HOMOLYTIC LIQUID-PHASE REACTIONS OF 1,3-DIOXACYCLANES (REVIEW)

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The literature data on the liquid-phase homolytic isomerization, addition, substitution, and oxidation reactions of 1,3-dioxacyclanes are examined. The problems involved in the formation, stabilities, kinetics, and mechanisms of the transformations of free radicals in a series of cyclic acetals are discussed. Possibilities for the application of the homolytic transformations of 1,3-dioxacyclanes in organic synthesis are demonstrated.

New areas for the effective application of various 1,3-dioxacyclanes as solvents, plasticizers, and corrosion inhibitors and in the synthesis of diene monomers, biologically active compounds, medicinal preparations, herbicides, etc. have been found in recent years. The increased interest of researchers in compounds of this series is also connected with their wide accessibility from petrochemical products (olefins, aldehydes, and glycols), on the one hand, and the presence of two heteroatoms in the ring, on the other. The latter is valuable from the point of view of the establishment of the general principles of the synthesis and transformations of saturated heterocyclic compounds.

The problems associated with the free-radical transformations of 1,3-dioxacyclanes in solution have been practically ignored in the published reviews and monographs [1-7] devoted to the chemistry and technology of cyclic acetals. The large amount of new data on the rates and directions of homolytic liquid-phase reactions of cyclic acetals are undoubtedly deserving of individual discussion.

Structures and Reactivities of Free Radicals Formed from 1,3-Dioxacyclanes

The radicals generated in 1,3-dioxacyclane media by various methods (thermal dissociation and photodissociation of peroxides, sensitized UV irradiation, redox systems) split out hydrogen from the substrate molecules to give cyclic free radicals.

The formation of nitroxyl radicals, which are sufficiently stable to be studied at room temperature by means of their ESR spectra, from substituted 1,3-dioxolanes and their heteroanalogs was observed in [8] by means of a free-radical acceptor (2-nitroso-2-methylpropane) in the benzophenone-initiated photochemical reaction and in the case of the thermal decomposition of di-tert-butyl peroxyoxalate. Only splitting due to spin–spin coupling with the nuclei of the nitrogen atoms was observed in the spectra, in which the reduced a_N value (13-14.5 G) as compared with the values for dialkylnitroxyl radicals (a_N = 15.5-17 G) was due to the inductive effect of the heteroatoms adjacent to the α-carbon atom [9] (Table 1). The radical formed from 2-cyclopropyl-1,3-dioxolane probably has a nonplanar structure, and this decreases the ability of the cyclopropyl ring to undergo opening, as a result of which only the signal of a nitroxyl radical containing an unsubstituted cyclopropane fragment is present in the ESR spectrum.

The ESR spectra of the radicals obtained by detachment of a hydrogen atom from the corresponding 1,3-dioxacycloalkane by the action of a hydroxyl radical at room temperature [10] or by reaction with the tert-butoxyl radical generated in the photolysis of di-tert-butyl peroxide (DTBP) [11] indicate that cyclic alkoxyalkyl and dialkoxyalkyl radicals are formed simultaneously [12] (Table 2).

These data, in conjunction with the constants of hyperfine splitting of the unpaired electron on the ^{13}C nuclei, made it possible to conclude that the radicals have a nonplanar structure.

The deciding factors in the degree of nonplanarity of the trivalent carbon atom are localization of the unpaired electron within the confines of a small ring with an increase in the p character of the carbon bonds and the presence in the α position relative to the radical center of one or two atoms that promote an increase in

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Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1011-1025, August, 1977. Original article submitted August 23, 1976.

TABLE 1. Nitroxyl Radicals Formed from Cyclic Acetals (DH) and Their Heteroanalogs as a Result of Detachment of a Hydrogen Atom in the Presence of 2-Nitroso-2-methylpropane in Benzene [8]

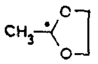
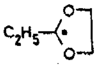
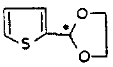
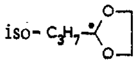
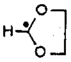
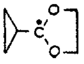
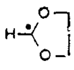
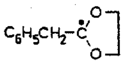
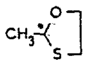
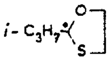
D' radical	a_N values of the tert-butyl-D-nitroxyl radical, G	D' radical	a_N values of the tert-butyl-D-nitroxyl radical, G
	14,1		14,1
	13,9		14,0
	14,1		13,2
	14,1		13,2
	13,8		14,4
			14,3

TABLE 2. Proton Splitting Constants and g Factors of Cyclic Radicals [12]

