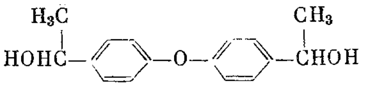
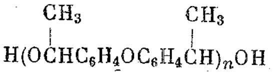
4. P. S. Starcher and B. Phillips, J. Am. Chem. Soc., 80, 4079 (1958).
5. A. I. Kirillov, Zh. Org. Khim., 3, 325 (1967).
6. M. Weygand and G. Hilgetag, Preparative Organic Chemistry, Wiley, New York (1972).

ACID-CATALYZED REACTIONS OF A DISECONDARY AROMATIC DIOL WITH ALKANOLS

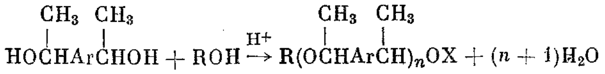
B. A. Zaitsev and L. L. Dantsig

UDC 542.97:547.568.5:547.26

Disecondary aromatic diols such as bis[4-(1-hydroxyethyl)phenyl ether  (I), undergo several successive and parallel reactions in the presence of acids, ending with the formation of aromatic monomeric and oligomeric compounds [1, 2]. In the presence of carboxylic acids (condensation telogens), esters are formed in addition to divinylaromatic compounds [3, 4].

Here we report a study of the p-toluenesulfonic acid-catalyzed reactions of the diol (I) with alkanols. On heating the diol (I) in nonpolar aromatic solvents with small amounts (10^{-2}-10^{-3} mole/liter) of p-toluenesulfonic acid, oligomeric ethers  $\mathrm{H(O\overset{CH_3}{\overset{|}{C}}HC_6H_4OC_6H_4\overset{CH_3}{\overset{|}{C}}H)_nOH}$ with a mean molecular mass M_n = 600-3400 are first formed rapidly with the elimination of water which is removed by azeotropic distillation [2, 5]. When the diol (I) and carboxylic acids are condensed simultaneously under the same conditions, oligomeric ethers with terminal ester groups (III) are formed with M_n = 1000-1300 [3, 4].

It would therefore be expected that systems containing (I), an alkanol, aromatic solvent, and p-toluenesulfonic acid would on reaction initially afford oligomeric ethers with terminal alkoxy-groups

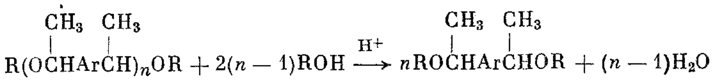


$$\mathrm{HO\overset{CH_3}{\overset{|}{C}}HAr\overset{CH_3}{\overset{|}{C}}HOH + ROH \xrightarrow{H^+} R(O\overset{CH_3}{\overset{|}{C}}HAr\overset{CH_3}{\overset{|}{C}}H)_nOX + (n+1)H_2O}$$

(IV)

in which Ar is $C_6H_4OC_6H_4$, R is alkyl, and X is alkyl or H. Table 1 shows that as telomerization proceeds, the number of OH groups in the reaction mixture decreases while those of alkoxy-groups increase. The negligible unsaturation of the products at this stage and on subsequent alcoholysis of the condensed telomer (IV) indicate the small contribution of degradative side-reactions, which are discussed below.

On heating the telomer (III) formed in the system diol(I)—carboxylic acid, acidolysis and esterificationof the carboxylic acid with the hydroxylated acidolysis products takes place [3, 4]. Under the same conditions, on heating with an excess of the alkanol the telomer (IV) undergoes alcoholysis. Complete alcoholysis of the telomers, followed by condensation of (V) is described by the equation



$$\mathrm{R(O\overset{CH_3}{\overset{|}{C}}HAr\overset{CH_3}{\overset{|}{C}}H)_nOR + 2(n-1)ROH \xrightarrow{H^+} nRO\overset{CH_3}{\overset{|}{C}}HAr\overset{CH_3}{\overset{|}{C}}HOR + (n-1)H_2O}$$

(VI)

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 88-94, January, 1986. Original article submitted July 17, 1984.

