

# HOMOLYTIC ADDITION OF ACETALS TO CARBON-CARBON MULTIPLE BONDS

By

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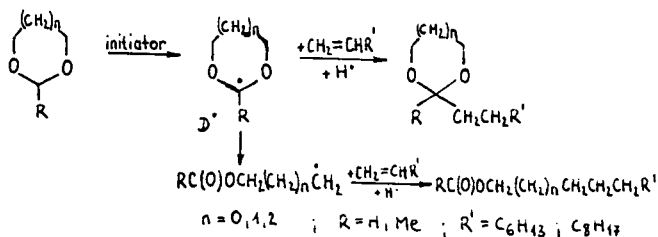
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Carbon and oxygen-centred radicals selectively attack the methylene or methyne group adjacent to two heteroatoms in cyclic and linear acetals, which leads to the formation of the corresponding dialkoxyalkyl radicals [1—3]. The latter have high reactivities and take part in various transformations [2]. The works devoted to the addition of similar radicals to various unsaturated compounds are summarized in this review.

## I. Addition of cyclic acetals

1,3-Dioxacyclanes add to  $\alpha$ -olefins in the presence of free-radical initiators, forming 2-alkyl-1,3-dioxacyclanes and esters [4—6].



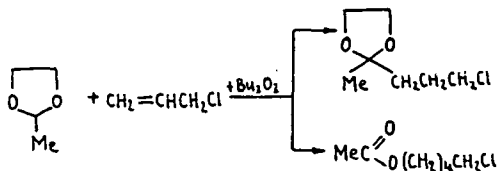
The formation of linear compounds is a result of cyclic dialkoxyalkyl radicals ( $\text{D}^\bullet$ ) rearranging into acyloxyalkyl radicals ( $\text{E}^\bullet$ ), and of the addition of the latter to the olefin double bond.

The reduced reactivity of the six-membered cycle in comparison with the five- and seven-membered ones [4] indicates that the formation of dialkoxyalkyl radicals is the limiting stage of the addition. It follows from the data in [4] that the ratio of the cyclic and linear products is not determined by the alkyl substituent structure in position 2 of the cycle.

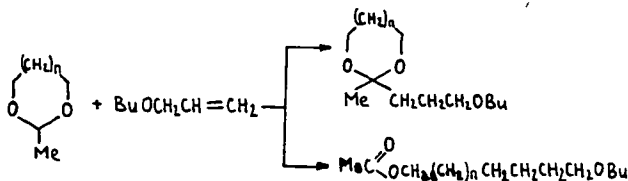
The high yield of linear compounds in the addition of cyclic acetals to olefins at 130—160 °C is accounted for by the rapid rearrangement of the cyclic radical into a linear one under these conditions [6]. The polar effects are the determining factor of the direction of addition to olefins containing functional substituents [7].

The addition of a cyclic dialkoxyalkyl radical with clearly expressed nucleophilic properties to the double bond of an olefinic hydrocarbon enriched by electrons is not favoured. In the intermediate state of the addition reaction the division of charges leads to the excess electron density at the olefin, an unfavourable combination of polar factors being realized. In contrast, electrophilic substituents in olefins promote the addition of nucleophilic dialkoxycycloalkyl radicals to the double bond.

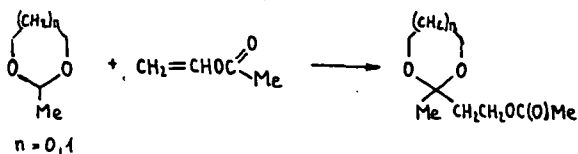
2-Methyl-1,3-dioxolane adds to allyl chloride (120—140 °C) with the formation of 5-chloropentanol acetate and 2-methyl-2-chloropropyl-1,3-dioxolane [7]:



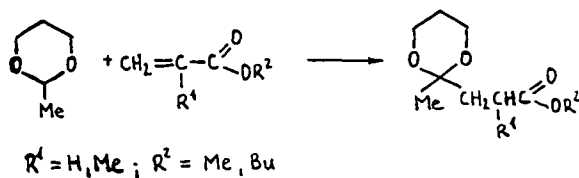
Here, the influence of the  $\alpha$ -chloro-atom upon the reduction of the double bond electron density is not essential and as a result mainly linear products are formed. In the products addition of five- and six-membered acetals of acetaldehyde to butyl ether, ester and 1,3-dioxane derivatives are present in equal amounts [4].



