Summary

The method of analysis given here leads to a fairly complete knowledge of the composition of neoarsphenamine and it has been found:

1. That the arsenite method of analysis gives a more accurate distribution of the sulfur in neoarsphenamine than has been previously possible.
2. That the so-called "sulfarsphenamine sulfur" is, in fact, nuclear sulfur.
3. That there are probably two types of combination between arsphenamine base and sodium formaldehyde sulfoxylate, one being of the N-methylene type, and the other resembling a double salt formation.
4. That there is a type of sulfur present in neoarsphenamine which owes its origin to some reaction or decomposition of sodium formaldehyde sulfoxylate but it is no longer present as sulfoxylate.

Brooklyn, New York

[Contribution from the Chemical Laboratory of Barnard College]

THE DIBROMIDES OF METHYLCOUMARIC AND METHYLCOUMARINIC ACIDS

By Marie Reimer and Marion Howard

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In connection with a study of *o*-methoxybenzalpyruvic acid it became necessary, for purposes of identification, to prepare α-bromo-*o*-methoxycinnamic acid (169–171°). As reactions for the preparation of this substance by the action of a 50% aqueous solution of potassium hydroxide on methylcoumaric acid dibromide, according to the directions of Perkin,[1] failed to give the substance he described, we have made a study of the action of bromine on methylcoumaric and methylcoumarinic acids and of the elimination of hydrogen bromide from the resulting compounds. Perkin[1] described two isomeric dibromo addition products, neither of which, however, he prepared in the pure condition. Fittig and Ebert[2] questioned Perkin's results, as they were able to obtain but one dibromo compound. Later investigators[3,4,5] were also unable to identify two products of the reaction, although Stoermer mentions an "impure methylcourmarinic dibromide" left in the filtrates. We find that the product of addition of bromine to methylcoumaric and methylcoumarinic acids is in each case a mixture of isomers which we have succeeded in separating and purifying; a dibromo acid melting, with vigorous decomposition, at 177° and, in smaller quantity, an isomeric acid melting, with very slight de-

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[1] Perkin, *J. Chem. Soc.*, **39**, 418 (1881).

[2] Fittig and Ebert, *Ann.*, **216**, 146 (1883).

[3] Werner, *Ber.*, **39**, 27 (1906).

[4] Stoermer and Friemel, *Ber.*, **44**, 1838 (1911).

[5] Biilmann and Lund, *Ann. chim.*, [9] **18**, 263 (1922).

composition, at 134° and changing above this temperature to the higher-melting isomer.

The isomeric dibromo acids differ markedly in solubility and in their behavior toward alkaline reagents. The higher-melting acid reacts rapidly with 50% aqueous potassium hydroxide, the chief product of the reaction being an oil which was proved to be α-bromo-*o*-methoxystyrene. This was accompanied by a very small amount of the potassium salt of an acid melting when pure at 136°, instead of a large percentage of acid melting at 169–171° as was expected from Perkin's description of this experiment. This low-melting acid was the chief product of the reaction when alcoholic instead of aqueous potassium hydroxide solution was used with the dibromo acid (177°). The dibromo acid (134°), treated with 50% aqueous potassium hydroxide, reacted slowly in the cold to give an almost quantitative yield of an acid melting at 171°, the same α-bromo-*o*-methoxycinnamic acid as described by Perkin (169–171°). That this acid is the geometrical isomer of that melting at 136° is proved by the ready conversion of the latter into the acid (171°) by exposure of its aqueous solution to the sunlight.

Since it was found possible to prepare the two dibromo acids in pure condition and since they differ so markedly toward alkaline reagents, it seemed of interest to carry out with both acids certain of the reactions previously studied by other investigators with the higher melting of the two. The products of the reactions of the two dibromo acids with water and with an aqueous solution of bromine were the same. With methyl alcohol isomeric compounds have been obtained.

Experimental Part

Preparation of Methylcoumaric and Methylcoumarinic Acids

Since coumarin is the least expensive of the substances from which these compounds can be prepared and dimethyl sulfate, for the same reason, is to be preferred to methyl iodide, a modification of the method of Stoermer and Friemel was used instead of that of Reychler[6] which gives better yields.

