a quartz reflux condenser, yielding 55.6 and 56.0% acetyl (CH_3CO) in comparison with 55.8, the calculated value for a heptose hexacetate.

Preparation of the Alpha Hexacetate of α-Glucoheptose.—Since it has already been shown by Fischer that this isomer is produced through the acetylation of the sugar with hot acetic anhydride and zinc chloride, we sought to obtain it by a method which has frequently been used in this laboratory to prepare alpha acetates, namely, by heating the acetic anhydride solution of the beta acetate with a little zinc chloride. Ten grams of the beta hexacetate were dissolved in 100 cc. acetic anhydride containing 2 g. $ZnCl_2$. The specific rotation of this solution was —10° to begin with, but after heating it three hours on the steam bath its rotation became constant at +25, indicating that the equilibrium in this solvent between the alpha and beta forms of the hexacetate had been established. On pouring the mixture into cold water an insoluble sirup precipitated and soon crystallized. The aqueous solution was extracted with chloroform, the extract washed with sodium bicarbonate solution and with water, and the crystals which formed when the chloroform was evaporated were united with those from the insoluble mass. One recrystallization from hot water of this product yielded crystals which had a specific rotation of +32, but on recrystallizing then five times from ether, a constant specific dextrorotation of +87.0° in chloroform was found. The pure substance melted at 164°, uncorrected, which is higher than the value found by Fischer, 156°, but our material was probably more nearly free from the beta isomer. Two acetyl estimations gave 55.6 and 55.5% CH_3CO in comparison with the calculated value 55.8.

WASHINGTON, D. C.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TRIPHENYLMETHYL. XXVI. TAUTOMERISM OF TRIARYLCARBINOLS.

BY M. GOMBERG AND N. E. VAN STONE.

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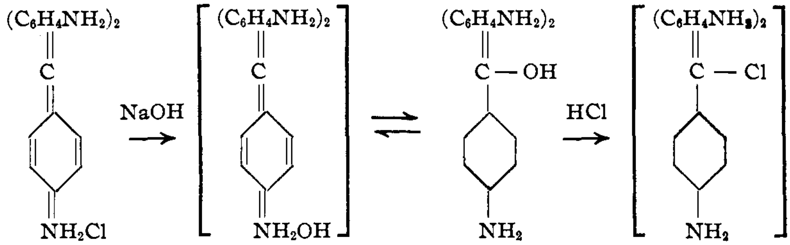
I. Introduction.

Historical.—The historical development of the application of the tautomeric hypothesis to the triphenylmethane derivatives may be said to fall mainly within the following periods:

(1) The complex dyes were considered as possessing of necessity a radically different constitution from that of the corresponding triarylcarbinols, for the very reason of the striking difference in properties. The dyes were *assumed* to possess a quinonoid constitution (I) in contradistinction from the benzenoid constitution of the carbinols (III). The possible existence of compounds isomeric with the carbinols but themselves colored and quinonoid, or the existence of salts isomeric with the

dyes but colorless and benzenoid, was neither looked for nor suspected. The hypothesis of tautomerism had no consideration in the discussion of the constitution of the dyes.

(2) With the advent of the tautomeric hypothesis the constitution of the dyes became a subject of new interest. Hantzsch and his cöworkers[1] have shown that crystal violet and other similar dyes, in solution, produce on addition of alkali, a colored, water-soluble base, which, like the original ammonium salt, is still dissociated to an appreciable extent and which only eventually changes over to the colorless, insoluble, non-dissociated carbinol. Hantzsch drew the conclusion that the water-soluble transitory compound possessing a marked electrical conductivity must be the true ammonium base. It, therefore, represents the labile desmotropic form (II), while the carbinol subsequently precipitating from the solution is the stable tautomer (III). In Hantzsch's nomenclature this evanescent ammonium hydroxide compound is the true base, while the stable carbinol is the *pseudo-base.* Henceforth the basic dyes of this series were considered merely as salts of the extremely unstable quinonoid colored ammonium base, the desmotropic colorless salts (IV) still remaining unknown. Similar considerations were extended to cover also the constitution of the acid, hydroxylated dyes.



(I). (II). (III). (IV).

(3) It was realized that triphenylcarbinol itself, devoid of either basic or acid auxochrome groups, gives on combination with some acids, as halogen acids, colorless ester-like compounds of benzenoid constitution (V), as might normally be expected of tertiary alcohols; on combination, however, with other acids, as sulfuric acid, it was found that intensely colored compounds are produced possessing at the same time salt-like nature. Here again it was sought to explain this strikingly divergent behavior by assuming the presence of the chromophor quinonoid nucleus in the colored derivatives[2] (VI), *i. e.*, by considering these salt-like substances as the salts of the quinocarbonium base, which is, of course, the hypothetical desmotrope of the carbinol itself. Although the quinonoid

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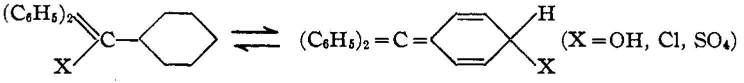
[1] Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899); Hantzsch and Ostwald, *Ibid.*, **33**, 278 (1900).

[2] Kehrmann, *Ber.*, **34**, 3815 (1901); Gomberg, *Ibid.*, **40**, 1847 (1909).

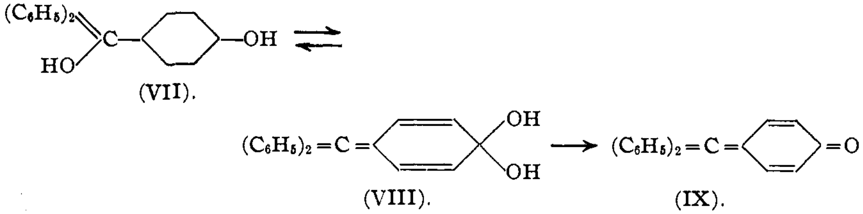
constitution of the sulfate received substantial corroboration of experimental nature, nontheless there still lacked for the firm basis of the tautomeric conception in this group a single instance of the actual existence of a desmotropic *pair* of carbinols, one colored and the other colorless, or a single desmotropic pair of strictly isomeric derivatives, *i. e.*, two chlorides or two sulfates. Evidence of the possible existence of two forms of such derivatives was finally obtained in the case of the chlorides[1] themselves. When dissolved in liquid sulfur dioxide triarylcarbinols were found to give rise to colored solutions and to show a totally different chemical behavior from that when in any other solvent and when at the same time colorless. Their peculiar behavior when in this solvent was shown to be, by diverse experimental evidence, totally consistent with, and to be explainable only on the assumption that the colored modification possesses the quinoid constitution, and is in mobile equilibrium with the benzenoid modification. The isolation, however, of the colored halides in the solid state proved impossible, for on evaporation of the sulfur dioxide the equilibrium shifts wholly in favor of the benzenoid modification.



(V). (VI).

(X =OH, Cl, SO$_4$)

(4) The indisputable and direct evidence for the correctness of the tautomeric view was at last obtained in the shape of the two desmotropic forms of a carbinol. It has been found that parahydroxytriphenylcarbinol is capable of existing in both the colorless and the colored modifications.[2] The two forms were isolated in crystalline solid state and to these carbinols have been assigned the structures (VII) and (VIII).



(VII). (VIII). (IX).

Analogy alone should be sufficient to justify the structure assigned to the colored modification, analogy with the colored chlorides described in the preceding paragraph, and also analogy with the colored fuchsone, the constitution of which could only be as indicated (IX). But, further, it has been shown that there exists a striking difference in the rate of dehydration on moderate heating of the two carbinols. The ease with which the colored modification, in contradistinction to the colorless carbinol, changes

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[1] Gomberg, *Ber.*, **40**, 1846 (1907); *Ibid.*, **42**, 406 (1909).

[2] Gomberg, THIS JOURNAL, **35**, 1035 (1913).

through loss of water into fuchsone is compatible only with a quinonoid structure for the former, wherein the two hydroxyl groups are linked to one and the same carbon atom.

(5) The fifth and final period in the development of the tautomeric conception as applied to the triarylmethane derivatives remains still unattained. It has not as yet proven possible to prepare two desmotropic chlorides in solid crystalline state, or two sulfates. As a near approach to the realization of this may be considered the fact that while the triarylcarbinol chlorides are colorless, another set of analogous acid derivatives, the sulfates, are always colored. A still nearer approach to this realization are some of the results described in connection with the study of the arylxanthenols.[1] It has been shown that while some arylxanthenol chlorides are colorless, others although entirely analogous, are colored; and again, with the same xanthenol the chloride may be colorless while the bromide is colored. But, in the dyes, there still remains unattained the isolation of the true ammonium bases tautomeric with the colorless carbinols, or of the colorless salts tautomeric with the dyes themselves.

Object of this Investigation.—A single carbinol has been reported as existing in two desmotropic forms and it seemed desirable to extend this study to the various substituted triphenylcarbinols, having in view the effects on the tautomeric tendency which might be brought about by various groups in the benzene ring. Since the greatest effect would probably be brought about through substitution in the same ring containing the parahydroxyl group, we have for the present studied the carbinols substituted in this ring, namely, those positions ortho to the hydroxyl group. It has been found possible to extend the instances of isolation of the desmotropic forms through a number of substituted carbinols, and at the same time to gain some knowledge what groups enhance or diminish the specific influence of the para hydroxyl groups. Whether of the simple groups only the hydroxyl, and only in the para position, has this specific influence, is difficult to say at present, and this must be left open for further study.

II. Substituted *p*-Hydroxytriphenylcarbinols.

Gomberg and Jickling[2] have lately reported a new method for the preparation of *p*-hydroxytriphenylcarbinol by the condensation of benzophenone chloride and phenol. They formulate the reaction as passing through several successive steps in virtue of various intramolecular rearrangements and they have been able to isolate the intermediate products formed:

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[1] Gomberg and West, THIS JOURNAL, 34, 1529 (1912).

[2] THIS JOURNAL, 37, 2575 (1915).

