factor responsible for the configuration of the next inserted monomer molecule, but that the catalytic complex, perhaps including a complexed or reacted monomer molecule,[17] can also play an appreciable role.

Work is in progress to establish whether stereoselectivity and stereoelectivity are dependent on the racemic and optically active monomer structure as well as on the nature of the catalyst and on the ratio (R_m) of the racemic monomer to the optically active one.

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Poly(2,6-diaryl-1,4-phenylene oxides)

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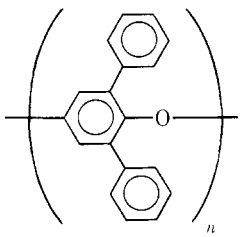
ABSTRACT: Some 2-aryl-6-phenylphenols have been synthesized by a variety of routes. Several phenols have been prepared by reaction of various substituted cyclohexanones with the Grignard reagent prepared from 2-chloro-6-phenylanisole followed by dehydrogenation and demethylation. The most general route identified is *via* condensation of acrolein with substituted dibenzyl ketones followed by dehydrogenation. High molecular weight polymers have been prepared by oxidative coupling only from phenols which do not have substituents in the *ortho* position of the pendant aryl group.

A recent publication[1] described the successful oxidative polymerization of 2,6-diphenylphenol (I) to a high molecular weight aromatic polyether, poly(2,6-diphenyl-1,4-phenylene oxide) (II). A search of the literature failed to disclose other syntheses of



II

2,6-diarylphenols without substituents in the other positions, and the synthesis of a number of such compounds by a variety of methods as well as their polymerization is the subject of the present paper.

A. Plesek[2] self-condensed cyclohexanone in the presence of sodium hydroxide to a mixture of cyclohexanone trimers which, as a structure proof, were converted to 2,6-diphenylphenol by a dehydrogenation reaction.

B. Treatment of 2-phenoxybiphenyl with phenylsodium yields 2,6-diphenylphenol as a product. Minor amounts of 2,6-diphenylphenol were also obtained from diphenyl ether and phenylsodium.[3] In addition, the compound has been observed as a by-product in the related commercial synthesis of phenol from chlorobenzene by treatment with aqueous alkali at elevated temperatures.[4]

C. The synthesis of 2,6-diphenyl-4-nitrophenol from nitromalonaldehyde and dibenzyl ketone was first described by Hill[5] and has been used by Luttringhaus[6] and Oki[7] as an intermediate in the synthesis of 2,6-diphenylphenol.

D. Betts and Davey[8] have also prepared 2,6-diphenylphenol by a sequence of reactions starting with the condensation of malonic ester with 2,4-diphenyl-3-oxobutyltrimethylammonium iodide which yields the intermediate 2,6-diphenyl-1,3-cyclohexanedione.

Results and Discussion

I. Synthesis of Phenols. None of these routes has been found to be readily adaptable as a general synthesis for 2,6-diarylphenols; hence a number of other routes were examined as follows.

E. Phenol or *o*-phenylphenol can be alkylated with cyclohexene to yield 2,6-dicyclohexylphenol or 2-cyclohexyl-6-phenylphenol, respectively,[9] both of which can be dehydrogenated to 2,6-diphenylphenol. Since appropriately substituted cyclohexenes are not readily available and the alkylation with substituted cyclohexenes would yield isomers, no other diarylphenols were synthesized by this route.

The self-condensation of cyclohexanone (method A) has been extended to 2-cyclohexylcyclohexanone. Subsequent dehydrogenation of the dimeric product gave a low yield of 2-(2-biphenylyl)-6-phenylphenol (IVd). Similarly from 2-methylcyclohexanone we have prepared 2-methyl-6-*o*-tolylphenol (V).

