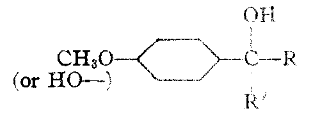
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

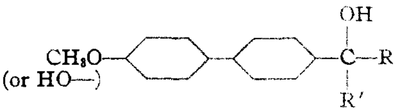
Quinoidation of Triaryl Compounds—Hydroxybiphenyldiarylmethyl Cations

BY LEIGH C. ANDERSON AND W. A. FISHER

Data have been presented from this Laboratory on the preparation and absorption spectra of *p*-hydroxyphenylbiphenylcarbinols.[1] This paper discusses investigations which have been made on biphenylcarbinols in which a hydroxyl or methoxyl group has been substituted on the terminal carbon of the biphenyl group in order to obtain data on the biphenoquinone type of structure. Two types of carbinols were used in this investigation: methoxy or hydroxyphenyldiarylcarbinols illustrated by I and methoxy or hydroxybiphenyldiarylcarbinols illustrated by II where the aryl groups R and R′ are either phenyl or *para*-biphenyl groups. The absorption spectra of the cations produced by solutions of these carbinols in acid have been ascertained.



I



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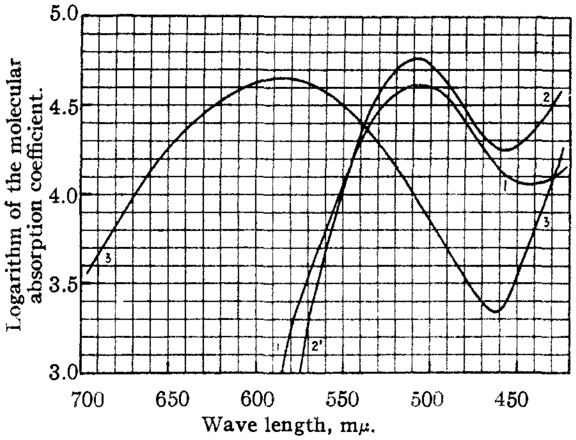

Fig. 1.—Absorption of acetic-sulfuric acid solutions of: 1, 4-phenyltriphenylmethyl sulfate; 2, 4-methoxy-4′-phenyltriphenylmethyl sulfate; 3, 4-(*p*-anisyl)-triphenylmethyl sulfate.

The effect on the absorption spectrum of the triphenylmethyl group when a *p*-anisyl group is substituted in a para position has been investigated for the first time. The chemical investigation of 4-(*p*-hydroxyphenyl)-triphenylcarbinol gave no evidence that the substance would become quinonoid through the biphenyl group. A study of the absorption curves gives evidence that the cations derivable from this compound and others containing the 4-hydroxybiphenyl or 4-methoxybiphenyl group contain predominating electronic structures which include quinoidation of the biphenyl group in a manner similar to that shown for fuchsones in the preceding paper. Considering the ions: 4-phenyltriphenylmethyl, 4-methoxy-4′-phenyltriphenylmethyl, and 4-(*p*-anisyl)-triphenylmethyl, the absorption of the first two is found to be similar while that of the third is markedly different (Fig. 1). It absorbs over a much broader region of the spectrum and has its absorption maximum much further toward the infrared. The structural change between the second and third ion is only in the position of the methoxy group; in the second it is on a phenyl group and in the third case it is on a biphenyl. The striking difference in absorption of the third ion as compared to that of the second is most logically explained by assuming that a predominating electronic structure for the third ion is that in which the biphenyl group has become quinonoid. A study of the absorption of the ions: 4,4′-diphenyltriphenylmethyl, 4-methoxy-4′4″-diphenyltriphenylmethyl, and 4-(*p*-anisyl)-4′-phenyltriphenylmethyl leads one to similar conclusions (Fig. 2).

