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 summerized. Reactions 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 isoprene[1]. Theoretical fundamentals have been developed and methods for manufacturing a whole series of other alkyl-, aryl-, halide- and polycyclic 1,3-dioxacycloalkanes[2-9] 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 monographies [10-22].

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 review[23].

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.

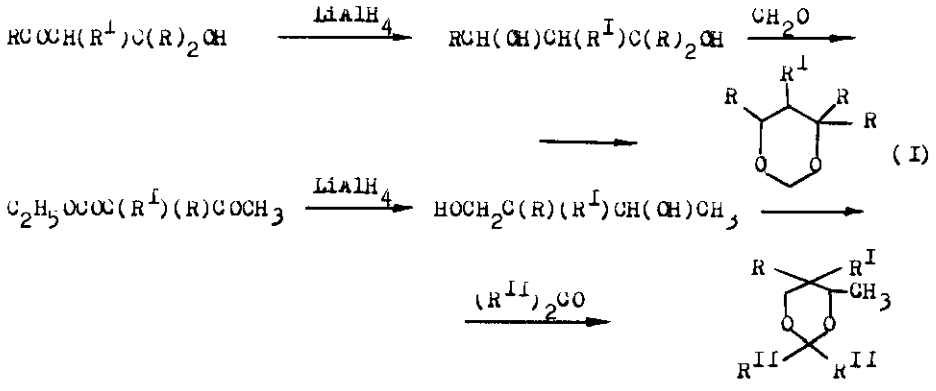
STEREOCHEMISTRY, KINETICS AND MECHANISM OF REACTIONS OF 1,3-DIOXACYCLANES WITH ALCOHOLS

Reactions of cyclic acetals with alcohols are a convenient method for obtaining glycols and another products[24-37], methanolysis being very widely employed in preparative organic chemistry [28-33].

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

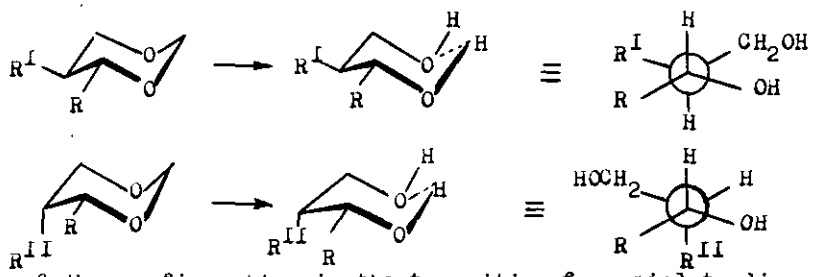
Initial data on the maintenance of the configuration of the diol part of the molecule in acetalization and alcoholysis were obtained by Garner and Lucas[34]. It was established that 4,5-dimethyl- and 2,4,5-trimethyl-1,3-dioxolanes obtained from an optically active 2,3-butandiol exhibit an optical activity[34], 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-dioxans in methanolysis has been noted in several works[22,35-37]. Thus the reduction by lithium aluminium hydride of oxyketones [35,36] or acetoacetic esters [37] 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 threo-1,3-diols, and from cis-erythro:



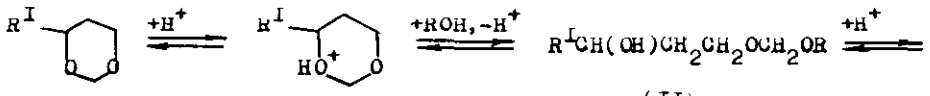
Retention of the configuration in the transition from diol to dioxycyclane and back evidences the fragmentation of the heterocycle ring on the carbon-oxygen bonds by the acetal carbon.

Five- and seven-link cyclic acetals show, during the methanolysis, a greater reactivity as compared to 1,3-dioxan[38]. Farberov and co-workers[39] 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).

