# FREE RADICAL TRANSFORMATIONS OF CYCLIC ACETALS

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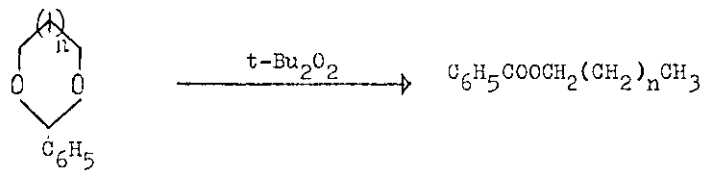
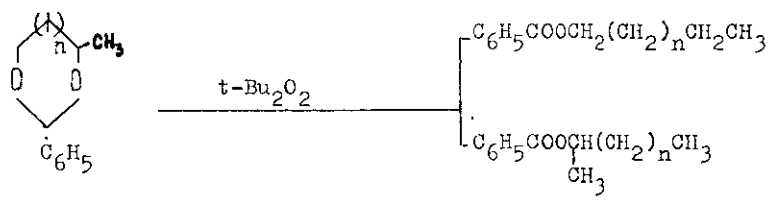
Abstract - Information of structure and properties of free radicals generated from cyclic acetals in reactions, which take place with their participation, is given. Data of kinetics and mechanism of chain-radical liquid-phase transformations of cyclic acetals are summarized and discussed. Possibilities and perspectives of using homolytical reactions of cyclic acetals in organic synthesis are shown.

Transformations of 1,3-Dioxacyclanes and Their Heteroanalogues Under the Influence of Radical Initiators. For the first time isomerization of benzaldehyde cyclic acetals into alkylbenzoates under the influence of tert.-butyl peroxide was mentioned in the work[1].

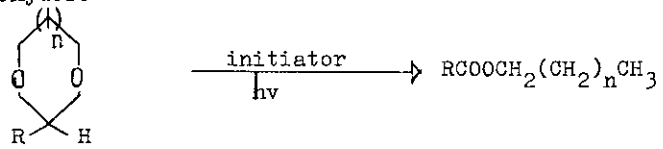


Benzoates of primary and secondary alcohols forming simultaneously from 2-phenyl-4-methyl-1,3-dioxacyclanes:



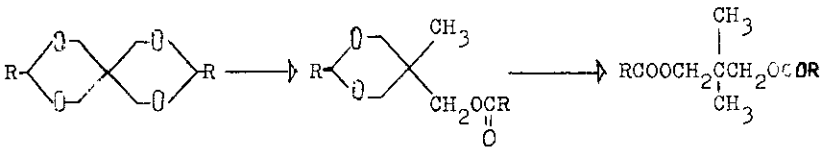
Later on in the works[2-5] homolytical transformations of various cyclic acetals in liquid phase were studied in detail. It has been shown that isomerization into esters, initiated by free radicals donors or by sensibilized UV-irradiation[2-5],

is a general reaction for cyclic acetals of aliphatic, aromatic and heteroaromatic aldehydes.

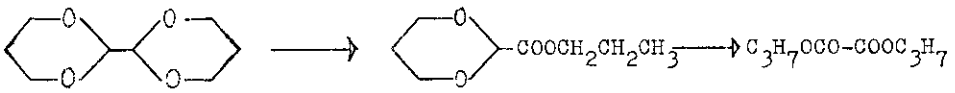


R=H, AlK; Ar, n=0,1,2,3

Spiro-1,3-dioxanes undergo a successive opening of the cycle and through the stage of 5-methyl-5-acyloxymethyl-1,3-dioxanes turn to diethers of 2,2-dimethylpropane-1,3-diol[6].

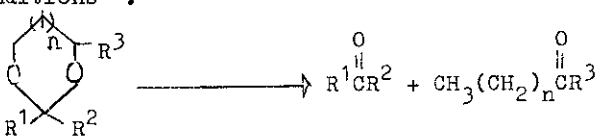


Glyoxal derivatives isomerization takes place in the same way with the successive opening of the cycles; dialkyloxalates being the final product[7].

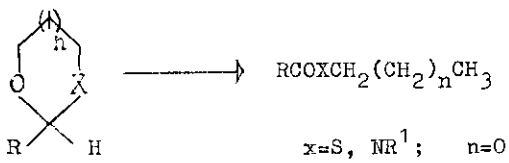


In all cases from 4-alkyl-1,3-dioxacycloalkanes both possible ethers are formed[8], but the primary alcohol derivatives formation selectivity is always higher than that of secondary ones, and from 4,4-disubstituted heterocycles tertiary alcohol ethers are not practically formed[9].

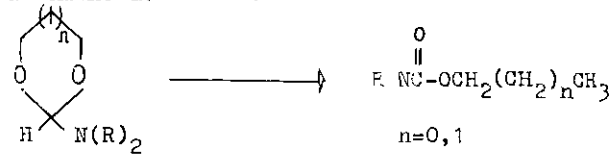
Cyclic ketals - 2,2-dialkyl-1,3-dioxacyclanes, in molecules of which $C^2$-H-carbon-hydrogen bonds are absent, decay into two carbonyl compounds under these conditions[10].



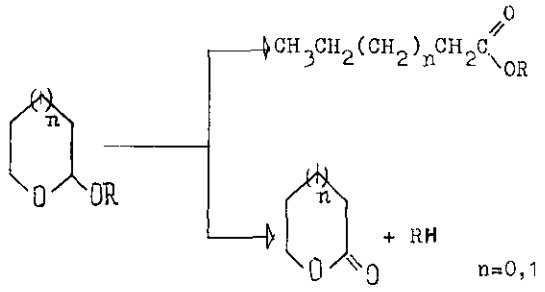
It has been established that from 1,3-oxaheterocycloalkanes amides and thioethers are formed under the influence of radical initiators[11-15].



