benzene eluate 5.56 g (23 mmoles, 23%) of white crystals of **2-phenyl-3-methylbutyrophenone (XI)**. Recrystallization from methanol yielded 4.12 g of pure material, mp 70–71°; lit.[25] 70–71°.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.65; H, 7.61. Found: C, 85.77; H, 7.61.

In addition 6.92 g (43 mmoles, 43%) of starting ketone X was isolated from the methylene chloride eluate.

Phenylation of Acetomesitylene (XII).—To a solution of 8.36 g (363 mg-atoms) of sodium in 1 l. of *t*-butyl alcohol, 58.94 g (0.36 mole) of XII was added with stirring under nitrogen. To the yellow solution 115 g (0.36 mole) of diphenyliodonium chloride was added and the reaction was boiled under reflux for 6 hr. Filtration of the brown mixture gave 21.6 g of a solid water-soluble material, which was assumed to be sodium chloride. After removal of the solvent from the filtrate, the residue was chromatographed on 500 g of Fluorisil. The hexane eluate contained 38.44 g (0.24 mole 65%) of unreacted XII.

The benzene, ether and acetone eluates together contained 26.5 g of a high-melting solid, **polymer XIII**. Crystallization from hexane of XIII gave light tan crystals which at 176–178° changed to opaque brown crystals, and melted at 200–210°.

Anal. Calcd for $C_{119}H_{114}O_7$: C, 86.28; H, 6.93; mol wt, 1656. Found: C, 86.62; H, 6.65; mol wt, 1640 and 1563.

When the phenylation was run in *t*-amyl alcohol at 0–5°, the reaction still gave solid XIII, mp 170–180°, of similar infrared spectrum.

Anal. Calcd for $C_{119}H_{114}O_7$: C, 86.28; H, 9.93; mol wt, 1656. Found: C, 83.95; H, 7.04; mol wt, 981.

Phenylation of Phenylacetomesitylene (XIV).—To a solution of 2.30 g (100 mg–atoms) of sodium in 500 ml of *t*-butyl alcohol, 23.8 g (0.1 mole) of XIV was added with stirring, under nitrogen. The dark brown mixture slowly turned orange upon the addition of 31.65 g (0.1 mole) of diphenyliodonium chloride. The reaction mixture was boiled under reflux for 6 hr and was worked up as before.

Chromatography of the residue after evaporation of the solvent gave 3.19 g (15 mmoles, 15%) of iodobenzene and 12.6 g (53 mmoles, 53%) of unreacted ketone XIV, identified by infrared spectra. In addition 15.0 g of an orange solid, **polymer XV**, was obtained, which on further chromatography and crystallization from ethanol melted 150–160°.

Anal. Calcd for $C_{92}H_{85}O_4$: C, 87.96; H, 6.90; mol wt, 1256. Found: C, 88.06; H, 6.90; mol wt, 1214 and 1112.

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[25] M. Tiffeneau and A. Orechow, *Bull. Soc. Chim. France*, **33**, 211 (1923)

By-product of the Bisphenol A Reaction. Syntheses and Structure Assignments of 2,4'-Isopropylidenediphenol and 4,4'-(4-Hydroxy-*m*-phenylenediisopropylidene)-diphenol

FRED W. NEUMANN AND WILLIAM E. SMITH

Benzene Research Laboratory, Midland Division,
The Dow Chemical Company, Midland, Michigan

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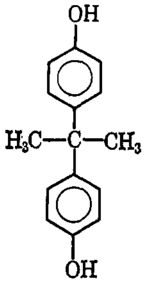
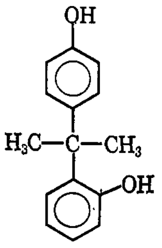
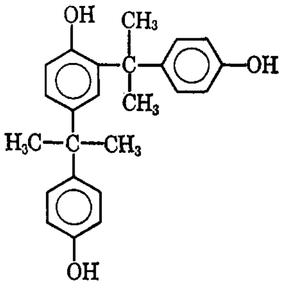
Bisphenol A is the commercial name for 4,4'-isopropylidenediphenol (I) and is commonly prepared by the condensation of phenol and acetone in the presence of a strong acid. A survey of the literature reveals that at least four organic impurities in commercial samples of Bisphenol A have been isolated and structural assignments have been proposed.[1] However, no chemical or physical evidence has been presented to support the assigned structures of the two major impurities, given as the 2,4'-isopropylidenediphenol (II, the 2,4' isomer) and 4,4'-(4-hydroxy-*m*-phenylenediisopropylidene)diphenol (III, trisphenol). Recently[1a] there has been reported the existence of a second triphenolic impurity; however, no chemical evidence or physical data were presented to support the structure given as 2,2,4-tris(4-hydroxyphenyl)-4-methylpentane (IV). If it is assumed that both *ortho* and *para* substitutions are possible during the formation of Bisphenol A and byproducts from acetone and phenol, then at least seven isomeric trisphenols are possible *via* carbonium ion intermediates. Compound IV would represent an eighth isomer.



