aminobenzoic acid. Kliegl[1] reduced "*o*-benzoyl-*p*-nitrobenzoic acid" (which he obtained from phenylnitro-fluoren) and isolated a product which melted at 195° with decomposition. This isomeric compound is 2-benzoyl-4-aminobenzoic acid and is the other acid obtained by the Freidel and Crafts reaction.

Summary.

1. The reactions of aluminum chloride and benzene with 3-nitro-phthalic anhydride, 4-nitro-phthalic anhydride, 3-acetylamino-phthalic anhydride and 4-acetylamino-phthalic anhydride, respectively, have been studied and the 2 possible derivatives of benzoylbenzoic acid have been obtained in each case.

2. In only one reaction was a derivative of diphenyl-phthalide isolated and, in this instance, Rubidge and Qua's method for increasing the yield of phthalide gave good results.

3. Seven new compounds have been prepared:

	M. p.
6-Benzoyl-2-nitrobenzoic acid	220–21° (decomp.)
2-Benzoyl-3-nitrobenzoic acid	157–60° (decomp.)
6-Benzoyl-2-aminobenzoic acid	159–60°
2-Benzoyl-3-aminobenzoic acid	193–4°
Diphenyl-?-amino-phthalide	86–9°
2-Carbethoxy-3-nitrobenzoyl chloride	76–7°
6-Carbethoxy-2-nitrobenzoyl chloride	Oil

4. Detailed directions are given for the preparation of several of the compounds used in the experiments and an improved method for the preparation of the benzoyl-3-aminobenzoic acids.

This research was done under the direction of Professor F. B. Allan. The author held a studentship from the Honorary Advisory Council for Scientific and Industrial Research.

TORONTO, CANADA.

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

TAUTOMERISM IN THE TRIARYL-CARBINOLS: MONO-PARA-HYDROXY-DIPHENYL-α-NAPHTHYL CARBINOL.

BY M. GOMBERG AND N. A. LANGE.

Received June 17, 1920.

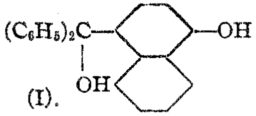
In a preceding paper[2] it has been shown that in the monohydroxy-triaryl carbinols, the naphthyl nucleus exerts a much more pronounced tautomerizing influence than does the phenyl nucleus when each carries an hydroxyl group; while *p*-hydroxy-triphenyl carbinol is stable both in its benzenoid and its quinonoid modification, *p*-hydroxy-naphthyl-diphenyl carbinol (I) is not stable in its benzenoid form, but spontaneously changes

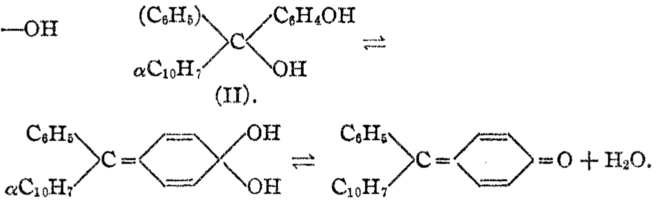
[1] *Ber.*, 38, 296 (1905).

[2] Gomberg and Sullivan, THIS JOURNAL, 42, 1864 (1920).

into the quinonoid. We have now prepared a carbinol isomeric with (I), namely, mono-*p*-hydroxy-diphenyl-naphthyl carbinol (II), wherein the hydroxyl group is situated in the phenyl and not in the naphthyl ring. We find that, in spite of the separateness of the hydroxyl group from the naphthyl nucleus, the latter nonetheless still exerts a noticeably greater favorable influence upon the quinoidation of the carbinol than is exerted by a phenyl nucleus. The benzenoid tautomer (II) spontaneously changes into the quinonoid tautomer (III), which, on heating, readily gives the corresponding fuchsone (IV).

The carbinol, obtained under diverse circumstances, is invariably colored and is amorphous. Whether it is entirely free from the colorless, benzenoid, tautomer seems impossible at present to determine. Judging, however, from the intensity of its color as compared with that of the fuchsone, one would infer that some benzenoid carbinol must be present.


(I).

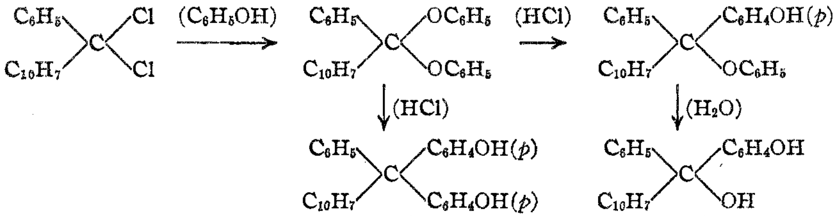

(II).