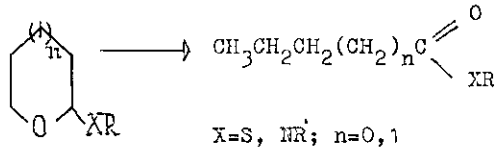
Cyclic acetals of formamides undergo the analogous isomerization into ethers of carbamino acid[16-17].



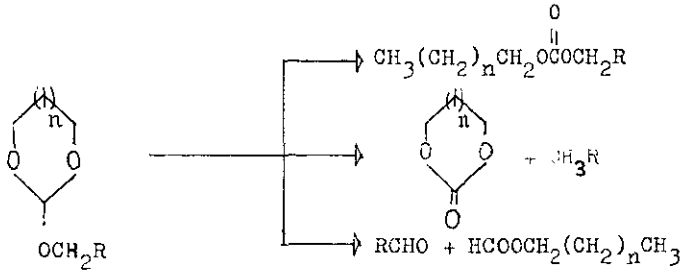

Linear-cyclic acetals - 2-alkoxyoxacycloalkanes - under the influence of free radicals form linear and cyclic esters in parallel; their correlation being determined by temperature, pressure and structure of an alkoxyl fragment and the cycle size[18-20].




In substitution of oxygen exocyclic atom into sulphur or nitrogen only isomerization with the cycle opening takes place[17, 21-22].




Cyclic orthoformates - 2-alkoxy-1,3-dioxacycloalkanes - turn simultaneously to cyclic and linear ethers of carbonic acid[23, 24] and also fragmentate with the formation of carbonyl compound and formate.

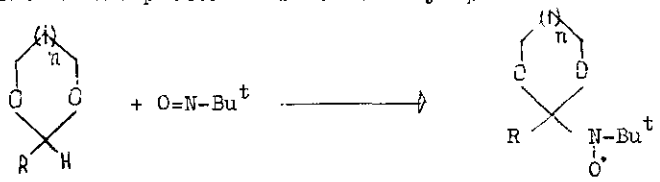



It is indicated that formally all these reactions are oxidizing-reducing processes, in which an acetal function is oxidized into an estereal one, and one

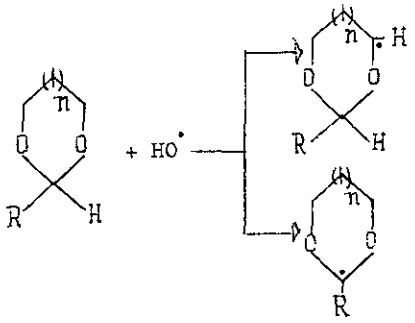
of the estereal functions is reduced to a hydrocarbon one, i.e., there is observed the transfer of a hydrogen atom from a carbon atom, adjacent to two heteroatoms, to a carbon atom, adjacent to an oxygen atom, which is accompanied by the breakdown of an endo- or exocyclic carbon-oxygen bond and the formation of a multiple carbon-oxygen bond. It has been proved that the above transformations[2-5, 12-15, 17, 18] take place according to a free-radical mechanism, the first stage of which is the breaking of hydrogen atom off $C^2$-atom cycle with the formation of the corresponding cyclic alkoxyalkyl radical.

Structure and Properties of Radicals Generated from Acetals. It has been shown that the latter reacts rapidly with 2-methyl-2-nitrosopropane transforming into corresponding nitroxyl radicals[25-28].

The formation of other radicals has not been established by this method (20°C, photolysis in the presence of tert.-butyl peroxide or acetone)[25-28].




Under the influence of tert.-butoxyl radicals the corresponding monoalkoxyalkyl radicals are generated from cyclic ketals[28]. However, in treating acetal water solutions by hydrogen peroxide in the presence of Ti(III) ions the parallel formation of cyclic di- and monoalkoxyalkyl radicals has been noted[12, 29-32].




n=0,1,2 R=H, AlK

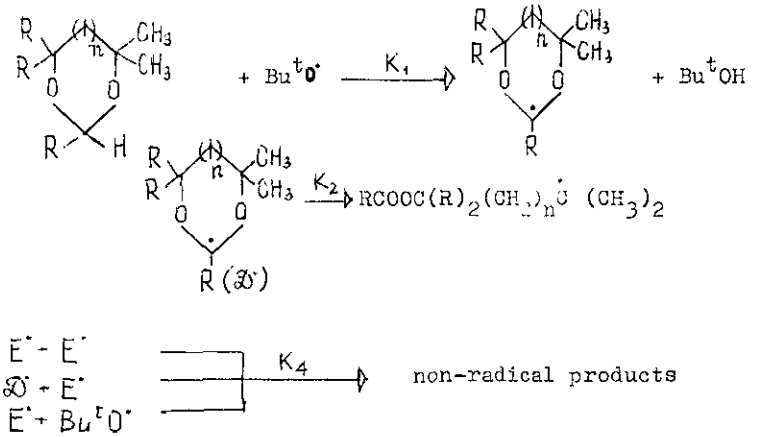
The selectivity of dialkoxyalkyl radicals formation increases when a methyl group is introduced into the second position of the heterocycle, and also in transition from hydroxyl(OH) to less active aminyl radicals[12, 31]. With the increase of the cycle size the selectivity of dialkoxyalkyl radicals formation decreases[12, 31].

In a number of works[33-39], devoted to the study of acetal activity in the reaction of hydrogen atom breaking off by various radicals, it has been also established that cyclic acetals are considerably more active than ketals and that a carbon-hydrogen bond, adjacent to two oxygen atoms, is the main reaction centre in the molecule. The partial contribution of a methylene or methine group, adjacent to two oxygen atoms, in reactions with tert.-butoxyl[33, 34, 37], undecyl[35, 38] and phenyl radicals[36-39] is more than 70% of the sum of partial contributions of all hydrocarbon groups.

