

and hydrogenated for 2 hours in a Parr apparatus using Adams' catalyst at room temperature and 50 p.s.i. The yield was 0.433 gram. The product was chromatographed on Florisil (10 grams, 1 × 15 cm. column) and eluted with 1500 ml. of hexane. The yield was 0.316 gram (63%). The infrared spectrum showed the following bands: aromatic ortho-substituted benzene (3.21, 6.22, 6.70, 13.35 μ); ester (5.72, 8.50 μ). Analysis by NMR gave the following τ values: aromatic protons (3.02 p.p.m.); methyl ester protons (6.40 p.p.m.); activated methyl and activated methylene protons (7.30 to 8.00 p.p.m.); methylene protons (8.00 to 8.90 p.p.m.).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 78.6; H, 10.4. Found: C, 78.9; H, 10.3.

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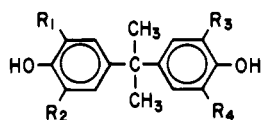
Syntheses of Some Brominated 4,4'-Isopropylidenebisphenols

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4, 4'-Isopropylidenediphenyl acetate (diacetate ester of bisphenol A) was converted to the monoester, α -(*p*-hydroxyphenyl)-*p*-cumenyl acetate, in 25% yield by selective methanolysis in the presence of a catalytic quantity of sodium methoxide. Bromination of the monoester with an equimolar amount of bromine followed by saponification yielded 2-bromo-4,4'-isopropylidenediphenol in 44% yield. Bromination with two molar equivalents of bromine and subsequent saponification gave 2,6-dibromo-4,4'-isopropylidenediphenol in 70% yield. 2,2',6-Tribromo-4,4'-isopropylidenediphenol slowly crystallized from an oil prepared by the bromination of bisphenol A with three molar equivalents of bromine (11% yield). All of the brominated bisphenols were further characterized by acetylation to the diacetate esters and complete bromination to the known tetrabromobisphenol A. The infrared absorption spectra of the subject compounds were also recorded.

PURE SAMPLES of the intermediates encountered in the bromination of 4,4'-isopropylidenebisphenol (bisphenol A, I) to 4,4'-isopropylidenebis-(2,6-dibromophenol) or tetrabromobisphenol A (VI) (2) were required for a thorough study of the reaction. The following intermediates were involved: monobrominated bisphenol A (II), two isomers of dibrominated bisphenol A (III and IV), and tribrominated bisphenol A (V), respectively.

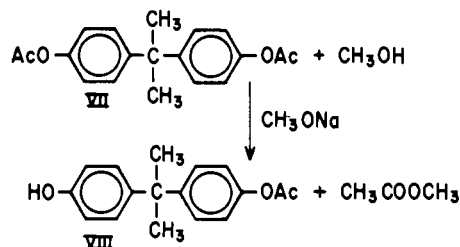


Compound	R ₁	R ₂	R ₃	R ₄
I	H	H	H	H
II	Br	H	H	H
III	Br	H	Br	H
IV	Br	Br	H	H
V	Br	Br	Br	H
VI	Br	Br	Br	Br

Only the symmetrically dibrominated intermediate III was known (3). Therefore, this study was primarily concerned with the preparation of unsymmetrically brominated bisphenols II, IV, and V. It is believed that the methods evolved may be applicable to other similar synthetic situations.

The approach considered most favorable to prepare monobrominated bisphenol A (II) and the unsymmetrically dibrominated compound IV was via the intermediate, α -(*p*-hydro-

xyphenyl)-*p*-cumenyl acetate (bisphenol A monoacetate, VIII). The two rings in this molecule should differ sufficiently in reactivity toward electrophilic substitution to permit selective bromination. The preparation of VIII was more difficult than anticipated. Monoesterification of bisphenol A with a number of acetylation reagents and monosaponification of bisphenol diacetate (VII) under a variety of conditions failed to give practical quantities of VIII. The only reliable synthetic method available was the methanolysis of bisphenol A diacetate in the presence of a catalytic amount of sodium methoxide. Chromatography over alumina of the reaction product removed unreacted starting material and bisphenol A and a 25% yield of VIII was achieved.



