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

Quinoidation of Triaryl Compounds—Hydroxynaphthyldiphenylcarbinols

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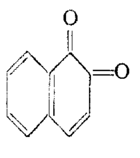
In this investigation, studies have been made of compounds which are capable of exhibiting the 1,5-, 2,6- and 1,7-naphthoquinonoid structures. Of the six theoretically possible naphthoquinones which are shown below, only two, the 1,2- and 1,4-naphthoquinones are well known.



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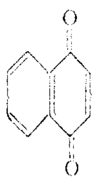

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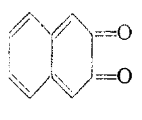

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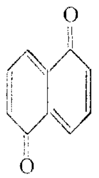

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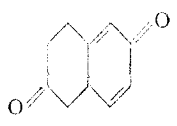

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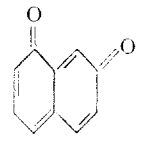

1,7- (2,8-)

A third, 2,6-naphthoquinone, was obtained in 1907 by Willstätter and Parnas[2] by the oxidation of 2,6-dihydroxynaphthalene in hot anhydrous benzene with excess lead peroxide and found to be unstable, particularly in solution. In a similar manner they prepared the more stable derivative, 1,5-dichloro-2,6-naphthoquinone which was also red-yellow and melted sharply at 206.5° with swelling and darkening. Evidence has been presented that the colored form of 3,11-dihydroxynaphthofluoran has the 2,6-naphthoquinone structure.[3]

Although the simple unsubstituted 2,3-naphthoquinone is unknown, Fries and Empson[4] in 1909 prepared a derivative, 6-bromo-4-chloro-1-methyl-2,3-naphthoquinone. Theoretical speculations drawn from a study of critical oxidation potentials of phenols led Fieser[5] to conclude that the 1,5-naphthoquinone was formed in solution, however brief its existence. In the same manner, evidence was obtained for the formation of 2,6-naphthoquinone, but none was found for that of 2,3-naphthoquinone. In 1921 Morgan and Vining[6] oxidized 1,7-dihydroxynaphthalene by a modification of the procedure of Willstätter and Parnas and obtained, not the expected quinone, but a compound stated to be dinaphtho-1,7,1′,7′-diquinone. Studies of the various quinones mentioned appear to have been complicated by the fact that the compounds are generally unstable and susceptible to oxidation, polymerization and decomposition.

Three naphthofuchsones which have been described in the literature[7] are colored crystalline compounds like the naphthoquinones which they closely resemble in structure and color. Two of the naphthofuchsones are derivatives of 1,2-naphthoquinone while the third is a derivative of 1,4-naphthoquinone. Each may be prepared conveniently by dehydration of the corresponding hydroxynaphthyldiphenylcarbinol on heating near or above its melting point.

Gomberg and co-workers studied four hydroxynaphthyldiphenylcarbinols having the hydroxyl and carbinol groups on the same ring of the naphthalene nucleus, and also studied the effect of the naphthalene nucleus on the stability of the three forms, benzenoidcarbinol, quinonoidcarbinol and fuchsone which is produced when water is eliminated from the quinonoid carbinol. In the case of 1-(2-hydroxynaphthyl)-diphenylcarbinol, both benzenoid and quinonoid forms were isolated along with the fuchsone and the xanthane, which may be postulated as a rearrangement product of the fuchsone. 2-(1-Hydroxynaphthyl)-diphenylcarbinol gave only the benzenoidcarbinol and the naphthofuchsone. 1-(4-Hydroxynaphthyl)-diphenylcarbinol existed only in the quinonoid form which is readily dehydrated to the naphthofuchsone. 2-(3-Hydroxynaphthyl)-diphenylcarbinol was isolated only in the benzenoid form and attempts to obtain the quinonoid carbinol and fuchsone gave only the xanthane.

The hydroxynaphthylcarbinols which have been prepared hitherto had the hydroxyl and carbinol groups on the same ring. This paper

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(1) The material presented in this paper constitutes a portion of a dissertation submitted by Donald G. Thomas to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, August, 1939.

(2) Willstätter and Parnas, *Ber.*, **40**, 1406, 3971 (1907).

(3) Fischer and König, *ibid.*, **47**, 1076 (1914).

(4) Fries and Empson, *ibid.*, **42**, 3375 (1909).

(5) Fieser, THIS JOURNAL, **52**, 5218 (1930).