According to their activity in the reactions with radicals of various nature 1,3-dioxacyclanes are arranged in the following order: 1,3-dioxacyclopentanes >1,3-dioxacycloheptanes >1,3-dioxacyclohexanes[33-39].

On the whole, under the influence of various free radicals, dialkoxyalkyl radicals are mainly formed from cyclic acetals. Monomolecular rearrangement of dialkoxyalkyl radicals into acyloxyalkyl radicals is the key stage of homolytical isomerization of cyclic acetals into esters. At relatively not high temperatures (20°C) 1,3-dioxa-2-cycloalkyl radicals have been proved to be stable enough, and it has appeared to be possible to study their rearrangement into acyloxyalkyl radicals by EPR-spectroscopy method[26].

The kinetics of D and E radicals formation and destruction has been studied and the constant of the isomerization rate of cyclic dialkoxyalkyl radicals has been determined (Table 1).

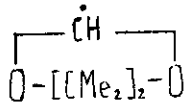
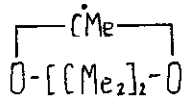
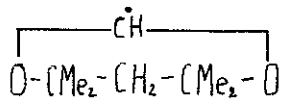
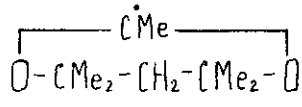
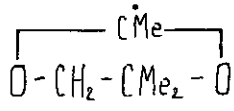



On the grounds of these results[26] it has been concluded that secondary dialkoxycycloalkyl radicals are rearranged more rapidly than tertiary ones (Table 1), the process is accelerated in the presence of methyl groups in the 4 and 5 po-

sitions of the cycle, and six-membered dialkoxycycloalkyl radicals are rearranged more rapidly than five-membered ones. These data have been explained in the following way[26]. For dialkoxyalkyl radicals D rearrangement the overlapping of the lone electron 2p-orbital with the loosening $\sigma^*$ -orbital of $O^3$-$C^4$ or $O^1$-$C^6$ bond is necessary[26].

The most effective maximum overlapping is when the lone electron 2p-orbital and $C^2$-$O^3$ and $O^3$-$C^4$ bonds are on one plane, and such a conformation is accessible most of all for acyclic dialkoxyalkyl radicals and less accessible for five-membered 1,3-dioxa-2-cycloalkyl radicals[26, 40]. The six-membered dialkoxycycloalkyl radicals occupy the intermediate position[40].

Table 1. Kinetic parameters of rearrangment of dialkoxyalkyl radicals[26]

| Dialkoxyalkyl radical | Acyloxyalkyl radical | $K_2$, $sec^{-1}$ (72°) |
|---|---|---|
| $(Bu^tO)_2\dot{C}H$ | $Bu^{t\cdot}$ | $5.0\ 10^5$ |
|  | $HC(=O)OC(Me)_2\dot{C}(Me)_2$ | $5.8\ 10^3$ |
|  | $MeC(=O)OC(Me)_2\dot{C}(Me)_2$ | $2.1\ 10^3$ |
|  | $HC(=O)OC(Me)_2CH_2\dot{C}(Me)_2$ | $5.7\ 10^4$ |
|  | $MeC(=O)OC(Me)_2CH_2\dot{C}(Me)_2$ | $5.3\ 10^3$ |
|  | $MeC(=O)OCH_2\dot{C}(Me)_2$ | $7.0\ 10^2$ |

In the works[12, 40] another method of study of 1,3-dioxa-2-cycloalkyl radicals structure connection with the rate of their isomerization is used. The ration of D and E radicals stationary concentrations ($X = \frac{E}{D}$) has been found by means of free radicals acceptors method; ethylene being used as this method. The value X has been determined as the ratio of summary yields of linear ($A_n$) and cyclic ($T_n$) telomerhomologes[12, 40].

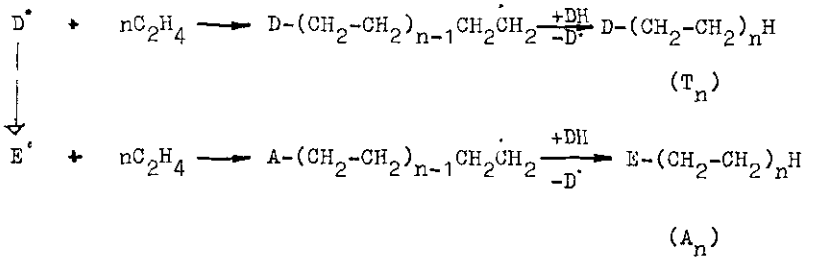
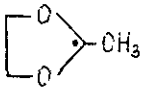
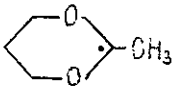
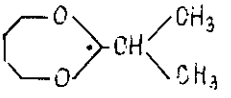
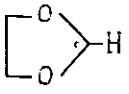


Table 2. Monomolecular rearrangement rate constants of cyclic dialkoxyalkyl radicals (130°C)[12, 38]

| Cyclic dialkoxyalkyl radicals | : $X=A_n/T_n$ | : $K_2$, $sec^{-1}$ |
|---|---|---|
|  | 0.15 | $0.4\ 10^3$ |
|  | 0.97 | $0.8\ 10^3$ |
|  | 1.96 | $1.3\ 10^3$ |
|  | 0.75 | $2.1\ 10^3$ |

