theory. The positions of these fragments were taken as those of the center of the segments and their orientations as those of the tangents to the curve at the center. With these values the sum[4] given in eq 2 was evaluated,

$$\Sigma_G = \frac{1}{6}\sum_{i,k=1}^{n}\frac{1}{R_{ik}^3}\left[\vec{b_i}\cdot\vec{b_k} - \frac{3(\vec{b_i}\cdot\overrightarrow{R_{ik}})\ (\vec{b_k}\cdot\overrightarrow{R_{ik}})}{R_{ik}^2}\right] \times \overrightarrow{R_{ik}}\cdot(\vec{b_i} \times \vec{b_k}) \quad (2)$$

where b_i is the direction of the unit vector at the center of the ith segment and R_{ik} is the distance between the center of the ith and kth segments. Taking the isotropic and anisotropic polarizability, α and β, of an equivalent length of a linear polymethylene chain[6] as characteristic of those of each of the segments, we then obtain the Kirkwood rotation as[4]

$$[\alpha]_D = 4.96 \times 10^5 \left(\frac{n^2 + 2}{3M}\right) \times \alpha^2\beta^2\Sigma_G \quad (3)$$

where n is the refractive index of the medium and M the molecular weight.

The values of the rotation are largely independent of the number of segments assumed, and we find for $m = 66$ a rotation $[\alpha]_D$ +2.1 for $r_0 = 5.7$ Å, $\epsilon = 2.09$ Å, and $\eta = 2.7$ Å. While smaller knots are possible, steric interactions prevent the particular atomic arrangement given by eq 1. The small value of $[\alpha]_D$ may be viewed as caused, in part, by the fact that some portions of I are right-handed helices and others are left-handed helices. Extensive cancellation thus results.

The small value arising from the cancellation reduces our confidence in the assignment of absolute configuration. Small deviations of the structure from that of eq 1, by straightening one portion of a curve or by rotating a portion by 90° about its chord, can lead to increases in α by factors of 10 or to decreases and changes in sign. The rotation is likely to be a sensitive function of the environment of the molecule for all but the smallest and tightest knots near C_{50}. Near the lower limit the deviations from eq 1 are sufficiently large that the calculation is of doubtful validity.

(6) C. W. Bann and R. de P. Daubeny, *Trans. Faraday Soc.*, **50**, 1173 (1954).

The Preparation and Redistribution of 4-(2,6-Diphenylphenoxy)-2,6-diphenylphenol

Donald A. Bolon

General Electric Research and Development Center,
Schenectady, New York 12301

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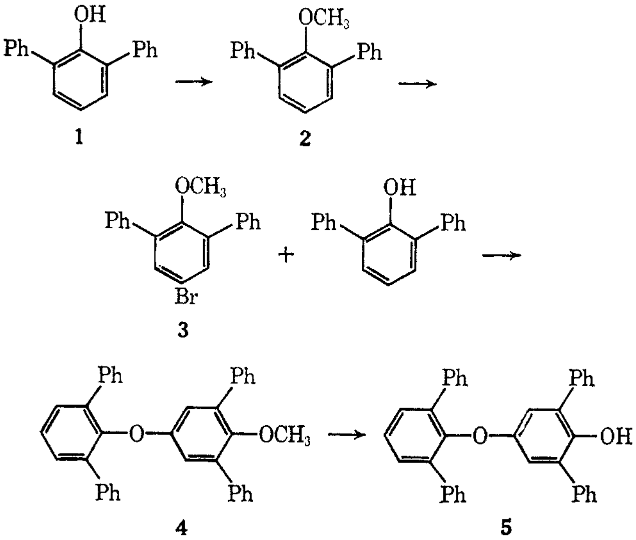
The discovery by Hay[1] that 2,6-diphenylphenol could be oxidatively coupled to form poly(2,6-diphenylphenylene oxide) led into a closer examination of the chemistry of 2,6-diphenylphenol. This molecule appears to be relatively hindered and the relative ease of its oxidative coupling was interesting. The backbone structure of poly(2,6-diphenylphenylene oxide) is identical with that of poly(2,6-dimethylphenylene oxide)[2] and this work was undertaken to see whether other reactions of 2,6-diphenyl-substituted phenols were similar to 2,6-dimethylphenol.

The phenyl-substituted analog of 2,6-xylenol dimer[3] was prepared. This is 4-(2,6-diphenylphenoxy)-2,6-diphenylphenol (5) and was prepared by the following sequence of reactions. The phenol **1** was converted to the methyl ether **2** which was brominated to give 4-bromo-2,6-diphenylanisole **3**. This was coupled with 2,6-diphenylphenol in an Ullmann reaction to give 4-(2,6-diphenylphenoxy)-2,6-diphenylanisole (**4**) which was cleaved to give the phenol dimer **5**.



When the dimer **5** was dissolved in benzene and treated with a radical source such as tri-*t*-butylphenoxyl it underwent redistribution.[3,4] The solution was silylated[5] with bis(trimethylsilyl)acetamide and examined by thin layer chromatography (tlc) or vapor phase chromatography (vpc). The vpc showed three components which were identified as monomer **1**, dimer **5**, and, by analogy, trimer **6**. These materials arise from a redistribution of the dimer radical **5a**.

