NOTES.

The Preparation of 2-Iodobenzoquinone. By HERBERT H. HODGSON and DONALD E. NICHOLSON.

2-*Iodobenzoquinone*, the remaining unknown monohalogeno-*p*-benzoquinone, has now been prepared by the oxidation of 3-iodo-4-aminophenol with ferric sulphate (cf. Smith and Irwin, *J. Amer. Chem. Soc.*, 1941, **63**, 1036). Ferric chloride and chromic acid, though suitable for the oxidation of the other three 3-halogeno-4-aminophenols, liberated a considerable amount of iodine when reacting with 3-iodo-4-aminophenol, with consequent production of an impure 2-iodobenzoquinone in very inferior yield.

3-Iodo-4-nitrosophenol (3 g.) (Hodgson and Nicholson, J., 1939, 1808) was made into a paste with hydrochloric acid (2 c.c., *d* 1·16) and water (8 c.c.), and the well-stirred mixture reduced near its b. p. by the addition of iron filings (2·5 g.) during 10 minutes. The mixture, after being heated for 5 minutes longer on the water-bath to complete the reduction, was submitted to rapid filtration on a previously warmed Buchner funnel. On cooling, the filtrate deposited 3-iodo-4-aminophenol in colourless plates, m. p. 145° after recrystallisation from boiling water (Hodgson and Kershaw, J., 1928, 2704, give m. p. 144·5°). A further quantity was obtained by three extractions of the residue from the iron reduction with boiling water (10 c.c. each time) (total yield, 1 g.) When the 3-iodo-4-aminophenol (1 g.) was mixed with water (15 c.c.) and ferric sulphate (5 g.) and steam-distilled (the flask could not be externally heated, since iodine then separated), 2-iodobenzoquinone passed over. It crystallised from hot water in orange-red prisms, m. p. 62° (Found: I, 54·1. $C_6H_3O_2I$ requires I, 54·2%), which had a pronounced quinone odour readily distinguished from that of iodine. Oximation was carried out by addition of a slight excess of hydroxylamine hydrochloride, dissolved in the minimum amount of water, to an alcoholic solution of 2-iodobenzoquinone which contained sodium acetate; after 12 hours, the monoxime separated as its stable tautomeride, 2-iodo-4-nitrosophenol; it crystallised from benzene in yellow needles, m. p. 152° (decomp.) [Hodgson and Moore, J., 1925, **127**, 2260, give m. p. 152° (decomp.)] (Found : N, 5·7; I, 50·9. Calc. : N, 5·6; I, 51·0%).

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Preparation and Properties of p-*Thiolbenzoic Acid.* By D. BRAMLEY and N. H. CHAMBERLAIN.

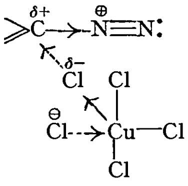
REPETITION of the procedure of Smiles and Harrison (J., 1922, **121**, 2024) for the preparation of this compound gave a white powder containing (by iodine titration) less than 1% of the required thiol. If, however, during reduction of the *p*-chlorosulphonylbenzoic acid, the temperature is maintained at 90—100°, the product is a yellow crystalline powder, m. p. 217°, freely soluble in alcohol, ether and acetone, and containing by iodine titration 99% of thiolbenzoic acid. The specimen contained traces of zinc, which repeated crystallisation from aqueous alcohol failed to remove (Found : C, 53·65; H, 4·0; S, 19·5. Calc. for $C_7H_6O_2S$: C, 54·5; H, 3·9; S, 20·8%).—LEEDS UNIVERSITY. [*Received, February* 5*th*, 1942.]

An Interpretation of the Sandmeyer Reaction. Part II. Some Corrections. By HERBERT H. HODGSON, STANLEY BIRTWELL, and JOHN WALKER.

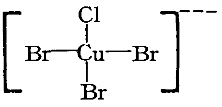
SINCE the publication of Part I (J., 1941, 770), Dr. F. G. Mann has kindly drawn our attention to the fact that there is little reliable evidence for the Cu–Cu link in cuprous compounds as depicted in (I) and (II) of Part I (p. 771), because in those compounds where detailed structure is known, the cuprous atoms are too far apart for such direct linkage; moreover, such structures usually enable the cuprous atoms to acquire 7 electrons and thus attain the krypton structure (cf. Wyckoff and Posnjak, *J. Amer. Chem. Soc.*, 1922, **44**, 30; Davey, *Physical Rev.*, 1922, **19**, 248; Goldschmidt, *Z. Elektrochem.*, 1928, **34**, 459; Mann, Purdie, and Wells, J., 1936, 1503). The active complex cuprous anion in a solution of cuprous chloride in hydrochloric acid will therefore be more correctly represented by (A) than by (I) (*loc. cit.*, p. 771), with the corresponding modification for (II) (*loc. cit.*, p. 771). This formulation would also be in harmony with the established compound, $K_3Cu(CN)_4$, which Grossmann and von der Forst (*Z. anorg. Chem.*, 1905, **43**, 94) have shown represents the most stable type of complex cuprous cyanide.

On analogy for the mixed Sandmeyer reactions, the formulæ for the complex anions of cuprous chloride with hydrobromic acid and of cuprous bromide with hydrochloric acid would then tentatively be (B) and (C), in which the bromine would tend to become δ-rather than the chlorine atoms.