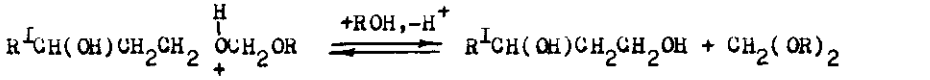
A highly negative value of S° (-24 to -27 e.u.), in the view of the authors, confirms that methanolysis follows a bimolecular mechanism. The quantitative effect of the substituents on the rate of reaction is described by the Taft equation:

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

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:



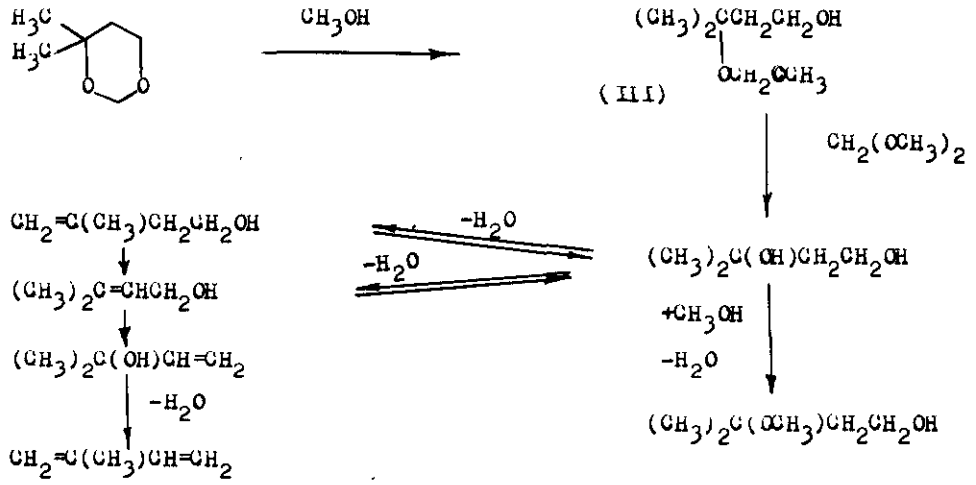
(II)



The addition of the first molecule of alcohol is, probably, the rate determing 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 dialkoxymethane. The possible formation of oxonium ion as a result of attack by a proton remote from the oxygen atom substituent is not discussed.

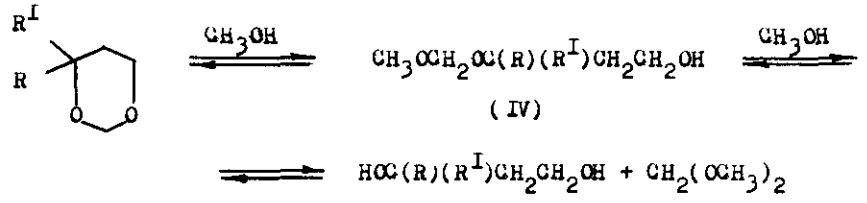
A detailed study of the products of the methanolysis of 1,3-dioxans[40, 41] has revealed 4,6-dioxaheptan-1-ols which are very important for determining the sequence of the reaction stages. The study of the behavior of the individual compo-

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-dioxa-1-hepthanol (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-dioxaheptan-1-ol (IV) which may be obtained, under certain conditions, also as the main product of the reaction[44]:

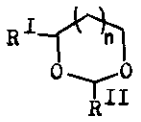


The authors explain the failure of 4-alkenyl-1,3-dioxans to conform to the rate constant vs. Taft constant correlation by a possible split of the heterocycle on O_3-O_4 bond and a formation of a stable allyl cation.

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-workers[45]. Cyclic acetals, similar to linear ones[46,47], react with thiols in the presence of acid catalysts p-toluene-

sulfonic acid, HCl, $ZnCl_2$:



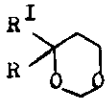
$$+ \ 2RSH \longrightarrow R^{I}-CH(OH)(CH_2)_nCH_2OH + R^{II}CH(SR)_2$$

$$n = 0,1$$

$$R=C_2H_5,\ C_4H_9,\ C_6H_5,\ tert\text{-}C_{12}H_{25};\ R^{I},R^{II}=H,\ CH_3,\ C_3H_7$$

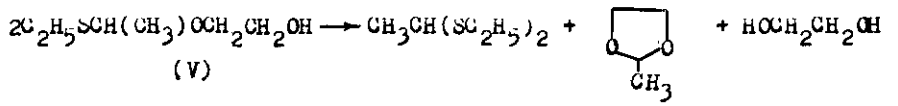
Table 1

KINETIC PARAMETERS OF METHANOLYSIS OF SUBSTITUTED 1,3-DIOXANS



R	R^{I}	$Kp.10^3$, l/mole	H, kcal/mole	$K_r\ 10^5$, l/mole s	E_r, kcal/mole	References
H	C_6H_5	8.40	8.1	0.39	22.7	42, 43
CH_3	CH_2Cl	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_3CH=CH	14.70	3.1	1.35	21.4	42, 43
CH_3	C_6H_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_2H_5				19.0	39
H	C_3H_7				19.0	39
H	C_3H_7				19.2	39