Fifty grams of coumarin was dissolved by warming with a solution of 30 g. of sodium hydroxide in 150 cc. of water. To the cooled solution 100 g. of dimethyl sulfate was added, the mixture shaken repeatedly and allowed to stand at room temperature for about three days. At the end of this time an oil, the methyl ester of methylcoumarinic acid, had separated. Water was added until the ester formed the lower layer; it was drawn off, the ethereal extract of the aqueous residue added to it, the ethereal solution washed repeatedly, dried over calcium chloride, and the ether distilled off. The clear oil remaining was hydrolyzed by boiling with 30% potassium hydroxide solution if methylcoumarinic acid was to be prepared or distilled

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[6] Reychler, *Bull. soc. chim.*, [4] 3, 551 (1908).

and then hydrolyzed to obtain methylcoumaric acid. The change of the methyl ester of methylcoumarinic acid to that of methylcoumaric acid on distillation was not complete but a fair yield of the latter could be obtained by rapid and repeated distillation. Although a boiling point of 275° is given as that of the methyl ester of methylcoumarinic acid, hydrolysis of the fraction distilled carefully at this temperature gives a mixture of the two acids. This agrees with the results of Biilmann. By rapid distillation the boiling point rises to 293°, that of methylcoumaric acid methyl ester. The yield of methylcoumarinic acid (m. p. 92–93°) obtained by hydrolysis of the undistilled ester was 78% calculated from the coumarin used; that of methylcoumaric acid (m. p. 182°) obtained from the ester two or three times distilled was 40 to 50%.

Action of Bromine on Methylcoumarinic and on Methylcoumaric Acids

Methylcoumarinic acid was dissolved in carbon disulfide, the calculated amount of bromine added slowly to the cooled solution and the solvent evaporated completely in a current of air. The pure white dibromo addition product, formed in quantitative yield, softened slightly at 120 to 130° and melted with decomposition at about 165°. Twenty-two grams of this product was treated with 25 cc. of toluene and the mixture thoroughly heated with stirring in boiling water. The liquid was drawn off, the undissolved residue extracted again at 100° with 25 cc. of toluene and a third time with 20 cc. The undissolved portion melted at 174–175°; on crystallization from boiling toluene it separated in compact clumps, melting with vigorous decomposition at 177°. The crystals that separated from the three toluene extracts were those of the impure, low-melting dibromide. They were purified by treatment at 100° with a quantity of toluene insufficient for complete solution; the portion undissolved was impure, high-melting dibromide. The crystals separating from the solution were again treated in the same way until after four or five recrystallizations the substance had a constant behavior on melting. The pure, low-melting dibromide melts to a clear liquid at 134° and immediately resolidifies; this solid begins to give off a gas at 169° and clears and decomposes vigorously at 170°. The melting at 134° is accompanied by slight decomposition, so that the final melting point is never as high as that of the pure high-melting isomer. That this behavior in the melting point tube is due to a transformation to the high-melting isomer was proved by heating a considerable quantity of the low-melting acid for about ten minutes to 136°. The cooled product, slightly brown, after washing with warm toluene melted at 177° and at the same temperature when mixed with the pure, high-melting dibromo acid.

Anal. (Subs. 134°.) Subs., 0.1794, 0.1446: CO_2, 0.2326, 0.1888; H_2O, 0.0523, 0.0396. Calcd. for $C_{10}H_{10}O_3Br_2$: C, 35.52; H, 2.96. Found: C, 35.36, 35.59; H, 3.23, 3.03. Subs. 7.628 mg.: AgBr, 8.588 mg. Calcd.: Br, 47.33. Found: 47.84 (micro-Carius). Subs. 8.434 mg.: AgI, 5.820 mg. Calcd.: OCH_3, 9.17. Found: 9.22 (micro-Zeisel).

The quantity of pure acid (134°) isolated from the reaction of bromine on methylcoumarinic acid was 18 to 20% of the crude product; by the action of bromine on methylcoumaric acid no more than 9 to 10% was obtained. The substance crystallizes from toluene in clumps of branching needles which separate on the surface of the solution and "creep" up the sides of the beaker, a behavior characteristic of this isomer as distinguished from that of the other. In fact it is possible to make a rough separation of the isomers by allowing a toluene solution of the mixture to stand until the solvent has completely evaporated. The crystals on the sides and over the top of the beaker are slightly impure, low-melting acid; the compact crystals on the bottom, the high-melting form. The low-melting acid is not as stable as its isomer but takes on a brown coloration on exposure to light and air.