(6) Morgan and Vining, *J. Chem. Soc.*, **119**, 1707 (1921).

(7) (a) Gomberg and McGill, THIS JOURNAL, **47**, 2392 (1925); (b) Gomberg and Sullivan, *ibid.*, **42**, 1864 (1920).

deals with hydroxynaphthylcarbinols which have the carbinol and hydroxyl groups in different rings of the naphthalene nucleus. Five new hydroxynaphthyldiphenylcarbinols have been synthesized: 2-(6-hydroxynaphthyl)-diphenylcarbinol, 2-(8-hydroxynaphthyl)-diphenylcarbinol, 1-(5-hydroxynaphthyl)-diphenylcarbinol, 1-(7-hydroxynaphthyl)-diphenylcarbinol and 1-(6-hydroxynaphthyl)-diphenylcarbinol. For brevity in this paper, the carbinols will be referred to as 2,6-, 2,8-, 1,5-, 1,7- and 1,6-carbinol, respectively. Theoretically, the first four of these carbinols should be capable of conversion to naphthofuchsones which would be derivatives of the unknown or but little known transnuclear naphthoquinones. The fifth, or 1,6-carbinol, cannot assume a quinonoid structure involving both the carbinol and hydroxyl groups. The properties of the five carbinols were compared with those of unsubstituted α- and β-naphthyldiphenylcarbinols as well as with hydroxynaphthyldiphenylcarbinols which are known to yield quinonoid fuchsones.

The carbinols studied in this investigation exhibit an interesting behavior on heating. The 1,6-carbinol, which cannot form a quinonoid structure, melts to a faint brownish colored liquid which then rapidly darkens although the unsubstituted α- and β-naphthyldiphenylcarbinols melt to colorless liquids; in fact, the α-carbinol was evaporatively distilled in a vacuum up to 225° without change. Three of the four carbinols, however, which theoretically can form a quinonoid structure, melt to colored liquids, dark red-purple in the case of the 2,6-carbinol; dark red in the 1,5-carbinol; and orange-red in the 1,7-carbinol. Furthermore, the color develops in these carbinols several degrees below their respective melting points. The behavior is similar to that observed in the case of 1-(2-hydroxynaphthyl)-diphenylcarbinol and 2-(1-hydroxynaphthyl)-diphenylcarbinol, both of which readily yield fuchsones. The 2,8-carbinol melts to a light yellowish-brown liquid which only develops a dark green-brown color above its melting point. This formation of color, a phenomenon concomitant with the quinonoid structure may possibly be regarded as indication of some tendency of these carbinols to assume a quinonoid structure.

The 2,6- and 1,5-carbinols were heated in a vacuum of 0.4 and 0.6 mm. at temperatures from 165 to 190°. The carbinols first darken and then melt to purple masses. No colored crystalline product, however, could be isolated from either of these melted materials. The action of sulfuric or phosphoric acids on the carbinols yielded for the most part only dark, amorphous products possessing high and very indefinite melting points.

The failure to isolate a naphthofuchsone may be due to the instability of these compounds under the conditions employed. Fluorenation may account, also, for the side reactions encountered in this work. Gomberg and McGill[7a] found that certain *o*-methoxylated carbinols containing two or three naphthyl groups fluorenated merely by boiling an acetic acid solution of the carbinol for a few minutes. Ullmann and Mourawiew-Winigradoff,[8] and Tschitschibabin and Magidson[9] had previously shown that mineral acids readily caused formation of fluorenes.

The behavior of acetic acid solutions of the carbinols concerned in this investigation was studied. The 1,6-carbinol and α- and β-naphthyldiphenylcarbinols produced no color on boiling in acetic acid until after several minutes when a slight yellow discoloration appeared. The 1,6-carbinol seems to show even less color than the other two. The 2,6-carbinol when heated in acetic acid quickly develops a purple color, most intense at the boiling point, which disappears on cooling. This behavior is similar to that of 1-(2-hydroxynaphthyl)-diphenylcarbinol which was studied by Gomberg and McGill. On boiling solutions of the 1,7- and 2,8-carbinols for a few minutes both develop a faint green-yellow color which almost entirely disappears when the solution is cooled. The 1,5-carbinol develops a faint pink color which deepens to a rose when boiled for a few minutes. On cooling, the color is permanent and is very similar to that which develops when a solution of this carbinol in acetic acid containing 6% sulfuric acid is allowed to stand.

