Synthesis of Dimeric and Trimeric 2-(*p*-Tolyloxy)ethyl Acetate-Formaldehyde Polymer Model Compounds

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The dimeric and trimeric 2-(*p*-tolyloxy)ethyl acetate–formaldehyde polymer model compounds and the halogenated compound of the dimer were synthesized. 2,2′-Methylenebis(5-methyl-1,2-phenyleneoxy)diethyl acetate was synthesized by the reaction of 2-(*p*-tolyloxy)ethyl acetate with formaldehyde in acidic media. 2-[2-(2-Acetoxyethoxy-3-chloro-5-methylbenzyl)-4-methylphenoxy]ethyl acetate was prepared by the reaction of 6-chloro-4,4′-dimethyl-2,2′-methylenediphenol with 2-chloroethanol, followed by treatment with acetic anhydride, and 2-[2,6-bis(2-acetoxyethoxy-5-methylbenzyl)-4-methylphenoxy]ethyl acetate from 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol.

A high molecular weight polymer was obtained[2] by the reaction of 2-(*p*-tolyloxy)ethyl acetate with formaldehyde in acetic acid solution in the presence of perchloric acid as a catalyst.

We have synthesized the dimeric and trimeric 2-(*p*-tolyloxy)ethyl acetate–formaldehyde polymer model compounds and the halogenated compound of the dimer.

Synthesis of the Dimeric Compounds. The dimer of 2-(*p*-tolyloxy)ethyl acetate–formaldehyde polymer model compounds and the halogenated compound were synthesized as shown in Chart 1. The reaction of 4,4′-dimethyl-2,2′-methylenediphenol(**1**) with 2-chloroethanol and sodium gave 2-[2-(2-hydroxy-5-methylbenzyl)-4-methylphenoxy]ethanol(**5**) in an 83% yield, but not 2,2′-methylenebis(5-methyl-1,2-phenyleneoxy)-diethyl acetate (**8**). 6-Chloro-4,4′-dimethyl-2,2′-methylenediphenol(**2**) gave 2-[2-(2-hydroxyethoxy-3-chloro-5-methylbenzyl)-4-methylphenoxy]ethanol(**6**) in a 75% yield. **6** was acetylated with acetic anhydride to form 2-[2-(2-acetoxyethoxy-3-chloro-5-methylbenzyl)-4-methylphenoxy]ethyl acetate (**7**).

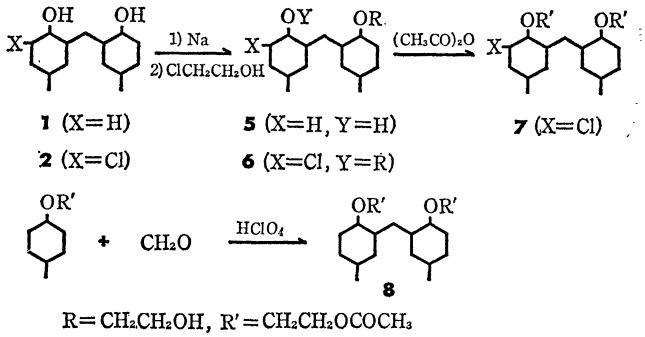


Chart 1.

The reaction of 2-(*p*-tolyloxy)ethyl acetate with formaldehyde in acetic acid solution in the presence of perchloric acid as a catalyst gave **8**.

Synthesis of the Trimeric Compounds. The reaction of 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol(**3**) with 2-chloroethanol and sodium gave mono, di, and tri ethanol derivatives; 2-(2-hydroxyethoxy-5-methylbenzyl)-6-(2-hydroxy-5-methylbenzyl)-4-methylphenol(**9**), 2,6-bis(2-hydroxyethoxy-5-methylbenzyl)-4-methylphenol(**10**), and 2-[2,6-bis(2-hydroxyethoxy-5-methylbenzyl)-4-methylphenoxy]ethanol(**11**). The tri

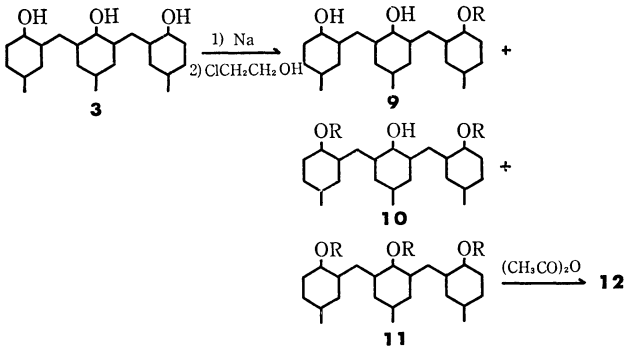


Chart 2.

ethanol derivative(**11**) was acetylated to give the desired compound; 2-[2,6-bis(2-acetoxyethoxy-5-methylbenzyl)-4-methylphenoxy]ethyl acetate(**12**)(see Chart 2).