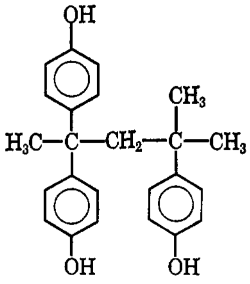
I



II



III



IV

The following work was carried out to verify the proposed structures and thus establish the by-product chemistry of Bisphenol A on a firmer basis. We have independently synthesized compounds II and III and have shown these products to be identical with two of the major, isolated by-products.

The 2,4'-isopropylidenediphenol (II) was synthesized by alkylation of phenol using 2-isopropenylphenol (VI) under acidic conditions. The unsaturated phenol was prepared from methyl salicylate;[2] the sequence of reactions is represented by eq 1 and 2. The yield of the desired compound (II) was low, the major product being 2'-hydroxy-2,4,4-trimethylflavan (VII), which is the known dimerization product[3] of VI. However a sufficient quantity of II was isolated using thin layer chromatography to obtain an infrared spectrum and an X-ray diffraction powder pattern which were congruent with those obtained from crystalline material isolated from a commercial sample of Bisphenol A.

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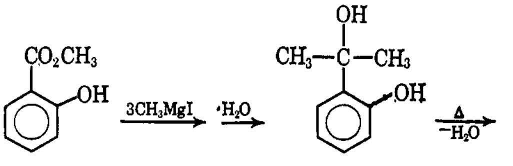
[1] (a) N. H. Reinking and A. E. Barnabeo, *Anal. Chem.*, **37**, 395 (1965); (b) F. Johan, H. Rosca, and O. Râdulescu, *Riv. Chim.* (Bucharest), **13**, 486 (1962); (c) A. S. Salova, *et al.*, *Lakokrasochnye Materialy i ikh Primenenie*, **1**, 71 (1962); (d) A. S. Salova, *et al.*, *Zh. Analit. Khim.*, **18**, 1128 (1963); translation in *J. Anal. Chem. USSR*, **18**, 974 (1963); (e) S. Tominaga, *Benseki Kagaku*, **12**, 137 (1963); (f) W. M. Anderson, *et al.*, *Anal. Chem.*, **31**, 1214 (1959); (g) H. H. Gill, *ibid.*, **36**, 1201 (1964); (h) G. Challa and P. H. Hermans, *ibid.*, **32**, 778 (1960); (i) H. Schnell and H. Krimm, *Angew Chem. Intern. Ed. Engl.*, **2**, 373 (1963); (j) H. Krimm and H. Schnell, West German Patent 1,197,469 (July 29, 1965).

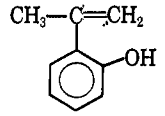
[2] (a) Béhal and Tiffeneau, *Bull. Soc. Chim.*, **3**, 311 (1908); (b) K. Fries, W. Gross-Selbeck, and O. Wicke, *Ann.*, **402**, 305 (1913).

[3] W. Baker, *et al.*, *J. Chem. Soc.*, 1774 (1952).

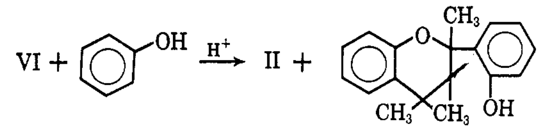


(1)

V



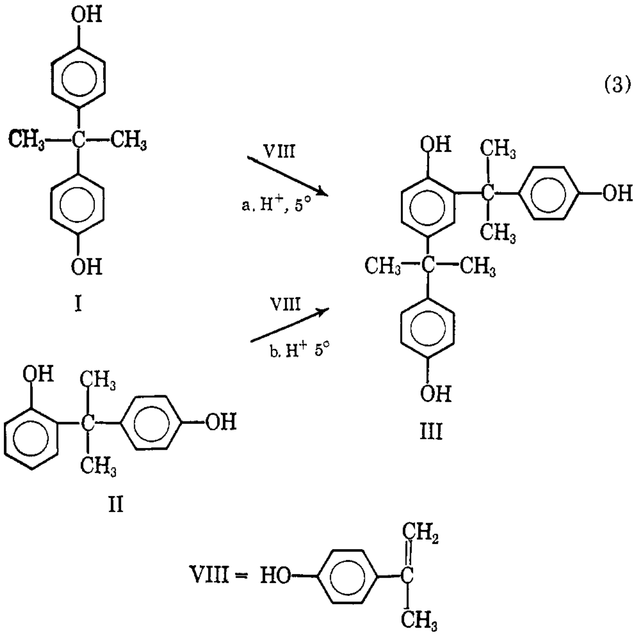
VI



(2)