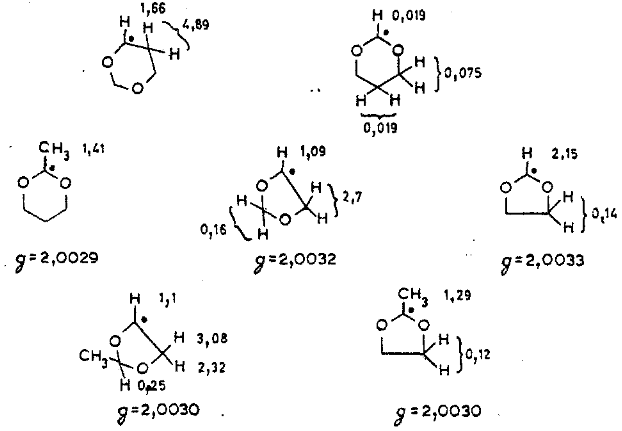
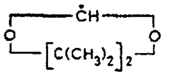
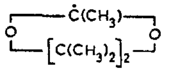
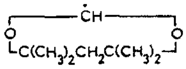
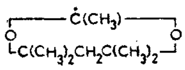


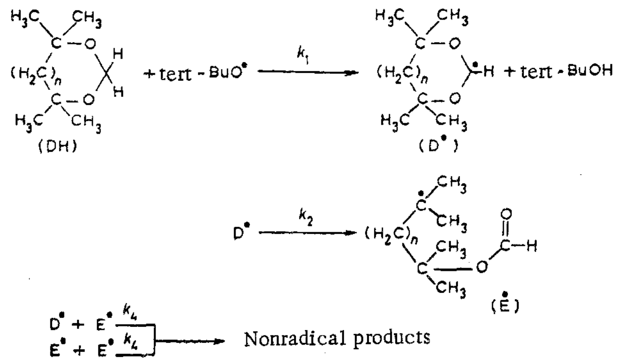
TABLE 3. Kinetic Parameters of the Rearrangement of Cyclic Dialkoxyalkyl Radicals [15]

Radical	$2k_4/\sqrt{k_2}$, liters·mole^{-1}·sec$^{-1/2}$ (72°)	k_2, sec^{-1} (72°)	lg $2A_4/\sqrt{A_2}$	E_2-E_4, kcal/mole
	$3{,}4\cdot10^5$	$5{,}8\cdot10^3$	—	—
	$9{,}7\cdot10^5$	$2{,}1\cdot10^3$	—	—
	$3{,}5\cdot10^4$	$5{,}7\cdot10^4$	+0,5	+6,5
	$3{,}8\cdot10^5$	$5{,}3\cdot10^3$	+1,2	+7,0

the electron density on the carbon atom via a conjugation mechanism; in this case the introduction of two oxygen atoms gives rise to a much stronger effect than the introduction of one oxygen atom.

Deviation from planarity in some cyclic dialkoxyalkyl radicals was confirmed in [13]. It follows from the ratio of the steady-state concentrations of the resulting radicals that detachment of a hydrogen atom from the carbon atom adjacent to the two heteroatoms is preferred over detachment from the other sites of the 1,3-dioxacycloalkane molecule. A similar conclusion was drawn as a result of an analysis of the quantitative principles of the thermal decomposition of DTPB in cyclic acetals [14].

Signals of cyclic radicals and the corresponding linear radicals have been identified in the ESR spectra of 1,3-dioxolanes and 1,3-dioxanes containing two methyl groups in the 4 and 5(6) positions [15].

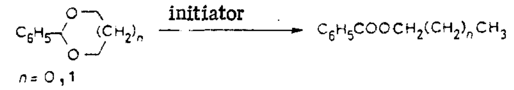


The kinetic parameters of the process (Table 3) have been determined in conformity with the proposed mechanism. Perkins and Roberts [15] have expressed the assumption that overlapping of the $2p_{\pi}$ orbital of the unpaired electron with the σ^* orbital of the adjacent oxygen atom should be realized during the monomolecular rearrangement. This overlapping is maximal for the conformation in which the $2p_{\pi}$ orbitals and the $C_{\alpha}-O$ and $O-C_{\gamma}$ bonds are coplanar. This sort of conformation is achieved in acyclic dialkoxyalkyl radicals, but the σ^* and $2p_{\pi}$ orbitals in the 1,3-dioxolanyl radicals are close to orthogonal. 1,3-Dioxanyl radicals occupy an intermediate position, and the rate constants for their rearrangement are therefore higher than those for the five-membered analogs.

It follows from a comparison of the energies (calculated by the Hoffman method) of the most stable conformations of the cyclic 1,3-dioxanyl and isometric linear 3-formylhydroxypropyl radicals that the rearrangement is accompanied by a considerable gain in energy [16]. These calculations are in agreement with the experimentally determined rate constants for monomolecular rearrangement, which at 70–150°C exceed the rate constant for chain transfer by two to three orders of magnitude.

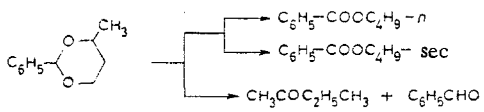
Kinetics and Mechanism of the Homolytic Isomerization of 1,3-Dioxacycloalkanes

Initiators of free-radical reactions (organic peroxides, peresters, and diazo compounds, as well as sensitized UV irradiation) cause rearrangement of cyclic acetals to isomeric esters. Similar transformation of cyclic acetals of benzaldehyde has been observed in the liquid phase (135°C) in the presence of DTBP [17].

