were melted together. (B) They were boiled for several hours in toluene. (C) The sodium salt of the compound to be condensed was heated with with diphenylcarbamine chloride in toluene solution. Upon filtering and evaporation of the toluene solution, the product usually crystallized out; otherwise, ether was added and the solution cooled with ice. The products were purified by recrystallization.

Diphenyl-*p*-phenetylacetylurea was prepared by method (C) and also by direct acetylation of diphenyl-*p*-phenetylurea.

Summary

1. Diphenylcarbamine chloride reacts with the sodium salt of acetanilide to give first an additive compound. This indicates that the salt possesses the enol structure.

2. A number of new derivatives of diphenylcarbamine chloride have been prepared.

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

ORGANIC OXIDATIONS BY IODIC ACID

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This acid has been used only rarely, exclusively in acid solutions and almost entirely for producing color effects.[2]

We have found that iodic acid can be applied in neutral solution, as, for example, its characteristic effect on amidol; in acid solutions, with most amines and phenols; in alkaline solutions, with mercaptans, thioureas and benzoin. Because it has no effect on alcohols, most alkaloids,[3] gluco-

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[1] The material presented in this paper is from part of a thesis submitted by Theodore W. Evans, du Pont fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

[2] For a voluminous bibliography on the color tests for morphine, see Merck's "Reagenzien Verzeichnis," **1924**. For Strychnine, see Selmi, *Ber.*, **11**, 1692 (1902). For emetine, Peroni, *Boll. chim. farm.*, 273 (1907). The naphthols, Vincent, "Merck's Report," **1902**, p. 59. Guaiacol, Guerine, *J. pharm. chim.*, 173 (1903). Adrenalin, Frankel and Allers, *Biochem. Z.*, **18**, 40 (1904); Ewins, *J. Physiol.*, No. 4, 110 (1910); Bayer, *Biochem. Z.*, **20**, 183 (1906); Krauss, *ibid.*, **22**, 131 (1903). Since iodic acid gives color tests with creatinine and uric acid [Vitali, *L'Orosi*, **21**, 73 (1898)], the following tests for components of urine by iodic acid are doubtful: glucose, Jaworowski, *Chem. Z.*, 269 (1907); *Z. anal. chem.*, **42**, 463 (1907); bile pigments, Copranica, *ibid.*, **22**, 626 (1883); acetoacetic acid, Riegler, *Pharm.-Ztg.*, **1902**, 249. Aniline was oxidized to aniline black, Ostrogovich and Silbermann, *Bul. chim. soc. Roman stiinte*, **16**, 128 (1913).

[3] Warneke, *Arch. Pharm.*, **226**, 281 (1888), oxidized wrightine to oxywrightine by iodic acid; this product by means of other oxidizing agents has been attempted in vain.

sides, carbohydrates, etc., it is concluded that it is very selective in its action. Symmetrical diaryl thioureas give the corresponding ureas, but asymmetrical diaryl thioureas, all tri- and tetra-substituted thioureas are without action, as also are the mustard oils, and disulfides, sulfoxides, etc.

Through the use of iodic acid we have been able to develop improved methods of preparation of the disulfides, aryl cyanamides, symmetrical diaryl ureas, purpurogallin and benzilic acid.

Experimental

A large number of amino and phenolic compounds, alkaloids and glucosides were tested for the oxidizing effect of iodic acid. The method employed was to place in a beaker some aqueous iodate solution, a few milligrams of the substance to be tested, a few drops of acetic acid and pieces of silk and cotton cloth. The mixture was boiled until the dye was fixed on the fabrics. With the different amino and phenolic compounds every imaginable shade of brown was obtained on the silk. In most cases no dye was fixed on the cotton; whenever fixed, light browns, buffs and ochers were obtained. The diamine and alkylated anilines, especially, gave beautiful shades of brown. Some of these amino and phenolic compounds will be investigated.

Color Tests on Silk.—Phenol, light brown; catechol, guaiacol, resorcinol, diresorcinol, deep brown. The naphthols, yellow-brown, eugenol, gold-brown. Quinol, brown. Procaine, butyn, anesthesine, *p*-aminobenzoic acid, light brown. Aminophenol and amidol, red-brown; *p*-aminophenol, dark brown. Phloroglucinol, blood-red. After hydrolysis with hydrochloric acid, phoridzin, through yellow to blood red. This is the only glucoside that gave a positive test. Apomorphine, beautiful light green, through chrome green to green-black on silk; greenish-gray on cotton. Boldine and apocodeine, brown.

