ORGANIC CHEMISTRY

ACID-CATALYZED DIMERIZATION AND ARALKYLATION IN DIVINYLAROMATIC COMPOUND—AROMATIC SOLVENT SYSTEMS

B. A. Zaitsev, R. F. Kiselëva,
V. M. Denisov, and A. I. Kol'tsov

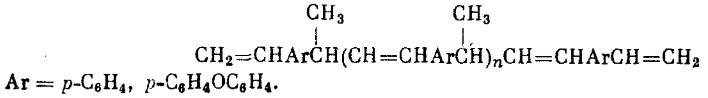
UDC 542.97:542.953:66.095.253:547.538

On heating styrene and bis(4-vinylphenyl) ether or a linear unsaturated aromatic oligomer with terminal vinyl groups in aromatic solvents, depending on the temperature and concentration of toluene-p-sulfonic acid, there are obtained predominantly dimers and linear oligomers, and/or products of the alkylation of the aromatic solvent by the unsaturated monomers, dimers, and oligomers.

On heating styrene with solutions of strong acids, there may be obtained, depending on the reaction conditions, the unsaturated styrene dimer trans-1,3-diphenylbut-1-ene (I) and/or the saturated dimer 1-methyl-3-phenylidane (II) [1-6]. The dimer (I) is formed preferentially on heating styrene in benzene or toluene in the presence of toluene-p-sulfonic acid (TSA) [7, 8].

The results of an examination of the cationic dimerization of styrene were utilized to develop methods for the preparation of linear unsaturated oligomers from divinylaromatic compounds [p-divinylbenzene and bis(4-vinylphenyl) ether (III)]. Oligomers of this type with a mean numerical molecular mass $\bar{M}_n$ of 430-1140, formed by successive dimerization steps, were obtained by heating the dehydration products of di-secondary aromatic diols [7, 9] or unsaturated secondary aromatic alcohols [10, 11] in aromatic solvents in the presence of TSA. Linear unsaturated oligomers and polymers were obtained subsequently by heating p-divinylbenzene in the presence of oxo-acids [12].

We have examined the conditions, mechanism, and kinetics of the formation, and the structure and properties of the linear unsaturated poly[bis(4-vinylphenyl) ether] (IV).



$$CH_2{=}CHAr\overset{CH_3}{\overset{|}{C}}H(CH{=}CHAr\overset{CH_3}{\overset{|}{C}}H)_nCH{=}CHArCH{=}CH_2$$

$Ar = p\text{-}C_6H_4,\ p\text{-}C_6H_4OC_6H_4.$

Such an unsaturated oligomer (polymer), which is of interest for the production of thermostable polymers, has been obtained at 80-140°C in aromatic solvents in the presence of TSA [13, 14].

It was of interest to establish the differences in the conditions for carrying out the dimerization of vinyl- and divinylaromatic compounds (monomers, dimers, and oligomers), such as (III), and the aralkylation of aromatic compounds by these unsaturated compounds in the presence of acid catalysts (the Balzon reaction [15, 16]).

Styrene, stilbene, and other alkenes are known to alkylate aromatic compounds in the presence of strong acids and Friedel—Crafts catalysts [15, 16], i.e., conditions similar to those used for the cationic dimerization of styrene.

In order to estabish the optimum conditions for the alkylation of aromatic compounds with unsaturated aromatic monomers (and oligomers), initially a study of the reactions of styrene with (I) in aromatic solvents in the presence of TSA (monohydrate) was carried out.

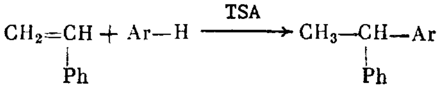
Table 1 shows the results obtained on heating styrene and (I) in the presence of sulfuric acid and TSA. The reactions occurring were studied by IR and PMR spectroscopy, determination of the degree of unsaturation of the product, and elemental analysis. The methods used in [1-4] were first used to obtain the model compounds (I) and (II), by heating styrene

---

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2566-2574, November, 1990. Original article submitted October 11, 1989.

