bis(2 - carbomethoxyethyl) - 2,4,8,10 - tetroxaspiro[5.5]undecane (X), m.p. 127–128° after crystallization from ether-hexane.

Anal. Calcd. for $C_{27}H_{32}O_8$: C, 66.92; H, 6.66. Found: C, 67.12; H, 6.80. Calcd. for saponification equivalent: 242 g. Found: 240 g.

The gross residue from the distillation was dissolved in ether, and from this solution 16 g. (12%) of X was obtained by crystallization.

The preparation of XVI, XVII, XVIII, XIX, and XX is illustrated by the following example.

5-Hydroxymethyl-5-methyl-2,2-bis(2-carbomethoxyethyl)-1,3-dioxane (XX). A solution of 120 g. (0.75 gole) of the ketal XV, 200 g. (1.0 mole) of dimethyl γ-ketopimelate,[11] 300 ml. of anhydrous methanol, and 0.2 ml. of 96% sulfuric acid was distilled slowly through the fractionating column used in the preparation of X until 200 ml. of distillate, b.p. 55–65°, had been collected. The residue was cooled to room temperature, and to it was added 10 ml. of saturated aqueous sodium bicarbonate solution, 500 ml. of water, and 200 ml. of saturated aqueous sodium sulfate solution in that order. This mixture was extracted with three 300-ml. portions of ether, and the combined extracts were filtered through anhydrous sodium sulfate and then evaporated on the steam bath under nitrogen, leaving a residue of about 300-ml. volume. This residue, when distilled under vacuum, yielded 120 g. (53%) of 5-hydroxymethyl-5-methyl-2,2-bis(2-carbomethoxyethyl)-1,3-dioxane (XX), b.p. 186–188° (0.1 mm).

Anal. Calcd. for $C_{14}H_{24}O_7$: C, 55.25; H, 7.95. Found: 55.47; H, 8.00. Calcd. for saponification equivalent: 152 g. Found: 151 g.

Polyesters. The following example illustrates the method of preparing polyesters from IX and X.

A mixture of 10 g. of the diester IX, 20 ml. of ethylene glycol, and 5.0 mg. of sodium methoxide was heated at 150° for 2 hr., all the while bubbling a fine stream of dry nitrogen through the mixture *via* a capillary tube. The mixture was then heated under vacuum according to this schedule: 1 hr. at 150° (0.1 mm.); 1 hr. at 190° (0.01 mm.); 1 hr. at 240° (0.1 mm.). The residue (10 g.), upon cooling, was a glassy solid slowly soluble in dioxane and chloroform.

The procedure for polymerizing the hydroxy esters XVI–XX was the same except that no ethylene glycol was added to the reaction mixture.

Acknowledgment. The author wishes to thank Dr. E. M. Balis and associates of this laboratory for the microanalyses reported.

SCHENECTADY, N. Y.

---

[11] For a method of preparation see R. M. Lukes, G. I. Poos, and L. H. Sarett, *J. Am. Chem. Soc.*, **74**, 1401 (1952).

[CONTRIBUTION FROM RESEARCH CENTER, KOPPERS CO., INC.]

Polymers from Bisphenols. Steric Inhibition of Condensation Polymerization[1]

SAMUEL C. TEMIN

Received December 15, 1960

A series of substituted bisphenols were utilized in the attempted preparation of polyesters with adipic and sebacic acids Both *p,p'*- and *o,o'*-bisphenols, with alkylene or sulfide bridging groups, were examined. It was observed that, although all of the bisphenols readily formed diacetates with acetic anhydride, the diacetates of some of the bisphenols did not undergo the trans-acidolysis reaction which is necessary for polymerization to occur. The failure to polymerize can be related to steric hindrance and is explained in terms of transition states.