Diphenoxydiphenylmethane, $(C_6H_5)_2C(OC_6H_5)_2$
p-Hydroxytriphenylcarbinol, $(C_6H_5)_2C(OH)(C_6H_4OH)$
Di-*p*-hydroxytetraphenylmethane, $(C_6H_5)_2C(C_6H_4OH)_2$.

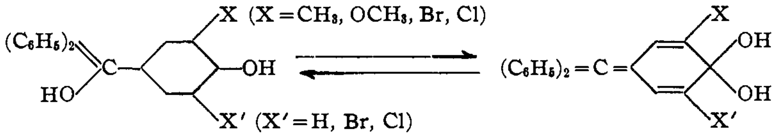
We have now studied the condensations of benzophenone chloride with other phenols and have found that this reaction offers a very general method for the synthesis of *p*-hydroxytriphenylcarbinols. We have prepared the carbinols required for our work by this method rather than to use the methods described for this purpose in the literature, which are laborious, involving many steps and giving only meager yields. We have studied the action between benzophenone chloride and the following phenols: *o*-cresol, guaiacol, *o*-bromophenol, *o*-chlorophenol, and *o*-nitrophenol. With the exception of the nitro compound, we have been able to show that a reaction analogous to the first step, as formulated by Gomberg and Jickling, takes place in every case without the aid of a catalytic agent. The various substituted diphenoxydiphenylmethanes have been isolated and are, generally speaking, similar in character and stability to the diphenyl ether of benzophenone. Likewise, the condensation with *o*-cresol, and with guaiacol, proceeded easily through the second step to the formation of the substitutes *p*-hydroxytriphenylcarbinols. With the monobromo- and monochlorophenols it was found that under similar conditions the reaction stopped with the first step, and only the substituted diphenoxydiphenylmethanes could be isolated. It was found that upon addition of the smallest amount of sulfuric acid the reaction between the chloro- or bromophenol and benzophenone chloride proceeded much more vigorously than when the reaction depended upon the hydrochloric acid generated during the course of the condensation. A satisfactory rearrangement of the chloro- and bromophenoxy compounds was only effected when, besides the addition of a drop of sulfuric acid, the reaction mixture was heated for twelve hours at 110°, but this unfortunately brought about decomposition products which made the isolation of the carbinols difficult. Much better results were obtained by substituting aluminum chloride for the sulfuric acid as the condensing agent. In the presence of anhydrous aluminum chloride, using carbon disulfide as a solvent, the reaction between the bromophenol or chlorophenol and benzophenone chloride yielded the desired carbinols, and for our further study this method was employed.

On long standing or when the reaction is carried on at elevated temperatures, benzophenone chloride and phenol yield a tetraphenylated derivative. Under similar conditions we have been able to carry the condensation between the benzophenone chloride and *o*-cresol or guaiacol to analogous compounds.

As previously mentioned, the reaction between *o*-nitrophenol and benzophenone chloride did not proceed in the desired manner. On mixing these two substances together and slightly warming there was only the slightest evolution of hydrochloric acid gas; with the addition of a drop of sulfuric acid this was only slightly increased. By heating on the water bath there were signs of a more vigorous reaction, but the final product was a charred mass and nothing could be isolated from it. The use of aluminum chloride and carbon disulfide did not yield the desired results. Recourse was finally had by carrying on the reaction between benzophenone chloride and *o*-nitrophenol in the presence of anhydrous aluminum chloride without the use of a solvent, and from this reaction the nitro-substituted carbinol for our work was obtained.

By brominating and by chlorinating the cresyl and guaiacyl carbinols we obtained carbinols substituted in both positions ortho to the para-hydroxyl group, and these also were studied as regards their tendency toward tautomerization. Similarly, the monobromo- and monochloro-carbinols were further brominated and chlorinated, respectively, and the dihalogenated carbinols thus resulting were in their turn investigated.

The Desmotropic Modifications of Substituted *p*-Hydroxytriphenylcarbinols.—The substitution of various groups in the position ortho to the hydroxyl group did not materially change the general characteristics of the carbinols from those of the *p*-hydroxytriphenylcarbinol itself. In every case save that of the nitro compound we were able to isolate two distinct forms, the colorless benzenoid (X) and the colored quinonoid (XI).



(X). (XI).

The colorless variety is best obtained by first dissolving the carbinol in normal alkali, precipitating with carbon dioxide and finally crystallizing from such solvents as benzene, ether or alcohol. The second crop of crystals in some cases shows a slight tinge of color, indicating that without doubt the solution contains both forms in equilibrium, but with a predominence of the colorless modification.

The quinonoid modification is always obtained by crystallizing the benzenoid variety from 60 to 70% acetic acid, and in some cases it is necessary to heat the solution for a considerable time to effect a complete change. If recrystallization takes place from more dilute acid, 30 to 40%, the colored modification separates out with less color, higher melting point, and is doubtless a mixture of the two modifications. If stronger acid is used there results in some cases the fuchsone, in others a carbinol acetate. On repeated recrystallization of the quinonoid desmotrope, even without previous treatment with alkali, from benzene, alcohol, or ether, there is a marked tendency to the formation of the benzenoid variety. The quinonoid carbinols in nearly all instances possess a lower melting point than the corresponding benzenoid modifications.

Although the transformations of the benzenoid modification into the quinonoid take place readily in solution, the identical changes may be brought about to some extent without the use of solvents. With the application of heat the white modification becomes colored, the melting point drops, and eventually, with the loss of a molecule of water, the fuchsone is formed, the rapidity of these various changes being determined by the temperature chosen.

The effect of light energy will also bring about the change from the colorless to the colored modification and, although here the effect, to be sure, is much slower, nevertheless with sufficient time and by occasional stirring in order to expose all of the material to sunlight or light from a mercury lamp, a complete change may be effected.[1]

We have assigned, in each case, the benzenoid structure to the white modifications and to the colored carbinols the quinonoid formulation. The benzenoid structure for the colorless carbinols requires no further explanation, it being in harmony with the generally accepted view as regards this class of compounds. Our justification for the quinonoid structure rests upon the analogy to the triaryl halides in the colored form, the relation to the fuchsone, and, particularly, *upon the rate of dehydration under the influence of heat as compared with that of the benzenoid modification.* We have carried out all the dehydrations at a temperature where the transformation from the benzenoid to the quinonoid modification is slow as compared to the loss of water from the colored compound, the temperature in each individual case being also so chosen as to minimize the possible decomposition of the resulting fuchsone. In most cases a temperature of 75° proved the most favorable for our purpose.

III. Reaction between Benzophenone Chloride and *o*-Cresol.

As has been said, the reaction between phenol and benzophenone chloride was found to take place in several successive steps. Between the reaction of phenol and *o*-cresol with benzophenone chloride there is no striking difference. Products which are similar to those isolated with the phenol reaction have been prepared in the course of this work through the reaction of benzophenone chloride upon *o*-cresol. Through the use of a solvent, from which the hydrochloric acid gas generated in the reaction between *o*-cresol and benzophenone chloride may be expelled either by boiling or by the rapid passage of dried air, we have been able to prepare the substituted diphenylether of benzophenone. Without the use

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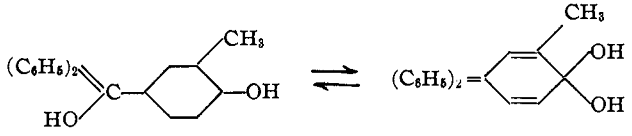
[1] Gomberg, THIS JOURNAL, **35**, 1039 (1913).

of a solvent the condensation proceeds through the second step, yielding 3-methyl-4-hydroxytriphenylcarbinol, and even through the third step, giving 3,3′-methyl-4,4′-hydroxytetraphenylmethane.

2,2′-Methyldiphenoxydiphenylmethane, $(C_6H_5)_2C(OC_6H_4CH_3)_2$.—To the warm solution of 24 g. (1 mol) of benzophenone chloride in 250 cc. of dry benzene are added gradually 27 g. (2.5 mol) of redistilled *o*-cresol. The flask is fitted with a reflux condenser and protected from the moisture of the air by a calcium chloride tube. The solution is gently heated on the water bath, and when no further acid fumes are given off, usually after three to four hours, the reaction may be considered to be at an end. The benzene is evaporated off under reduced pressure and to the yellow oil remaining a few cc. of alcohol are added. Any excess of *o*-cresol or benzophenone chloride that may be present goes into solution in alcohol while the ether separates out as a white solid partly crystalline. For purification it is recrystallized from hot alcohol, and it then melts at 142°. The yield is nearly quantitative. The cresoxy compound is characterized by its insolubility in the ordinary solvents. It is stable to steam distillation, is not soluble nor decomposed by alkalies, but acids decompose it to benzophenone and the *o*-cresol.

Calc. for $C_{27}H_{24}O_2$: C, 85.21; H, 6.36. Found: C, 85.23, H, 6.47.

3 - Methyl - 4 - hydroxytriphenylcarbinol (*o*-**Cresyldiphenylcarbinol**),



.—Bistrzycki and Zurbriggen[1] first prepared *o*-cresyldiphenylcarbinol through the condensation of benzilic acid with *o*-cresol and subsequent removal of the carbon dioxide from the resulting cresyldiphenylacetic acid by use of especially prepared 100% sulfuric acid. The preparation by this method is laborious and the yields are comparatively small. On the other hand, according to our method, an almost theoretical yield of the cresyldiphenylcarbinol is obtained.

24 g. (1 mol) of benzophenone chloride are mixed with 27 g. (2.5 mol) of redistilled *o*-cresol, the mixture is at first cooled, and then allowed to stand at room temperature for from two to four days, protected from the moisture of the air by a calcium chloride tube. After the addition of a little water, the mixture is steam distilled to remove the excess cresol. The residue, after steam distillation, is digested with warm normal alkali and the solution, after cooling, is filtered from benzophenone not carried over in the steam distillation. To remove all traces of benzophenone which may be held in suspension or in solution by the alkali, the solution is shaken with small amounts of ether, and the ether dissolved in the

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[1] *Ber.*, **36**, 3558 (1903).

alkaline solution of the carbinol is removed from the solution by passage of a brisk stream of air. To the alkaline solution small amounts of solid sodium chloride are gradually added; on standing the sodium salt of the carbinol crystallizes out in long needles with almost no color. These are filtered, washed with a little water, redissolved in warm water, and the free carbinol is precipitated by passing carbon dioxide into the alkaline solution. On standing, the oily carbinol solidifies and is then filtered and air-dried.