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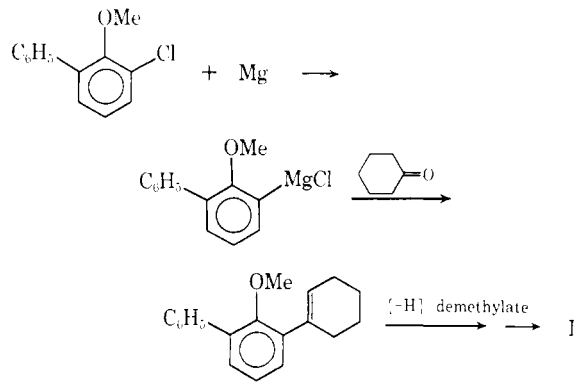
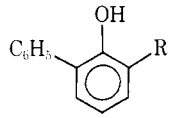
F. Several 2,6-diarylphenols were prepared by Scheme I which uses the synthesis of 2,6-diphenylphenol

SCHEME I



as an illustration. In this manner the following phenols (IV, R = a, *m*-tolyl; b, *p*-tolyl; c, *p*-*t*-butylphenyl; d, *o*-biphenylyl; e, 3′-*o*-terphenylyl; f, α-naphthyl) were prepared.

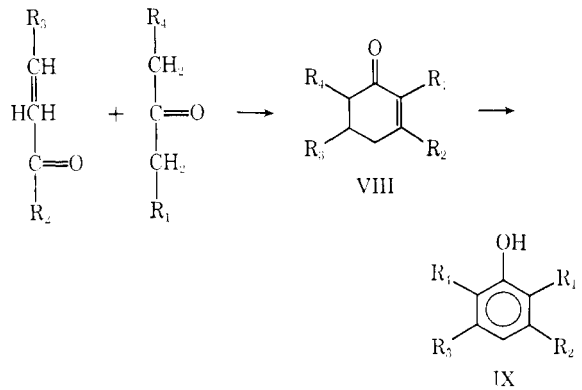


IV

G. The synthesis of 2-(3-biphenylyl)-6-phenylphenol (VII) was achieved *via* cleavage of 4,6-diphenyldibenzofuran (VI) with lithium–biphenyl adduct. The 4,6-diphenyldibenzofuran was obtained by metalation of dibenzofuran with butyllithium followed by reaction with cyclohexanone and subsequent dehydration and dehydrogenation. The synthesis of a number of substituted dibenzofurans and their cleavage will be the subject of another paper.

H. In 1904, Weland[10] reported on the facile condensation of dibenzyl ketone with cinnamaldehyde in the presence of diethylamine which yields VIII (R_1, R_3, R_4 = C_6H_5, R_2 = H). This ketone can be readily dehydrogenated to yield 2,3,6-triphenylphenol (IX) (Scheme II). By condensing dibenzyl ketone with

SCHEME II



acrolein we have synthesized 2,6-diphenyl-2-cyclohexenone which can be dehydrogenated to 2,6-diphenylphenol. This route is potentially useful as a general route to aryl phenols. The synthesis of 2,3,5,6-tetraphenylphenol (IX, R_1 = R_2 = R_3 = R_4 = C_6H_5–) from dibenzyl ketone and benzalacetophenone using sodium methoxide as the catalyst has been reported.[11]

TABLE I

Polymerizn method	Monomer	$[\eta]^a$	T_g^b
A′	IVa	0.16	
B′	IVa	0.17	219
A′	IVb	0.44	
B′	IVb	0.58	218
A′	IVc	0.43	
B′	IVc	0.59	240
A′	IVd	0.14	
B′	IVd	0.09	211
A′	IVe	0.24	
B′	IVe	0.28	212
A′	IVf	0.20	
B′	IVf	0.13	234

[a] Units of deciliters per gram measured in chloroform at 25°. [b] Differential scanning calorimetry.

II. Polymerization. The oxidative polymerization of 2,6-diphenylphenol can be effected with oxygen using an amine complex of a copper salt as catalyst,[1] or with lead dioxide as oxidant.[12] Silver oxide which has been used to prepare low molecular weight polymers from 2,6-dimethylphenol[13] can also be used.

These three methods, as described in the Experimental Section, give comparable results in the oxidative polymerization of a variety of 2,6-diarylphenols. Method C′ is included since it represents the preferred method for larger scale polymer synthesis. The results are outlined in Table I. Satisfactory elemental analyses were obtained for all polymers.