The solubilities of the two dibromo acids in the solvents which have been used by other investigators of this bromination reaction are given in the following table.

TABLE I

SOLUBILITIES

Substance	G. of subs. in 100 g. solvent CS_2 (20°)	$CHCl_3$ (20°)	Toluene (20°)	Toluene (100°)
177°	0.33	3.73	2.08	6.91
134°	1.54	14.50	4.88	45.91

It is evident that for the separation of these isomers toluene at 100° is the best solvent. The compound (134°) can be heated in toluene at 100° for many hours without isomerization. In boiling toluene, however, it gradually changes to the high-melting form. This fact, together with the decidedly greater solubility of the 134° acid, evidently accounts for the failure of other investigators to isolate the compound.

Reaction of Alkalies on the Dibromo Acids

α-Bromo-*o*-methoxycinnamic Acid, $2\text{-}CH_3OC_6H_4CH{=}CBrCOOH$ (171°).—When finely ground crystals of the acid (134°) were stirred in an excess of a 50% aqueous solution of potassium hydroxide, the crystals became opaque and slowly went into solution; after standing for twenty-four hours an almost solid mass of a colorless potassium salt had separated. This was filtered out and dissolved in water. A faint cloudiness due to the oil, α-bromo-*o*-methoxystyrene, was removed by filtration. Addition of hydrochloric acid precipitated a colorless acid which separated from boiling water in long, fine needles melting at 171°. The acid is in all respects like that described by Perkin as melting at 169–171°. From the solution left after filtration of the potassium salt, more of the same acid was precipitated. The yield was practically quantitative. By boiling the acid with 10% aqueous potassium hydroxide solution, a second molecule of hydrogen bromide was eliminated readily and *o*-methoxyphenylpropiolic acid (124–125°) formed, as described by Perkin.

α-Bromo-*o*-methoxycinnamic Acid (136°).—The dibromo acid melting at 177° was subjected to the same treatment as that described above. After twenty-four hours, the solution was clear except for a few crystals of a potassium salt. These, on solution and acidification, gave a trace of an acid melting at about 130°. On acidification of the potassium hydroxide solution, an oil separated. It was taken up with ether, the ethereal solution washed with sodium carbonate, dried, the ether distilled off and the residue, a pale yellow, fragrant oil, analyzed.

Anal. Subs. 0.1112; CO_2, 0.2069; H_2O, 0.0405. Calcd. for C_9H_9OBr: C, 50.70; H, 4.22. Found: C, 50.74; H, 4.04.

The substance on oxidation with potassium permanganate in the cold yields *o*-methoxybenzoic acid. It is, therefore, α-bromo-*o*-methoxystyrene, $2\text{-}CH_3OC_6H_4CH{=}CHBr$.

In the hope of getting a larger quantity of the low-melting acid, the dibromo acid (177°) was treated with potassium hydroxide in alcoholic solution; 3 g. of the finely powdered acid was covered with a saturated solution of potassium hydroxide in methyl alcohol and the mixture stirred vigorously. Soft, white crystals began to separate immediately and after three minutes there was a nearly solid mass of this substance. The solid, a potassium salt, was at once filtered and dissolved in water, a trace of bromostyrene filtered out and the cooled solution acidified. The mixture, at first cloudy, rapidly deposited pale yellow needles of an acid which was purified by crystallization from hot benzene. It separates in stiff, pale yellow needles melting at 136°; from hot water it separates in a pasty condition and slowly solidifies.

Anal. Subs. 0.1577, 0.1690; CO_2, 0.2692, 0.2897; H_2O, 0.0531, 0.0553. Calcd. for $C_{10}H_9O_3Br$: C, 46.68, H, 3.50. Found: C, 46.49, 46.66; H, 3.75, 3.63.

The yield of this acid was 80–90% of that calculated. From the aqueous filtrates a small amount of a higher-melting, colorless acid separated slowly. This was formed by the action of light on the solution of the yellow acid (136°) as was proved by subjecting a saturated aqueous solution of the latter in a quartz test-tube to bright sunlight. After two hours the liquid was filled with a mass of fine, white needles. This substance crystallized from hot water in long, stiff needles melting at 171°. A mixed melting point determination proved it to be identical with the α-bromo-*o*-methoxycinnamic acid (171°) previously described. This transformation shows that the new, more soluble yellow acid (136°) is the geometrical isomer of the slightly soluble, colorless acid (171°). The same transformation can be brought about in benzene solution.

