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

TAUTOMERISM OF ORTHO-HYDROXY-TRIARYL CARBINOLS WHICH CONTAIN NAPHTHYL GROUPS

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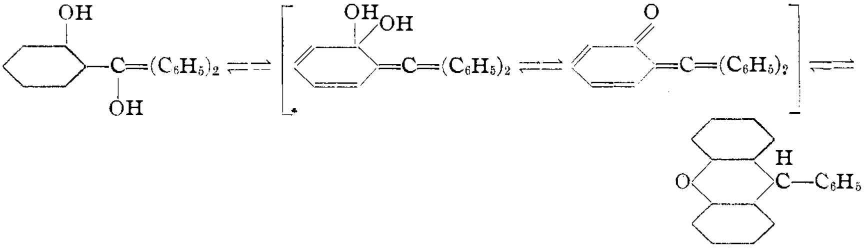
Introduction

The assumption of a quinonoid rather than benzenoid structure for the colored triarylmethyl salts affords a lucid explanation of their observed properties. The single fact necessary for the incontrovertible establishment of the quinonoid structure for these salts is still lacking, however. So far it has not been possible to isolate any triarylmethyl salt in the two tautomeric forms in the solid phase but only in solution. Indirect evidence for the potential existence of the salts in both the benzenoid and the quinoid modifications is found in a study of the substituted triarylmethyl carbinols, such as hydroxy carbinols. The stability of the benzenoid and quinonoid forms of the carbinols seems to be more nearly of the same order of magnitude than is the case with the corresponding forms of the salts themselves.

The first such quinocarbonium base obtained in both the quinonoid and benzenoid modifications was *p*-hydroxy-triphenyl carbinol. Several other *p*-hydroxylated triaryl carbinols have since been studied, and both modifications proved to exist by their isolation in the solid state. More recently it has been found[2] in this Laboratory that *o*-hydroxy-triphenyl carbinol presumably exhibits such tautomeric change, but neither the colored carbinol nor the fuchsone could be obtained in the solid form. Their presence in solution as intermediate phases between the benzenoid carbinol and the xanthane was indicated.



A homolog of this carbinol, *p*-methoxy-*o*-hydroxy-triphenyl carbinol, whose preparation has been reported previously[3] has been observed by us to show similar tendencies toward tautomerization.

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[1] The material here presented is from the dissertation submitted by W. J. McGill to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1924.

[2] Gomberg and Nishida, This Journal, **45**, 190 (1923).

[3] Tiemann and Parrisius, *Ber.*, **13**, 2376 (1880). Gomberg and Johnson, This Journal, **39**, 1674 (1917).

The Object of this Investigation.—The question as to the catholicity of this tautomerization in the entire class of *o*-hydroxy-triaryl carbinols, and more especially the effect of naphthyl groups upon the tautomerization, has been the principal object of investigation in this paper. For this purpose we have studied a number of *o*-hydroxy-triaryl carbinols which contain 1, 2 or 3 naphthyl groups; namely, the monomethoxy derivative of hydroxydiphenyl-α-naphthyl carbinol (I), *o*-hydroxyphenyl-di-α-naphthyl carbinol (II) and its methoxy and benzyloxy derivatives, 3-hydroxynaphthyl-diphenyl carbinol (III) and its methoxy and benzyloxy derivatives, 3-hydroxynaphthyl-2-di-α-naphthyl carbinol (IV) and its methoxy derivative, 2-hydroxynaphthyl-1-diphenyl carbinol (V) and its methoxy and benzyloxy derivatives, and 1-hydroxynaphthyl-2-diphenyl carbinol (VI) and its methoxy derivative.

At the same time we have been afforded an opportunity to study the hexa-arylethanes containing naphthyl substituents. The unexpected stability of the chloride of 3-hydroxynaphthyl-2-diphenyl carbinol made it possible also to prepare, for the first time, a free radical which contains a free hydroxyl group, and to study its reactions in aqueous solution.