2-(2-Hydroxyethoxy-3-chloro-5-methylbenzyl)-6-(2-hydroxyethoxy-5-methylbenzyl)-4-methylphenol(**13**) was isolated in a low yield from the reaction product of 2-(2-hydroxy-3-chloro-5-methylbenzyl)-6-(2-hydroxy-5-methylbenzyl)-4-methylphenol(**4**) with 2-chloroethanol and sodium.

Hydrogen Bonds of the Oligomeric Phenols. The presence of hydrogen bonds has been postulated to explain the peculiar behavior of certain phenolic resin intermediates.[3] Infrared spectroscopic,[4–7] potentiometric,[8–10] and kinetic[11] results showed the presence of intramolecular OH···OH-bonds in a number of polyphenols of novolak type. The IR spectral data of the oligomeric phenols are given in Table 1. Compound **1** exhibits three OH absorptions in carbon tetrachloride in line with the previous IR studies.[7] The concentration-independent band at 3553 cm^{-1} has been assigned to an intramolecular OH···OH-bond. The band at 3605 cm^{-1} can be assigned to the stretching vibrations of the free OH group, while the broad concentration-dependent band at 3300 cm^{-1} is assigned to the closed ring of H-bonds resulting from dimeric association. On account of the intramolecular OH··· OH-bond as illustrated in I, the reactivity of the hydrogen-bonded OH group of **1** might be lower than that of the free OH group.

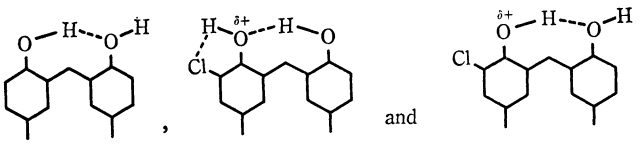
Compound **2** has a more complex spectrum, show-

Table 1. Hydroxy stretching frequencies, ν(OH) of the oligomeric phenols in carbon tetrachloride

Compound	Concn. (mM)	ν (cm^{-1})	ε	Concn. (mM)	ν (cm^{-1})	ε	Assignments
p-Cresol	25	3615	211				Free
		3480	8				Inter
2-Chloro-*p*-cresol	25	3610	12				Free
		3553	108				Intra OH···Cl
1	25	3605	98	2.5	3605	180	Free
		3460	116		3470	132	Intra OH···OH
		3300 br	154				Inter
2	25	3610	63	2.5	3615	68	Free
		3532	151		3532	160	Intra OH···Cl
		3490	121		3495	116	Intra OH···OH
		3375	123				Inter
		3240	85				Inter
3	4.0	3590	32				Free
		3350 sh					Intra OH···OH
		3214 br	241				Inter
4	3.0	3525	152				Intra OH···Cl
		3418 br	206				Intra OH···OH
		3240	152				Inter

All the samples were examined in 1.0 mm. cells. br, broad. sh, shoulder.

ing three concentration-independent bands in the OH region. The band at 3610 cm^{-1} is characteristic of the free OH group. Two bands at 3545 and 3490 cm^{-1} can be assigned to an intramolecular OH···Cl-bond and an intramolecular OH···OH-bond, respectively. Thus, we suggest that two conformers (II-a and II-b) are present in compound **2**.



I II-a and II-b

The intramolecular OH···OH-bond of type II-a might be weaker than that of **1** on account of the electron withdrawing of Cl-atom and the fact that the OH···Cl-bond is weaker than the OH···OH-bond, while the H-atom having the H-bond of type II-b might easily be released from phenol nucleus.

Actually, 2-chloro-*p*-cresol, which has mainly a *cis*-form[12] involving an intramolecular OH···Cl-bond (3553 cm^{-1}), gave 2-chloro-4-methylphenoxy-ethanol in a 70% yield.[13] The bonding shift of the intramolecular H-bond of **1** (Δ145 cm^{-1}) is higher than that of **2** (Δ120 cm^{-1}).

This stronger intramolecular H-bond might disturb the addition reaction.