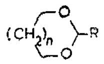


Ultraviolet radiation sensitized by acetone, acetophenone, or benzophenone gives rise to the same processes at lower temperatures (20°C); the rate of isomerization is considerably lower in this case [18, 19].

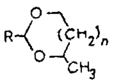
In the case of 2-phenyl-4-methyl-1,3-dioxane the isomeric butyl benzoates, methyl ethyl ketone, and benzaldehyde are simultaneously formed [17].



With respect to their relative reactivities in the case of isomerization in the presence of DTBP (10 mole %) at 130°C, six-membered cyclic acetals can be arranged in the following order [20, 21]: 2-furyl-1,3-dioxane ≥ 2-phenyl-1,3-dioxane > 2-methyl-1,3-dioxane > 2-isopropyl-1,3-dioxane > 1,3-dioxane. The results

TABLE 4. Kinetic Parameters of the Liquid-Phase Radical Isomerization of 1,3-Dioxacyclanes [23] 

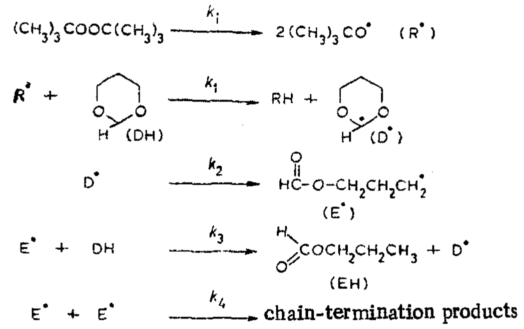
n	R	$k_3/\sqrt{k_4} \cdot 10^3$, liters/mole · sec$^{1/2}$ (130°C)	$E = E_3 - {}^1/_2E_4$, kcal/mole	$\lg A_3/\sqrt{A_4}$	$k_3/\sqrt{k_4}$, liters/mole · sec$^{1/2}$
0	H	5,92	14.4±0,2	5,7	$4.26 \cdot 10^5 \exp(-14\,400/RT)$
0	iso-C_3H_7	6,73	11,2±0.3	3,8	$6{,}92 \cdot 10^3 \exp(-11\,200/RT)$
0	C_6H_{13}	8.53	11,2±0.3	3.9	$8{,}51 \cdot 10^3 \exp(-11\,200/RT)$
2	H	2,58	12,1±0,3	3,8	$6.92 \cdot 10^3 \exp(-12\,100/RT)$
1	H	0,98	13 6±0.4	4,4	$2.40 \cdot 10^4 \exp(-13\,600/RT)$

TABLE 5. Kinetic Parameters of the Liquid-Phase Isomerization of 4-Methyl-1,3-dioxacyclanes [25] 

n	R	(k_n/k_{iso})			$\Delta E = E_{iso} - E_n$, kcal/mole
		120°	130°	150°	
1	iso-C_3H_7	3.8	3,6	3.2	2,2±0,3
1		6.0	5.6	4.9	2,4±0,3
0	CH_3	1,9	1,8	1.7	1,3±0,2
0	iso-C_3H_7	1,8	1,7	1,6	1,2±0,2

indicate that groups that are capable of delocalizing the unpaired electron, thereby stabilizing the intermediate cyclic radical, increase the rate of isomerization.

A study of the kinetic principles of the DTBP-initiated liquid-phase transformations of the 1,3-dioxacyclanes at 120-150°C showed [22] that the initial rate of formation of the ester depends linearly on the substrate concentration to the first power and on the initiator concentration to the 0.5 power. These results were found to be valid for a large number of compounds and indicate a radical-chain unbranched mechanism with quadratic chain termination by the rearranged radicals.



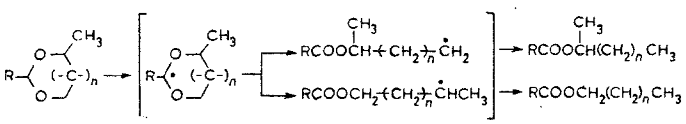
Hence, $W_{EH} = k_3/\sqrt{k_4} \cdot [DH] \cdot \sqrt{W_i}$.

The experimentally determined $k_3/\sqrt{k_4}$ value (Table 4) is a kinetic parameter that characterizes the reactivities of the cyclic acetals in liquid-phase homolytic isomerization reactions [23].

1,3-Dioxolane is appreciably more reactive than its seven- and six-membered analogs. This is explained by the fact that the change in the sp^3 hybridization of the ring $C_{(2)}$ atom to sp^2 that occurs during detachment of a hydrogen atom is least advantageous for the six-membered ring, whereas linear $E^\bullet$ radicals with different numbers of methylene groups differ insubstantially with respect to their reactivities both in chain-propagation and chain-termination reactions.

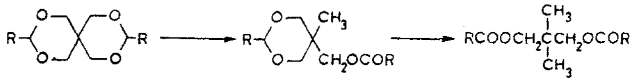
It follows from [24] that the chief product of chain termination is a diester. This confirms the dominant role of dimerization in processes involving quadratic chain termination by primary alkyl radicals.