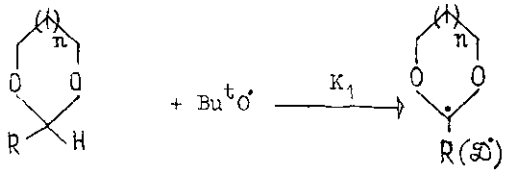
The results obtained (Table 2) show that with the increase of the cycle size the rate of dialkoxycycloalkyl radicals rearrangement increases[12], and the fragmentation of linear dialkoxyalkyl radicals proceeds still more rapidly[41, 42]. Thus, in recording EPR spectra of the radicals, generated from 1,1-dialkoxyalkanes, alongside with mono- and dialkoxyalkyl radicals the signals of alkyl radicals are present, forming as a result of alkyl radicals fragmentation[41]. Under analogous

conditions in EPR-spectra of 1,3-dioxacyclanes the signals of acyloxyalkyl radicals have not been found[31]. In the reactions of ethylene radical telomerization by 1,1-dialkoxyalkanes the products of dialkoxyalkyl radicals addition to ethylene are not formed[42-44]. At the same time esters, which are the products of their monomolecular fragmentation, are accumulated in the reaction mass[45, 46]. This is explained by the high rate of dialkoxyalkyl radicals fragmentation[42], which evidently exceeds the rate of their addition to ethylene more than an order. Although the constants of dialkoxyalkyl radicals rearrangement ($K_2$) have been obtained in the works[12, 26, 40] by various methods and at various temperatures, the higher rate of rearrangement is characteristic for those dialkoxyalkyl radicals which are less stable thermodynamically. or lead to more stable radicals. Apparently, alongside with the stereoelectronic control of dialkoxyalkyl radicals splitting, determining the transition state of this reaction, thermodynamic factors play an important role. This is indicated by the data of the works[1, 46], in which it has been shown that the direction of asymmetric acetals fragmentation depends considerably on the nature of a forming radical. Dialkoxyalkyl radicals fragmentation proceeds more preferably to the formation of the most stable radical[1, 46].

In the work[47] the minimums of energies have been calculated by Hofmann method, which corresponds to the most stable conformations of 1,3-dioxa-2-cyclohexyl and isomeric to it 3-formyloxypropyl radical and it is shown that the ring splitting is accompanied by the energy isolation.

In the work[48] the difference of complete energies of cyclic mono- and dialkoxyalkyl and isomeric to them linear radicals has been calculated by Hofmann method. Proceeding from the energetic effects of these transitions it has been concluded that cyclic monoalkoxyalkyl radicals are less inclined to rearrangement than dialkoxyalkyl ones[48]. In transition from 1,3-dioxa-2-cyclopentyl radicals to 1,3-dioxa-3-cyclohexyl ones the gain in the energy, isolated as a result of rearrangement, increases[48].

The Mechanism of Homolytical Isomerization of Acetals into Ethers. While studying the kinetics of ether accumulation during 1,3-dioxacyclanes isomerization initiated by the peroxide it has been established[2-5, 33] that the initial rate of ether formation is linear with the acetal concentration and directly proportional to the quadratic root from the iniator concentration.



$$+ Bu^tO^{\cdot} \xrightarrow{K_1} \quad + Bu^tOH \qquad (1)$$

$$D^{\cdot} \xrightarrow{K_2} \underset{(E)}{RCOOCH_2(CH_2)_n\dot{C}H_2} \qquad (2)$$

$$\dot{E} + DH \xrightarrow{K_3} RCOOCH_2(CH_2)_nCH_3 + D^{\cdot} \qquad (3)$$

$$\dot{E} + \dot{E} \xrightarrow{K_4} \text{the products of termination} \qquad (4)$$

The dependences obtained testify to the fact that the breaking of hydrogen atom off the substrate by acyloxyalkyl radicals is the limiting stage of the process (reaction 3), and the chain breaking off takes place as a result of the rearranged radicals recombination (reaction 4).

The initial rate of ether formation ($W_{eth.}$) is satisfactorily depicted by the equation [2-6, 33].

$$W_{eth.} = \frac{K_3}{\sqrt{K_4}} [DH] \sqrt{W_{Bu^tOH}/2}$$

In the work [6] the reactions of breaking chain of radical isomerization have been studied. It has been established that the rate of formation of glycol diethers is equal to a half of the initiation rate, and the part of disproportionation in the chain breaking does not exceed 10%.

$$\dot{E} + \dot{E} \longrightarrow E - E$$

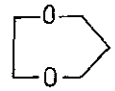
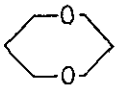
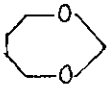
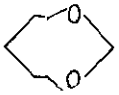
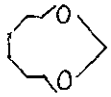
The Relation of Acetals Structure with Their Reactivity. The parameter $\frac{K_3}{\sqrt{K_4}}$ is the measure of reactivity of cyclic acetals in free-radical isomerization [2-5].

Under consideration of reactivity of cyclic acetals in isomerization [2-5] the influence of the following factors has been taken into account:

- the nature of the radicals ($\dot{E}$ ), leading the chain
- the structure of rearranged radicals ($\dot{E}$ )
- the tension of the rings of various size and polar effects.

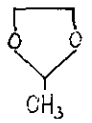
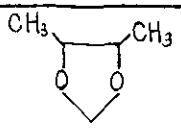
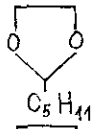
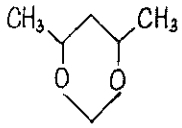
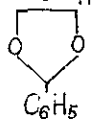
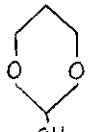
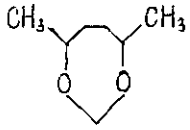
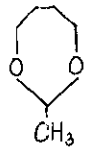
The rearranged primary formyloxyalkyl radicals (E ), which lead the chain and differ in number of methylene links between the centre and HCOO group, do not differ greatly in activity, and the reaction rate is determined mainly by the reactivity of $C^2$-H carbon-hydrogen bonds[2-5]. The dependence of the reactivity in the series of formals (Table 3) is in qualitative accordance with the dependence of the rates of carbonium ions formation and azocompounds decomposition on the cycle size[49,50]. According to the literatures[49, 50] the transition state of the limiting stage (reaction 3) is achieved at practically complete breakdown of $C^2$-H bond and is nearer to the final products than to the initial reacting particles.
The breakdown of $C^2$-H carbon-hydrogen bond in the cycle is accompanied by the transition of carbon $C^2$-atom from the state of $Sp^3$-hybridization to the state $Sp^2$. This transition is the most difficult in case of 1,3-dioxacyclohexanes, it is facilitated in case of five- and seven-membered cycles, which are more tense.

