Dr. Gerald O. Dudek, Department of Chemistry, Harvard University, for mass spectral analysis; Dr. Elwyn T. Reese of this laboratory for enzymatic studies; and Mr. Carmine DiPietro of this laboratory for elemental microanalyses.

Phenylation of Monoketones with Diphenyliodonium Chloride[1]

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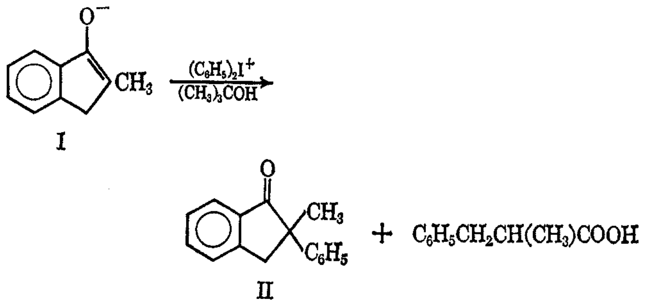
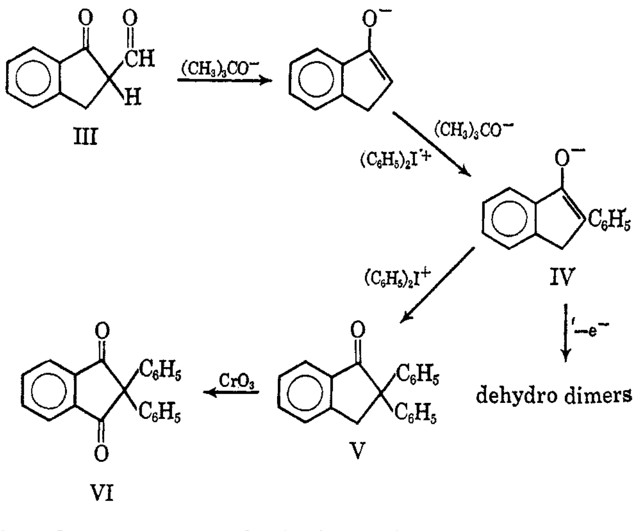
Previous papers from this laboratory have reported on the phenylation of the carbanions of the β-diketones dibenzoylmethane,[3] dimedone,[3,4] and 1,3-indandiones,[5] the triketone tribenzoylmethane,[3] and esters.[6] We have also studied the mesitylation,[7] ethynylation,[8] and vinylation[8] of 2-phenyl-1,3-indandione with iodonium salts. Hauser and co-workers have recently reported on the arylation of a series of β-diketone dicarbanions with diaryliodonium chloride in the presence of sodium amide in liquid ammonia to form γ-phenyl derivatives.[9] The mechanism proposed for the arylations involves ion-pair formation followed by electron transfer from carbanion to iodonium cation with subsequent coupling of the radical pair formed.[5] In the reactions of the dicarbanions it is suggested that coupling occurs between an aryl radical and an anion radical.[9]

In this study we report on the phenylation of the carbanions of a series of monoketones with diphenyliodonium chloride. The results of these phenylations described below can also be interpreted in terms of the previously proposed electron-transfer, radical-pair mechanism for arylation.

The Phenylation of 1-Indanones.—The reaction of 2-methyl-1-indanone (I) with diphenyliodonium chloride in the presence of potassium *t*-butoxide in *t*-butyl alcohol gave the unknown 2-methyl-2-phenyl-1-indanone (II) in 68% yield. There was also formed 20% of α-methylhydrocinnamic acid, a cleavage product of I by potassium *t*-butoxide.



Analogous reaction of 2-formyl-1-indanone (III) gave as the only phenylated product 54% of 2,2-diphenyl-1-indanone (V). In addition 4.5% of 2-(1-keto-2-indanylmethylene)-1-indanone, a known thermal condensation product of III, was obtained. Two other minor products are believed to be dehydrodimers of 2-phenyl-1-indanone (IV). Formation of these products might be explained by decarbonylation of III to 1-indanone, which in the presence of *t*-butoxide gave the monophenyl derivative IV, not isolated but further phenylated to V. It has been reported previously that in the phenylation of 1,3-indandione only the diphenyl derivative was formed.[5] A separate phenylation of IV under similar conditions gave V in 74% yield, plus a small amount of a material also believed to be dehydrodimers of IV. Dehydrodimer formation in the phenylation of the analogous diketone, 2-phenyl-1,3-indandione, has also been reported;[5] its formation, structure, and reactions have been studied in detail.[10] Compound V was oxidized with chromium trioxide to 2,2-diphenyl-1,3-indandione.[5]