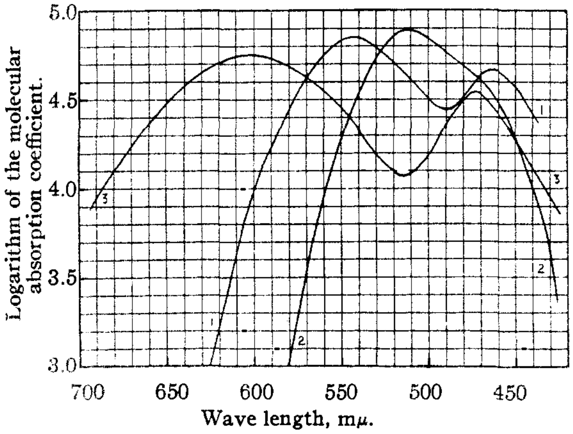

Fig. 2.—Absorption of acetic-sulfuric acid solutions of: 1, 4,4′-diphenyltriphenylmethyl sulfate; 2, 4-methoxy-4′,4″-diphenyltriphenylmethyl sulfate; 3, 4-(*p*-anisyl)-4′-phenyltriphenylmethyl sulfate.

If the methoxy group can fix the positive charge out at the end of the biphenyl group as the evidence indicates, there is no reason for assuming that the methoxy situated on the phenyl group has any less effect in causing the phenyl group to become quinonoid. This determines the predominating electronic structure of the 4-methoxy-

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[1] Anderson and Fisher, THIS JOURNAL, 66, 589 (1944).

4′-phenyltriphenylmethyl ion. A preferred position for the location of the charge on the 4-phenyltriphenylmethyl ion is not indicated by these data although the lack of similarity of its absorption to that of the substituted biphenyl compound makes it improbable that the charge is on the end of the biphenyl group.

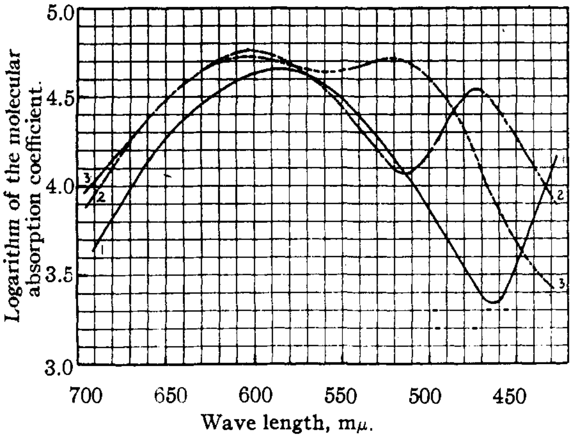


Fig. 3.—Absorption of acetic-sulfuric acid solutions of: 1, 4-(*p*-anisyl)-triphenylmethyl sulfate; 2, 4-(*p*-anisyl)-4′-phenyltriphenylmethyl sulfate; 3, 4-(*p*-anisyl)-4′,4″-diphenyltriphenylmethyl sulfate.

A para-anisyl group substituted in a para position of the triphenylmethyl ion is more strongly bathochromic than that of any other single substituent which has been reported (Fig. 3). This is consistent with data of Morton and Emerson, who found the maximum absorption of the 4,4′,4″-tri-(*p*-anisyl)-triphenylmethyl ion at 638 mμ.[2] These data appear to rule out conclusively any structural theory relating color to the central carbon atom. It is not reasonable to assume that replacing the methoxyphenyl group in a carbinol by a methoxybiphenyl group and thus increasing the distance between the substituted methoxy group and the central carbon atom would increase the effect of the methoxy on this atom. Dilthey and Harenberg[3] have claimed that groups far away from the central carbon atom have only a slight influence on the color. This is undoubtedly correct in the case of the methoxy groups in the 4,4′,4″-tri-(*p*-methoxyphenoxy)-triphenylmethyl ion they were investigating. They concluded that this was evidence against the quinonoid theory on the assumption that the diphenylether group might be expected to become quinonoid by having a tetracovalent ether oxygen. There is no evidence for this since tetravalent oxygen has usually been assumed to possess three covalences, the fourth being an ionic valence.