Table 3. The dependence of cyclic formals reactivity on the cycle size (130°C)

| Formals | $(K_3/\sqrt{K_4})\ 10^3$ (l/mol s)$^{0.5}$ |
|---|---|
|  | 5.9 |
|  | 1.0 |
|  | 2.5 |
|  | 5.5 |
|  | 8.0 |

In the works[2-5] it has been established that the substituents in the second position of the heterocycle, which are able to delocalize a lone electron, increase the reactivity of 1,3-dioxacyclanes (Table 4).

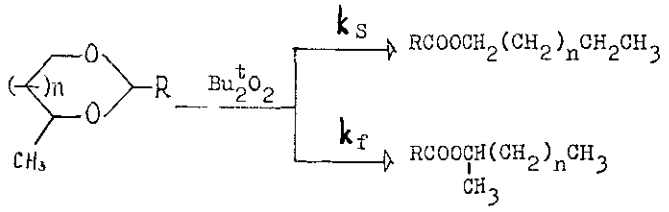
Table 4. The reactivity of substituted 1,3-dioxacyclanes (130°C)

| Acetal | : | $(K_3/\sqrt{K_4})10^3$ $(l/mol\cdot s)^{0.5}$ | : | Acetal | : | $(K_3/\sqrt{K_4})10^3$ $(l/mol\cdot s)^{0.5}$ |
|---|---|---|---|---|---|---|
|  | | 7.0 | |  | | 4.0 |
|  | | 8.5 | |  | | 0.4 |
|  | | 8.1 | | | | |
|  | | 1.8 | |  | | 1.4 |
|  | | 3.2 | | | | |

On the whole, 2-substituted 1,3-dioxacyclanes are isomerized two - four times faster than the corresponding formals. A slight acceleration caused by a phenyl group at $C^2$-atom of the ring is explained[3] by a non-plane structure of the cyclic radical $\underline{OCH_2CH_2O}CH\text{-}C_6H_5$ [29, 31], in consequence of it the conjugation of a lone electron $\pi$-orbital with a phenyl ring is minimum.

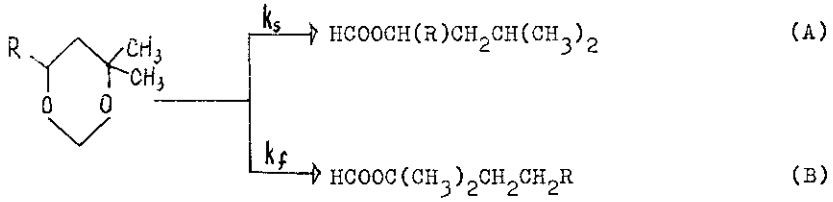
The cyclic acetals of disecondary glycols, containing the methyl groups in $\gamma$ - position to the reaction centre, show the reduced activity [2, 3, 9], which is explained by the fact that in this case the chain is led not by primary but secondary acyloxyalkyl radicals $RCOOCH(CH_3)(CH_2)_n\text{-}CHCH_3$, which are less active in the reaction of hydrogen atom breaking off.

The asymmetric cyclic acetals, which are the derivatives of primary-secondary glycols, are isomerized in two directions [1, 8, 9], which lead to the formation of ethers which differ in the structure of the alcohol part:



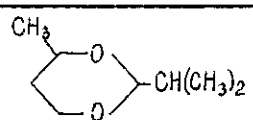
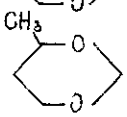
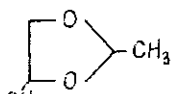
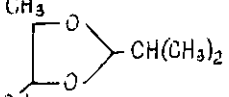
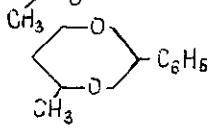
The ethers of normal structure are preferably formed, the predecessors of which are more stable than primary and secondary acyloxyalkyl radicals[8, 9]. Discovered in the work[8] ratios of the constants of the cycle opening reactions rates with the formation of primary and secondary acyloxyalkyl radicals (Table 5) show that the rearrangement takes place more selectively in six-membered cycles than in five-membered ones.

This dependence is explained by the fact[8] that in the rearrangement of the six-membered cycle the transition state is nearer to the final products than for five-membered one. In isomerization of formals of primary-tertiary and secondary-tertiary glycols of 4,4-dimethyl and 4,4,6-trimethyl-1,3-dioxanes the tertiary alcohols are not formed [9].




R = H, $CH_3$

Table 5. Isomerization of the acetals of primary-secondary glycols

| Acetal | $K_S/K_f$ | | | $\Delta E = E_f - E_S$ |
|---|---|---|---|---|
| | 120° | 130° | 150° | |
|  | 3.8 | 3.6 | 3.2 | 2.2 |
|  | 6.0 | 5.6 | 4.9 | 2.4 |
|  | 1.9 | 1.8 | 1.7 | 1.3 |
|  | 1.8 | 1.7 | 1.6 | 1.2 |
|  | - | 5.0 (135°C) | | |

Therefore, the rate of formation of tertiary formyloxyalkyl radicals from the corresponding 1,3-dioxacycloalkyl radicals exceeds more than one order the rate of primary and secondary radicals formation [9]. The parameter $K_3\sqrt{E_4}$ for these compounds is essentially lower than in case of non-substituted formals, as far as in the act of the chain prolongation less active primary and tertiary formyloxyalkyl radicals take place [9]. So, the substituents, situated in $\gamma$-position from the reaction centre of 1,3-dioxacyclane, influence the rate and direction of isomerization.