0568-5230/90/3911-2323$12.50

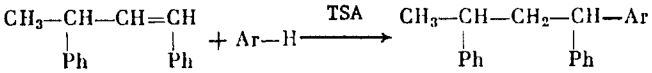
in sulfuric acid solutions. Styrene and (I) were then heated in aromatic solvents in the presence of TSA, and the reaction products fractionated by vacuum distillation. It will be seen from Table 1 that on heating styrene in benzene or toluene under mild conditions ([TSA] ∿ $1 \cdot 10^{-2}$ mole/liter, 80-110°C, reaction time 1-2 h), (I) was the main product. When the concentration of TSA was increased (to ∿ 0.05-0.15 mole/liter), the temperature raised, and/or the reaction times increased, alkylation products of the aromatic solvent appeared in the reaction products [i.e., addition of styrene to the solvent of type (A)].



$$\underset{\displaystyle Ph}{CH_2=CH} + Ar-H \xrightarrow{TSA} CH_3-\underset{\displaystyle Ph}{CH}-Ar$$

(A)

where Ar = C_6H_5 (1,1-diphenylethane (V)), p-$C_6H_4CH_3$ (1-phenyl-1-(p-tolyl)ethane (VI)), o-$C_6H_3(CH_3)_2$ (1-phenyl-1-(o-xylyl)ethane (VII)), p-$C_6H_4OCH_3$ (1-phenyl-1-p-(anisyl)ethane (VIII), or p-$C_6H_4OC_6H_5$ (1-phenyl-1-(p-phenoxyphenyl)ethane (IX)), or of (I) to the aromatic solvent of type (B) (or C*)).



$$CH_3-\underset{\displaystyle Ph}{CH}-CH=\underset{\displaystyle Ph}{CH} + Ar-H \xrightarrow{TSA} CH_3-\underset{\displaystyle Ph}{CH}-CH_2-\underset{\displaystyle Ph}{CH}-Ar$$

where Ar = C_6H_5 (1,1,3-triphenylbutane(X), p-$C_6H_4CH_3$ (1,3-diphenyl-1-(p-tolyl)butane (XI)), o-$C_6H_3(CH_3)_2$ (1,3-diphenyl-1-(o-xylyl)butane (XII)), p-$C_6H_4OCH_3$ (1,3-diphenyl-1-(p-anisyl) butane (XIII), p-$C_6H_4OC_6H_5$ (1,3-diphenyl-1-(p-phenoxyphenyl)butane (XIV)).

Under these conditions, the amounts of (I) decreased, and (II) sometimes appeared. Accordingly, the degree of unsaturation of the product decreased, or at high conversions approximated to zero, while the IR and PMR spectra showed characteristic peaks. The PMR spectra of the compounds (A) showed: a doublet at δ 1.55 ppm for the CH_3 group in $CH_3-CH(Ar)_2$, a quartet at δ 3.9-4.1 ppm characteristic of the tertiary CH group, and a signal at δ 7.0 ppm for the aromatic protons. Substituents in the benzene ring in compounds (A) and (B) give rise to additional signals (singlets) at δ 2.1-2.2 ppm (o, p-CH_3) and 3.52-3.65 ppm (p-OCH_3). The aromatic protons of the p-substituted benzene ring are seen in the spectrum at δ 6.7-6.9 ppm.

In the case of compounds (B), in addition to the signals given above, further signals are seen at δ, ppm: 1.15-1.20 (CH_3 in $CH_3\underset{\displaystyle Ph}{CH}CH_2$), 2.2-2.3 (CH_2 group), 3.3-3.6 (tertiary CH in $CH_3-\underset{\displaystyle Ph}{CH}-CH_2-$). The signal for the protons of the —CH=CH—(trans) group in the starting material at δ 6.2-6.3 ppm either disappear, or become very small.

In the IR spectra of the products of aralkylation of the aromatic solvents by the dimer (I), the intensities of the absorption at 3020 (H—C=), 1648 (C=C), and 965 (H—C=, trans) cm^{-1} fall markedly, while those of the absorptions at 2830 (CH_2), 2925 (CH_2) and 2960 cm^{-1} (CH_3) (in the aralkylation of toluene, o-xylene, and anisole) increase as a result of the increased numbers of CH_3 groups in the reaction products.

Note that on heating (I) with 62% sulfuric acid, the main product is the dimer (II) (Table 1). The PMR spectrum showed no signal at δ 6.3 ppm (—CH=CH—trans), but a multiplet appeared at δ 4.1 ppm (CH-t in $Ph-\overset{|}{C}H-Ph$) together with a complex multiplet at δ 1.4-3.4 ppm ($-CH_2-\overset{|}{C}H-CH_3$) and a signal at δ 2-2.25 ppm ($-CH_2-$).

On heating (I) at 110°C in the presence of TSA (concentration ∿0.08 mole/liter) (Table 1, expts. 16, 17), a polymeric product formed slowly, whereas under similar conditions (II) remained unchanged. During the reaction of (I), the viscosity of the product increased, and its unsaturation decreased. The PMR spectrum showed weakening of the signal at δ 6.3 ppm

---

*Compounds of type (C) $(CH_3\underset{\displaystyle Ph}{CH}-\underset{\displaystyle Ar}{CH}-CH_2Ph$ are usually formed in small amounts. Their PMR spectra show an additional signal at 2.55 ppm (CH_2Ph).