That the hydroxy or methoxy group is strongly concerned in attracting the charge is further evidenced by the absorption of corresponding pairs of these compounds, one containing a hydroxy group and the other a methoxy. The absorption curves of ether solutions of 4-(*p*-hydroxyphenyl)-triphenylcarbinol and the corresponding methoxy compound cannot be distinguished from one another. On the other hand, the change from hydroxy to methoxy groups in the case of the ions causes a displacement of the absorption bands. The direction of the displacement depends upon whether a phenyl or a biphenyl group is substituted (Fig. 4). The change from the 4-(*p*-hy-

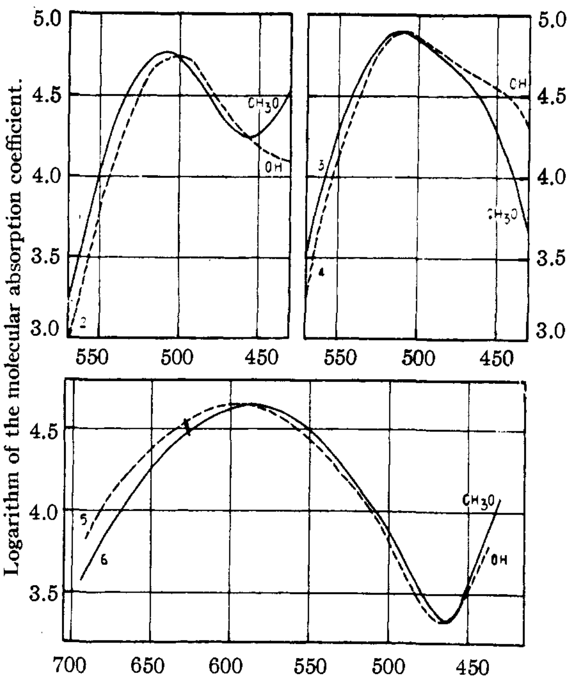
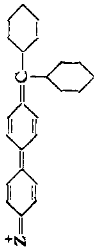
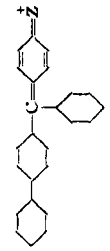
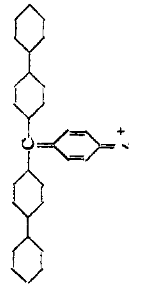


Fig. 4.—Comparison of the absorption of methylated and unmethylated hydroxytriarylmethyl sulfates: 1, 4-methoxy-4′-phenyltriphenylmethyl sulfate; 2, 4-hydroxy-4′-phenyltriphenylmethyl sulfate; 3, 4-methoxy-4′,4″-diphenyltriphenylmethyl sulfate; 4, 4-hydroxy-4′,4″-diphenyltriphenylmethyl sulfate; 5, 4-(*p*-hydroxyphenyl)-triphenylmethyl sulfate; 6, 4-(*p*-anisyl)-triphenylmethyl sulfate.

TABLE I

POSITIONS OF THE ABSORPTION MAXIMA OF THE QUINONOID BANDS OF OH—CH_3O PAIRS OF COMPOUNDS (mμ)

			
HO-	592	502	508
CH_3O-	587	508	512

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[2] Morton and Emerson, THIS JOURNAL, 59, 1947 (1937); 60, 284 (1938).

[3] Dilthey and Harenberg, *J. prakt. Chem.*, 136, 49 (1933).

droxyphenyl)-triphenylmethyl ion to the 4-(*p*-anisyl)-triphenylmethyl ion has an hypsochromic effect on the absorption band nearest the infrared. If the oxygen group is on a phenyl group, the change from the hydroxy to the methoxy derivative has a bathochromic effect on the absorption band nearest the infrared. In every case, however, the hydroxy group appears to separate the first two bands in the spectrum more than does the methoxy group.

No data obtained in this work can be used in deciding whether the positive charge in these ions is located on the oxygen atom or on the carbon atom to which the oxygen is attached. It appears more reasonable to assign the charge to the oxygen, since the arrangement of electrons with the charge on the oxygen allows every atom to have a group of eight outer electrons around it while retaining the charge on the carbon causes that atom to exist with only six outer electrons.

4-(*p*-Hydroxyphenyl)-triphenylcarbinol was investigated to see whether the strong quinonizing influence of an hydroxy group in the *para* position of a phenyl group is still evident when a biphenyl group intervenes. The compound is perfectly colorless, has a high melting point (224-227°), and shows no tendency whatsoever to exist in a quinonoid form in the solid state. If it is maintained above its melting point, it decomposes quite rapidly with the evolution of gas. The product, however, could not be obtained crystalline and it did not have an intense color as should be characteristic of such a compound as diphenylbiphenoquinomethane. The color, though a deep purple-brown, seemed to be possessed by only a small amount of the material even when the copious gas evolution had ceased. It is thought likely that any evolution of water took place between molecules resulting in condensation rather than intramolecularly leading to a quinonoid biphenyl group. An attempt to make diphenylbiphenoquinomethane by the reaction between biphenoquinone and diphenylketene was also unsuccessful.