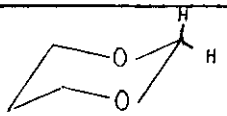
In the work[51] it is shown that the substituents in the 5-position of 1,3-dioxanes do not practically influence the reactivity because of their remoteness from the reaction centre in 1,3-dioxane and from the radical centre in radicals, forming from them as a result of rearrangement.

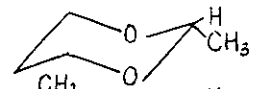
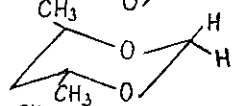
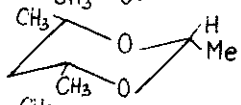
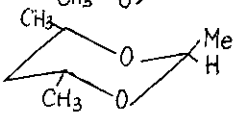
In the work[52] the combination of EPR method with gas-liquid chromatography has been used to determine the relative rates of hydrogen atom breaking off 1,3-dioxanes of various structure (Table 6). By means of EPR method the ratios of stationary concentrations of radical forming under the conditions when the mixture of di-tert-butyl peroxide and two dioxanes has been subjected to UV-irradiation in the cell of EPR-spectrometer, have been measured.

The relative constants of the rate, obtained by joining up two systems of data, are given in Table 6, where $\rho$ is the reactivity of the proper hydrogen atom of each compound in relation to 1,3-dioxane.

Great differences in the rates of reaction with tert.-butoxyl radicals are observed in epimeric 2,4,6-trimethyl-1,3-dioxanes, and the ratio values for them $\rho_{AH}/\rho_{BH}$, determined by the gas-liquid chromatography and EPR methods, are equal to 11 and 7 respectively.

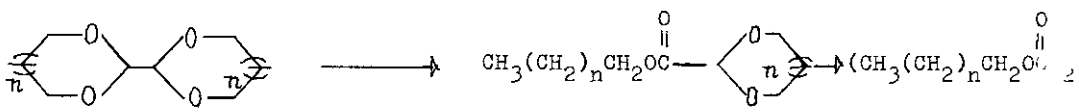
Table 6. The relative activity of 1,3-dioxanes in the reaction of hydrogen atom breaking off by tert.-butoxyl radicals (20°C)

| Dioxane | : | $\rho$ (GLCh) | : | $\rho$ (EPR) |
|---|---|---|---|---|
| 1 | : | 2 | : | 3 |
|  | | 1.0 | | 1.0 |

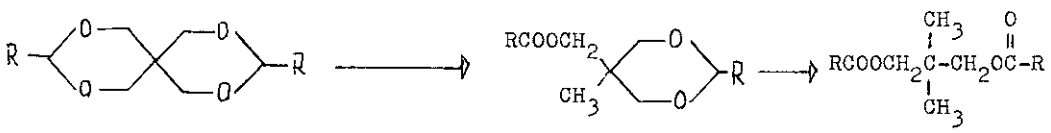
| 1 | : | 2 | : | 3 |
|---|---|---|---|---|
|  | | 1.5 | | 2.4 |
|  | | 2.6 | | 1.6 |
|  | | 2.8 | | 2.1 |
|  | | 0.25 | | 0.3 |

It is evident from these results that cis-form (4) is more active than trans-form (5) and that the axial C-H bond at C-2 breaks much quicker than the equatorial one,. Apparently, the stereoelectronic control takes place here and the heightened reactivity of the axial C-H bond is connected with its interaction with electron non-divided pairs of adjacent oxygen atoms in the transition state[52]. There is no such an interaction between the equatorial C-H bond and adjacent non-divided pairs of electrons.

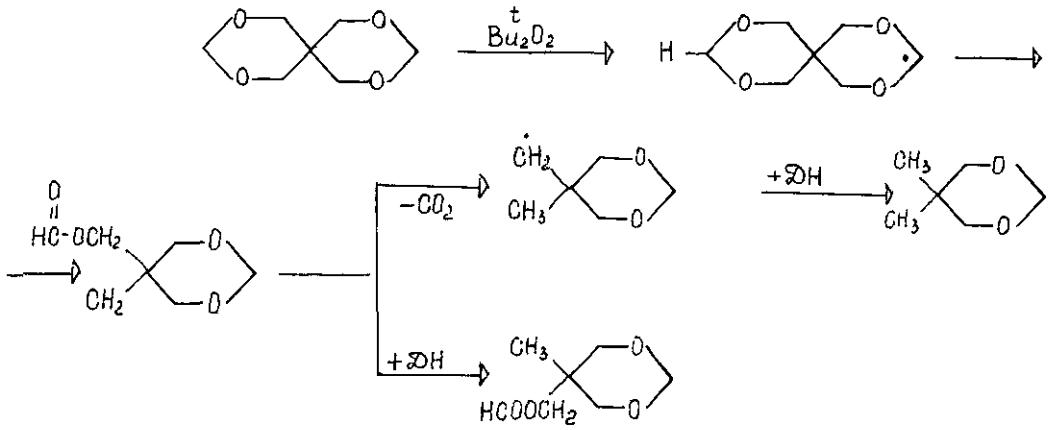
Cases of Acetals Isomerization, Which are accompanied by Other Reactions. Bis-spiroacetals, in molecules of which there are two 1,3-dioxacyclane rings in each, are isomerized with the successive opening of cycles [6, 7, 53, 54].