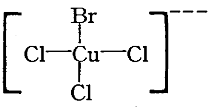
These anionic formulæ would even more readily account for the preponderance of bromo- and chloro-products found respectively when the anions (B) and (C) react with diazonium salts. The proposed mechanism for the reaction is of course undisturbed by this proposal for bringing the structures of the complex anions into line with current data.



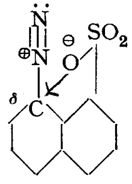
(A.)



(B.)



(C.)



(D.)

Prof. W. M. Cumming also has pointed out to us that the statement concerning the general reaction of iodides with diazonium compounds reported by Saunders ("The Aromatic Diazo-compounds," E. Arnold and Co., London, 1936, p. 154) as found by Cumming and Muir (*J. Roy. Tech. Coll.*, 1936, **3**, 562) requires considerable modification. The actual sentence from Saunders (*op. cit.*) on which we had relied, as the original paper was then not accessible to us, runs as follows : "An exception to this very general reaction has been recently reported by Cumming and Muir, who have found that 1-diazonaphthalene-8-sulphonic acid when treated with potassium iodide in pyridine solution affords *not* the iodo-compound but naphthalene-1 : 8-sultone." It would not be inferred from this statement that the yield of 1 : 8-iodonaphthalene sulphonate had been 70% and that the so-called pyridine solution was composed of 1 c.c. of pyridine in 150 c.c. of water, and the amount of the 1 : 8-naphthasultone, which was not estimated, could not be greater than 30%. Further, when pyridine was absent "the yield of naphthasultone was higher with a corresponding poor yield of iodo-salt, while the formation of 1 : 8-naphthasultone occurred readily when 1-diazonaphthalene-8-sulphonic acid was heated alone or in aqueous solution." This last reaction conforms to the scheme of interpretation given in the Sandmeyer paper, *viz.*, the anionoid sulphuric bound-ion seeks the kationoid carbon to which the diazo-group is attached (D; VII*c*, p. 774 of the first paper).

It would appear, therefore, that in the decomposition of 1-diazonaphthalene-8-sulphonic acid by potassium iodide in the presence of less than 1% of pyridine, two simultaneous reactions occur : (1) the normal decomposition by iodide as given in the Sandmeyer paper and (2) the reaction above. The pyridine would thus appear to play the rôle depicted in (VII*a*) (*loc. cit.*, p. 774), *viz.*, formation of an ephemeral diazoamino-compound, which would retard reaction (2) and promote reaction (1), since in its absence the main product is 1 : 8-naphthasultone.

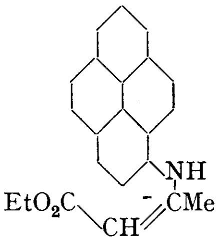
The authors cordially thank Prof. W. M. Cumming and Dr. F. G. Mann for their interest in this work.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, February* 16*th*, 1942.]

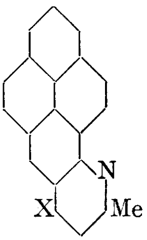
Derivatives of 1′-*Aza*-3 : 4-*benzpyrene.* By M. WEIZMANN and F. BOGRACHOV.

THE application of the Skraup synthesis to 3-aminopyrene (Vollmann and co-workers, *Annalen*, 1937, **531**, 52) leads to 1′-aza-3 : 4-benzpyrene. We have found that the same ring system is readily obtainable from 3-aminopyrene and ethyl acetoacetate.

Ethyl β-3-*Pyrenylaminocrotonate* (I).—To a filtered solution of 3-aminopyrene (3 g.) (Vollmann and co-workers, *ibid.*, p. 109) in ethyl alcohol, ethyl acetoacetate (3·5 c.c.) was added at room temperature. The yellowish-green product was collected after 24 hours and recrystallised from *iso*propyl alcohol; it had m. p. 129°; yield, 85% (Found : C, 79·8; H, 5·5. $C_{22}H_{19}O_2N$ requires C, 80·2; H, 5·8%).

(I.)





(II.)

4′-*Hydroxy*-2′-*methyl*-1′-*aza*-3 : 4-*benzpyrene* (II, X = OH).—(I) was diluted with liquid paraffin (5 parts) and heated at 220° for 30 mins. The crystalline product was washed with benzene and recrystallised from nitrobenzene; m. p. 350°; yield, 90% (Found : C, 84·5; H, 5·0; N, 5·2. $C_{20}H_{13}ON$ requires C, 84·8; H, 4·6; N, 5·0%).

4′-*Chloro*-2′-*methyl*-1′-*aza*-3 : 4-*benzpyrene* (II, X = Cl).—The foregoing substance (12·5 g.) was heated with phosphorus pentachloride (10 g.) in ethylene dichloride (20 g.) for 2 hours at 130—140° and for 1 hour at 160—170°. The mixture was poured on ice, and the solid product dissolved in alcohol and reprecipitated with water. It formed yellow crystals, m. p. 207°, from pyridine (Found : Cl, 11·7. $C_{20}H_{12}NCl$ requires Cl, 11·8%).—THE HEBREW UNIVERSITY, JERUSALEM. [*Received, March* 6*th*, 1942.]