The pmr spectrum of V shows a singlet at τ 6.26 for the methylene protons and a singlet at 2.97 for the phenyl hydrogens in the ratio of 1:5. Ketone IV shows a more complicated spectrum in the region τ 6.32–6.81, owing to the mutual splitting of the methylene and methinyl hydrogens. Absorption at τ 2.98 is attributed to the phenyl protons.

Phenylation of 2-Cyano-1-tetralone (VI).—Reaction of 2-cyano-1-tetralone (VI) with potassium *t*-butoxide and diphenyliodonium chloride in *t*-butyl alcohol gave the previously unknown compound 2-cyano-2-phenyl-1-tetralone (VII) in 50% yield.

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[1] This article is taken from the theses of W. J. Daniel and G. Rubin, submitted in partial fulfillment of the requirements for the degree of Master of Science (Chemistry) and in part from the doctoral dissertation of S. A. Galton, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry). This is publication XXVIII in the series on iodonium salts.

[2] Eastman Kodak Co. Fellow, 1961–1962; Texaco Co. Fellow, 1963; National Institutes of Health, Postdoctoral Fellow, 1963–1965.

[3] F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).

[4] The phenylation of dimedone has also been reported by O. Neilands, G. Vanags, and F. Gudriniece, *J. Gen. Chem. USSR*, **28**, 1201 (1958); *Chem. Abstr.*, **52**, 19988 (1958); and J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *J. Am. Chem. Soc.*, **84**, 1504 (1962).

[5] F. M. Beringer, S. A. Galton, and S. J. Huang, *ibid.*, **84**, 2819 (1962).

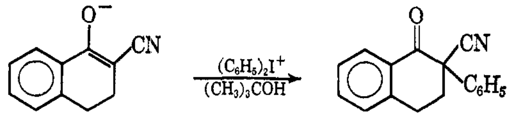
[6] F. M. Beringer and P. S. Forgione, *J. Org. Chem.*, **28**, 714 (1963); *Tetrahedron*, **19**, 739 (1963).

[7] F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **28**, 3417 (1963).

[8] F. M. Beringer and S. A. Galton, *ibid.*, **30**, 1930 (1965).

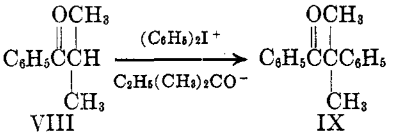
[9] K. G. Hampton, T. M. Harris, and C. R. Hauser, *ibid.*, **29**, 3511 (1964).

[10] (a) F. M. Beringer, S. A. Galton, and S. J. Huang, *Tetrahedron*, **19**, 809 (1963); (b) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **28**, 3250 (1963).



VI VII

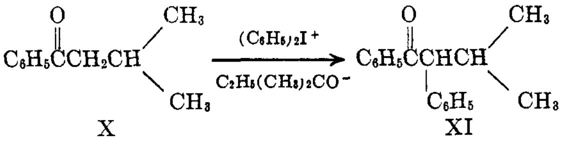
Phenylation of Isobutyrophenone (VIII).—Reaction in *t*-butyl alcohol in the presence of sodium *t*-butoxide and diphenyliodonium chloride at the freezing temperature of the reaction mixture (~26°) gave 2-methyl-2-phenylpropiophenone (IX) in 57% yield. On changing to *t*-amyl alcohol and phenylating at 0–5°, the yield of IX rose to 81%.



$$\mathrm{C_6H_5\overset{\overset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}H \xrightarrow[C_2H_5(CH_3)_2CO^-]{(C_6H_5)_2I^+} C_6H_5\overset{\overset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}C_6H_5}$$

VIII IX

Phenylation of Isovalerophenone (X).—The phenylation run in *t*-amyl alcohol in the presence of sodium *t*-pentoxide and diphenyliodonium chloride at 0–5° gave 2-phenyl-3-methylbutyrophenone (XI) in 23% yield. No 2,2-diphenyl-3-methylbutyrophenone was found.