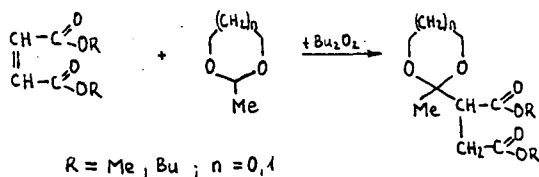
The addition to vinyl acetate leads mainly to 2,2-disubstituted 1,3-dioxacyclanes [4].



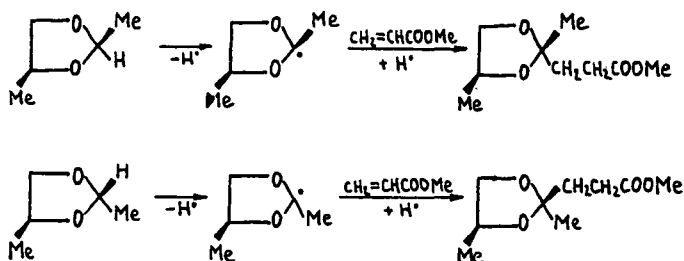
The addition of cyclic acetals to double bond of  $\alpha$ ,  $\beta$ -unsaturated acids leads exclusively to cyclic compounds [8].



The reaction of cyclic acetals with esters of maleic acid proceeds selectively [4].

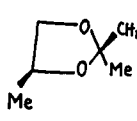
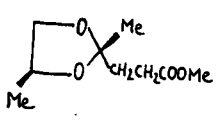
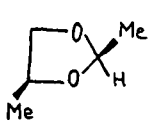
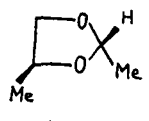


The photochemical addition of *cis*- and *trans*-2,4-dimethyl-1,3-dioxolanes to methyl acrylate at  $-78^\circ\text{C}$  leads to a mixture of geometrical isomers with partial retention of the initial dioxolane primary configuration [9].



At room temperature the mixtures obtained contain about equal amounts of geometrical isomers (Table I). The degree of retention of the initial 1,3-dioxolane configuration increases with the increase of the methyl acrylate concentration.

Table I  
 Photochemical addition of *cis*- and *trans*-2,4-dimethyl-1,3-dioxolanes  
 to methyl acrylate in acetone medium

2,4-Dimethyl-1,3-dioxolane	T, °C		
	20 -78	60 73	40 26
	20 -78	62 43	37 56



a) addition to the monomer double bond (reaction 2) with the formation of telomeric radicals ( $\dot{T}_n$ );

b) monomolecular rearrangement into acyloxyalkyl radicals ( $\dot{E}$ ) (reaction 3).

Acyloxyalkyl radicals ( $\dot{E}$ ) split off a hydrogen atom and form the ester (EH), or add to the monomer carbon-carbon double bond and as a result a telomeric radical is formed ( $\dot{A}_n$ ). The transmission of the chain by the radicals (reactions 5, 6) leads to the formation of telomer homologues of 2-alkyl-1,3-dioxacyclane series (I) and esters ( $\dot{A}_n$ ).

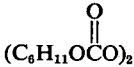
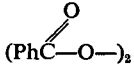
The composition of the mixture of telomer homologues of the  $T_n$  series (or  $A_n$ ) at constant monomer/telogen ratio depends on the reaction temperature. With the increase of the monomer concentration, under otherwise equal conditions, the yields of both high homologues (1,3-dioxacyclanes and esters) increase, while their ratio  $A_n/T_n$  does not change [10].