TABLE 1. Conditions of Formation, Composition, and Properties of the Acid-Catalyzed* Reactions of Styrene and Dimer (I) in Aromatic Solvents

Expt. No.	Alkene	[Alkene]	[Acid]·10^3	Solvent†	T, °C	Time, h
		mole/liter				
1	Styrene	7.800	1464	H_2O	120	3,3
2	Styrene	0,800	8000	H_2O	120	16,0
3	Styrene	0,4550	5,7	Benzene	80	4,0
4	Styrene	0,1880	92,9	Benzene	80	28,5
5	Styrene	1,4140	17,8	Toluene	110	4,0
6	Styrene	0,1996	72,4	Toluene	110	6,0
7	Styrene	0,1860	133,5	Toluene	110	15,0
8	Dimer (I)	0,0932	133,8	Toluene	110	10,5
9	Styrene	0,1915	94,8	o-Xylene	110	11,5
10	Dimer (I)	0.0933	134.0	o-Xylene	110	9,0
11	Styrene	0.1862	133,6	Anisole	110	16,0
12	Dimer (I)	0,0940	133,8	Anisole	110	10,5
13	Styrene	3,61	125,9	Diphenyl ether	100	7,5
14	Styrene	0,6200	138,0	Diphenyl ether	100	4,0
15	Dimer (I)	0.0100	115.1	Diphenyl ether	100	4,5
16	Dimer (I)	4,735	72,0	Dimer (I)	110	2.0 5,0
17	Dimer (I)	4,735	72,7	Dimer (I)	110	13,5

---

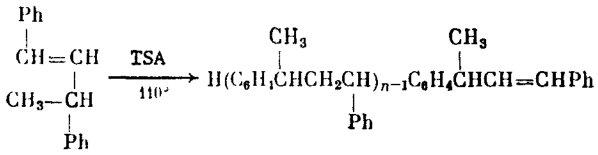
*Catalyst H_2SO_4 (expt. 1), 62% H_2SO_4 (expt. 2), TSA (expts. 3-17).

†The molar proportions of solvent (benzene, toluene, o-xylene, or anisole) to alkene were 45-95; in expts 13, 14, and 15 the diphenyl ether/alkene ratios were 1, 9.4, and 10 respectively.

(—CH=CH—) as compared with the same signal in (I), while signals appeared at δ, ppm: 1.2 (CH_2 in $CH_3\underset{\underset{Ph}{|}}{C}HCH_2$), 2.2 (—$CH_2$—), and 3.6 (—CH—). In the IR spectrum, the intensity of the absorption at 3020 (H—C=), 965 (H—C=), and 755 cm^{-1} decreased considerably. These findings, in conjunction with the reactions described above, indicate that polyaralkylation takes place by successive aralkylations by the unsaturated group of the dimer (I) (or its reaction product) of the aromatic ring in another molecule of the dimer (I) (or its reaction product). This polyaralkylation results in the formation of an oligomer (or a polymer) by cationic polyaddition:

TABLE 1 (continued)

Reaction products and their amounts in the mixture, %	Fraction No.	Yield, %	Properties of product		
			unsaturation, moles C=C per 100 g of product	n_D^{20}	Bp, °C (p, mm Hg)
(I)	–	70	0,440	1.591	140(2)
(II)	–	69	0,000	1,579	128(2)
(I)	–	10	0.410	–	–
(V) (contains 10% (I) and <5% (II))	1	6	–	1,577	115 117(2)
50% (V), 40% (I) and 10% (II)	2	5(V)		1,583	127 137(2)
50% (X), 30% (I) and 20% (II)	3	8(X)	0.110	1,589	170 190(2)
(I)	–	–	0,398	1,587	–
(VI) (contains <10% (I))	1	10	0,063	1,569	120 123(2)
70% (VI) and 30% (I)	2	9(VI)	0,150	1,574	125 128(2)
(VI) (contains <5% (I))	2	13(VI)	0.015	1,567	115 117(1)
70% (XI), 30% (VI)	4	64(XI) 10(VI)	0.018	1,581	200 205(3)
(II)	2	17	0,000	1,580	140–145 (3–4)
(XI)	3	50	0,000	1,582	188–193(2)
(VII)	2	37	0,007	1,568	110–115(1)
40% (VII), 60% (XII)	3	39(XII) 10(VII)	0.008	1,578	205–210(2)
(II)	1	20	0,036	1,580	150(4)
(XII)	2	50	0,010	1.576	200(1–2)
(VIII)	1	80	0,000	1,572	135(2)
80% (II), 20% (I)	1	55(II)	0,083	1,578	150–155(4)
(XIII)	2	43	0.005	1,588	195–200(2)
95% (IX)	2	12	0.005	1,602	190(2)
60% (IX), 40% (XIV)	3	14(IX) 26(XIV)	0,000	1,612	230–240(2)
(IX)	2	57	0,024	1,599	182(2)
10% (I), 90% (II)	2	20(II)	0,049	1,581	140(3)
(XIV)	3	68	0,020	1,597	240(2)
(XV) and (I)	–	–	0.300	1,587	–
(XV) and (I)	–	–	0.179	1,599	–
93% (XV), 7% (I)	–	–	0,018	1,609	–



