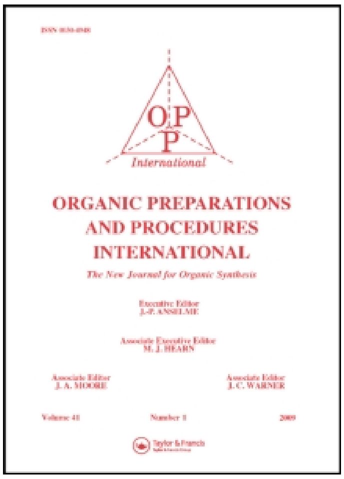

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REDUCTIVE METHYLATION OF HYDROXYBIPHENYL WITH ALUMINA AND METHANOL

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REDUCTIVE METHYLATION OF HYDROXYBIPHENYL WITH ALUMINA AND METHANOL.[1]

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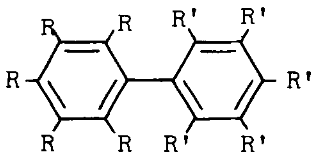
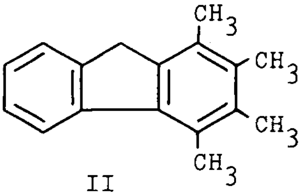
In previous studies it was shown that phenol, naphthols, and indanol react with methanol at 275-550° in the presence of an alumina catalyst to give ring methylation, with or without attendant O-extrusion (i.e. reduction). The procedure is a convenient synthetic route to hexamethylbenzene,[2,3] various polymethylnaphthalenes,[4,5] tetramethylindan, and tetramethylindene.[6] We now report the extension of this method to the syntheses of (a) 2,3,4,5,6-pentamethylbiphenyl (I) and 1,2,3,4-tetramethylfluorene (II) from 2- or 4-hydroxybiphenyl or 2,4-dihydroxybiphenyl and (b) decamethylbiphenyl (III) from 2,2'- or 4,4'-dihydroxybiphenyl.

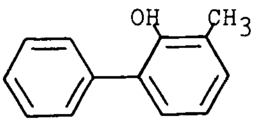


I: R=CH_3, R'=H

III: R=R'=CH_3



II



IV

The distribution of products formed depends on the reaction temperature and the alumina used, as well as the starting material. Yields of products obtained from the monohydroxybiphenyls are given in Table 1. It will be noted that at 280-300° 2-hydroxybiphenyl produces mainly I and the monomethyl derivative IV. As the reaction temperature is increased with either of the hydroxybiphenyl isomers the ratio of I:II obtained decreases markedly, with the best yield of II (21%) produced from the 2-isomer at 470°. The maximal yield (98% crude) of III resulted from use of 2,2'-dihydroxybiphenyl at 400°.

Mechanistic pathways to I, III, and IV are readily rationalized in terms of our earlier proposals.[4,5] However, the route to II is not yet clear, since I is not transformed into II (or *vice versa*) under reaction conditions. Mixtures of I and II are separable by column chromatography on alumina, to which the planar II is more strongly adsorbed.[7] The structure of I was established by direct comparison with a sample synthesized from 2-butyne and 1-phenylpropyne; while that of II follows from its PMR and UV spectra (latter virtually superimposable on that of 4-methylfluorene,[8] but shifted bathochromically by 3-7 nm). The structure of IV is assigned on the basis of IR spectra, which show the presence of an unsubstituted phenyl group (very strong bands at 705 and 760 $\mathrm{cm^{-1}}$)[9] and a 2,6-disubstituted phenol (very strong, sharp band at 3560 $\mathrm{cm^{-1}}$).[10]

EXPERIMENTAL

General Procedure.--Reactions were conducted in a flow system consisting of a vertically mounted, thermally controlled (to ca. ±10°) combustion furnace (30 cm long) bearing a pyrex reactor tube (53 cm x 2.7 cm outside diameter) packed with Houdry Process Corp. (Philadelphia) grade HA-100 alumina[11] (45 g, 28 cm in length, pre-activated in situ in a stream of nitrogen gas for 16 hr. at the reaction temperature). To the preheated reactor was added dropwise (15-30 drops/min.) over a period of 5-8 hr. a solution of 2.5 g of dihydroxybiphenyl or 5 g of monohydroxybiphenyl in 210 ml of methanol in a stream of nitrogen carrier gas (27 ml/min.). Effluents (trapped in air- and ice-cooled baths) plus acetone extracts of the cooled catalyst were combined, evaporated, and dissolved in ether. The ether solution was washed successively with 10% aqueous sodium hydroxide solution and water, dried, and evaporated. Neutral products were obtained from the res-

