ADDITION OF THIOLS TO DIVINYL ETHERS OF GLYCOLS

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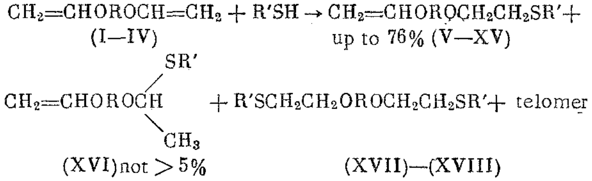
The addition of various reagents to divinyl ethers of glycols (DEG) selectively at one of the vinyloxy groups may become a new, rather general method of synthesis of functionally substituted alkoxyethylenes. However, the selection of the conditions of addition is limited: nucleophiles do not react with vinyl ethers, while electrophilic agents, on the contrary, are too active to carry out a selective process. There are no data in the literature on the addition of various reagents to DEG, with the conservation of one of the vinyloxy groups.* The reactions of DEG with hydrogen sulfide [7] and silicon hydrides [8, 9] did not lead to the production of monoadducts.

In our opinion, this problem can be solved only on the basis of homolytic reactions. We began a verification of this assumption with a study of the radical reaction of DEG with thiols. Previous studies [10-13] on the thiylation of α,β-unsaturated ethers served as a starting point and basis for these investigations. At a mole ratio thiol : DEG equal to 1 : 3, double addition and telomerization were suppressed to a substantial degree, and the yield of monoadducts (Table 1) exceeded 70%.



$$\underset{(I—IV)}{CH_2{=}CHOROCH{=}CH_2} + R'SH \rightarrow \underset{\text{up to 76\% (V—XV)}}{CH_2{=}CHOROCH_2CH_2SR'} +$$

$$\underset{\text{(XVI) not} > 5\%}{CH_2{=}CHOROCH(SR')CH_3} + \underset{(XVII)—(XVIII)}{R'SCH_2CH_2OROCH_2CH_2SR'} + \text{telomer}$$

$R = (CH_2)_2$ (I), $(CH_2)_3$ (II), $(CH_2)_4$ (III), $(CH_2)_2O(CH_2)_2$ (IV)
$R = (CH_2)_2$, $R' = C_2H_5$ (V), n-C_3H_7 (VI), n-C_4H_9 (VII),
t-C_4H_9 (VIII), n-C_5H_{11} (IX), C_6H_5 (X);
$R = (CH_2)_3$, $R' = n$-C_3H_7 (XI): $R = (CH_2)_4$, $R' = n$-C_3H_7 (XII)
$R = (CH_2)_2O(CH_2)_2$, $R' = C_2H_5$ (XIII) n-C_3H_7 (XIV),
n-C_4H_9 (XV), (XVI) : $R = (CH_2)_2O(CH_2)_2$, $R' = n$-C_3H_7
(XVII) : $R = (CH_2)_2$, $R' = n$-C_3H_7 и (XVIII) : $R = (CH_2)_2O(CH_2)_2$,
$R' = n$-C_3H_7

Thiylation occurs in the presence of azoisobutyrodinitrile (AIBN) or under the influence of irradiation by ultraviolet (UV), as well as under conditions of thermal initiation (see Table 1). The maximum yield (76%) of 1 : 1 adducts was obtained in the case of noncatalytic addition. The use of UV irradiation substantially reduces the time of the reaction (from 25 or 12 h to 3 h or less), while maintaining satisfactory yield (40-60%) of the monoadduct. The use of AIBN as a catalyst increases the yield of oligomers, while in the case of the ethers (III) and (IV) it leads to the formation of transparent colorless insoluble (benzene, ether, CCl_4) elastomers containing sulfur (up to 9%, for example, experiment 17, see Table 1). The ethers (I)-(IV) themselves, in contrast to vinyl alkyl ethers [14, 15], polymerize well in the presence of the indicated initiator, forming transparent colorless homopolymers of various consistencies (from jelly-like to solid, vitreous), depending upon the time of polymerization (70-80°, 2-12 h). In the presence of benzoyl peroxide (BP) (1% of the weight of themixture), there is a complete inhibition of the process (experiment 3).