$$\mathrm{PhCH{=}CH\underset{Ph}{\underset{|}{C}}H{-}CH_3}\ \xrightarrow[110^{\circ}]{\text{TSA}}\ \mathrm{H(C_6H_4\overset{CH_3}{\overset{|}{C}}HCH_2\underset{Ph}{\underset{|}{C}}H)_{n-1}C_6H_4\overset{CH_3}{\overset{|}{C}}HCH{=}CHPh}$$

Other modes of addition of the units, involving phenyl groups, leading to the formation of branched and even grafted polymers, are possible. However, experiments carried out in the presence of a radical polymerization inhibitor (hydroquinone) excluded the possibility of the formation of the polymer by a radical mechanism.

It therefore follows from Table 1 that on heating styrene in an aromatic solvent (the benzene nucleus of which does not contain an electron-acceptor substituent) in the presence of TSA, depending on the conditions either one or several successive, parallel reactions may occur: a) aralkylation of the aromatic solvent by styrene to give an addition product of type (A); b) dimerization of the styrene to give the unsaturated dimer (I); c) isomerization

TABLE 2. Conditions of Formation, Composition, and Properties of Addition Products of Aromatic Solvents to Bis(4-vinylphenyl) Ether (III) and the Linear Unsaturated Poly[bis(4-vinylphenyl)Ether] (IV)*

Expt. No.	Starting material	Concentration of starting material, g/liter	[TSA]·10³ mole/liter	Solvent	T, °C	Time, h	Reaction products	Properties of product			
								softening point, °C	unsaturation †	elemental analysis, %	
										C	H
1	Ether (III)	0,0634 ‡	5,2	Benzene	80	1	Oligoether (IV)	128–140	0.450	86,20	6,57
2	Oligoether (IV)	10,83	74.7	Benzene	80	2	(XVI)	–	–	–	–
3	»	10,80	74.7	Toluene	110	2	(XVII)	–	0,100	86,36	6,63
4	»	10,80	74.7	o-Xylene	110	2	(XVIII)	–	0,120	88,90	7,03
5	»	10,85	110,4	o-Xylene	110	2	(XVIII)	–	0,100	–	–
6	Ether (III)	0,05 ‡	76,7	Anisole	110	4	85% Type (A) 15% Type (B)	25–40	0,035	82,93	7,17
						10	70% Type (A) 30% Type (B)	–	0,014	82,57	7,15
7	Oligoether (IV)	10,83	74,6	Anisole	110	11	(XIX)	135–140	0.032	83,12	6,77
8	Ether (III)	0,53 ‡	128,8	Diphenyl ether	100	3	(XX)	145–160	0,056	85,13	6,48
9	Oligoether (IV)	10,83	74,6	»	110	2	(XX)	115–130	0,0574	–	–
10	»	10,83	74,6	»	100	2	(XX)	–	0,0536	85.30	6,62
						5	(XX)	125–135	0,0417	85,40	6,81
11	»	10,83	74,6	Diphenyl sulfide	110	4	(XXI)	90–97	0,071	82,45	5,96; 56,8 **

---

*Oligoethers (IV) with the following aromatic units (Ar), adding at the site of the double bonds, Ar: C_6H_5 (XVI); p-$C_6H_4CH_3$ (XVII); o-$C_6H_3(CH_3)_2$ (XVIII); p-$C_6H_4OCH_3$ (XIX); p-PhOPh (XX); p-PhSPh (XXI).

†Moles of $\rangle C{=}C\langle$ bonds per 100 g of products.

‡Mole/liter.