Experimental

4-Methoxy-4′-phenyltriphenylcarbinol.—This carbinol was described by Bowden, Harris and Roberts[4] while this investigation was being carried on. We prepared it by two procedures: (1) the reaction between *p*-anisylmagnesium bromide and *p*-phenylbenzophenone, and (2) the methylation of 4-hydroxy-4′-phenyltriphenylcarbinol by means of dimethyl sulfate.

4-Methoxy-4′,4″-diphenyltriphenylcarbinol.—A mixture of 15 g. of *p*-anisylmagnesium bromide in ether–benzene solution and 20 g. of 4,4′-diphenylbenzophenone was refluxed for three hours. After standing overnight, the product was hydrolyzed with ice and dilute hydrochloric acid and then steam distilled. The carbinol was extracted from the unreacted ketone by ether, in which the ketone is almost insoluble. The ether in the carbinol solution was replaced by benzene, 60–75° petroleum ether was added, and 10 g. of carbinol crystallized. Recrystallization of the carbinol from 90–100° petroleum ether containing a small amount of benzene gave small white needles, m. p. 144–146°. In contrast to 4-methoxytriphenylcarbinol and 4-methoxy-4′-phenyltriphenylcarbinol, this compound crystallizes readily and is less soluble in the common solvents.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92. Found: C, 87.08; H, 6.14.

4-(*p*-Hydroxyphenyl)-triphenylcarbinol.—Thirty grams of 4-hydroxy-4′-benzoylbiphenyl dissolved in 200 cc. of benzene was added to the Grignard reagent made from 55 g. of bromobenzene, 7.9 g. of magnesium and 100 cc. of ether. The mixture was refluxed overnight. After the addition compound had been decomposed by means of ice and dilute hydrochloric acid, the solvent and biphenyl were removed by steam distillation. The residue was digested with 500 cc. of 2.5% sodium hydroxide solution to dissolve unreacted ketone; the carbinol is practically insoluble in the cold dilute alkali. The alkali insoluble material was recrystallized from ethylene chloride giving 30 g. of material as short white needles melting at 224–227°. This carbinol is not very soluble in benzene or alcohol and appears to have a small temperature coefficient of solubility in these solvents. Its solubility in ether is about 3.5 g. per liter.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. *Found:* C, 84.79; H, 5.99.

Acetyl Derivative of 4-(*p*-Hydroxyphenyl)-triphenylcarbinol.—This compound was prepared from the carbinol by means of acetic anhydride and anhydrous sodium acetate. It was recrystallized from alcohol, m. p. 154–156.5°.

Anal. Calcd. for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62. Found: C, 82.13; H, 5.73.

4-(*p*-Anisyl)-triphenylcarbinol.—4-Methoxy-4′-benzoylbiphenyl was prepared from 4-methoxybiphenyl according to the method of Fieser and Bradsher.[5] This ketone was treated with a large excess of phenylmagnesium bromide. After the addition compound had been hydrolyzed with ice and ammonium chloride, the solvent and biphenyl were removed by steam distillation. The carbinol was recrystallized four times from 90–100° petroleum ether, m. p. 108–109°.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.08; H, 6.14.

4-(*p*-Hydroxyphenyl)-triphenylcarbinol from 4-(*p*-Anisyl)-triphenylcarbinol.—Aluminum chloride was more satisfactory than acetic–sulfuric acid and acetic–hydrobromic acid mixtures in our attempts to demethylate 4-(*p*-anisyl)-triphenylcarbinol. A partial demethylation occurred when a mixture of two parts by weight of anhydrous aluminum chloride and one of the methoxy carbinol dissolved in benzene was refluxed for one hour. The product was decomposed with ice and dilute hydrochloric acid and the benzene layer was washed with water and dried. The hydroxycarbinol crystallized from the solution prior to the methoxycarbinol upon the addition of petroleum ether. The hydroxycarbinol was recrystallized several times from benzene–petroleum ether. Experiments showed it to be the same as the previously described 4-(*p*-hydroxyphenyl)-triphenylcarbinol.