VII

Trisphenol (III) was synthesized by alkylation of both the 4,4′ isomer (I) and the 2,4′ isomer (II) with 4-isopropenylphenol (VIII) under acidic conditions.



(3)

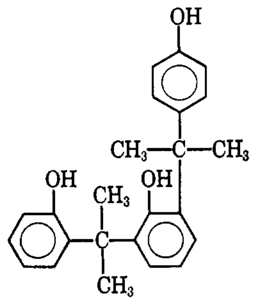
I

II

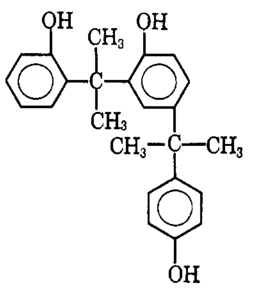
III

The yield of trisphenol (III) from the reaction with the 2,4′ isomer (II) was 67% whereas the yield obtained using the 4,4′ isomer under identical conditions (I) was only 15%. Schnell, *et al.*, have carried out alkylations of both *ortho*- and *para*-substituted monohydric phenols and dihydric phenols with 4-isopropenylphenol to give unsymmetrical 4,4′-isopropylidenediphenols.[4] Our experiments now illustrate selective *para* alkylation in biphenolic molecules such as compound II. The relative yields suggest that one *para* position in the 2,4′ isomer (II) is at least four times more reactive than the combined effect of the four *ortho* positions available in I.

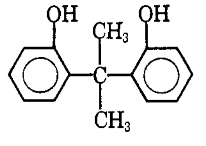
If reaction 2 between phenol and 2-isopropenylphenol (VI) had resulted in the formation of the 2,2′-isopropylidenediphenol (IX), the subsequent reaction with 4-isopropenylphenol (VIII) would have produced the isomeric trisphenols X and XI. In this event, the products of reactions 3a and 3b would have not been identical.



XI



X



IX

If it is assumed that these alkylations go *ortho* and *para* but not *meta*, then the monoalkylation of (I) can give only one isomer (III). The only other diphenolic isomer that can lead to the formation of III by alkylation with 4-isopropenylphenol is the 2,4′-isopropylidenediphenol. Thus the structures previously assigned are now shown to be correct, with the major trisphenolic isolated impurity having the structure of III.

Experimental Section

All melting points are corrected.

***o*-Hydroxy-α,α-dimethylbenzyl Alcohol** (V).—This compound was made from methyl salicylate using the procedures of Béhal, *et al.*,[2a] and Fries, *et al.*[2b] The crude product was used directly to prepare 2-isopropenylphenol. The infrared spectral features have not been reported previously. The infrared spectrum (split Nujol–Fluorolube mulls for all spectra) shows bands which occur at 3590 and 3355, 1382 and 1369, 1240, 1160, and 762 cm^{-1}, characteristic of both free and hydrogen bonded hydroxy groups, two methyl groups on the same carbon atom, a phenyl-oxygen linkage, a carbinol group, and *ortho* substitution, respectively.

2-Isopropenylphenol (VI).—This compound was prepared by the distillative dehydration of the carbinol (V) as described in the literature.[2b,3] Our product was collected at 97–118° (18 mm); the boiling points reported are 204° at atmospheric pressure[2b] and 39° at 0.4 mm.[3] It was characterized by conversion to 2′-hydroxy-2,4,4-trimethylflavan (VII) as described later.

The infrared spectral properties of the 2-isopropenylphenol have not been reported previously. The bands which occur at 3610, 3590, 3350, and 3265 cm^{-1}, and 1375, 1190, 910, and 755 cm^{-1} are characteristic of a hydroxy group with some indication of hydrogen bonding, a methyl group, a phenyl-oxygen linkage, an isopropenyl CH_2 group, and *ortho* substitution, respectively.