The methyl ester of the acid (136°) could not be prepared by allowing the acid to stand in contact with methyl alcohol saturated with hydrogen chloride; almost the whole amount of the acid was recovered unchanged after many hours. The pure ester, a lemon-yellow, mobile oil, was prepared in quantitative yield by the action of diazomethane on the purified acid.

Anal. Subs. 0.1311; CO_2, 0.2342; H_2O, 0.0499. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.70; H, 4.05. Found: C, 48.64; H, 4.23.

Elimination of hydrogen bromide from the acid (136°) was much more difficult than from the isomeric acid. After boiling a solution of the acid in 10% potassium hydroxide solution for thirty minutes, practically the entire amount was recovered unchanged. After boiling the solution for two hours, the acetylenic acid was precipitated from the acidified solution together with a considerable quantity of methoxybromostyrene.

The differences in properties of the two isomeric acids might indicate that the acid (136°) is the *cis*, the acid (171°) the *trans* isomer but no conclusion can be drawn without direct experimental evidence.

Reaction of Aqueous Bromine Solution on the Two Dibromo Acids

5-Bromo-2-methoxycinnamic Acid Dibromide,

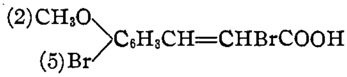
$$\left.\begin{matrix}(2)\mathrm{CH_3O}\\(5)\mathrm{Br}\end{matrix}\right\rangle \mathrm{C_6H_3CHBrCHBrCOOH}$$

(201°).—The dibromo acid (177°) on treatment with an aqueous solution of bromine, according to the directions of Biilmann,[5] gave a practically quantitative yield of a product with a bromine atom in the ring. After crystallization from benzene it melted at 201°. (M. p. given by Biilmann, 198°; Perkin, 188°.)

The dibromo acid (134°), subjected to the same treatment, became pasty and even on vigorous shaking could not be made to react completely with the bromine solution. The only product isolated melted at about 184° and was shown by analysis to be a mixture of a tribromo and a dibromo compound. By repeated recrystallization of this mixture a small amount of the tribromo acid (201°) was obtained in pure condition.

By the action of hot aqueous potassium hydroxide solution on this tribromo acid, Perkin obtained 5-bromo-2-methoxyphenylpropiolic acid. By a less strenuous method we have prepared two isomeric ethylenic acids.

α-Bromo-5-bromo-2-methoxycinnamic Acid,



$$\begin{matrix}(2)CH_3O \\ (5)Br\end{matrix}\!\!>C_6H_3CH{=}CHBrCOOH$$

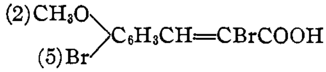
(163–164°).—Two grams of the tribromo acid was covered with a saturated solution of potassium hydroxide in methyl alcohol and the mixture stirred. The tribromo acid dissolved at once and a very few crystals of a potassium salt separated. After five minutes, addition of water produced no cloudiness, indicating that there had been no formation of a styrene derivative as was the case with the acids in which there was no bromine in the ring. Acidification of the solution gave a pasty precipitate which slowly solidified after cooling and vigorous stirring. The substance, obtained in practically quantitative yield, separates from boiling benzene in fine, pale yellow needles, melting at 163–164°.

Anal. Subs. 0.1554; CO_2, 0.2052; H_2O, 0.0380. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.71; H, 2.38. Found: C, 36.01; H, 2.66.

The **methyl ester** was obtained in small quantity when the acid was treated with a saturated solution of hydrogen chloride in methyl alcohol but about one-half of the acid was recovered unchanged. A quantitative yield of the ester separated from the ethereal solution in lustrous, pure white needles when the acid was treated with diazomethane. It crystallizes from a small volume of methyl alcohol in fine, soft needles melting at 94°.

Anal. Subs. 0.1488; CO_2, 0.2079; H_2O, 0.0427. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 38.10; H, 3.19.