Polyesters derived from a diphenolic material and a dicarboxylic acid were first investigated by Bischoff.[2] Later, polyesters were prepared by reaction of hydroquinone diacetate with dicarboxylic acids.[3] This technique was used by Levine and Temin[4] to prepare bisphenol polyesters. Conix[5] and Eareckson[6] synthesized polyesters from acid chlorides and diphenates by interfacial polycondensation. Korshak and co-workers,[7] and others,[8] also prepared polyphenyl esters using acid chlorides. In addition, a large number of bisphenols have been used in preparing polycarbonates.[9] In this previous work it appeared that substitution in the benzene rings of a bisphenol lowered the softening point of the corresponding polyesters.

In the present work a variety of bisphenol alkanes and bisphenol sulfides were studied in an effort to prepare liquid polyesters. It was hoped that the introduction of sufficient bulky groups, particularly in the *o,o'*-bisphenols, would yield liquid polymers. This objective was not attained but it was noted that certain of the bisphenols

---

[1] Presented at 138th National Meeting of the American Chemical Society, New York, September, 1960.

[2] C. A. Bischoff and A. von Hedenstrom, *Ber.*, **35**, 3455 (1902).

[3] J. G. N. Drewitt and J. Lincoln, British Pat. **621,102** (1947); *Brit. Abstr.*, **1949**, BII, 1114; E. R. Wallsgrove and F. Reeder, British Pat. **636,429** (1950); *Chem. Abstr.*, **44**, 7878d (1950).

[4] M. Levine and S. C. Temin, *J. Polymer Sci.*, **28**, 179 (1958).

[5] A. Conix, *Ind. chim. belge*, **22**, 1457 (1957); *Ind. Eng. Chem.*, **5**, 147 (1949).

[6] W. M. Eareckson, *J. Polymer Sci.*, **40**, 399 (1959).

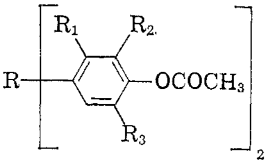
[7] V. V. Korshak and S. V. Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, **123**, 849 (1958); *Chem. Abstr.*, **53**, 8700c (1959); *Vysokomolekulyarnye Soedineniya*, **1**, 1482 (1959).

[8] N. I. Volynkin and G. I. Braginskii, U.S.S.R. Pat. **121,556** (1959); *Chem. Abstr.*, **54**, 7357d (1960).

[9] H. Schnell, *Angew. Chem.*, **68**, **633** (1956); *Ind. Eng. Chem.*, **51**, 157 (1959).

TABLE I

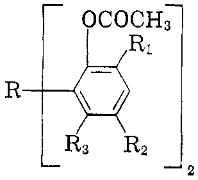
p,p'-BISPHENOL DIACETATES



No.	R	R_1	R_2	R_3	M.P.	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
1	S	CH_3	H	$—C(CH_3)_3$	88	70.5	70.6	7.7	7.8
2	$CHCH_3$	CH_3	H	$—CH(CH_3)_2$	99–100	76.1	76.3	8.3	8.3
3	$C(CH_3)_2$	H	CH_3	CH_3	59–60	75.0	75.2	7.7	7.6
4	—	H	$C(CH_3)_3$	$C(CH_3)_3$	215–216	77.7	77.8	9.4	9.4
5	S	H	$C(CH_3)_3$	$C(CH_3)_3$	88–89	70.5	70.4	7.7	7.7

TABLE II

o,o'-BISPHENOL DIACETATES



No.	R	R_1	R_2	R_3	M.P.	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
6	—	H	H	H	94–95	[a]			
7	CH_2	H	CH_3	H	59–60	73.1	73.2	6.5	6.5
8	CH_2	Cl	Cl	Cl	175–177	41.5	41.7	2.1	2.2
9	CH_2	Cl	$C(CH_3)_3$	H	92.3	64.5	64.3	6.5	6.5
10	S	$C(CH_3)_3$	CH_3	H	116	70.5	70.9	7.7	7.8
11	CH_3	$C(CH_3)_3$	CH_3	H	None	76.4	76.1	8.6	8.7
12	$CHCH_3$	$C(CH_3)_3$	H	CH_3	150	77.0	76.6	8.8	8.8
13	$C(CH_3)_3$	$C(CH_3)_3$	CH_3	H	163–164	77.0	77.2	8.9	9.0

[a] G. Kraemer and R. Weissgerber, *Ber.*, **34**, 1667 (1901).

could not be made to polymerize under the conditions used.