Attempts to Make Diphenylbiphenoquinomethane.—Two methods were employed in attempting to make this compound: (1) the dehydration of 4-(*p*-hydroxyphenyl)-triphenylcarbinol, and (2) the reaction between diphenylketene and biphenoquinone. The dehydration procedure was tried by heating the carbinol in inert solvents for extended periods of time, and by heating the solid carbinol under reduced pressure in inert atmospheres. For example, a sample of carbinol was placed in a flask immersed in a sulfuric acid bath; the flask was evacuated and a small amount of carbon dioxide introduced. When the sample was heated at 220–230°, a vigorous evolution of water occurred. After heating for thirty minutes, the product was a purple gum which could not be crystallized. It did not have the intense color which diphenylbiphenoquinomethane might be expected to have, and the purple color seemed to be a property of only part of the material.

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[4] Bowden, Harris and Roberts, *J. Chem. Soc.*, 302 (1939).

[5] Fieser and Bradsher, THIS JOURNAL, **58**, 2337 (1936).

It is thought likely that the decomposition which occurred took place by evolution of water between molecules rather than intramolecularly.

The biphenoquinone necessary for the other attempted preparation was made according to the directions of Willstätter and Kalb[6] by the oxidation of 4,4′-dihydroxybiphenyl which was prepared from benzidine as described by Hirsch.[7] This dihydroxy compound is much less soluble in water than Hirsch indicated. Recrystallization of the material from water using a soxhlet extractor gave a better product than recrystallization from glacial acetic acid as suggested by Bratz and von Niementowski.[8]

The formation of fuchsones from diphenylketene and quinones has been investigated by Staudinger and by Staudinger and Bereza.[9] In contrast to the quinones used previously, biphenoquinone is quite insoluble in most solvents. For this reason the reaction was run in nitrobenzene in which it is somewhat soluble. A suspension of biphenoquinone in nitrobenzene containing diphenylketene was stirred under a carbon dioxide atmosphere for forty-eight hours. No diphenylbiphenoquinomethane was isolated from the yellow gum which precipitated when petroleum ether was added to the filtered product.

4-(*p*-Anisyl)-4′-phenylbenzophenone.—4-Phenylbenzoyl chloride was prepared by refluxing a mixture of 20 g. of 4-phenylbenzoic acid and 50 cc. of thionyl chloride for thirty minutes. The excess thionyl chloride was then removed by distillation under reduced pressure. To the acid chloride were added 19 g. of 4-methoxybiphenyl and 400 cc. of tetrachloroethane, and the resulting solution was cooled to −10°; 16 g. of anhydrous aluminum chloride was added and the mixture allowed to warm to room temperature while being stirred vigorously. After standing overnight, the product was decomposed with ice and dilute hydrochloric acid and the tetrachloroethane was removed by steam distillation. The solid residue was dried and then digested with 600 cc. of ether. The ether insoluble 4-(*p*-anisyl)-4′-phenylbenzophenone was recrystallized from *o*-dichlorobenzene giving plates which melted at 246–248°. *Anal.* Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.30; H, 5.61.

2-Methoxy-4′,5-diphenylbenzophenone.—This compound is the ether soluble fraction from the above reaction. The ether was evaporated and the residue recrystallized from methyl alcohol giving white needles, m. p. 127–130°. The assignment of the formulas for these two compounds was made on the basis of their melting points and the analogy between this reaction and that occurring between benzoyl chloride and 4-methoxybiphenyl. The total yield in this reaction was 75%; 50–65% of this was 4-(*p*-anisyl)-4′-phenylbenzophenone. *Anal.* Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.48; H, 5.57.

4-(*p*-Anisyl)-4′-phenyltriphenylcarbinol.—A solution of 4 g. of 4-(*p*-anisyl)-4′-phenylbenzophenone dissolved in 75 cc. of ether was added to the Grignard reagent prepared from 5.4 g. of bromobenzene and 0.8 g. of magnesium. The mixture was refluxed for two hours and allowed to stand. After the addition compound had been hydrolyzed with ice and dilute hydrochloric acid, the solvent and biphenyl were removed by steam distillation. The residue was twice recrystallized from benzene–petroleum ether giving 4 g. of material, m. p. 141–143°.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92. Found: C, 86.94; H, 6.08.