High molecular weight polymers are only obtained from monomers which are free of substituents in the *ortho* position of the pendant phenyl. Apparently the introduction of any substituent in these *ortho* positions offers enough steric hindrance to hinder the carbon–oxygen coupling reaction leading to polymer. The effect of steric hindrance on polymer formation has previously been observed.[14]

All of the polymers are unsymmetrical since in each case one of the pendant aryl groups is phenyl and the other carries substituents. The glass temperatures (Table I) are all in the same region as the parent polymer II;[1] however, analysis by differential scanning calorimetry indicated no trace of crystallinity in any of these polymers whereas the parent polymer II crystallizes readily and melts in the neighborhood of 500°.[1]

Experimental Section

Method A. Synthesis of 2-(2-Biphenylyl)-6-phenylphenol (IVd) from 2-Cyclohexylcyclohexanone. To a 1-l. round-bottomed flask equipped with a condenser and Dean–Stark trap was added 500 g (2.77 mol) of 2-cyclohexylcyclo-

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(13) B. O. Lindgren, *Acta. Chem. Scand.*, 14, 1203 (1960).

(14) A. S. Hay, *J. Polym. Sci.*, 58, 581 (1962).

hexanone, 20 g of potassium hydroxide, 50 ml of toluene, and 10 ml of water. The reaction was refluxed for 5 hr, cooled, washed with dilute hydrochloric acid, then water, dried, and distilled. After removal of unreacted 2-cyclohexylcyclohexanone a fraction (159.4 g, 0.47 mol), bp 180–220° (0.4 mm), which corresponded to the dimer was collected. This fraction was heated with 20 g of 3% palladium on carbon catalyst for 8 hr at 225° (15 mm), then at 310° at atmospheric pressure for 4 hr. The reaction mixture was diluted with the same volume of toluene and extracted with Claisen's alkali. There was obtained 13 g (0.04 mol, 8.7% yield based on dimer) of a solid which after recrystallization from methanol had mp 117°. It was identical with IVd prepared by method F.

2-Methyl-6-(2-methylphenyl)phenol V. Condensation of 2-methylcyclohexanone followed by catalytic dehydrogenation of the dimer as in the preceding example resulted in a 65% yield of V, bp 110° (1 mm). *Anal.* Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.39; H, 7.33.

Method E. Dehydrogenation of 2-Cyclohexyl-6-phenylphenol to 2,6-Diphenylphenol. To a 250-ml three-necked flask equipped with a magnetic stirrer, thermometer, and condenser was added 50 g (0.02 mol) of 2-cyclohexyl-6-phenylphenol and 6 g of palladium on alumina. The reaction flask was evacuated (15 mm) and heated 5 hr at 260°. The reaction mixture was worked up as described in method F to yield 33.5 g (0.136 mol, 69% yield) of 2,6-diphenylphenol.

Method F. General Procedure. 2-*t*-Butylphenyl-6-phenylphenol. To a thoroughly dried, 1-l., three-necked flask equipped with a condenser, stirrer, and nitrogen inlet was added 24.3 g (1.0 mol) of magnesium turnings and 30 ml of anhydrous ether. To the stirred mixture there was added dropwise 218 g (1.0 mol) of 2-chloro-6-phenylanisole dissolved in 240 ml of purified tetrahydrofuran. After all of the anisole was added the reaction mixture was allowed to stir at room temperature for 2 hr and then heated at reflux for a further 2 hr. After cooling to room temperature there was added dropwise over a 1.5-hr period 154.0 g (1.0 mol) of 4-*t*-butylcyclohexanone. A vigorous reaction ensued and the reaction mixture was maintained at reflux for 2 hr. The reaction mixture was cooled to room temperature and dilute hydrochloric acid cautiously added. The reaction mixture was flooded with water and extracted with ether, the ether layer was dried over anhydrous magnesium sulfate, and the product distilled (148.5 g, bp 200–225° (0.2 mm)). To this intermediate product was added 20 g of 5% palladium-on-carbon catalyst and the reaction mixture was slowly heated to 300° and held there (2 hr) until no more hydrogen evolution could be detected. After cooling to room temperature the catalyst was separated and the product treated with 225 ml of 57% aqueous hydrogen iodide and 225 ml of glacial acetic acid at reflux for 24 hr. The reaction mixture was then flooded with water and the oily product taken up in 900 ml of *n*-heptane. The heptane was washed four times with 200 ml of 12% aqueous sodium hydroxide; then the product was separated by washing with three 500-ml portions of Claisen's alkali.[15] The Claisen's alkali layer was flooded with water and the product taken up in ether. After evaporation of the ether there was obtained 90.7 g (0.30 mol, 30% yield) of 2-(4-*t*-butylphenyl)-6-phenylphenol (IVc). After one recrystallization from *n*-heptane it had mp 80.0–81.6°. *Anal.* Calcd for $C_{22}H_{22}O$: C, 87.4; H, 7.3. Found: C, 87.1; H, 7.4.

