ON TRIPHENYLMETHYL. XXIII. TAUTOMERISM OF THE HYDROXY-TRIPHENYL CARBINOLS.

By M. Gomberg.

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Bistrzycki and Herbst,[1] in their first paper on *p*-hydroxytriphenylcarbinol describe it as an orange colored compound which on repeated recrystallization (six times) from 50% acetic acid, finally becomes colorless and melts at 139–40°. Baeyer and Villiger[2] prepared the same carbinol by a different method and speak of it as a colorless compound when crystallized from benzene, and on subsequent recrystallization from acetic acid it was found by them to melt at 143–4°. They do not mention any change of color in the carbinol with the change of solvent from benzene to acetic acid. Auwers and Schröter[3] found that when the carbinol is liberated from its solution in sodium hydroxide by means of carbon dioxide instead of by acetic acid, it possesses a higher melting point, 157–8°. They contend that the lower melting compound of Bistrzycki and Herbst is a hydrate, $C_{19}H_{16}O_2 + {}^1/_2H_2O$, while the higher melting substance is the true carbinol. In support of this they cite data from elementary analyses, and also state that they found it possible to change one substance into the other by the proper choice of solvents containing water, *i. e.*, alcohol, dilute acetic acid, etc.; or anhydrous solvents, *i. e.*, benzene, chloroform, etc. No mention is made whether there is any difference in the color between the two products. Later Bistrzycki with Zurbriggen[4] and with Herbst[5] found that *o*-cresyldiphenylcarbinol exists in two forms, *i. e.*, α-yellow, melting at 197–8°, and β-colorless and melting at 148–9°. At the same time a correction was made relative to their previous statements as regards the color of the hydroxytriphenyl carbinol. In this article they say that the carbinol was obtained finally pale in color, but never entirely colorless. They confirmed Auwers and Schröter's discovery of the higher melting modifications, but disputed their statement that there is any difference in composition between the higher melting hydroxycarbinol and the lower melting modification. To explain the difference between the two modifications, a tentative suggestion was put forward, involving the orthoquinol structure, not unlike that employed by Zincke for similar cases.

The various conflicting statements cited above, relative to the color, melting points, and stability of hydroxytriphenylcarbinol, become, however, readily explicable when viewed in the light of the quino-carbonium

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[1] *Ber.*, 34, 3073; 35, 3133.

[2] *Ibid.*, 36, 2791.

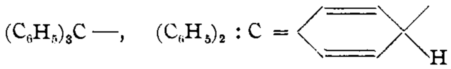
[3] *Ibid.*, 36, 3247.

[4] *Ibid.*, 36, 3558.

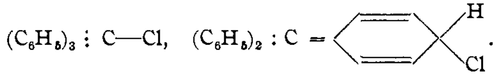
[5] *Ibid.*, 36, 3565.

hypothesis. The following facts have been established, in the opinion of the writer, in previous papers dealing with this hypothesis:

1. Triphenylmethyl exists in two tautometic forms, the quinonoid, and the benzenoid:[1]

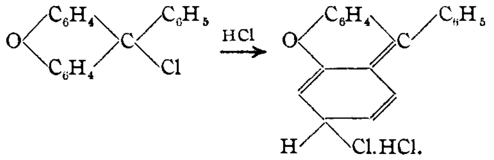


2. The triaryl carbinol halides are equally capable of showing similar tautomerism, being respectively colored and colorless:[2]



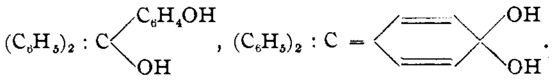
3. The triaryl methyl sulfates (perchlorates, double salts with metals, etc.) exist only in the quinonoid state, and are always colored.[3]

4. The so-called "carboxonium" and "carbothionium" salts of the xanthenols and thioxanthenols are in reality quino-carbonium salts, tautomerized to that state by excess of mineral acid or by metallic halides, if present:[4]



5. The hydroxy groups in the para position to the central carbon atom exert an unusually favorable influence as regards the tautomerizing tendency of the triaryl methyl compounds in general.[5]

In view of the above cited phenomena of quinoidation it seemed not improbable that the conflicting statements as regards the properties of hydroxytriphenyl carbinol could be explained by the existence of two forms of the carbinol, the benzenoid and the quinonoid:



The results so far obtained confirm this assumption.