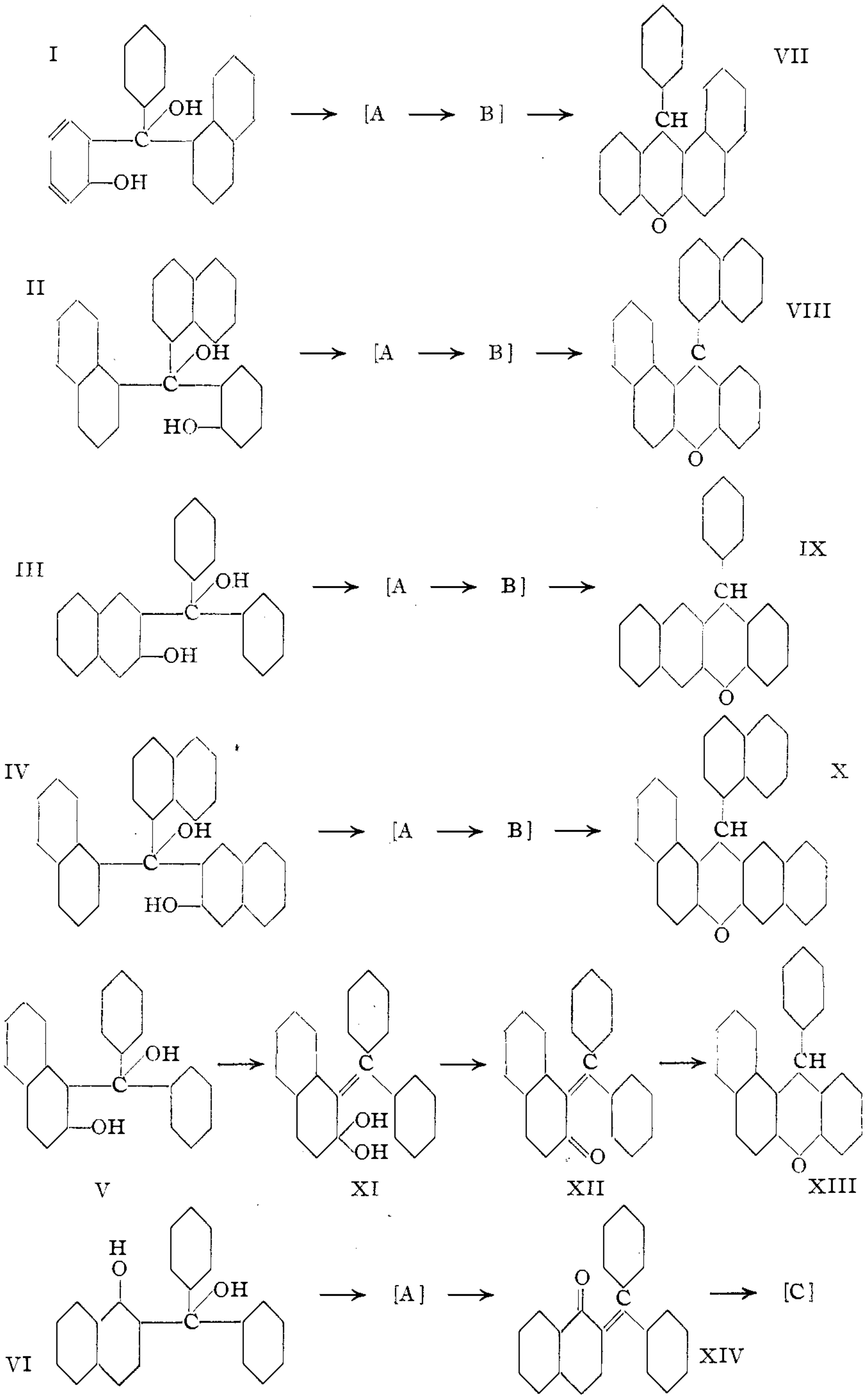
Discussion of Results

In their study of *o*-hydroxy-triphenyl carbinol, already referred to, Gomberg and Nishida observed that at slightly elevated temperatures in acetic acid, benzene or toluene solutions of the colorless carbinol, the colored modification is produced, but the equilibrium is completely reversed when the solution is cooled. As the temperature is increased to 110°, however, dehydration takes place and the fuchsone is formed, but since its stability at the temperature necessary for dehydration is of a low order, there is a rearrangement to form the more stable xanthane.

Quinoidation and subsequent fuchsonation seem, then, to be necessary preliminaries to the formation of xanthanes from *o*-hydroxy-triaryl carbinols, although the quinonoid carbinol and the fuchsone may have but an exceedingly transitory existence. The possibility of isolating any one of the four successive states, benzenoid carbinol, quinonoid carbinol, fuchsone and xanthane, depends entirely upon their relative stabilities.

The substitution of a naphthyl group for one of the oxygen-free phenyl rings gives mono-*o*-hydroxydiphenyl-naphthyl carbinol (I). We have attempted to make this compound by demethylating its methoxy derivative and obtained, not the hydroxy carbinol, but the xanthane VII. We are forced to conclude that the quinonoid form of this carbinol and the fuchsone are even more unstable than their triphenyl analogs, and that the benzenoid-hydroxy carbinol, as soon as it is formed, dehydrates under the influence of the reagents employed and gives the more stable xanthane.

The substitution of two naphthyl groups for the oxygen-free phenyl



A = Quinonoid carbinol B = Fuchsone C = Xanthane nuclei of *o*-hydroxy-triphenyl carbinol gives a still greater effect of this nature, and *o*-hydroxyphenyl-di-α-naphthyl carbinol (II) is therefore unstable. Dehydration takes place even in neutral solvents at slightly elevated temperatures with the formation of the xanthane VIII, and a barely observable color change is the only indication of the formation as intermediate phases of the unstable quinonoid carbinol and the fuchsone. By comparison, it requires one and two-thirds hours' boiling in glacial acetic acid to dehydrate the triphenyl analog.

Carbinols in which the Hydroxy Group is a Substituent of a Naphthyl Nucleus.—There are three possibilities in the substitution of an *o*-hydroxylated naphthyl group for the *o*-hydroxyphenyl group in *o*-hydroxytriphenyl carbinol. The hydroxyl may occupy the 1, 2 or 3 position in the naphthyl ring, corresponding to VI, V and III. Of these, the last obviously resembles the triphenyl analog most closely, since the central carbon atom with its hydroxyl group is farthest removed from any possible influence of the second benzene ring in the naphthalene nucleus.

This assumption of similarity is supported by the behavior of the two compounds. Like its triphenyl analog, 3-hydroxynaphthyl-2-diphenyl carbinol (III) is stable under ordinary conditions; it forms a stable chloride, and it can be converted quantitatively to the xanthane IX by heating for some time at a temperature slightly below its melting point. Neither the quinonoid carbinol nor the fuchsone could be isolated. Unlike the triphenyl analog, its hot solutions in various solvents exhibit only traces of color, so that we have very little direct evidence for the existence of a stable quinonoid form or of the fuchsone, even in solution. It is probable, however, that in this instance we are dealing with a special case complicated by the effects of valence orientation in the naphthalene ring itself, and that the high degree of instability of the quinonoid carbinol and of the fuchsone is a direct consequence of the same structural configuration which hinders the formation of 2,3-naphthoquinones in general.[4]

The effect of naphthyl groups in producing intra-condensation is reflected in the ease with which 3-hydroxynaphthyl-di-α-naphthyl carbinol (IV) forms the xanthane X. Here the xanthane possesses an even greater stability than its mono-naphthyl analog, and the visible evidence for the existence of the intermediate quinonoid carbinol and the fuchsone is still less.

