An Improved Synthesis of 2,6-Diarylphenols

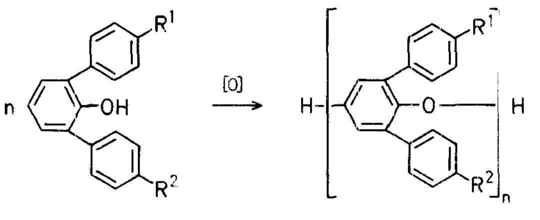
D. E. DANA

Polymer Science & Engineering Department, University of Massachusetts, Amherst, Massachusetts 01002, U.S.A.

A. S. HAY*

General Electric Co., Corporate Research & Development, P.O. Box 8, Schenectady, New York 12308, U.S.A.

Oxidative polymerization of 2,6-diphenylphenol (**1**; $R^1 = R^2 = H$) yields a polyether **2** ($R^1 = R^2 = H$) that has a glass transition temperature of 235 °C[1].

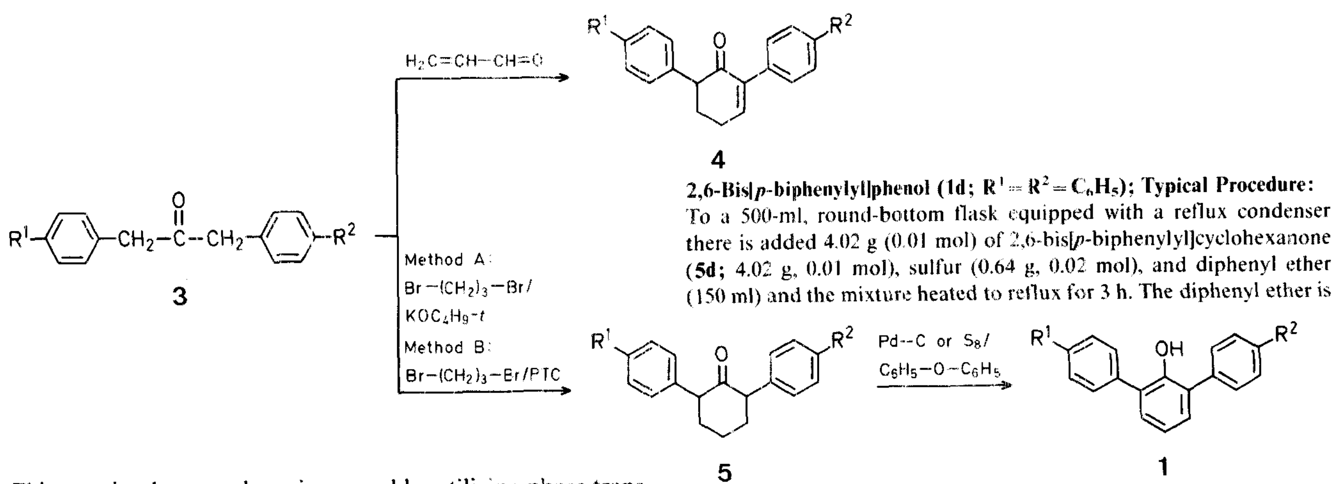


1 **2**

The polymer readily crystallizes and has a melting point of 480 °C. A number of 2-aryl-6-phenylphenols containing a variety of substituents on the pendant aryl group have also been synthesized[2]. The corresponding unsymmetrically substituted polymers are all amorphous and show no tendency to crystallize. In order to study this class of polymers further, we have synthesized some symmetrically substituted 2,6-diarylphenols in which the substituents on the pendant phenyl groups are in the *para* positions.

Most of the syntheses of 2,6-diarylphenols used previously are not adaptable to the synthesis of the desired phenols. The condensation of acrolein with dibenzyl ketone (**3**; $R^1 = R^2 = H$) to yield the cyclohexenone, **4** ($R^1 = R^2 = H$) and subsequent dehydrogenation was used previously to prepare 2,6-diphenylphenol in modest yield[2]. Extensive polymerization of the acrolein under the reaction conditions precludes this route from being used as a general approach.

The synthesis of 2,6-diphenylcyclohexanone (**5**; $R^1 = R^2 = H$), a potential precursor to 2,6-diphenylphenol, has been accomplished in low yield via a double nucleophilic displacement reaction on 1,3-dibromopropane with dibenzyl ketone (**3**; $R^1 = R^2 = H$), catalyzed by potassium *t*-butoxide[3] (Method A).



4 **3** **5** **1**

This reaction has now been improved by utilizing phase transfer catalysis (Method B). The dibenzyl ketones **3** are readily available from the corresponding phenylacetic acid esters[4].

Utilizing this general route, we have synthesized symmetrically *para*-substituted diarylphenols **1** ($R^1 = R^2 =$ methyl-, methoxy-, phenyl). The polymerization of these monomers and the properties of the resulting polymers will be discussed in a forthcoming paper.

