the exception of petroleum ether, and very difficultly soluble in water. On heating with acids, benzaldehyde is split off.

Calculated for $C_{18}H_{17}O_2N_3$: C, 70.36; H, 5.54; N, 13.68.
Found: C, 70.04; H, 5.52; N, 13.69.

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON.]

SOME CHARACTERISTIC COLOR REACTIONS PRODUCED BY SODIUM HYPOBROMITE.

BY WILLIAM M. DEHN AND SILAS F. SCOTT.

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Since hippuric acid gave with sodium hypobromite a very characteristic color reaction,[1] it was thought that other substances also would be affected characteristically by this reagent. This has proved to be the case and to such an extent that sodium hypobromite alone or combined with the use of ammonia can now be considered one of the most valuable reagents for detecting and distinguishing many phenolic and nitrogenous aromatic compounds.

For the purpose of uniformity and of determining the limits of tests and comparing their respective delicacies, solutions of the various substances were prepared in the following concentrations: I, 1 gram in 100 cc. of water; II, in 1,000; III, in 10,000; IV, in 100,000; V, in 1,000,000. Alcohol was added when necessary to produce complete solution; with bases, hydrochloric acid was used for the same purpose. With various concentrations of solutions quite different color effects may often be obtained and thus one sometimes obtains results quite different from the results described in the literature. For this reason the concentrations of solution should always be indicated, also the quantity used, method of applying the reagent, quantity of reagent and the temperature. In the following experiments the reagent was applied, a drop at a time, to about 5 cc. of the solutions tested. When a series of colors are given they indicate the progressive effect either on standing or on adding more of the hypobromite solution. The following abbreviations are used to indicate the conditions and manner of applying tests.

A. Treated with sodium hypobromite at ordinary temperature.

A′. Treated with ammonia, then with sodium hypobromite at ordinary temperature.

B. First heated to boiling, then treated with sodium hypobromite.

B′. Treated with ammonia, then heated and finally treated with sodium hypobromite.

Of course solutions should not be acid in reaction for then bromine is liberated from the hypobromite. Excess of ammonia should be avoided

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[1] THIS JOURNAL, this Number, *Note 1.*

for the reason that it destroys the hypobromite. Care should be exercised that the hypobromite is added gradually for the reasons not only that often a series of colors may thereby be developed but that the possible destruction of color by an excess of hypobromite may be avoided. Conditions of experiments and concentrations of solutions yielding negative results are omitted in the following descriptions. When heat and the addition of ammonia give effects that are the same as A, only the effects of the latter are described.

Phenolic Compounds.

Phenol.[1]—B and B′–I, deep chrome-green; II, same; III, light sea-green. Ammonia is necessary and heat assists this color reaction.

Pyrocatechinol.—A, A′, B, B′–I, II, bright green followed immediately by a deep brown. B, B′–III, pink-brown followed by amber-brown. Most sensitive with ammonia and heat. Color is changed to yellow by an excess of sodium hypobromite.

Resorcinol.—A–I, bromine-brown; II, amber-brown; III, straw-yellow, A′–I, deep brown-black; II, deep amber-green. B–I, amber-brown; II-amber-green; III, green-amber; IV, straw-yellow. B′–I, deep brown. black; II, deep amber-green; III, green-amber; IV, faint pink. Color is intensified by the use of ammonia and heat; destroyed by an excess of sodium hypobromite and continued heat.

Hydroquinol. — A–I, chrome-green, changing immediately through bromine-brown to deep brown-black; II, chrome-green to deep brown; III, transient light green. A′–I, deep brown; II, same; III, very transient light green. B–ammonia itself imparts a golden-amber hue; I, dark brown; II, deep amber; III, light amber. Less sensitive with ammonia and heat; an excess of sodium hypobromite discharges the color, yielding odor resembling quinone.

To Distinguish the Dihydric Phenols.—To about 0.1 per cent. solution of each add one drop of ammonia; hydroquinol gives a golden yellow color. Add 2–3 drops of sodium hypobromite; pyrocatechinol gives a dark brown, resorcinol gives a green, and hydroquinol gives a brown-red color.

Pyrogallol.—A–I, amber, brown-red, deep black-brown; II, amber, deep brown-red; III, amber. A′–same as A but less sensitive. B–ammonia alone imparts an amber color; I–III, same as above; IV, amber.

Phloroglucinol.—A–I, green-amber, green-brown, deep violet, deep violet-brown; II, violet, red-brown, amber. A′–I, black-brown; II, brown-red. B and B′–I, deep violet, deep brown-black; II, deep violet; III, violet. The violet color, best formed with ammonia in a warm solution, easily distinguishes phloroglucinol from the other phenols.

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[1] A blue color with bleaching powder is described: Lex, *Ber.*, 3, 458; Salkowski, *Z. anal. Chem.*, 11, 316; *Jsb. chem.*, 1873, 722.

Orthocresol.—A–I, dirty chrome green, brown, dirty brown; II, brown-amber, brown. B–I, Paris green, deep black-green, dirty green, yellowish precipitate; II, brilliant chrome-green, grass-green, amber; III, sea-green, straw-yellow.