It has been shown[4a] that the 1,2-naphthoquinone represents a stable arrangement of the naphthalene linkages. From 2-hydroxynaphthyl-1-, and 1-hydroxynaphthyl-2-diphenyl carbinols (V and VI), we should expect to obtain reasonably stable quinonoid carbinols as well as the corresponding fuchsones. We have, in fact, succeeded in isolating the benzenoid

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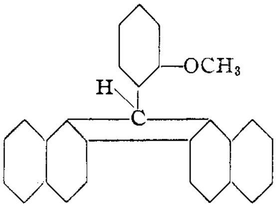
[4] (a) Marckwald, *Ann.*, **274**, 331 (1893); **279**, 1 (1894). (b) Fries. *Ann.*, **389**, 305 (1912).

V and quinonoid XI forms of the 2,1-carbinol, and the fuchsone XII and xanthane XIII. We have proved conclusively the separate existence of all of these modifications by a comparison of their physical, chemical and optical properties. The tautomerizing influence in the case of this carbinol is so marked that merely heating its methoxy and benzyloxy derivatives in acetic acid suffices to split off the methyl and benzyl groups with quantitative formation of the fuchsone.

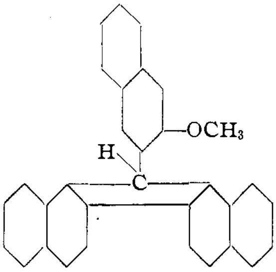
We have also obtained the benzenoid carbinol and the fuchsone XIV of the 1,2-carbinol. Here the fuchsone apparently possesses the greatest stability of the four possible forms and we were unable to make the xanthane.

Fluorenation.—Tautomerization to the ortho-quinonoid form is hindered when a methyl or a benzyl group has replaced the hydroxyl hydrogen. Both the *o*-methoxy and *o*-benzyloxy carbinols are perfectly stable and do not give the quinonoid carbinol, the fuchsone or the xanthane.[1] The methoxy and benzyloxy derivatives of our carbinols I, III and VI are likewise stable compounds. Only the methoxy and benzyloxy derivatives of our most active carbinol, namely, V, show a tendency to split off the methyl or benzyl groups, and to revert to the fuchsone.

When a similar substitution is made in the carbinols II and IV, the resulting methoxy and benzyloxy derivatives can no longer easily form the xanthane, but the inclination toward intramolecular condensation resulting from the presence of two and three naphthyl groups, respectively, is satisfied by the formation of the stable, five-membered fluorene ring. This change, resulting in the formation of *o*-methoxy- or *o*-benzyloxyphenyl-di-α-naphthofluorene (XV), and 3-methoxynaphthyl-2-di-α-napthofluorene (XVI), requires little energy. That the fluorenation occurs as indicated has been proved by synthesizing XV from di-α-naphthofluorenone and *o*-iodo-anisole by means of the Grignard reaction and the subsequent reduction of the fluorenol thus obtained.



XV



XVI

The Carbinol Chlorides and the Corresponding Free Radicals.—A decided relationship exists between the stability of the carbinols themselves and that of the corresponding carbinol chlorides and the free radicals. Where the carbinol does not readily undergo tautomeric change, stable chlorides can ordinarily be obtained, and possibly stable free radicals. Thus, from the stable carbinol III and its methoxy and benzyloxy derivatives, and from the methoxy derivative of the carbinol I we have made chlorides of reasonable stability, and from these the corresponding free radicals. On the other hand, the existence of tautomeric forms of the carbinol, particularly when the quinonoid form and the fuchsone are fairly stable, presages an even greater tendency toward tautomerization on the part of the carbinol chlorides. This condition is exemplified by the carbinols V and VI which form the corresponding fuchsones so readily that the carbinol chlorides exist only momentarily in solution, presumably in the quinonoid form.

We succeeded in crystallizing two of the free radicals referred to, 3-methoxynaphthyl-2-diphenyl-methyl and 3-benzyloxynaphthyl-2-diphenyl-methyl. Molecular-weight determinations showed that the solid hexa-arylethanes almost completely dissociate to the free radicals at the freezing points of *p*-dichlorobenzene and naphthalene, the solvents employed. Previous observations on the effect of naphthyl groups as hexa-arylethane substituents are thus confirmed.[5] We were unable to obtain 3-hydroxy-naphthyl-2-diphenyl-methyl or mono-*o*-methoxy-diphenyl-α-naphthyl-methyl in solid form but indirect molecular-weight determinations showed dissociations ranging from 85 to 90% and of more than 100%, respectively. Whether the figures above 100% indicate merely decomposition, or actually "ultra-dissociation" must remain undecided.[6]

The stability of 3-hydroxynaphthyl-2-diphenyl-methyl in solution has afforded for the first time an opportunity to test the possibility of obtaining such a free radical, in virtue of its phenolic hydroxyl, in aqueous solution as the sodium salt. The actual product obtained with sodium hydroxide solution is not the sodium salt of the free radical, however, but a mixture of the methane and the carbinol, so that the reaction must proceed according to the following formulation: $2\ C_{10}H_6OH.(C_6H_5)_2 = C + H_2O = C_{11}H_6OH.$-$(C_6H_5)_2 = C.OH + C_{10}H_6OH(C.H.)_2CH$. This reaction is not unlike that which takes place in anhydrous solutions between hydrogen chloride and many free radicals, $2\ (Ar)_3C + HCl \longrightarrow (Ar)_3CCl + (Ar)_3CH$.