The polymerization reaction employed was the acidolysis of the bisphenol diacetate, with either adipic or sebacic acid, using magnesium metal as catalyst. The diacetates were prepared in essentially quantitative yields by reaction of the bisphenol with excess acetic anhydride in the presence of sulfuric acid.[4] The bisphenols and diacetates, mostly new compounds, are listed in Tables I and II.

A discussion of the phenomenon observed here involves the question of steric hindrance in phenols. Completely sterically hindered phenols were first observed by Stillson and co-workers.[10] They reported that hindrance of the phenolic function seemed to reach its maximum effect with an *o-t*-butyl group after examination of the chemical properties of several hindered bisphenols. They also reported that these hindered phenols did not readily yield acyl derivatives. They succeeded in preparing acetates only by elaborate techniques involving liquid ammonia or sodium-potassium alloy.

Coggeshall,[11] using spectroscopic means, classified phenols as unhindered, partially hindered, or hindered. The classification was based on the wave length shift, at approximately 2.7 μ, in going from a dilute solution to the crystalline state. Later, Sears and Kitchen[12] refined these measurements and described a "hydrogen bonding index" which was based on the infrared shift in going from a dilute solution to the liquid state. Coggeshall[11] considered a 2,6-dimethylphenol as "unhindered," a 2-methyl-6-*t*-butylphenol as "partially hindered," and a 2,6-di-*t*-butylphenol as "hindered." Sears and Kitchen[12] confirmed these generalizations but found also that the "*t,t*-octyl" group offered more hindrance than the *t*-butyl group. Recently, Puttnam,[13] basing his results on a

---

[10] G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Am. Chem. Soc.*, **67**, 303 (1945).

[11] N. D. Coggeshall, *J. Am. Chem. Soc.*, **69**, 1620 (1947).

[12] W. C. Sears and L. J. Kitchen, *J. Am. Chem. Soc.*, **71**, 4110 (1949).

[13] N. A. Puttnam, *J. Chem. Soc.*, 486 (1960).

spectroscopic measure of hydrogen bonding, concluded that alkyl groups, other than *t*-butyl in *ortho*-substituted phenols have only a slight effect on hydrogen bonding. Further, he reported that one *o-t*-butyl produces the same effect as an *o*-methyl coupled with a methyl, isopropyl, or *sec*-butyl group in the other *ortho* position.

The results obtained in the present work, based essentially on chemical reactivity, are in good agreement with the results of spectroscopic measurements. In general, one *o-t*-butyl group is insufficient to prevent polymerization, but if coupled with any other adjacent alkyl group, provides enough steric hindrance to inhibit the reaction. The results with one bisphenol (No. 3) indicate that two adjacent methyl groups are insufficient to prevent polymerization, a degree of hindrance in agreement with Puttnam.[13] Further, a chlorine group is shown to exert about the same steric effect as a methyl group on bisphenol reactivity. In summary, hindrance due to substitution, that leads to a spectroscopic classification of "hindered," is sufficient to inhibit the polymerization reaction.

Table III also illustrates that where hindrance is sufficient completely to prevent alkali solubility of a bisphenol, it is generally sufficient to inhibit the acidolysis reaction of its diacetate.