The bromination of bisphenol A monoacetate appeared to proceed in a marked stepwise fashion. The second bromine substitution proceeded noticeably slower than the first. This is due to the deactivation of the ring by the inductive effect of the bromine atom already present (1). The mono- and dibrominated monoacetates were saponified without isolation to yield monobrominated bisphenol A (II) and unsymmetrically dibrominated bisphenol A (III) in 44 and 70% yields, respectively.

During the attempted preparation of tribromobisphenol A (V), a solid began to separate from the crude viscous product obtained from the reaction of bisphenol A and 3 molar equivalents of bromine. This solid, tribrominated bisphenol A, was isolated in 11% yield. Previous attempts to separate the compound by crystallization, chromatography, and conversion to easily separable derivatives were unsuccessful.

EXPERIMENTAL

Melting points were determined in a Vanderkamp "Melt-pointier" apparatus and are corrected.

All brominated bisphenols were fully brominated to yield tetrabromobisphenol A. A mixed melting point of an intimate mixture with authentic tetrabromobisphenol A was undepressed.

α -(*p*-Hydroxyphenyl)-*p*-cumenyl Acetate (Bisphenol A Monoacetate, VIII). A solution of 0.45 gram of sodium methoxide dissolved in 7.7 grams (0.24 mole) of methanol (ACS grade) was added dropwise with stirring to a solution of 75 grams (0.24 mole) of 4,4'-isopropylidenediphenyl acetate (4) (bisphenol A diacetate, VII) dissolved in 150 ml. of dry toluene heated at the reflux temperature. The reaction mixture was stirred and heated at the reflux temperature for 1.75 hours, cooled to 25° C. and then carbonated with dry carbon dioxide. Insoluble inorganic material was collected on a Büchner funnel, and the solvent was removed by distillation under reduced pressure (~ 25 mm.). The residue was dissolved in 45 ml. of carbon tetrachloride, and this solution was chromatographed through activated alumina (Alcoa grade F-20). Using methylene chloride as an elution solvent, unreacted bisphenol A diacetate (VII) eluted first, followed by bisphenol A monoacetate (VIII). Bisphenol A remained in the column under these conditions. The crude bisphenol A monoacetate was recrystallized from a mixture of 45 ml. of perchloroethylene and 25 ml. of Skellysolvent (b. p. 60–100° C.) to yield 16.4 grams (25%) of white crystalline solid, m.p. 98–100° C.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.39; H, 6.57.

2-Bromo-4,4'-isopropylidenediphenol (II). A solution of 2.38 grams (0.0148 mole) of bromine dissolved in 20 ml. of chloroform was added dropwise with stirring to a solution of 4.00 grams (0.0148 mole) of bisphenol A monoacetate (VIII) dissolved in 30 ml. of chloroform while the reaction temperature was maintained at 10° C. The solvent was removed by distillation, and the oily residue was added to 40 grams of 5% sodium hydroxide solution. The mixture was gently warmed, and solution indicating reaction completion was quickly attained. The solution was carbonated with carbon dioxide, and the gummy crystals which separated were collected on a Büchner funnel and dissolved in 75 ml. of tetrachloroethylene. Insoluble inorganic material was collected on a Büchner funnel. Considerable difficulties were encountered in the purification of this compound. White needles were finally obtained by allowing a tetrachloroethylene solution to evaporate slowly during which time the compound precipitated. Evaporation of about 75% of the solvent over an 8-day period permitted the isolation of 2.0 grams (44%) of product, m.p. 80–83° C.; $\lambda_{\max}^{CS_2}$ 2.77 (m), 2.83(m), 7.32(w), 7.49(w), 7.72(m), 7.91(m), 8.43(s), 8.49(s), 12.05(m,sh.), 13.01(w), 13.72(w), 14.01(w) μ .

