Polymer Bulletin 9, 487–494 (1983)

Polymer Bulletin

Preparation of Co-Dimers of Styrene and *p*-Chlorostyrene with Regulated Monomer Sequences Using Phosphates

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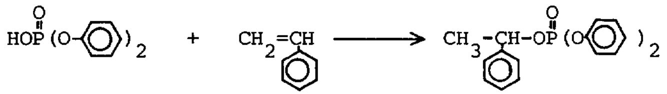
SUMMARY

Two co-dimers of styrene and p-chlorostyrene having regulated monomer sequences were obtained by the reactions of 1-(4-chlorophenyl)ethyl diphenyl phosphate with styrene and of 1-phenylethyl diphenyl phosphate with p-chlorostyrene. The structures of the co-dimers were confirmed by GC-MS and analyses of the oxidative cleavage products.

INTRODUCTION

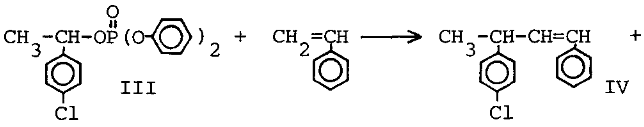
In the previous paper (N. YAMAZAKI et al. 1980), we have reported that linear dimers of styrene and the derivatives were obtained with an oxo acid such as diphenyl hydrogen phosphate, I. The reaction was assumed to proceed through a stable intermediate, 1-phenylethyl diphenyl phosphate, II, which was produced by the reaction of styrene with I. Then, another styrene monomer was inserted to II followed by elimination of β-proton giving styrene dimer (Eqs. 1 and 2). Compared with direct dimerization of styrene by I, the reaction of styrene and II, which was prepared separately from diphenyl phosphorochloridate and 1-phenyl ethylalcohol, occurred more rapidly to afford styrene dimer. The protonation of styrene with I is supposed to be slow and may be a rate determining step. Such a difference in the reactivity of I and II toward styrene may enable the preparation of co-dimers of difinite monomer sequence according to Eqs. 3 and 4. Two co-dimers IV and V, were actually prepared by the reactions of III and II with styrene and p-chlorostyrene respectively. This paper presents indentification of the co-dimers obtained and influence of the reaction conditions on the preparation of the co-dimers.



I II

(1)

(2)



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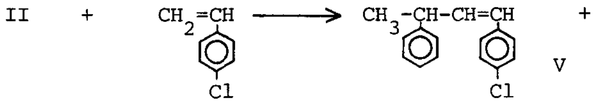

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RESULTS AND DISCUSSION

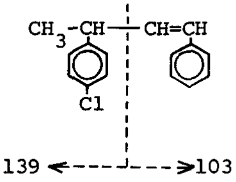
Identification of Co-dimers

The structures of the co-dimers obtained by the reactions 3 and 4 were determined by GC-MS and NMR as well as the analysis of oxidative cleavage products. The results of GC-MS of the co-dimers are summarized in Table 1. Two characteristic mass fragments of m/e 139 and 103 were observed in appreciable intensities in the case of III + styrene, while only weak signals were found at m/e 139 and 103 for II + p-chlorostyrene. These m/e values are attributable

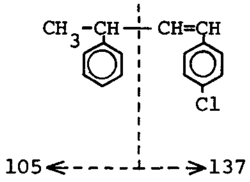
Table 1 Mass Spectral Data of Co-dimers

m/e	Relative Intensity	
	III + styrene	II + p-chlorostyrene
242	47	81
227	91	100
207	100	41
192	63	62
178	14	13
165	19	20
149	53	52
139	68	5
137	2	2
129	61	49
115	95	86
105	13	12
103	43	15
91	75	51

Postulated Structures of Co-dimers

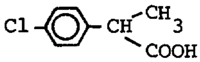
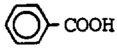
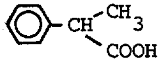


IV



V

Table 2 Oxidative Products of Co-dimers

Cleavage Product	Yield of Products[a], %	
	III + styrene	II + p-chlorostyrene
	71	10
	66	6
	~0	81
	~0	77

a) Based on mol number of co-dimer oxidized.

to each fragment divided with a broken line in the postulated structure IV in Table 1. On the other hand, m/e 105 and 137 fragments corresponding to the structure V were negligible in both cases. Lack of the fragments may presumably be due to ready fission of C-Cl bond under the measuring condition.

