Conclusions.

1. A few methods have been outlined for the preparation of a 6-atom heterocyclic ring containing mercury in place of a non-metal.

2. The preparations of a number of new derivatives of *m*-bromo-dimethyl-aniline, *m*-bromo-monomethyl-aniline Bindshedler's green, mercury derivatives of nitroso-phenol, nitroso-aniline, phenylamine and nitro-diphenylamine have been described. These compounds were obtained as a result of carrying out the above procedures.

Work on the problem is being continued.

CHICAGO, ILL.

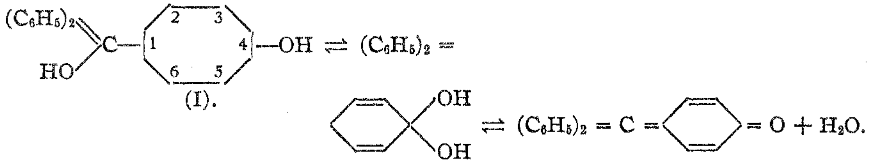
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TAUTOMERISM IN THE TRIARYL CARBINOL SERIES; DIPHENYL-4-HYDROXY-1-NAPHTHYL CARBINOL AND DIPHENYL-2-HYDROXY-1-NAPHTHYL CARBINOL.

BY M. GOMBERG AND F. W. SULLIVAN, JR.

Received June 15, 1920.

It has been shown in previous papers[1] from this laboratory that *p*-hydroxy-triphenyl carbinol exists in 2 tautomeric forms mutually convertible into each other, the benzenoid (I) and the quinonoid (II). The former, colorless, is converted into the latter, colored, by the agency of proper solvents, by heat, and by ultra-violet light. The quinonoid tautomer loses water on heating, to yield fuchsone (III). It is obvious that the benzenoid carbinol, on heating, should also yield the identical fuchsone, through the phase of temporary existence as the quinonoid carbinol.



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

Such is really the case. Moreover, the benzenoid carbinol loses water much more slowly than the quinonoid tautomer does, a difference in behavior fully consistant with the constitutions assigned to the 2 carbinols, respectively.

Little is known as to how extensively this tendency to tautomerization is shared by substituted hydroxy-triaryl carbinols. Three possible variations of the occurrence of this phenomenon suggest themselves: first, as in the case of *p*-hydroxy-triphenyl carbinol itself, when the benzenoid and the quinonoid carbinol, as well as the fuchsone, all possess sufficient individual stability to permit the isolation of each in the solid state; second, when the equilibrium between the 2 carbinols is preëminently in favor

---

[1] THIS JOURNAL, **35**, 1035 (1913); **37**, 2575 (1915).

of the benzenoid tautomer; the conversion of that into quinonoid requires then such energetic means that the reaction proceeds further and the fuchsone is produced; third, the equilibrium is largely or completely in favor of the quinonoid carbinol; in such cases it becomes impossible to isolate the colorless carbinol, and the colored carbinol obtainable consists either wholly of the quinonoid tautomer or of that with some slight admixture of the benzenoid.

A knowledge of the factors that influence or determine in a particular carbinol the occurrence of the one or the other of these 3 possible tautomeric relationships should be of considerable interest, as this is intimately connected with the question of color-production in the triphenylmethane compounds, and also, in view of the contemporary discussion as to the "quinoncarbonium or oxonium" constitution of many dyes.[1]

At the present time our knowledge in this respect is very limited. It has been shown by Gomberg and Van Stone[2] that any of the groups CH_3, OCH_3, Br, Cl, in positions 3, or 3 and 5, in the hydroxylated nucleus (see Formula I), does not interfere with the stable existence of each of the 2 carbinols and fuchsone. On the other hand, even one NO_2 group in the same position prevents the stable occurrence of the quinonoid carbinol. The same is true, as has recently been found by P. Demont,[3] when the groups CH_3 and NO_2, Br and NO_2, or COOH and CH_3, are present in positions 3 and 5. Again, if the groups CH_3 or OCH_3 are present in position 2, *i. e.*, *meta* instead of *ortho* to the *p*-hydroxy groups, they have been found to impede tautomerization to such an extent that only the benzenoid carbinol and the fuchsone can be isolated.[4]

Thus, there are at present a number of hydroxy-triaryl carbinols on record of which all of the 3 components that constitute the tautomeric equilibrium are known; a still larger number are on record of which the stable existence of only 2 components is definitely established, a colorless carbinol and the fuchsone. But, strangely, there are no instances described in which the third possible variation has been observed; namely, the stable existence of a colored carbinol and the corresponding fuchsone. And yet the number of fuchsones described in the literature is quite extensive, although their formation has always been unforeseen since, in each case, the corresponding carbinol was sought. Bearing in mind the possible existence of a colored, in addition to the colorless tautomeric carbinol, it appeared to us probable that, in many instances, the existence of the colored carbinol had been overlooked; that, probably, the quinonoid carbinol,

---

[1] Diethey, *Ber.*, **53**, 261 (1920).