With the increase of the reaction temperature, the yield of linear telomer homologues increases, while the yield of cyclic ones decreases. Hence, the radical telomerization of ethylene by 2-methyl-1,3-dioxolane at 50 °C leads mainly to telomer homologues of cyclic structure ( $T_n$ ), and at 150 °C 2-methyl-2-alkyl-1,3-dioxanes and alkyl acetates are formed in commensurable amounts (Table II). This is connected with the fact that with the increase of temperature the rate of monomolecular rearrangement of cyclic dialkoxyalkyl radicals  $\dot{D}$  increases to a greater extent than the rate of their addition to the monomer. This leads to an increase in the ratio of the stationary concentrations of the radicals  $\left(\frac{\dot{E}}{\dot{D}}\right)$  [10].

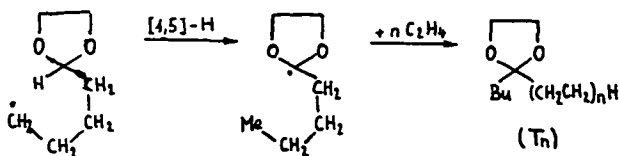
The selectivity of the formation of cyclic ( $T_n$ ) and linear telomers depends essentially on the cycle dimensions [10]. Under otherwise equal conditions, the yield of telomers of the ester series increases with increase of the cycle dimensions [10].

Table II

Composition of the products of ethylene radical telomerization by 2-methyl-1,3-dioxolane at various temperatures [10]

T °C	Initiator	Molar ratios of telomers in reactions mixture				
		$T_1/A_1$	$T_2/A_2$	$T_3/A_3$	$T_4/A_4$	$T/A$
50		40.1	25.1	18.8	16.6	100.0
90		37.3	23.4	14.3	19.9	94.9
		1.8	1.1	0.9	1.3	5.1
15	$(Me)_3COOC(Me)_3$	28.5	22.4	18.5	8.2	77.6
		6.1	4.2	3.8	8.3	22.4

The telomerization of ethylene by cyclic formal (1,3-dioxolane) at 150°C is complicated by the fact that it is accompanied by the rearrangement of the second cyclic telomeric radical with 1,5-migration of the hydrogen atom [12].



This leads to the formation of the third series of telomer homologues: 2-butyl-2-alkyl-1,3-dioxolanes ( $T_n'$ ) [13].

The most important characteristic of the telomerization process is the quotient of the constants of the chain transmission,  $C_n = K_{trans}/K_p$  [14], where  $K_{trans}$  is the constant of the reaction rate of chain transmission (reaction 5 or 6),  $C_n$  is the constant of the reaction rate of chain increase by the radical containing  $n$  monomeric units (reactions 2 or 4). Values of  $C_n$  found for ethylene telomerization by 1,3-dioxacyclanes are given in Table III.

Table III

Quotient of the constants of chain transmission in the radical telomerization of ethylene by 1,3-dioxacyclanes [11, 13, 15]

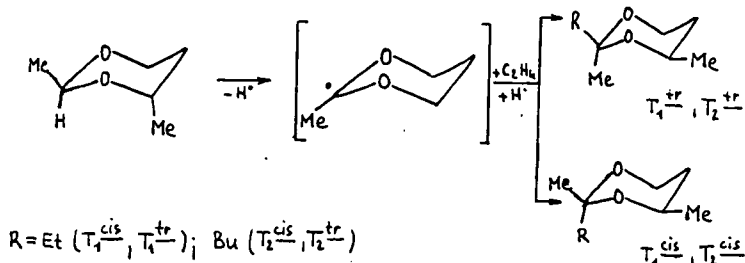
Telogen	T °C	$C_n = K_{trans}/K_p$			
		$C_1$	$C_2$	$C_3$	$C_4$
	90	0.15	0.1	0.10	0.10
	50	0.22	0.20	0.20	—
	90	0.23	0.23	0.22	—
	120	0.19	0.18	0.20	—
	150	0.23	0.19	0.19	—
	90	0.20	0.23	0.23	0.23
	150	0.23	0.23	0.23	0.23

The given values of  $C_n$  show that 1,3-dioxacyclanes are telogens of average activity [7]. As the values  $C_n < 1$ , the developing radicals react more easily with ethylene than with telogen.