To determine the relative reactivity of DEG in the thiylation reaction, we conducted a series of experiments with n-propyl mercaptan under comparable conditions (Table 2). As is shown by the value of the

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*Simple divinyl ether, which participates in several such reactions [1-6], differs substantially from DEG.

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TABLE 1. Conditions of Thiylation of DEG

Experiment No.	DEG	R' in R'SH	Conditions of experiment			Ratio ether /thiol	Yield† of 1:1 adduct, %	Total yield of bis-adduct and oligomers
			initiation	temperature, °C	time, h			
1	I	C_2H_5	Without initiator	40-45	10	2:1	50	35
2	I	C_3H_7	The same	40-55	6	1:1	45	37‡
3	I	C_4H_9	BP	60-65	6	2:1	Reaction did not take place	
4	I	C_4H_9	AIBN*	60-65	8	3:1	53	41
5	I	C_4H_9	UV	Room temperature	6	3:1	44	44
6	I	C_4H_9	The same	The same	3	2:1	72	27
7	I	C_5H_{11}	Without initiator	60-70	25	2:1	76	21
8	I	C_5H_{11}	AIBN*	60-70	25	2:1	44	46
9	I	C_6H_5	UV	Room temperature	2	3:1	55	33
10	I	C_6H_5	Without initiator	60-65	25	3:1	57	29
11	I	t-C_4H_9	UV	Room temperature	3	2:1	29	64
12	II	C_3H_7	The same	The same	3	2:1	43	46
13	III	C_3H_7	" "	" "	3	2:1	47	45
14	IV	C_2H_5	Without initiator	40-50	13	2:1	64	22
15	IV	C_3H_7	The same	60-65	12	3:1	64	36
16	IV	C_3H_7	" "	50-60	12	1.5:1	42	27**
17	IV	C_3H_7	AIBN*	69-65	12	3:1	–	92
18	IV	C_4H_9	Without initiator	60-65	12	3:1	73	17
19	IV	C_4H_9	AIBN*	60-65	12	3:1		98

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* In each case 0.2% of the weight of DEG was taken.

† On the basis of reacted DEG.

‡ Yield of the bis-adduct 31%.

** Yield of the bis-adduct 13%.

TABLE 2. Relative Reactivity of DEG in the Thiylation Reaction*

DEG	Yield† of 1:1 adduct, %	Total yield of bis-adduct and oligomers, %	Conversion of ether, %	DEG	Yield† of 1:1 adduct, %	Total yield of bis-adduct and oligomers, %	Conversion of ether, %
I	55	38	56	III	47	45	57
II	43	46	64	IV	63	28	50

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* Thiol – n-C_3H_7SH, UV irradiation, room temperature, 3 h, ratio, M, DEG: n-C_3H_7SH = 2:1.

† On the basis of reacted DEG.

conversion, there is some tendency for increasing reactivity in the series: (IV) < (I) = (III) < (II); however, the yield of the 1 : 1 adduct varies in the opposite order. As we go from systems with a β-arrangement of the oxygen atoms (I) and (IV) to γ- and δ-systems (II) and (III), respectively, the selectivity of the process drops sharply. Actually, if we arbitrarily take the ratio of the yield of the monoadduct to the summary yield of the bis-adduct and oligomers as the characteristic of selectivity, we can easily see that the selectivity of the reaction in the case of divinyl ethers of 1,3-propane- and 1,4-butanediols (II) and (III) is approximately the same (0.9 and 1.0), whereas for divinyl ethers of ethylene glycol and diethylene glycol (I) and (IV) it is substantially higher (1.5 and 2.2, respectively). Such a "β-effect" is difficult to explain. If we consider that it is entirely due to differences in the inductive influence on the reaction center, the substantial difference in the selectivity between ethers (I) and (IV), in which the inductive influence on the vinyloxy group should be approximately the same, remains incomprehensible. At the same time, the observed differences in the selectivity definitely reflect the change in the degree of stabilization of the intermediate radical

$$[R'SCH_2\dot{C}H{-}OR'' \leftrightarrow R'SCH_2CH{=}\dot{O}R'']$$
$$(XIX)$$

From this standpoint, as the experiment indicates, systems with a β-arrangement of the oxygen atoms (I),