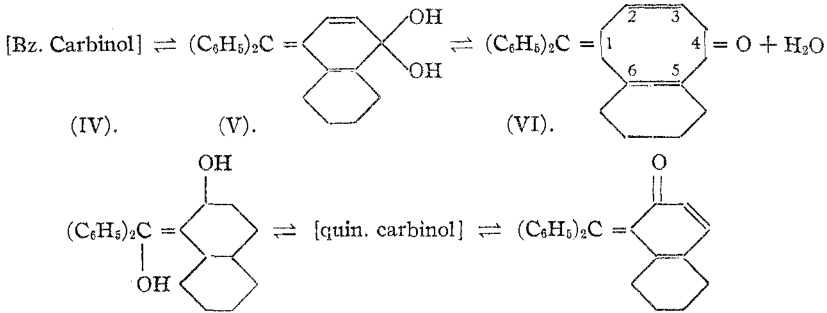
[2] Gomberg and Van Stone, THIS JOURNAL, **38**, 1577 (1916).

[3] Demont, *Dissertation*, "Synthèse de quelques dérivés de la Parafuchsone, Fribourg," (Suisse) 1919.

[4] THIS JOURNAL, **39**, 1674 (1917).

and not the fuchsone, was the first product of the reaction. When such a carbinol is dried for the purpose of analysis, or recrystallized from such solvents as benzene, acetic acid, etc., anhydrolysis would naturally take place and the carbinol would change to the fuchsone without becoming appreciably more intense in color.

With this idea in view, we subjected *p*-naphthofuchsone (VI) and *o*-1-naphthofuchsone-2- (IX) to a careful examination. Our surmise was verified; carbinols corresponding to these fuchsones were isolated, in the first case the quinonoid and in the second, the benzenoid tautomer only.



(IV). (V). (VI).

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

The statement that, in the case of the *p*-naphthofuchsone, only the quinonoid carbinol was obtained requires a modification. A definite answer to the question whether in a given instance both tautomeric carbinols exist is readily had, when the two tautomers happen to be clearly differentiated by the presence and absence of color, respectively, or by a distinct difference in the melting points, or by both. Equally definite is the answer in such cases when only the benzenoid carbinol is obtainable. But, on the other hand, when apparently only one carbinol is obtainable and that one possesses color, and is amorphous—as is usually the case—then it becomes difficult to give an unequivocal answer as to whether the substance under examination is the quinonoid carbinol alone or whether it contains an admixture of some of the benzenoid.

Occasionally[1] it may prove to be possible to establish the presence of some benzenoid tautomer in the colored substance when the latter is precipitated in part from an alkaline solution and in part from an acid solution. If the 2 samples, apparently alike in intensity of color, lose water at different rates, then certainly we are dealing with mixtures and not with a single tautomer. But when the 2 samples lose water at equal rates, the question is left open. If we may venture to assume that a quinonoid carbinol possesses an intensity of color near that of the corresponding fuchsone, then from the comparison of the 2 colored compounds an inference might be drawn as to whether the carbinol is wholly quino-

---

[1] Gomberg and Todd, This Journal, **39**, 2392 (1917).

noid or whether it contains some of the colorless tautomer. Such a comparison of the 2 solids would give at best only approximately correct results. A comparison of their solutions, while more certain, is not feasible, because the action of the solvent may induce partial tautomerization in an otherwise homogeneous carbinol.

It is obvious, then, that when only a colored carbinol is obtainable it often becomes difficult, if not impossible, to establish positively whether some of the benzenoid tautomer also is or is not present. This difficulty, however, is of no great moment to our problem. With the existence of the colored carbinol a demonstrable fact, it is clearly established that the formation of a fuchsone is dependent invariably upon the previous tautomerization of the benzenoid to the quinonoid carbinol.

The Condensation of Benzenone Chloride with α- and β-Naphthol.—This subject has been investigated by Clough,[1] who prepared *p*-naphthofuchsone and *o*-naphthofuchsone by the condensation of α- and of β-naphthol with benzophenone chloride. In the case of the former fuchsone he obtained a yield of only 15%, while he does not state the yield of the latter. Bistrzycki[2] also prepared *p*-naphthofuchsone by the condensation of benzilic acid with 1-hydroxy-2-naphthoic acid. Although the yields by this method are satisfactory, the method is quite complicated. Neither of these observers isolated the carbinols corresponding to these fuchsones. Carbinols isomeric with the two just mentioned have been prepared. Kaufmann and Egner[3] and Preizecker[4] prepared 1-hydroxy-2-naphthyl-diphenyl carbinol and 2-hydroxy-2-naphthyl-diphenyl carbinol by the action of phenyl-magnesium bromide on the esters of 1-hydroxy-2-naphthoic acid and 3-hydroxy-2-naphthoic acid, respectively.