Action on Mercaptans.—A mixture of 3 g. of *p*-thiocresol, 6 g. of sodium iodate, 6 g. of sodium hydroxide and 90 cc. of water was heated on the water-bath for an hour. When cooled and neutralized, the di-*p*-tolyldisulfide precipitated. After recrystallization from alcohol it melted at 46°.

In an analogous manner dibenzyldisulfide, melting at 71°, was prepared.

Action on Thioureas.—Equal weights of thiocarbanilide, sodium iodate and sodium hydroxide in 100 cc. of water were heated to boiling until a plastic mass in the water was obtained. If this is filtered hot and washed with water, pure diphenylurea is obtained.

In a similar manner, 3,3′-dinitrothiocarbanilide yielded 3,3′-dinitrodiphenylurea, melting at 233°; phenyl-*p*-tolylthiourea gave phenyl-*p*-tolylurea melting at 212°.

Ethyl-N,N′-diphenylthiourea, N,N-methylphenylthiourea and N,N′-diphenylbenzylthiourea failed to react with iodate.

Preparation of Aryl Cyanamides.—When a mixture of equal weights of phenylthiourea, sodium iodate, sodium hydroxide and a double mass of water was heated to boiling for ten minutes, then cooled, filtered[3] and neutralized with acetic acid, a plastic

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[3] In the preparation of these aryl cyanamides, small quantities of the corresponding diarylureas always were formed—these constitute the precipitates found at this point.

mass precipitated. After decanting, washing with water and letting stand, it solidified. Its identity was established by heating with aniline, thus forming diphenylguanidine, melting at 147°.

In a similar manner *o*-tolylcyanamide and *p*-tolylcyanamide were prepared.

The Preparation of Purpurogallin.—When 100 cc. of a cold aqueous solution containing 8 g. of sodium iodate is slowly added with constant stirring to 10 g. of pyrogallol[4] dissolved in a little cold water, the reaction proceeds smoothly with a precipitation of 7.6 g. of purpurogallin. Assuming the reaction to be

$$2C_6H_6O_3 + NaIO_3 = C_{11}H_8O_5 + CO_2 + NaI + H_2O$$

this is equivalent to a 92% yield.

In order to test the validity of this equation, the carbon dioxide evolved was determined by absorbing it in a potash bulb. In two determinations each starting with 10 g. of pyrogallol and 8 g. of iodate, 1.2902 and 1.2899 g. of carbon dioxide were obtained. In each case the yield of purpurogallin was 6.5 g. These figures represent a 78% yield of purpurogallin and a 74% yield of carbon dioxide. This would seem to indicate that for each molecule of purpurogallin formed a corresponding molecule of carbon dioxide is liberated.

The Preparation of Benzilic Acid.—Benzoin is directly convertible into benzilic acid by the action of sodium iodate in concentrated sodium hydroxide. When it is added to a hot concentrated solution of these, the reaction proceeds spontaneously, and substantially a quantitative yield of benzilic acid is obtained, in accordance with the reaction

$$3C_6H_5CHOHCOC_6H_5 + NaIO_3 + 3NaOH = 3(C_6H_5)_2COHCOONa + 3H_2O + NaI$$

From Pure Benzoin.—To a beaker containing 20 g. of sodium hydroxide and 7 g. of sodium iodate, sufficient water is added to make a boiling hot solution; then 20 g. of benzoin is put in and stirred with a rod. The purplish colored mixture is then heated and stirred. Finally, when the purple color is entirely discharged, sufficient water is added to dissolve the solids to a clear solution. Concentrated hydrochloric acid is gradually added and the iodine and traces of benzoic acid are expelled by boiling. On cooling, filtering and drying, about 20 g. of crude benzilic acid is obtained. This is dissolved in boiling benzene, filtered and cooled rapidly, when about 18 g. of pure benzilic acid is obtained. From the benzene filtrate 2 g. of impure benzilic acid may be recovered. The crude benzoin obtained from benzaldehyde may be used directly in this preparation, but a lessened yield is obtained.

Summary

Iodic acid has been shown to be a very selective oxidant. By its use various improved preparations have been developed.

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[4] Various oxidizing reagents have been used to prepare purpurogallin from pyrogallol. These were compared by Perkin and Stevens, who contributed what they considered the best reagent, namely sodium nitrite and acetic acid. Their best yields were 30–40% [*J. Chem. Soc.*, **83**, 194 (1903)].