Experimental Part

4-Methoxy-1-hydroxy-triphenyl Carbinol.—The carbinol was made by the method previously used by Gomberg and Johnson.[3b] Glacial acetic acid solutions of the carbinol become light reddish-brown when warmed to 100–110° and the color disappears when the solution is cooled. Even in solutions heated at 120° for some minutes, the color is completely removed by cooling. Benzene and toluene solutions of the carbinol, heated

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[5] (a) Gomberg and Schoepfle, THIS JOURNAL, **39**, 1652 (1917). (b) Gomberg and Sullivan, *ibid.*, **44**, 1829 (1922).

[6] P. Walden, "Chemie der freien Radikale," S. Hirzel, **1924**, p. 286.

at their respective boiling points, exhibit the same color change, reversible on cooling. A sample of the colorless carbinol after boiling with 70% acetic acid for 15 minutes precipitated as orange-yellow crystals of the quinonoid carbinol when the solution was cooled. The solid carbinol, heated at 140° for one hour, fused to a red mass which gave, when recrystallized from glacial acetic acid, the corresponding fuchsone, m. p. 156°, which is also the melting point of the original carbinol as well as of the quinonoid carbinol. The assumption seems justified that both the colored and the colorless forms of the carbinol are transformed by heat into the fuchsone, and it is this latter which melts at 156°. A comparison of the rates of dehydration of the two carbinols shows a notable difference in the two.

TABLE I

COMPARATIVE RATE OF DEHYDRATION OF THE CARBINOLS

Temp. °C.	Time, min.	Loss in % Colored	Loss in % Colorless
100	45	56.1	34.2
	60	74.8	55.7
	90	91.2	76.4
	120	101.6	94.3

Mono-*o*-methoxydiphenyl-α-naphthyl Carbinol

The Carbinol.—Forty g. of phenyl-α-naphthyl ketone[7] was slowly added in ether solution to the Grignard reagent prepared from 47 g. of *o*-iodo-anisole and 4.5 g. of magnesium turnings. The reaction was moderate and the precipitate which formed redissolved when heated for one-half hour after the ketone had been added. The mixture was decomposed with ice and acetic acid and was steam-distilled. The carbinol solidified in the distillation flask. It was filtered off, dried, and recrystallized from benzene; yield, 85%; m. p., 156°. The carbinol is soluble in warm benzene and carbon disulfide, and slightly soluble in chloroform, alcohol, ether and acetone. When it is boiled with acetic acid, only a slight color is produced; this does not disappear as the solution cools, and the carbinol can be recovered unchanged. With sulfuric acid the carbinol gives a deep blue color.

Mono-*o*-methoxydiphenyl-α-naphthyl-methane, obtained from the carbinol by reduction with zinc dust and acetic acid, crystallized from acetone in colorless needles; m. p., 134°.

Mono-*o*-methoxydiphenyl-α-naphthyl-chloromethane.—This was made from the carbinol, in benzene, by means of dry hydrogen chloride in the presence of calcium chloride. The chloride crystallized when the solution was concentrated under reduced pressure. It was purified by recrystallizing from petroleum ether, and the pure chloride melted at 142°.

Anal. Calcd. for $C_{24}H_{19}OCl$: Cl, 9.88. Found: 9.72.

Mono-*o*-methoxydiphenyl-α-naphthyl-methyl.—The carbinol chloride, shaken with molecular silver in benzene, gives a deep, reddish-brown solution of the free radical. Attempts were made to recrystallize the free radical obtained by evaporating this solution, from acetone, ether, petroleum ether and carbon disulfide, but in every case only a red, gummy residue resulted which absorbed various amounts of oxygen. Oxygen-absorption determinations made on solutions of the free radical obtained from the

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[7] Montagne, *Rec. trav. chim.*, **26**, 280 (1907).

carbinol chloride and silver showed that more than the calculated amount of oxygen was absorbed. In one instance the absorption was 137% and in another it was 120% of the calculated volume.

Although we failed to isolate the solid hexa-arylethane, we have determined its degree of dissociation, using an indirect cryoscopic method.[8]

TABLE II

MOLECULAR-WEIGHT DETERMINATIONS ON DIMETHOXY-TETRAPHENYL-DINAPHTHYL-ETHANE

Solvent G.	Halide G.	Calcd. concn. of hexa-aryl	ΔT °C.	ΔT, with Ag °C.	Dissocn. in %
1. Solvent, benzene; f. p., 4.9°. $K = 53$					
20.32	0.3317	1.44	0.241	0.261	108
20.61	.6714	2.85	.481	.505	105
20.17	.9527	4.08	.698	.725	104
2. Solvent, *p*-dichlorobenzene; f. p., 53°. $K = 82$					
21.02	.3453	1.45	.375	.408	109
20.71	.6871	2.90	.758	.818	108
20.52	.9716	4.09	1.082	1.179	109

Mono-*o*-methoxydiphenyl-α-naphthyl Peroxide.—The peroxide was obtained by shaking the solution of the carbinol chloride in benzene with molecular silver, filtering off the silver and bubbling oxygen through the solution until the latter was decolorized; evaporation of the solvent left a resinous mass which became solid after repeated washing with warm petroleum ether, and which melted at 111° after recrystallization from chloroform and petroleum ether.