Further purification of the carbinol is best accomplished by converting it into the insoluble acetate (see below) and then regenerating the carbinol. The crude carbinol is dissolved in a small amount of hot glacial acetic acid. On cooling and stirring the entire mass becomes suddenly solid, and the beautiful red crystals of the acetate thus formed may be filtered from the acid, while any tetraphenylmethane derivative that may possibly be present remains in solution in the acid. The red crystals of the carbinol acetate lose their acetic acid when allowed to stand exposed to the air. The resulting fuchsone is now hydrolyzed back to the carbinol by gently warming it with dilute alkalies and some alcohol or acetone, and is then reprecipitated from the solution with carbon dioxide. Further treatment of this carbinol is conditioned upon which of the two desmotropes it is desired to obtain.

The Quinonoid and Benzenoid Desmotropes.—On recrystallization of the purified carbinol from 60% acetic, the quinonoid modification of the carbinol is obtained pure, melting at 108–109° and colored a beautiful yellow. Bistrzycki and Zurbriggen reported that their carbinol melted at 108–109°, was yellow, and on recrystallization the melting point was raised. As a solvent they used acetic acid of 50% strength, and we have also found that with this strength acid the tendency to produce the colorless variety is only hindered by long heating. When the carbinol was precipitated from its alkaline solution by means of dilute acetic acid, Bistrzycki and Herbst[1] obtained a compound identical in composition with the original carbinol yet which, on recrystallization from benzene, was colorless and melted at 148–149°. We have been able to prepare this white variety of the carbinol, namely the benzenoid desmotrope, by taking the product precipitated from alkaline solution by carbon dioxide and, after drying, recrystallizing it from alcohol, benzene, or ether and petroleum ether. In every case we were able to obtain a compound identical in composition to the colored carbinol, perfectly white and melting at 148–149°, although often the second batch of crystals showed signs of the colored modification. By dissolving the colorless modification in 60% acetic acid and warming for a short time, the colored carbinol, melting at 108–109°, is obtained. If acid of less strength is used the melting

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[1] *Ber.*, 36, 3566 (1903).

point is lowered to 120–130° and the result is a mixture of the two desmotropes possessing a light yellow color. On the other hand, by repeated recrystallization from alcohol or benzene the colored carbinol gradually changes to the white, higher melting, benzenoid desmotrope. On long exposure in a quartz dish to the rays of the sun, the white modification becomes yellow, but a similar change is noticed in the course of a few hours if the same compound is warmed to 60°.

Calc. for $C_{20}H_{18}O_2$: C, 82.72; H, 6.25. Found: Quinonoid desmotrope, C, 82.56; H, 6.18; Benzenoid desmotrope, C, 82.7; H, 6.24.

Dehydration of the Two Forms of the *o*-Cresyldiphenylcarbinol.—Equal amounts of the two desmotropes were heated at the same time in an especially constructed glycerol bath which allowed a very accurate control of the temperature. This bath consisted of a rectangular copper tank measuring 9 × 6 × 4 inches, through the entire length of which extended two copper tubes. When the bath was filled with glycerol and heated, by means of a Bunsen burner beneath, a thermometer which was immersed through an opening in the top into the glycerol showed less than a degree change of temperature during periods extending over several weeks. One gram of each desmotrope was placed in a porcelain boat about five inches long, the boats placed each in one of the separate tubes, and a slow stream of carefully purified and dried air was passed throughout the period of heating. The rate of dehydration, *i. e.*, the loss of water, was carefully noted at different intervals. While the colored desmotrope loses water rapidly, the white modification loses it slowly, *in proportion as it is being transformed under the influence of heat energy into the quinonoid desmotrope.* In the tables below showing the rates of dehydration the time represents the different intervals of heating, while the percentages given show the total loss of weight in per cent. at the end of that interval. On longer heating the further loss in either case was on the average of 1 mg. per day, which, as will be shown, is due to the decomposition of the fuchsone itself.

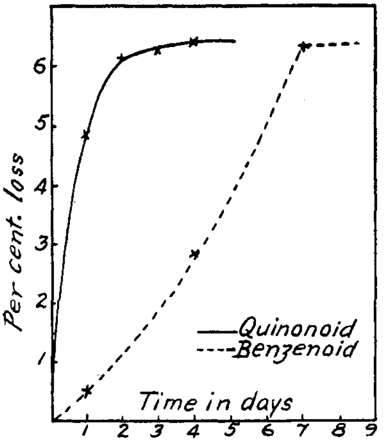


Fig. 1.

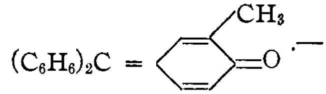
Temperature.	Time.	Quinonoid.	Benzenoid.
70°	24 hrs.	4.86%	0.47%
70°	24 hrs.	6.12%	1.31%
70°	24 hrs.	6.24%	1.81%
70°	24 hrs.	6.38%	2.85%
70°	70 hrs.	6.42%	6.30%

Calculated loss for one molecule of water is 6.25%.

Decomposition of Fuchsones on Heating.—When the dehydration of various carbinols was undertaken at temperatures ranging from 100°

to 150°, it was found that there resulted always a loss considerably more than that calculated for one molecule of water. We have been able to show that at temperatures from 75° and up appreciable decomposition of the fuchsone may take place with the production of small amounts of benzoquinone or its homologs, which are quite volatile, and the loss in weight, on heating the carbinols, in excess of that calculated for one molecule of water is thus accounted for. We have been able to isolate and completely identify benzoquinone resulting in this manner from *p*-hydroxytriphenylcarbinol; tolylquinone, from *o*-cresyldiphenylcarbinol; and methoxyquinone, from 2-methoxy-*p*-hydroxytriphenylcarbinol.

In view of this fact care has to be exercised to select for the dehydration experiments such a temperature that this decomposition would be a minimum, and our results justify the selection of 75°. The facts just described clear up a discrepancy in the observations made by Gomberg, on the one hand, and by Baeyer on the other. Gomberg[1] reported that by the action of silver sulfate on *p*-bromotriphenylchlormethane a *p*-quinone sulfate is produced and that this on hydrolysis yields fuchsone. The latter was not isolated at that time but its presence was inferred from several reasons, among them, by the distinct odor resembling that of benzoquinone. Baeyer[2] disputed the correctness of this observation claiming that the fuchsone has no odor. The fact that fuchsone on gentle heating does give rise to benzoquinone explains the discrepancy in the two observations. We have now verified that *freshly prepared fuchsone* is without odor, but when kept in a closed bottle, even if only at room temperature, in the course of several days it suffers sufficient autooxidation to give rise to an unmistakable trace of benzoquinone.

7,7-Diphenyl-2-methyl-quinomethane,  .—When either of the two modifications of the *o*-cresyldiphenylcarbinol are dehydrated, either by heat or by glacial acetic acid, there results the diphenyl-2-methylquinomethane. If the dehydration of the solid forms of the carbinol takes place at a low temperature, this transformation takes place without fusion of the material, and the resulting fuchsone melts at 173–175°. On recrystallization from benzene, it is obtained as deep red crystals melting at 176°, as described by Bistrzycki and Zurbriggen. It is very soluble in alcohol, ether or acetic acid.

Calc. for $C_{20}H_{16}O$: C, 88.19; H, 5.927. Found: C, 88.02; H, 5.935.

Diphenyl-2-methylquinomethane Acetate.—When either form of the carbinol is dissolved in hot glacial acetic acid and the solution afterwards cooled and stirred the entire mass becomes solid. The deep red crystals

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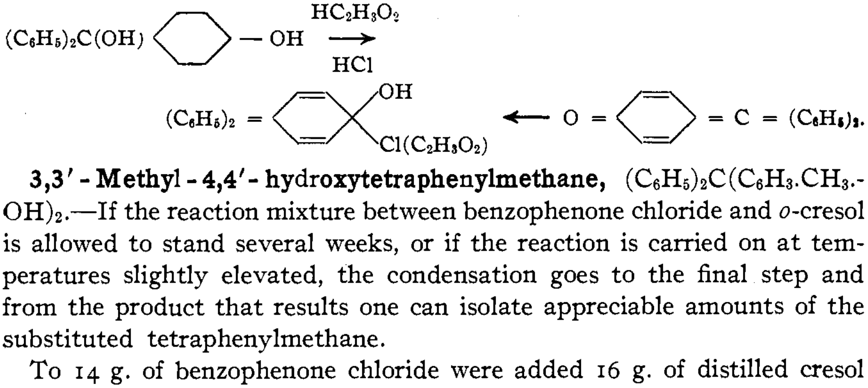
[1] *Ber.*, 40, 1853 (1907).

[2] *Ibid.*, 40, 3086 (1907).

resulting may be filtered off, washed with petroleum ether, dried between filter papers and used for analysis. The same product results if the carbinols are dissolved in the cold and the acid solution is allowed to stand, when the acetate resulting separates out, owing to its lesser solubility. On heating to 75° or on exposure to air the acetate loses the acid, leaving the fuchsone. The loss in weight can be checked by passing the acid evolved into a standard alkali solution.

Calc. for $C_{20}H_{16}O + C_2H_4O_2$: $C_2H_4O_2$, 18.08. Found: $C_2H_4O_2$, 18.07, 18.13.

The influence of the *p*-hydroxyl group in inducing tautomerization of this cresyl carbinol to the quinoid state is well brought out by the existence of this colored acetate. Triphenylcarbinol itself also gives an acetate but that one is perfectly white. On the other hand, *p*-hydroxytriphenylcarbinol, when dissolved in sufficient cold glacial acetic acid to make a saturated solution, deposits on standing the acetate intensely colored. Still better results are obtained by starting with the cold saturated solution of the diphenylfuchsone. The reaction in this case with acetic acid is not unlike that with hydrochloric acid.