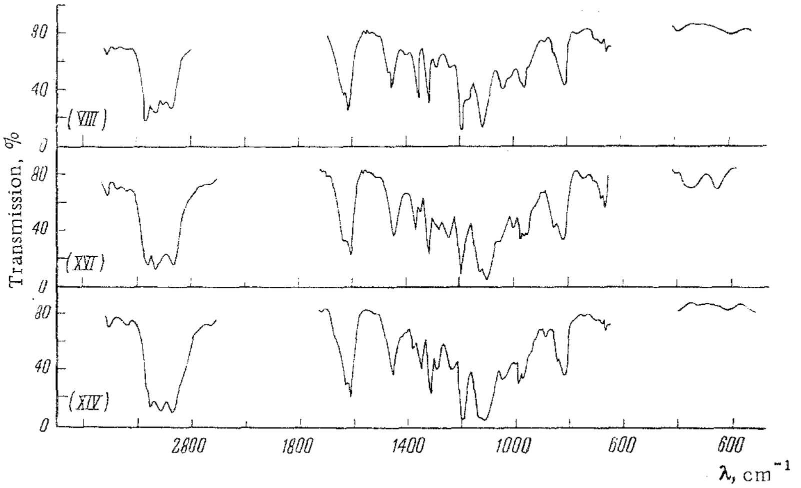
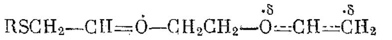


Fig. 1. IR spectra: (VIII) $\mathrm{t\text{-}C_4H_9SCH_2CH_2OCH_2CH_2OCH{=}CH_2}$; (XVI) $\mathrm{CH_3-\underset{\displaystyle SC_3H_7}{\underset{|}{C}}HOCH_2CH_2OCH_2CH_2OCH{=}CH_2}$; (XIV) $\mathrm{n\text{-}C_3H_7SCH_2CH_2OCH_2CH_2{-}}$ $\mathrm{OCH_2CH_2OCH{=}CH_2}$.

(IV), in comparison with the ethers (II) and (III), possess increased possibilities for supplementary stabilization of the intermediate (XIX). The possibility remains that this may occur by partial transfer of an electron to the oxygen atom in the β-position and ultimately to the second multiple bond



$$\mathrm{RSCH_2{-}CH{=}\dot{O}{-}CH_2CH_2{-}\overset{\cdot\delta}{O}{\overset{...}{=}}CH{\overset{...}{=}}\overset{\cdot\delta}{C}H_2}$$

Such an effect of transfer of an electron along the chain of σ-bonds in vicinal systems was first detected in an investigation of the EPR spectra of certain aromatic anion radicals [16, 17]. The increased ability of systems with β-alternation of oxygen atoms to transmit the influence of the substituent has already been noted in kinetic investigations as well [18, 19]. In the series of DEG, the divinyl ether of diethylene glycol should give the most stable radical with reduced ability to initiate polymerization, which is in good agreement with the experimental data. The isomeric purity of the sulfides formed was established by PMR and IR spectroscopy, thin-layer chromatography, and chemical functional analysis. In the PMR spectrum of the sulfide (XIV), in full agreement with the structure assumed for it, there is no doublet from the CH_3 group, nor the quartet of the methine proton of the fragment $-O-CH(CH_3)-S-$, but the signals of the protons of the $-CH_2-O$ groups were detected. In a comparison of the IR spectra (Fig. 1) of the sulfides: $\mathrm{C_3H_7SCH_2CH_2OR'}$ (XIV), $\mathrm{C_3H_7S-\underset{\displaystyle CH_3}{\underset{|}{C}}H-OR'}$* (XVI) and $\mathrm{t\text{-}C_4H_9SCH_2CH_2OR}$ (VIII), $\mathrm{R{=}CH_2CH_2OCH{=}CH_2}$, $\mathrm{R'{=}(CH_2)_2O(CH_2)_2OCH{=}CH_2}$, a difference in their structure is distinctly noticeable. In the spectrum of compound (VIII), the three methyl groups are represented by an intense band at 1,360 cm^{-1}; in the case of (XVI) this band (1,374 cm^{-1}) is less intense (two methyl groups); in the spectrum of (XIV) there is only a weak absorption in this region (one methyl group). In addition, the spectrum of (XVI) contains a band at 630 and 670 cm^{-1} of substantial intensity, which is absent in the case of (VIII) and (XIV). The vinyloxy group is unambiguously identified in the spectra of all the monoadducts (V)-(XVI) with frequencies 815-820, 965-975, 1,200-1,205, 1,320, 1,615-1,620, 1,635-1,640, 3,040-3,050, 3,100-3,120 cm^{-1}. In chromatography in a thin layer of Al_2O_3 (Table 3), the presence of α-isomers in the adducts (VII), (XI), (XII), (XIV)-(XVI) was not detected. It was established preliminarily with the sulfides (XIV) and (XVI) as an example that the corresponding β- and α-isomers differ substantially in R_f values (0.26 and 0.46, respectively, benzene : chloroform, 5 : 1). An analysis of the isomeric composition of the sulfides (V)-(XV) with the aid of mercuric chloride [20] proved to be unfeasible, since the vinyloxy group partially reacted under the conditions used, liberating the acid. Therefore we used the method of hydrolytic oxime formation [21]. The analytical data (see Table 3) once again confirm the scheme of β-addition.