The carbinols mentioned above and three naphthofuchsones were dissolved in a 6% acetic acid solution of sulfuric acid with the formation of salts whose colors varied in their degree of stability. Unpublished work in this Laboratory has shown that the absorption spectra of sulfuric acid solutions of a quinonoid carbinol, for example *p*-hydroxytriphenylcarbinol, and of sulfuric acid solutions of its fuchsone are identical; the product

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[8] Ullmann and Mourawiew-Winigradoff, *Ber.*, **38**, 2215 (1905).

[9] Tschitschibabin and Magidson, *J. prakt. Chem.*, **90**, 168 (1914); Magidson, *Ber.*, **58B**, 433 (1925).

is a sulfuric acid salt of the triarylcarbinol. In some cases, the color of the acid solution is quite different from that of the simple fuchsone. The fuchsones of the 1,4-, 1,2- and 2,1-carbinols were used as comparison materials because they are readily obtained in a pure condition. The relative permanence of colors of the salts of the other hydroxynaphthyldiphenylcarbinols used in this investigation was also determined for the products obtained after heating the carbinols above their melting points. The residues were dissolved in acetic acid containing 6% sulfuric acid and the same results were obtained as with the unmelted carbinols. Table I summarizes the colors which first developed together with the final color and time when evidence of change was first noted.

TABLE I

ACETIC--SULFURIC ACID SOLUTION

Solute	Original color	Final color	Time when change was first noted
1,6-Carbinol	Greenish-brown	Cherry-red	1–2 min.
α-Naphthyldiphenylcarbinol	Brownish-green	Orange	15–30 min.
β-Naphthyldiphenylcarbinol	Red-brown	Orange	15–30 min.
2,3-Carbinol	Brown	Brown-red	90 min.
1,5-Carbinol	Green	Purple-red	90 min.
2,8-Carbinol	Green	Brown-red	4 hrs.
1,7-Carbinol	Green	Purplish-red	4–5 hrs.
2,6-Carbinol	Red-purple	Purple-red	1–3 days
1,2-Fuchsone	Blue-green	Blue-green	No change
2,1-Fuchsone	Blue-green	Blue-green	No change
1,4-Fuchsone	Violet	Violet	No change

It will be noted that the solutions of the 1,6-carbinol and α- and β-naphthyldiphenylcarbinols, which cannot assume a quinonoid structure involving an hydroxyl group, changed color most rapidly. The solutions of those carbinols which gave stable fuchsones yielded permanent colors, and ranking next to them in stability of color is the 2,6-carbinol whose simple unsubstituted quinone is known. In between these two groups are the carbinols which theoretically can form fuchsones. The data indicate that (1) a compound capable of possessing a quinonoid structure in one ring of naphthalene is stabilized in acid solution by this structure, (2) a compound in which a quinonoid structure is impossible is not stable in acid solution and side reactions, probably fluorenation, take place, and (3) a compound which can possess a quinonoid structure across both rings in naphthalene is stabilized somewhat in acid solution by this structure but is also susceptible to side reactions. It is not unlikely that these results may be interpreted as indications of the relative ability of the carbinols to form a quinonoid structure involving the hydroxyl group.

Experimental

2-(6-Hydroxynaphthyl)-diphenylcarbinol

6-Bromo-2-naphthol.—1,6-Dibromo-2-naphthol, prepared according to the directions of Franzen and Stäuble,[10] was reduced in alcohol by tin and concentrated hydrochloric acid and yielded the monobromonaphthol desired; m. p. 127–128°. An interesting by-product from this reaction, not reported by the above investigators, was 6-bromo-2-ethoxynaphthalene which was produced by simultaneous reduction and etherification. Its identity was shown by comparison with an authentic specimen prepared by the method of Davis[11]; m. p. 79–80°.

6-Bromo-2-methoxynaphthalene.—The methyl ether was obtained by methylation of 6-bromo-2-naphthol with dimethyl sulfate in potassium hydroxide solution; m. p. 105–106°.