The Two Carbinols.—The hydroxy carbinol is best prepared from *p*-anisyl-diphenyl carbinol by demethylating the latter with aluminium chloride in benzene.[6] The mixture of the carbinol and the diphenyl

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[1] *Ber.*, 40, 1881.

[2] *Ibid.*, 40, 1860.

[3] *Ibid.*, 40, 1847.

[4] Gomberg and Cone, *Ann.*, 370, 141; 376, 183.

[5] Gomberg and West, THIS JOURNAL, 34, 1529.

[6] Gomberg, THIS JOURNAL, 35, 209.

quinomethane obtained in this way is digested with warm sodium hydroxide solution (3%) until the quinone has been changed to the carbinol and nearly all has gone into solution. The filtered alkaline solution may now be treated in one of two ways, depending upon which modification, the quinonoid, or the benzenoid is desired. In the first instance, the carbinol is best liberated by the addition of some acid in excess, preferably acetic acid. In the second, by the addition of an ammonium chloride solution. Subsequent purification of each is carried out as follows: The quinonoid modification is recrystallized from 40-50% acetic acid, as was done by Bistrzycki. But, it should be stated, no amount of recrystallization from this solvent diminishes or destroys the yellow color, the latter is an inherent property of the quinonoid substance. The benzenoid form is purified by dissolving it in alcohol to which a few drops of ammonia water have been added, and then slowly adding water until a permanent turbidity is produced. On standing, the hydroxy-carbinol separates out in shining needles or plates, absolutely colorless. These must be filtered and washed with dilute alcohol containing some ammonia, and dried in a desiccator over soda lime, or otherwise they assume a tinge of yellow.

The yellow form melts at 139–40°, occasionally a couple of degrees higher or lower, depending a good deal upon the rate of heating. The colorless modification turns yellow on heating at about 110–20°, melts usually at 157–9°. In rare instances we observed samples melting as high as 162–3°. The same was observed by Auwers and Schröter.

The Two Modifications are not Physical Isomers.—The colorless and the yellow modifications were found to be about equally soluble in benzene, 1 gram in about 150 cc. of the solvent at room temperature. When a concentrated solution of the yellow modification is inoculated with the colorless form, or a solution of the colorless with the yellow form, such inoculation has no effect upon the nature of the crystals that are subsequently obtained: each solution deposits the modification which has been originally dissolved in the solvent. Nor does either of the two modifications contain water of crystallization. Solutions of each modification in benzene were dried over calcium chloride two weeks, and then concentrated under reduced pressure at a temperature not exceeding 40°. The crystallin deposits were washed with petroleum ether, dried and analyzed. The sample of the quinonoid modification was, after this treatment, just as colored as before solution, and melted at 140–42°, with evolution of water; the benzenoid was almost colorless and melted at 159–161°.

Quinonoid: I. 0.1691 gram substance gave 0.5118 CO_2 and 0.0891 H_2O.
Benzenoid: II. 0.3071 gram substance gave 0.9291 CO_2 and 0.1690 H_2O.
Benzenoid: III. 0.2100 gram substance gave 0.6375 CO_2 and 0.1115 H_2O.

	Calculation $C_{19}H_{16}O_2$.	Found.		
		I.	II.	III.
C	82.57	82.55	82.52	82.79
H	5.84	5.90	6.16	5.94

Influence of Heat.—That the two different modifications behave differently when heated to a moderate temperature, has been observed by Auwers and Schröter, who noticed that the higher melting form remains unchanged, while the lower melting modification becomes insoluble in alkalies. We find that the causal difference is in the rate with which water is given off. As might be expected, the quinonoid, yellow, modification loses water far more readily than the benzenoid form, explainable by the fact that the two hydroxyl groups in the quinonoid form are linked to the same carbon atom.