***p*-Naphthofuchsone** (*Formula VI*).—Using a slight modification of the method given by Gomberg and Jickling for the preparation of *p*-hydroxy-triphenyl carbinol we obtained a quantitative yield of *p*-naphthofuchsone from benzophenone chloride and α-naphthol. Six g. of benzophenone chloride and 7.5 g. of α-naphthol were mixed in a flask protected from moisture by a tube of calcium chloride. After the reaction mixture had stood overnight, it was made slightly alkaline with dil. sodium hydroxide, decomposed with water and distilled with steam. The alkaline solution was decanted and the insoluble residue was dissolved in acetic acid, from which the fuchsone crystallized on the addition of water. The yield by this method was 7.8 g., or 100%. *p*-Naphthofuchsone is colored orange-yellow and melts at 179°. It gives a violet color with sulfuric acid.

---

[1] Clough, *J. Chem. Soc.*, **89**, 771 (1906).

[2] Bistrzycki, *Ber.*, **45**, 1429 (1912).

[3] Kaufmann and Egner, *ibid.*, **46**, 3779 (1913).

[4] Preizecker, *Monatsh.*, **35**, 900 (1914).

3-Bromo-*p*-naphthofuchsone.—*p*-Naphthofuchsone was dissolved in glacial acetic acid in the proportion of 1 g. to 10 cc. and the calculated amount of a dil. solution of bromine in acetic acid was added. Gradually, bromo-naphthofuchsone separated as reddish-brown crystals, which melted at 176°. Yield, 70%. The compound gives an intense blue color with sulfuric acid.

3-Chloro-*p*-naphthofuchsone.—In a similar manner, but with the substitution of chlorine for bromine, chloro-naphthofuchsone was obtained as a bright red crystalline substance melting at 161°. The color produced with sulfuric acid is very similar to that produced by bromonaphthfuchsone.

o-(1)-**Naphthofuchsone**-(2) (*Formula IX*).—When *β*-naphthol and benzophenone chloride were mixed under the conditions given for the preparation of *p*-naphthofuchsone, condensation did not take place, but, under the influence of a catalyst, the reaction occurred, with the formation of the fuchsone. Six g. (1 mol.) of benzophenone chloride, 4.4 g (1.2 mols.) of *β*-naphthol and 4.1 g. (1.2 mols) of aluminum chloride were mixed in a flask and 50 cc. of carbon disulfide was added. The reaction mixture was protected from moisture with a tube of calcium chloride, and was allowed to stand overnight. Then it was boiled for one hour under a reflux condenser, decomposed with ice and distilled with steam. After the insoluble residue had been digested with dil. alkali, it was recrystallized from acetic acid; this gave 4 g. (a 50% yield) of brilliant orange red crystals of *o*-naphthofuchsone, melting at 198°. Clough gives the melting point as 194°, otherwise our observations agree with the properties of this compound as described by him. The fuchsone gives a green color with sulfuric acid.

Conversion into Carbinols.—In contrast with *p*-fuchsone it was found that *p*-naphthofuchsone and *o*-naphthofuchsone were quite insoluble in *N* alkali solution. The procedure finally adopted to dissolve the naphthofuchsones was to shake them overnight with 50% alcoholic 0.5 *N* sodium hydroxide. After solution was once effected dilution did not cause precipitation.

4-Hydroxy-1-naphthyl-diphenyl Carbinol.—*p*-Naphthofuchsone was dissolved in alcoholic sodium hydroxide and the solution was filtered. The clear liquid was diluted and stirred constantly while a solution of ammonium chloride was added. A very voluminous precipitate of the carbinol separated and was filtered after a short time. The carbinol was dried, but it could not be crystallized because it changed to the fuchsone in all solvents. The dried amorphous yellow powder obtained by precipitation was heated at 120°, and the moisture evolved was collected by passing it over calcium chloride and weighed.

Calc. for H_2O in $C_{23}H_{18}O_2$: 5.5. Found: (1) 5.6; (2) 5.8; (3) 6.0; Av., 5.8.

3-Bromo-4-hydroxy-1-naphthyl-diphenyl Carbinol.—According to the procedure given above, 3-bromo-4-hydroxy-1-naphthyl-diphenyl carbinol was obtained from bromo-naphthofuchsone as a canary-yellow powder. This carbinol also lost one molecule of water when heated to 120°

Calc. for H_2O in $C_{23}H_{17}O_2Br$: 4.4. Found: (1) 4.3; (2) 4.2.