Anal. Calcd. for $C_{48}H_{38}O_4$: C, 84.91; H, 5.64. Found: C, 85.02; H, 5.77.

Attempts to make mono-*o*-hydroxydiphenyl-α-naphthyl carbinol by demethylation of the methoxy carbinol, either with aluminum chloride and antimony chloride, or with hydrobromic acid of various strengths (30 to 48%), failed. The substance obtained by either method was phenyl-pheno-α-naphtho-xanthane (VII).

o-Hydroxyphenyl-di-α-naphthyl Carbinol (II)

The carbinol was prepared by Kaufmann and Egner's method,[9] substituting the ether in the Grignard reaction by benzene; yield, 85%. The carbinol was recrystallized from acetone, using as little heat as possible; m. p., 142°. It loses water very easily and forms the xanthane. Dehydration is produced by dilute acids, or partially even by recrystallizations from neutral solvents such as alcohol, benzene or acetone. Heating the solid at 120° for one hour converts the carbinol completely to the xanthane, which has been described by Kaufmann and Egner.

***o*-Methoxyphenyl-di-α-naphthyl-fluorene (XV).**—Five g. of the methoxylated carbinol,[9] boiled with 15 cc. of glacial acetic acid, gave a green solution which quickly changed to a red and which upon cooling deposited colorless, leaf-like crystals of the fluorene; m. p., 318°. The same fluorene is obtained when the carbinol in benzene or chloroform is treated with hydrogen chloride or with a few drops of acetyl chloride. The identity of this compound was proved by comparing it with a sample of the fluorene obtained by reduction with zinc dust of the fluorenol which had been synthesized from *o*-iodo-anisole and di-α-naphthofluorenone.[10]

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[8] Gomberg and Cone, *Ber.*, **37**, 2037 (1904).

[9] Kaufmann and Egner, *Ber.*, **46**, 3785 (1913).

[10] Schmidlin and Huber, *Ber.*, **43**, 2833 (1910).

o-Benzyloxyphenyl-di-α-naphthyl Carbinol.—This carbinol was made from o-hydroxyphenyl-di-α-naphthyl carbinol in acetone solution with sodium hydroxide and benzyl chloride. It melts at 149–150°. The colorless crystals are soluble in chloroform and in acetone; they are less soluble in ether and alcohol.

o-Benzyloxyphenyl-di-α-naphthyl-fluorene.—Five g. of the carbinol boiled with glacial acetic acid gave a green solution which slowly changed to red and from which, as it cooled, crystals of the fluorene precipitated. These melt at 210° and are soluble in chloroform and in acetone.

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.03; H, 5.39. Found: C, 91.18; H, 5.45.

Attempts to make the carbinol chloride with hydrogen chloride or with acetyl chloride resulted only in the production of the fluorene.

3-Hydroxynaphthyl-2-diphenyl Carbinol (III)

Cold glacial acetic acid solutions of the carbinol[9] become colored a light brown after long standing and this change is produced immediately in such solutions by boiling. Upon continued boiling the acid solution becomes slowly decolorized, and there is formed phenyl-pheno-β-naphtho-xanthane, the same compound that was obtained by Kaufmann and Egner by heating the dry carbinol at 165°. Benzene, toluene and xylene solutions of the carbinol remain colorless at ordinary temperatures and exhibit traces of color when the solutions are heated to their respective boiling points. The color produced in all of these solvents is not destroyed when the solutions are cooled to 0°.

3-Hydroxynaphthyl-2-diphenyl-methyl.—The chloromethane[11] shaken in dry benzene with molecular silver gave a deep brown solution which decolorized upon exposure to air. Oxygen-absorption determinations upon such solutions showed that the calculated amount of free radical was formed after two hours' shaking with molecular silver. The decomposition of the free radical sets in very quickly, so that after eight hours' shaking, only two-thirds of the substance is left undecomposed, and after 12 hours only one-third.

Although the free radical was thus shown to be stable for a short time in solution, efforts to isolate it according to the usual procedure failed. In every case the yellow solid obtained did not absorb oxygen. We have used benzene, ether, carbon disulfide and absolute alcohol as solvents for the preparation of the free radical in solution, and we have endeavored to recrystallize the solid hexa-arylethane from all of these as well as from acetone, but with no better results. Examination of the product resulting from the spontaneous decomposition of the free radical revealed that it contained two sub-

TABLE III

MOLECULAR-WEIGHT DETERMINATIONS ON DIHYDROXY-DINAPHTHYL-TETRAPHENYL-ETHANE

1. Solvent, benzene; f. p., 4.9°. K = 53

Solvent G.	Halide G.	Calcd. concn. of hexa-aryl compd.	ΔT °C.	ΔT with Ag °C.	Dissocn. in %
20.01	0.3401	1.50	0.261	0.244	87.6
20.12	.6941	3.00	.530	.493	86.2
20.36	1.0012	4.22	.756	.698	84.8
2. Solvent, p-dichlorobenzene; f. p., 53°. K = 82					
20.42	0.3516	1.52	.409	.388	90.2
20.06	.7027	3.04	.833	.783	88.1
20.61	1.1001	4.10	1.270	1.179	85.7

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[11] Lammer, *Monatsh.*, **35**, 177 (1914).

stances, namely, 3-hydroxynaphthyl-2-diphenyl-methane, m. p. 125°, and the xanthane just described and melting at 171°. The auto-oxidation of the free radical can thus be formulated as follows: $2\ (C_6H_5)_2.C.C_{10}H_6.OH \longrightarrow (C_6H_5)_2.CH.C_{10}H_6.OH + C_6H_5\text{-}\overline{CHC_6H_4.O.C}{}_{10}H_6$.