Alternatively, the structures of the co-dimers were estimated from the oxidative cleavage products. As shown in Table 2, the cleavage products of the III + styrene system were found to be 2-(4-chlorophenyl) propionic acid and benzoic acid, justifying the validity of the structure IV. On the other hand, 2-phenylpropionic acid and p-chlorobenzoic acid were main products in case of the II + p-chlorostyrene system indicating that the co-dimer had the reverse monomer sequence V. Contamination of small amounts of 2-(4-chlorophenyl) propionic acid and benzoic acid may be due to the homo-dimers of styrene and p-chlorostyrene which could not be excluded by fractional distillation of V.

Preparation of Co-dimers

As shown in Table 3, III was allowed to react with various amount of styrene without solvent giving V in 33~35% yield. In each case, III was found to convert to I completely. Total mole number of V, 0.34 mmol, and p-chlorostyrene, 0.61 mmol, was approximately equal to that of the starting phosphate, III, 1.0 mmol (No. 5, in Table 3), indicating that III undergoes two reactions; One is the co-dimer formation (Eq. 5) and the other is a direct β-proton elimination to afford p-chlorostyrene and I (Eq. 6). Homo-dimers and oligomers of higher molecular weights were minor products under a mild condition. However, at a higher temperature, appreciable amount of styrene dimer was produced (No. 4, in Table 3). The reactions were, therefore, carried out below 50°C. Although p-chlorostyrene generated via reaction (6) reacted in part with III and/or I to give p-chlorostyrene dimer, the yield decreased with increase of the amount of styrene added. Thus co-dimer IV was obtained in preference to other oligomers though the yield leveled out at around 35%.

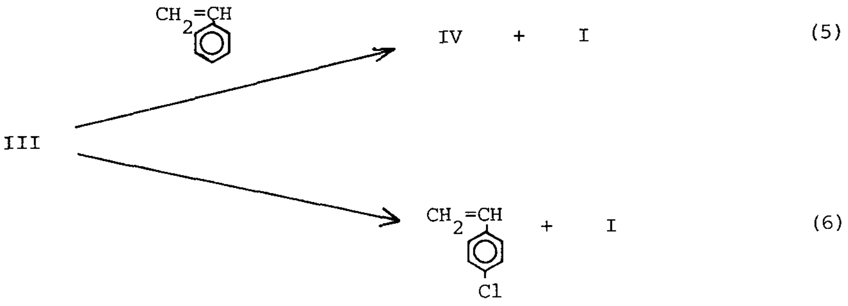


Table 3 Yields of Dimers by the Reaction of III with Styrene[a]

No.	[Styrene]/[III]	Time ,day	Yields of Dimers[b], %		
			Co-dimer(IV)	Styrene dimer	p-Chlorostyrene dimer
1	1.0	4	33	4	9
2	4.0	5	34	3	2
3	8.0	6	35	4	1
4[c]	8.0	0.5	30	18	0
5[d]	16	8	34	2	0

a) Reaction was carried out at 50°C without solvent.
b) Based on mole number of III and determined by GC.
c) Reaction was carried out at 90°C.
d) Yield of p-chlorostyrene was 61% based on mole number of III.

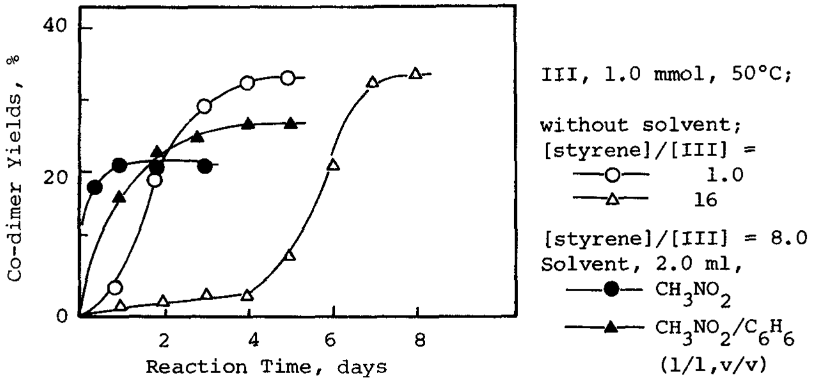
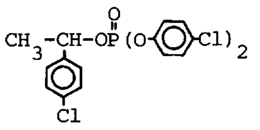


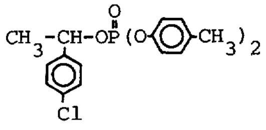
Fig. 1. Time-Conversion Curves for Co-dimer IV

As shown in Figure 1, increasing the amount of styrene added caused retardation of the co-dimer formation. This may presumably be due to the decrease of polarity of the reaction system. On the contrary, the reaction was enhanced in polar solvents, which seems to promote the polarization of 1-(4-chlorophenyl)ethyl-O bond facilitating insertion of styrene.