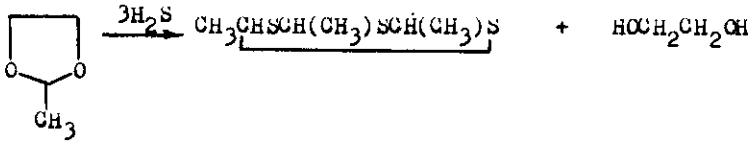
The authors have advanced a suggestion on the primary formation of intermediate product (V). However, the authors failed to isolate this compound because of its decomposition in distallation[45]:



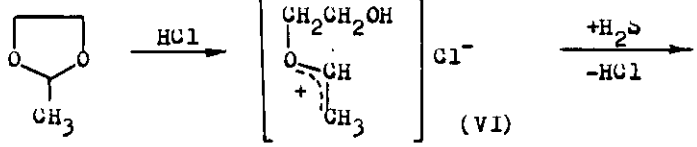
$$2C_2H_5SCH(CH_3)OCH_2CH_2OH \longrightarrow CH_3CH(SC_2H_5)_2 + \qquad + HOCH_2CH_2OH$$

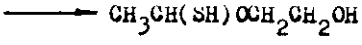
(V)

After treatment of 2-methyl-1,3-dioxolane by hydrogen sulfide the product was 2,4,6-trimethyl-1,3,5-trithiane and glycol[48].



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



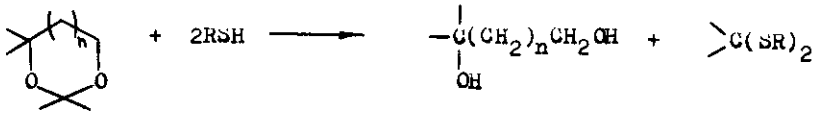


However, no VI and VII were found in reaction products. The cationite KY-2[49] may serve as a splitting catalyst.

Unsubstituted trithiane is formed from cyclic formals in a good yield[50].

The information thiolysis carries as regards the ascertainment of the stage mechamism of acid-catalysed transformations of 1,3-diocyclanes, 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 glycols [51-56]:

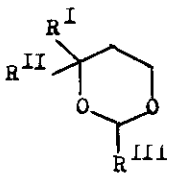


It was established that the structures of the 1,3-dioxacyclane tells, in the first place, on the selectivity of formation of glycol. Dithioacetals are formed mostly at a yield close on 90%[57] (Table 2).

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 substituent[53]. 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 DIETHYLTHIOACETALS IN THIOLYSIS OF 1,3-DIOXACYCLANES IN THE PRESENCE OF KY-2 CATIONITE



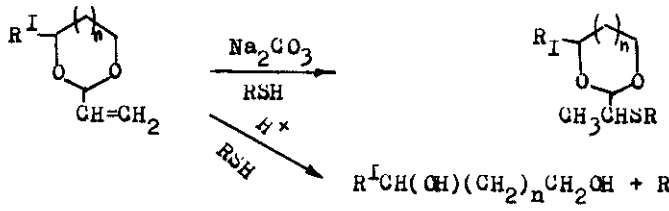
n	R^I	R^{II}	R^{III}	Temperature, °C	Duration, h	Yield of glycol	Yield of thioacetal
0	H	H	H	100	1.5	32.3	99.5
1	H	H	H	100	1.0	67.6	95.5
2	H	H	H	80	1.5	37.8	80.2
1	H	H	CH_2	60	3.5	61.2	98.5
1	H	H	C_6H_5	60	3.5	92.5	96.5
1	H	CH_3	H	80	1.5	85.8	98.0
1	CH_3	CH_3	H	80	0.8	34.4	69.2
1	C_6H_5	H	H	80	3.0	-	98.1
1	H	CH_3	CH_3	60	2.0	82.6	95.1
1	H	H	C_4H_3O	60	4.0	-	78.2
1	H	H	C_3H_7	80	3.0	71.2	82.5
1	H	H	C_8H_{17}	60	4.0	68.8	84.0
1	H	H	C_6H_{13}	60	3.5	70.5	88.7
1	H	H	C_5H_{10}	100	2.0	-	63.5

In a homogeneous catalysis, the activities of thioalcohols up to butanethiol differ but negligibly[56]. 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 stops[56].