With increase of the temperature from 50 to 150°C, the values  $C_n$  are practically unchanged, which testifies to the closeness of the value of the chain increase (2, 4) and continuation (5, 6) reaction activation energies. The values of  $C_n$  do not depend on the developing radical ( $T_n$ ) chain length ( $n$ ) either; that is, the first radical

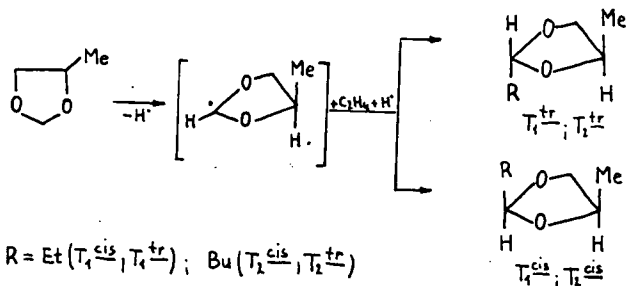
no longer feels the influence of the polar effect from the 1,3-dioxacyclane substituent.

In the radical telomerization of ethylene by 2,4-dimethyl-1,3-dioxane, the parallel formation of stereoisomeric 2,4-dimethyl-2-alkyl-1,3-dioxanes has been found [16]:



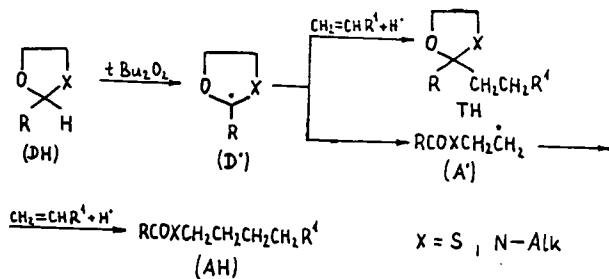
The formation of isomers with axial-equatorial arrangement of the methyl groups ( $T_1^{trans}/T_1^{cis} = T_2^{trans}/T_2^{cis} = 3$ ) is preferred, which is explained by the screening effect of the H<sup>4</sup> and H<sup>6</sup>-axial hydrogen atoms.

The radical telomerization of ethylene by 4-methyl-1,3-dioxolane also leads to the formation of stereoisomeric 4-methyl-2-alkyl-1,3-dioxolanes. Mainly isomers with the *trans*-arrangement of the alkyl substituents are formed  $T_1^{trans}/T_1^{cis} = T_2^{trans}/T_2^{cis} = 5:4$  [17].



The effect observed is explained by steric hindrance which coincides with that of the 4-CH<sub>3</sub>-group on D-radical addition to ethylene.

In the interaction of 1,3-diheterocyclanes with terminal olefins, 2-alkyl-1,3-diheterocycloalkanes and the corresponding linear products (thioethers or N,N-dialkylamides) are formed.



This essentially influences the composition of the products of a heteroatomic nature [18, 19]. Thus, in comparison with oxygen, the sulphur atom leads to the formation of adducts with cyclic structure [19], while the N-adducts have a linear structure (Table IV).

Table IV

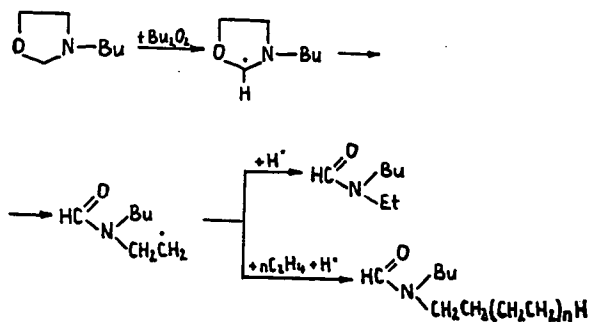
Composition of products of homolytic addition of  
1,3-diheterocycloalkanes to 1-hexene [19]

$t = 150^\circ\text{C}$ ,  $[\text{tBu}_2\text{O}_2] = 0.2 \text{ mol/l}$   $[\text{1-hexene}] = 0.5 \text{ mol/l}$