TABLE 1. Reactions of Bis[4-(1-hydroxyethyl)phenyl] Ether with Alkanols

Expt. No., (sample)	Conditions for synthesis of monomer-oligomer mixture				Properties of monomer-oligomer mixture					
	alkanol	molar ratio diol (I) : alkanol	p-toluenesulfonic acid, $C_{cat}\cdot10^3$, mole/liter	time, min	amount, %				unsaturation, moles C=C bonds/100 g of product	n_D^{20}
					OH groups	alkoxy-groups	C	H		
1^a (1)	EtOH	1 : 2	1,387	3	–	3,6	–	–	0,02	1,576
(4)	"	1 : 2	1,387	13	–	7,8	–	–	–	1,571
(7)	»	1 : 2	1,387	38	–	12,1	–	–	0,04	–
(15)	»	1 : 2	1,387	355	–	11,0	81,05	7,33	0,57	1,580
(16)	»	1 : 2	1,387	415	0,5	7,4	83,00	6,93	0,73	1,593
2^b (1)	»	1 : 2	6,900	120	–	7,4	80,21	7,40	–	1,577
(2)	»	1 : 2	6,900	180	–	3,4	82,47	7,00	–	1,592
(3)	»	1 : 2	6,900	300	–	2,3	84,25	6,72	0,65	1,617
3^c (1)	»	1 : 2	1,370	5	7,9	4,4	–	–	0,02	1,580
(4)	»	1 : 2	1,370	21	3,7	7,8	–	–	0,03	1,574
(7)	»	1 : 2	1,370	50	2,4	10,6	–	–	0,05	1,569
(11)	»	1 : 2	1,370	110	1,2	14,3	–	–	0,08	1,560
4^d	*t*-BuOH	1 : 2	1,366	6	8,7	0,6	–	–	–	1,585
	"	1 : 2	1,366	28	3,6	1,3	–	–	–	1,588
5^e	»	1 : 2,33	6,835	5	3,5	1,6	–	–	0,04	1,582
	»	1 : 2,33	6,835	60	–	3,5	–	–	0,39	$1,586^{45}$
	»	1 : 2,33	6,835	90	–	2,8	–	–	0,56	$1,587^{60}$
6^f	»	1 : 0,4	13,470	85	–	–	85,65	6,40	–	1,644

Notes. Initial concentration of diol (I), mole/liter: a) 0.2043, b) 0.2039, c) 0.2026, d) 0.2011, e) 0.2011, f) 0.3967.

TABLE 2. Catalytic Cleavage of Bis[4-(1-alkoxyethyl)phenyl] Ethers in an Aromatic Solvent

R in $(\mathrm{RO\overset{CH_3}{\overset{\vert}{C}}HC_6H_4})_2\mathrm{O}$ (VI)	Initial concentration, mole/liter		Temperature, °C	Time, h	Content, %		Unsaturation, moles $>C=C<$ bond/100 g product
	ether (VI)	p-toluenesulfonic acid, $C_{cat}\cdot10^3$			alkoxy groups	carbon	
Et – (VIa)	$0,4505^a$	17,4	98	0,0	28,8	76,48	0,00
	0,4505	17,4	98	0,5	20,5	78,70	0,24
	0,4505	17,4	98	1,0	18,5	79,88	0,32
	0,4505	17,4	96	1,5	17,4	80,10	0,36
	0,4505	17,4	96	2,0	14,6	81,40	–
i-Pr (Vb)	$0,4052^a$	15,7	98	0,0	34,5	77,21	0,00
	0,4052	15,7	96	0,5	18,7	80,96	0,39
	0,4052	15,7	94	1,18	11,4	82,18	0,49
	0,4052	15,7	93	1,70	10,1	82,55	0,52
	0,4052	15,7	93	2,00	9,7	82,67	0,54
The same	$0,4052^b$	15,7	82,5	0,5	32,2	77,28	0,00
	0,4052	15,7	82,5	1,16	30,1	78,52	0,00
	0,4052	15,7	82,5	2,00	29,0	79,29	0,04
	$0,4058^c$	16,2	80	0,50	28,8	78,77	–
	0,4058	16,2	80	1,00	26,0	79,20	0,10
	0,4058	16,2	80	1,50	23,2	79,52	0,18
	0,4058	16,2	80	2,00	22,3	79,69	0,24