The reaction products of the thiolysis of 4,4-dimethyl-1,3-dioxan contained a compound with a structure of 4-thio-2,3-dimethylhex-1-ene[59]. Tetrahydrofuran is

formed in substantial amounts from 1,3-dioxepane as a result of a fast dehydration of the resulting 1,4-butanediol[60, 61].

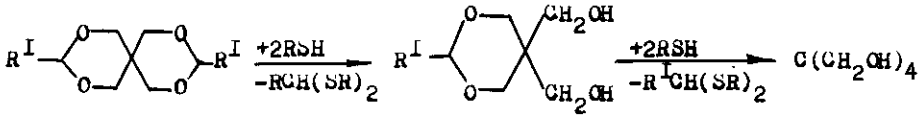
It is of interest to note that the addition of thiols to 2-vinyl-1,3-dioxacyclanes can be carried out only in an alkali catalysis reaction. The use of an acid catalyst leads to di(alkylthio)acetals[62, 63]:

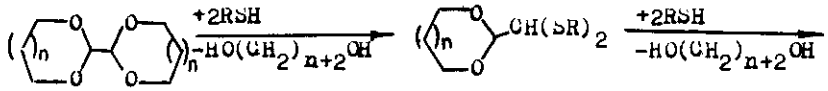


$$R^{I}CH(OH)(CH_2)_nCH_2OH + RSCH(CH_3)CH(SR)_2$$

n = 0, 1, 2; R = alkyl; R^{I} = H, CH_3

The thiolysis of bis- and spiro-1,3-dioxacyclanes proceeds as a consecutive fragmentation of cyclic compound[64, 65]:



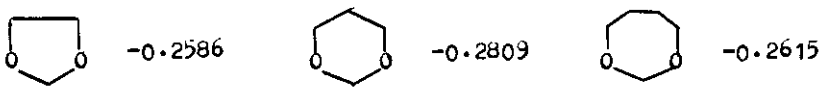


$$\longrightarrow (RS)_2CH\text{-}CH(SR)_2$$

n = 0, 1, 2; R, R^{I} = alkyl

The rate of thiolysis by the use of the KY-2 cationite is described by the equation for first order reactions. The zero order in terms of thiol is related to a high rate of saturation of the catalyst by mercaptane, as evidenced by a change in the time of the nuclear spin-lattice reaction of protons[58]. The energy of activation of thiolysis depends but slightly on the structure of 1,3-dioxacyclane, whereas the relative reactivity differs by approximately an order of magnitude (Table 3).

The electron density of oxygen atoms fails to correlate with the reactivity of the heterocyclic compound[60,65]:



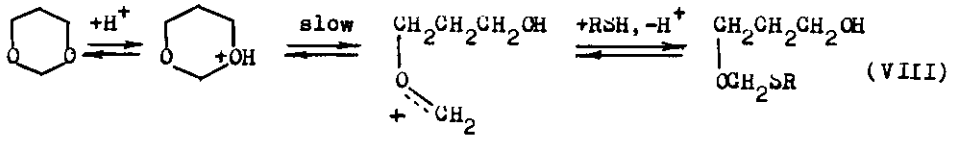
3.04 1.00 2.69

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:



(VIII)

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-diocacyxlanes with such an abundant class of organic compound as esters have appeared in the literature but recently. Esterolysis expands sustantially the potentialities of the synthesis of some very valuable compounds and the understanding of the acid-catalyzed transformations of 1,3-dioxacyclanes[66].

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];

$CH_2(OR)_2$; $CH_3COOCH_2(CH_2)_nCH_2OOCCH_3$ (IX);