The α-isomers are inclined to disproportionation, as was discovered in the production of the thioacetal (XVI).

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*Specially synthesized under the conditions of catalysis by $SOCl_2$.

The ability of the monoadducts obtained to give polymers under the influence of cationic catalysts (BF_3 etherate, $SnCl_4$) was verified with compounds (VI) and (VII) as examples. Viscous polymeric liquids were obtained at room temperature.

EXPERIMENTAL

In the work we used freshly-redistilled, thoroughly purified reagents. Typical procedures are cited below.

Noncatalytic Addition. A mixture of 15.8 g (IV) and 3 g butanethiol was heated in an ampoule, purged with nitrogen for 12 h at 60-65°. After removal of the unreacted substances (11 g), we obtained 5.5 g (73%) of the adduct (XV) (Table 4). In addition, we isolated 1.2 g of nonredistilling oligomer.

Addition Initiated by UV Irradiation. A mixture of 6.1 g (I) and 2.6 g butanethiol was irradiated in a quartz test tube (PRK-2) for 3 h at room temperature. After removal of the unreacted substances (3.7 g), we obtained 3.1 g (72%) of the adduct (VII) (see Table 4) and 1.3 g (27%) of the oligomer.

Addition in the Presence of AIBN. A mixture of 5.7 g (I), 2.6 g amyl mercaptan, and 0.011 g AIBN was heated in an ampoule, purged with nitrogen for 25 h at 60-70°. After removal of the unreacted substances (2.5 g) we obtained 2.7 g (44%) of the adduct (IX) (see Table 4) and 2.3 g (46%) of the oligomer.

Attempt at Addition in the Presence of BP. A mixture of 5 g (I), 2.1 g butanethiol, and 0.07 g BP was heated at 60-65° for 6 h with mixing. The reaction did not take place; the starting materials were recovered.

Synthesis of the Sulfide (XVI). To a mixture of 14.6 g (IV), 33.5 g benzene, hydroquinone (~ 0.3 g), and $SOCl_2$ (4-5 drops) we added 3.6 g propanethiol with mixing. The reaction mixture was heated for 6 h at 45-50°, after which it was treated with an aqueous solution of K_2CO_3. The organic layer was dried with K_2CO_3. The organic layer was dried with K_2CO_3 and redistilled. Yield 4.4 g (30%) of the adduct (XVI) (see Table 4).