---

a) Synthesis carried out in toluene.
b) Synthesis carried out with the addition of propan-2-ol (molar ratio (VIb):propan-2-ol = 1:20.
c) Synthesis carried out in benzene.

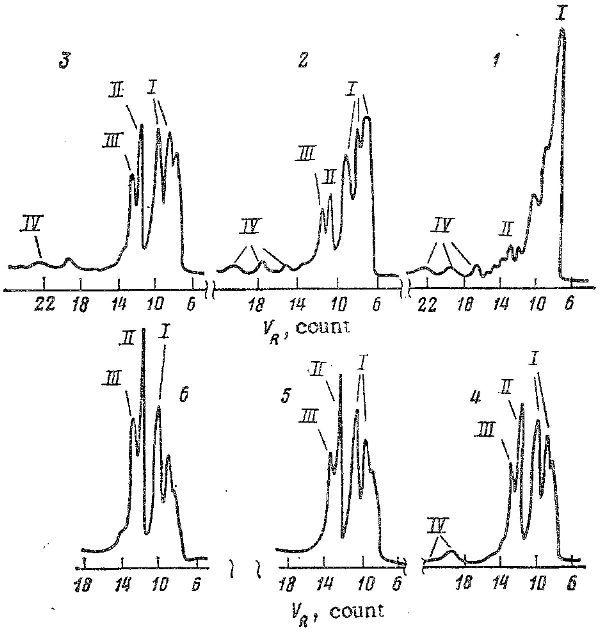
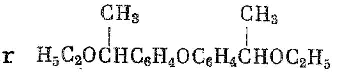


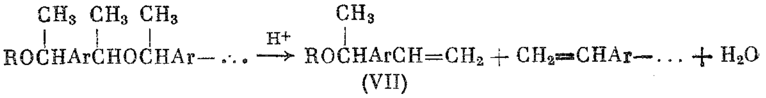
Fig. 1. Gel chromatograms of the products of the alcoholysis (or decomposition) of the oligomeric ether (II) (C_0 48.1 g/liter) with ethanol (COC_2H_5OH 1.856 mole/liter) in the presence of p-toluenesulfonic acid (C_{cat} $6.31 \cdot 10^{-3}$ mole/liter) at 95-110°C for (min): 1) 40, 2) 80, 3) 121, 4) 140, 5) 161, 6) 194; peaks: (I) oligomeric and dimeric alcoholysis products of the ether (II); (II) ether (VIa); (III) ether (VIIa); (IV) hydroxylated alcoholysis products of (V).

The alcoholysis step was also studied using the model system ether (II) [5]—ethanol. It will be seen from Fig. 1 that the chromatographic peak for (I), corresponding to the comparatively high molecular weight oligomer (II), on alcoholysis is split into several peaks corresponding to lower molecular weight products (oligomeric and dimeric), together with the hydroxylated product (V) [Fig. 1, peak (IV)]. As alcoholysis proceeds, the amounts of dimers and the final alcoholysis product, bis[4-(1-hydroxyethyl)phenyl] ether  $H_5C_2OCH(CH_3)C_6H_4OC_6H_4CH(CH_3)OC_2H_5$ (VIa), increase in the products at this stage (Fig. 1, chromatograms 4-6).