$CH_2[OCH_2(CH_3)\ CH_2OOCCH_3]_2$ (X);

$$ROCH_2OCH_2(CH_2)_nCH_2OOCCH_3 \quad (XI)$$

A separate study of the behaviour of (XI) in an esterolysis is indicative of its formation in the first stage of the reaction[66]:

$$+ R^{I}COOR \rightleftharpoons R^{I}COOCH_2(CH_2)_nCH_2OCH_2OR$$

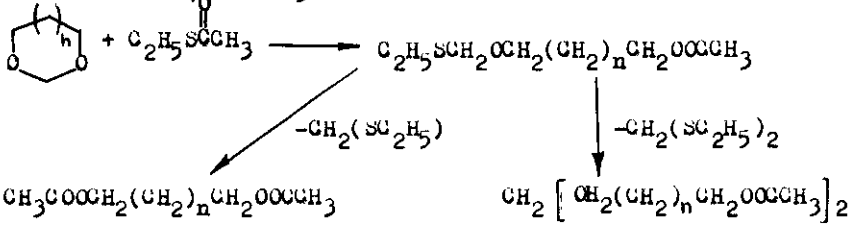
Interacting with the second molecule of ester, (X) turns to a diester (IX) and acetal:

$$XI + R^{I}COOR \rightleftharpoons IX + CH_2(OR)_2$$

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

$$2XI \rightleftharpoons X + CH_2(OR)_2$$

Products, similar to compounds (IX), (X) and (XI), are formed in esterolysis by thioesters[68]. 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 O_1 and O_3 :



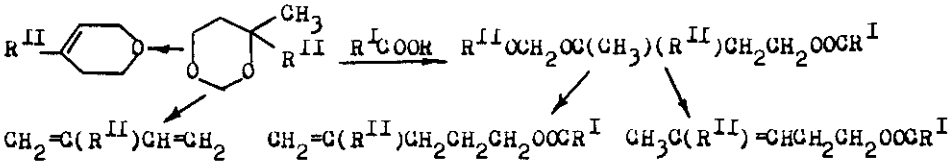
$$+ C_2H_5SCCH_3 \longrightarrow C_2H_5SCH_2OCH_2(CH_2)_nCH_2OOCCH_3$$

$$-CH_2(SC_2H_5) \qquad -CH_2(SC_2H_5)_2$$

$$CH_3COOCH_2(CH_2)_nCH_2OOCCH_3 \qquad CH_2\left[OCH_2(CH_2)_nCH_2OOCCH_3\right]_2$$

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 resins[68].

The introduction of the propenyl, methyl or phenyl substituent in the fourth position of the ring results in cracking products[68]:

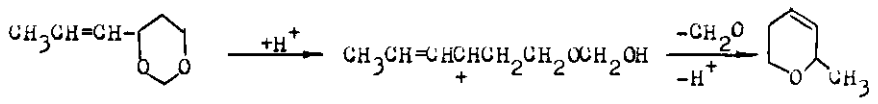


$$R^{II}\text{-}\underset{\underset{R^{II}}{|}}{\overset{CH_3}{|}}\text{-}O \xrightarrow{R^{I}COOR} R^{II}OCH_2OC(CH_3)(R^{II})CH_2CH_2OOCR^{I}$$

$$CH_2{=}C(R^{II})CH{=}CH_2 \qquad CH_2{=}C(R^{II})CH_2CH_2CH_2OOCR^{I} \qquad CH_3C(R^{II}){=}CHCH_2CH_2OOCR^{I}$$

R, R^{I} = alk.; R^{II}=CH_3, C_6H_5, $CH_3CH{=}CH$

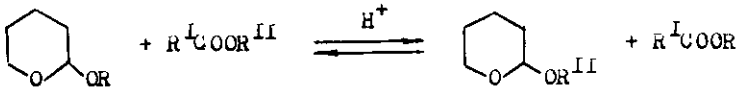
The formation of 2-methyl-5,6-dihydro-2H-pyran is the result of the elimination of the formaldehyde molecule from 4-propenyl-1,3-dioxan:



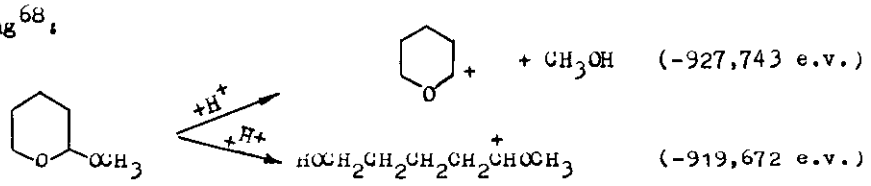
As the molecular weight of the ester increases, its activity in the esterolysis falls off[68].

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 acid[71]. 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 alkoxyl groups[72]:



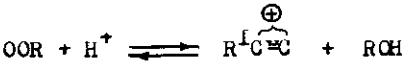
It was shown by quantum-chemical calculations that the splitting of exo-cyclic acetal bond is energetically more favourable (by 100 kcal/mol) than the opening of the ring[68]:



The esterolysis of 2-alkoxytetrahydropyrans is described by an equation for reversible third-order reactions[68].