3-Chloro-4-hydroxy-1-naphthyl-diphenyl Carbinol.—In the same manner as the preceding, 3-chloro-4-hydroxy-1-naphthyl-diphenyl carbinol was prepared from chloro-naphthofuchsone. It resembles the bromo-carbinol in appearance and, on heating, loses one molecule of water.

Calc. for H_2O in $C_{23}H_{17}O_2Cl$: 5.0. Found: (1) 4.6; (2) 4.6.

All these carbinols give the same colors with sulfuric acid as do the corresponding fuchsones. It was not found possible to isolate the benzenoid and quinonoid modifications. It is probable that the carbinols obtained consisted in each case largely, if not entirely, of the quinonoid tautomer.

2-Hydroxy-1-naphthyl-diphenyl Carbinol.—2-Hydroxy-1-naphthyl-diphenyl carbinol was readily prepared from *o*-naphthofuchsone in the same way that the preceding carbinols were prepared from their corresponding *p*-naphthofuchsones. It was found that the *o*-hydroxy carbinol was quite stable and could be crystallized from benzene and petroleum ether in the form of pure white plates, which give off water when heated, became red and melted slightly below the true melting-point of the fuchsone (194°). All efforts to convert this benzenoid carbinol to the quinonoid tautomer resulted in the formation of the fuchsone; even when heated to 150° with water in a sealed tube it suffered this change. Heated to 120° by itself, it becomes red, loses water and gives the fuchsone directly.

Calc. for H_2O in $C_{23}H_{18}O_2$: 5.5. Found: (1) 6.3; (2) 6.6.

Calc. for $C_{23}H_{18}O_2$: H, 5.52; C, 84.7. Found: H, 5.76, 5.92, C, 84.9, 85.2.

The behavior of this compound shows a distinct resemblance to that of *o*-hydroxy-triphenyl carbinol described by Baeyer.[1] It appears from the comparison of *ortho* and *para*-hydroxy-triphenyl carbinols with *ortho*- and *para*-hydroxy-naphthyl-diphenyl carbinols that in both cases the *ortho* isomer is more stable than the *para*, and that the substitution of the naphthyl for the phenyl group decreases the stability of the carbinol.

When *o*-naphthofuchsone was dissolved in alcohol to which a few drops of ammonia had been added, it was found that, on standing, feathery white crystals, presumably the ammonium salt, were formed. The same substance is readily prepared from the fuchsone by shaking the latter with alcohol saturated with ammonia. When the salt is heated in an open tube, it is converted into the fuchsone, but when it is heated in a sealed melting-point tube, it melts at 171°.

Hydrogen Chloride Addition Compounds of the Naphthofuchsones.—*p*-Fuchsone readily absorbs 2 mols. of hydrogen chloride when placed in

---

[1] Baeyer, *Ann.*, **354**, 167 (1907).

an atmosphere of the gas,[1] Similarly, when *p*-naphthofuchsone was placed in a porcelain boat and dry hydrogen chloride was passed over it, the absorption of the acid proceeded rapidly and was complete in 3 hours; the contents of the boat acquired the appearance of a black viscous mass. The absorption was somewhat more than that calculated for 2 molecules of hydrogen chloride. The boat was then placed in a desiccator over soda lime, but the loss in weight was only slight. Under diminished pressure about $^1/_3$ of the total acid was lost in the first 24 hours, and in 4 to 5 days all the acid was given up. *o*-Naphthofuchsone also absorbed hydrogen chloride, but it did not take up so large an excess over 2 molecules. It gave off its acid *in vacuo* much more slowly than the *para*-compound, and 23 days were required for elimination of 80% of the acid. It was found that chloro- and bromo-naphthofuchsones do not form additive compounds with hydrogen chloride.

Summary.

1. Improved methods of preparing *p*-naphthofuchsones and *o*-naphthofuchsones are described.

2. It was found that the fuchsones can be converted into their corresponding carbinols. The *para*-fuchsone gives the quinonoid almost entirely, while the *ortho*- changes to the benzenoid carbinol exclusively.

3. It was found that the influence of an hydroxy-naphthyl group is much greater than that of an hydroxy-phenyl group. In *p*-hydroxy-triphenyl carbinol, both tautomers are stable; in the *p*-hydroxy-naphthyl-diphenyl carbinol, the quinonoid only is stable. A similarly greater tautomerizing tendency was observed when *o*-hydroxy-triphenyl carbinol was compared with *o*-hydroxy-naphthyl-diphenyl carbinol; the former does not give the fuchsone on heating, while the latter does.

This investigation was done with the assistance of The National Aniline and Chemical Company Fellowship, and we wish to express our obligations for the generous aid we have thus received.

ANN ARBOR, MICHIGAN.

---

[1] THIS JOURNAL, 37, 2585 (1915).