It is noteworthy that during the acidolysis of the telomers (III) only traces of hydroxylated compounds are found, apparently owing to the rate of esterification of the diol (I) by the carboxylic acids under these conditions exceeding the rate of acidolysis. In contrast to acidolysis, in the alcoholysis of the oligomers (II) and telomers (IV), samples of the reaction mixture purified from catalyst and alkanol still contain substantial amounts of hydroxylated products, as shown by exclusion liquid chromatography (ELC) [Fig. 1, peaks (IV)], IR spectroscopy, and analysis for OH groups. This leads to the conclusion that the rates of alcoholysis of the telomers (IV) and the subsequent condensation of hydroxylated compounds are comparable.

When alcoholysis is complete, the number of alkoxy-groups in the reaction product reaches a maximum, and the OH group content falls almost to zero (Table 1).

It may be assumed that, by analogy with the reaction of the diol (I)—carboxylic acid system, subsequent reactions of the system diol (I)—alkanol would involve intramolecular dehydration (cleavage) of the oligomeric ethers



$$ROCH(CH_3)ArCH(CH_3)OCH(CH_3)Ar-\ldots \xrightarrow{H^+} \underset{(VII)}{ROCH(CH_3)ArCH=CH_2} + CH_2=CHAr-\ldots + H_2O$$

and cleavage of the final alcoholysis products and condensation of (VI) to alkene and alkanol, as follows:

$$\underset{(VI)}{ROCHArCHOR} \xrightarrow[-ROH]{H^+} \underset{(VII)}{ROCHArCH{=}CH_2} \xrightarrow[-ROH]{H^+} \underset{(VIII)}{CH_2{=}CHArCH{=}CH_2}$$

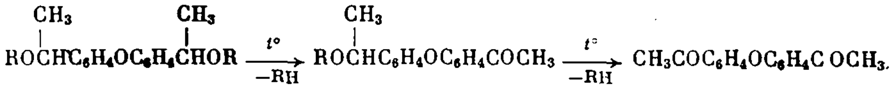
Accordingly, when the diol (I)—alkanol system is heated for prolonged periods, the unsaturation of the products increases (Table 1), the IR spectra of the products at this stage showing absorption for $CH_2{=}CHAr-$ at 1630 ($C{=}C$), 995 ($H_2C{=}$), and 910 ($H_2C{=}$) cm^{-1}, and according to ELC the concentrations of vinyl- and divinylaromatic compounds in the products increase (Table 1).

In order to provide further confirmation of the cleavage mechanism described above, a study was carried out of the catalytic reactions of the model compounds bis[4-(1-ethoxyethyl)-phenyl] ether (VIa, R = Et) [6] (Table 2) and bis[4-(1-isopropoxyethyl)phenyl] ether (VIb, R = $i\text{-}C_3H_7$). The formation of the alkanol by β-elimination was demonstrated by GLC and mass spectroscopy. Also observed in the reaction products (ELC, IR, and PMR spectroscopy) were 4-(1-alkoxyethyl)-4'-vinyldiphenyl ether $CH_2{=}CHC_6H_4OC_6H_4\overset{\overset{CH_3}{|}}{C}HOR$ (VIIa) and bis(4-vinylphenyl) ether (VIII).

As in the case of the analogous catalytic cleavage of esters of the diol (I) [7], semilogarithmic transformations of the kinetic plots for the cleavage of the dialkoxy-derivatives of the diol (I) remained linear only in the early stages of cleavage. As the reaction proceeded the plots increasingly diverged from linearity, and it may be assumed that the reduction in the rate of cleavage is due to the accumulation in the system of the alkanol, which modifies the activity of the p-toluenesulfonic acid and lowers the reaction temperature [in the cleavage of (VIa) and (VIb)]. The effect of the alkanol on the rate of reaction was studied in reactions carried out in toluene in the presence of an excess of propan-2-ol (a) and in benzene without the addition of propan-2-ol (b). It will be seen from Table 2 that although the reaction temperatures and concentrations of the ether (VIb) and catalyst were similar in both experiments, the rate of cleavage was higher in the absence of added alkanol.