6-Methoxy-2-benzoylnaphthalene.—Five and nineteenths grams of ground magnesium was first activated with iodine and then treated with 1 cc. of ethyl bromide in ether. After the magnesium had started to react with the ethyl bromide, 47.4 g. of 6-methoxy-2-bromonaphthalene in 500 cc. of ether was added and then another cc. of ethyl bromide. The mixture was refluxed for several hours, during which time a brown oil separated. The oil was brought into solution by the addition of 200 cc. of benzene which also produced a purple luminescence. The mixture was heated and when only a very small amount of magnesium remained, 26 cc. of cyanobenzene in 100 cc. of benzene was added which caused the formation of a white precipitate. After refluxing for forty-eight hours the reaction product was hydrolyzed with ammonium chloride solution followed by a few cc. of acetic acid. The organic layer was separated, treated with a few cc. of hydrochloric acid and steam distilled. Ether was added to the residue remaining after steam distillation and the ether solution was treated with norite and dried with calcium chloride. Evaporation of the ether gave the ketone which was recrystallized from alcohol, a small amount of colorless insoluble material being filtered off in the recrystallization process; yield, 45%; m. p. 81–82°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.44; H, 5.34. Found: C, 82.33; H, 5.39.

6-Ethoxy-2-benzoylnaphthalene was obtained in similar fashion from the reaction between the Grignard reagent prepared from 6-ethoxy-2-bromonaphthalene and cyanobenzene. It was recrystallized from alcohol; yield, 30%; m. p. 88–89°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.61; H, 5.8. Found: C, 82.68; H, 5.82.

6-Hydroxy-2-benzoylnaphthalene.—This ketone was obtained by refluxing 1 g. of either the methoxy or ethoxy ketone with 3 cc. of constant boiling hydrobromic acid and 10 cc. of glacial acetic acid for periods varying from six to twenty-four hours. The resulting solution was poured into water and the precipitated solid dissolved in

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(10) Franzen and Stäuble, *J. prakt. Chem.*, [2] **103**, 368 (1922).

(11) Davis, *J. Chem. Soc.*, **77**, 39 (1900).

ether which was then extracted with sodium hydroxide solution. The alkaline extract was acidified to precipitate the hydroxy ketone which was once more dissolved in ether. After decolorization with norite and drying with calcium chloride the ether was evaporated and the ketone was crystallized from alcohol; yield, 70–80%; m. p. 158–159°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.26; H, 4.84. Found: C, 82.1; H, 4.89.

2-(6-Hydroxynaphthyl)-diphenylcarbinol.—The most satisfactory procedure found for this carbinol involved the treatment of 6-hydroxy-2-benzoylnaphthalene with phenylmagnesium bromide in excess. The Grignard reagent was first prepared in ether as usual after which an equal volume of benzene was added and the ether distilled off. A warm benzene solution of the ketone was then added directly to the benzene solution of the phenylmagnesium bromide and a greenish-yellow addition product formed at once. This soon changed to a creamy-white when the mixture was refluxed on the steam-bath. After refluxing for three hours the mixture was cooled and the precipitate allowed to settle. The supernatant benzene solution was decanted and hydrolyzed with water and a small volume of acetic acid. After the organic layer had been washed with sodium bicarbonate solution, dried with calcium chloride, and treated with norite, the solvent was evaporated. The resulting oil quickly solidified on scratching and was washed a few times with petroleum ether to remove biphenyl. The carbinol was then crystallized from benzene. Ether was added to the precipitate described above and this mixture was hydrolyzed with water and acetic acid and then worked up in the manner just described for the solution that had been decanted; combined yield, 75%. The carbinol darkens before melting and melts at 170–171° to a dark red-purple liquid (sealed tube). Color with concentrated sulfuric acid: red to purplish-red.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.73; H, 5.57.

In another synthesis, this carbinol was prepared by the action of phenylmagnesium bromide on the ethyl ester of 6-hydroxy-2-naphthoic acid which in turn had been synthesized from 2-naphthylamine-6-sulfonic acid by the procedure of Butler and Royle.[12] This synthesis of the carbinol was not regarded as satisfactory because of the low yield of hydroxynaphthoic acid.

In a third procedure, β-naphthylmethyl ether was treated in nitrobenzene solution with acetyl chloride and aluminum chloride to give 6-methoxy-2-acetylnaphthalene. This was oxidized with sodium hypochlorite to give the methyl ether of 6-hydroxy-2-naphthoic acid which was demethylated by hydrobromic acid in acetic acid solution to the hydroxy acid. Esterification of the latter acid with methyl alcohol and treatment of the ester with phenylmagnesium bromide gave the carbinol. This procedure was not as satisfactory as that described first due to low yields encountered in the first two steps.