α-Bromo-5-bromo-2-methoxycinnamic Acid,



$$\begin{matrix}(2)CH_3O \\ (5)Br\end{matrix}\!\!>C_6H_3CH{=}CBrCOOH$$

(221°).—This acid separated slowly from the benzene filtrates of the yellow acid (163–164°) just described. After repeated crystallization from benzene it was obtained in the form of fine, pure white needles melting at 221°. The high-melting point led to the belief that the substance might be a polymer of the acid (163–164°) formed by the action of light on the benzene solution of the latter. A molecular weight determination, however, and the fact that the substance readily decolorizes a solution of potassium permanganate in the cold to form 2-methoxy-5-bromobenzoic acid proved it to be an isomeric, not a polymeric, form of that acid.

Anal. Subs. 2.692 mg.; CO_2, 3.560 mg.; H_2O, 0.540 mg. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.71; H, 2.38. Found: C, 36.07; H, 2.24. Mol. wt. (Rast method). Subs. 0.570 mg.: camphor, 7.596 mg. Δ_t 9°. Calcd.: 336. Found: 333.5.

It was found possible to prepare this acid in quantity by exposing a saturated benzene solution of the yellow acid (163–164°) to bright sunlight. The first crystals to separate on spontaneous evaporation of the benzene, after two or three days' exposure, were those of the high-melting, colorless acid which is considerably less soluble in benzene than its isomer. By repeated exposures good yields of the acid (221°) were obtained.

The **methyl ester** of the acid (221°) may be formed in quantitative yield by the reaction of methyl alcohol saturated with hydrogen chloride or by diazomethane. It separates from methyl alcohol in firm, stiff needles, melting at 106–107°.

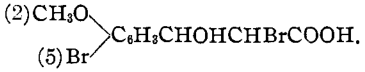
Anal. Subs. 0.1342; CO_2, 0.1856; H_2O, 0.0364. Calcd. for $C_{11}H_{10}O_3Br_2$: C. 37.71; H, 2.85. Found: C, 37.71; H, 3.01.

By treatment of both the acids (163–164°) and (221°) with a boiling 10% aqueous solution of potassium hydroxide a molecule of hydrogen bromide was readily eliminated from each and 5-bromo-2-methoxyphenylpropiolic acid formed; it was crystallized from boiling benzene. The substance turns bright yellow and effervesces violently at 174°; it is evidently Perkin's acetylenic acid "melting with decomposition at about 168°."

Anal. Subs. 0.1244; CO_2, 0.2134; H_2O, 0.0317. Calcd. for $C_{10}H_7O_3Br$: C, 47.06; H, 2.74. Found: C, 46.98; H, 2.83.

Reaction of Water on the Two Dibromo Acids

α-Bromo-β-hydroxy-*o*-methoxyhydrocinnamic Acid, 2-$CH_3OC_6H_4CHOHCHBrCOOH$ (134°).—Biilmann prepared this hydroxy acid by shaking the high-melting dibromo acid with water. The low-melting dibromo acid (134°) gives the same substance under the same treatment.

By reaction of the hydroxy acid with an aqueous bromine solution Biilmann prepared α-bromo-β-hydroxy-5-bromo-2-methoxyhydrocinnamic acid,  $\begin{matrix}(2)CH_3O\\(5)Br\end{matrix}\!>C_6H_3CHOHCHBrCOOH$. The acid melted at 137°, solidified and melted again at 154°. This behavior and especially the fact that after he had prepared the 154° substance he was not able to obtain the compound (137°) in the same laboratory led Biilmann to conclude that the acids were dimorphic not isomeric. The behavior of the compound (137°) on melting is so like that of our dibromo acid (134°) that the question of possible isomerism in the case of the two hydroxy acids arose. To test the point we have prepared the two hydroxy acids and treated both with an ethereal solution of diazomethane. From both solutions an oil separated which solidified completely. The solid, in each case, was crystallized from boiling ligroin from which it separated in firm clumps of crystals melting at 93–95°. A mixed melting point determination showed that the two were identical. The substance is the methyl ester of α-bromo-β-methoxy-5-bromo-2-methoxyhydrocinnamic acid  $\begin{matrix}(2)CH_3O\\(5)Br\end{matrix}\!>C_6H_3CHOCH_3CHBrCOOCH_3$.

Anal. Subs. 0.1559; CO_2, 0.2131; H_2O, 0.0517. Calcd. for $C_{12}H_{14}O_4Br_2$: C, 37.69; H, 3.66. Found: C, 37.29; H, 3.71.