**S content, %.

TABLE 3. IR and PMR Spectra of Products Obtained

Compound	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm
(I)	965, 1500, 1600, 1648, 2870, 2930, 2962, 3020	1,4 (3H), 3.5 (1H), 6,2 (2H), 7,1 (10H, Ar)
(II)	1500, 1600, 2855, 2930, 2962, 3060	1,2–1,3 (3H), 1.4–3,4 (3H, CH$_2$CH), 2,0–2,2 (2H), 2,3 (1H, CH-*t*), 3,85–4,4 (1H, CH-*t*), 7,0 (9H, Ar)
(III)	905, 990, 1115, 1240, 1265, 1405, 1500, 1595, 1630, 2975, 3000, 3045, 3085	5,1 (1H), 5,55 (1H), 6,45 (1H), 7.0 (8H, Ar)
(IV)	900, 940, 965, 1100, 1240, 1495, 1595, 1625, 1645, 2865, 2900, 2925, 2955, 3000, 3030	1,45 (3H, CH$_3$), 3.5 (1H, CH-*t*), 5,1 (1H), 5.5 (1H), 6,3 (2H), 6,45 (1H), 7,0 (*p*-H, Ar)
(V)	695, 750, 910, 970, 1025, 1075, 1370, 1445, 1475, 1487, 1600, 2870, 2930, 2965, 3000, 3025	1,55 (3H, CH$_3$), 3,9 (1H, CH-*t*), 7,1 (10H, Ar)
(VI)	690, 755, 900, 960, 1020, 1370, 1445, 1500, 1575, 1600, 1650, 2870, 2925, 2960, 3000, 3025	1,55 (3H), 2,25 (3H, CH$_3$ **in** CH$_3$Ph), 3,95 (1H, CH-*t*), 6,9 **and** 7,0 (9H, Ar)
(VII)	700, 760, 870, 905, 980, 1000, 1030, 1060, 1370, 1445, 1485, 1575, 1600, 1650, 2870, 2925, 2965, 3000	1.5 (3H), 2,13 (3H, 3,90 (1H), 6.75–7,0 (8H, Ar)
(VIII)	695, 750, 830, 1025, 1115, 1240, 1370, 1450, 1500, 1580, 1600, 2870, 2900, 2930, 2965, 3000	1.56 (3H), 3,62 (3H, CH$_3$), 4,0 (1H, CH-*t*), 6,79 **and 7,0** (9H, Ar)
(IX)	735, 800, 860, 905, 1030, 1085, 1125, 1240, 1500, 1575, 3025, 3040, 3055, 3075, 3100	1,5 (3H, CH$_3$), 4,0 (1H, CH-*t*), 6,9 **and** 7,0 (14H, Ar)
(X)		1,15 (CH$_3$ **in** CH$_3$CHPh), 1,8 (CHCH$_2$Ph), 2,35 (CH$_2$), 3,5 (CH-*t*), 7,0 (H, Ar)
(XI)	7, 25, 745, 790, 900, 1030, 1370, 1505, 1600, 2870, 2900, 2925, 2960, 3000, 3030, 3065, 3085	1,15 (3H, CH$_3$), 1,85 (3H; CHCH$_2$Ph), 2,15 (3H, CH$_3$ **in** CH$_3$Ph), 2,35 (2H, CH$_2$), 3,5 (1H), 6,9 **and** 7,1 (14H, Ar)
(XII)	695, 720, 810, 877, 1025, 1370, 1450, 1500, 1600, 2850, 2900, 2925, 2965, 3000, 3027, 3065	1,2 (3H), 1,85 (3H), 2,2 (3H), 2,3 (2H), 3,6 (1H), 6,9 **and** 7,1 (13H, Ar)
(XIII)	690, 720, 800, 900, 1025, 1115, 1240, 1370, 1450, 1505, 1595, 2830, 2870, 2900, 2925, 2955	1,2 (3H), 1,85 (3H), 2,15 (3H), 2,3 (2H), 2,5 (1H, CH-*t*), 3,6 (1H), 3,65 (3H, CH$_3$ **in** OCH$_3$), 4,0 (1H)
(XIV)	695, 730, 825, 905, 1020, 1105, 1200, 1240, 1450, 1505, 1590, 2870, 2900, 2925, 2955, 3000	1,2 (3H), 2,3 (2H), 2,5 (1H), 3,6 (1H), **6.9 and 7,0 (19H, Ar)**
(XV)	580, 620, 670, 695, 745, 780, 825, 835, 900, 1020, 1060, 1100, 1175, 1300, 1370, 1420, 1445, 1500, 1595, 2860, 2900, 2925, 2950, 3000, 3020	1,2 (CH$_3$), 1.45 (CH$_3$), 1,85 (CHCH$_2$), 2.2 (CH$_2$), 2,5 (CH-*t*), 3.5–3,8 (CH-*t*), 4.2 (CH-*t*), 6.4 (CH=CH), 6.9 **and** 7.0 (*p*-H, Ar)
(XVI)	680, 725, 870, 940, 965, 1010, 1100, 1170, 1240, 1375, 1450, 1475, 1595, 1645, 2850, 2920, 2955, 3075, 3100	
(XVII)	690, 730, 870, 910, 940, 965, 1015, 1105, 1240, 1370, 1450, 1495, 1600, 1655, 2850, 2870, 2925, 2955, 2990	1,2, 1,4, 2,15, 2,2, 2,5, 3,6, 3.0–4,1 (CH-*t*), 5,6, 6,2, 7,0
(XVIII)	725, 870, 940, 965, 1105, 1240, 1370, 1450, 1495, 1600, 1650, 2850, 2870, 2925, 2955, 2990, 3030, 3055, 3100	1.25, 1,65, 2,2 (*o*-CH$_3$), 3,7, 4,1, 6,2, 7.0
(XIX)	770, 800, 845, 870, 1010, 1100, 1240, 1370, 1450, 1500, 1605, 1655, 2830, 2875, 2900, 2925, 2955, 2995, 3030, 3055	1,25, 1.56, 2,2, 3,65, 6,9
(XX)	680, 870, 900, 1010, 1065, 1100, 1240, 1370, 1450, 1500, 1590, 1645, 1655, 2850, 2865, 2920, 2950, 2995, 3025	1,2, 1,5, 2,3, 3,7, 4,15, 7,0
(XXI)	680, 870, 1010, 1045, 1060, 1075, 1105, 1235, 1370, 1440, 1490, 1590, 2850, 2870, 2900, 2915, 2950, 2995, 3020, 3040	