3,3′-Methyl-4,4′-hydroxytetraphenylmethane, $(C_6H_5)_2C(C_6H_3.CH_3.OH)_2$.—If the reaction mixture between benzophenone chloride and *o*-cresol is allowed to stand several weeks, or if the reaction is carried on at temperatures slightly elevated, the condensation goes to the final step and from the product that results one can isolate appreciable amounts of the substituted tetraphenylmethane.

To 14 g. of benzophenone chloride were added 16 g. of distilled cresol and the mixture was warmed on the water bath for three days. The reaction mixture was then steam distilled to remove the excess of cresol, taken up in normal alkali, the latter shaken with ether to remove the benzophenone, and the product thrown down by the addition of dilute acetic acid to the alkaline solution. On crystallization from dilute acetic acid, it separated out as white crystals melting at 183°, which, on recrystallization from benzene, alcohol, acetic acid or toluene, melt at 190°. Unlike di-*p*-hydroxytetraphenylmethane, this compound is extremely soluble.

Calc. for $C_{29}H_{24}O_2$: C, 85.22; H, 6.36. Found: C, 84.82; H, 6.56.

Attempts to Isolate the Free Radical.

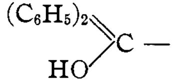
3-Methyl-*p*-carboethoxytriphenylcarbinol, $C_2H_5O.CO.OC_6H_3CH_3.(C_6H_5)_2COH$.—As the carbinol chloride itself could not be expected to give the free radical the hydroxyl group was protected by the carboethoxy group. To 30 g. of *o*-cresyldiphenylcarbinol dissolved in as small amount of normal alkali as possible and mixed with ice were added 10 g. (1.1 mol) of chlorocarbonic ester. On standing a granular precipitate separated out which, on recrystallization from acetic acid, melted at 136°.

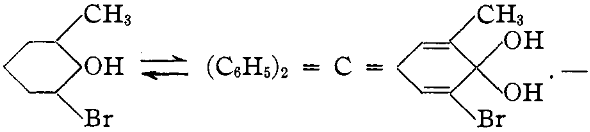
3-Methyl-*p*-carboethoxytriphenylcarbinol Chloride.—The usual procedure for the preparation of triaryl chlorides was followed, and dry hydrochloric acid gas was passed into a benzene solution of the carbinol. The water formed in the reaction was taken up with a few pieces of fused calcium chloride in the bottom of the flask, and to the benzene solution an equal amount of petroleum ether was added. The chloride separated out in white rosets. Melting point 131–2°.

Calc. for $C_{23}H_{21}O_3Cl$: Cl, 9.34. Found: Cl, 9.7.

The Free Radical.—The above carbinol and the corresponding chloride were prepared in the hope of obtaining from the latter the free radical which should on gentle hydrolysis yield a hydroxylated triarylmethyl. A preliminary experiment with molecular silver showed that in benzene solution the chloride is readily removed to the extent of 98.5% within ten minutes. When shaken with molecular silver in this way, the solution becomes lemon yellow and, on subsequent exposure to oxygen or air, loses this color and at the same time absorbs oxygen quickly to the extent of 85% of that calculated for one molecule of oxygen, as is usually taken up by the free triarylmethyl radicals. On evaporation of the benzene, a product separates out which bears all the characteristics of a peroxide. The same peroxide is obtained in purer state by shaking the benzene solution of the chloride with silver and simultaneously passing oxygen through the solution, and it then melts at about 161–162°. There can be no doubt therefore that the free radical actually exists, but all our efforts to isolate it in the solid crystalline state proved fruitless. The reason for this failure lies, we believe, in the inherent tendency of this radical to spontaneously polymerize or isomerize when heated, as has been found to be the case with other similar radicals.[1] Indeed, the longer a solution of the radical in ether or benzene is heated the less of the peroxide does it furnish on exposure to air, and at the same time more of a white inactive compound is obtained which is produced at the expense of the free radical.

3 - Methyl - 5 - bromo - *p* - hydroxytriphenylcarbinol,





. —Bromination of the *o*-

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[1] Gomberg, *Ber.*, 36, 378 (1903); Schlenk, *Ibid.*, 47, 1665 (1914).

cresylidphenylcarbinol takes place in either acetic acid or chloroform. For this purpose the carbinol was dissolved in glacial acetic acid and to this solution was added gradually a large excess of bromine dissolved in the same solvent. After standing at room temperature with occasional shaking, it was warmed on the water bath for a few hours. On cooling slowly there separated out deep red crystals. These were shown, by analysis, to contain bromine substituted in the benzene ring and removable only by drastic treatment, as fusion with sodium peroxide; also bromine which could be easily hydrolyzed off, and in addition bromine that could be titrated by sodium thiosulfate. There can be no doubt that this red compound is a perbromide of a quinonoid-carbinol bromide with apparently three atoms of perbromine, as shown by titration with thiosulfate. Often on cooling too rapidly there separated out along with the crystals of the perbromide a black oil, but this can be put back into solution on application of heat and additional acid.

To obtain the bromocresylcarbinol from this perbromide, two methods may be employed. The red crystals are boiled with a large amount of water; or the perbromide may be taken up in ether, washed with a strong solution of sodium bisulfite in order to remove the bromine, and, after drying the ether solution, the carbinol may be precipitated by addition of petroleum ether. The product resulting in either case is likely to contain a considerable amount of the brominated fuchsone. It is, therefore, advisable to redissolve the whole in warm alkali in order to hydrolyze the fuchsone, and the carbinol is then precipitated out by addition of dilute acid or by passing carbon dioxide into the solution. On recrystallization from acetic acid 60%, the carbinol is colored red and melts at 138–139°. It represents the quinonoid modification. As was shown to be the case with the *o*-cresylcarbinol, more dilute acid brings about some loss of color in the carbinol and a variable rise in melting point, owing to the formation of a mixture of the two desmotropes.

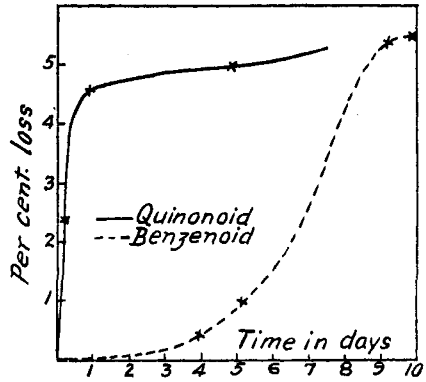


Fig. 2.

Dehydration of the Two Modifications of the Carbinols.

Temperature.	Time of heating.	Quinonoid.	Benzenoid.
75°	3 hrs.	2.4	No loss
75°	22 hrs.	4.54	No loss
75°	24 hrs.	4.75	No loss
75°	24 hrs.	4.90	No loss
90°	48 hrs.	4.97	1.00
105°	120 hrs.	5.40	5.30
105°	48 hrs.	5.40	5.45

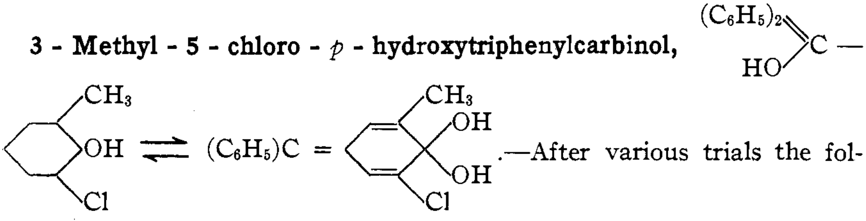
Calculated loss for one molecule of water is 4.89%.

To obtain the colorless desmotrope, the carbinol is dissolved in normal alkali, precipitated by means of carbon dioxide, and the product obtained filtered, dried, and recrystallized from benzene or ether and petroleum ether. On repeated recrystallization it is obtained entirely white and melts at 145°. The manner of the mutual transformation between these two modifications does not differ greatly from that observed and previously cited in the case of the *o*-cresylcarbinols. On the whole, however, the presence of the bromine in the nucleus imparts to the benzenoid desmotrope somewhat greater stability in the sense that it shows a lesser tendency to tautomerize to the quinonoid form than the non-brominated carbinol, and may be kept colorless for a longer time than the latter.

Diphenyl-2-methyl-6-bromo-quinomethane, $(C_6H_5)_2C : C_6H_2BrCH_3 : O$. —Dehydration of the carbinol in either desmotropic modification can be carried on at such a temperature that no fusion occurs and yet there results the brominated fuchsone compound. This, on recrystallization from benzene, is orange-red and melts at 202°. It dissolves in the ordinary organic solvents very easily but is insoluble in petroleum ether.

Calc. for $C_{20}H_{15}OBr$: Br, 22.72. Found: Br, 23.3.

3 - Methyl - 5 - chloro - *p* - hydroxytriphenylcarbinol,



.—After various trials the following procedure was adopted for the chlorination of the *o*-cresylcarbinol: To 16 g. (1 mol) of cresyldiphenylcarbinol suspended in carbon tetrachloride was added chlorine (1 mol) previously dissolved also in carbon tetrachloride. As the reaction proceeds the suspended carbinol goes into solution with evolution of hydrochloric acid gas. Towards the end of the reaction the solution was warmed on the water bath, and then concentrated to a small bulk. On standing there separated out the chlorofuchsone, an orange-colored compound. To hydrolyze it to the carbinol, it was found necessary to warm the fuchsone for a long time with alkali. The carbinol was then precipitated from the alkaline solution by means of carbon dioxide, dried and recrystallized from 60% acetic acid. Unless heated for some time with acetic acid of this strength, quinoidation is likely to be incomplete. The quinonoid desmotrope thus obtained possesses a yellow color and melts at 133°. If recrystallization of the quinonoid carbinol takes place from alcohol, benzene or ether, the carbinol is partially changed into the colorless desmotrope. It is, however, difficult to obtain an entirely white compound in this way except by repeated recrystallizations. If, however, the colored carbinol is first dissolved in normal alkali and then, after reprecipitation with carbon dioxide, is dissolved in any of the above-mentioned solvents, it appears as an entirely white compound, melting at 149°.