Anal. Calcd. for $C_{15}H_{15}BrO_2$: C, 58.63; H, 4.92; Br, 26.01. Found: C, 59.04; H, 4.90; Br, 25.56.

The diacetate ester derivative was prepared by the reaction with acetic anhydride in the presence of a small amount of *p*-toluenesulfonic acid. The crude oily product required one month to solidify, and it was recrystallized from a toluene-Skellysolvent (b.p. 60–100° C.) mixture to yield a white crystalline solid, m.p. 80–81° C.

Anal. Calcd. for $C_{27}H_{19}BrO_4$: C, 58.32; H, 4.89; Br, 20.42. Found: C, 58.01; H, 4.75; Br, 20.03.

2,6-Dibromo-4,4'-isopropylidenediphenol (IV). The bromination of bisphenol A monoacetate (VIII) to prepare this compound was similar to the preparation of the monobromo derivative except that 4.76 grams (0.0296 mole) of bromine was used. The oil which remained after evaporation of the chloroform solvent was dissolved in 40 grams of 5% aqueous sodium hydroxide solution with warming. Carbon tetrachloride (100 ml.) was added to this solution, and the mixture was acidified to pH 6 by the addition of 5% hydrochloric acid. The layers were separated, and the organic solution was washed once with warm water and then diluted while hot with Skellysolvent (b.p. 60–100° C.). Product precipitated when the solution cooled to yield 4.0 grams (70%) of white crystalline solid, m.p. 132–133° C.; $\lambda_{\max}^{CS_2}$ 2.77(m), 2.84(m), 7.56(sh.,w), 7.91(m), 8.01(w), 8.53(s), 12.05(m), 12.91(w), 13.60(w), 14.09(w) μ .

Anal. Calcd. for $C_{15}H_{14}Br_2O_2$: C, 46.66; H, 3.66; Br, 41.38. Found: C, 46.70; H, 3.65; Br, 41.38.

The diacetate ester derivative was prepared in the previously described manner and recrystallized from a toluene-Skellysolvent (b.p. 60–100° C.) mixture as a white solid, m.p. 115–116° C.

Anal. Calcd. for $C_{19}H_{18}Br_2O_4$: C, 48.54; H, 3.86; Br, 33.97. Found: C, 48.30; H, 3.85; Br, 33.23.

2,2',6-Tribromo-4,4'-isopropylidenediphenol (V). Bromine (726 grams, 4.50 moles) was added dropwise with stirring to a solution of 344 grams (1.50 moles) of bisphenol A (I) dissolved in 508 grams of 2B 95% ethanol. Cooling was required to maintain the reaction temperature of 24–26° C. Water (406 grams) was added, and the solid which precipitated was collected on a fritted glass funnel and washed with 130 grams of water. The solid (tetrabromobisphenol A) was discarded, and the water wash was added to the filtrate. The layers which formed were separated, and the organic solution was allowed to stand at room temperature for 3 months. Solid material started to separate after 1 month. This solid was collected and recrystallized from a chloroform-Skellysolvent (b.p. 60–100° C.) mixture to yield 79.3 grams (11%) of white plates, m.p. 107–110° C. $\lambda_{\max}^{CS_2}$ 2.83(m), 7.55(sh.,w), 7.73(m), 8.42(s), 8.52(s), 9.63(w), 11.48(w), 12.18(m), 12.89(w), 13.65(w), 14.16(w) μ .

Anal. Calcd. for $C_{15}H_{13}Br_3O_2$: C, 38.82; H, 2.82; Br, 51.67. Found: C, 39.21; H, 3.13; Br, 51.21.

The diacetate derivative was prepared in the manner previously described and recrystallized from a toluene-Skellysolvent (b.p. 60–100° C.) mixture to yield a white solid, m.p. 97–98° C.

Anal. Calcd. for $C_{19}H_{17}Br_3O_4$: C, 41.56; H, 3.12; Br, 43.61. Found: C, 42.00; H, 3.01; Br, 43.32.

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