of the unsaturated dimer (I) to the saturated dimer (II); d) aralkylation of the aromatic solvent by dimer (I) to give an addition product of type (B), and e) polyaralkylation by (I) to give linear oligomers, branched and grafted polymers. A further possibility is the involvement of (II) in aralkylation of unsaturated aromatic compounds.

On heating (I) under similar conditions, the same reactions occur as with styrene, except for reaction (A).

Turning from model systems, we now consider the reactions of the divinylaromatic monomer (III) and the linear oligoether (IV) obtained when it undergoes cationic oligomerization in similar systems.

As has already been reported [13, 14], on heating (III) in benzene or toluene at the boiling point and [TSA] $< 1 \cdot 10^{-3}$ mole/liter, the principal product is (IV) containing 95 ± 5% of unsaturated units (Table 2, expt. 1). On heating (III) and (IV) under more severe conditions, it might be expected that aromatic solvents would be aralkylated by these compounds. In fact, as will be seen from Table 2, as the extent of reaction increases, the unsaturation of the products approaches zero. The occurrence of these reactions is confirmed by IR and PMR spectroscopy: in the IR spectra, the intensity of the absorption for the terminal $CH_2{=}CH$ groups (3080, 3025, 1630, 990 and 905 cm^{-1}) decreases sharply, together with that for the internal trans-$\rangle C{=}C \langle$ bonds (at 1645 and 965 cm^{-1}). In the PMR spectra of the products of reaction of (III) and (IV), the characteristic signals at δ 6.3, 5.55, and 5.1 ppm attributed to unsaturated groups are much reduced, while signals appear at δ 1.2 (CH_3 in $CH_3CH(Ph(CH_2-)$ and 2.2 ($-CH_2-$) ppm, together with signals for the substituents in the aromatic compounds at δ 2.3 (CH_3 in CH_3-Ph-) and 3.65 (CH_3 in CH_3OPh-) ppm.

EXPERIMENTAL

PMR spectra were recorded on a Jeol C-HL (60 MHz) instrument in CCl_4 (internal standard TMS), and IR spectra on a Specord 75 IR (layers and films). The unsaturation of the samples was estimated by ozonolysis at 0°C in an ADS-3 apparatus in CCl_4 as solvent.

p-Toluenesulfonic acid was used as the monohydrate, with a content of the main component of 92%. 1,3-Diphenylbut-1-ene (trans) (I) and 1-methyl-3-phenylindane (II) were obtained as described in [1-4]. Bis-(4-vinylphenyl) ether (III) was obtained as described in [13, 17], and purified by sublimation and crystallization, mp 88.5-89.0°C.