The approximate degree of dissociation of the hexa-arylethane was determined by the freezing-point method, indirectly.

3-Hydroxynaphthyl-2-diphenyl-methyl Peroxide.—Two g. of the chloromethane, shaken in benzene with molecular silver in the presence of air, gave 1.6 g. of the peroxide. The compound is soluble in chloroform, carbon tetrachloride and alcoholic sodium hydroxide. Recrystallized from chloroform, it melted at 145°.

Anal. Calcd. for $C_{46}H_{34}O_4$: C, 84.88; H, 5.27. Found: C, 84.61; H, 5.39.

3-Methoxynaphthyl-2-diphenyl Carbinol

The carbinol was methylated in dil. acetone with methyl sulfate and potassium hydroxide. By concentrating the acetone, a quantitative yield of the methoxy carbinol was obtained; m. p., 175–176°.

3-Methoxynaphthyl-2-diphenyl-chloromethane.—The chloride was prepared from the carbinol by our usual procedure, with hydrogen chloride and calcium chloride in benzene solution. After recrystallization from petroleum ether it melts at 129–130°.

Anal. Calcd. for $C_{24}H_{19}OCl$: Cl, 9.88. Found: 9.75.

When reduced with zinc dust in a glacial acetic acid solution, the carbinol gives the methane; m. p., 179–180°.

3-Methoxynaphthyl-2-diphenyl-methyl.—The free radical was prepared from the chloride, with molecular silver in benzene solution. The yellow solid obtained upon evaporation of the benzene in an atmosphere of carbon dioxide was recrystallized from acetone.

Solutions of the free radical absorb nearly the calculated amounts of oxygen; 95, 97 and 95% of the calculated results were obtained in three experiments.

Solutions of the free radical absorb less than the calculated amounts of iodine. Equilibrium is reached when about 68–70% of the iodide is formed. The presence of the iodide in solutions which had been titrated with iodine was shown by the formation of the anilide and its isolation. It proved identical with that made from the chloride and aniline.

Because of the slight solubility at ordinary temperatures, molecular-weight determinations of the radical were carried out in naphthalene and *p*-dichlorobenzene as solvents.

TABLE IV

MOLECULAR WEIGHTS OF DIMETHOXY-DINAPHTHYL-TETRAPHENYLETHANE

Solvent G.	Solute G.	Concn. in %	ΔT °C.	Mol. wt. °C.	Dissocn. in %
	1. Solvent, *p*-dichlorobenzene; f. p., 53°. $K = 82$				
21.76	0.2250	1.02	0.286	339.0	90.6
	.5128	2.30	.565	341.8	89.0
	.7874	3.49	.872	340.1	90.0
	1.1654	5.08	1.256	349.5	84.9
	2. Solvent, naphthalene; f. p., 80°. $K = 70.5$				
21.84	0.2316	1.04	0.228	327.0	97.6
	.4712	2.09	.463	327.3	97.4
	.79166	3.49	.771	330.5	95.5
	1.1234	4.89	1.089	332.1	94.6

The molecular weight of the monomolecular form is 323.

3-Methoxynaphthyl-2-diphenyl-methyl Peroxide.—One g. of the carbinol chloride shaken with molecular silver in benzene gave 0.7 g. of the peroxide upon oxidation, a yield of 75%. The substance is soluble in chloroform, carbon tetrachloride and acetone; it is insoluble in benzene or ether; m. p., 169–170°.

Anal. Calcd. for $C_{48}H_{38}O_4$: C, 84.91; H, 5.64. Found: C, 84.95; H, 5.68.

3-Benzyloxynaphthyl-2-diphenyl Carbinol

The carbinol was made from the hydroxy carbinol in dil. acetone with benzyl chloride and potassium hydroxide. After recrystallization from acetone it melted at 165°. It is soluble in ether, benzene, chloroform and acetone, and less so in alcohol.

Anal. Calcd. for $C_{30}H_{24}O_2$: C, 86.49; H, 5.81. Found: C, 86.55; H, 5.76.

When reduced with zinc dust in acetic acid it gives the methane; m. p., 141°.

3-Benzyloxynaphthyl-2-diphenyl-chloromethane.—The chloride was made in the usual way, in ether solution with dry hydrogen chloride and calcium chloride; m. p., 115°. Heating it in xylene for ten hours at 100° expelled only 8–10% of the chlorine as hydrogen chloride. Samples that stood in a desiccator for some days, however, acquired a perceptible odor of benzaldehyde.

Anal. Calcd. for $C_{30}H_{23}OCl$: Cl, 8.15. Found: 8.01.

3-Benzyloxynaphthyl-2-diphenyl-methyl.—The solid hexa-arylethane was obtained in exactly the manner described for the methoxy-hexa-arylethane. The benzyloxy compound is likewise soluble only in warm solvents and is stable in dry air for short periods. Its solution in benzene is deep red and in high dilutions, yellow. Such solutions absorb the calculated amounts of oxygen, the reaction being almost instantaneous.

The molecular weight of the hexa-arylethane was determined in naphthalene and in *p*-dichlorobenzene.