The same solution was examined on tlc and showed a spectrum of 11 spots in decreasing amounts. The first two were identified as monomer **1** and dimer **5**. The other spots were assigned as being the higher oligomers of 2,6-diphenylphenol. This was further substantiated by degrading a sample of 2,6-diphenylphenol polymer with 2,6-diphenylphenol according to the method of Cooper, Gilbert, and Finkbeiner.[4] The resulting mixture gave the same series of compounds on tlc.

The final proof that the reactions of 2,6-diphenylphenol dimer **5** are identical with those of the 2,6-dimethylphenol dimer is that **5** can be polymerized to poly(2,6-diphenylphenylene oxide) by the use of metal oxides such as lead dioxide.[6] The polymer obtained from this oxidation is identical with polymer obtained from the copper–amine-catalyzed polymerization of 2,6-diphenylphenol.

(1) A. S. Hay, unpublished work.

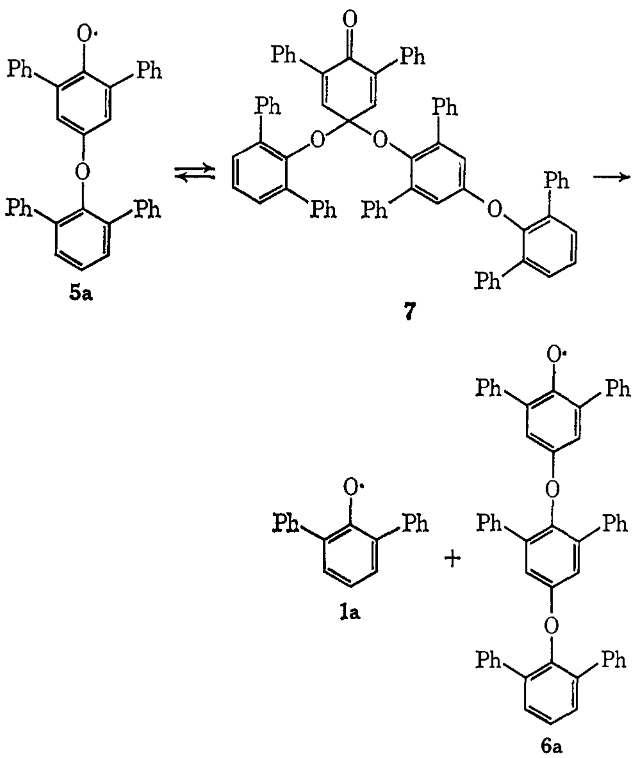
(2) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Amer. Chem. Soc.*, **81**, 6335 (1959).

(3) D. A. Bolon, *J. Org. Chem.*, **32**, 1584 (1967).

(4) G. D. Cooper, A. R. Gilbert, and H. Finkbeiner, Polymer Preprints, Winter Meeting of the American Chemical Society, Phoenix, Ariz., 1966, p 166.

(5) J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

(6) H.-D. Becker, U. S. Patent 3,390,425 (1968).



This reaction clearly demonstrates that a hindered phenoxy radical can and does react at the *para* position of another phenoxy radical. The relative ease of the redistribution of **5a** is at some variance with what might be predicted by an examination of molecular models. However, an examination of a model of the quinone ketal **7** shows that one of the pendant phenoxy rings is nearly coplanar with the cyclohexadienone ring and consequently is less hindered than the planar written form of **7** would appear.

Experimental Section

2,6-Diphenylphenol (1).—This material was prepared as described by Plešek.[7]

2,6-Diphenylanisole (2).—To a stirred solution of sodium methoxide (0.75 mol) and 2,6-diphenylphenol (88.6 g, 0.56 mol) in methanol (240 ml) under nitrogen was added slowly dimethyl sulfate (76 ml). The reaction was stirred 6 hr and the methanol was distilled. The residue was treated with water, the organics were taken up in pentane, and any phenolic material was extracted with Claisen alkali.[8] The pentane was evaporated and the residue was distilled yielding a colorless oil (bp 175–177° (2.2 mm), mp 40–41°, $n^{20}{}_{D}$ 1.6329, 63% yield).

Anal. Calcd for $C_{19}H_{16}O$: C, 88.2; H, 6.2; mol wt, 260. Found: C, 88.0; H, 6.4; mol wt, 256.

4-Bromo-2,6-diphenylanisole (3).—2,6-Diphenylanisole (54 g, 0.02 mol) was brominated (32 g, 0.02 mol) in glacial acetic acid (200 ml). After 4 hr at room temperature, the reaction was refluxed for 2 hr and then poured into sodium bisulfite solution (300 ml, 1%). The brown oil which formed slowly crystallized and was recrystallized from 80% ethanol giving 58.5 g (85%) of white crystals, mp 98–99°.

Anal. Calcd for $C_{19}H_{15}OBr$: C, 67.3; H, 4.4; mol wt, 339. Found: C, 67.3; H, 4.9; mol wt, 334.