Table 1. Products from Alumina-Catalyzed Reactions of Hydroxybiphenyls with Methanol[a]

Starting Hydroxy-biphenyl	Reaction temp., °C	Yields of Identified Products, mol %[b]			Molar ratio, I:II	Unidentified products, weight %
		I	II	IV		
2-	280	30.0	traces	28.1	300	24.1
2-	300	46.3	2.9	22.4	16.0	20.9
2-	400	46.3	11.1	1.1	4.2	14.8
2-	470	6.1	21.2	1.1	0.3	60.1
4-	300	43.8	14.2	-	3.1	19.8
4-	400	36.2	18.8	-	1.9	13.2
4-	500	18.9	14.0	-	1.4	20.8

[a]Molar ratio used: MeOH/hydroxybiphenyl = 175. [b]Analyzed by gas chromatography.

idue and phenolic products were recovered from the alkaline wash solution. For runs reported in the Table both neutral and phenolic products were analyzed by means of gas chromatography on a column (2.4 m x 1 cm) packed with 10% DC-550 silicone oil on Chromosorb W at 200°.

<u>Decamethylbiphenyl (III)</u>.--Crude product (98% from 2,2'-dihydroxybiphenyl at 400°; 39% at 300°; 46% from 4,4'-dihydroxybiphenyl at 470°) was obtained directly from the neutral residue. An analytically pure sample (mp 258-259°, sealed tube) resulted from recrystallizations from acetonitrile and absolute ethanol, identified by direct comparison with an authentic sample.[12]

<u>2-Hydroxy-3-methylbiphenyl (IV)</u>.--This substance was isolated as a nearly colorless liquid by preparative gas chromatography (*vide supra*); ir (CCl_4) 3560, 1470, 1430, 1324 cm^{-1}; ir (CS_2) 1220, 1090, 760, 705 cm^{-1}; pmr (CCl_4) δ 2.24 (s, 3, $C\underline{H}_3$), 5.09 (s, 1, $O\underline{H}$), 6.5-7.8 (m, 8, aromatic protons).

<u>Anal</u>. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 85.15; H, 6.68.

<u>2,3,4,5,6-Pentamethylbiphenyl (I)</u>, reference sample.--To a mixture of anhydrous aluminum chloride (2.67 g, 0.02 mol) and benzene (10 ml) was added in succession (with stirring at 0°) sufficient 2-butyne to produce a dark red mixture and then dropwise (over a period of 30 min.) a solution of 1-phenylpropyne (2.72 g, 0.02 mol) and 2-butyne (total quantity of 5.4 g, 0.1 mol), in benzene (5 ml). Stirring was continued for 4 hr. while the mixture warmed to room temperature. The mixture was then refluxed for 1 hr., poured onto ice, and

extracted into ether. Evaporation of the ether gave 8.6 g of crude product, containing 36% hexamethylbenzene and 52% I as based on VPC. The hexamethylbenzene was removed by fractional crystallization from acetonitrile and as part of the forerun from distillation (in vacuo) of the mother liquor. The higher boiling I produced needles from absolute ethanol; yield: 1.8 g (40%); mp 71-73°, lit.[13] mp 72-73°.

Catalytic Reductive Methylation of 2,4-Dihydroxybiphenyl.--From interaction of 10 g of 2,4-dihydroxybiphenyl with methanol (molar ratio 1:175) at 400° was obtained only neutral product (10.4 g crude), chromatographed on Brinkmann neutral alumina (310 g) with pentane as eluent. Fractions 6-9 (100 ml each) yielded I (identical with the reference sample), while fractions 11-12 gave 1,2,3,4-tetramethylfluorene (II), recrystallized from ethanol, mp 119-120°; uv (EtOH) λ_{max} 211 nm (log ε 4.63), 263 sh (4.27), 271 (4.34), 280 sh (4.19), 302.5 (3.64); pmr (CCl_4) δ 2.15 (s, 9, 3 CH_3), 2.50 (s, 3, CH_3 at C-4), 3.48 (s, 2, CH_2), 6.9-7.4 (m, 3, aromatic protons), 7.6-7.9 (m, 1, H-5).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.53; H, 8.17.

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