2′-Hydroxy-2,4,4-trimethylflavan (VII).—Fries, *et al.*,[2b] previously prepared this compound from 2-isopropenylphenol using hydrogen chloride and ether as solvent. Baker, *et al.*,[3] did not use a solvent. We utilized ethyl alcohol as solvent to similate other reaction conditions with the omission of phenol.

A solution containing 0.5 g of 2-isopropenylphenol in 10 ml of ethanol was saturated overnight with hydrogen chloride while the temperature was kept at −2 to +8°. The ethanol was removed by evaporation and the residue was recrystallized twice

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[4] H. Schnell, H. Krimm, and H. Ruppert, West German Patent 1,150,093 (Dec 27, 1963).

by dissolving in acetic acid and subsequent addition of water. The yield of the crude product isolated was 60%. The melting point of this purified product was 95.5–96.5° which is comparable to the reported value of 97.0°.[3] The authenticity of the material was confirmed by conversion to the acetate which melted at 93.5–95.0° (crude); the reported value is 97°.[3] A mixture melting point determination of the acetylated and unacetylated samples showed a marked depression of 78–93°.

The infrared spectral features of this flavan have not been reported previously. The bands which occur at 3380, 1370 and 1378, 1205, and 755 cm^{-1} are characteristic of a hydrogen-bonded hydroxyl group, methyl group, phenyl–oxygen linkage, and *ortho* substitution, respectively.

2,4′-Isopropylidenediphenol (II).—To a 250-ml, three-neck, round-bottomed flask fitted with a stirrer, a condenser capped with a calcium chloride drying tube, a dropping funnel, a gas inlet tube, and a thermometer, a solution of 3.3 g (0.035 mole) of phenol and 75 ml of 2B anhydrous ethanol (used in all the experiments) was added. The solution was cooled to 8° and saturated with hydrogen chloride. Then a solution of 4.0 g (0.043 mole) of 2-isopropenylphenol in 35 ml of anhydrous ethanol was added over a 35-min period, keeping the temperature of the reaction mixture at 5°. The mixture was then stirred for an additional 5 hr while kept below 10° and then at the end of this period 25 ml of water was added. The ethanol and water were removed by vacuum evaporation. The residue was allowed to air dry on filter paper; the paper absorbed the oily fraction. The crude solid residue amounted to 0.7 g, mp 90–98°.

A sample was analyzed using paper chromatography[1a] and compared to another sample of the purified material. There was estimated to be 10% of the desired compound present in the crude sample. Using thin layer chromatography (tlc plate of silica gel HF254; eluent, 10% acetone in chloroform) a more concentrated fraction was isolated, and then purified by recrystallization using benzene and isooctane. The resulting crystals were shown to be identical with the purified material isolated from commercial Bisphenol A by demonstration of congruent infrared scans and X-ray diffraction powder patterns. The infrared spectrum of the purified material has spectral features which support the structural assignment. The bands which occur at 3420 and 3295, 1360 and 1350, 1200, 830, and 750 cm^{-1} are characteristic of hydrogen-bonded hydroxy groups, two methyl groups on the same carbon atom, phenyl–oxygen linkage, *para* substitution, and *ortho* substitution, respectively. The X-ray diffraction pattern interplanar spacings (relative intensities) were 13.8 (40), 9.2 (16), 6.8 (6), 6.25 (8), 5.8 (100), 5.55 (20), 4.93 (2), 4.72 (8), 4.51 (60), 4.43 (8), 3.97 (16), 3.79 (8), 3.58 (8), and 3.50 (4), with other minor spacings not reported. The 60-MHz nmr spectrum of the compound saturated in carbon tetrachloride with TMS as internal reference showed the protons of the methyl groups as a single absorption at -1.59 ± 0.02 ppm; the aromatic protons as a complex spectrum, with three protons in the range -6.4 to -6.9 ppm and five protons in the range -6.9 to -7.5 ppm; the hydroxyl protons as two single lines, of one proton each at -4.31 ± 0.02 and -4.80 ± 0.02 ppm. The melting point of the purified 2,4′ isomer is 111°.

Anal. Calcd for $C_{15}H_{16}O_2$: C, 79.5; H, 7.06; mol wt, 228. Found: C, 79.1; H, 6.97; mol wt, 222.

A portion of the crude material from the initial reaction mixture was recrystallized from aqueous acetic acid to give a compound melting at 95.5–97.0°. This product was characterized as compound VII by its melting point and by no depression of a mixture melting point when a determination was made using an authentic sample.