Metacresol.—A–I, pink-amber, light brown; II, amber. B–I, blue-green, deep black-green, brown, amber, dirty white precipitate; II, brilliant emerald-green, green-amber, amber; III, light green, amber.

Paracresol.—A–I, pink, pink-amber, light brown, dirty white precipitate; II, pink, amber; III, light yellow. B–I, light amber, brown; II, amber.

The cresols are distinguished by the lack of formation of a green color with the para, when treated with ammonia and sodium hypobromite; the ortho forms a dark brown, the meta a light brown, when treated with sodium hypobromite.

"*Cresol.*"—A–I, pink, wine-red, deep brown-red; II, amber, pink, amber, red, brown; III, light yellow. B–I, sea-green, deep dirty green, deep brown; II, light pink-amber, amber-brown; III, amber.

α-Naphthol.—A–I, purple, purple-black, brown-black; II, purple, dirty green-black, green-brown, purple-violet; III, sea-green, amber, pink-violet; IV, faintly pink. A′–I, dirty green, brown, black-brown, brown-black; II, sea-green, brown-amber; III, yellow-green. B–I, blue-green, indigo-blue, green-black; II, blue-green, dirty green. B′–I, dirty green, deep brown; II, sea-green, dark amber-brown.

β-Naphthol.—A–I, yellow-green, dark amber-brown, brown-black; II, green amber, deep brown; III, amber; IV, straw-yellow. A′–I, pink-brown, wine-red, deep red-brown; II, pink-amber, red-brown; III, pink-amber. B–I, amber, yellow-green, green-brown; II, amber, brown-amber. *The naphthols are distinguished* best in A–II solutions; purple with the *α*, brown with the *β*.

Derivatives of Phenols.

Salicylic Acid.—B, B′–I, II, light chrome-green. Color changed to amber by an excess of sodium hypobromite, restored to green by the addition of more ammonia.

Thymol, 2-isopropyl-5-methylphenol. B′–I, II, brilliant nickel-green; III, faintly green color. Excess of ammonia is to be avoided. This is a very beautiful and characteristic test for thymol.

Salol.—B′–I, same as phenol and salicylic acid. Color develops best after heating and standing.

Guaiacol, *o*-methoxyphenol.—A, A′–I, deep red-brown; II, amber-brown. B, B′–I, deep blue-green or black-green; II, chrome-green. The colors of guaiacol resemble the colors of phenol more closely than of pyrocatechol.

Vanillin, 3-methoxy-4-oxybenzaldehyde. B′–I, II, beautiful amber color.

Arbutin, A–I, pink, amber; II, same. B–I, deep nickel-green; II, same.

Eugenol, 4-propenyl-2-methoxyphenol. A, A′, B, B′–I, II, golden yellow, changing to deep brown.

Oil of Bay, contains eugenol. B′–I, clear deep red-brown; II, brown-yellow. Ammonia alone gives a bright lemon-yellow.

Oil of pimento, contains eugenol. B′–I, red-amber, brown, deep red-brown; II, red-amber, brown, amber. Ammonia alone gives a bright lemon-yellow.

Scores of other fixed and volatile oils, tested as described above, failed to give characteristic color tests. Homogeneous aromatic oils like safrol, apiol and anethol failed to give the color tests even after boiling for some time with concentrated alkalis. Under these conditions oil of wintergreen gave the same green color as salicylic acid.

Gallic Acid.—A–I, pink, amber, brown, black-brown; II, pink, pink-amber, grass-green, amber-green, brown, amber; III, pink, brown, amber. Alkalis alone give first a pink, then a grass-green and finally a brown color, but the action is greatly quickened and intensified by means of sodium hypobromite.

Tannic Acid.—A–I, II, pink, amber, brown, deep brown; III, pink, pink-amber, amber; IV, pink. Alkalis alone give first a pink, then a brown color; here as with gallic acid, owing to the oxidizing power of the hypobromite, the action is greatly quickened and intensified.

Aromatic Nitrogen Compounds.

Aniline.—A–I, orange-red, deep red-brown; II, smoky amber, deep orange; III, amber, dirty orange; IV, light yellow. A′–I, orange, deep brown; II, orange, deep brown; III, amber. With A′–I solutions, odor of phenylisocyanide.

o-Toluidine.—A–I, brick-red, violet, purple, purple-black, deep brown-black; II, brown-red or orange-red; III, red-amber; IV, light straw-yellow. A′–I, violet, purple, purple-black; II, yellow, pink-amber, brown-red; III, golden yellow. With A′–I solutions, odor of phenylisocyanide.

p-Toluidine.—A–I, pink, rose-red, red-brown; II, pink, dirty yellow. A′–I, violet, dark brown; II, pink-amber, golden brown.