(III). (IV).

The demonstration of the existence of the quinonoid tautomer of *p*-hydroxy-diphenyl-naphthyl carbinol adds another instance in support of the generalization that the colored fuchsones—which are the mother substances of the triphenyl-methane dyes—are but the final step in the chain of reactions: benzenoid carbinol ⟶ quinonoid carbinol ⟶ fuchsone. It may yet prove possible to adduce direct experimental evidence of similar tautomerization in the formation of the dyes themselves.

The carbinol under consideration has been prepared by the condensation of α-naphthyl-phenyl-ketone chloride with phenol. The condensation was found to proceed in the same manner as described for the condensation of benzophenone chloride with phenol.[1] Here again, the mechanism of the reaction is

(V). (VI).


(VIII). (VII).

---

[1] Gomberg and Jickling, THIS JOURNAL, 37, 2575 (1915).

Depending upon the conditions of procedure, the result of the condensation is the diphenoxy-compound (V), or the carbinol (VII), or the tetraaryl-methane derivative (VIII).

α-Naphthyl-phenyl-ketone Chloride, $(C_6H_5)(C_{10}H_7) : C : Cl_2$.—α-Naphthyl-phenyl ketone, prepared by the method of Montague,[1] and the calculated quantity of phosphorus pentachloride, were heated at 100° until the reaction mixture was liquid and the pentachloride had gone into solution. The phosphorus oxychloride was removed by distillation under reduced pressure at a temperature of 100°, which left the ketone chloride as viscous brown liquid. This was then poured into low boiling petroleum ether and the solution was boiled for a short time with charcoal and filtered. On standing, small colorless needles of the ketone chloride separated. A second crystallization from petroleum ether yielded practically pure chloride. The yield was 60%. On heating, the chloride begins to soften at about 86° and melts at 92°. Attempts to purify the chloride by distillation under reduced pressure were not successful because of its decomposition at elevated temperatures.

Calc. for $C_{17}H_{12}Cl_2$: Cl, 24.7. Found: 24.3.

Phenyl-α-naphthyl-diphenoxy-methane, $(C_6H_5)(C_{10}H_7) : C :-(O.C_6H_5)_2$.—Six g. of phenol was dissolved in 30 cc. of dry benzene and the solution heated to boiling under a reflux condenser; to this boiling solution, protected from moisture by a calcium chloride tube, 7 g. of ketone chloride, dissolved in 30 cc. of benzene, was added in small portions during the course of several hours. This solution was kept boiling until hydrogen chloride was no longer evolved. After the solution was cooled ammonia was added to neutralize any hydrogen chloride still in solution, and the mixture was then distilled with steam in order to remove the excess of phenol. The solid residue was digested with cold *N* sodium, hydroxide solution, and then boiled with a small quantity of alcohol which removes the yellow color caused by the presence of a small amount of the fuchsone. Finally, the product was purified by recrystallization from amyl alcohol, which formed white crystals that melt at 169–70°. The yield was 80–85%. The substance is readily soluble in benzene, chloroform, carbon tetrachloride, carbon disulfide, acetone; is fairly soluble in ether, ethyl acetate and amyl alcohol, and is slightly soluble in petroleum ether and in alcohol. On treatment with aqueous solution of acids, the diphenoxy compound hydrolyzes to give the ketone and phenol. When placed in an atmosphere of dry hydrogen chloride, it is converted into phenol and the fuchsone described below.

Calc. for $C_{29}H_{22}O_2$: C, 86.53; H, 5.51. Found: C, 86.31; H, 5.33.

α-Naphthyl-phenyl-quinomethane, $(C_6H_5)(C_{10}H_7) : C : C_6H_4 : O$.—Eight g. of ketone chloride and 13.5 g. of phenol were placed in a round-

---

[1] *Rec. trav. chim.*, 26, 280 (1917).

bottom flask and protected from moisture by a tube of calcium chloride. The reaction was allowed to proceed for 12 hours at room temperature, when the mixture was heated to about 50° for one hour. The contents of the flask were distilled with steam in order to remove the excess of phenol. This caused the fuchsone to remain as a dark red viscous liquid, which gradually solidified on standing. On recrystallization from dil. alcohol, yellow crystals are obtained which melt at 169–70°. The yield was 85–90%. The fuchsone is readily soluble in chloroform, carbon tetrachloride, benzene; is fairly soluble in alcohol, acetone, ethyl acetate, and only slightly soluble in petroleum ether.