The formation of esters that differ with respect to the alcohol portion is characteristic for 1,3-dioxacyclanes that contain a substituent in the 4 position. The reason for this is the possibility of competitive decomposition of the cyclic radical at two nonequivalent C—O bonds. Since linear alkyl radicals whose properties determine the direction of the process are formed in this step, esters with normal structures (Table 5) are primarily formed, since their precursors are the more stable secondary radicals [25]:



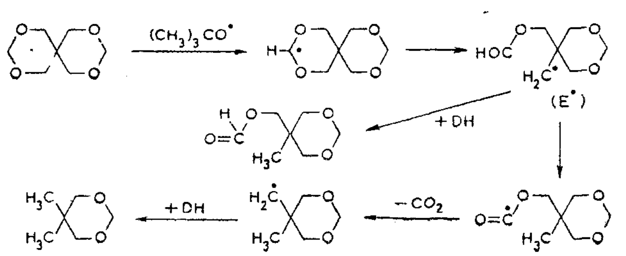
The rates of isomerization of the stereoisomeric 2,5-disubstituted 1,3-dioxanes are practically identical, i.e., the geometry of the ring 5 position does not affect the homolytic cleavage of the $C_{(2)}-H$ bond [26].

The radical isomerization of pentaerythritol diacetals, in which 2,5,5-trisubstituted 1,3-dioxanes are formed in the first step [27], may serve as a method for the preparation of 2,2-dimethyl-1,3-propanediol diesters:



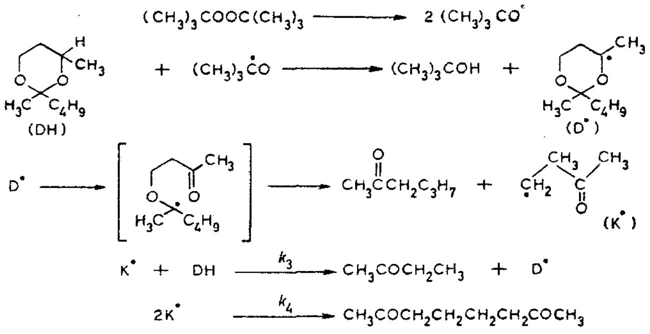
$R = CH_3$; C_2H_5 ; C_3H_7 ; C_6H_{13}

In the case of pentaerythritol diformal (R = H), 5,5-dimethyl-1,3-dioxane [28] is formed in addition to the expected 5-methyl-5-formyloxymethyl-1,3-dioxane and 2,2-dimethyl-1,3-propanediol diformate, evidently as a consequence of intramolecular rearrangement of monocyclic radical $E^{\bullet}$:



In the case of 2,2,4-trisubstituted 1,3-dioxanes it was shown that under the influence of radical initiators cyclic ketals undergo fragmentation at the two C–O ring bonds to give the corresponding ketones [29]. In this case the reaction center is the alkyl-substituted carbon atom adjacent to the heteroatom.

The kinetic principles of the rearrangement have been studied in the case of 2,4-dimethyl-2-butyl-1,3-dioxane. The rate of formation of methyl ethyl ketone (W_{MEK}) depends linearly on the concentration of the starting ketal and is extrapolated to the origin. The rate of formation of methyl butyl ketone (W_{MBK}) also depends linearly on the ketal concentration and cuts out a value equal to the rate of initiation on the axis of ordinates. Linear dependences of W_{MEK} on the initiator concentration to the 0.5 power and of $W_{MBK}/\sqrt{W_i}$ on $\sqrt{W_i}$ are satisfied. These results made it possible to assume a radical-chain mechanism for the reaction.



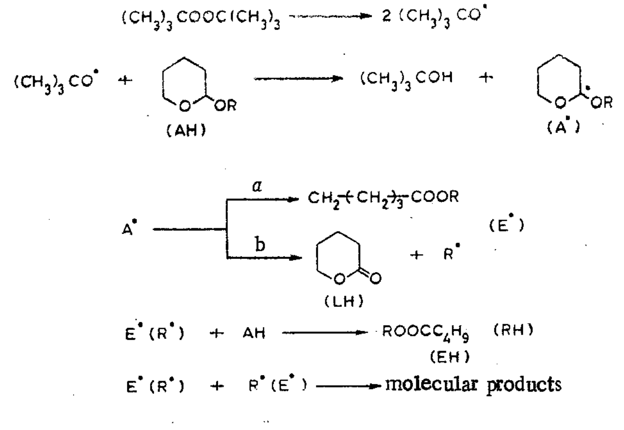
Hence, $W_{MEK} = k_3/\sqrt{k_4} \cdot [DH] \cdot \sqrt{W_i}$.

The kinetic parameter $k_3/\sqrt{k_4}$(130°C) = $0.64 \cdot 10^{-3}$ (liter/mole · sec)$^{1/2}$ for the formation of methyl ethyl ketone from 2,4-dimethyl-2-butyl-1,3-dioxane is considerably lower than for 2-methyl-1,3-dioxane; this is due to the increased strength of the $C_{(4)}-H$ bond as compared with the $C_{(2)}-H$ bond [29].