TABLE V

MOLECULAR WEIGHT OF DI-BENZYLOXYNAPHTHYL-TETRAPHENYLETHANE

1. Solvent, *p*-dichlorobenzene; m. p., 53°. $K = 82$

Solvent G.	Solute G.	Concn.	ΔT	Mol. wt.	Dissocn. in %
23.17	0.2619	1.11	0.228	405.2	97.0
	.5341	2.25	.455	412.1	93.7
	.8116	3.38	.687	415.6	92.0
	1.2001	4.92	1.020	414.2	92.7

2. Solvent, naphthalene; f. p., 80°. $K = 70.5$

Solvent G.	Solute G.	Concn.	ΔT	Mol. wt.	Dissocn. in %
22.81	0.2812	1.21	0.218	398.2	100.5
	.5546	2.37	.432	396.1	101.5
	.8362	3.53	.644	401.2	98.9
	1.1182	4.68	.857	403.1	98.0

The molecular weight of the monomolecular form is 399.

α-Naphthyl-α-naphtho-β-naphthoxanthane (X).—The carbinol,[9] heated on the steam-bath in acetone solution for two hours, gave colorless crystals of the xanthane. These turn brown at 250° and melt at 262°. They are insoluble in sodium hydroxide solution, and are soluble with difficulty in the usual solvents. The xanthane is also formed when solutions of the carbinol are heated in acetic acid, chloroform or benzene.

Anal. Calcd. for $C_{31}H_{20}O$: C, 91.14; H, 4.93. Found: C, 91.29; H, 5.04.

Because of the instability of the carbinol, even in inert solvents, the carbinol chloride could not be prepared.

3-Methoxynaphthyl-2-di-α-naphthyl Carbinol.—This was prepared from the hydroxy carbinol by means of methyl sulfate and alkali in acetone. After recrystallization from a mixture of chloroform and absolute alcohol, it melted at 252°. The carbinol is soluble in chloroform and carbon tetrachloride, slightly soluble in acetone and practically insoluble in alcohol. With sulfuric acid it gives deep blue solutions.

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.46; H, 5.49. Found: C, 87.61; H, 5.61.

3-Methoxynaphthyl-2-di-α-naphthofluorene (XVI).—A sample of the solid carbinol was heated in acetic acid at the boiling point for 30 minutes. The fluorene separated in light, crystalline masses as the solution cooled; m. p., 241–242°. The crystals gave no color with sulfuric acid. The fluorene is soluble in chloroform and carbon tetrachloride.

Anal. Calcd. for $C_{32}H_{22}O$: C, 90.95; H, 5.25. Found: C, 91.07; H, 5.37.

The lability of the methoxy compound made it impossible to prepare the methoxycarbinol chloride, in spite of all precautions. Acetyl chloride in chloroform, at 0°, converted the carbinol into the fluorene. We could not verify the statement of Lammer that the carbinol chloride is formed from the carbinol with acetyl chloride in moist phosphorus oxychloride as the solvent. By this method we obtained only the fluorene as was to be expected.

2-Hydroxynaphthyl-1-diphenyl Carbinol (V)

The carbinol was prepared by us from the methyl ester of 2,1-oxynaphthoic acid and phenylmagnesium bromide in preference to the method previously recorded.[12] The reaction proceeded gently and after the mixture had been heated for three to four hours on the steam-bath, a yellow precipitate appeared in the green solution. The mixture was decomposed with ice and ammonium chloride, the ether layer washed with water, dried over calcium chloride and the ether evaporated under reduced pressure, the yellow mass remaining crystallized when treated with warm petroleum ether. Several recrystallizations from alcohol to which a few drops of ammonium hydroxide had been added gave colorless crystals of the carbinol. These turned red at 120° and melted at 195–198°.

Tautomerization of the Carbinol and the Quinonoid Carbinol (XI).—Solutions of the carbinol in acetic acid of various concentrations, ranging from 50% to glacial, become red upon heating to the boiling point, and when cooled deposit red crystals of *o*-naphthofuchsone; m. p., 198°. With hydrochloric acid, the change to fuchsone is very rapid. Experiments were carried out to determine whether the color change in glacial acetic acid were reversible upon cooling. It was found that in a 1% solution in glacial acetic acid, the color appeared at 40° and disappeared at the same temperature when the solution was cooled, but after the solution had been heated past this equilibrium temperature several times with alternate cooling below it, the color change was no longer completely reversible. When the alternate increases and decreases of temperature were repeated 30 or 40 times the color finally became a permanent red, with no noticeable decrease upon cooling.

When samples of the colorless carbinol were recrystallized from alcohol which contained a few drops of acetic acid, the resultant crystals were of a reddish-orange color, m. p. 140–145°, depending upon the rate of heating. Heated at 140–150° for a few minutes the crystals gave off water and fused to a reddish mass which solidified and then melted again at 195°, indicating that the fuchsone had been formed. Dry samples of the colored and of the colorless carbinols were heated for various periods of time at temperatures between 50° and 100°. The water driven off was carried by a current of dry air into a weighed calcium-chloride tube and thus determined.

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[12] Gomberg and Sullivan, THIS JOURNAL, **41**, 1869 (1920).