Compound **3** shows the presence of three OH absorptions. From the previous results,[4] we assign two bands at 3590 and 3350 cm^{-1} to an intramolecular OH···OH···OH-bond, two H-atoms being involved in an intramolecular H-bond. Compound **4** shows three OH absorptions. Two bands at 3525 and 3148 cm^{-1} are assigned to an intramolecular OH···OH···OH···Cl-bond. The broad, concentration-dependent, band at 3240 cm^{-1} is assigned to the intermolecular H-bonds.

However, these spectroscopic studies can give no explanation for the present synthetic results.

Experimental

General. Melting points are uncorrected. ^{1}H-NMR spectra were taken on a JEOL Model PS-100 spectrometer in a deuterochloroform or carbon tetrachloride solution, with tetramethylsilane as an internal standard. Chemical shift values are given in terms of τ. IR spectra were obtained on a Hitachi EPI-G2 or a Hitachi Model 225 spectrophotometer. Mass spectra were obtained on a Hitachi RMU-6 mass spectrometer at 70 eV.

Materials. 2-(*p*-Tolyloxy)ethyl acetate; bp 92—94 °C/2 mmHg[2] [lit,[2] 104—110 °C/5 mmHg], 2-chloro-*p*-cresol; bp 82—83 °C/13 mmHg[14] [lit,[14] 195—197 °C], 4,4′-dimethyl-2,2′-methylenediphenol(**1**); mp 123—125 °C[15] [lit,[15] 126 °C], 6-chloro-4,4′-dimethyl-2,2′-methylenediphenol (**2**); mp 168—172 °C[16] [lit,[16] 170 °C], 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol(**3**); mp 214—217 °C[15] [lit,[15] 215 °C], and 2-(2-hydroxy-3-chloro-5-methylbenzyl)-6-(2-hydroxy-5-methylbenzyl)-4-methylphenol(**4**); mp 188—190 °C[17] [lit,[17] 187 °C] were prepared by the methods in the literature. All other reagents were commercial products.

*2-[2-(2-Hydroxy-5-methylbenzyl)-4-methylphenoxy]ethanol(**5**).* A mixture of **1** (45.6 g) and sodium (11 g) in ethanol (140 ml) was stirred for 16.5 hr at 80 °C. 2-Chloroethanol (41.6 g) was then added to the solution and refluxed for 20.5 hr. After being cooled, the product which separated was recrystallized from ligroin to give colorless plates (**5**); yield, 44 g (83%), mp 99—100 °C. IR(KBr); 3375 and 3240 cm^{-1}. NMR ($CDCl_3$, 5.0%); 2.88—3.48 (6H, m, phenyl), 5.01 (2H, b, OH), 5.76—6.30 (6H, m, CH_2CH_2 and $PhCH_2Ph$), 7.74(3H, s, CH_3), and 7.79 (3H, s, CH_3). MS; *m/e* 272 (M^+). Found: C, 75.18; H, 7.38%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.

5 (2.7 g) was refluxed with acetic anhydride (20 ml) for 5 hr to give 2-[2-(2-acetoxy-5-methylbenzyl)-4-methylphenoxy]ethyl acetate; yield, 3.1 g, mp 50—51.8 °C (from ligroin). IR(KBr); 1750 cm^{-1}. Found: C, 70.69; H, 6.66%.

Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79%.

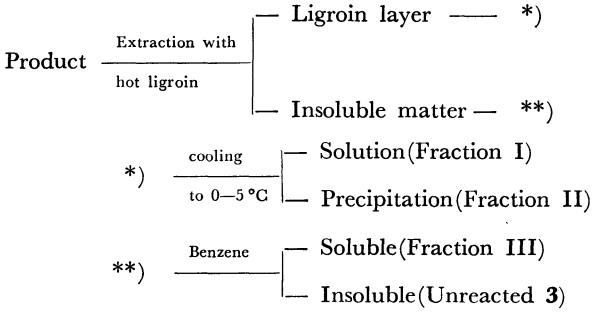
2-[2-(2-Acetoxyethoxy-3-chloro-5-methylbenzyl)-4-methylphenoxy]-ethyl Acetate (7). **2** (105 g) was added to a solution of sodium (22.1 g) in ethanol (280 ml). After being stirred for 14 hr at refluxing temperature, 2-chloroethanol (80.5 g) was added to the reaction mixture at room temperature and the mixture was refluxed for 17 hr. The precipitated sodium chloride was removed and the filtrate was cooled to 0 °C to give white crystal (105 g); 2-[2-(2-hydroxyethoxy-3-chloro-5-methylbenzyl)-4-methylphenoxy]ethanol (**6**). yield, 85%; mp 114—116 °C (from a mixture of benzene and ligroin). IR(KBr); 3440 and 3390 cm^{-1}. Found: C, 64.52; H, 6.78%. Calcd for $C_{19}H_{23}O_4Cl$: C, 65.05; H, 6.61%.