Like 1,3-dioxacyclanes, linear cyclic acetals – 2-alkoxyoxacyclanes – in the liquid phase in the presence of radical initiators are rearranged to linear or cyclic esters. Thus methyl valerate is formed selectively from 2-methoxytetrahydropyran in the presence of DTBP (at 130°C) [30]. As a result of transformations initiated by sensitized UV irradiation (at 20°C), the predominant process is the formation of δ-valerolactone [31].

The results of a study of the effect of the structure of 2-alkoxytetrahydropyrans on the rate and direction of homolytic transformations [32] make it possible to draw a conclusion of fundamental significance: the direction of cleavage of a cyclic dialkoxyalkyl radical is determined by the stability of the alkyl radicals formed. Thus substituents in the 6 position determine the formation of a linear radical, whereas a carbonyl group in the β position of the alkoxy substituent determines the selective transformation to a lactone.

The following reaction mechanism has been established by kinetic studies [33]:



Hence, $W_{EH} \simeq \frac{k_{2a}}{k_2} \cdot \frac{k_3}{\sqrt{k_4}} [DH] \cdot \sqrt{W_i}$.

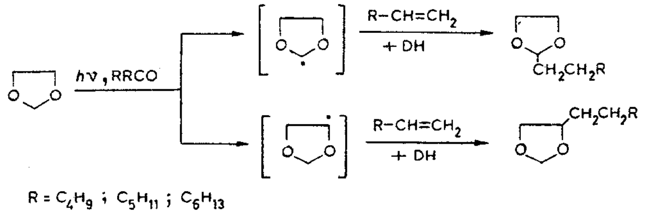
In the case $R = CH_3$, $k_{2a} \simeq k_2 \gg k_{2b}$, and the scheme of the process is completely analogous to the scheme for cyclic acetals. When $R = \text{tert-}C_4H_9$, $k_{2b} \simeq k_2 \gg k_{2a}$, and the scheme coincides with the mechanism of the transformation of cyclic ketals (see above).

The reactivity of 2-n-pentyloxytetrahydropyran is close to the reactivity of 2-methyl-1,3-dioxane. This makes it possible to conclude that the factor that determines the homolytic cleavage of precisely the $C_{(2)}-H$ bond is the presence of two oxygen atoms in the α position.

Radical Addition and Substitution Reactions of 1,3-Dioxacyclanes

Cyclic alkoxy- and dialkoxyalkyl radicals formed from the corresponding 1,3-dioxacyclanes participate in reactions involving addition to the multiple bonds and in reactions involving detachment of a halogen atom.

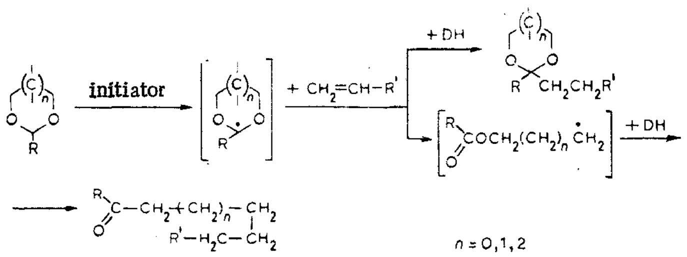
Mainly 2-alkyl derivatives (1 : 1 addition products) are formed in up to 50% yields in the photosensitized addition of 1,3-dioxolane and 1,3,5-trioxane [34, 35] to olefins with a terminal double bond; 4-alkyl-1,3-dioxolanes are formed in considerably smaller amounts.



When diethyl maleate is used in place of unsaturated hydrocarbons in this reaction, diethyl 1,3-dioxan-2-ylsuccinate is obtained in up to 90% yield. A photoexcited molecule of the sensitizer attacks the substrate, cleaving the weakest $C_{(2)}-H$ or $C_{(4)}-H$ bonds, and the corresponding cyclic radical adds to the carbon–carbon double bond of the unsaturated compound.

It has been demonstrated that cyclic dialkoxyalkyl radicals can also add to the carbonyl group of aldehydes [36] and ketones [37] to give hydroxyalkyl derivatives.

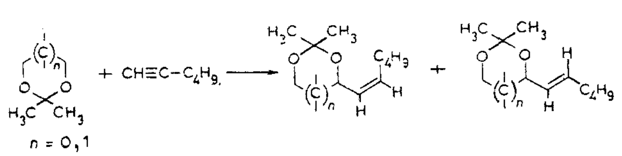
The addition of 1,3-dioxacyclanes to linear and cyclic unsubstituted compounds under the influence of DTBP or benzoyl peroxide [38-41] at 90-160° gives, in addition to alkylacetals, adducts with ester character:



The latter are formed as a result of rearrangement of the intermediate cyclic radical to a linear radical (see above); the role played by this reaction becomes greater as the temperature rises. The ratio of the products of addition to the 2 and 4 ring positions also indicates (see above) that the $C_{(2)}-H$ bond more easily (by a factor of two to three) undergoes homolytic cleavage than the $C_{(4)}-H$ bond. The formation (in up to 5% yields) of compounds with isoalkyl substituents was observed in all cases.