4-Methoxy-4′-carboxybiphenyl.—This compound was made by the oxidation of 4-methoxy-4′-acetylbiphenyl. Fieser and Bradsher have prepared this acid by alkaline permanganate oxidation of the acetyl compound.[10] In the present work the oxidation was carried out with permanganate and with sodium hypoiodite.

Methyl Ester of 4-Methoxy-4′-carboxybiphenyl.—This compound has been reported by Fieser and Bradsher, Because of the insolubility of both the ester and the acid in methanol, it was found convenient to carry out the esterification of large quantities of the acid by the use of a soxhlet apparatus; 20 g. of the acid was placed in the soxhlet extractor and 600 cc. of methanol containing 5 cc. of sulfuric acid was used in the flask. The ester crystallized from the solution in plates with the previously reported melting point, 172–173°.

4-(*p*-Anisyl)-4′,4″-diphenyltriphenylcarbinol.—An excess of *p*-biphenylmagnesium bromide was added to 5 g. of the methyl ester of 4-methoxy-4′-carboxybiphenyl and the mixture was refluxed for five hours. The product was decomposed with ice and dilute hydrochloric acid and then steam distilled. The residue was extracted with one liter of ether leaving most of the tetraphenyl undissolved. The ether solvent was replaced by benzene and 6 g. of the carbinol was precipitated by the addition of petroleum ether. The product was recrystallized several times from benzene–petroleum ether, m. p. 130–132°.

Anal. Calcd. for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83. Found: C, 87.63; H, 6.06.

All the compounds whose absorption spectra were determined showed no change in absorption after recrystallization from suitable solvents. Curve 1, Fig. 2, was taken from the published work of Burawoy.[11]

The absorption curves for the triarylmethyl ions were obtained from solutions of the carbinols in an acetic–sulfuric acid mixture which was prepared by dissolving 5 cc. of concentrated sulfuric acid in 95 cc. of glacial acetic acid. Increasing the amount of sulfuric acid in the solvent had no effect on the absorption. The absorption of 4-(*p*-hydroxyphenyl)-triphenylcarbinol was also determined in a solution of *p*-toluenesulfonic acid in glacial acetic acid and found to be identical with that of the acetic–sulfuric acid solution except for intensity. Using 10 g. of *p*-toluenesulfonic acid in 100 cc. of glacial acetic acid gave an absorption maximum of 4.3 units as compared to 4.65 units for the acetic–sulfuric acid solution. By using 25 g. of the sulfonic acid in 100 cc. of acetic acid, this maximum was raised to 4.55 units. The acetic–sulfuric acid solutions of these carbinols were stable for weeks.

Summary

1. 4-(*p*-Hydroxyphenyl)-triphenylcarbinol and the corresponding methoxy compound have been made, as well as the series of related compounds secured by replacing one and then both of the phenyl groups in the methoxy compound by *p*-biphenyl groups.

2. A comparison of the visible absorption of the 4-phenyltriphenylmethyl, 4-methoxy-4′-phenyltriphenylmethyl and 4-(*p*-anisyl)-triphenylmethyl ions and the corresponding ions containing an additional 4-phenyl substituent indicates that the biphenyl group is quinonoid in the 4-(*p*-anisyl) compounds.

3. Replacing an hydroxyl group by a methoxy group in these ions causes a shift in the absorption maximum of the principal band, which is different in direction depending on whether the substituted group is on a phenyl or biphenyl group.

4. 4-(*p*-Hydroxyphenyl)-triphenylcarbinol shows no tendency to exist in a quinonoid form in the solid state and attempts to prepare diphenylbiphenoquinomethane from it by dehydration failed.

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(6) Willstätter and Kalb, *Ber.*, **38**, 1233 (1905).

(7) Hirsch, *ibid.*, **22**, 335 (1889).

(8) Bratz and von Niementowski, *ibid.*, **52**, 192 (1919).

(9) Staudinger, *ibid.*, **41**, 1359 (1908); Staudinger and Bereza, *Ann.*, **380**, 258 (1911).

(10) Fieser and Bradsher, THIS JOURNAL, **58**, 1738 (1936).

(11) Burawoy, *Ber.*, **64**, 1640 (1931).