Linear Unsaturated Poly-[bis(4-vinylphenyl) Ether] (IV) (Table 2, expt. 2). To a solution of 0.3808 g of TSA and 0.1510 g of hydroquinone (HQ) in 200 ml of benzene was added at 70°C with stirring a solution of 5.00 g of (III) in 150 ml of benzene, and the mixture was heated for 1 h. The benzene solution of the product was washed successively with water, 5% $NaHCO_3$ solution, and water, and dried over $MgSO_4$. The solvent was removed, and the (IV) dissolved in chloroform and precipitated with ethanol to give 4.40 g of (IV), $\bar{M}_n \sim 1500$ (according to the PMR spectrum and vapor osmometry).

Compounds (V)-(XIV) were obtained by the same method (the reaction conditions, composition, and properties of the products are shown in Tables 1 and 3).

1-Phenyl-1-(4-tolyl)ethane (VI) (Table 1, expt. 6). A solution of 6.472 g of styrene, 4.656 g of TSA, and 0.065 g of HQ in 300 ml of toluene was heated for 6 h at 110°C. The toluene solution of the products was then worked up as for the synthesis of (IV); removal of the solvent and vacuum fractionation of the residue gave 1.35 g of fraction 1, containing 1.2 g of (VI), and 3.20 g of fraction 2, containing 2.24 g of (VI) (with (I) as a by-product). In expt. 7 (Table 1), in which a solution of 4.977 g of styrene, 7.097 g of TSA, and 0.149 g of HQ in 245 ml of toluene was heated for 15 h at 110°C, 1.24 g of fraction 2 contained 1.18 g of (VI) and 3.24 g of fraction 4 contained ~1.0 g of (VI).

1-Phenyl-1-(o-xylyl)ethane (VII) (Table 1, expt. 9). A solution of 3.495 g of styrene, 3.438 g of TSA, and 0.100 g of HQ in 170 ml of o-xylene was heated for 11.5 h at 110°C, to give 2.62 g of fraction 2 and 1.70 g of fraction 3.

1,2-Diphenyl-1-(p-tolyl)butane (XI) (Table 1, expt. 8). A solution of 5.030 g of the dimer (I), 7.173 g of TSA, and 0.151 g of HQ in 245 ml of toluene was heated for 10.5 h at 110°C to give 0.86 g of fraction 2, consisting of (II), and 3.622 g of fraction 3, consisting of (XI).

1,3-Diphenyl-1-(o-xylyl)butane (XII) (Table 1, expt. 10). A solution of 5.714 g of (I), 8.147 g of TSA, and 0.171 g of HQ in 280 ml of o-xylene was heated for 9 h at 110°C to give 1.142 g of fraction 1, consisting of (II), and 4.36 g of fraction 2, consisting of (XII).

1-Phenyl-1-(p-anisyl)ethane (VIII) (Table 1, expt. 11). A solution of 5.246 g of styrene, 7.482 g of TSA, and 0.157 g of HQ in 260 ml of anisole was heated for 16 h at 110°C, to give 8.55 g of (VIII). Found: C 84.30; H 7.60%. $C_{14}H_{16}O$. Calculated: C 83.96; H 8.05%.

1,3-Diphenyl-1-(p-anisyl)butane (XIII) (Table 1, expt. 12). A solution of 5.500 g of (I), 7.843 g of TSA, and 0.165 g of HQ in 270 ml of anisole was heated for 10.5 h at 110°C to give 1.875 g of fraction 1, consisting of a mixture of (I) and (II), and 1.80 g of fraction 2, consisting of (XII). Found: C 87.48; H 8.11%. $C_{23}H_{24}O$. Calculated: C 87.35; H 7.59%.

1-Phenyl-1-(p-phenoxyphenyl)ethane (IX) (Table 1, expt. 14). To a solution of 0.182 g of TSA and 0.004 g of HQ in 3.200 g of diphenyl ether was added at 100°C with stirring a solution of 0.416 g of styrene in 3.20 g of diphenyl ether, and the mixture kept for 4 h at 100°C, to give 0.620 g of fraction 2, consisting of (IX). Found: C 88.08; H 6.79%. $C_{20}H_{18}O$. Calculated: C 87.55; H 6.61%. Compound (IX) was also obtained in another experiment (Table 1, expt. 13), in which a solution of 0.181 g of TSA and 0.03 g of HQ in 4.183 g of diphenyl ether was treated at 100°C with 2.605 g of styrene over 2.5 h, and the mixture kept at 100°C for 5 h. Fraction 2 of the product (0.825 g) consisted mainly of (IX). Found: C 87.41; H 6.42%.