A mixture of **6** (70 g) and acetic anhydride (204 g) was refluxed for 13 hr. After the solvents had been removed, benzene solution of the residue was washed successively with sodium hydroxide solution and water, dried over anhydrous sodium sulfate, and then distilled to give **7** (70 g) as a colorless viscous liquid; bp 205—210 °C/0.001 mmHg. IR(neat); 1735 cm^{-1}. NMR (CCl_4, 10%); 3.04—3.50 (5H, m, phenyl), 5.58—6.15(8H, m, $C\underline{H}_2C\underline{H}_2$), 6.13(2H, s, $PhC\underline{H}_2Ph$), 7.72(3H, s, $PhC\underline{H}_3$), 7.82(3H, s, $PhC\underline{H}_3$), 8.02(3H, s, $COC\underline{H}_3$), and 8.06 (3H, s, $COC\underline{H}_3$). MS; *m/e* 434(M^+). Found: C, 63.21; H, 6.19%. Calcd for $C_{23}H_{27}O_6Cl$: C, 63.52; H, 6.26%.

2,2'-Methylenebis(5-methyl-1,2-phenyleneoxy)diethyl Acetate (8). Perchloric acid (10 ml) was added to a solution of 2-(*p*-tolyloxy)ethyl acetate (14.4 g) and paraformaldehyde (0.7 g) in acetic acid (70 ml). The reaction mixture was stirred for 30 hr at 30 °C. After completion of the reaction, the mixture was poured into water and washed with water. Oily product was recrystallized from benzene to give **8** (7.2 g); colorless plates, mp 98—101 °C. IR(KBr); 1730 cm^{-1}. NMR (CDCl$_3$, 15%); 2.98—3.41(6H, m, phenyl), 5.53—6.04(8H, m, $C\underline{H}_2C\underline{H}_2$), 6.01(2H, s, $PhC\underline{H}_2Ph$), 7.78(6H, m, $PhC\underline{H}_3$), and 7.95(6H, s, $COC\underline{H}_3$). MS: *m/e* 400(M^+). Found: C, 68.72; H, 7.21%. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05%.

After **8** (2.0 g) was refluxed in methanol (17 ml) containing NaOH (0.5 g) for 2 hr, the reaction mixture was poured into ice water. White precipitate was recrystallized from benzene to give 2,2'-methylenebis(5-methyl-1,2-phenyleneoxy)diethanol (1.5 g); mp 105—107 °C. IR(KBr); 3350 cm^{-1}. Found: C, 72.26; H, 7.68%. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65%.

Reaction of 3 with 2-Chloroethanol. **3** (52 g) was added to a solution of sodium (12.4 g) in ethanol (250 ml). After being kept at 80 °C for 25 hr, 2-chloroethanol (45 g) was added to the solution and refluxed with stirring for 20 hr. After the reaction, the reaction mixture was concentrated to give a residue which separated three compounds according to the given scheme.



The compound(Fraction I) easily soluble in ligroin was recrystallized from ligroin. Colorless needle crystals were obtained, mp 146—149 °C. Yield, 0.82 g. IR(KBr): 3360 and 3250 cm^{-1}. NMR(CDCl$_3$, 14%); 1.98—2.44(2H, b, O$\underline{H}$), 2.90—3.36(8H, m, phenyl), 5.82—6.18 (8H, m, $C\underline{H}_2$-$C\underline{H}_2$), 6.17(2H, s, $PhC\underline{H}_2Ph$), 6.20(2H, s, $PhC\underline{H}_2Ph$), 7.40—7.60(1H, b, O$\underline{H}$), 7.73(3H, s, $C\underline{H}_3$), and 7.77(6H, s, $C\underline{H}_3$). MS; *m/e* 392(M^+). Found: C, 76.14; H, 7.14%. Calcd for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19%. The compound was concluded to be 2-(2-hydroxyethoxy-5-methylbenzyl)-6-(2-hydroxy-5-methylbenzyl)-4-methylphenol (**9**). A solution of **9** (0.2 g) in acetic anhydride (10 ml) was treated by the previous method to give acetylated compound (0.1 g); colorless needle, mp 95—97 °C. IR(KBr); 1750 cm^{-1}. Found: C, 71.73; H, 6.62%. Calcd for $C_{31}H_{34}O_7$: C, 71.80; H, 6.60%.