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:



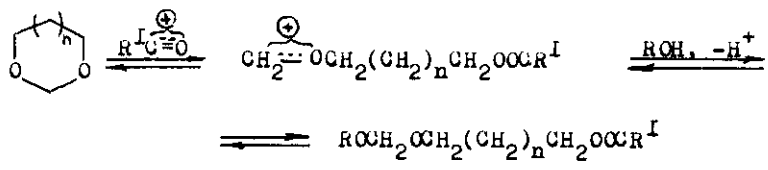


Table 4

DEPENDENCES OF THE EQUILIBRIUM CONSTANT (K_p) AND OF THE RATES OF FORWARD (K_1) AND OF THE REVERSE REACTIONS (K_{-1}) OF 2-METOXY-TETRAHYDROPYRAN WITH PROPYL ACETATE UPON THE TEMPERATURE

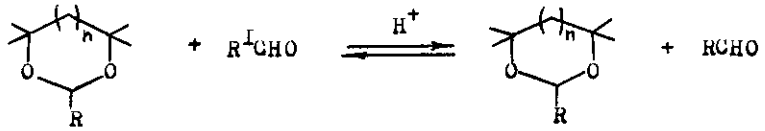
Temperature, °C	K_p	$K_1\ 10^4$	$K_{-1}\ 10^4$
40	1.11	0.31	0.28
50	1.29	0.58	0.45
60	1.49	1.06	0.71
70	1.68	1.75	1.04
80	1.91	1.78	1.46

In contrast to other acid-catalyzed reactions, it is possible in esterolysis to isolate and identify the product formed as a result of the splitting of one of the carbon-oxygen bonds of the cyclic compound.

REACTIONS OF REACETALIZATION AND EXCHANGE

The cycloacetal fragment is present in the structure of many natural and biologically active compounds[21]. It is most probable that there occur exchange reactions in the activity of plant and animal organisms. However, no attention was devoted, up to recently, in the literature to reacetalization and exchange reactions.

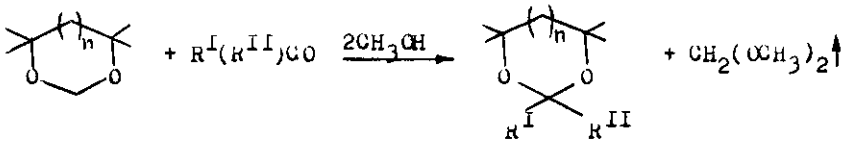
It was found recently that the interaction of 1,3-dioxacyclanes with aldehydes in an acid catalysis leads to a new pair of 1,3-dioxacyclane-aldehyde [74-76]:



n = 0, 1, 2, R, R^I = H, alkyl, aryl ...

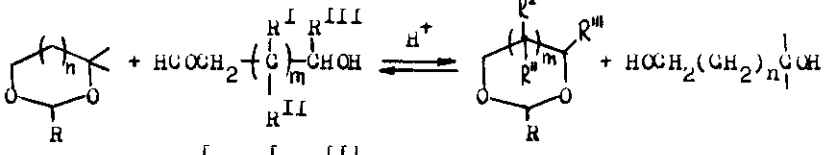
The reactions may be catalysed by mineral acids, boron trifluoride etherate, p-toluenesulfuric acid and cation-exchange resins in acid form. When cyclic formals

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 yield[77];



When ketones are employed, the formation of 1,3-dioxacyclanes proceeds smoothly for both 1,3-dioxacyclanes unsubstituted and substituted at C_4[78].

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];

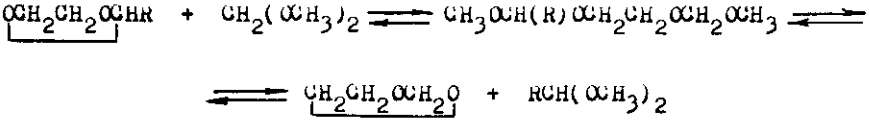


R= H, alkyl; R^I, R^{II}, R^{III}= H, CH_3, OH, CH_2OH; m,n = 0, 1, 2

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 C_2. Because of a high yield of 1,3-dioxalane, said method may be recommended as means for analyzing high-boiling cyclic formals[79].

