From our work we conclude that this method of replacement of amino groups by bromine is excellent in certain cases when the nucleus is not attacked by bromine under the conditions of the experiment, and when applicable is preferable to other procedures because of the simplicity of operation and the saving of time.

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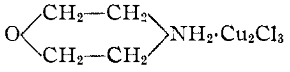
Morpholine Hydrochloride Complexes of Cuprous and Cupric Chloride

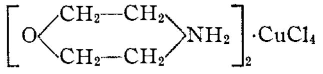
BY WALTER H. C. RUEGGEBERG, GORDON N. JARMAN AND RICHARD B. WEARN[1]

Complexes of morpholine with several divalent metals have been reported[2] but detailed data on copper complexes are lacking.

It was found that two complexes of cuprous chloride were obtained after reaction with morpholine hydrochloride. One of these substances, I, constituting about 90% of the reaction product, is the normal reaction product expected from cuprous chloride while the other, II, obtained in about 10% yield, is that derived from cupric chloride which was originally present in the cuprous chloride used.



I (white)



II (green)

There are also strong indications that I can be transformed into II. This transformation can easily be observed visually by the color change from white to green occurring when I is exposed to the atmosphere.

The cuprous and cupric complexes are also differentiated by their solubility in water. While the green cupric complex is soluble in water, a 10% solution of hydrochloric acid is required to dissolve the cuprous complex.

Experimental

Preparation of Compound I.—To morpholine (728.6 g.), obtained from the Carbide and Carbon Chemicals Corporation was added dropwise concentrated hydrochloric acid (305.3 g.) in a round bottom flask equipped with a mechanical stirrer, dropping funnel, thermometer, gas inlet and gas escape tubes and at such a rate that by means of moderate cooling with an ice–water-bath, the temperature did not exceed 50°. After all of the hydrochloric acid had been added, a stream of nitrogen was passed through the flask and subsequently, cuprous chloride (655.4 g.), C. P. grade obtained from the Fischer Scientific Co., was added at 50°. The entire deep-brown reaction mixture was stirred for several hours. All but about 10 to 20 g. of a solid material, probably cuprous chloride, went into solution. Upon cooling, a copious separation of crystals occurred. The yield was about 90%.

About 20 g. of the crude crystalline product was sucked dry on a Büchner funnel in an atmosphere of nitrogen. The crude crystals so obtained were washed with acetone and the acetone washings were set aside for the isolation of compound II. The cuprous chloride–morpholine hydrochloride complex so formed is a white crystalline material which tends to darken upon prolonged exposure to air. After some darkening at 103°, it was found to melt, with decomposition, at 110.5–112°.

Anal. Calcd. for $C_4H_{10}NOCu_2Cl_3$: Cu, 39.53; Cl, 33.07; N, 4.36. Found: Cu, 39.63; Cl, 32.62; N, 4.15.

It was found that compound I will react in concentrated solution with acetylene to form an orange-yellow substance which upon 5-fold dilution with water deposited a purplish red crystalline complex. This complex is probably $I \cdot C_2H_2$. Further work is required to identify this material.

Isolation of Compound II.—After concentrating and cooling the acetone washings obtained in the purification of the cuprous complex, I, above, a crop of fine bright green crystals was obtained. After drying, it was found that this complex melted to a dark brown liquid at 160–165°. If complex II is allowed to cool after having been heated to 160°, the green color characteristic of the cupric complex reappears. If, however, this material is heated above 160°, decomposition occurs to such an extent that, after cooling, only a brownish black fluid remains.

Anal. Calcd. for $C_8H_{20}N_2O_2CuCl_4$: Cu, 16.66; Cl, 37.16; N, 7.34. Found: Cu, 16.5; Cl, 36.81; N, 7.03.

CHEMICAL CORPS TECHNICAL COMMAND
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[2] Haendler and Smith, THIS JOURNAL, **63**, 1164 (1941).

Derivatives of 5-Chloro-8-hydroxyquinoline

BY M. WEIZMANN AND E. BOGRACHOV

A number of syntheses in the series of 5-chloro-8-hydroxyquinoline was carried out. Derivatives of this substance were expected to have some antimalarial activity, and also to be effective against trypanosomae[1] and amoebae.[2] These compounds thus supplement the recent work by Lauer[3] and by Elderfield.[4]

The condensation of 4-chloro-2-aminophenol with ethyl acetoacetate proceeded easily at relatively low temperature, giving the substituted amino-crotonate, while 4-chloro-2-amino*anisole* reacted only at 160° and gave 2-methoxy-5-chloroacetoacetanilide. Cyclization of the two products led to 4,8-dihydroxy-5-chloroquinaldine (I) and 2-hydroxy-4-methyl-5-chloro-8-methoxyquinoline (II), respectively.

The corresponding Skraup syntheses of 8-hydroxy and 8-methoxy-5-chloroquinoline proceeded with equal ease (yield, 35 and 40%, respectively), as did the Doebner–Miller reaction (condensation with paraldehyde) which led to 8-hydroxy- and 8-methoxy-5-chloroquinaldine. The latter condensed with ortho and para-nitrobenzaldehyde

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[1] Chiang and Hartung, *J. Org. Chem.*, **10**, 21 (1945); Browning and co-workers, *Proc. Roy. Soc.* (London), **113B**, 293 (1933); *J. Path. Bact.*, **27**, 121 (1924); *Brit. Med. J.*, II, 326 (1923).

[2] Vioform is a derivative of 5-chloro-8-hydroxyquinoline.

[3] Lauer, Arnold, Tiffany and Tinker, THIS JOURNAL, **68**, 1268 (1946).

[4] Elderfield and co-workers, *ibid.*, **68**, 1584 (1946).