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

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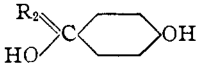
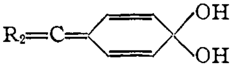
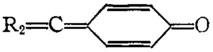
It has been shown[1] that when *p*-hydroxytriphenylcarbinol is crystallized from 50% acetic acid, the product obtained is yellow in color, melts at 139–140°, and when warmed it loses a molecule of water in a comparatively short time, forming fuchsone (III). On the other hand, when this carbinol is crystallized 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.

graphed through the photometer, its spectrum was continuous and intense to a frequency of about 4350. The electrical set-up was patterned after the one used for similar purposes at the Bureau of Standards.[3] Some of the curves where absorption was in the visible region of the spectrum were checked by the use of a Nutting photometer and Hilger wave-length spectrometer with a Pointolite lamp as the source of light.

About 0.1 g. of the material under investigation was weighed into a 25 or 50cc. volumetric flask and the flask filled with the solvent. A one centimeter absorption tube filled with this solution was inserted in one section of the photometer and a similar tube filled with the solvent was placed in the other. The sector in the beam of light passing through the solvent was set at extinction coefficient values of 0.1, 0.2, etc., up to 1.2 and the two spectra were photographed at each setting. Five cc. of the solution was then diluted to 25 cc. and a new series of exposures taken on another plate. Further dilutions were made until the peaks of the absorption bands had been photographed. When this procedure is followed, the first one or two exposures taken of a diluted solution coincides with the last exposures taken of the solution before diluting. The overlapping sections of the curves assisted us materially in checking our dilutions and in obtaining continuous curves. At least two and sometimes six or seven samples of a substance have been used before a quantitative absorption curve was considered to have been obtained.

The points at which the comparison beam and the beam which had passed through the solution were of equal intensity were determined under a low power lens in a comparator similar to the one used at the Bureau of Standards. The scale of the comparator was fitted with a vernier reading to a tenth of a millimeter. A curve showing the relationship between the comparator readings and frequencies was made by means of the spectrum of the copper spark.

As regards the choice of suitable solvents, very few are transparent to the shorter ultraviolet rays. Of these methyl alcohol and ethyl alcohol, although transparent, are of necessity eliminated, since in solutions of the hydroxytriarylcarbinols in alcohols, an equilibrium is established between the two tautomers.[4] Water cannot be used for two reasons: first, the insolubility of the carbinols in it and, second, the possibility of its reaction with the solutes. Ether has been found very satisfactory and, in every case studied thus far, the absorption spectrum of the ether solution that has been standing for several weeks has been found to be identical with that of the fresh solution.

Purification of Materials.—The compounds discussed in this paper were purified until their quantitative absorption spectra remained constant.

p-Hydroxytriphenylmethane[5] obtained from the carbinol by reduction with zinc dust and acetic acid was recrystallized from ether; m. p. 110°.

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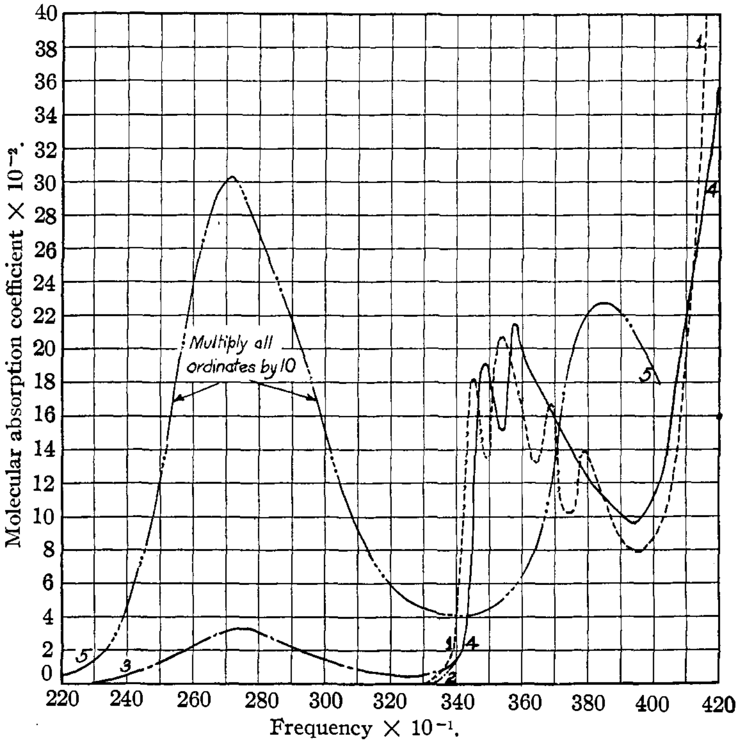
[3] Bureau of Standards Scientific Paper No. **440,** June, **1922.**

[4] (a) Ref. 1a, p. 1037; (b) Orndorff, Gibbs, McNulty and Shapiro, THIS JOURNAL, **49,** 1545 (1927).