Cyclic ketals are considerably less active in addition reactions than acetals, and the formation of appreciable amounts of 2,2,4-trisubstituted 1,3-dioxacyclanes is observed only under severe conditions (150-160°C); in this case 2,2-dimethyl-1,3-dioxolane is twice as reactive as 2,2-dimethyl-1,3-dioxane.

The radical addition of 2,2-dimethyl-1,3-dioxolane and 2,2-dimethyl-1,3-dioxane to 1-hexyne (160°C, acetal : olefin : DTBP molar ratio = 10 : 1 : 0.25, 4 h) may serve as a method for the preparation of 3-octene-1,2-diols and 4-nonene-1,3-diols; according to the NMR spectra, cis- and trans-4-hexenyl-2,2-dimethyl-1,3-dioxacyclanes are formed in approximately equal amounts [42].



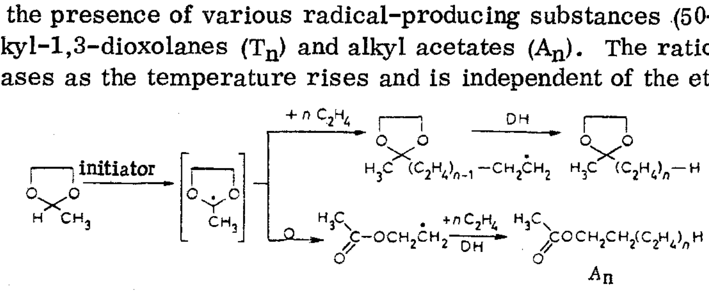
The homolytic addition of 2,2-disubstituted 4-alkoxymethyl-1,3-dioxolanes to 1-nonene to give 2,2,4,4-tetrasubstituted 1,3-dioxolanes, the yields of which were not indicated, has been described [43].

When unsaturated compounds with double bonds to which an electron-acceptor group is attached (α,β-unsaturated ketones and esters and nitriles of α,β-unsaturated acids) are used, the reaction proceeds selectively to favor the formation of 2-substituted 1,3-dioxacyclanes, which in a number of cases are difficult to obtain by other methods [44, 45]. This indicates the nucleophilic character of the cyclic dialkoxyalkyl radical, the addition of which takes place through a transition step with charge separation, as a consequence of which electron-donor substituents attached to the double bond increase the reaction rate.

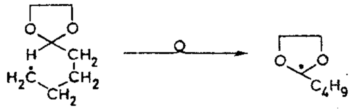
Examples of homolytic addition to the double bond of 2-alkenyl-1,3-dioxacyclanes are known [45-47]. The acetal function does not have a substantial effect on the rate and direction of the reaction, and the process is similar in many respects to the corresponding reactions of allyl ethers.

The homolytic addition of 2-alkoxytetrahydropyrans to olefins leads mainly to 2-alkyl-2-alkoxytetrahydropyrans [30].

A special case of these reactions, which is, however, of independent significance, is the radical telomerization of the widely accessible lower α-olefins with cyclic acetals. Telomerization of ethylene with 2-methyl-1,3-dioxolanes [48, 49] in the presence of various radical-producing substances (50-150°C) gave two series of telomers — 2-methyl-2-alkyl-1,3-dioxolanes (T_n) and alkyl acetates (A_n). The ratio of the yields of the linear and cyclic telomers increases as the temperature rises and is independent of the ethylene concentration.

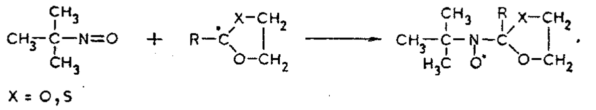


The practical constancy of the partial constants of chain transfer as the temperature rises and the molecular masses of the growing radicals increase ($C_n = 0.2$) indicates approximately identical activation energies for the addition of the monomers and chain transfer, as well as that the dioxolane ring does not have a substantial effect on the reactivity of the growing radical. Similar results were obtained in the telomerization of ethylene with 2-ethyl-, 2-isopropyl-, and 2-butyl-1,3-dioxolanes. An increase in the fraction of linear telomer homologs (A_n) was observed in all cases as the temperature rose. Monomolecular rearrangement of the growing radical with two ethylene links was noted in addition to chain transfer and chain propagation in the telomerization of 1,3-dioxolanes [50, 51].



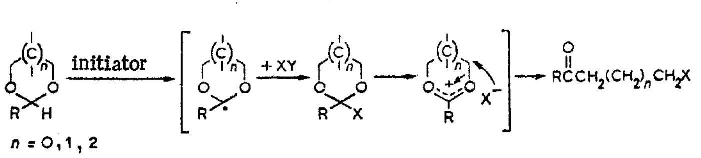
This leads to the appearance in the reaction mass of a new series of telomer homologs – 2-butyl-2-alkyl-1,3-dioxacyclanes. The telomerization of ethylene by six- and seven-membered cyclic acetals proceeds in the same way as the telomerization of 2-substituted 1,3-dioxolanes. However, the yield of linear telomer homologs is appreciably higher in the case of dioxepane. The partial constants for the investigated compounds range from 0.15 to 0.25; this characterizes them as relatively inefficient chain carriers whose reactivities are close to those of aliphatic carboxylic acid esters.