The white modification of the chlorocresylcarbinol shows a stability far greater than any of the colorless modifications so far mentioned. This stability shows itself in the dehydration experiment, the white carbinol changing but very slowly into the quinonoid carbinol under the influence of heat; furthermore, even on recrystallization from 60% acetic acid the colorless form persists in crystallizing out unless the solution is previously warmed for some time.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL. TEMP. 75°.

Time of heating.	Quinonoid.	Benzenoid.	Time of heating.	Quinonoid.	Benzenoid.
1½ hrs.	0.71%	No loss	24 hrs.	5.6%	0.32%
4 hrs.	1.53%	No loss	48 hrs.	5.6%	0.62%
18 hrs.	3.1%	0.12%	72 hrs.	5.7%	1.72%
24 hrs.	4.3%	0.2%	after 12 days	5.7%	5.62%

Theoretical loss due to one molecule of water is 5.54%.

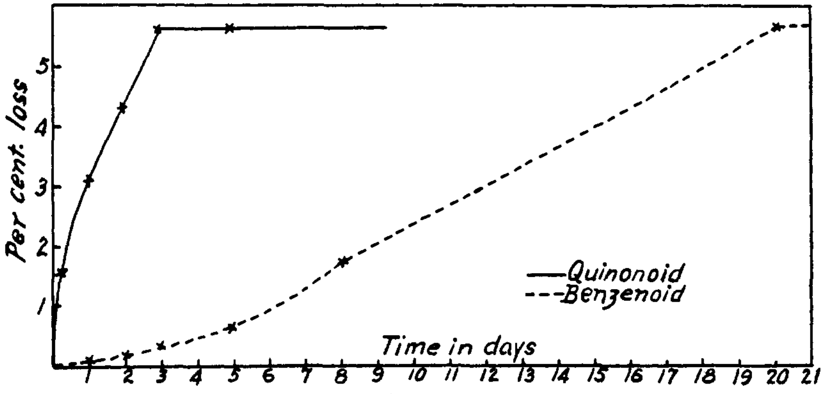


Fig. 3.

Diphenyl-2-methyl-6-chloroquinomethane.—This fuchsone, which results from the dehydration of either modification of the chlorocresylcarbinol, melts at 197° and is far more stable towards heat than most of the other analogs studied. It is easily soluble in most of the usual organic solvents. It is hydrolyzed with difficulty to the carbinol by alkali alone, but if a slight amount of alcohol is added to the alkali solution the carbinol is easily formed and passes into solution.

Calc. for $C_{20}H_{15}OCl$: Cl, 11.58. Found: Cl, 11.42.

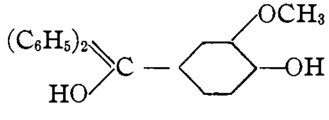
IV. Reaction between Benzophenone Chloride and Guaiacol.

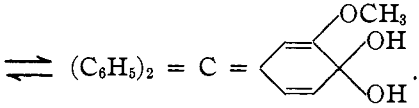
The reaction between benzophenone chloride and guaiacol follows the same course as the condensation of the keto-chloride with either phenol or *o*-cresol. We have been able to so arrange the conditions as to obtain similar products to those isolated in these previously mentioned cases.

2,2′-Methoxydiphenoxy-diphenylmethane, $(C_6H_5)_2C(OC_6H_4OCH_3)_2$.—To the warmed solution of 24 g. (1 mol) of benzophenone chloride in benzene are added 30 g. (2.5 mol) of distilled guaiacol and the mixture heated on the water bath until the evolution of hydrochloric acid ceases. On evaporation of the excess of benzene a yellow oil separates out which on addition of small amounts of alcohol becomes solid and partly crystalline. This is filtered and recrystallized from hot alcohol or ether, in either of which it is only slightly soluble. When obtained in this manner it is a white compound melting at 189°. Like its analogs already mentioned, it stands steam distillation, is insoluble in alkalies, but acids decompose it into benzophenone and guaiacol.

Calc. for $C_{27}H_{24}O_4$: C, 78.6; H, 5.87. Found: C, 78.15; H, 5.90.

3-Methxoy-*p*-hydroxytriphenylcarbinol,





.—If the reaction between the benzophenone chloride and guaiacol proceeds in absence of a solvent there results the substituted *p*-hydroxytriphenylcarbinol. This reaction takes place, however, much more slowly than in the case of phenol or *o*-cresol.

In a long-necked round-bottom flask 24 g. (1 mol) of benzophenone chloride are mixed with 30 g. (2.5 mol) of redistilled guaiacol and allowed to stand at room temperature for from two to three weeks. No attempt at cooling is necessary, since the reaction proceeds very slowly and apparently without generation of much heat. The manipulation for isolation of the carbinol differs but little from that employed in the isolation of the *o*-cresol carbinol. After steam distillation to remove the excess of guaiacol the product remains as a yellow oil which solidifies even while warm. This is digested with normal alkali, the solution is cooled and filtered, and the carbinol precipitated by means of carbon dioxide. On standing, this precipitate becomes solid and may be filtered, dried, and recrystallized from benzene. There is probably only the slightest trace of the tetraphenylated derivative present and this remains in solution while the triphenylcarbinol separates out from the hot benzene on slight cooling, being, unlike its analogs, but slightly soluble in this solvent. When obtained in this way the guaiacol compound is entirely white, and melts at 159°. It dissolves in 60% acetic acid with the production of color and after slight warming crystallizes out in the quinonoid modification, melting at 147°, and is colored brown. The effects of heat, light, and solvents do not differ in general from those in the case of the carbinols previously mentioned.

Calc. for $C_{20}H_{18}O_3$: C, 78.38%; H, 5.93%. Found (colored desmotrope): 77.92 and 5.72; (white desmotrope): 78.11 and 5.89.

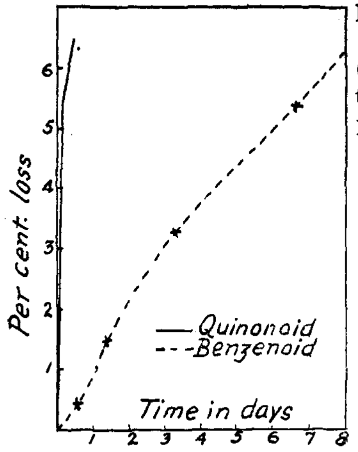


Fig. 4.

Dehydration of the Two Forms of the Carbinol.

Temperature.	Time of heating.	Quinonoid.	Benzenoid.
75°	15 min.	0.32%	No loss
75°	15 min.	1.97%	No loss
75°	30 min.	2.94%	0.10%
75°	30 min.	3.94%	0.12%
75°	45 min.	5.39%	0.15%
75°	12 hrs.	....	0.39%
75°	18 hrs.	....	1.46%
75°	46 hrs.	....	3.27%
75°	78 hrs.	....	5.37%

The loss calculated for 1 mol. of water is 5.24%.

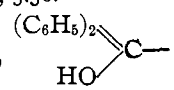
Diphenyl-2-methoxy-quinomethane, $(C_6H_5)_2C : C_6H_3OCH_3 : O$.—The fuchsone which results from the dehydration of either form of the guaiacyl carbinol when recrystallized from benzene melts at 183°. It is very soluble in ordinary solvents, is with difficulty hydrolyzed to the carbinol by alkali, but more easily with the addition of slight amounts of alcohol. Of all the fuchsones studied we have found none of them as unstable towards heat as the guaiacyl fuchsone. We have been able to isolate the methoxybenzoquinone which results from this decomposition and have found that its melting point is 145°, as reported recently by Moore,[1] and not 140°, as has appeared in the older literature.

2,2′-Methoxydi-*p*-hydroxydiphenylmethane, $(C_6H_5)_2C(C_6H_3OCH_3OH)_2$.—We have been able to obtain this compound in small amounts by carrying on the reaction between benzophenone chloride and guaiacol at elevated temperatures.

12 g. of benzophenone chloride and 15 g. of guaiacol were mixed and allowed to react for a week at a temperature of 60° to 65°. In working up the reaction mixture in the usual way, there is precipitated from the acetic acid solution on the addition of water small amounts of a high melting compound. It is characterized by its solubility in benzene which renders its separation from the corresponding triphenylcarbinol derivative very simple. On heating it softens at 200° and melts at 208°.

Calc. for $C_{27}H_{24}O_4$: C, 78.6; H, 5.87. Found: C, 78.73; H, 5.56.

3 - Methoxy - 5 - bromo - *p* - hydroxytriphenylcarbinol,


$$\begin{matrix}(C_6H_5)_2\diagdown \\ \quad C— \\ HO\diagup\end{matrix}$$

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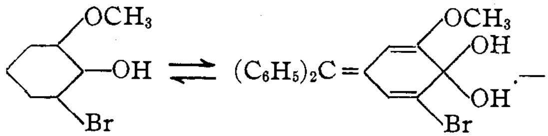
[1] *J. Chem. Soc.*, 99, 1045 (1911).



.—12 g. (1 mol) of the guaiacyl carbinol were suspended in a small amount of carbon tetrachloride and to this was added bromine (1.1 mol) dissolved in the same solvent. The reaction mixture is warmed on the water bath and finally concentrated to a small bulk. On cooling there separates out the brominated guaiacyl fuchsone. The fuchsone is hydrolyzed with normal alkali and the free carbinol is obtained in the benzenoid state by precipitation from the alkaline solution by means of carbon dioxide. On recrystallization from ether and petroleum ether it melts at 156° and is entirely white.

The quinonoid modification of the carbinol is obtained when the colorless carbinol is warmed with 60° acetic acid, and on crystallizing from this solvent it is an orange colored substance melting at 151°.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL:

Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
75°	14 hrs.	1.48	0.15	75°	6 days	4.65	2.22
75°	4 days	3.6	0.4	95°	4 days	....	3.52
75°	1 day	3.62	0.57	95°	3 days	....	4.45
75°	3 days	4.1	0.85	95°	2 days	....	4.85

Theoretical loss for one molecule of water is 5.87%.