[5] Bistrzycki and Herbst, *Ber.*, **35,** 3137 (1902).

p-Hydroxytriphenylcarbinol, benzenoid tautomer, was recrystallized three times from alcohol containing a trace of ammonia. It was filtered in an atmosphere which was free from acid fumes and the substance dried over soda lime. The crystals acquired a very pale greenish-yellow color; m. p. 159–160°.

p-Hydroxytriphenylcarbinol, quinonoid tautomer, was recrystallized from water solutions of acetic acid containing 50, 60 and 70% of acid, and from solutions containing 50 and 60% of propionic acid. The crystals were allowed to stand in contact with the mother liquor for from twenty-four to forty-eight hours and were washed on the filter plate with a small quantity of solvent. They were dried to constant weight in a desiccator which contained a saturated solution of potassium hydroxide and in which the pressure was reduced to 3–4 mm.: m. p. 139–140°.



1. - - - -Methane. 2. — — — —Benzenoid form of the carbinol. 3. — — —Quinonoid form of the carbinol. 4. ———Both forms—benzenoid and quinonoid carbinols. 5. — — — — —Fuchsone of the carbinol.

Fig. 1.—*p*-Hydroxytriphenylmethane and its derivatives.

Diphenylquinomethane, or the fuchsone of *p*-hydroxytriphenylcarbinol, was obtained by the dehydration of the carbinol. It was recrystallized twice from ether; m. p. 168°.

3-Methyl-4-hydroxytriphenylmethane[6] was prepared by reducing *o*-cresyldiphenylcarbinol with zinc dust and acetic acid. It was recrystallized from ether; m. p. 100°.

3-Methyl-4-hydroxytriphenylcarbinol, benzenoid tautomer, was obtained when

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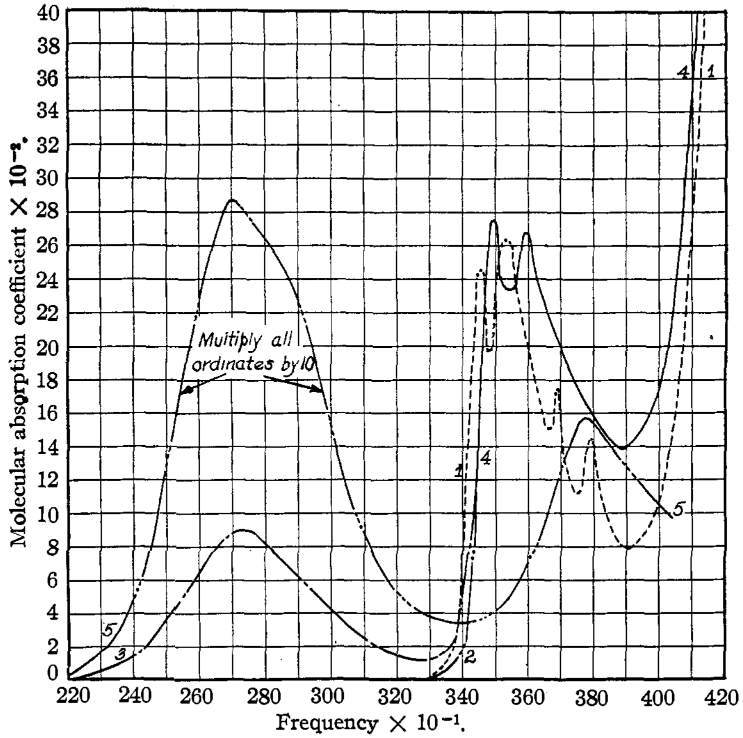
[6] Bistrzycki and Zurbriggen, *Ber.* **36**, 3561 (1903).

carbon dioxide was passed into an alkaline solution of the fuchsone. The colorless crystals were recrystallized from ether; m. p. 151°.

3-Methyl-4-hydroxytriphenylcarbinol, quinonoid tautomer, was obtained when either the colorless modification of the carbinol, or the corresponding fuchsone, was crystallized from 50, 60 or 70% aqueous solutions of acetic acid, or 50 or 60% aqueous solutions of propionic acid. The crystals were washed with pure solvent and dried in an evacuated desiccator containing soda lime. The literature[7] records 108–109° as the melting point of this modification. All samples prepared by us melted at 138–139°. The color of the crystals obtained varied with the acid concentration but by means of quantitative absorption spectra we have been able to show that this difference in color is due to the size of the crystals; the finely divided material from the 50% acetic acid solution having a lighter yellow and the larger crystals from the 70% acid having a deeper yellow color than the material from the 60% acid; a similar relationship held true for the material crystallized from the propionic acid solutions. Ether solutions of all these samples, however, have identical quantitative absorption spectra.



1. - - - - -Methane. 2. — — — —Benzenoid form of the carbinol. 3. — — —Quinonoid form of the carbinol. 4. ———Both forms—benzenoid and quinonoid carbinols. 5. — — — — —Fuchsone of the carbinol.

Fig. 2.—*o*-Cresyldiphenylmethane and its derivatives.