For each of the following experiments, about 0.9 gram of substance was taken. The material was placed in a boat and kept at definit temperatures for intervals of $^1/_2$ hour each. A stream of dry air was passed constantly through the tube and the liberated water was collected in a weighed calcium chloride tube.

Temperature.	Time of heating, minutes.	Loss of water in per cent.	
		Benzenoid.	Quinonoid.
60°	30	..	0.53
75°	30	..	1.44
90°	30	0.38	2.68
100°	30	0.78	3.44
110°	30	1.29	4.90
120°	30	1.67	5.72
130°	30	3.52	7.48

The results clearly show the striking differences as regards the stability of the two carbinols. The fact that the benzenoid form upon heating to about 100° begins to turn yellow and at the same time begins to give off water, indicates that it is first gradually tautomerized to the quinonoid form. This change is probably accompanied by absorption of energy, as will be discussed below, in speaking of the effect of light.

Transformation of the Modifications into Each Other.—The yellow modification is always the resulting product when either modification of the carbinol is recrystallized from dilute acetic acid, while the high melting, colorless, modification is invariably obtained when an alkaline solution of either modification is treated with dilute ammonium chloride solution, or when it is recrystallized from alcohol containing some ammonia. In other words, an alkaline medium favors the formation of the benzenoid form, while acid favors the formation of the quinonoid form. From alcohol containing hydrochloric acid, a mixture of the two forms is obtained usually, yellow and colorless crystals separating simultaneously. The yellow modification has also been obtained by recrystallization of the colorless form from benzene containing a little acetic acid. On the other hand, by the recrystallization of the yellow form from benzene containing some pyridine, a change from the yellow to the colorless form is observed. Repeated recrystallization of the quinonoid form from a mixture of benzene and petroleum ether induces tautomerization but slowly, but in alcohol the tautomerization is marked. 1.5 grams of the quinonoid form melting at 138–9° was found to have lightened considerably in color on the second recrystallization from alcohol, and melted at 142–4°; on the fourth, at 150°, with but very slight evolution of water; on the sixth, the two kinds of crystals came down together and they were readily separated mechanically from each other, the quinonoid melting at 136–7°, and the benzenoid melting at 156°.

It is obvious that the relation between the two modifications of the carbinols is hardly that of tautomerism in the very strict sense of the word. And yet, the recent advances in the field of enol-keto tautomerism have demonstrated that there is no sharp line of division between the phenomena of structural isomerism and that of what is designated as tautomerism. Tautomers may be separated from each other, and possess each an individual existence. The two carbinols under discussion represent, in that sense, an illustration of a pair of stable tautomers. No doubt, the various carbinols belonging to this series will be found to differ in the degree of stability of the two tautomeric modifications, respectively.

The Influence of Light.—Stoemer and his coworkers[1] have shown that ethylene derivatives are readily affected by ultraviolet light, the higher melting individual of a pair of such stereoisomers being readily changed to the lower melting one. Such a change is accompanied by an absorption of energy and the lower melting isomer invariably possesses a higher heat of combustion than the higher melting isomer. The influence of ultraviolet light upon the tautomeric hydroxy-carbinols is not unlike that upon the stereoisomeric ethylenes. Dry samples of the benzenoid carbinol exposed to direct sunlight rapidly turn yellow on the surface, and the colored upper layer now possesses the melting point of the quinonoid carbinol. Much more striking is the change when a solution of the carbinol in benzene, in a quartz flask, is exposed to direct sunlight. In a few minutes the solution begins to turn yellow, and after a few hours it is a deep orange, and the tautomeric change is complete. The solution now contains only the quinonoid modification.