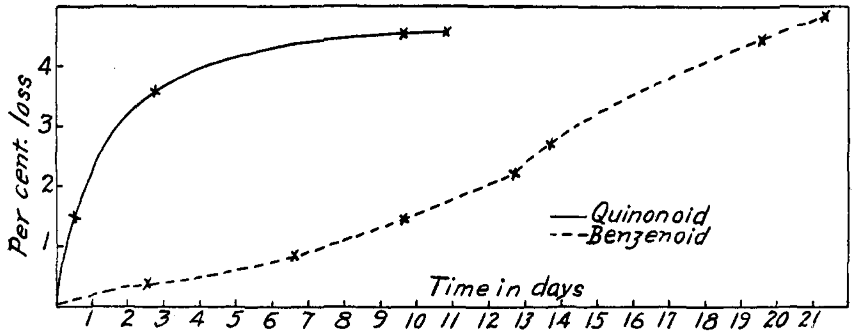
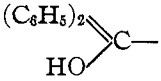


Fig. 5.

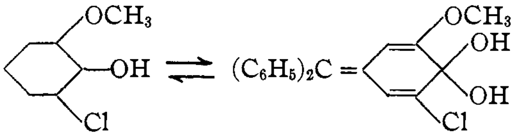
Diphenyl-2-methoxy-6-bromoquinomethane. — This bromoguaiacylfuchsone is obtained by dehydration of either modification of the carbinol. It is stable at 75°, is soluble in benzene and acetic acid, and, when crystallized from either of these solvents, is a dark red compound, melting at 232°.

Calc. for $C_{20}H_{15}O_2Br$: Br, 21.77. Found: Br, 22.22.

3 - Methoxy - 5 - chloro - p - hydroxytriphenylcarbinol,



$(C_6H_5)_2(HO)C-$



. — 12 g. of the guaiacyl carbinol were suspended in a small amount of carbon tetrachloride and to this was gradually added the calculated amount (1 mol) of chlorine in solution in carbon tetrachloride. As the reaction proceeds the guaiacyl carbinol goes into solution and there is an evolution of hydrochloric acid gas. Towards the end of the reaction the mixture is warmed on the water bath. The carbon tetrachloride is evaporated and the fuchsone thus obtained recrystallized from benzene. On long heating, this goes into solution in normal alkali and the chlorinated guaiacyl carbinol is obtained on reprecipitation by means of carbon dioxide. It is then recrystallized from 60% acetic acid, and the quinonoid modification is thus obtained. It is orange colored and melts at 159–161°. It dissolves in alcohol, benzene, or ether, the solution is only slightly colored, and on recrystallization from these solvents there is a marked rise in the melting point of the carbinol accompanied by loss of most of the color. The colorless modification is, however, best obtained by reprecipitation of the carbinol from its alkaline solution with carbon dioxide, and subsequent recrystallization from ether by addition of petroleum ether. When obtained in this manner, it melts at 166–168° and is perfectly white.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL.

Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
75°	9 hrs.	1.5%	0.101%	75°	96 hrs.	5.19%	1.90%
75°	42 hrs.	3.26%	0.496%	95°	220 hrs.	5.35%	4.90%
75°	70 hrs.	4.74%	1.09%	95°	48 hrs.	5.45%	5.21%

Theoretical loss calculated for one molecule of water is 5.26%.

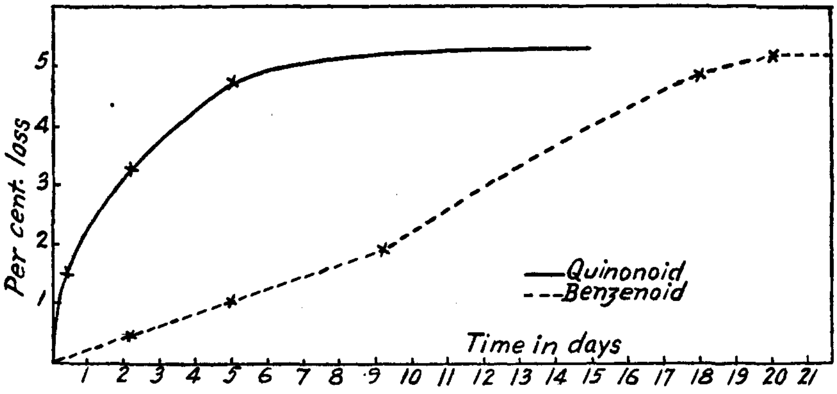


Fig. 6.

Diphenyl-2-methoxy-6-chloroquinomethane.—The chloroguaiacylfuchsone results from the dehydration of either modification of the carbinol.

It remains unaffected when heated for a long period at 75°, is soluble in hot benzene, in both these respects differing from the unchlorinated guaiacyl fuchsone. It melts at 227° and on hydrolysis with alkali yields the carbinol.

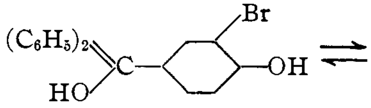
Calc. for $C_{20}H_{15}O_2Cl$: Cl, 10.98. Found: Cl, 11.01.

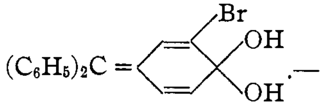
V. Reaction between Benzophenone Chloride and *o*-Bromophenol.

2,2'-Bromodiphenoxydiphenylmethane, $(C_6H_5)_2C(OC_6H_4Br)_2$.—6 g. of benzophenone chloride were mixed with 7 g. of *o*-bromophenol, which had been prepared from *o*-amidophenol by Sandmeyer's reaction. The reaction mixture was allowed to stand at room temperature for several days, no cooling being necessary. During this interval hydrochloric acid was continually given off. The excess of bromophenol was steam distilled, the product digested with normal alkali, but no material soluble in alkali could be isolated, *i. e.*, the condensation under these conditions did not yield any triarylcarbinol. On cooling, the yellow oil solidified and it was found to consist mostly of benzophenone and some of the diphenoxyether, the two being separated from each other by the insolubility of the latter in alcohol. On recrystallization from hot alcohol the ether melts at 184–185°. The theoretical yield of this same product may be obtained by carrying on the reaction between benzophenone chloride and *o*-bromophenol in benzene solution and at a temperature sufficient to expel all the hydrochloric acid formed in the reaction.

Calc. for $C_{25}H_{18}O_2Br_2$: Br, 31.37. Found: Br, 31.82.

3-Bromo-*p*-hydroxytriphenylcarbinol,





.—The fact that the condensation of benzophenone chloride with *o*-bromophenol under the usual conditions, fails to proceed beyond the first step, led us to study more fully the means whereby the phenoxy derivatives may be transformed into the corresponding triphenylcarbinols. A series of experiments on diphenoxydiphenylmethane has shown that this ether gives rise to the carbinol not only under the influence of hydrochloric acid but also when heated in the presence of a very small amount of sulfuric acid. However, when applied to the bromophenoxyether, even this treatment failed to produce more than only a small amount of the carbinol accompanied by a large amount of decomposition products. Nor was the result improved by adding sulfuric acid to the mixture of benzophenone chloride and *o*-bromophenol.[1] We have finally been able to prepare the desired carbinol

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[1] Sachs and Thonet, *Ber.*, 37, 3329 (1904).

by use of these same materials in the presence of anhydrous aluminum chloride in carbon disulfide solution at ordinary temperatures, thus avoiding the decomposition products obtained in the other case.

The procedure used was as follows: 24 g. (1 mol) of benzophenone chloride are dissolved in carbon disulfide and the containing flask surrounded by ice-water. Alternatively there are added small amounts of *o*-bromophenol and finely powdered aluminum chloride until 1.2 mols of each have been added. After the reaction has subsided the mixture is allowed to warm up to room temperature and finally warmed on the water bath. After the evolution of hydrochloric acid gas has ceased the product is cooled and decomposed in the usual manner. The product which separates out as a thick oil is then subjected to steam distillation in order to remove the excess of bromophenol and the product remaining digested with normal alkali. From the filtered solution the sodium salt of the carbinol is precipitated through the addition of solid sodium chloride. The sodium salt is filtered, washed with small amounts of water, redissolved in warm water and the carbinol precipitated by means of carbon dioxide. On standing, the precipitate becomes solid, and is then filtered, dried, and recrystallized from a small amount of carbon tetrachloride. The carbinol resulting is slightly yellow in color, melts at 107–109°, and is entirely white when further recrystallized from ether and petroleum ether. It then melts at 109°.

The colored modification is obtained when acetic acid 60% is used as a solvent. When recrystallized from this solvent, the carbinol is orange in color, and the melting point is 104.5–105°.

That the constitution of this carbinol is that of a *p*-hydroxy compound and not that of the isomeric *p*-bromocarbinol, the production of which is not at all excluded by the process of preparation which has been employed, is proven by the following: On brominating our monobromo compound we get a dibromo compound which is entirely identical with the diphenyl-3-5-dibromo-4-hydroxycarbinol, described by Auwers and Schröten,[1] and the constitution of which can be no other than as given below.

Calc. for $C_{19}H_{15}O_2Br$: Br, 22.51. Found: Br, 23.01.

Dehydration of the Two Modifications of the Carbinol.—Although there is but little variance in the melting points of the two modifications of the bromophenolcarbinols and although the transformation of the white compound to the colored modifications under the influence of heat takes place comparatively easily, yet the difference in rates of dehydration points unmistakably to a difference in structure.

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[1] *Ber.*, 36, 3237 (1903).

Temperature 75°.

Time of heating.	Quinonoid.	Benzenoid.
6 hrs.	1.68%	0.43%
19 hrs.	2.95%	1.66%
7 hrs.	3.15%	1.76%
24 hrs.	4.26%	2.13%
13 hrs.	4.71%	2.51%
20 hrs.	5.03%	3.15%
12 hrs.	5.18%	3.43%
7 days	5.21%	5.01%

Calculated loss for one molecule of water is 5.07%.