Such polarization should also induced by substitution of an electron withdrawing group on the phenyl ring of III. In fact, an inductive effect was observed in the reaction of 1-(4-chlorophenyl)ethyl di-p-chlorophenyl phosphate, VI, and 1-(4-chlorophenyl)ethyl



VI



VII

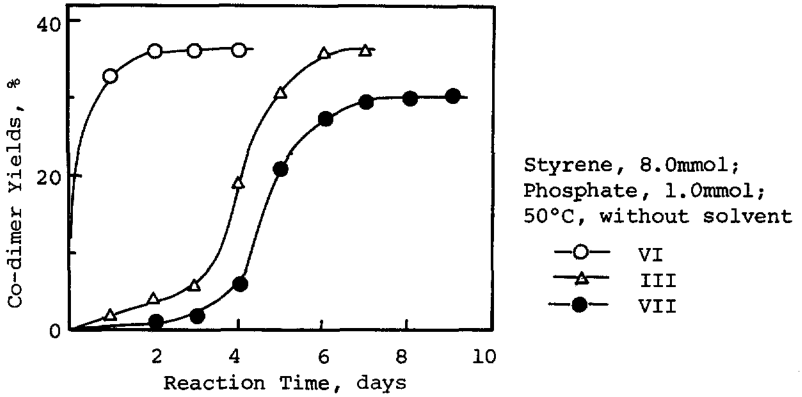


Fig. 2. Time-Conversion Curves for Co-dimer IV.

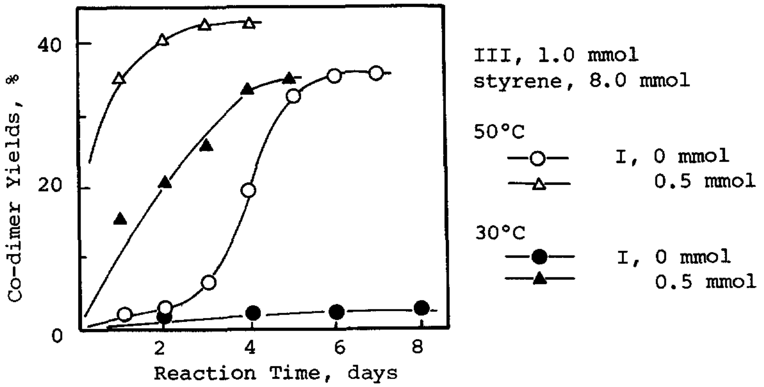


Fig. 3. Time-Conversion Curves for Co-dimer IV.

di-p-methylphenyl phosphate, VII, with styrene (Figure 2). The reaction rate increased in the order of VII$<$III$<$VI according to the Brown's σ^+ values (BROWN and OKAMOTO, 1958; STOCK and BROWN, 1963).

Addition of I diminished the induction period to afford IV in high yield (Figure 3). Similarly, IV was produced by addition of I at 30°C, whereas the reaction does not virtually undergo without I at the same temperature.

Table 4 Yields of Dimers Formed by the Reaction of II with p-Chlorostyrene[a]

No.	[p-Chlorostyrene]/[II]	Time ,day	Yields of Dimers[b], %		
			Co-dimer(V)	p-Chlorostyrene dimer	Styrene dimer
6	1.0	5	23	2	16
7	2.0	5	35	3	13
8	4.0	5	43	5	9
9	8.0	7	24	4	3
10	16	7	25	4	2

a) Reaction was carried out at 50°C without solvent.

b) Based on mole number of II and determined by GC.

As shown in Table 4, a co-dimer V with reverse sequence of monomer unit was also obtained preferentially by the reaction of 1-phenylethyl diphenyl phosphate II with p-chlorostyrene. High selectivity of the production of V was attained at the mole ratio of [p-chlorostyrene]/[II] = 4 with only 9% and 5% yields of homodimers of styrene and p-chlorostyrene respectively.

EXPERIMENTAL

Syntheses of Phosphates

The phosphates II, III, VI, and VII were all prepared by the similar method described previously (N. YAMAZAKI et al. 1980).