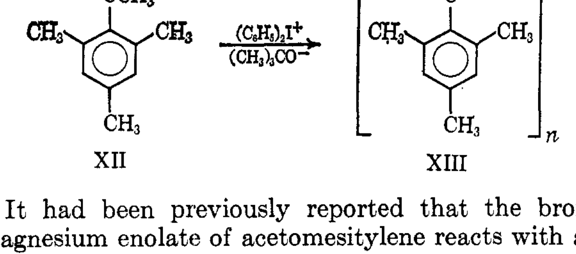


$$\mathrm{C_6H_5\overset{\overset{O}{\|}}{C}CH_2CH\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array} \xrightarrow[C_2H_5(CH_3)_2CO^-]{(C_6H_5)_2I^+} C_6H_5\overset{\overset{O}{\|}}{C}\underset{\underset{C_6H_5}{|}}{C}HCH\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}}$$

X XI

Phenylation of Acetomesitylene (XII).—The phenylation of acetomesitylene run in *t*-butyl alcohol containing sodium *t*-butoxide yielded a high molecular weight polymer (XIII). Infrared spectra of this polymer in Nujol showed bands at 1715, 855, 755, and 700 cm^{-1} characteristic of carbonyl, mesityl, and phenyl adsorption. The ultraviolet spectrum taken in 0.1 *N* sodium ethoxide showed no shift in adsorption, which indicated the absence of acidic hydrogens. Paper chromatography did not show the presence of more than one compound. Attempts to split the polymer by sodium amide and by acidic and basic oxidation did not succeed. Pmr spectrum of the polymer showed very broad absorption at τ 7.8 and 2.5, characteristic of aromatic methyl and phenyl hydrogens. Spectra taken at 75 and 145° did not resolve this absorption band. Carbon, hydrogen, and molecular weight analyses are in accord with a repeating unit of mesitoylphenylmethylene.

The phenylation run at 0–5° in *t*-amyl alcohol containing *t*-pentoxide produced a similar polymer of lower molecular weight.



XII XIII

It had been previously reported that the bromomagnesium enolate of acetomesitylene reacts with acyl chlorides to form diacyl derivatives of acetomesitylene. Initially the phenylation of acetomesitylene was tried by forming the bromomagnesium enolate of acetomesitylene and then adding diphenyliodonium chloride to the reaction mixture. The failure of the reaction was probably due to the insolubility in ether of the reactants.

Phenylation of Phenylacetomesitylene (XIV).—The phenylation of phenylacetomesitylene run in *t*-butyl alcohol containing sodium *t*-butoxide yielded a high molecular weight polymer (XV). Infrared spectrum of this polymer showed bands at 1700, 855, 760, and 700 cm^{-1} characteristic of carbonyl, mesityl, and phenyl adsorption. The ultraviolet spectrum taken in 0.1 *N* sodium ethoxide showed no shift in absorption, which indicated absence of acidic hydrogens. Carbon, hydrogen, and molecular weight analyses indicated the skeleton of the repeating unit to be that of diphenylacetomesitylene.

The results of the phenylations reported here are summarized in Table I.

TABLE I

PHENYLATION OF MONOKETONES

Carbanion	Phenylated product	% yield	Solvent	Temp, °C
I	II	68[a]	*t*-BuOH	80
III	V	54	*t*-BuOH	60
IV	V	74	*t*-BuOH	80
VI	VII	50[a]	*t*-BuOH	80
VIII	IX	57	*t*-BuOH	26
VIII	IX	81	$C_2H_5(CH_3)_2COH$	0–5
X	XI	23	$C_2H_5(CH_3)_2COH$	0–5
XII	Polymer XIII			
XIV	Polymer XV			

[a] Previously not reported in the literature.

All of the above phenylations are accompanied by iodobenzene formation; benzene formation has also been reported in previous phenylations mentioned in the introduction of this paper and has been detected here in the phenylation of IV.