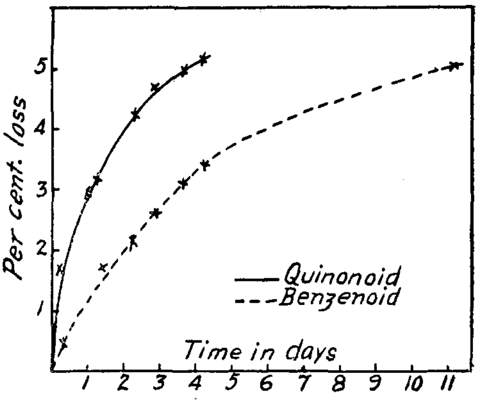
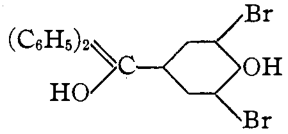
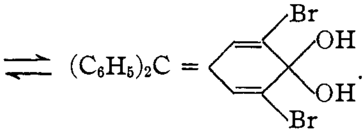


Fig. 7.

Diphenyl-2-bromoquinomethane, $(C_6H_5)_2C : C_6H_3Br : O$.—The product remaining from the dehydration of either form of the bromocarbinol melts at 140° when recrystallized from benzene. This fuchsone is characterized by its low melting point, for all other fuchsones studied melt well over 160°.

3,5-Dibromo-p-hydroxytriphenylcarbinol,





.—This carbinol can be prepared, as has been mentioned above, by brominating monobromo-*p*-hydroxytriphenylcarbinol. The more preferable method, however, is to brominate directly *p*-hydroxytriphenylcarbinol. The identity of the dibromides obtained by these two methods proves that the constitution assigned by us to the monobromocarbinol as that of *p*-hydroxycarbinol is correct.

Both Bistrzycki[1] and Auwers[2] have worked with the dibromocarbinol, have recrystallized it from various solvents, but have failed to notice the existence of it in the two desmotropic forms.

The procedure for the purification of these compounds is as follows: *p*-Hydroxytriphenylcarbinol in acetic acid or in carbon tetrachloride is brominated with the required amount of bromine. The crude solid product is boiled with a small amount of glacial acetic acid. On cooling the insoluble dark orange-red dibromofuchsone crystallizes out, while any unbrominated carbinol remains in solution. The fuchsone is now hydrolyzed to the carbinol by gentle warming with dilute alkali and alcohol,

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[1] Bistrzycki and Herbst, *Ber.*, 35, 3133 (1902).

[2] Auwers and Schröter, *Ibid.*, 36, 3237 (1903).

and the carbinol is precipitated by means of a stream of carbon dioxide or with very dilute acetic acid.

In order to obtain the benzenoid desmotrope the carbinol is recrystallized from benzene or from carbon tetrachloride, from which solvents it separated, however, with solvent of crystallization in each case. The crystals from benzene contain one-half molecule of solvent of crystallization, and this is held with considerable tenacity. Samples which have been kept in a desiccator for two weeks still contained about 8% of benzene, while the amount calculated for one-half molecule is 8.24%. The benzene, however, can be driven off at elevated temperatures, about 70°, but the carbinol acquires on this treatment a slight tinge of color. For our dehydration experiments, the carbinol freed from benzene was further recrystallized from ether and petroleum ether.

The preparation of the quinonoid desmotrope requires some care. The carbinol as obtained on the addition of dilute acid to its alkaline solution, is digested while still moist with 80% acetic acid, the filtered solution is gently warmed, and to it hot water is gradually added until the strength of the acid is reduced to about 60%. On cooling the quinonoid modification separates out in red crystals.

Although the two desmotropes differ strictly in their appearance, they both melt at about the same temperature. The purest benzenoid desmotrope melts at 138°, but in most instances the fusion point is found to be 134–136°, and this is the temperature at which the quinonoid modification melts. The colorless carbinol begins to turn quite red at about 90° and it is probable that the benzenoid desmotrope is almost completely converted into the quinonoid desmotrope before the fusion point is reached, and hence the identity of the melting points.

The two desmotropes may be differentiated from each other not only by their difference in color but also by their respective rates of dehydration on heating, as is the case with the pairs of tautomers of the other carbinols described in this paper. In the following experiment we employed, in obtaining the first set of curves, a sample of the benzenoid carbinol which has been obtained from its alkaline solution by treatment with carbon dioxide, washing thoroughly the precipitate and drying in a vacuum desiccator for two weeks. The quinonoid desmotrope employed was the crystalline compound ground to a powder in a mortar. Although the colorless compound was in a much finer state of division, yet the dehydration was slower than that of the colored. It is interesting to note the sudden breaks in the curves with the changes of temperature on heating. In the second experiment both desmotropes employed were crystalline and were reduced to about the same degree of fineness in a mortar and were kept at a constant temperature.

	Experiment 1.				Experiment 2		
Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
90°	23 hrs.	1.69	0.47	85°	22 hrs.	0.84	0.18
90°	24 hrs.	2.21	1.01	85°	58 hrs.	2.3	1.06
100–5°	24 hrs.	3.24	2.42	85°	24 hrs.	2.52	1.50
90°	21 hrs.	3.61	3.06	85°	24 hrs.	2.70	1.80
100°	70 hrs.	3.84	3.72	85°	144 hrs.	3.60	3.52
100°	140 hrs.	3.91	3.81				

Calculated loss for one molecule of water was 4.1°.

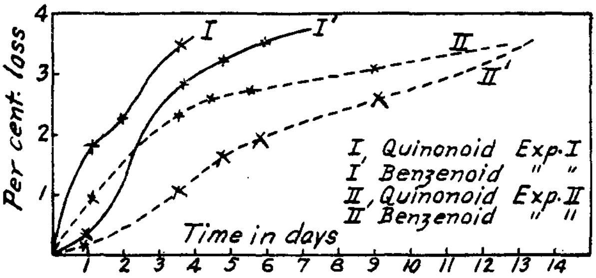

Fig. 8.

VI. Reaction between Benzophenone Chloride and *o*-Chlorophenol.

In the reaction between *o*-chlorophenol and benzophenone chloride the same difficulties and limitations were encountered as in the condensation with bromophenol. The chlorinated phenoxy compound was readily produced, but we were unable to effect its rearrangement except under conditions which rendered the isolation of the triarylcarbinol difficult. Again, as with the bromophenol, we had recourse in the use of anhydrous aluminum chloride.

Preparation of *o*-Chlorophenol.—By direct chlorination of phenol there results mostly the *p*-chlorinated compound with relatively small amount of the *o*-chlorophenol. We have tried the various methods reported in the literature, and have found that the method reported by Lossen,[1] chlorinating in carbon tetrachloride solution by means of chlorine dissolved in this same solvent, yielded the best results, 100 g. of phenol yielding as much as 35 g. of the desired compound. For separation from the *p*-chlorophenol, as well as from the unchanged phenol, the method employed by Holleman[2] was used. The reaction mixture is suspended in potassium carbonate solution and shaken with ether, whereby the unchanged phenol is removed by the ether while the chlorophenols remain in the alkaline solution. This is now acidified, the liberated chlorophenols extracted with ether, the solution dried, and the phenols carefully fractionated.

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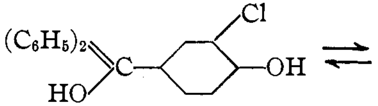
[1] Friedlander's *Fortschritte*, 7, 89 (1903).

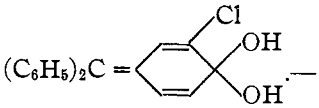
[2] Holleman and Rinkes, *Rec. trav. chim.*, 30, 79 (1911).

2,2′-Chlorodiphenoxydiphenylmethane, $(C_6H_5)_2C(OC_6H_4Cl)_2$. — The phenoxy compound could be isolated when the reaction between the benzophenone chloride and *o*-chlorophenol was carried out without the use of a solvent, but was more easily prepared, with theoretical yields, if the reaction took place in benzene solution warmed sufficiently to expel the hydrochloric acid gas given off in the reaction as soon as formed. On evaporation of the benzene and the addition of small amounts of alcohol, the chlorophenoxy compound separates out. On recrystallization from hot alcohol, it is obtained quite pure and it then melts at 191–192°.

Calc. for $C_{25}H_{18}O_2Cl_2$: Cl, 16.86. Found: Cl, 16.94.

3-Chloro-*p*-hydroxytriphenylcarbinol,





.—12 g. of benzophenone chloride were dissolved in a small amount of carbon disulfide and the temperature of the solution kept down by means of ice-water. To this solution gradually and alternately small amounts of *o*-chlorophenol and aluminum chloride, finely powdered, were added until slightly more than one molecule of each had been used. The product is isolated in the same manner as the bromophenol compound, and it also is crystallized from carbon tetrachloride, from which it separates as a slightly colored material without a sharp melting point. On recrystallization from 60% acetic acid, the quinonoid desmotrope, deep orange and melting at 118°, is obtained. If the product obtained from the carbon tetrachloride solution is dissolved in alcohol, on standing there separates out the benzenoid desmotrope in large, transparent, colorless crystals, melting at 70–72°, with apparent loss of solvent of crystallization.

Calc. for $C_{19}H_{15}O_2Cl + {}^1/_2C_2H_6O$: ${}^1/_2C_2H_6O$, 6.9. Found: ${}^1/_2C_2H_6O$, 6.88.

If the alcohol of crystallization is driven off at a low temperature or by long exposure of the crystalline carbinol over calcium chloride, the product remaining is a white powder melting at 126°, and on recrystallization from benzene, or ether and petroleum ether, the melting point is not changed. Similar to the case with the analogous monobromocarbinol, the method employed for the preparation of the 3-chloro-*p*-hydroxytriphenylcarbinol did not exclude the possibilities of production of the isomeric 3-hydroxy-*p*-chlorocarbinol. That the carbinol prepared by the methods just given is nonetheless the *p*-hydroxy compound was definitely shown by further chlorinating the product obtained from this reaction. We obtained in this manner a dichlorocarbinol identical in every respect with the product obtained by direct chlorination of the *p*-hydroxytriphenylcarbinol, the constitution and properties of which are given later in this paper.

The transformation of the 3-chloro-*p*-hydroxytriphenylcarbinol from the white form to the colored modification takes place not quite as readily as with the corresponding bromocarbinol, as can be seen on comparison of the two sets of curves showing the relative values of dehydration.

TEMPERATURE 80°.