From the analogy in behavior between the stereoisomeric ethylenes on the one hand and the tautomeric hydroxy-carbinols on the other, we may reasonably infer that in the case of the hydroxy carbinols also, the lower melting, quinonoid, modification is the *labil* form and should

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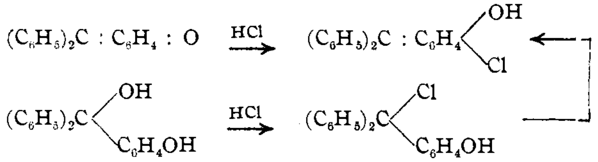
[1] *Ber.*, 42, 4865; 44, 637, etc.

possess a higher heat of combustion than the *stable*, the benzenoid, form. This inference has not yet been tested.

Action of Hydrochloric Acid.—As the triaryl carbinol halides in general possess a much greater tendency towards tautomerization than the carbinols themselves[1] it may well be surmized that the chloride of the *p*-hydroxytriphenyl carbinol would exist only in the quinonoid state, *i. e.*, as the quino-carbonium salt. We find, in fact, that both tautomers of the carbinol behave toward hydrochloric acid alike, and that the chloride obtained in this way is apparently identical with the chloride obtained from fuchsone:



$$(C_6H_5)_2C : C_6H_4 : O \xrightarrow{HCl} (C_6H_5)_2C : C_6H_4\begin{matrix}OH\\ Cl\end{matrix}$$

$$(C_6H_5)_2C\begin{matrix}OH\\ C_6H_4OH\end{matrix} \xrightarrow{HCl} (C_6H_5)_2C\begin{matrix}Cl\\ C_6H_4OH\end{matrix}$$

We can confirm Bistrzycki's and Auwers' results that it is impossible to isolate this chloride by treating the carbinol in solution with hydrochloric acid, for under these conditions it separates as an oil, probably as a chloride-hydrochloride. We have obtained it fairly pure in the following manner: A weighed amount of the dry fuchsone is placed in a porcelain boat and dry hydrochloric acid is passed over it. The fuchsone at once assumes a deep red color and absorbs the acid with great avidity, with slight liquefaction. The amount of absorbed acid is usually about one and one-half molecules, due to partial formation of the chloride-hydrochloride. The extra amount is however gradually given off from the compound when it is kept in a desiccator, much faster when the desiccator is exhausted. When the composition of the chloride has reached approximately that of the normal salt, further loss of hydrochloric acid takes place only very slowly. Thus, a 0.5 gram sample of fuchsone gained, through absorption of acid, 18.76% of its weight; after one hour in a vacuum desiccator the gain was reduced to only 13.90%, while the theoretical amount for one molecule of hydrochloric acid is 13.68%. After two hours further *in vacuo* the acid dropped to 13.50%, and after fourteen hours more, to 11.70%.

The same chloride is obtained when either modification of the carbinol is treated with hydrochloric acid in the same manner as fuchsone. It is, however, advisable in this case to treat the solid carbinol with the acid for a short time only, and then place it in a vacuum desiccator in order to remove the water produced in the reaction. This treatment is repeated several times. Obviously, the formation of the chloride from the carbinol

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[1] Compare, for instance, the colorless phenyl-4-hydroxyquinoxanthenol with its colored carbinol halide. Gomberg and West, THIS JOURNAL, 34, 1565.

in the pure state is less certain than from fuchsone; but none the less, quite fair results have been obtained.

The solid chloride is deep red, irridescent, and looks very much like fuchsine. It slowly loses its hydrochloric acid when dry, somewhat more rapidly when a stream of air is passed through its solution in benzene, and especially when the latter is warmed. Treated with molecular silver, it behaves entirely unlike the benzenoid triarylmethyl halides. While the latter lose chlorine and give rise to a triarylmethyl, the *p*-hydroxytriphenylcarbinol chloride loses hydrochloric acid, and gives rise to fuchsone. It behaves therefore, in this respect, similarly to the colored, quinonoid chlorides of *p*-hydroxybenzo-γ-pyranols[1] and of *p*-hydroxyxanthenols.[2]

Auwers and Schröter[3] reported that the dibromo-*p*-hydroxytriphenyl carbinol gives with hydrobromic acid a *colorless* carbinol bromide. If this be true, it is then confirmatory evidence that halogens in the nucleus are negative in their influence as regards tautomerization.[4]

Conclusion.