The formation of the same compound by the action of diazomethane on the two hydroxy acids is an argument for their dimorphism rather than isomerism.

Reaction of Methyl Alcohol on the Two Dibromo Acids

α-Bromo-β-methoxy-2-methoxyhydrocinnamic Acid, 2-$CH_3OC_6H_4CHOCH_3CHBrCOOH$ (118°).—Werner[7] prepared the methyl ester (m. p. 64°) of this acid by warming the impure high-melting dibromo acid with methyl alcohol and hydrogen chloride; on hydrolysis of this ester the acid (m. p. 118°) was obtained. We have prepared this acid, in good yield, by shaking the pure dibromo acid (177°) with an excess of cold methyl alcohol for nine hours.

α-Bromo-β-methoxy-2-methoxyhydrocinnamic Acid (136°).—On repeating Werner's experiment we obtained not only the acid described by him, melting at 118°, but in very small quantity an isomeric acid melting at 136°. The ester (64°) formed by the action of methyl alcohol saturated with hydrogen chloride on the high-melting dibromo acid gives, on hydrolysis with alcoholic potassium hydroxide, a heavy deposit of the potassium salt of the acid (118°). On acidifying the alkaline filtrate from the separation of the potassium salt, a small amount of an acid separates slowly in fine, shining needles melting, after recrystallization from water, at 136°. Analysis proves it to be isomeric with Werner's acid (118°).

Anal. Subs., 5.207 mg.: CO_2, 8.680 mg.; H_2O, 2.160 mg. Calcd. for $C_{11}H_{13}O_4Br$: C, 45.67; H, 4.53. Found: C, 45.46; H, 4.64.

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[7] Werner, *Ber.*, **39**, 27 (1906).

When the low-melting dibromo acid (134°) was shaken with an excess of cold methyl alcohol, this methoxy acid (136°) was the sole product of the reaction.

Summary

Two isomeric dibromo acids have been prepared in the pure condition by the action of bromine on methylcoumaric and on methylcoumarinic acids.

The reactions of these acids with potassium hydroxide, water, an aqueous solution of bromine and methyl alcohol have been studied.

New York, N. Y.

[Contribution from the Chemistry Laboratory of the University of Michigan]

TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS

By L. C. Anderson and M. Gomberg

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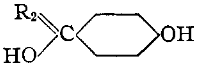
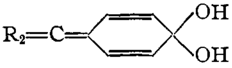
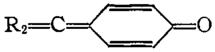
It has been shown[1] that when *p*-hydroxytriphenylcarbinol is crystallized from 50% acetic acid, the product obtained is yellow in color, melts at 139–140°, and when warmed it loses a molecule of water in a comparatively short time, forming fuchsone (III). On the other hand, when this carbinol is crystallized from alcohol containing a trace of ammonia, it is obtained colorless, melts at 157–159°, and when warmed loses a molecule of water at a very slow rate, fuchsone being the product. It has been demonstrated that neither of the modifications contains water of crystallization and that they are not simply two different crystalline forms of the same material. One modification can be changed into the other by the proper choice of solvent; heat or light favors the colored form. Structures (I) and (II) have been assigned to these forms:



I. Benzenoid (colorless)



II. Quinonoid (colored)



III. Fuchsone

It has been our purpose to study these tautomeric forms by means of the quantitative absorption spectra of their solutions. The present paper deals with *p*-hydroxytriphenylcarbinol and with *o*-cresyldiphenylcarbinol (3-methyl-4-hydroxytriphenylcarbinol). Work on other carbinols will appear in subsequent papers.

Procedure.—For the measurement of absorption spectra in the ultraviolet, we used a Judd-Lewis sector photometer (Hilger)[2] and a Hilger quartz spectrograph, Size C. The source of light was a condensed spark between tungsten electrodes under distilled water and, when photo-

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[1] (a) Gomberg, This Journal, **35,** 1035 (1913); (b) Gomberg and co-workers, **37,** 2575 (1915); (c) **38,** 1577 (1916); (d) **39,** 1674 (1917); (e) **39,** 2392 (1917); (f) **42,** 1864 (1920); (g) **42,** 1879 (1920); (h) **45,** 190 (1923); (i) **47,** 2392 (1925).

[2] Adam Hilger, Ltd., London, Catalog No. H-40.