1,3-Diphenyl-1-(p-phenoxyphenyl)butane (XIV) (Table 1, expt. 15). To a solution of 0.452 g of TSA and 0.021 g of HQ in 8.500 g of diphenyl ether was added at 100°C a solution of 2.081 g of (I) in 8.500 g of diphenyl ether over 2 h, and the mixture heated at 100°C for 2 h to give 2.558 g of fraction 3, consisting of (XIV). Found: C 88.87; H 6.83%. $C_{28}H_{26}O$. Calculated: C 88.85; H 6.92%.

Oligomer (XV) (product of homoaralkylation of (I)) (Table 1, expt 17). A solution of 0.061 g of TSA in 3.963 g of (I) was heated for 13.5 h at 110°C. The resulting highly viscous product was diluted with 20 ml of toluene, and the TSA and solvent removed as described above to give 3.344 g of (XV). Found: C 92.90; H 7.75%. When the reaction time was increased to 45 h, a product was obtained which consisted (according to exclusion liquid chromatography) of ∿7% of (I), ∿35% of tetramer, ∿40% of hexamer, and ∿18% octamer and higher molecular weight oligomers.

Oligoether (IV) with Methylphenyl Units (XVII) (Table 2, expt. 3). To a solution of 14.20 g of TSA and 0.300 g of HQ in 500 ml of toluene was added at 90°C a solution of 10.0 g of (IV) in 400 ml of toluene, and the mixture heated for 2 h at 110°C to give 8.50 g of (XVII).

Oligoether (IV) with Diphenyl Sulfide Units (XXI) (Table 2, expt. 11). To a solution of 7.13 g of TSA and 0.155 g of HQ in 300 ml of diphenyl sulfide was added at 110°C a solution of 5.01 g of (IV) in 150 ml of diphenyl sulfide, the mixture heated for 4 h at 110°C, the TSA and solvent removed, and the residue diluted with 30 ml of chloroform and precipitated with ethanol to give 4.02 g of (XXI).

LITERATURE CITED

1. M. J. Rosen, J. Org. Chem., 18, 1705 (1953).
2. B. B. Corson, H. J. Heintzelman, H. Moe, and C. R. Sousseau, J. Org. Chem., 27, 1636 (1962).
3. I. C Calder, W. Y. Lee, and F. E. Treloar, Aust. J. Chem., 22, 2689 (1969).
4. P. E. Spoerri and M. J. Rosen, J. Am. Chem. Soc., 72, 4918 (1950).
5. M. Sawamoto, T. Masuda, J. Nishii, and T. Higashimura, J. Polym. Sci., Polym. Lett. Ed., 15, 329 (1977); 13, 279 (1975).
6. T. Higashimura and H. Nishii, J. Polym. Sci., Polym. Chem. Ed., 15, 329 (1977).
7. B. A. Zaitsev, L. L. Dantsig, G. I. Khramova, and G. A. Shtraikhman, Zh. Prikl. Khim., 50, 411.
8. H. Hasegawa and T. Higashimura, J. Polym. Sci., Polym. Chem. Ed., 18, 611 (1980).
9. R. G. Luchko, V. I. Symova, B. A. Zaitseva, and G. A. Shtraikhman, Inventor's Certificate No. 622,258 (USSR); Byull. Izobret., No. 1, 290 (1979).
10. G. I. Khramova, B. A. Zaitsev, and G. A. Shtraikhman, Zh. Prikl. Khim., 49, 2675 (1976).
11. B. A. Zaitsev, G. I. Khramov, and G. A. Shtraikhman, Inventor's Certificate No. 480,276 (USSR); Byull. Izobret., No. 30, 76 (1975).
12. H. Hasegawa and T. Higashimura, Macromolecules, 13, 1350 (1980).
13. B. A. Zaitsev and R. F. Kiseleva, Acta Polymerica, 34, 616 (1983).
14. B. A. Zaitsev, R. F. Kiseleva, and V. M. Denisov, Vysokomol. Soedin., 26A, 1602 (1984).
15. G. A. Olah (ed.), Friedel—Crafts and Related Reactions, Vol. 2, part 1, Chap. XIV, Publ. Inc., New York—London—Sydney (1964), pp. 3, 138.
16. K. V. Vatsuro and G. L. Mishchenko, Name Reactions in Organic Chemistry [in Russian], Khimiya, Moscow (1976), p. 31.
17. B. A. Zaitsev, S. V. Lukasov, R. F. Kiseleva, et al., Acta Polym., 36, No. 10, 521 (1985).