The cyclic radicals formed by sensitized UV irradiation of 1,3-dioxacyclanes and their heteroanalogs actively add to the oxygen–nitrogen double bond of 2-nitroso-2-methylpropane [8]:



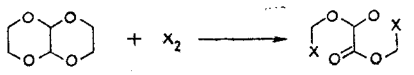
The resulting nitroxyl radicals were identified from the parameters of their ESR spectra, and, as indicated above, this made it possible to draw an unambiguous conclusion regarding the structure of the intermediate radicals.

The 1,3-dioxacyclane radical formed as a result of homolytic cleavage of the weakest $C_{(2)}-H$ bond is capable of detaching a halogen atom from a halogenating agent to give the extremely unstable cyclic dialkoxyalkyl halide [52], which evidently has the character of a carbonium ion [53]. The rapid isomerization of the latter to the corresponding halogen-containing ester evidently proceeds as intramolecular nucleophilic substitution through attack of the X^- anion on the ring $C_{(4)}[C_{(6)}]$ atom.



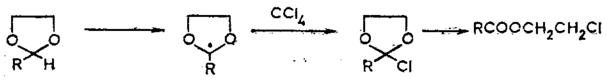
Hence, it follows that the position of the halogen atom in the ester molecule unambiguously indicates the site of cleavage of the C–O bonds.

In the reaction of chlorine, bromine, or N-bromosuccinimide (NBS) with trans-1,4,5,8- tetraoxadecalin, bis(2-haloethyl) oxalate was obtained as the principal product instead of the expected cyclic mono- and dihalo derivatives [54]:



2-Chloroethyl or 2-bromoethyl formate is formed under the influence of the same reagents from 1,3-dioxolane. The liquid-phase chlorination of 1,3-dioxanes with molecular chlorine also leads to the corresponding chloro esters [55].

In the reaction of cyclic acetals with NBS in carbon tetrachloride the formation of chloro esters along with bromo derivatives is noted: this is explained by chain transfer to the solvent [56]:

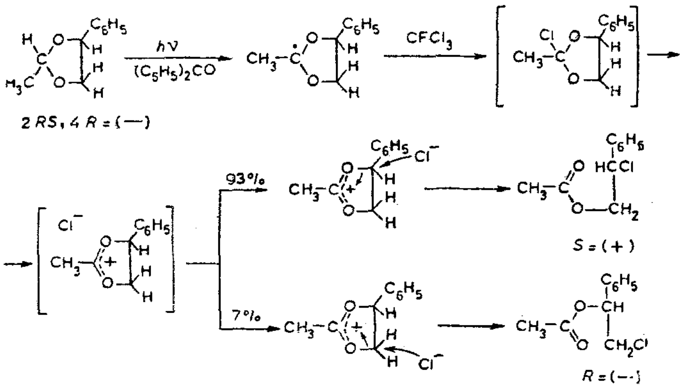


The yields of reaction products are determined by the ability of the substituent in the 2 position to stabilize the unpaired electron in the cyclic radical; hence, it can be concluded that the rate-determining step is homolysis of the $C_{(2)}-H$ bond.

As a result of a study of the action of NBS in benzene solution at 50°C in the presence of benzoyl peroxide on a number of acetals and ketals of ethylene glycol and propylene 1,2-glycol it was found that there is practically no involvement of the $O_{(3)}-C_{(4)}$ bond during ring opening and that the bromine atom in the resulting esters is attached to the primary carbon atom [57]. Only bromination of the alkyl groups in the 2 position occurs in the case of cyclic acetals.

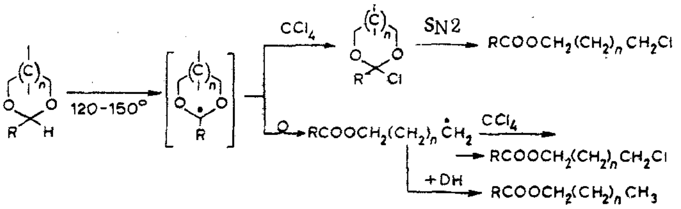
It is interesting that the bromination of 4-phenyl-1,3-dioxane with NBS takes place simultaneously in the 2 and 4 positions, as indicated by the simultaneous formation of bromo esters and 4-bromo-4-phenyl-1,3-dioxane [58].

The photochemical reactions of a number of five-membered cyclic acetals and their heteroanalogs in $CFCl_3$ in the presence of benzophenone lead exclusively to the formation of the corresponding chlorine-containing acyclic esters [8]. The photolysis of optically active 2-phenyl-4-methyl-1,3-dioxolane gives 2-acetoxy-1-chloro-1-phenylethane with complete inversion of configuration. This is convincing proof that a reaction via an S_N2 mechanism takes place at the $C_{(4)}$ atom:



Whereas a phenyl group in the 4 position is replaced by a CH_3 or CH_2Cl group, the chloride ion attacks the least substituted carbon atom in the intermediate carbonium ion; as a result, only primary chloro esters are formed [8].