These two toluidines and aniline are easily distinguished by the orange color with aniline and by the changes of color and deeper colors of *o*-toluidine.

p-Phenylenediamine.—A–I, bright blue-green, deep purple, black-purple, brown-black; II, deep grass-green, deep purple, dirty brown; III, grass-green, amber-brown, violet purple, curdy white precipitate;

IV, bright amber. A′–I, dark blood-red, purple, brown-black; II, deep brown-red; III, amber. B′–I, II, deep purple, brown; III, brown, amber. Very characteristic color effects.

m-Nitraniline.—A–I, yellow, dirty brown; II, ochre-yellow; III, light yellow; A′–I, red-brown; II, dirty brown; III, light yellow.

p-Sulpanilic Acid.—B′–I, deep red-brown; II, amber; III, light yellow.

Benzamide.—A′–I, II, yellow, deep brown, brown-black, precipitate; III, amber yellow. The color is not easily discharged by an excess of hypobromite. An intense odor of phenylisocyanide is given off.

Phenylurethane.—A′–I, brown or brown-red color, odor of phenylisocyanide; II, cloudy yellow. B′–I, orange, brown.

Phenylhdyrazine.—A′–I, II, dirty orange.

Ammonol, ammonia-phenylacetamide. B′–I, yellow-red colored precipitate; II, amber.

Fatty amides and amines fail to yield color effects with sodium hypobromite, in fact no *aliphatic* compound responds to this reagent. It is specifically an *aromatic* test reagent.

Alkaloids.

Some forty of the most common alkaloids and glucosides were tested with sodium hypobromite; only the following ones gave definite color reactions.

Morphine.—A′, B′–I, deep amber-brown; II, amber; III, light yellow. The test is best made with the use of ammonia; the color is discharged by an excess of hypobromite.

Codeine and Dionine gave the same as morphine, only less sensitive.

Apomorphine.—A–I, deep brown, deep chrome-green; II, pink-amber, deep brown, deep chrome-green, lighter green, amber; III, light pink, light yellow. This is a very characteristic reaction, particularly in solution II.

Physostigmine or Eserine.[1]—A–I, light red; II, pink. A′–I, deep blood-red; II, bright bichromate-red; III, rose-pink. Alkalis give a red color but the hypobromite with heat deeply intensifies the red.

Antipyrine.—A′–I, pink-amber. Color discharged by an excess of hypobromite.

Phenacetine.—B′–I, deep amber-brown; II, amber.

Acetphenetidine.—B–I, deep amber-brown; II, amber.

Though not giving characteristic color effects, some of the other alkaloids gave off characteristic odors. For instance scopolamine and hyoscyamine gave a phenylisocyanide-like odor, caffeine a methylamine odor, and atropine and cinchonidine other characteristic odors. From consideration of the above-described color reactions and negative results obtained with

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[1] With bleaching powder, an intensely red color. Eber, *Z anal. Chem.*, 28, 134; Ferreira, *Bl.* [3], 9, 753.

scores of other organic groups, it is concluded that hypobromite is an invaluable reagent for detecting and distinguishing phenolic and aromatic amino compounds. None of the aliphatic or terpene compounds tested gave color effects; only compounds of the types:

$$>OH \qquad >NH_2 \qquad >CONH_2$$

With *p*-phenylenediamine, it yields nearly quantitatively a white crystalline solid melting with decomposition at 105°. This and other products of the hypobromite reaction are being investigated.

SEATTLE, WASH., July 4, 1908.

THE OXIDATION AND THE REDUCTION OF β,γ-DIPHENYL-γ-CYANBUTYRIC ACID.

BY S. AVERY AND G. R. MCDOLE.

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Oxidation.—As additional evidence of the correctness of the constitution of the acid under consideration, the formation of which by the action of sodium hydroxide on cinnamic ester mixed with benzyl cyanide has been described by us[1] in a previous communication, we will briefly give the results obtained by oxidation.

The alkali salt of the acid was found to be attacked very readily by alkaline permanganate. Difficulty, however, was experienced in stopping the action till the greater part of the substance had been oxidized to benzoic acid. The oxidation of the acid with neutral permanganate is more easily controlled. The following procedure was found to give the most satisfactory results:

One and one-half grams of potassium permanganate were dissolved in about 100 cc. of water and 1 gram of the cyan acid stirred into the solution. After mixing as thoroughly as possible, the whole was heated on the water bath. The acid gradually went into solution and the odor of hydrocyanic acid became evident. Towards the end of the reaction an odor resembling acetophenone was noticed. As soon as the permanganate was completely reduced, the acid in the meantime having gone into solution, the product of the reaction was filtered from the manganese dioxide formed and precipitated by means of hydrochloric acid. Yield, 0.6 gram. By repeated recrystallization from alcohol, 0.3 gram of pure benzoyl hydrocinnamic acid was obtained. This substance was identified by the melting point 162°,[2] crystalline form (octahedrons),[3] and analysis of a silver salt which gave 30.1 per cent. Ag. Calculated, 29.9. The formation of benzoyl hydrocinnamic acid by oxidation of the cyan acid can be explained only on the supposition that the latter

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[1] THIS JOURNAL, 30, 596.

[2] *Ber.*, 21, 1350.

[3] *Ibid.*, 29, 2586.