The results presented in this paper show conclusively that there exist two modifications of *p*-hydroxytriphenyl carbinol and that these are not physical isomers. The ease with which the colorless is changed to the colored modification, and *vice versa*, suggests a mutual relation of tautomerism. Such a conclusion, plausible as it is, would of course be very venturesome, were this phenomenon of isomerization limited to only one carbinol. But this is not the case.

We can confirm Bistrzycki and Zurbriggen's results as regards *o*-cresyldiphenyl carbinol. We find that the same methods which we employed with the hydroxytriphenyl carbinol, give best results in the homologous *o*-cresylcarbinol for the isolation of its two modifications. We find here the same relation between the high and low melting modifications as regards color, and a similar effect as regards the influence of light. Moreover, we have examined several other *p*-hydroxytriphenyl carbinols (to be described in a subsequent paper) and apparently they all exist in two modifications, related to each other like the two *p*-hydroxytriphenyl carbinols.[5] We are therefore forced to the conclusion that the tautomerization of *p*-hydroxytriphenyl carbinols is a general phenomenon. From the behavior of the modifications and also from analogy with similar isomerization in the triaryl methyls, triaryl methyl salts, xanthenols, etc., it seems justifiable to infer that in the case of the hydroxytriphenyl carbinols also, we are dealing with tautomerization to the para-quinoid

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[1] Gomberg and Cone, *Ann.*, 370, 203.

[2] Gomberg and West, THIS JOURNAL, 34, 1562.

[3] *Ber.*, 36, 3243.

[4] Gomberg and Cone, *Ann.*, 370, 185.

[5] We have not as yet investigated the dihydroxy and trihydroxy compounds, such as benzaurine and aurin.

state, *i. e.*, that the colored modification is the simplest *quinocarbonium base.*

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

A COLOR REACTION OF HYPOCHLORITES WITH METHYLANILINE AND ETHYLANILINE.

BY PAUL NICHOLAS LEECH.

Received May 30, 1913.

Methylaniline.—In connection with an investigation on the molecular rearrangement of derivatives of triphenylmethylhydroxylamine pursued with, and under the guidance of, Professor Stieglitz, mono-methylaniline and aniline were possible products, which had to be taken into consideration and tested for. According to Hofmann,[1] upon the addition of bleaching powder solution, pure methylaniline gives no color reaction and a careful search of the literature failed to show any observation contrary to this statement. However, in preliminary trials on methods for detecting aniline and methylaniline, side by side, the action of chloride of lime solution on an aqueous solution of methylaniline was tried, and it was noticed that if the water solution of methylaniline was made alkaline (not strongly) and a small amount of one-half saturated bleaching powder solution was added, after a number of seconds, a navy blue color would appear, gaining in intensity, and then fading, finally leaving a pale yellow solution (and a white precipitate, probably calcium carbonate). To verify this observation, the following method of preparing *pure* methylaniline was employed:

(1) Kahlbaum's "Special" mono-methylaniline was dried over fused potassium hydroxide, and twice fractionated by distillation, with the aid of a Glinsky distilling tube. The methylaniline obtained, almost colorless, was treated in the usual manner with nitrous acid, and converted into nitrosomethylaniline. This was reduced with tin and hydrochloric acid, the regenerated free base was liberated by means of alkali, and distilled over with steam, etc. The methylaniline thus obtained was dried and twice fractionated. The treatment assured the absence of aniline and dimethylaniline.

(2) Kahlbaum's "Special" mono-methylaniline was dried over fused potassium hydroxide, twice fractionated as before, and the methylaniline obtained was subjected to the same method of purification as was used by Hofmann.[2] That is, it was converted into methylacetanilide, which was thrice recrystallized from water, giving the melting point 103°, and

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[1] *Ber.*, 7, 526 (1874).

[2] *Ibid.*, 7, 523 (1874).