1-(4-chlorophenyl)ethyl diphenyl phosphate (III)

Anal. ^1H NMR ($CDCl_3$) δ 1.50 (d, CH_3, 3H), 4.65 (m, CH, 1H), 7.15~7.30 ($-C_6H_4Cl$ and $2-C_6H_5$, 14H)

1-Phenylethyl diphenyl phosphate (II)

Anal. ^1H NMR ($CDCl_3$) δ 1.60 (d, CH_3, 3H), 4.65 (m, CH, 1H), 7.1~7.3 (3 C_6H_5, 15H)

1-(4-Chlorophenyl)ethyl di-p-chlorophenyl phosphate (VI)

Anal. ^1H NMR ($CDCl_3$) δ 1.70 (d, CH_3, 3H), 5.6 (m, CH, 1H), 6.9~7.3 ($-C_6H_4Cl$ and 2 $-C_6H_4Cl$, 12H)

1-(4-Chlorophenyl)ethyl di-p-methylphenyl phosphate (VII)

Anal. ^{1}H NMR ($CDCl_3$) δ 1.60 (d, CH_3, 3H), 2.3 (s, 2 $-CH_3$, 6H), 5.6 (m, CH, 1H), 6.9~7.3 ($-C_6H_4Cl$ and 2 $-C_6H_4-$, 12H)

Synthesis of Co-dimer (IV)

A mixture of III (30 mmol) and styrene (240 mmol) was kept at 50°C. After a designed period of time, the reaction mixture was extracted with ether and washed with aqueous solution of sodium hydrogen carbonate and dried. A co-dimer, V, was isolated by evaporation of styrene and p-chlorostyrene in vacuo followed by distillation under a reduced pressure. bp 86~88°C/0.2 mmHg; isolation yield, 17%; anal. ^{1}H NMR ($CDCl_3$) δ 1.43 (d, CH_3, 3H, J=7 Hz), 3.50 (m, CH, 1H), 6.27 (m, -CH=CH-, 2H), 7.16 ($-C_6H_5$ and $-C_6H_4Cl$, 9H)

Co-dimer (V)

bp, 85~88°C/0.2 mmHg; isolation yield, 19%; anal. ^{1}H NMR ($CDCl_3$) δ 1.40 (d, CH_3, 3H, J=7 Hz), 3.56 (m, CH, 1H), 6.27 (m, -CH=CH-, 2H), 7.18 (m, $-C_6H_5$ and $-C_6H_4Cl$, 9H)

Oxidation of Co-dimer (IV)

The oxidation of co-dimer was carried out according to the method of Sen (SEN and RASTOGI, 1953). To a acetone solution containing 0.44 g of IV was added an aqueous solution of $KMnO_4$ (0.8 g) during a period of one hour with constant stirring, and the reaction mixture was allowed to stand overnight at room temperature. The precipitated manganese dioxide was dissolved by addition of sulfuric acid. After evaporating acetone the resulting clear solution was extracted with ether. The extracts were combined and dried over anhydrous sodium sulfate. After evaporation of ether, 0.38 g of cleavage products (A and B) were obtained.

Oxidation of Co-dimer (V)

Co-dimer V, 0.15 g, was oxidized in a similar manner to afford 0.17 g of the cleavage products (C, D, and small amount of A and B).

Analysis of the Oxidative Cleavage Products

The cleavage products and the methyl esters were analyzed by means of HLC (TOYO SODA HLC-803;column, G2000H8) and GC-MS (PEG-20M; column, a length, 2 m; a diameter, 3 mm). The products were identified by comparison with authentic samples.

Product A: HLC, 36.1 ml (THF, elution vol.); GC-MS of the methyl ester, 11 min (retention time); m/e 198(14.5), 139(100), 103(56.5), 77(22.6).

Product B: HLC, 37.6 ml (THF, elution vol.); GC-MS of the methyl ester, 3.0 min (retention time); m/e 136(61), 105(100), 77(78), 51(42).

Product C: HLC, 36.6 ml (THF, elution vol.); GC-MS of the methyl ester, 4.3 min (retention time); m/e 164(58.6), 105(100), 77(45.1), 51(24.8), 39(12.8), 27(17.3).

Product D: HLC, 36.4 ml (THF, elution vol.); GC-MS of the methyl ester, 6.0 min (retention time); m/e 170(63.3), 138(100), 111(70), 75(53.3), 50(33.3).

Authentic Samples

2-(4-Chlorophenyl)propionic acid was prepared according to Campbell (CAMPBELL and KENYON, 1946) and identified by NMR and IR. Anal ^{1}H NMR (CDCl$_3$) 1.50 (d, CH$_3$, 3H), 3.67 (m, CH, 1H), 7.16 (s, -C$_6$H$_4$Cl, 4H); IR (KBr) 1700 cm^{-1} ($\nu_{C=O}$). Commercial benzoic acid, 2-phenylpropionic acid, and p-chlorobenzoic acid were used as authentic samples. Comparing the results of GC, HLC, and GC-MS spectroscopies, the cleavage products were identified as follows: Product A: 2-(4-chlorophenyl)propionic acid. Product B: benzoic acid. Product C: 2-phenylpropionic acid. Product D: p-chlorobenzoic acid. The yields of the products were measured by GC-MS and listed in Table 2.

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Received December 21, 1982, accepted January 28, 1983 *S*