The thermal elimination of the ethers (VI) was also examined. It was found that the mechanism of the cleavage of (VI) is dependent upon the pyrolysis temperature. Elimination at 200-250°C and a residual pressure of about 15 Pa proceeded as described above, but when this ether was heated at 320-350°C for 5 h there were obtained (as shown by IR and PMR spectroscopy) acetyl- and diacetylaromatic compounds. Mass spectrometry of the cleavage products showed the presence of the alkane (for example, ethane).

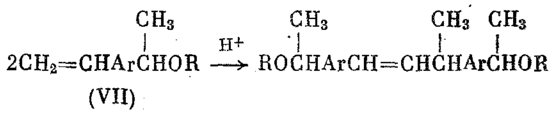
Hence, on heating the ether (VI) above 300°C, the β-elimination mechanism, involving cleavage of a hydrogen atom and an alkoxy group from adjacent carbon atoms, begins to encounter competition from another β-elimination mechanism involving cleavage of a hydrogen atom and an alkyl group from adjacent carbon and oxygen atoms, as follows:



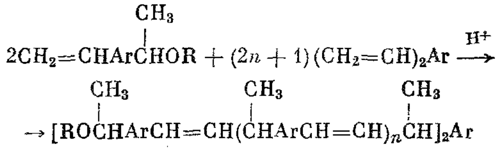
$$\underset{(VI)}{RO\overset{\overset{CH_3}{|}}{C}HC_6H_4OC_6H_4\overset{\overset{CH_3}{|}}{C}HOR} \xrightarrow[-RH]{t^\circ} \underset{(IX)}{RO\overset{\overset{CH_3}{|}}{C}HC_6H_4OC_6H_4COCH_3} \xrightarrow[-RH]{t^\circ} \underset{(X)}{CH_3COC_6H_4OC_6H_4COCH_3.}$$

Above 300°C, the acetylaromatic compounds (IX) and (X) undergo condensation to give dypnone-type compounds, 1,3,5-triphenylbenzoyl groups, and water [8, 9]. As pyrolysis of the ether (VI) proceeds at 350°C, therefore, the numbers of acetyl groups in the reaction products first increase to 5%, then fall slowly to 1%. It is noteworthy, for comparison, that in the pyrolysis of the diol (I) acetylaromatic compounds are also obtained as a result of dehydrogenation (2-4% of acetyl groups are present).

The concluding stage of the acid-catalyzed, relatively low-temperature reaction in the system diol (I)—alkanol in the one-step process involves cationic polyaddition of vinyl and divinylaromatic compounds [2, 4, 10], these being the cleavage products of the ethers (preceding step in the reaction). The mechanism of the polyaddition is styrene dimerization, resulting in the preferential formation of unsaturated dimers and oligomers (see scheme on following page). The extent of unsaturation of the products at this stage is high, and the refractive indices are extremely high (Table 1, expt. 2, sample 3, and expt. 6). The IR spectra of the products show absorption for the $-CH{=}CH-$(trans) grouping at 965 cm^{-1}, the intensity of which gradually increases as the oligomerization products are formed, the amounts of unsaturated, straight-chain oligomers in the reaction mixture, and its viscosity, increasing.



$$\underset{\text{(VII)}}{2CH_2{=}CHAr\overset{CH_3}{\overset{|}{C}}HOR} \xrightarrow{H^+} RO\overset{CH_3}{\overset{|}{C}}HArCH{=}CH\overset{CH_3}{\overset{|}{C}}HAr\overset{CH_3}{\overset{|}{C}}HOR$$



$$2CH_2{=}CHAr\overset{CH_3}{\overset{|}{C}}HOR + (2n+1)(CH_2{=}CH)_2Ar \xrightarrow{H^+}$$
$$\to [RO\overset{CH_3}{\overset{|}{C}}HArCH{=}CH(\overset{CH_3}{\overset{|}{C}}HArCH{=}CH)_n\overset{CH_3}{\overset{|}{C}}H]_2Ar$$

Hence, the acid-catalyzed reactions of the diol (I)—alkanol and diol (I)—carboxylic acid systems are analogous. Furthermore, both series of reactions result in the formation of the same divinylaromatic compounds and the products of their polyaddition by the formation of straight-chain unsaturated styrene dimers.

