

showed the following peaks: 3.3, 3.45, 6.18, 6.35, 6.55, 6.7, 6.95, 7.45, 7.75, 7.9, 8.2, 8.5, 8.7, 9.35, 12.15, 13.05, 13.4, 4.35 μ (potassium bromide pellet).

Anal. Calcd. for $C_{10}H_9O_6Cu$: C, 71.98; H, 5.07; Cu, 7.62. Found: C, 71.80; H, 5.09; Cu, 7.52.

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The Nitration of 3-Chloro-4-iodonitrobenzene

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Halonitrobenzenes are important intermediates in the synthesis of a variety of compounds such as phenylhydrazine,² phenylsemicarbazide,³ benzotriazole,^{4,5} phenoxazine,⁶ and anthranil.⁷ In a program^{8,9,10} on preparation of such compounds, the nitration of 3-chloro-4-iodonitrobenzene was undertaken for detailed investigation. Although it might give a mixture of dinitroisomers, only 1-iodo-2-chloro-4,6-dinitrobenzene¹¹ was isolated. It reacts with hydrazine hydrate to give 2-chloro-4,6-dinitrophenylhydrazine.¹²

EXPERIMENTAL¹³

Nitration of 3-chloro-4-iodonitrobenzene. To a suspension of 3-chloro-4-iodonitrobenzene (10 g.) in conc. sulfuric acid (42 ml., d., 1.82), fuming nitric acid (14 ml., d., 1.5) was added dropwise with vigorous shaking. When all the nitric acid was added, it was heated on a water bath for an hour and poured on crushed ice. The yellow crystalline solid was filtered and recrystallized successively from acetic acid, methanol, and ethanol to give 1-iodo-2-chloro-4,6-dinitrobenzene (7 g.) in yellow needles, m.p. 118°. Mixed melting point with an authentic sample of 1-iodo-2-chloro-4,6-dinitrobenzene remained undepressed.

Anal. Calcd. for $C_6H_2N_2O_4ClI$: Cl + I, 49.4. Found: Cl + I, 49.2.

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(2) R. S. Kapil and S. S. Joshi, *J. Indian Chem. Soc.*, **36**, 417 (1959).

(3) R. S. Kapil and S. S. Joshi, *J. Indian Chem. Soc.*, **36**, 505 (1959).

(4) S. S. Joshi and S. P. Gupta, *J. Indian Chem. Soc.*, **35**, 681 (1958).

(5) H. Singh and R. S. Kapil, *J. Org. Chem.*, **25**, 657 (1960).

(6) S. S. Joshi and S. P. Gupta, *J. Indian Chem. Soc.*, **36**, 329 (1959).

(7) S. S. Joshi and I. R. Gambhir, *J. Am. Chem. Soc.*, **78**, 2222 (1956).

(8) R. S. Kapil and S. S. Joshi, *J. Indian Chem. Soc.*, **36**, 593 (1959).

(9) R. S. Kapil, *J. Chem. Soc.*, **24**, 4127 (1959).

(10) R. S. Kapil, *J. Org. Chem.*, in press (1960).

(11) S. S. Joshi and D. S. Deorha, *J. Chem. Soc.*, 2414 (1957).

(12) S. S. Joshi and D. S. Deorha, *J. Indian Chem. Soc.*, **28**, 34 (1951).

(13) All melting points are uncorrected.

2-Chloro-4,6-dinitrophenylhydrazine. To a cooled solution of 1-iodo-2-chloro-4,6-dinitrobenzene (1 g.) in ethanol twice the equivalent quantity of hydrazine hydrate was added. 2-Chloro-4,6-dinitrophenylhydrazine was filtered after an hour, m.p. 175° (lit.¹² m.p., 175°). After two recrystallizations from ethyl acetate, yellow needles (0.5 g.) melting at 190° were obtained.

Anal. Calcd. for $C_6H_5N_4O_4Cl$: Cl, 15.2. Found: Cl, 15.1.

The *acetyl* derivative prepared by the acetic acid-acetic anhydride method crystallized in lemon yellow needles from ethanol, m.p. 189°.

Anal. Calcd. for $C_8H_7N_4O_5Cl$: Cl, 12.9. Found: Cl, 12.7.

The *benzoyl* derivative prepared by the pyridine method crystallized in colorless needles from ethanol, m.p. 208°.

Anal. Calcd. for $C_{13}H_9N_4O_5Cl$: Cl, 10.5. Found: Cl, 10.2.

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Reactions of Nitrohydroxychalcones. Oxidation by Hydrogen Peroxide in Alkaline Medium

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In earlier publications,³ we had communicated our observations regarding the isomerization of some nitrohydroxychalcones to flavanones and the conversion of nitrohydroxychalcones to flavones. The behavior of some of these chalcones towards alkaline hydrogen peroxide oxidation is now reported. The chalcones studied were 2',4'-dihydroxy-3'-nitrochalcone derivatives (type I) and 2',6'-dihydroxy-3'-nitrochalcone derivatives (type II). The type I chalcones on oxidation yielded the corresponding 3,7-dihydroxy-8-nitroflavone derivatives (type III), while the type II chalcones gave 2-benzylidene-4-hydroxy-7-nitro-3(2H)-benzofuranone derivatives (type IV). The constitutions were fully supported by color tests and analytical values.

The oxidation of type I chalcones gave products that gave a yellow coloration with concentrated sulfuric acid, and with ferric chloride a pale purplish-brown color characteristic of 3-hydroxy flavones. The enhanced halochromism of the 3-hydroxyflavones with *ortho* and *para* alkoxy substitution is shown in Table I.

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