The hot ligroin soluble compound(Fraction II) was recrystallized from benzene to give 2,6-bis(2-hydroxyethoxy-5-methylbenzyl)-4-methylphenol(**10**); colorless plate, mp 115—120 °C, yield, 3.5 g. IR(KBr); 3400 cm^{-1}. NMR(CDCl$_3$, 5.0%); 2.90—3.45(8H, m, phenyl), 4.60—5.50(3H, b, O$\underline{H}$), 5.85—6.30(8H, m, $C\underline{H}_2C\underline{H}_2$), 6.14(2H, s, $PhC\underline{H}_2Ph$), 7.75 (6H, s, $C\underline{H}_3$), and 7.83 (3H, s, $C\underline{H}_3$). MS; *m/e* 436(M^+). Found: C, 74.09; H, 7.46%. Calcd for $C_{27}H_{32}O_5$: C, 74.29; H, 7.39%. The acetylation of **10** gave oily product. IR(neat); 1730 cm^{-1}. Found: C, 70.04; H, 6.87%. Calcd for $C_{33}H_{38}O_8$: C, 70.44; H, 6.81%.

2-[2,6-Bis(2-hydroxyethoxy-5-methylbenzyl)-4-methylphenoxy]ethanol(**11**) was obtained by repeated crystallizations from the fraction III, with benzene as a solvent; mp 118—121 °C, yield, 2.2 g. IR(KBr): 3400 cm^{-1}. NMR (CDCl$_3$, 2.0%); 2.85—3.45(8H, m, phenyl), 5.90—6.40(15H, m, $C\underline{H}_2C\underline{H}_2$ and O$\underline{H}$), 6.60(4H, s, $PhC\underline{H}_2Ph$), 7.72(3H, s, $C\underline{H}_3$), and 7.83(6H, s, $C\underline{H}_3$). MS; *m/e* 480(M^+). Found: C, 72.45; H, 7.48%. Calcd for $C_{29}H_{36}O_6$: C, 72.48; H, 7.55%.

2-[2,6-Bis(2-acetoxyethoxy-5-methylbenzyl)-4-methylphenoxy]ethyl Acetate(12). A sample of **11** (1 g) was refluxed with acetic anhydride (20 ml) to give **12** (0.8 g); colorless plate, mp 64—65 °C (from ligroin). IR(KBr); 1735 cm^{-1}. NMR (CDCl$_3$, 5.0%); 2.90—3.40(8H, m, phenyl), 5.50—6.00(12H, m, $C\underline{H}_2C\underline{H}_2$), 6.04(4H, s, $PhC\underline{H}_2Ph$), 7.78(6H, s, $PhC\underline{H}_3$), 7.86(3H, s, $PhC\underline{H}_3$), 7.97(3H, s, $COC\underline{H}_3$), and 7.99(6H, s, $COC\underline{H}_3$). MS; *m/e* 606(M^+). Found: C, 69.02; H, 6.93%. Calcd for $C_{35}H_{42}O_9$: C, 69.29; H, 6.98%.

Reaction of 4 with 2-Chloroethanol. **4** (46 g) was added to a solution of sodium (9.9 g) in ethanol (150 ml). The resulting solution was stirred at 80 °C for 22 hr, 2-chloroethanol (36 g) then being added. The mixture was refluxed for 22 hr. After being cooled, the residue which separated was recrystallized from a mixture of ligroin and dioxane to give 2-(2-hydroxyethoxy-3-chloro-5-methylbenzyl)-6-(2-hydroxyethoxy-5-methylbenzyl)-4-methylphenol (**13**); colorless plate, mp 143—145 °C, yield, 3 g. IR(KBr): 3400 cm^{-1}. NMR (CDCl$_3$, 7.0%); 2.89—3.45(7H, m, phenyl), 5.26—6.35 (15H, m, $PhC\underline{H}_2Ph$ and $C\underline{H}_2C\underline{H}_2$), 7.25(3H, s, $C\underline{H}_3$), 7.79(3H, s, $C\underline{H}_3$), and 7.84(3H, s, $C\underline{H}_3$). MS; *m/e* 470(M^+). Found: C, 68.90; H, 6.67%. Calcd for $C_{27}H_{31}O_5Cl$: C, 68.85; H, 6.63%. Acetylated compound of **13** was an oily substance. IR (neat); 1750 cm^{-1}. Found: C, 66.52; H, 6.22%. Calcd for $C_{33}H_{37}O_8Cl$: C, 66.38; H, 6.25%.

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