Calc. for $C_{23}H_{16}O$: C, 89.61; H, 5.23. Found: C, 89.67; H, 5.32.

The fuchsone dissolves in sulfuric acid with a deep red color. On treating the fuchsone with an aqueous solution of sodium hydroxide, it is converted into the carbinol as described below.

4,4′-Dihydroxy-triphenyl-α-naphthyl Methane, $(C_6H_5)(C_{10}H_7):C-(C_6H_4OH)_2$.—Four g. of the ketone chloride and 30 g. of phenol, previously saturated with dry hydrogen chloride, were heated at 110° for 24 hours. The contents of the flask were protected from moisture by a tube of calcium chloride. After the excess of phenol had been removed by steam distillation, the semi-solid residue, while still warm, was poured into 500 cc. of a 5% sodium hydroxide solution and thoroughly stirred to break up all lumps. After it had stood for about $^1/_2$ hour the white precipitate was removed from the alkaline solution by filtration, and washed with water. The precipitate was recrystallized several times from glacial acetic acid by careful addition of water to the hot solution. The crystals were dissolved in ether, and the solution was boiled with charcoal, filtered and evaporated to dryness. Another recrystallization of the solid residue from acetic acid gave white microscopic needles, which begin to soften at 206° and melt with decomposition to a red liquid at 209–10° (uncorr.). The yield was 15–20%. The compound is readily soluble in ether, methyl or ethyl alcohols; is fairly soluble in chloroform, carbon tetrachloride, *m*-xylene, toluene, benzene or acetic acid; is very slightly soluble in 10% sodium hydroxide solution and insoluble in petroleum ether. For analysis it was dried one hour at 110–5°.

Calc. for:		Found:
$C_{29}H_{22}O_2$:	C, 86.53; H, 5.51	Sample A—C, 88.71; H, 5.14
$C_{29}H_{22}O_2\,0.5H_2O$:	C, 88.55; H, 5.34	C, 88.82; H, 5.24
$C_{29}H_{22}O_2H_2O$:	C, 90.62; H, 5.20	Sample B—C, 88.41; H, 5.23
		C, 88.74; H, 5.06

Apparently the dihydroxy compound has been produced first, but on subsequent treatment, in the process of purification, it has suffered dehydration. From the fact that it is still somewhat soluble in sodium hydroxide solution, it must be concluded that the dehydration has occurred between 2 molecules of the tetra-aryl-methane compound, and not within one molecule through the destruction of both phenolic hydroxyl groups.

Diphenyl-α-naphthyl Carbinol, $(HOC_6H_4)(C_6H_5)(C_{10}H_7) : C.OH$. — The fuchsone was dissolved in a small quantity of alcohol and then heated to boiling with *N* sodium hydroxide solution until the color of the solution had changed from red-yellow to a very light yellow. This solution was diluted with an equal volume of water and the carbinol was precipitated as a light yellow amorphous material upon the addition of a saturated solution of ammonium chloride. Attempts to recrystallize the carbinol from the common organic solvents were not successful. The method previously employed[1] for the isolation of the colored and colorless tautomers of a similarly amorphous carbinol was not successful in this case, because of partial dehydration of the carbinol to form the fuchsone when it is dissolved in acetic acid. Whether precipitated from an alkaline solution or from acid solution, the carbinol looks equally intense in color, loses water at about the same rate and readily changes to the fuchsone. However, the sample from dil. acetic acid, presumably quinonoid, begins to soften and turn red at 70°, while the sample from an alkaline solution, and presumably containing some benzenoid carbinol, begins to soften and turn red at 87°.

Thus, it has been demonstrated that a naphthyl group exerts a stronger tautomerizing influence than a phenyl group; also, that in this case as well, similarly to those described in previous papers, the formation of fuchsone is preceded by the intermediate stage, namely, the formation of the quinonoid carbinol.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A MOSAIC DISEASE OF CABBAGE AS REVEALED BY ITS NITROGEN CONSTITUENTS.[2]

BY S. L. JODIDI.
(With the coöperation of S. C. Moulton and K. S. Markley.)

Received June 23, 1920.

Introductory.

It is generally accepted in plant hygiene that only healthy and vigorous plants, as a rule, yield maximum returns. Hence, it goes without saying that measures looking to the amelioration of our cultivated plants will, of course, lead to crops superior both in quality and quantity. This object may be attained by finding proper remedies for the existing plant

---

[1] Gomberg and Todd, THIS JOURNAL, 39, 2392 (1917).

[2] Presented before the Division of Biological Chemistry at the Chicago Meeting of the American Chemical Society, September 6–10, 1920.