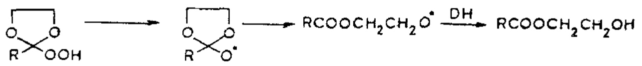
When tetra-, tri-, and dichloromethanes, the strengths of the C—Cl bonds in which range from 70 to 80 kcal/mole [59], are used as the halogenating agents and the reaction is initiated by DTBP (at 120–150°C), the rate of rearrangement of the cyclic radical and the rate of detachment of a chlorine atom by it turn out to be close; this leads to the simultaneous formation of esters and chloro esters, during which the latter are formed via parallel ionic S_N2 and radical mechanisms.



Liquid-Phase Initiated Oxidation of 1,3-Dioxacyclanes

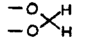
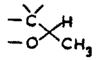
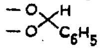
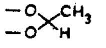
The free-radical-donor-initiated liquid-phase oxidation of 1,3-dioxacyclanes with molecular oxygen leads to hydroperoxide and peroxide derivatives. This reaction has served as the basis for a method for the preparative synthesis of 2-hydroperoxy-1,3-dioxolanes, the concentration of which in the substrate undergoing oxidation reaches 80% [61].

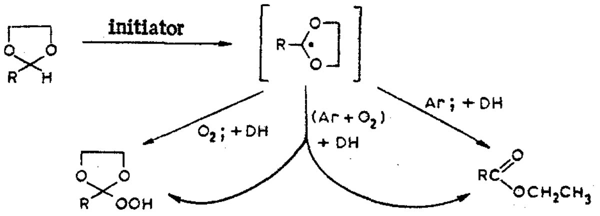
The corresponding ethylene glycol esters are formed in more profound oxidation steps as a result of decomposition of the hydroperoxides:



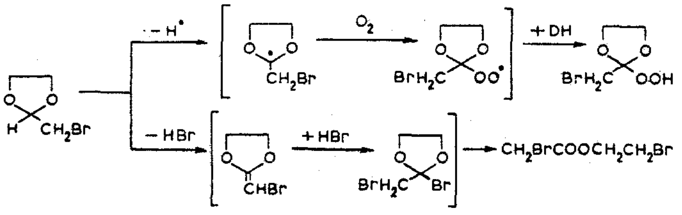
The oxidation and isomerization reactions proceed simultaneously [62], and the ratio of the ester and hydroperoxide depends on the conditions and the oxygen concentration:

TABLE 6. Partial Values of the Relative Rate Constants for Oxidation of the Corresponding C—H Bonds of 1,3-Dioxacyclanes

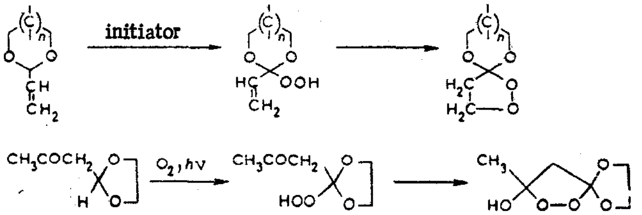
Type of bond	$k_2/\sqrt{k_6} \cdot 10^3$, (liters/mole · sec)$^{1/2}$
	1,93
	1,54
	7,20
	3,90



The occurrence of a number of new transformations that accompany liquid-phase oxidation was established in the case of cyclic acetals containing an α-halomethyl group in the 2 position [63]. In the opinion of Seyfarth [63], the formation of β-bromoethyl monobromoacetate from 2-dibromomethyl-1,3-dioxolane proceeds through a step involving the formation of a ketene acetal.



The formation of spirocyclic peroxides has been established in the autoxidation of 2-alkenyl- [64] and 2-β-oxoalkyl-1,3-dioxolanes [65]:



It has been found as a result of a study of the initiated oxidation of a number of cyclic acetals by kinetic methods that the latter are oxidized via a free-radical mechanism with quadratic termination by peroxide radicals [66, 67]. The primary site of attack by the peroxy radical ($DO_2^{\bullet}$) in 1,3-dioxacyclanes is the $C_{(2)}$—H bond, especially when there is an alkyl or phenyl substituent present, as well as a substituent-activated $C_{(4)}$—H bond (Table 6); the strength of the carbon—hydrogen bond undergoing cleavage ranges from 80 to 90 kcal/mole.

The rate constants of the two reactions — homolytic cleavage of the C—H bond by a peroxy radical and recombination of the $DO_2^{\bullet}$ radicals [68, 69] — were determined separately by the intermittent illumination method. The fact that the rate constant for cleavage of the $C_{(2)}$—H bond by a peroxy radical decreases on passing from cyclic formals to cyclic acetals was explained by the steric hindrance created by the substituent. Additional activation of this bond by an alkyl substituent is not substantial in the case of such a powerful factor as two ring oxygen atoms.

The corresponding glycol monoesters are formed as a result of the liquid-phase oxidation of cyclic acetals with ozone, but the available data [70] indicate that the reaction does not proceed via a radical mechanism.

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