EXPERIMENTAL

The compositions and structures of the products were determined by functional group analysis (OH, OR, and $CH_2{=}CH$), and by IR and PMR spectroscopy. IR spectra were obtained in microlayers on a Specord 75-IR. Mass spectra of the cleavage products of the dialkoxy-derivatives of the diol (I) were obtained on an MX-1320 mass spectrometer in a pyrolysis cell (ampul) attached to the direct inlet into the mass spectrometer. Exclusion liquid chromatography was carried out on a ZhKh-1307 chromatograph [stainless steel column, ℓ 0.6 m, d 8 mm; sorbent Sephadex LH-20, eluent chloroform, elution rate 20 ml/h, efficiency 6500 theor. plates (for toluene), sample concentration 2.6 mass %, differential refractometer detector]. The unsaturation of the samples was determined by ozonolysis at 0°C in an ADS-3 apparatus, solvent CCl_4.

p-Toluenesulfonic acid (the catalyst) was used in the form of its monohydrate, pure grade ($p\text{-}CH_3C_6H_4SO_3H\cdot 1H_2O$ content 99.6%).

Bis[4-(1-hydroxyethyl)phenyl] ether [diol (I)] was obtained by the catalyzed hydration of bis(4-acetylphenyl) ether in the presence of Raney nickel [1], mp 87-89°C (from toluene), n_D^{20} 1.5839 (supercooled melt).

Oligomeric ether (II) was obtained as described previously [2, 5]. A mixture of 40.0 g of the diol (I), 700 ml of toluene, 0.40 g of hydroquinone, 0.40 g of CuCl, and 0.2000 g of p-toluenesulfonic acid was heated for 20 min at the boil, with azeotropic distillation of the water (2.3 ml). After cooling, the reaction mixture was filtered, and the filtrate washed successively with water, about 5% aqueous $NaHCO_3$, and water, and dried over $CaCl_2$. The solvent was removed in vacuo. To remove the low-molecular-weight fraction, the product was reprecipitated from chloroform (40 ml) with ethanol (330 ml), and dried in vacuo. The oligomeric ether melted at about 57°C, and contained 0.12 mole of $>C{=}C<$ bonds/100 g of product. Its mean molecular mass was almost 1400.

Alcoholysis of the Oligomeric Ether (II). To a mixture of 21.0 g of the ether (II), 368 ml of toluene, 0.211 g of hydroquinone, 0.527 g of CuCl, and 37.4 g of ethanol heated to about 75°C was added 0.5250 g of p-toluenesulfonic acid. The mixture was heated at the boil, samples being removed at fixed intervals for analysis.

Bis[4-(1-ethoxyethyl)phenyl] Ether (VIa). To a mixture of 130 ml of toluene, 51.6 g of ethanol, and 0.725 g of p-toluenesulfonic acid, heated to the boil, was added with stirring over 1 h 20 min a solution of 29.0 g of the diol (I) in 100 ml of toluene and 30 ml of ethanol. The mixture was heated for 1 h at the boil, a Dean and Stark apparatus being used to remove 60 ml of condensate containing water, ethanol, and toluene. The mixture was then washed and the solvent removed as in the synthesis of the oligomeric ether (II). There was obtained 32.4 g of crude product, which was redistilled under reduced pressure (about 15 Pa) to give a fraction bp 125°C, n_D^{20} 1.5315. Found, %: C 76.48, H 8.27. $C_{20}H_{26}O_3$. Calculated, %: C 76.40, H 8.33.