TABLE III

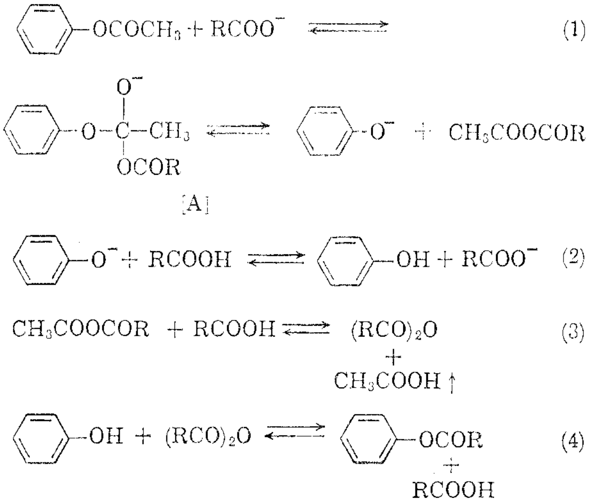
BISPHENOL POLYESTERS

Bisphenol				
No.	Alkali Soluble	Acid	Sb_2O_3, %[a]	Polymer, $\eta_{sp/c}$
1	P[b]	S[c]	0.05	0.094
2	P	S	0.17	0.098
3	P	S	0.05	0.064
4	No	S	0.17	None
5	No	S	0.17	None
6	Yes	S	0.17	0.22
7	Yes	A[d]	0	0.092
8	Yes	A	0	0.090
9	Yes	S	0	0.056
10	No	S	0.17[e]	None
11	No	A	0	None
12	No	A	0.05	None
13	No	S	0.05	None

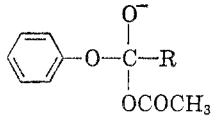
[a] All experiments included ~0.8% Mg ribbon as well. [b] Partially soluble. [c] Sebacic acid. [d] Adipic acid. [e] Same results obtained with no Sb_2O_3 present.

Nevertheless, all of the bisphenols readily yielded diacetates in essentially quantitative yield. It is somewhat puzzling that hindered bisphenols would readily undergo acylation but, as diacetates, not undergo acidolysis which is part of the polyesterification reaction. Reflection, however, indicates that different mechanisms must operate for the two reactions. Inhibition of polymerization in this case is an effect based on the difference in energy levels of initial and transition states. The importance of transition states in predicting steric hindrance to reactivity is well known.

Unfortunately, the mechanism of acidolysis reactions involving phenols seems to have been neglected in the literature although much attention has been given to the similar reactions of esterification, hydrolysis, and alcoholysis.[14] A scheme has been postulated for the acidolysis, Equations 1 to 4, which involves mixed anhydride formation and then interchange to liberate the more volatile acid. It is illustrated for a simple phenol acetate below:

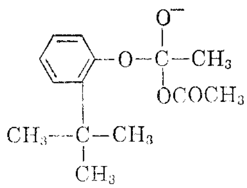


It is possible that, as Equation 1 is an equilibrium reaction, the phenoxide ion and mixed anhydride may also form the intermediate [A′], shown below. In this case an alternate route to the product, involving decomposition of [A′] to yield product and acetate ion, can be visualized.



[A′]

It is possible that the role of the catalyst is to furnish the positive cation not shown in Equations 1 and 2. Thus the initial attack may be by a catalyst cation rather than by carboxyl anion. In either case the transition state intermediate, [A], must involve a considerable amount of compressional energy as shown, for example, [B], with one *o-t*-



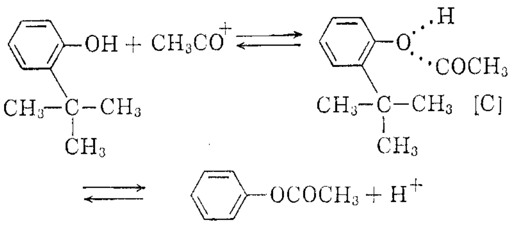
[B]

---

[14] See, for example, (a) J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, N. Y., 1956, chap. 12; (b) P. H. Hermans, *Introduction to Theoretical Organic Chemistry*, Elsevier, New York, 1954, Chap. 19; (c) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, New York, 1953, pp. 752 *ff*.

butyl group. Inspection of models[15] shows that the carbon of the acetate carbonyl is extremely hindered in 2,6-di-*t*-butylphenol acetate. The carbonyl group is forced out of coplanarity[16] with the ring and the transition state cannot be constructed. Kadesch[1] has discussed the relation of coplanarity to steric hindrance.