Reacetalization of 1,3-dioxalanes by linear acetals is carried out under milder conditions as compared to that by aldehydes[80].

The primary product of the reaction is probably mixed acetal forming as a result of the addition of fragments of linear acetal on the C_2-O bond of 1,3-dioxacyclane[81];

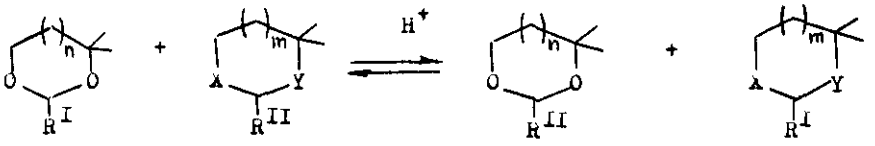


When using methyl alcohol acetals and cyclic formals, the resulting methylal is driven from the reaction zone and the yield of final 1,3-dioxacyclane rises to 80-90%.

Ethylene and propylene oxides react with 1,3-dioxacyclanes to form up to 25-40% 1,3-dioxalanes and 4-methyl-1,3-dioxalanes[82]. When use is made of the stabler 3,3-bis (chloromethyl)oxacyclobutane and 1-chloro-2,3-epoxypropane, formed are

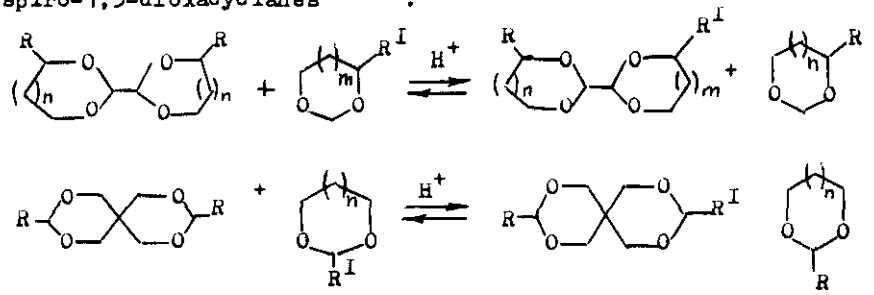
2-substituted 5,5-bis(chloromethyl)-1,3-dioxans and 2-substituted 4-chloromethyl-1,3-dioxolanes with yields of 65-75%. It proves impossible to isolate the expected alkyl-substituted α,β-oxides from the reaction products because of a high rate of their polymerization. The reaction between 1,3-dioxepane with halide-substituted oxides results in tetrahydropyran[82].

Exchange reactions of 1,3-dioxacyclanes with 1,3-dioxacyclanes, 1,3-oxathianes, 1,3-dithions [83-85]:



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

Exchange reactions of 1,3-dioxacyclanes make it possible to obtain asymmetric bis- and spiro-1,3-dioxacyclanes [86-88]:



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:

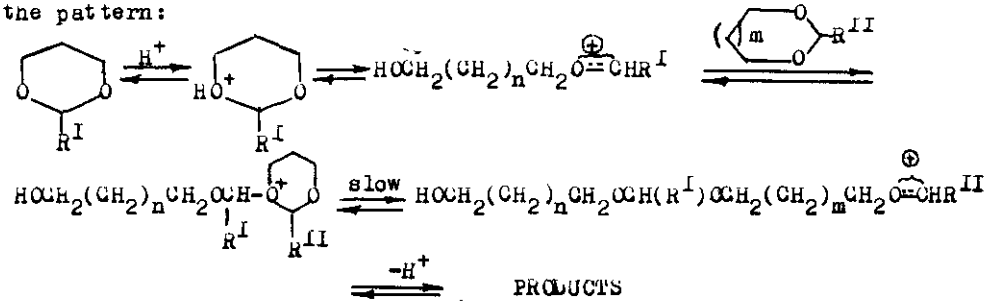


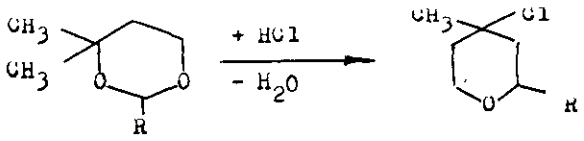
Table 5

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-dimetnyl-1,3-dioxan	1.3
1,3-dioxolane + 2,4,4-tertmethyl-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