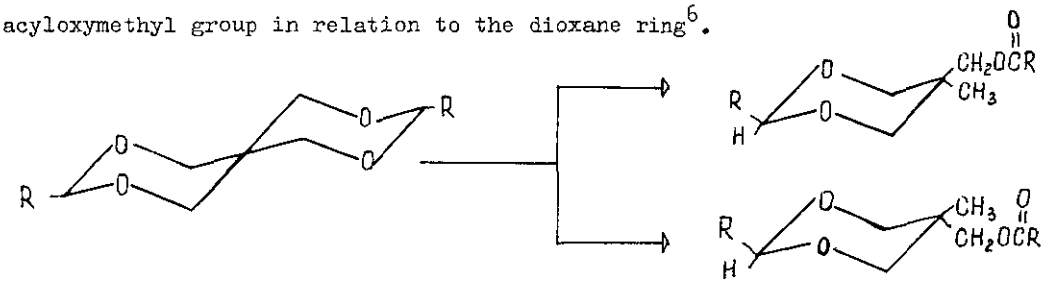
or:



In case of pentaerythritoldiformal the isomerization is accompanied by the rearrangement with 1,5-migration of hydrogen atom, as a result 5,5-dimethyl-1,3-dioxane is formed alongside with 5-methyl-5-formoxymethyl-1,3-dioxane[6].

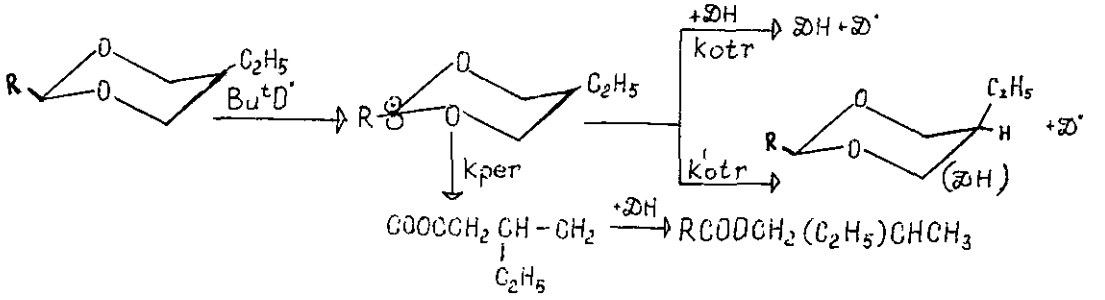


The reactivity of spirodioxanes is two times higher than that of 1,3-dioxanes, which indicates the closeness of $C^2$-H carbon-hydrogen bonds activity in them [6]. At the first stage of isomerization of pentaerythritol acetals the mixture of stereoisomers is simultaneously formed, which differs in the position of methyl and acyloxymethyl group in relation to the dioxane ring[6].



The stereoisomers with the equatorial acyloxymethyl group are preferably formed, which is caused by the energetic advantage of the volume substituent situation in the equatorial position [55].

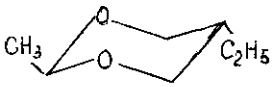
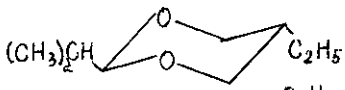
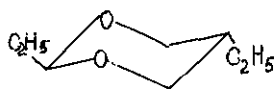
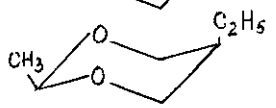
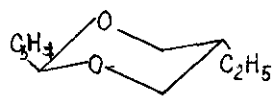
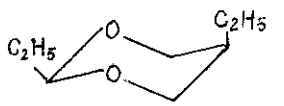
While studying homolytical isomerization of individual stereoisomers 2,5-dialkyl-1,3-dioxanes it has been established that alongside with isomeric ethers stereoisomeric 1,3-dioxanes are formed in the reaction mass[12, 56]. The formation of the latter is explained by the participation of cyclic dialkoxyalkyl radicals in the reaction of breaking hydrogen atom off the molecules of the initial compound[12,56].



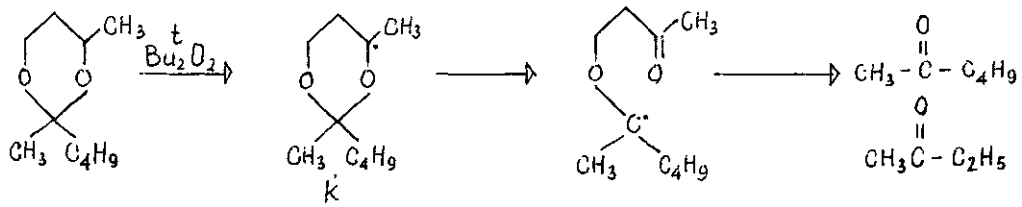
The obtained values (Table 7) of the constants ratios ($K_{rear.}/K_{br.}$) are the same for cis and transisomers and show that the stage of rearrangement is considerably quicker than the stage of the chain transfer.

With the increase of the alkyl substituent volume the value $K_{rear.}/K_{br.}$ decreases (Table 7) which is connected with the fact that the opening of the ring, demanding the coplanarity of carbon trivalent atom bonds, is realized more easily in case of substituents of the less volume [12, 56].

Table 7. The ratio of the constants of rates of monomolecular rearrangement and bimolecular breaking hydrogen atom $K_{rear.}/K_{br.}$ for 2,5-dialkyl-1,3-dioxa-2-cyclohexyl radicals [12, 56] (135°C)