2-(6-Hydroxynaphthyl)-diphenylmethane.—Two-tenths of a gram of carbinol was refluxed with 20 cc. of glacial acetic acid and 2 g. of granulated zinc until the purple color which first appeared upon heating had disappeared, about forty-five minutes being required. The product was precipitated by pouring into water and extracted with ether which was then washed with sodium bicarbonate solution, dried and treated with norite. Evaporation of the ether left an oil which crystallized when a drop of methanol was added. The methane was crystallized from methanol; m. p. 101.5–103° with solvent of crystallization; m. p. 52° without solvent of crystallization.

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.03; H, 5.81. Found: C, 88.91; H, 5.97.

2-(8-Hydroxynaphthyl)-diphenylcarbinol

2-Naphthylamine-8-sulfonic Acid.—β-Naphthylamine was sulfonated with concentrated sulfuric acid at 80° following the procedure of Green and Vakil[13] and the 2-naphthylamine-8-sulfonic acid was separated from the predominant 2,5-isomer by the insolubility of the sodium salt of the former in 94% alcohol.

Methyl 8-Hydroxy-2-naphthoate.—8-Hydroxy-2-naphthoic acid, which had been prepared from the sodium salt of 2-naphthylamine-8-sulfonic acid by following the procedure of Butler and Royle, was esterified by refluxing for twenty-four hours with absolute methanol containing a small amount of sulfuric acid. The solution was poured into water and the precipitated ester dissolved in ether. The ethereal solution was washed with sodium bicarbonate solution, dried with magnesium sulfate, decolorized with norite and the ether then evaporated off. The ester crystallized from chloroform in fine, colorless needles; yield, 65%; m. p. 151–152.5°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.29; H, 4.95. Found: C, 71.21; H, 5.05.

2-(8-Hydroxynaphthyl)-diphenylcarbinol.—To the Grignard reagent prepared from 1.25 g. of ground magnesium ribbon and 6.6 cc. of bromobenzene in 40 cc. of ether was added an ether–benzene solution of 1.85 g. of methyl 8-hydroxy-2-naphthoate. The mixture, in which a fine yellowish precipitate appeared, was refluxed for six hours, and then hydrolyzed with ammonium chloride solution and a little acetic acid. The organic layer was washed with sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was evaporated and the resulting oil solidified on scratching. The solid carbinol was washed with petroleum ether to remove biphenyl and then recrystallized from benzene; yield, 67%; m. p. 162–163° to a light yellowish-brown liquid (sealed tube). Color with concentrated sulfuric acid: green, rapidly changing to red-brown.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.30; H, 5.55.

1-(5-Hydroxynaphthyl)-diphenylcarbinol

5-Hydroxy-1-naphthoic Acid.—1-Naphthylamine-5-sulfonic acid was converted to the sodium salt and recrystallized several times from water. The amino group was diazotized according to the procedure of Royle and Schedler[14] for similar compounds, but the solid diazonium salt was added to a cold cuprous cyanide solution rather than to one at 50–60° as stated. Nitrogen was evolved immediately and after standing half an hour or so at room temperature the mixture was warmed on the steam-bath over-

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[12] Butler and Royle, *J. Chem. Soc.*, **123**, 1649 (1923).

[13] Green and Vakil, *ibid.*, **113**, 35 (1918).

[14] Royle and Schedler, *ibid.*, **123**, 1641 (1923).

night. After cooling, the solid cyanosulfonic acid was filtered off and hydrolyzed to the sulfonaphthoic acid in preference to hydrolyzing the entire reaction mixture. The sulfonaphthoic acid resulting from the alkaline hydrolysis was dried and fused with potassium hydroxide at 240–260° to give the desired hydroxynaphthoic acid. The yield by this procedure, based on the sodium salt of 1-naphthylamine-5-sulfonic acid, was 35%; m. p. of the crude acid which was sufficiently pure for esterification, 232–235°.

Methyl 5-Hydroxy-1-naphthoate.—The ester was prepared by refluxing the above hydroxynaphthoic acid for twenty-four hours with concentrated sulfuric acid in absolute methanol in the proportion of 10 g. of acid, 1 cc. of concentrated sulfuric acid and 100 cc. of methanol. The product was worked up in the manner described for methyl 8-hydroxy-2-naphthoate. The oil which resulted on evaporation of the ether was treated with carbon tetrachloride from which crystals immediately precipitated when a seed crystal was added; yield, 90%; m. p. 130–131.5°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.29; H, 4.95. Found: C, 71.03; H, 5.07.