(15) Claisen's alkali is prepared by dissolving 88 g of potassium hydroxide in 63 ml of water, cooling, and diluting to 250 ml with methanol.

TABLE II

Phenol	Yield, %	Mp, °C
IVa	25.0	
IVb	12.6	62–63
IVd	16.6	117
IVe	13.6	161–163
IVf	9.4	94–95

The following new phenols (Table II) were prepared in a similar fashion. Satisfactory analyses were obtained in all cases.

Method H. 2,3,6-Triphenylphenol (IX). To a 500-ml round-bottomed flask equipped with a condenser was added 113.5 g (0.54 mol) of dibenzyl ketone, 72 g (0.54 mol) of cinnamaldehyde, and 50 ml of diethylamine. An exothermic reaction took place. After 30 min there was added 1 l. of ethanol and the mixture was cooled and filtered. There was obtained 155 g (0.48 mol, 88.9% yield) of 2,3,6-triphenyl-2-cyclohexenone. This product was mixed with 10 g of 3% palladium-on-carbon catalyst and heated to 270°. A rapid evolution of hydrogen ensued which ceased after 30 min. The reaction mixture was cooled and dissolved in hot ethyl acetate, filtered, and cooled to yield 94.0 g of IX (0.29 mol, 60.4% yield based on 2,3,6-triphenyl-2-cyclohexenone), mp 164°. *Anal.* Calcd for $C_{22}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.1; H, 5.1.

2,6-Diphenylphenol. To a 250-ml round-bottomed flask equipped with a condenser and magnetic stirrer was added 100 g (0.48 mol) of dibenzyl ketone and 30 ml of N,N,N′,N′-tetramethylethylenediamine. With vigorous stirring over a 1-hr period there was added 26.7 g (0.48 mol) of acrolein. After standing for 48 hr at room temperature the reaction mixture was distilled to yield 57.7 g (0.23 mol, 48.6% yield) of 2,6-diphenyl-2-cyclohexenone, bp 190–210° (0.2 mm), mp 65–66.5°. Dehydrogenation of 40 g (0.16 mol) of this product for 20 min at 270° in the presence of 10 g of 3% palladium on carbon catalyst gave after work-up as described in method F 0.066 mol (41.4% yield based on 2,6-diphenyl-2-cyclohexenone) of 2,6-diphenylphenol, mp 101°.

Polymerization. Three methods of polymerization were used as illustrated in the following general procedures.

Method A′. The phenol (2.0 g) was dissolved in 50 ml of benzene in a 150-ml screw-cap bottle and 10.0 g of silver oxide was added. The bottle was shaken overnight (16.0 hr); then the excess silver and silver oxide were removed by filtration and the polymer was isolated by precipitation into 500 ml of methanol. The polymer was redissolved in chloroform, filtered through Supercel, and the polymer again isolated by precipitation with methanol. The polymer was separated by filtration and dried *in vacuo* at 110° for 3 hr.

Method B′. This method is essentially the same as method A′ except 10.0 g of lead dioxide + 1.5 g of water was used as the oxidant.

Method C′. To a test tube fitted with a sintered glass disk in the bottom for use as an oxygen inlet and a condenser as a gas outlet was added 50 ml of benzene, 1.0 g of the phenol, 0.006 g of CuCl, and 0.004 g of N,N,N′,N′-tetramethylethylenediamine. Oxygen was bubbled vigorously through the reaction mixture which was maintained at 80° with a water bath for 8 hr. The polymer was precipitated in methanol, dissolved in chloroform, and reprecipitated in methanol. The polymer was isolated by filtration and dried *in vacuo* at 110°.