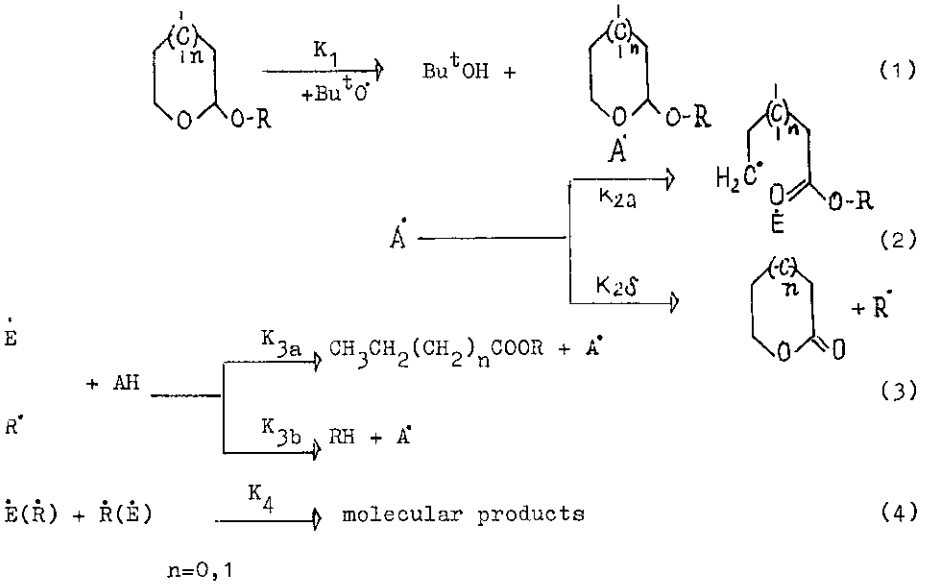
| 2,5-Dialkyl-1,3-dioxane | $\frac{K_{rear.}}{K_{br.}}$ | 2,5-dialkyl-1,3-dioxane | $\frac{K_{rear.}}{K_{br.}}$ |
|---|---|---|---|
|  | 47 |  | 22 |
|  | 37 |  | 47 |
|  | 28 |  | 36 |

Transformations of Cyclic Acetals. 2,2-Dialkyl-1,3-dioxacyclanes transformations take place in another way[10]. The absence of $C^2$-H carbon-hydrogen bonds in the molecule leads to C-H bonds, adjacent to an oxygen atom, becoming the main reaction centres[10]. Thus, during 2,4-dimethyl-2-butyl-1,3-dioxane transformations at the first stage 2,4-dimethyl-2-butyl-1,3-dioxa-4-cyclohexyl radical (K) is formed, which fragmentates with the formation of methylethyl- and methylbutylketones [10].



In transition of six-membered ketals to seven-membered ones the rate of transformation increases. However, five-membered ketals are less reactive than six-membered ones[10]. The latter is evidently connected with the fact that in this case the radicals are formed as a result of rearrangement, in which a lone electron is in allyl conjugation with a carbonyl group which decreases its reactivity[10].

Transformations of Linear-Cyclic Acetals - 2-Alkoxyoxacyclanes. As a result of the study of the kinetics of linear and cyclic ethers accumulation, forming in 2-alkoxyoxacyclanes isomerization, the general mechanism of the process has been established[57-61].




(1)

(2)

(3)

(4)

The parameter $K_{2a}/K_{2b}$ indicates the degree of the rearrangement of the radical A with the breakdown of the endocyclic carbon-oxygen bond $C^6$-$O^1$ (Table 8). In the works [58-60] it has been shown that R substituent structure influences greatly the process direction, so, if R=prim.alkyl then $K_{2a}/K_{2b}$=3-4, which leads to the formation of alkylvalerates with the selectivity not lower than 60%. If R=sec.alkyl, then $K_{2a}/K_{2b}$=0.3-0.8 and lactones are the main products.

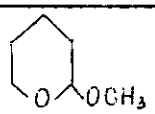
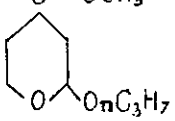
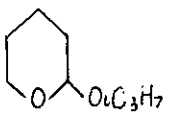
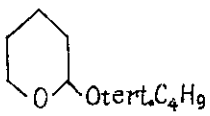
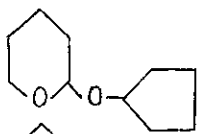
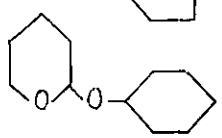
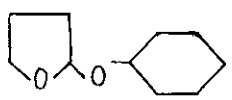
The five-linked radicals of A type undergo the cycle breakdown several times worse than the six-linked ones. It has been shown that the value $K_{2a}$ does not depend on the R structure and the values of the parameter $K_{2a}/K_{2b}$ are connected with the change of the value $K_{2b}$. It follows from the parameter value $(K_{3a}+K_{3b})/\sqrt{K_4}$ that the carbon-hydrogen $C^2$-H bond strength does not depend upon R substituent structure and is determined by the nature of the attacking radical and the

heterocycle size [60-61].

With the increase of pressure within the interval 1-10000 atm the selectivity of lactone formation increases greatly [26], which is explained by the difference in tension in the transition state of the stage 2, ruptured endo- and exocyclic carbon-oxygen bonds.

By means of EPR-spectroscopy it has been shown that the axial $C^2$-H bond in cis-4-methyl-2-metoxytetrahydropyrane is eight times more active than the analogous equatorial $C^2$-H bond in its trans-isomer .

Table 8. The kinetic parameters of homolytical transformations of 2-alkoxyoxacyclanes (130°C)

| Compound | $K_3/\sqrt{K_4}\ 10^3$ $(l/mol\ s)^{0.5}$ |
|---|---|
|  | 1.8 |
|  | 1.6 |
|  | 0.7 |
|  | 0.2 |
|  | 1.0 |
|  | 1.1 |
|  | 1.9 |

On the whole, as it has been shown in the work [26], cis-2-methoxy-4-methyltetra-

hydropyrane reacts with tert.-butoxyl radicals six times faster than tetrahydropyrane does, that is, the breaking of hydrogen equatorial atom at $C^2$-atom of 2-alkoxy derivative takes place with the same rate as the breaking of axial hydrogen off 2-methylene group of tetrahydropyrane.

It has been shown that the direction of the decay of the radicals A depends considerably on the number and nature of substituents in 6 position of tetrahydropyrane ring [27]. Substituents capable to stabilize a lone electron in the radicals E increase sharply the value $K_{2a}$. It is interesting that cis-2,6-dimethoxytetrahydropyrane is two times more active than trans isomer and that both forms are turned mainly into corresponding ethers.

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