Substrate	Addition products	Yield	Ratio of yields of products with linear and cyclic structures
	 Me MeCOOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Bu	3 86	30
	 Et EtC(O)N(C <sub>3</sub> H <sub>7</sub> )C <sub>6</sub> H <sub>13</sub>	8 89	11
	 Me MeCOSCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>13</sub>	65 9	0.14

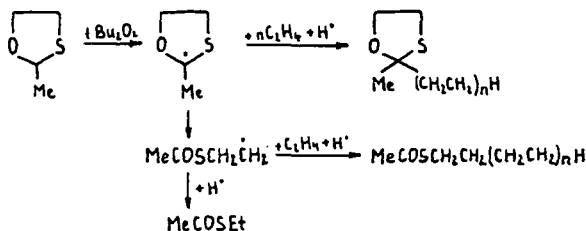
In [20], studying the homolytic addition of 1-hexene to 3-propyl-1,3-oxazolidine, it has been shown that high pressure leads to cyclic adduct formation; this is connected with the rate decrease of the monomolecular rearrangement of 1,3-oxazo-2-cyclopentyl radicals.

As a result of radical ethylene telomerization, N-butyl-1,3-oxazolidine telomers of the N-butyl-alkyl-formamide series have been discovered [21].



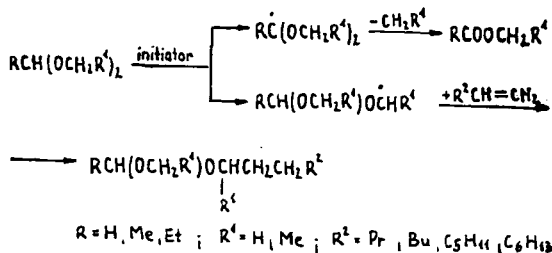


In contrast, radical 2-methyl-1,3-oxathiolane ethylene telomerization results in parallel alkyl acetate and 2-methyl-2-alkyl-1,3-oxathiolane formation; the selectivity of formation of the latter is 3—5 times as high as that of alkyl thioacetates [22], which indicates higher rate of addition of intermediate radicals than rearrangement.



## II. Homolytic addition of linear acetals

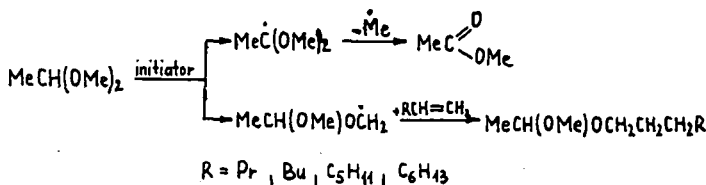
In homolytic addition reactions to carbon-carbon double bonds, the linear 1,1-dialkoxyalkane acetals behave differently from their cyclic analogues. While radical addition of cyclic acetals proceeds mainly at heterocycle positions, 1,1-dialkoxyalkanes in the presence of peroxide initiators give addition products at the  $\alpha$  carbon-atom of the alkoxy group [23].



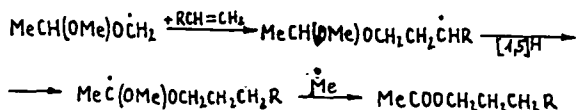
Simultaneous mono- and dialkoxy radical formation from 1,1-dialkoxyalkanes has been proved by EPR [24].

The absence of homolytic addition products of 1,1-dialkoxyalkyl radicals testifies to the fact that their molecular splitting into alkyl radical and ester proceeds rather quicker than their addition to the olefinic double bond.

In the interaction of 1,1-dimethoxyethane with  $\alpha$ -olefins, methyl acetate and 1-methoxy-1-alkoxyethanes are formed in an ordinary scheme.