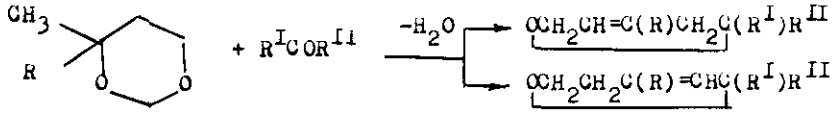
REACTIONS AND RECYCLIZATION OF 1,3-DIOXACYCLANES

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



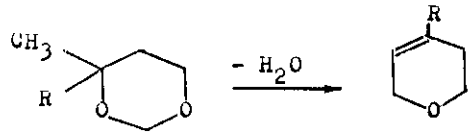
$R = CH_3$; i - C_3H_7, n-C_3H_7

Probably, the reaction of reacetalization is common to 1,3-dioxans with electron-donor substituents at C_4. 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]:



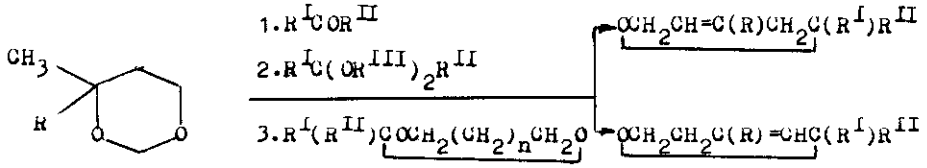
$R = CH_3$, C_6H_5; R^I, $R^{II} = CH_3$, C_2H_5, $-(CH_2)_4$, $-(CH_2)_5-$

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:

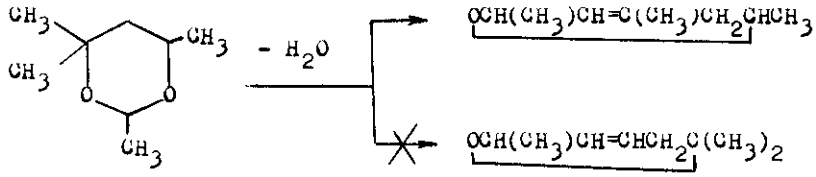


$R = CH_3, C_6H_5$

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 $2\text{-}R^{I}\text{-}2\text{-}R^{II}\text{-}4\text{-}$phenyl-3,6-dihydro- and $2\text{-}R^{I}\text{-}2\text{-}R^{II}\text{-}4\text{-}$phenyl-5,6-dihydropyrans [92]:



2,4,6-Trimethyl-5,6-dihydro-2H-pyran only is obtainable from 2,4,4,6-tetramethyl-1,3-dioxan [92]:



Thus, the formation of dihydropyrans is the result of the breakdown of the $O_3\text{-}C_4$ 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 phase [93]. The technology developed by Soviet scientists features good performance indicators [94] and makes

it possible to obtain specific high-purity products[95]. A disadvantage of the process is the formation of considerable amounts of hard-to-utilize by-products and the need of frequently regenerating the catalyst[1].

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-DIOXANES 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-1[97]. 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 ones[98]. 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], hexamethylenetetramine[100], formalzene[101] and others.

Of interest is the splitting of dioxans in the presence, instead of amine salts, of bifunctional organic compounds containing, along with the NH_2 group, acid residues such as sulfanilic acid[102]. 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:

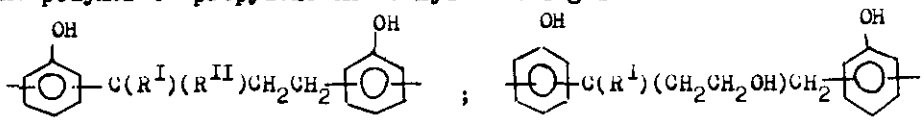


Table 6

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	55.8	58.3	51.6	83.4	93.3	98.1
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
Hydroxilamine	77.2	82.9	71.3	75.1	83.3	87.6
Non-organic amine	99.3	98.6	96.8	86.7	97.9	95.7
Ammonia	57.9	58.9	58.3	44.3	50.2	50.2

It was shown later[105] 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 hydrocarbons[105].

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-Dioxacyclane	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-Dichlorophenol	1,3-Propandiol	31.4
1,3-Dioxan	2,6-Di-tert-butylphenol	1,3-Propandiol	99.3
1,3-Dioxan	2,4-Di-tert-butylphenol	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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