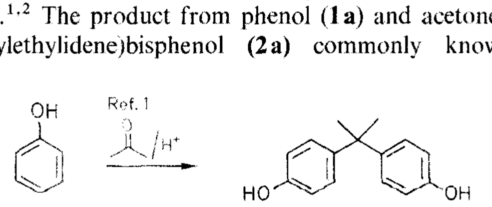
Synthesis of 2,6-Diphenyl-4,4′-(1-methylethylidene)bisphenol and 2,2′,6,6′-Tetraphenyl-4,4′-(1-methylethylidene)bisphenol

Z.Y. Wang, A.S. Hay*

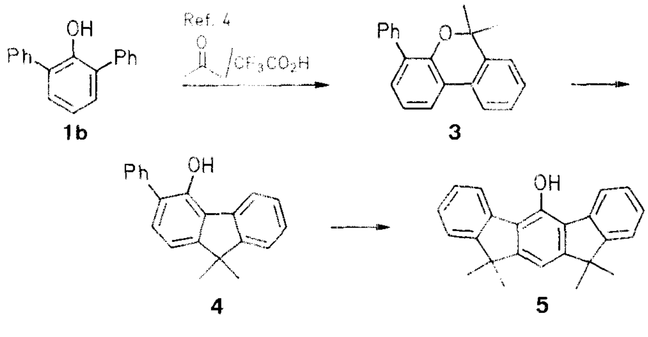
Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec H3A 2K6, Canada

Transalkylation of 4,4′-(1-methylethylidene)bisphenol (**2a**) with 2,6-diphenylphenol (**1b**) in the presence of methanesulfonic acid gives 2,2′,6,6′-tetraphenyl-4,4′-(1-methylethylidene)bisphenol (**2b**) or the intermediate 2,6-diphenyl-4,4′-(1-methylethylidene)bisphenol (**6**) as product depending on the acid concentration.

The reaction of aldehydes and ketones with phenols in the presence of acid catalysts to yield bisphenols is a well studied reaction.[1,2] The product from phenol (**1a**) and acetone, 4,4′-(1-methylethylidene)bisphenol (**2a**) commonly known as bisphenol-A or BPA, is manufactured in very large quantities for use as a monomer in the synthesis of a large variety of polymeric materials. Kahovec and Poposil[3] found that 2,6-diphenylphenol (**1b**) did not react with acetone in the presence of acidic catalysts under a variety of conditions. However, Webb and Hall[4] reported that in the presence of trifluoroacetic acid the reaction did proceed to give the substituted fluorene **4** as the principal product via the dibenzopyran **3**. Further reaction with acetone for extended periods gives the bisfluorene **5**. A transalkylation process for the production of bisphenols has been reported by Mark.[5] He found that bisphenols such as **2a** in the presence of a large excess of an alkyl or chlorosubstituted phenol and a strong acid are transformed into the corresponding bisphenol of the substituted phenol via the intermediate unsymmetrical bisphenol.

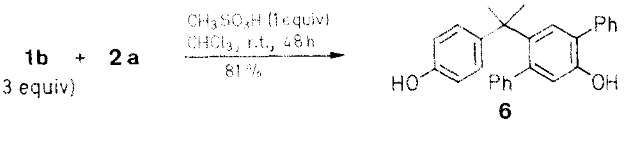


1a **2a**

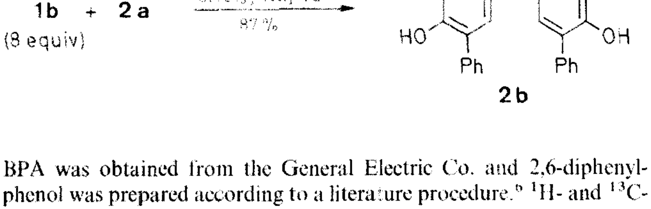


1b **3** **4** **5**

We have now found that the transalkylation reaction between **2a** and 3 equivalents of **1b** with 1 equivalent of methanesulfonic acid gives 2,6-diphenyl-4,4′-(1-methylethylidene)bisphenol (**6**). 2,2′,6,6′-Tetraphenyl-4,4′-(1-methylethylidene)bisphenol (**2b**) is produced in the presence of a larger excess of **1b** and of acid. Direct reaction between acetone and **1b** gives **3** as the principal product, in accordance with Ref. 4.