In contrast, the acetylation reaction must proceed by attack of an acetylium ion,[17] as sulfuric acid is used as a catalyst, on the phenolic oxygen. The reaction is shown, Equation 5, for an *o*-*t*-butylphenol. Inspection of models[5] shows that [C] is sterically possible even in the case of a 2,6-di-*t*-butylphenol. Although the —OH of the phenol is forced out of the plane of the ring, it is considerably more accessible than the carbonyl carbon of the phenol acetate. This is of some theoretical interest since the latter is one atom further removed from the ring than the phenolic oxygen.



(5)

Although the work reported here dealt only with bifunctional reagents, and consequently with a polymerization reaction, the application of this reaction to monofunctional reagents might be a useful tool in determining the steric effect of groups in positions adjacent to the functional group. It would also be of interest, in connection with mechanisms, to study the reaction of hindered phenols or bisphenols with acid chlorides and to investigate the hydrolysis of the hindered phenol acetates. Such a program is beyond the scope of the present investigation.

EXPERIMENTAL

All of the bisphenols were commercial samples or available in the Koppers laboratory.

The adipic and sebacic acid were pure commercial samples.

The bisphenol diacetates, Tables I and II, were obtained in essentially quantitative yields as previously described.[4] Frequently, the addition of sulfuric acid to the slurry of bisphenol in acetic anhydride caused a rise in temperature and immediate solution. Bisphenol No. 11, 2,2′-methylene bis-(6-*t*-butyl-4-methylphenol), did not give a crystalline diacetate although distillation gave a glass that could be ground to a powder.

The polymerization technique was similar to that previously described.[4] After about 3 hr. heating (200–230°) at atmospheric pressure (during which time the odor of acetic acid became apparent in the experiments where polymer resulted), the melts were subjected to heating *in vacuo*. The final 30 min., at least, was at 1 mm. pressure or less. The polymers described in Table III were all brittle glasses at room temperature.

In the experiments involving bisphenols No. 3, 4, 5, and 10, where no polymer was formed, an attempt was made to identify the material remaining in the tubes. Quantitative recovery was not attempted because part of the starting materials had distilled or sublimed out of the tube. However, it was possible to isolate, and identify, both starting materials in good yields. As an example, the manipulations, after attempted polymerization of bisphenol No. 5 diacetate and sebacic acid, are described. The solid remaining after heating was dissolved in acetone to remove inorganic matter and the acetone solution taken to dryness. The residue was triturated in the cold with sodium carbonate solution and the mixture filtered. The solid remaining on the filter was recrystallized from methanol-water to yield a product, m.p. 80–82°. A second recrystallization from petroleum ether gave a material melting at 84°. A mixed melting point with the original diacetate (m.p. 88°) gave 85–88°. The filtrate from the sodium carbonate treatment was acidified with sulfuric acid to precipitate a solid, m.p. 130–132°. A mixed m.p. with authentic sebacic acid gave 130–133°.

CONCLUSIONS

The results of the polymerization attempts are given in Table III. The data clearly demonstrate that in a bisphenol where the hydroxy groups are situated between a *t*-butyl group and one other group, no polymer is formed. Thus all *o,o′*-bisphenols with *t*-butyl groups in the 3-position (Nos. 10, 11, 12, and 13) did not yield polymers. A 3-(or 5-)*t*-butyl alone (No. 1) in a *p-p′*-bisphenol is not sufficient to prevent polymerization.

Where polymers were not obtained, the starting materials could be recovered (see Experimental). These results, therefore, present an instance of steric inhibition of a reaction used to effect condensation polymerization. Numerous examples of steric hindrance to addition polymerization have been reported,[18] but this appears to be the first report of steric inhibition in condensation polymerizations.

Acknowledgment. The author is grateful to Dr. R. D. Hinkel and his staff for analyses and to Dr. A. V. DiGiulio for helpful discussions of the mechanism presented here.

PITTSBURGH, PA.

---

(15) Fisher-Taylor-Hirschfelder Models.

(16) R. G. Kadesch, *J. Am. Chem. Soc.*, **66**, 1207 (1944).

(17) See C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, New York, 1953, p. 295.

(18) P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 246–248; C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, pp. 127–131.