Experimental Section[11]

Starting Materials.—Diphenyliodonium chloride was prepared according to the procedure reported by Beringer and co-workers.[12] 2-Methyl-1-indanone[13] was prepared by cyclization of the acid chloride of α-methylhydrocinnamic acid[14] with aluminum chloride in hexane according to the procedure of Kipping.[15] 2-Formyl-1-indanone was prepared from 1-indanone and ethyl formate in the presence of sodium methoxide according to Ruhemann and Levy.[16] 2-Cyano-1-tetralone was prepared by the ring opening of 4,5-dihydronaphthoisoxazol which was formed by the condensation of hydroxylamine with 2-hydroxymethylene-1-tetralone according to the method of Auwers.[17] Acetomesitylene was

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(11) Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were taken on a Perkin-Elmer Model 521 grating spectrophotometer and a Perkin-Elmer 137 Infracord spectrophotometer. Ultraviolet spectra were taken on a Cary, Model 14, spectrophotometer. Nmr spectra were run on a Varian High Resolution spectrometer at a frequency of 60 Mc/sec, in carbon tetrachloride, using tetramethylsilane as internal standard. Melting points were taken in capillary tubes and were corrected.

(12) F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

(13) R. C. Fuson, W. E. Ross, and C. H. McKeever, *J. Am. Chem. Soc.*, **60**, 2935 (1938), and N. Kishner, *J. Russ. Phys. Chem. Soc.*, **46**, 1411, 1423 (1914).

(14) R. S. Toermer and E. Laage, *Ber.*, **50**, 981 (1917).

(15) F. S. Kipping and G. Clarke, *J. Chem. Soc.*, **83**, 913 (1903).

(16) S. Ruhemann and S. I. Levy, *ibid.*, **101**, 2542 (1912).

(17) K. Auwers, *J. Prakt. Chem.*, **150**, 57, 144 (1937).

prepared by the method of Noller and Adams[18] and phenylacetomesitylene was prepared by the method of Klages and Lickroth.[19] 2-Phenyl-1-indanone was prepared by the cyclization of α,β-diphenylpropionic acid chloride[20] with aluminum chloride according to the method of Campbell and Ciganek.[21] 1-Indanone and 1-tetralone were obtained from Eastman Organic Chemicals. Isobutyrophenone, isovalerophenone, and mesitylene were used as obtained from Distillation Products Industries. *t*-Butyl alcohol and *t*-amyl alcohol were purchased from Matheson, Coleman and Bell and were distilled from calcium hydride.

Phenylation of 2-Methyl-1-indanone (I).—To a solution of 11.2 g (0.10 mole) of potassium *t*-butoxide and 14.6 g (0.10 mole) of I in 200 ml of dry *t*-butyl alcohol there was added with stirring 31.6 g (0.10 mole) of diphenyliodonium chloride. After 20 hr at room temperature most of the iodonium salt remained unreacted. After 3 hr of heating at reflux the solution turned from yellow to tan, and no unreacted iodonium salt was found when a sample was tested with a saturated potassium iodide solution. The solution was filtered and concentrated in a rotary evaporator on a steam bath *in vacuo*. The resulting red oil was dissolved in ether and extracted twice with 200 ml of 0.1 *N* sodium hydroxide. The ether was dried over magnesium sulfate and after evaporation of the solvent yielded 12.6 g of a dark brown solid, representing the neutral fraction. After decolorization and recrystallization from ethanol there was obtained 12.2 g (55 mmoles, 68% based on reacted I) of colorless **2-methyl-2-phenyl-1-indanone** (II), mp 109–110°.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.34. Found: C, 86.07; H, 6.37.

The aqueous phase was acidified with concentrated hydrochloric acid and extracted with methylene chloride to yield after evaporation of the solvent 5.4 g of a yellow liquid. Distillation yielded 3.1 g (20.0 mmoles, 20%) of **α-methylhydrocinnamic acid**. The infrared spectrum was identical with that of an authentic sample.

Ring Cleavage of II.—Compound II (4.5 mmoles, 1 g) and 504 mg (4.5 mmoles) of potassium *t*-butoxide were dissolved in 30 ml of *t*-butyl alcohol and heated under reflux for 12 hr. The solvent was removed by distillation, and the residue was partitioned between ether and water. The aqueous layer was acidified and extracted with methylene chloride. The extract yielded 1.0 g of a liquid whose infrared spectrum showed the characteristic band for a carboxylic acid in the 3500–3000-cm^{-1} region, one carbonyl band at 1730 cm^{-1} assigned to the acid carbonyl, and CH_3 stretching bands at 1420 and 1390 cm^{-1}. The spectrum was very similar to that of α-methylhydrocinnamic acid except it contained a third band in the substituted benzene region, 760–700 cm^{-1}, probably due to the additional phenyl ring.