6



2b

BPA was obtained from the General Electric Co. and 2,6-diphenylphenol was prepared according to a literature procedure.[6] ^{1}H- and ^{13}C-NMR spectra were obtained on Varian XL-200 or XL-300 spectrometers. Mass spectra were obtained on a HP 5984A spectrometer.

2,6-Diphenyl-4,4′-(1-methylethylidene)bisphenol (6):

To a suspension of **2a** (0.91 g, 4 mmol) and **1b** (2.95 g, 12 mmol) in dry $CHCl_3$ (5 mL), is added dropwise methanesulfonic acid (0.26 mL, 4 mmol). The resulting reddish suspension is stirred at room temperature for 48 h. The mixture is then diluted with $CHCl_3$ (150 mL) and washed with 1 N NaOH (2 × 50 mL). The organic phase is dried (Na_2SO_4) and the solvent removed at reduced pressure. Flash chromatography of the residue (15 % EtOAc in *n*-hexane) affords **6** as a white solid: yield: 1.23 g (81 %); mp 53–55 °C.

$C_{27}H_{24}O_2$	calc.	C 85.23	H 6.36
(380.5)	found	85.14	6.53

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.68 (s, 6 H, 2 CH_3), 5.33 (br s, 2 H, 2 OH), 6.74 (d, 2 H, H-2′, H-6′), 7.13 (s, 2 H, H-3, H-5), 7.17 (d, 2 H, H-3′, H-5′), 7.36–7.51 (m, 10 H, C_6H_5).

^{13}C-NMR (300 MHz, $CDCl_3$): δ = 31.19, 41.89, 114.78, 127.56, 127.99, 128.37, 128.45, 128.82, 129.41, 137.99, 143.09, 143.16, 147.78, 153.27.

MS: *m/z* (%) = 380 (M^+, 25), 365 (M^+ $-CH_3$, 39).

2,2′,6,6′-Tetraphenyl-4,4′-(1-methylethylidene)bisphenol (2b):

To a septum-sealed flask containing **2a** (2.74 g, 12 mmol) and **1b** (23.62 g, 96 mmol) in dry $CHCl_3$ (35 mL), is added dropwise via syringe methanesulfonic acid (3.89 mL, 60 mmol). The resulting reddish solution is stirred at room temperature for 4 d. The mixture is diluted with $CHCl_3$ (300 mL) and washed with 1 N NaOH (2 × 150 mL). The organic phase is dried (Na_2SO_4), and the solvent removed *in vacuo*. Excess of **1b** is removed from the above residue by Kugelrohr distillation (~ 250 °C/0.13 mbar), and the residue crystallized from cyclohexane to give **2b**: yield: 5.55 g (87%). An analytical sample is obtained by recrystallization from toluene and petroleum ether (bp 35–60 °C); mp 200–200.5 °C.

$C_{39}H_{32}O_2$	calc.	C 87.94	H 6.06
(532.7)	found	88.03	6.13

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.74 (s, 6 H, $2CH_3$); 5.29 (s, 2 H, OH); 7.20 (s, 4 H, H-2, H-6, H-2′, H-6′); 7.36–7.56 (m, 20 H, PH).

^{13}C-NMR (300 MHz, $CDCl_3$): δ = 31.33, 42.11, 127.55, 128.05, 128.48, 129.44, 138.02, 142.91, 147.19.

MS: *m/z* (%) = 532 (M^+, 20); 517 (M^+ $-CH_3$, 60).

This work was supported by the General Electric Company and the Natural Sciences and Engineering Research Council of Canada.

Received: 4 October 1988; revised: 2 February 1989

(1) Bode, K.-D., in: *Houben-Weyl*, 4th ed., Vol. VI/1c, Georg Thieme Verlag, Stuttgart, 1976, p. 1022.
(2) Schnell, H., Krimm, H. *Angew. Chem.* **1963**, *75*, 662; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 373.
(3) Kahovec, J., Poposil, J. *Collect. Czech. Chem. Commun.* **1969**, *34*, 2843.
(4) Webb, J.L., Hall, W.L. *J. Org. Chem.* **1973**, *38*, 1621; *US Patent* 3723465 (1973); *C.A.* **1973**, *78*, 147736.
(5) Mark, V. *US Patent* 4560808 (1985); *C.A.* **1986**, *104*, 225385.
(6) Hay, A.S., Clark, R.F. *Macromolecules* **1970**, *3*, 533.