1-(5-Hydroxynaphthyl)-diphenylcarbinol.—To the Grignard reagent prepared from 2.5 g. of ground magnesium and 14 cc. of bromobenzene in 50 cc. of ether was added a solution of 4 g. of the above ester in 75 cc. of ether followed by 50 cc. of benzene. A yellow precipitate formed at once and the mixture was refluxed for four hours. The liquid was decanted from the addition product and both were separately hydrolyzed and worked up in the manner previously described for the other carbinols. The carbinol was crystallized from benzene; yield, 63%. It darkens before melting and melts at 199–200° to a dark red liquid (sealed tube); color with concentrated sulfuric acid, green.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.48; H, 5.52.

1-(7-Hydroxynaphthyl)-diphenylcarbinol

Methyl 7-Hydroxy-1-naphthoate.—This ester was prepared from 1-naphthylamine-7-sulfonic acid in the manner described for the preparation of methyl 5-hydroxy-1-naphthoate. The ester crystallized from chloroform in fine needles; m. p. 124–126°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.29; H, 4.95. Found: C, 71.33; H, 5.05.

1-(7-Hydroxynaphthyl)-diphenylcarbinol.—The carbinol was obtained in the manner described for the preparation of 1-(5-hydroxynaphthyl)-diphenylcarbinol except that the entire reaction mixture was hydrolyzed and worked up instead of hydrolyzing and working up the addition product and solution separately. The carbinol is quite insoluble in benzene from which it was recrystallized with the addition of a small amount of ether; yield, 67%. It darkens before melting and melts to a deep orange-red liquid at 231.5–232.5° (sealed tube and pre-heated bath); color with concentrated sulfuric acid, green.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.50; H, 5.64.

1-(6-Hydroxynaphthyl)-diphenylcarbinol

Methyl 6-hydroxy-1-naphthoate resulted from the esterification of 6-hydroxy-1-naphthoic acid with methyl alcohol and concentrated sulfuric acid; m. p. 112–113°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.29; H, 4.95. Found: C, 71.24; H, 4.90.

1-(6-Hydroxynaphthyl)-diphenylcarbinol.—The carbinol was obtained from the action of phenylmagnesium bromide in excess on the above ester and recrystallized from chloroform; m. p. 188–190° to a faintly yellow tinged liquid which rapidly becomes very dark (sealed tube). Color with concentrated sulfuric acid: reddish-brown.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.32; H, 5.43.

The 1,4-, 1,2- and 2,1-carbinols and fuchsones required for the comparative studies were prepared by the methods given in the literature.[7] An interesting observation was made in the preparation of 1-hydroxy-2-benzoylnaphthalene, however. This compound was prepared by heating a mixture of α-naphthyl benzoate and aluminum chloride at 150–165° until evolution of hydrogen chloride ceased. The ketone prepared under these conditions melted at 64–65°. In one run in which the temperature was kept at 100° a product melting at 160° was obtained; the 4-hydroxy-1-benzoylnaphthalene melts at 164–165°. The higher temperature favored ortho rearrangement while para rearrangement was favored by the lower temperature. The results of this experiment are in harmony with the findings of Rosenmund and Schnurr,[15] who studied the effect of temperature on the rearrangement of esters. In some cases it was found by these investigators that the ratio of ortho to para rearrangement product could be readily controlled by proper selection of the temperature.

2-(3-Hydroxynaphthyl)-diphenylcarbinol.—This carbinol was readily prepared from the methyl ester of 3-hydroxy-2-naphthoic acid and phenylmagnesium bromide following the procedure of Lammer[16]; m. p. 181–182°.

Summary

1. Five new hydroxynaphthyldiphenylcarbinols have been synthesized.

2. Attempts to isolate naphthofuchsones from the carbinols have not been successful. However, results have been obtained which indicate that the color of acid solutions of these carbinols is more permanent when the hydroxyl and carbinol groups are oriented at positions corresponding to the oxygen atoms in naphthoquinones. These data may indicate the existence of a quinonoid structure in acid solutions of those carbinols which are theoretically capable of assuming such a structure.

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[15] Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928).

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