-boiling cyclic formals⁷⁹.

Reacetalization of 1,3-dioxalanes by linear acetals is carried out under milder conditions as compared to that by aldehydes⁸⁰.

The primary product of the reaction is probably mixed acetal forming as a result of the addition of fragments of linear acetal on the C₂-O bond of 1,3-dioxacyclane⁸¹:

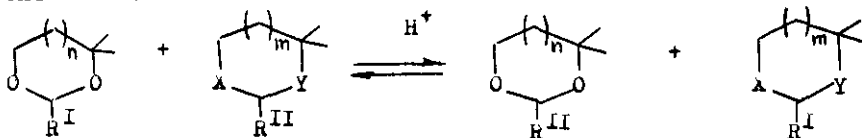


When using methyl alcohol acetals and cyclic formals, the resulting methylal is driven from the reaction zone and the yield of final 1,3-dioxacyclane rises to 80-90%.

Ethylene and propylene oxides react with 1,3-dioxacyclanes to form up to 25-40% 1,3-dioxalanes and 4-methyl-1,3-dioxalanes⁸². When use is made of the stabler 3,3-bis(chloromethyl)dioxacyclobutane and 1-chloro-2,3-epoxypropane, formed are

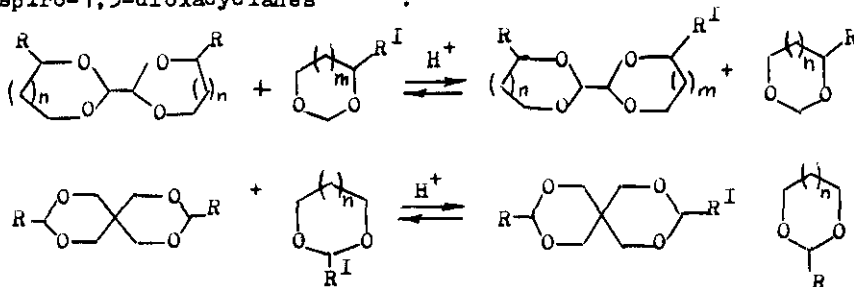
2-substituted 5,5-bis(chloromethyl)-1,3-dioxans and 2-substituted 4-chloromethyl-1,3-dioxolanes with yields of 65-75%. It proves impossible to isolate the expected alkyl-substituted α, β -oxides from the reaction products because of a high rate of their polymerization. The reaction between 1,3-dioxepane with halide-substituted oxides results in tetrahydropyran⁸².

Exchange reactions of 1,3-dioxacyclanes with 1,3-dioxacyclanes, 1,3-oxathianes, 1,3-dithions⁸³⁻⁸⁵;



$m, n = 0, 1, 2$; $R^I, R^{II} = \text{alkyl, aryl...}$; $X, Y = O, S, N$ -

Exchange reactions of 1,3-dioxacyclanes make it possible to obtain asymmetric bis- and spiro-1,3-dioxacyclanes⁸⁶⁻⁸⁸;



The resultant compounds are very interesting objects from the viewpoint of determining the reactivities of each of the cyclic compounds and investigation of stereochemical problems.

The activation energy of exchange reactions lies within the limits of 2 to 12 kcal/mole (Table 5).

The rate of the slow stage is proportional to the concentration in the first order of each of the reagents and the catalyst. In all probability, the reaction follows the pattern:

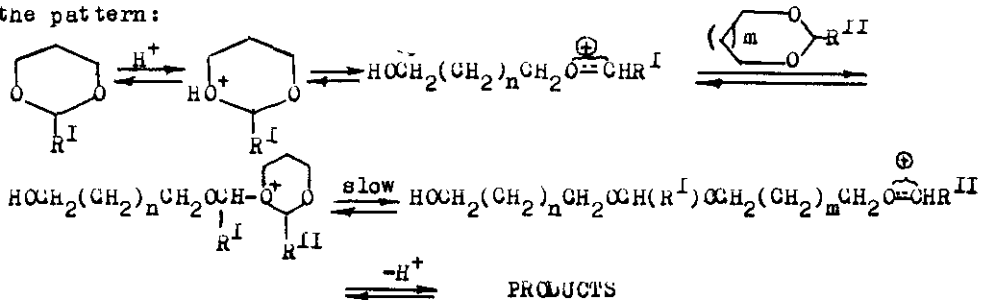


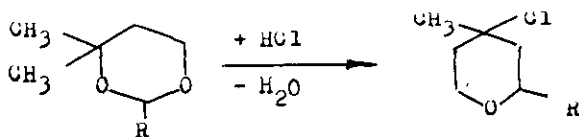
Table 5

DIFFERENCE IN ACTIVATION ENERGIES OF FORWARD AND REVERSE EXCHANGE REACTIONS OF 1,3-DIOXACYCLANES

Reaction	$E = E_f - E_r,$ kcal/mole
1,3-dioxolane + 2-methyl-1,3-dioxan	12.7
1,3-dioxolane + 2,4-dimethyl-1,3-dioxan	1.3
1,3-dioxolane + 2,4,4-tert-methyl-1,3-dioxan	7.7
1,3-dioxolane + 4-methyl-2-isopropyl-1,3-dioxan	5.5
1,3-dioxolane + 4-methyl-2-propyl-1,3-dioxan	7.8
1,3-dioxolane + 4-methyl-2-amyl-1,3-dioxan	8.9
4-methyl-1,3-dioxolane + 2-isopropyl-1,3-dioxan	4.8
4-methyl-1,3-dioxolane + 2-isopropyl-1,3-dioxepane	9.4
4-methyl-1,3-dioxolane + 2-isopropyl-1,3-dioxolane	7.9
4-methyl-1,3-dioxolane + 2,4-dimethyl-1,3-dioxan	5.8

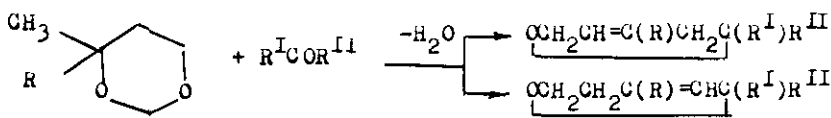
REACTIONS AND RECYCLIZATION OF 1,3-DIOXACYCLANES

It was established that 2-alkyl-4,4-dimethyl-1,3-dioxans recyclize in the presence of hydrochloric acid into 2-alkyl-4-chloro-4-methyltetrahydropyrans^{89,90}:



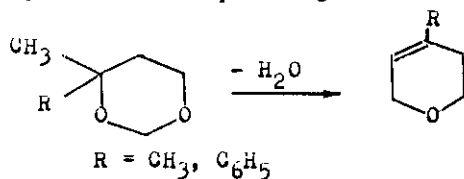
R = CH₃; i - C₃H₇, n-C₃H₇

Probably, the reaction of reacetalization is common to 1,3-dioxans with electron-donor substituents at C₄. Thus, in the reacetalization of 4-R-4-methyl-1,3-dioxans by ketones there are formed not the 2,2,4,4-tetraalkyl-1,3-dioxans, but isomeric alkyl-substituted dihydropyrans^{91, 92}:

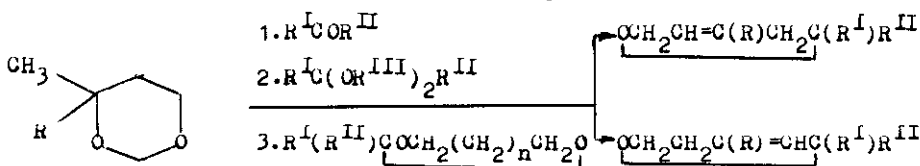


R = CH₃, C₆H₅; R^I, R^{II} = CH₃, C₂H₅, -(CH₂)₄, -(CH₂)₅-

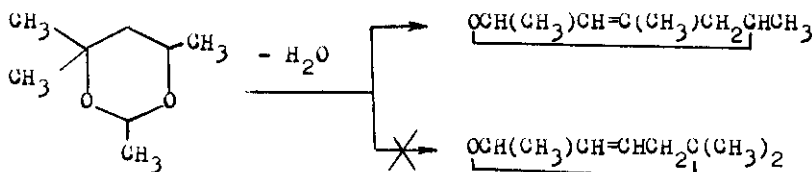
4-Methyl- and 4-phenyl-5,6-dihydro-2H-pyrans are formed as a result of intramolecular dehydration of 4,4-dimethyl-, or 4-methyl-4-phenyl-1,3-dioxan in the process of their synthesis and splitting:



In the presence of aldehydes, ketones or linear (cyclic) acetals, there is noted the formation, along with 4-phenyl-5,6-dihydro-2H-pyran, of 2-R^I-2-R^{II}-4-phenyl-3,6-dihydro- and 2-R^I-2-R^{II}-4-phenyl-5,6-dihydropyrans⁹²:



2,4,6-Trimethyl-5,6-dihydro-2H-pyran only is obtainable from 2,4,4,6-tetramethyl-1,3-dioxan⁹²:



Thus, the formation of dihydropyrans is the result of the breakdown of the O₃-C₄ bond, which is possible only if a sufficiently stable (for example, a tertiary) carbonium ion is formed.

Recyclization seems to be a convenient transition from the readily available petroleum olefins to substituted dihydropyrans and their derivatives. In addition, the study of said reaction makes it possible to go into greater detail on the formation of dihydropyrans in thermocontact splitting of 4,4-disubstituted 1,3-dioxans into diene hydrocarbons.

REACTIONS OF 1,3-DIOXACYCLANES WITH AMINES AND PHENOLS

Among the known methods of obtaining diene hydrocarbons, and in particular, of isoprene, promising is the "dioxan method" consisting in the splitting of 4,4-dimethyl-1,3-dioxan over solid catalysts in the vapour phase⁹³. The technology developed by Soviet scientists features good performance indicators⁹⁴ and makes

it possible to obtain specific high-purity products⁹⁵. A disadvantage of the process is the formation of considerable amounts of hard-to-utilize by-products and the need of frequently regenerating the catalyst¹.

In scientific literature, there are data on the possibility of obtaining diene hydrocarbons as a result of the decomposition of alkyl-1,3-dioxans in liquid phase by water or alcohols^{21, 96}. However, the selectivity of formation of diene is then lower than that in thermocatalytic processes. This underlies the search for compounds which react with formaldehyde but do not react with dienes. Most promising for said purpose proved to be amines and phenols.

THE REACTION OF 1,3-DIOXANS WITH AMINES

The best yields of dienes are achieved at a molar ratio of amine to dioxan within the limits of 0.2 to 0.4-to-1⁹⁷. At lower amine concentration, the diene yield drops because of the presence in the reaction zone of a large quantity of unbonded formaldehyde.

The number of alkyl substituents in the heterocyclic compound has negligible effect upon its reactivity. Nonetheless, it is well to note a somewhat lower selectivity of formation of divinyl from 4-methyl-1,3-dioxan because of the difficulty of dehydration of the primary-secondary glycols as compared to the primary-tertiary ones⁹⁸. The determining influence upon the selectivity of formation of diene is the nature of the amine (Table 6).

The attendant diene products are, depending on the nature of the amine, oximes^{98, 99}, hexamethylenetetramine¹⁰⁰, formalzene¹⁰¹ and others.

Of interest is the splitting of dioxans in the presence, instead of amine salts, of bifunctional organic compounds containing, along with the NH₂ group, acid residues such as sulfanilic acid¹⁰². The diene yield is in this case as high as 80-85%.

THE REACTION OF 1,3-DIOXANS WITH PHENOLS

The aim of the first investigation of the reaction of 1,3-dioxans with phenols was the manufacture of phenol resins^{103, 104}. The obtained phenol resins were worse in quality than industrial specimens, the reason for this being the presence in the polymer of propylene and ethylene bridges:

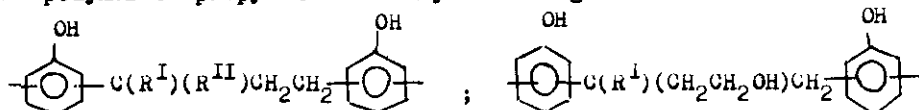


Table 6

MANUFACTURE OF DIENES BY AMINOLYSIS OF 4-METHYL-, 4,4-DIMETHYL- AND 4,4,5-TRIMETHYL-1,3-DIOXANS

Amine	Conversion of dioxans, %			Selectivity of formation of diens, %		
	4-methyl-1,3-dioxan	4-dimethyl-1,3-dioxan	4,4,5-trimethyl-1,3-dioxan	divinyl	isoprene	2,3-dimethyl-1,3-butadiene
Butylamine	39.6	40.3	38.5	52.7	68.5	72.4
Dibutylamine	31.4	34.5	32.8	59.4	67.4	68.5
Tributylamine	50.4	51.8	48.6	11.8	12.6	15.8
Octylamine	39.6	42.3	42.4	62.8	66.9	70.5
Decylamine	40.5	42.8	39.8	60.3	66.4	69.2
aromatic amines						
Methylaniline	49.7	63.4	49.9	68.5	78.6	73.9
Dimethylaniline	52.3	51.0	48.5	54.4	62.8	55.7
Pyrrolidone	72.4	77.0	69.2	52.8	65.2	61.3
Methylpyrrolidone	59.4	61.0	57.8	59.5	63.6	61.3
Morpholine	48.4	45.0	48.2	77.4	95.4	98.8
Ethylenediamine	62.5	60.5	59.4	68.2	71.4	72.6
Hydroxylamine	77.2	82.9	71.3	75.1	83.3	87.6
Non-organic amine						
Ammonia	99.3	98.6	96.8	86.7	97.9	95.7

It was shown later¹⁰⁵ that the reaction may be directed toward the formation, depending on conditions, of glycols or dienes (Tables 7, 8).

The presence in phenol of substituents influences substantially the yield of glycols. The condensation of m,p- and o-chlorophenols and 2,4-dichlorophenol with

aldehyde on the α -carbon atom of the aromatic ring is difficult, and the yield of glycol falls off to 30-40%.

When the temperature is raised and the experiment is conducted under non-equilibrium conditions favouring the dehydration of glycols, the end products of the reaction are diene hydrocarbons¹⁰⁵.

Lower yields of dienes in phenolysis as against aminolysis are, in all probability, the consequences of a high rate of processes of alkylation of phenols by compounds containing unsaturated bonds and hydroxyl groups.

The study of the reaction of alkyl-1,3-dioxans with various substituted phenols (Table 8) tends to indicate that dienes are formed effectively when using phenols free from most active α -hydrogen atoms, e.g., 2,6-di-tert-butylphenol.

Table 7

MANUFACTURE OF GLYCOLS BY PHENOLYSIS OF 1,3-DIOXACYCLANES

1,3-Dioxacyc- lane	Phenol	Glycol	Yield, %
1,3-Dioxan	Phenol	1,3-Propandiol	96.7
1,3-Dioxan	m-Cresol	1,3-Propandiol	95.8
1,3-Dioxan	o-Cresol	1,3-Propandiol	36.3
1,3-Dioxan	p-Chlorophenol	1,3-Propandiol	41.5
1,3-Dioxan	o-Chlorophenol	1,3-Propandiol	39.6
1,3-Dioxan	2,4-Dichlorophe- nol	1,3-Propandiol	31.4
1,3-Dioxan	2,6-Di-tert-bu- tylphenol	1,3-Propandiol	99.3
1,3-Dioxan	2,4-Di-tert-bu- tylphenol	1,3-Propandiol	63.5
1,3-Dioxolane	Phenol	Ethyleneglycol	92.1
4-Methyl-1,3- dioxan	Phenol	1,3-Butandiol	91.6
4,4-Dimethyl- 1,3-dioxan	Phenol	3-Methyl-1,3- butandiol	12.6

Table 8
 MANUFACTURE OF DIENES THROUGH PHENOLYSIS OF ALKYL-1,3-DIOXANS
 BY VARIOUS PHENOLS

Phenol	Diene yield, %		
	divinyl	isoprene	2,3-dimethyl- 1,3-butadiene
Phenol	52.3	60.2	61.8
m-Cresol	53.6	53.8	61.2
o-Cresol	49.2	52.3	54.1
m-Chlorophenol	31.6	38.4	38.9
o-Chlorophenol	38.9	42.3	42.8
2,4-Dichlorophenol	38.3	39.4	38.6
2,6-Di-tert-butylphenol	53.6	61.3	63.8

In the case in hand, bis(3,6-di-tert-butyl-4-oxyphenyl)methane was isolated from the still residue.

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