4-(2,6-Diphenylphenoxy)-2,6-diphenylanisol (4).—Potassium *t*-butoxide (11.2 g, 0.1 mol) and dimethylformamide (DMF) (20 ml) were combined under nitrogen and a mixture of 2,6-diphenylphenol (24.6 g, 0.1 mol) in hexamethylphosphortriamide (18 g) was added. This mixture was heated until all of the *t*-butyl alcohol distilled out. The reaction was cooled and 4-bromo-2,6-diphenylanisole (33.9 g, 0.1 mol), DMF (30 ml), and cuprous bromide (2.0 g) were added. The mixture was stirred and heated to reflux while 3 ml of DMF was distilled to remove any traces of *t*-butyl alcohol. The reaction was cooled after 18 hr and a mixture of methanol (600 ml) and concentrated HCl (25 ml) was added. The reaction was filtered and the organic material was extracted with benzene. Residual 2,6-diphenylphenol was removed with Claisen alkali[8] from the benzene which was then dried and distilled. There were three fractions obtained after the benzene: 2,6-diphenylanisole,[9] 4-bromo-2,6-diphenylanisole, and 4-(2,6-diphenylphenoxy)-2,6-diphenylphenol bp 237–260°/(3 mm). This material was recrystallized from 4:1 hexane–toluene giving white crystals, 11 g, 22%, mp 149–150°.

Anal. Calcd for $C_{37}H_{28}O_2$: C, 88.1; H, 5.6; mol wt, 504. Found: C, 87.8; H, 5.4; mol wt, 470.

4-(2,6-Diphenylphenoxy)-2,6-diphenylphenol (5).—Anisole 4 (8.2 g, 0.016 mol) was heated to reflux under nitrogen with pyridine hydrochloride (5.5 g, 0.048 mol) for 18 hr. The residue was poured into water (150 ml). The tan solids were recrystallized from hexane–toluene giving white plates, mp 162–164°, 4.0 g, 50%. A thin layer chromatography showed that the dimer was contaminated with unreacted starting material which was separated by elution chromatography on alumina with hexane–benzene: mp 175–177°.

Anal. Calcd for $C_{36}H_{26}O_2$: C, 88.2; H, 5.3; mol wt, 490. Found: C, 87.8; H, 5.5; mol wt, 470.

Redistribution.—4-(2,6-Diphenylphenoxy)-2,6-diphenylphenol (5, 10 mg) in benzene (1 ml) under nitrogen at 25° was treated with the tri-*t*-butylphenoxy radical[10] (10 μl of 0.1 *M* solution). The blue color of the radical was discharged immediately and after a few minutes the orange-red color of the diphenoquinone appeared.[3] The sample was treated with bis(trimethylsilyl)acetamide and the silylated phenols were examined by tlc and vpc. A complete redistribution sequence was observed which corresponded to seeing oligomers up to 11 monomer units long. This sequence was identical with the one obtained from the reaction of 2,6-diphenylphenol, poly(2,6-diphenylphenylene oxide) and an oxidizing agent.[5]

A vpc analysis of the silylated mixture showed three components as their silyl ethers: 2,6-diphenylphenol, 4-(2,6-diphenylphenoxy)-2,6-diphenylphenol, and the trimer **6**. The monomer and dimer were shown to be identical with the known materials by retention times and by infrared spectra.

Polymerization.—Dimer **5** (0.5 g) was stirred in toluene (30 ml) with lead dioxide (5 g) for 24 hr. The colorless solution was filtered. The polymer was isolated by precipitation into methanol: yield 0.42 g, 84%. Intrinsic viscosity in $CHCl_3$, 0.97.

A sample of 2,6-diphenylphenol treated in an identical manner gave a red solution which yielded 0.35 g (70%) of polymer which had an intrinsic viscosity of 0.48.

Registry No.—**2**, 20104-40-9; **3**, 20104-39-6; **4**, 20104-41-0; **5**, 20104-42-1.

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[7] J. Plešek, *Chem. Listy*, **50**, 252 (1956), reprinted in *Coll. Czech. Chem. Commun.*, **21**, 375 (1956).

[8] See L. F. Fieser "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 191.

(9) The 2,6-diphenylanisole results from debromination of the bromo compound. In spite of the fact that both the bromoanisole and the phenol are present in the reaction at this point, further addition of cuprous bromide only results in debromination and not in production of more dimer.

(10) C. D. Cook and R. C. Woodworth, *J. Amer. Chem. Soc.*, **75**, 6242 (1953).

Transesterification with an Anion-Exchange Resin

W. Pereira, V. Close, W. Patton, and B. Halpern

Department of Genetics, Stanford University School of Medicine, Stanford, California 94305

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Although the modification of esters of edible oils by alcoholysis using anion exchange resins is used commercially,[1] synthetic applications of such base-catalyzed transesterifications are rare.[2]

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(1) A. T. Gros and R. O. Feuge, *J. Amer. Oil Chem. Soc.*, **26**, 97, 704 (1949).

(2) C. J. Schmidle and R. C. Mansfield, *Ind. Eng. Chem.*, **44**, 2868 (1952); M. J. Astle and J. E. Zaslowsky, *ibid.*, **44**, 2868 (1952).