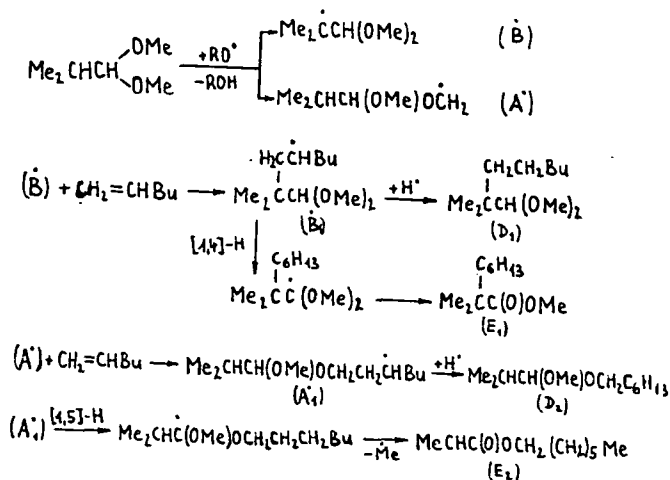
Considerable amounts of alkyl acetates accumulate in the reaction mixture, the formation of which is connected with intermediate radicals rearranging with 1,5-hydrogen atom migration.



Such type of rearrangement has frequently been observed in homolytic processes [25—27].

Data analysis of 1,1-dimethoxyethane addition to various olefins ( $\text{R}-\text{CH}=\text{CH}_2$ ) makes it possible to determine the influence of the size of the alkyl substituent group on the carbon atom which carries the lone electron on the degree of rearrangement of the radical containing alkoxy fragments [23]. The ratio [acetate]/[acetal] characterizing the extent of rearrangement of the radical  $\text{CH}_3\text{CH}(\text{OCH}_3)\text{OCH}_2\text{CH}_2\dot{\text{C}}\text{HR}$  with 1,5-H-migration decreases with the increase in molecular mass of the compound (Table V) and for 1-octane is equal to 0.3, *i.e.* 5 times less, than for 1-pentene and 1-hexene. This shows that in  $\text{CH}_3\text{CH}(\text{OCH}_3)\text{OCH}_2\text{CH}_2\dot{\text{C}}\text{HR}$  radicals the size of the substituent at the paramagnetic centre determines the rate of rearrangement. It is apparent that short substituents ( $\text{R}=\text{C}_3\text{H}_7, \text{C}_4\text{H}_9$ ) in the transition state do not hamper the rupture of acetal hydrogen in the 1,1-dimethoxyethane molecule. The increase in size of R results in a decrease of the reaction products (Table V). It has been established that the degree of radical rearrangement with 1,5-H-migration is practically unchanged as the process temperature decreases [23].

The radical addition of 1,1-dimethoxy-2-methylpropane to 1-hexene leads to linear acetals ( $D_1, D_2$ ) and esters ( $E_1, E_2$ ) [23].



The formation of esters is probably connected with rearrangement of radicals  $\dot{\text{A}}_1$  and  $\dot{\text{B}}_1$  with 1,5- and 1,4-H-migration, respectively. The decrease in the selectivity

Table V

 Radical addition of 1,1-dimethoxyethane to  $\alpha$ -olefins

 T = 150 °C, [tBu<sub>2</sub>O<sub>2</sub>] = 0.3 % mol, time = 1.5 h

Olefin CH <sub>2</sub> =CH-R R	Charge, mmol		Conversion, %		Yield*, mol % [MeCH(OMe) OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> R + MeC(O)OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> R]
	RCH=CH <sub>2</sub>	MeCH(OMe) <sub>2</sub>	RCH=CH <sub>2</sub>	MeCH(OMe) <sub>2</sub>	
Pr	9.0	74.4	25	10	22 $\left(\frac{62}{38}\right)^{**}$
	9.0	70.0	23	11	24 $\left(\frac{66}{44}\right)$
Bu	8.9	73.3	24	12	19 $\left(\frac{61}{39}\right)$
	9.9	67.5	28	15	20 $\left(\frac{59}{41}\right)$
C <sub>5</sub> H <sub>11</sub>	9.4	63.9	38	21	11 $\left(\frac{42}{58}\right)$
	12.8	64.9	31	25	10 $\left(\frac{45}{55}\right)$
C <sub>6</sub> H <sub>13</sub>	8.9	65.2	61	23	7 $\left(\frac{26}{74}\right)$
	12.0	65.2	53	21	7 $\left(\frac{25}{75}\right)$

\* Mol. on reacted olefin

\*\* In brackets is the ratio [acetate]/[acetal] for the same R substituent

 of formation of ester E<sub>1</sub> with the decrease of the reaction temperature from 150 to 60 °C is caused by an abrupt decrease in the degree of 1,4-hydrogen migration.