Phenylation of 2-Formyl-1-indanone (III).—To a solution of 4.38 g (39 mmoles) of potassium *t*-butoxide in 200 ml of dry *t*-butyl alcohol and 6.08 g (38 mmoles) of III there was added with stirring 12.0 g (38 mmoles) of diphenyliodonium chloride. After 18 hr of stirring at room temperature much unreacted iodonium salt was still present. After the mixture was stirred at 60° for 8 hr, the solution turned red, and no unreacted iodonium salt was found. The reaction was worked up as before, and the neutal fraction was chromatographed on a 400-g Fluorisil column. The benzene eluate gave 4.43 g (17 mmoles, 54% based on 1-indanone) of a pale yellow solid of **2,2-diphenyl-1-indanone** (V), mp 95–98°. Recrystallization from isopropyl alcohol raised the melting point to 98–99°, lit.[22] 95–96°.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.73; H, 5.73.

The infrared spectrum of the 2,2-diphenyl-1-indanone was identical with that of an authentic sample. The ultraviolet absorption maximum was $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ ($\epsilon_{\max}$ 29,600).

From the ether eluate small amounts of a white and yellow solid was obtained, mp 227–229 and 117–120°, respectively. The infrared specta of these materials were similar to that of 2-phenyl-1-indanone (IV) and on this basis they are postulated to be **dehydrodimers of IV**.

Chromatography of the acidic fraction on a 200-g Fluorisil column gave in the benzene eluate 0.5 g of a red solid, which upon recrystallization from xylene yielded 0.47 g (1.7 mmoles, 4.5%) of **2-(1-keto-2-indanylmethylene)-1-indanone**, mp 232°, with softening at 225°; lit.[16] softening at 217° and melting at 232°.

Anal. Calcd for $C_{19}H_{14}O_2$: C, 80.28; H, 4.92. Found: C, 80.12; H, 4.86.

Phenylation of 2-Phenyl-1-indanone (IV).—To a solution of 2.3 g (100 mg-atoms) of sodium in 1 l. of *t*-butyl alcohol and 20.8 g (0.1 mole) of IV there was added with stirring 31.2 g (0.1 mole) of diphenyliodonium chloride. The color of the solution turned from a light yellow to a light green. After the mixture had been heated under reflux for 1 hr, no unreacted iodonium salt remained. The solution was concentrated to a thick syrup by distillation of the solvent. The distillate contained 5% of benzene, as determined by optical density of the solution at 254 mμ. The residue was separated into neutral and acidic fractions as before.

Chromatography of the neutral fraction on Fluorisil gave in the hexane eluate a small amount of iodobenzene, identified by its infrared spectrum. The benzene fraction yielded 23 g of pale orange, oily crystals. When these were dissolved in 400 ml of hexane a small amount of insoluble solid was collected, mp 229–230°. The ultraviolet and infrared spectra of this material were identical for those obtained for the **dehydrodimer of IV** obtained in the previous reaction. The hexane solution was concentrated to 200 ml and allowed to crystallize; the white solid formed was collected to yield 21 g (74 mmoles, 74%) of **2,2-diphenyl-1-indanone** (V), mp 96–97°.

Chromic Acid Oxidation of 2,2-Diphenyl-1-indanone (V).—A solution prepared by dissolving 1.5 g of chromium trioxide in 35 ml of hot glacial acetic acid containing 3 ml of concentrated sulfuric acid was added dropwise to a solution of 2.0 g (7.0 mmoles) of V in 25 ml of glacial acetic acid. The solution became dark green immediately, and the temperature rose gradually to 53° during the addition. After being stirred for 1 hr at room temperature, the reaction mixture was poured over 250 ml of ice and water. The precipitate was recrystallized twice from ethanol to yield 412 mg (1.38 mmoles, 19.5%) of **2,2-diphenyl-1,3-indandione**, mp 123–124°, lit.[5,23] 125 and 118°, respectively. No depression of melting point was observed when mixed with an authentic sample. The infrared spectrum was identical with that of an authentic sample.