3-Methyl-4-hydroxyquinodiphenylmethane was prepared by heating *o*-cresyldi-

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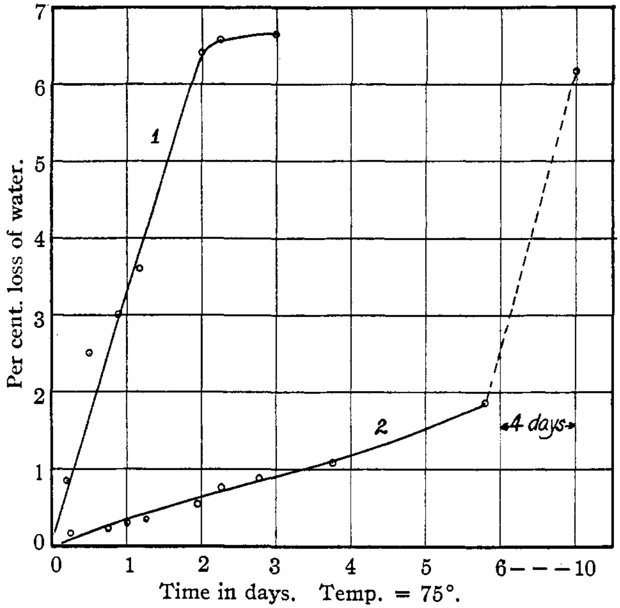
[7] Ref. 1 c, p. 1585; ref. 6, p. 3558.

phenylcarbinol at 75° until it had reached constant weight. It was crystallized from ether; m. p. 176°.

Further proof has been obtained that the quinonoid modification of *o*-cresyldiphenylcarbinol is not a mixture of the benzenoid form and the fuchsone. By the application of Beer's law we calculated that the intensity of the absorption band of the quinonoid form of *o*-cresyldiphenylcarbinol at frequency 2730 is equal to that of a mixture composed of 3.17% of fuchsone and 96.83% of the benzenoid form. Mixtures of approximately this composition were made and the absorption spectrum of these mixtures was found to be very similar to that of the quinonoid carbinol. When the melting point of this mixture was determined, however, it was observed that the mixture began to soften several degrees below the temperature at which it melted, whereas the melting point of the quinonoid modification is always quite sharp. Moreover, the mixture made by us loses water when placed in a current of warm air at a rate quite different from the rate of loss by the true quinonoid carbinol (Diagram I).



Curve 1 = Quinoid form of *o*-cresyldiphenylcarbinol.
Curve 2 = 3.16% of fuchsone + 96.84% of benzenoid form of *o*-cresyldiphenylcarbinol.

Fig. 3.

We therefore conclude that within a fairly wide range of acid concentration only a single product, namely, the quinonoid tautomer, is formed when either the *p*-hydroxytriphenylcarbinol or *o*-cresyldiphenylcarbinol is recrystallized from dilute acetic or propionic acid.

Summary

The quantitative absorption curves of ether solutions of the methane, the benzenoid carbinol, the quinonoid carbinol and the fuchsone of each—the *p*-hydroxytriphenylcarbinol and *o*-cresyldiphenylcarbinol—have been carefully determined. The spectroscopic results constitute further evidence that *p*-hydroxytriphenylcarbinol and *o*-cresyldiphenylcarbinol exist each in two tautomeric forms, a quinonoid and a benzenoid.

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

THE ABSORPTION SPECTRA OF SOME TRIPHENYLMETHANE DERIVATIVES

By L. C. Anderson

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The curves which we have obtained for the quantitative absorption of ultraviolet light by solutions of triphenylmethane and some of its derivatives differ in many respects from those which other investigators have recorded. These differences are due partly to variations in equipment and procedures used at different laboratories but partly, however, to the fact that in some of the recently published work no account was taken of the fact that reaction between the solute and the solvent had given rise to compounds which differed from the original solute and which consequently possessed different absorption spectra.

As previously mentioned,[1] we have found ether to be a very satisfactory solvent to use in this type of work. We have examined layers of pure ethyl ether as thick as two centimeters and in no case has the pure liquid shown selective absorption[2] in the spectrum included by our equipment,[1] which allows measurements to be made at frequencies from 4550 $mm.^{-1}$ to the visible.

The ultraviolet absorption spectra of solutions of triphenylmethane and triphenylcarbinol have been described by Hartley,[3] Baker[4] and Hantzsch[5] who give curves which show absorption only in broad bands. Orndorff, Gibbs, McNulty and Shapiro[6] have given curves which show the quantitative absorption of ultraviolet light by absolute ethyl alcohol solutions of these compounds. They report ten peaks for the solution of triphenylmethane and seven for triphenylcarbinol between 3700 and

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[1] Anderson and Gomberg, This Journal, **50**, 203 (1928).

[2] See for discussion, Smith, Boord, Adams, and Pease, This Journal, **49**, 1335 (1927); De Laszlo, *ibid.*, **49**, 2106 (1927).

[3] Hartley, *J. Chem. Soc.*, **51**, 152 (1887).

[4] Baker, *ibid.*, **91**, 1490 (1907).

[5] Hantzsch, *Ber.*, **52**, 509 (1919).

[6] Orndorff, Gibbs, McNulty and Shapiro, This Journal, **49**, 1541 (1927).