Ethylene telomerization products by linear formals are alkyl formates and compounds of the asymmetric series of 1,1-dialkoxymethanes [28, 29].

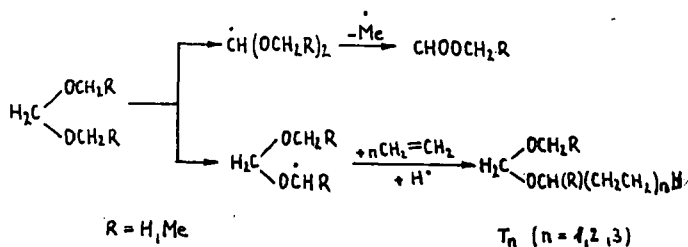




Table VI  
Ethylene telomerization by dimethoxymethane  
 $T=150^{\circ}\text{C}$ ,  $[t\text{Bu}_2\text{O}_2]=0.2\text{ mol}\%$ , time = 30 min.

S initial* mmol	M initial* mmol	$K_m^*$ mol, %	$\left(\frac{M}{S}\right)_{\text{av.}}$	Content of telomer homologues with monomeric units, mol %				$C_1$	$C_2$	$C_3$	Yield, weight** %	
				$T_1$	$T_2$	$T_3$	$T_{n>3}$				$\sum_{n=1}^{\infty} T_n$	$\Sigma Y_m$
61.0	10.4	40	0.13	44.2	28.7	12.6	14.5	0.11	0.14	0.11	27.6	72.4
66.2	18.2	41	0.22	37.4	23.5	12.5	26.6	0.13	0.13	0.11	44.5	55.5
66.4	23.6	25	0.31	46.2	24.4	12.4	27.0	0.17	0.19	0.14	42.5	57.5
49.4	25.5	22	0.46	20.1	20.0	13.9	46.0	0.11	0.15	0.14	51.2	48.8
53.0	30.4	21	0.52	17.5	16.1	12.4	54.0	0.11	0.12	0.12	51.4	48.6

Average arithmetical values of constants:  $C_{\text{av.}}$

Average arithmetical error

0.11      0.14      0.12

$\pm 0.02$      $\pm 0.02$      $\pm 0.01$

\*  $M_{\text{init.}}$ ,  $S_{\text{init.}}$  = initial amounts of monomer and telogen;  $K_m$  = monomer conversion.

\*\* yield of  $T_n$  telomers and  $Y_m$  hydrocarbons for the sum of identified products till  $T_3$ .

However (in contrast to ethylene), non-rearranged asymmetric acetal  $T_3$  is not formed, which testifies to the full rearrangement of the developing radical  $\dot{T}_3$  with 1,9-H-migration. This is explained by a favourable combination of polar factors: the nucleophilic radical formed in the transition state attacks the electrophilic part of the radical, including the mobile hydrogen atom.

In the reaction of isobutylene with 1,1-dimethoxyethane, products containing two or more isobutylene members are not found. This is explained [23] by a combination of unfavourable steric factors in the growth stage. At the same time, for radical reactions with isobutylene, allyl chain rupture and cross-recombination of the radicals produced are characteristic, which has an essential influence on the character of the reaction products.

### References

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### ГОМОЛИТИЧЕСКОЕ ПРИСОЕДИНЕНИЕ АЦЕТАЛЕЙ К ДВОЙНОЙ СВЯЗИ УГЛЕРОД-УГЛЕРОД

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Органические радикалы со свободным электроном на углеродном или кислородном атоме селективно атакуют метильные или метинные группы, присоединенных к двум гетероатомам в циклических и линейных ацеталей, что приводит к образованию соответствующих диалкоксалкильных радикалов. Последние обладают высокой реакционной способностью и принимают участие в различных превращениях. В обзоре рассмотрены результаты работ, относящихся к реакциям присоединения подобных радикалов к различным ненасыщенным соединениям.