Phenylation of 2-Cyano-1-tetralone (VI).—To a solution of 3.36 g (30 mmoles) of potassium *t*-butoxide in 200 ml of dry *t*-butyl alcohol and 5.13 g (30 mmoles) of VI there was added with stirring 9.48 g (30 mmoles) of diphenyliodonium chloride. The mixture was heated at reflux overnight, and worked up as before.

Chromatography of the neutral fraction (5.8 g) yielded 3.74 g (15 mmoles, 50%) of **2-cyano-2-phenyl-1-tetralone** (VII), mp 65–68°. Sublimation at 200° (0.3 mm) raised the melting point to 69–70°.

Anal. Calcd for $C_{17}H_{13}NO$: C, 82.24; H, 5.26; N, 5.67. Found: C, 82.44; H, 5.44; N, 5.74.

Phenylation of Isobutyrophenone (VIII).—To a solution of 2.30 g (100 mg-atoms) of sodium in 500 ml of *t*-amyl alcohol 14.82 g (0.1 mole) of VIII was added with stirring. After the solution had been cooled to 0–5°, 31.65 g (0.1 mole) of diphenyliodonium chloride was added. The ice bath was allowed to melt, and the reaction temperature gradually rose to room temperature. The reaction mixture was agitated under nitrogen for an additional 6 hr.

The excess base was neutralized with saturated ammonium chloride. The reaction mixture was filtered, and the filtrate after removal of the solvent was chromatographed as before. The benzene fraction gave 18.1 g (81 mmoles, 81%) of straw-colored **2-methyl-1-phenylpropiophenone** (IX). Crystallization from methanol yielded 16.4 g of pure material: mp 44–45°, lit.[24] 46–47°; oxime 192–193°, lit.[24] 192–193°.

Anal. Calcd for $C_{16}H_{16}O$: C, 85.69; H, 7.19. Found: C, 85.80; H, 7.16.

Phenylation run in *t*-butyl alcohol at the freezing temperature of the reaction mixture (~26°) gave 57% of IX.

Phenylation of Isovalerophenone (X).—The same procedure was used as above. To a solution of 2.30 g (100 mg-atoms) of sodium in 500 ml of *t*-amyl alcohol there was added with stirring 16.22 g (0.1 mole) of X, and the solution was cooled to 0–5°. The reaction turned dark orange as 31.65 g (0.1 mole) of diphenyliodonium chloride was added. The reaction was worked up as before. Chromatography of the neutral fraction gave in the

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(18) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **45**, 1889 (1924).

(19) A. Klages and G. Lickroth, *Ber.*, **32**, 1549 (1899).

(20) W. Wislicenus and K. Goldstein, *ibid.*, **28**, 815 (1895).

(21) N. Campbell and E. Ciganek, *J. Chem. Soc.*, 3834 (1956).

(22) M. Vaillant, *Ann. Chim.*, **9**, 5 (1954).

(23) (a) A. Schönberg and R. Moubasher, *J. Chem. Soc.*, 71 (1943); (b) R. Moubasher, *J. Am. Chem. Soc.*, **73**, 3246 (1951).

(24) M. Ramart-Lucas and M. E. Salmen-Legagneur, *Bull. Soc. Chim. France*, **45**, 730 (1929).

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 $C_{92}H_{86}O_4$: 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

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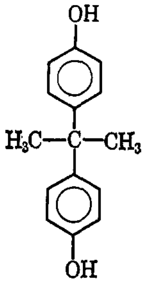
Bisphenol A is the commercial name for 4,4'-isopropylidenediphenol (I) and is commonly prepared by the condensation of phenol and acetone in the presence of a strong acid. A survey of the literature reveals that at least four organic impurities in commercial samples of Bisphenol A have been isolated 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.



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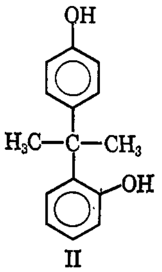
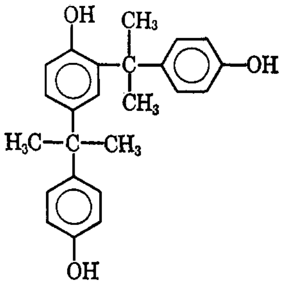
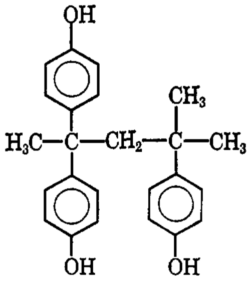


II



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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[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).