Bis[4-(1-isopropoxyethyl)phenyl] Ether (VIb). To 160 ml of a 40% solution of propan-2-ol in toluene containing 0.4300 g of p-toluenesulfonic acid was added at the boil with stirring over 45 min 15.0 g of the diol (I) in 50 ml of a 40% solution of propan-2-ol in toluene. The mixture was heated for 0.5 h at the boil (bp 80.5-82°C). The water liberated was collected in a Dean and Stark trap partly filled with sodium chloride (to separate the water from the propan-2-ol—toluene mixture). In order to remove the water more completely, the condensate, containing propan-2-ol and water, was periodically removed (about 130 ml), and the lost propan-2-ol replaced. There was obtained 17.7 g of crude product, mp 67-69°C (after recrystallization from ethanol). Found, %: C 77.21, H 8.63. $C_{22}H_{30}O_3$. Calculated, %: C 77.15, H 8.82. n_D^{70} 1.4955 (after distillation at 60°C (about 20 Pa)).

Catalytic Reactions in the Bis-[4-(1-hydroxyethyl)phenyl]Ether—Ethanol System. A mixture of 35.0 g (0.1355 mole) of the diol (I), 621 ml of toluene, 15.8 ml of ethanol, 0.350 g of hydroquinone, and 0.200 g of CuCl was heated to 95-97°C, and 0.1750 g of p-toluenesulfonic acid added with stirring. The mixture was then heated at the boil, samples being removed for analysis. The samples were washed with water, 5% $NaHCO_3$, and water; the toluene solution of the product was dried over $CaCl_2$, and the toluene removed under reduced pressure. The catalyzed reactions of the other systems were carried out similarly.

Catalytic Cleavage of Bis[4-(1-alkoxyethyl)phenyl]Ethers (VI). A mixture of the ether (VI), an aromatic solvent, p-toluenesulfonic acid, hydroquinone [1% of the weight of the ether (VI)], and CuCl [1% of the weight of the ether (VI)] was heated with stirring at the boil in a flask fitted with a reflux condenser. Samples were removed and were worked up as described above.

CONCLUSIONS

1. On heating a disecondary aromatic diol with an alkanol in an aromatic solvent in the presence of an acid catalyst, condensation telomerization takes place with the formation of oligomeric ethers, alcoholysis of which and condensation of hydroxylated intermediate products gives dialkyl ethers of the diol, followed by cleavage of these ethers to give vinyl- and divinylaromatic compounds, and cationic polyaddition of these monomers to give straight-chain unsaturated oligomers, giving mixtures of vinylaromatic compounds and unsaturated straight-chain oligomers.

2. The rate of cleavage of dialkoxy-derivatives of the aromatic diol decreases as the reaction progresses as a result of the increasing concentration of the liberated alkanol, which modifies the activity of the catalyst.

LITERATURE CITED

1. B. A. Zaitsev, L. L. Dantsig, G. I. Khramova, and G. A. Shtraikhman, Zh. Prikl. Khim., 50, 411 (1977).
2. B. A. Zaitsev and R. F. Kiseleva, Vysokomol. Soedin., 23A, 1783 (1981).
3. B. A. Zaitsev, L. L. Dantsig, and G. I. Khramova, Zh. Org. Khim., 19, 2340 (1983).
4. B. A. Zaitsev, G. I. Khramova, and L. L. Dantsig, Vysokomol. Soedin., 24A, 2467 (1982).
5. B. A. Zaitsev, A. V. Fedorova, R. F. Kiseleva, and G. I. Khramova, Vysokomol. Soedin., 25A, 1076 (1983).
6. B. A. Zaitsev and L. L. Dantsig, Izv. Akad. Nauk SSSR, Ser. Khim., 959 (1983).
7. B. A. Zaitsev, L. L. Dantsig, I. O. Gusarova, M. B. Tennikov, and V. G. Belen'kii, Izv. Akad. Nauk SSSR, Ser. Khim., 1881 (1982).
8. B. A. Zaitsev, The Mechanics of Composite Materials [in Russian], No. 5, 973 (1983).
9. B. A. Zaitsev, Yu. N. Sazanov, L. A. Shibaev, L. L. Dantsig, and T. A. Antonova, Thermochim. Acta, 19, 319 (1977).
10. B. A. Zaitsev and R. F. Kiseleva, Acta Polym., 34, 616 (1983).