Trisphenol (III) from 2,4′-Isopropylidenediphenol.—To a 500-ml, three-neck, round-bottom flask fitted with a stirrer, condenser capped with a calcium chloride drying tube, a dropping funnel, a gas inlet tube, and a thermometer, was added 40.0 g (0.175 mole) of purified 2,4-isopropylidenediphenol in 200 ml of ethanol.

The solution was cooled to 5.5° and saturated with hydrogen chloride. A solution containing 16.1 g (0.12 mole) of 4-isopropenylphenol[5] was added at 7° over a 75-min period. The solution was stirred for an additional 5 hr at 6–8° and then placed in a refrigerator for 16 hr.

To the pink solution 100 ml of water was added, and the water and ethanol were removed by vacuum evaporation. To the residue 150 ml of glacial acetic acid was added, and the resulting mixture was warmed to 80° to effect solution. To this solution 200 ml of warm water was added and the mixture was allowed to cool. The resulting precipitate was collected and dried *in vacuo*, yielding 29.3 g (67.0%), mp 180–190.5°. Twenty grams of this crude material was dissolved in 400 ml of acetic acid and the solution was stirred for 5 min with 4 g of activated charcoal. The charcoal was removed by filtration and 520 ml of water was added to the filtate. The solution was allowed to stand and cool for 6 hr to precipitate the product which was then collected. A sample which was recrystallized four times from acetic acid–water in this manner melted at 184–186°.

Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.56; H, 7.60. Found: C, 79.60; H, 7.15.

A portion of the material was melted in a test tube and then ground; the melting point of this premelted sample was 190.5–193°.

Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.56; H, 7.60; mol wt, 362.4. Found: C, 79.29; H, 7.42; mol wt, 350.

The difference in melting points suggested the existence of allotropic forms, but X-ray diffraction patterns did not substantiate this conclusion. The infrared spectrum of this purified material has spectral features which support the structural assignment. The bands which occur at 3300, 2870, 1240, 820, and 833 cm^{-1} are characteristic of a hydrogen-bonded hydroxyl group, methyl group, a phenyl–oxygen linkage, 1,2,4-trisubstituted benzene, and 1,4-disubstituted benzene, respectively. The X-ray diffraction pattern interplanar spacings (relative intensities) were 10.4 (65), 7.3 (100), 5.74 (25), 5.50 (75), 5.15 (65), 4.91 (50), 4.30 (65), 3.85 (85), 3.73 (10), 3.61 (25), 3.47 (25), 3.36 (25), and 3.25 (3), with other minor spacings not reported. The 60-MHz nmr spectrum of the compound dilute in dioxane with TMS as internal reference showed the methyl protons as two lines of equal intensity at -1.55 ± 0.02 and -1.59 ± 0.02 ppm, each line being assigned to one *gem*-dimethyl grouping (the existence of a shift between them shows they are not in identical environments); the aromatic protons as a complex spectrum, with approximately equal absorption in the ranges -6.3 ppm to -6.75 and -6.75 ppm to -7.3 ppm; the hydroxy protons as a single absorption at -7.6 ppm in one run and -7.4 ppm in another run.

Trisphenol (III) from 4,4′-Isopropylidenediphenol.—To a flask equipped as for the previous reaction was added a solution of 9.12 g (0.04 mole) of 4,4′-isopropylidenediphenol (99.8% pure) in 100 ml of ethanol. The solution was cooled by an ice bath to 8° and then saturated with hydrogen chloride. A solution of 4.0 g (0.03 mole) of 4-isopropenylphenol in 25 ml of 2B anhydrous ethanol was added over a period of 30 min. The final mixture was stirred for 1.5 hr at 4° and then the flask placed in a refrigerator for 17 hr.

To the cold solution 50 ml of water was added, and the ethanol and water were removed by vacuum evaporation. The residue was triturated with 3 ml ethanol and 1 ml of water, and then allowed to stand overnight at room temperature. The resulting precipitate was collected on a filter and dried for 2 hr at 100°. The melting point of this crude product was 138–158°. Paper chromatographic analysis indicated this crude material to contain about 15% of trisphenol when using purified material for calibration. Using thin layer chromatography, a more concentrated material was isolated which was then purified by recrystallization from acetic acid and water. The resulting crystals were proven to be identical with material synthesized in the previous experiment as well as to material isolated from commercial Bisphenol A by demonstration of congruent X-ray diffraction powder patterns and infrared scans.

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(5) H. Schnell and H. Krimm, British Patent 905,994 (Sept 12, 1962).