TABLE 3

Ether	Thiol	Initiation	R_f	No. of fragments hydrolyzable with liberation of acetaldehyde
I	C_3H_7SH	Without initiator	—	1,04
I	C_4H_9SH	UV	0,46	0,96
I	C_6H_5SH	»	—	0,99
II	C_3H_7SH	»	0,44	0,96
III	C_3H_7SH	»	0,58	1,00
IV	C_3H_7SH	Without initiator	0,26	1,00
IV	C_4H_9SH	The same	0,34	1,01
IV	C_3H_7SH	$SOCl_2$	0,46	1,90

TABLE 4. Adducts of DEG with Thiols

Compound No.	Bp, °C (mm, Hg)	$n^{20}D$	d_4^{20}	MR		Found, %			Calc., %		
				found	calc.	C	H	S	C	H	S
V	73(2)	1,4721	0,9893	49,90	50,25	54,84	9,10	17,96	54,50	9,14	18,18
VI	72—72,5(1)	1,4723	0,9728	54,809	54,902	56,71	9,24	16,76	56,80	9,53	16,84
VII	84,5—85(1)	1,4710	0,9631	59,30	59,55	58,95	9,70	15,75	58,78	9,86	15,69
VIII	88—88,5(1,5—2)	1,4686	0,9559	59,49	59,55	58,79	9,76	15,48	58,78	9,86	15,69
IX	101—101,5(1)	1,4705	0,9543	63,899	64,198	60,02	10,35	14,84	60,50	10,55	14,68
X	121—122(1)	1,5460	1,0825	65,62	65,09	64,30	7,17	14,10	64,25	7,18	14,29
XI	88—90(1)	1,4693	0,9571	59,49	59,55	58,73	10,00	15,28	58,78	9,86	15,69
XII	109—109,5(1,5)	1,4699	0,9541	63,84	64,19	60,76	10,12	14,43	60,50	10,15	14,68
XIII	99(1)	1,4730	1,0118	61,09	61,33	54,58	9,17	14,47	54,50	9,14	14,54
XIV	110(1)	1,4723	1,0018	65,54	65,98	56,42	9,50	13,84	56,37	9,46	13,68
XV	126,5(1,5)	1,4711	0,9893	70,19	70,63	57,97	9,88	13,04	58,02	9,74	12,91
XVI	113—115(1,5)	1,4700	0,9943	65,76	65,98	56,35	9,56	13,66	56,37	9,46	13,68
XVII	135,5—137(1,5)	1,4876	0,9939	76,97	77,25						
XVIII	170—172(1,5)	1,4851	1,0186	87,39	88,33						

Methods of Investigation. The PMR spectra were obtained on a JEOLC-60 spectrometer with a working frequency of 60 MHz, solvent CCl_4, internal standard $Si(CH_3)_4$. The IR spectra were taken on a UR-10 spectrophotometer in a microlayer. Chromatography of the mono-adducts (VII), (XI), (XII), (XIV)-(XVI) was conducted on Al_2O_3 (activity II). The solvent systems used were mixtures of benzene-chloroform, 5:1; benzene; benzene:ether, 5:1; 10:1; cyclohexane:benzene, 1:1. The chromatograms were developed with iodine. Analysis for the content of fragments hydrolyzable with liberation of acetaldehyde was carried out as follows: 0.1575 g (XIV) and 25 ml 0.5 N $NH_2OH \cdot HCl$ (acidified with HCl) was heated at 50-70° for 2-5 h with mixing. After which, the acid liberated was titrated with 0.5 N NaOH in the presence of bromophenol blue.

Polymerization. In the ampoule we took 2.5 g (IV) and 0.005 g (0.2% of the weight of the ether) AIBN. After 12 h of heating at 60-65° we obtained a transparent vitreous brittle polymer, insoluble in benzene, ether, and CCl_4.

When a drop of an ether solution of $BF_3(C_2H_5)_2O$ was added to a small amount of the monomers (VI) and (VII), the mixture heated up, forming a liquid polymer.

CONCLUSIONS

1. The conditions of homolytic addition of thiols to divinyl ethers of glycols, permitting the production of monoadducts with yields of up to 76%, were found.

2. Increased selectivity of the reaction was noted in the case of divinyl ethers of ethylene glycol and diethylene glycol.

3. On the basis of the experimental data, the possibility of supplementary stabilization of the intermediate radical on account of partial transfer of an electron along the chain with β-alternation of oxygen atoms was hypothesized.

4. The ability of the monoadducts obtained to polymerize according to a cationic mechanism was demonstrated.

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