Time of heating.	Quinonoid.	Benzenoid.
1 hr.	1.08	.....
16 hrs.	3.74	2.024
20 hrs.	4.98	2.376
40 hrs.	5.80	3.42
48 hrs.	....	4.35

Calculated loss for one molecule of water is 5.78%.

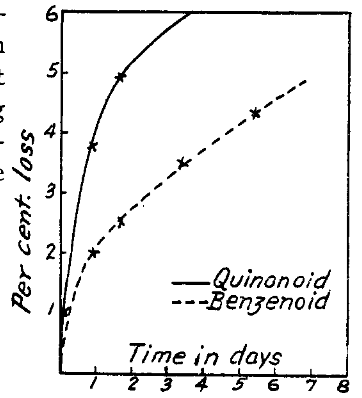
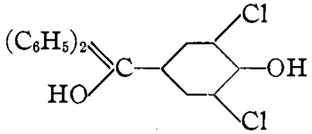


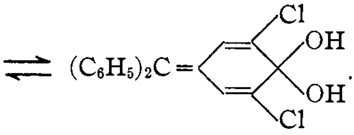
Fig. 9.

Diphenyl-2-chloroquinomethane.—The product remaining from the dehydration of either form of the chlorocarbinol consists of the chlorofuchsone. It does not differ in properties from the bromofuchsone, both of them showing remarkable stability over the guaiacylfuchsone under the influence of heat. When crystallized from benzene it melts at 162–3°. On recrystallization from hot glacial acetic acid there separated out deep red crystals containing acetic acid, which is easily driven off at 75°. Here again, as in the instance of the *o*-cresylfuchsone acetate, we are inclined to attribute to this compound the constitution of a quinocarbonium salt, namely, diphenyl-2-chloroquinomethane acetate.

Calc. for $C_{19}H_{14}OCl$: Cl, 11.42. Found: Cl, 11.70.

3,5-Dichloro-*p*-hydroxytriphenylcarbinol,





.—This carbinol is best prepared from *p*-hydroxytriphenylcarbinol directly. The latter is suspended in carbon tetrachloride and to the cooled mixture a solution of chlorine in the same solvent is slowly added. The carbinol, on chlorination, goes into solution. The solvent is now evaporated and the residue is boiled up with glacial acetic acid. On cooling, dichlorofuchsone, m. p. 217°, very little soluble in cold acetic acid, crystallizes out. The hydrolysis of the fuchsone to the carbinol, further purification, and the isolation of the two desmotropes is carried out in the same manner as has been described under the 3,5-dibromocarbinol. The dichlorofuchsone is darker red than the corresponding dibromo compound, and the quinonoid carbinol possesses also a brighter red color than the dibromocarbinol. Here again, as has been found to be the case with the analogous dibromocarbinol, the benzenoid dichloro compound crystallizes from benzene and from carbon tetrachloride with solvent of crystallization. Furthermore, the two desmotropes cannot be differentiated from each other by their melting points, for both melt at approximately the same temperature, 134°. They can be differentiated, however, not merely by the difference in color but also by their respective rates of dehydration on heating.

VII. Nitro-*p*-Hydroxytriphenylcarbinol.

The reaction between benzophenone chloride and *o*-nitrophenol was in no way similar to any other condensations previously studied. When mixed in the cold without the use of a solvent there was only slight action as judged from the amount of hydrochloric acid given off. Upon the addition of catalytic agents, a drop of sulfuric and addition of hydrochloric acid gas, this action was only slightly increased. At temperatures ranging from 75–100° the evolution of gas was increased, but the resulting product was a charred mass from which nothing could be isolated. Recourse was had to methods similar to those employed with the *o*-bromo- and *o*-chlorophenols, but without satisfactory results, whether carbon disulfide or heptane (b. p. 90°) was used. The condensation was finally brought about in the presence of aluminum chloride without the use of solvents, and resulted in the formation of the nitrohydroxycarbinol. 12 g. (1 mol) of benzophenone chloride and 7.5 g. (1.1 mol) of *o*-nitrophenol are mixed in a round-bottom flask and kept cool by surrounding with ice-water. To this mixture were gradually added 7 g. (1 mol) of anhydrous aluminum chloride. After the reaction is at an end, the mixture is heated on the water bath at 60°. Too high a temperature should be avoided; otherwise the result is a charred mass. After cooling, the aluminum salt is decomposed in the usual manner, the excess of nitrophenol removed by steam distillation, the product digested with normal alkali, precaution being taken to remove the benzophenone, and the sodium salt of the carbinol finally precipitated by addition of sodium chloride. The sodium salts already mentioned of the various carbinols were in every case white needle-like crystals. In the case of the nitrophenolcarbinol the sodium salt was bright red. The carbinol which results from the water solution of the sodium salt on the addition of acids is almost colorless. On recrystallization from 60% acetic acid, it does not change in color but always precipitates out with only a slight amount of color. It melts at 97–98°. Recrystallization from any solvent does not change the melting point.

Calc. for $C_{19}H_{15}O_4N$: C, 71; H, 4.71; N, 4.36. Found: C, 70.68; H, 4.353; N, 4.273.

It is barely possible that here we have another instance of substituted triphenylparahydroxycarbinols occurring in but one modification, as is the case in certain carbinols studied in this laboratory by L. C. Johnson and which will be described later. The intense color of the sodium salt, in contradistinction from the carbinol itself, suggests the relation of aci-nitro to the true nitro compounds, so thoroughly studied by Hantzsch. The substance is now under further investigation.

Summary.

1. It has been shown in this paper that benzophenone chloride condenses with various ortho-substituted phenols, in some instances requiring no catalytic agent, in others the use of aluminum chloride makes the yields more satisfactory. Under proper conditions this offers an excellent method for the preparation of various *p*-hydroxytriphenylcarbinols.

2. It has been shown that substitution of the groups, CH_3, OCH_3, Br, Cl in the ortho positions to the hydroxyl group does not deprive the carbinol of the tendency to tautomerize, and with each carbinol two desmotropic forms have been isolated. The various pairs of tautomers show remarkable similarity, as for example, in their melting points, in every instance the colored compound melting lower than the corresponding white desmotrope. Furthermore, the white higher melting compound, through heat or light energy, is invariably changed to the lower melting isomer.

3. Although as mentioned, the substitution did not hinder the tautomeric tendency in the carbinols studied, it resulted nevertheless in a gradation of this tendency. The various curves of dehydration, if placed on one diagram, would show clearly that at the temperature chosen, 75°, the various white desmotropes differ in their readiness to transform into the corresponding colored modifications, as judged by their rate of loss of water. For example, the monobromo-*p*-hydroxytriphenylcarbinol suffers transformation and subsequent dehydration in one-third the time as the chlorocresylcarbinol. Similarly, the colored modifications differ among themselves, as may be noted from the readiness of dehydration of the guaiacyl colored desmotrope as compared with the chloroguaiacyl colored compound under similar conditions. This, to be sure, does not indicate tautomeric tendency, but rather serves as a measure of the stability with which the two hydroxyl groups linked to one and the same *p*-quinone-carbon atom are held in the various quinoid carbinols, respectively.

4. The colored desmotropic modifications of the carbinols have been shown to possess the quinonoid constitution. The existence of so large a group of desmotropes removes the phenomenon of tautomerism in this series of compounds from the realm of chance, and offers a very strong support of experimental nature to the whole quinocarbonium theory

and to the quinonoid interpretation of the cause of color in the triphenylmethane series in general. This applies in no lesser degree to the free triarylmethyl radicals themselves. In the solid state they are nearly all colorless or only pale yellow, but when they are dissolved in some solvent, like benzene, intensely colored solutions result. We must assume from the evidence presented in this paper that the radicals dissolve with a simultaneous partial transformation to the quinonoid state.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 267.]

RESEARCHES ON QUINAZOLINES. XXXIII. A NEW AND SENSITIVE INDICATOR FOR ACIDIMETRY AND ALKALIMETRY, AND FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS BETWEEN THE LIMITS OF 6 AND 8 ON THE SORENSEN SCALE.[1]

BY MARSTON TAYLOR BOGERT AND GEORGE SCATCHARD.[2]

Received June 19, 1916.

Introductory.

As a means of measuring hydrogen-ion concentration, the use of an indicator possesses the obvious advantage of convenience of operation, practically instantaneous readings and inexpensive apparatus.

Ostwald's explanation[3] of indicator action as due to an equilibrium between an ion of one color and an un-ionized molecule of another color (or colorless), has been quite generally abandoned in favor of the theory that an equilibrium exists between the two forms in both states.[4]

$$\begin{tikzcd} \mathrm{H}^+ + \mathrm{In}^- \arrow[r, shift left] \arrow[d, shift left] & \mathrm{HIn} \arrow[l, shift left] \arrow[d, shift left] \\ \mathrm{H}^+ + \mathit{In}^- \arrow[u, shift left] & \mathit{HIn} \arrow[u, shift left] \end{tikzcd}$$

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[1] Sörensen's system of expressing hydrogen-ion concentration has been used throughout, the "Index" (P_H) being the negative common logarithm of the concentration of hydrogen ion, *i. e.*, the negative exponent of the power to which 10 must be raised to express this concentration (Sörensen, *Compt. rend. Laboratoire de Carlsberg*, **8** (1909); Fales and Nelson, THIS JOURNAL, **37**, 2771 (1915)). Thus, the index 6 represents a hydrogen-ion concentration of 10^{-6}, and 8 of 10^{-8}. This provides a single unit for expressing acidity and alkalinity, and one which can be measured directly by the use of the hydrogen electrode. Further, it is the relative and not the absolute change in hydrogen-ion concentration which affects both the electromotive force of the hydrogen electrode and the color of the indicator.

[2] The experimental work upon which this paper is based was carried out by Mr. George Scatchard in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University.

Acknowledgments are also due to Dr. H. A. Fales, of this University, for much valuable assistance and advice.

[3] *Wissenschaftliche Grundlagen der analytischen Chemie*, 1901, 117.

[4] Stieglitz, THIS JOURNAL, **25**, 1112 (1903); A. A. Noyes, *Ibid.*, **32**, 816 (1910).