TABLE VI

DEHYDRATION OF THE BENZENOID AND QUINONOID CARBINOLS

Time heated, hrs.	Temp. °C.	Loss, % Benzenoid	Loss, % Quinonoid	Temp. °C.	Loss, % Benzenoid	Loss, % Quinonoid
2	50	2.2	2.3	70	4.8	9.4
6		6.0	9.4		17.3	24.7
12		14.3	22.6		62.1	79.5
24		21.3	38.4		89.4	102.4
2	60	2.1	2.6	80	27.4	41.6
6		8.9	12.4		43.1	79.8
12		29.2	29.8		75.1	101.2
24		63.1	77.2		104.2	103.0

***o*-Naphthofuchsone.**—This was obtained in practically quantitative yield by boiling a concentrated solution of the carbinol in glacial acetic acid for a few minutes. As the solution cooled, shining red needles of the fuchsone precipitated. These are soluble in chloroform, alcohol, benzene and ether; m. p., 198°.

Optical Constants of the Benzenoid and Quinonoid Carbinols.—In order to establish further the radical differences exhibited by the colored and the colorless forms of the carbinol in both their chemical and physical properties, the crystal forms and optical properties of the two have been determined, and also those of the fuchsone.[13]

TABLE VII

OPTICAL CONSTANTS OF THE BENZENOID AND QUINONOID CARBINOLS AND OF THE FUCHSONE

	Benzenoid carbinol	Quinonoid carbinol	Fuchsone
Color	Colorless	Orange	Red
Crystal form	Lath-shaped, occasionally terminated (Dome angle 126°)	Lath-shaped, singly or doubly terminated (Dome angle, 64°)	Acicular, elongated; cross-section rhombic. (Dome angle, 74°; angles between prism planes, 70° and 110°)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic or monoclinic
Extinction	Parallel	Sometimes parallel, sometimes inclined. Max. angle, 33°	Parallel for needles; symmetrical in cross section
n_D	1.685±.005	1.662±.003	1.634
	1.740±.005	1.728±.003	>1.77
	1.758±.005	1.750±.003[a]	>1.77 about 1.85
Bi-refringence	0.07	0.09	About 0.2
Optical character	Biaxial, negative from indices	Biaxial, negative	Biaxial, negative from indices

[a] Index parallel to elongation on needles with parallel extinction is 1.696 ± 0.03.

Phenyl-pheno-α-naphthoxanthane (XIII).—A sample of the solid carbinol gave a colorless solution after prolonged boiling with acetic acid. After filtering and cooling the solution, colorless crystals of the xanthane precipitated; m. p., 172–173°.

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[13] We are indebted to Professor E. H. Kraus and Mr. E. F. Holden of the Department of Mineralogy, University of Michigan, for the data given in Table VII.

Anal. Calcd. for $C_{23}H_{16}O$: C, 89.57; H, 5.23. Found: C, 89.40; H, 5.35.

2-Methoxynaphthyl-1-diphenyl Carbinol.—It was prepared from the hydroxy carbinol by methylating the latter with methyl sulfate in acetone. The carbinol melts at 148–150°, and is soluble in chloroform, acetone and benzene, but only slightly soluble in alcohol or ether.

Solutions of the carbinol in glacial acetic acid become green when heated and the color disappears as the solution cools. After six or seven of such alternate changes in temperature, a yellow tint appears, which persists in both hot and cold solutions. This gradually deepens to a pronounced red, the green color slowly becoming less prominent. Further heating increases the intensity of the red color, and when the red solution is concentrated and cooled, red crystals of *o*-naphthofuchsone separate. Evidently the methyl group is removed from the methoxy side chain, presumably as methyl alcohol.

Attempts to make 2-methoxynaphthyl-1-diphenyl-chloromethane from the carbinol, either by means of dry hydrogen chloride or by the action of acetyl chloride, resulted in failure. In either case *o*-naphthofuchsone was produced. Evidently methyl chloride was split off.

2-Benzyloxynaphthyl-1-diphenyl Carbinol.—This compound was obtained in a yield of about 95%; m. p., 142°. The carbinol is soluble in acetone, benzene and chloroform; it is less soluble in ether and alcohol. When heated with acetic acid or with acetyl chloride it suffers a change similar to that of the methoxy carbinol—the benzyl group is split off and *o*-naphthofuchsone is formed.

1-Hydroxynaphthyl-2-diphenyl Carbinol (VI).—The red color produced by warming a trace of the carbinol to 50–60°[9] in 50% acetic acid does not disappear when the solution is cooled. All attempts to obtain a colored form of the carbinol resulted in the production of the fuchsone, which can be changed back to the colorless carbinol with difficulty. Employing our usual method of dissolving the fuchsone in alcoholic alkali and precipitating with ammonium chloride, it required two days' shaking with the alkali to decolorize the original red solution completely.

Summary

1. Tautomerization to an *o*-quinonoid form of the carbinol has been shown to be a general phenomenon in the class of the *o*-hydroxy-triaryl carbinols. Such tautomerization appears to be a necessary preliminary stage in the intramolecular-condensation which occurs in the carbinols when the latter form the corresponding xanthanes, which are formed by nearly all of them.

2. Of the six *o*-hydroxy-triaryl carbinols investigated, in one case, that of the 3-hydroxynaphthyl-2-diphenyl carbinol, all of the intermediate products between the carbinol and the xanthane have been isolated.

3. Two triaryl-methyls hitherto unknown, the 3-methoxynaphthyl-2-diphenyl-methyl and the corresponding benzyloxy compound, have been isolated in the solid form as the hexa-arylethanes. Two others, the mono-*o*-methoxydiphenyl-α-naphthyl-methyl and the 3-hydroxynaphthyl-2-diphenyl-methyl have been prepared in solution. All four have been found to exist almost wholly in the monomolecular state.

4. 3-Hydroxynaphthyl-2-diphenyl-methyl is the first instance of a triaryl-methyl containing a free hydroxy group.

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