The ketones 1,3-bis[*p*-methoxyphenyl]-2-propanone, 1,3-bis[*p*-tolyl]-2-propanone and 1,3-bis[*p*-biphenylyl]-2-propanone were prepared according to Refs.[4,5].

2,6-Bis[*p*-methoxyphenyl]cyclohexanone (5c; $R^1 = R^2 = H_3CO$); Typical Procedure:
In a 250-ml, 3-neck, round-bottom flask equipped with a nitrogen inlet, a mechanical stirrer, and an addition funnel are combined 1,3-bis[*p*-methoxyphenyl]-2-propanone (13.5 g, 0.05 mol), tetrabutylammonium bromide (6.45 g, 0.02 mol), 50% sodium hydroxide (25 ml), and chlorobenzene (15 ml). The mixture is stirred vigorously under nitrogen and to this solution is added, dropwise, 1,3-dibromopropane (10.1 g, 0.05 mol) at such a rate that the temperature does not exceed 40 °C. Following addition, the mixture is allowed to stir for 16 h. The mixture is then poured into water (200 ml) and the organic phase is dissolved in chloroform (50 ml). The chloroform solution is washed with water until neutral. After drying with anhydrous magnesium sulfate, the solvent is evaporated and the crude yellow solid is triturated with ether. Filtration produces a white powder; yield: 7.9 g (51%); m.p. 165–166 °C; 169 °C after recrystallization from hexane.

$C_{20}H_{22}O_3$	calc.	C 77.39	H 7.14
(310.4)	found	77.51	7.16

^{1}H-N.M.R. ($CDCl_3$): $\delta = 2.1$ (m, 6H); 3.77 (s, 6H); 3.79 (t, 2H); 7.0 ppm (m, 8H).

2,6-Bis[*p*-methoxyphenyl]phenol (1c; $R^1 = R^2 = H_3CO$); Typical Procedure:
To a 50-ml, round-bottom flask equipped with a reflux condenser there is added 2,6-bis[*p*-methoxyphenyl]cyclohexanone (**5c**; 3.1 g, 0.01 mol), 5% palladium on carbon (0.63 g), and diphenyl ether (10 ml). The mixture is heated under reflux with vigorous stirring for 24 h. The spent catalyst is removed by filtration and the diphenyl ether removed by vacuum distillation. The orange residue is dissolved in hot absolute ethanol. Upon cooling, pale brown crystals deposit. After filtration and drying there is obtained the off white solid phenol **2c**; yield: 2.5 g (80%); m.p. 105–107 °C, 109 °C after two recrystallizations from heptane (colorless needles)

$C_{20}H_{18}O_3$	calc.	C 78.41	H 5.92
(306.3)	found	78.41	5.88

M.S.: $m/e = 306$ (M^+).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 3.85$ (s, 6H); 5.34 (s, 1H); 6.9–7.9 ppm (m, 11H).

2,6-Bis[*p*-biphenylyl]phenol (1d; $R^1 = R^2 = C_6H_5$); Typical Procedure:
To a 500-ml, round-bottom flask equipped with a reflux condenser there is added 4.02 g (0.01 mol) of 2,6-bis[*p*-biphenylyl]cyclohexanone (**5d**; 4.02 g, 0.01 mol), sulfur (0.64 g, 0.02 mol), and diphenyl ether (150 ml) and the mixture heated to reflux for 3 h. The diphenyl ether is removed in vacuo and the brown residue recrystallized from heptane/chloroform: pale brown plates; yield: 3.3 g (84%); m.p. 221–230 °C

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After two recrystallizations from chloroform; yield: 3.0 g (75%); off-white plates; m.p. 242–243 °C.

$C_{30}H_{22}O$	calc.	C 90.42	H 5.57
(398.5)	found	90.36	5.48

M.S.: $m/e = 398$ (M^+).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 5.48$ (s, 1 H); 7.2–7.7 ppm (m, 21 H).

Table. 2,6-Diarylcyclohexanones **5** and 2,6-Diarylphenols **1** prepared

Product No.	$R^1 = R^2$	Yield [%]	m.p. [°C]	Molecular formula[a]	M.S. [m/e]
5a	H	36	119–121°[b]	$C_{18}H_{18}O$ (250.3)	–
5b	H_3C	42	139°	$C_{20}H_{22}O$ (278.4)	–
5c	H_3CO	see experimental			
5d	C_6H_5	30	191–193°	$C_{26}H_{26}O$ (354.5)	–
1b	H_3C	55	95°	$C_{20}H_{18}O$ (274.3)	274
1c	H_3CO	see experimental			
1d	C_6H_5	see experimental			

[a] Satisfactory microanalyses obtained: C ±0.14, H ±0.22.

[b] Ref.[3], m.p. 123–124 °C.

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* To whom correspondence should be addressed.

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