

A New Method for the Oxidation of 2-Keto-1,2,3,4-tetrahydroquinoxaline, Investigations on the Complex Formed Between 2-Hydroxyquinoxaline and Cuprous Chloride

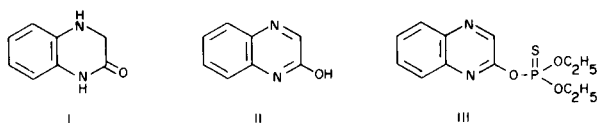
Naleen Borthakur, Alok K. Bhattacharya, Rajendra Prasad,
Avinash Garg and Ramesh C. Rastogi

Regional Research Laboratory, Jorhat, Assam 785006, India
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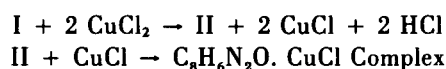
2-Keto-1,2,3,4-tetrahydroquinoxaline I is rapidly oxidised to 2-hydroxyquinoxaline II on reaction with cupric chloride. This is an oxidation-reduction reaction in which the cupric chloride in the process is reduced to cuprous chloride. The latter instantaneously reacts with II forming an insoluble brick red complex. Compound II can be regenerated from the complex by treatment with alkali. The properties of this new complex are discussed.

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2-Keto-1,2,3,4-tetrahydroquinoxaline I was reported (1) to be easily oxidised to II in the presence of alkaline hydrogen peroxide, silver nitrate or even air. An attempt to study this oxidation in the presence of cupric chloride as the catalyst led to the formation of a brick red complex. Complexes between nitrogen heterocycles and Cu^{++} are known (2) and a quinoxaline derivative was also reported to react with Cu^{++} ion (3). We report here for the first time the oxidation of I with cupric chloride and also the complex formation between II and cuprous chloride.



Cupric chloride is known to easily reduce to cuprous chloride with the evolution of hydrogen chloride in the presence of a variety of reducing agents (4). It has also been used for dehydrogenation of hydrocarbons (5). In the reaction of I with cupric chloride also hydrogen chloride was liberated, thus making the reaction mixture highly acidic (*vide* Experimental). The reaction proceeded as follows:



The same complex was instantaneously obtained by mixing cuprous chloride with II. Quinalphos III an organophosphorus pesticide obtained from II also gave the same complex on reaction with cupric chloride. Compounds of the type III were reported (6) to be hydrolysed by Cu^{++} ions. Thus, during the hydrolysis of III by cupric chloride, II must have been formed and also the cuprous chloride, which then reacted to give the complex. The identity of the complexes from the above different sources were confirmed by their superimposable ir spectra as well as their DTA curves; the rate of weight loss in all the three cases were the same.

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The complex formation was observed even when the I and cupric chloride were mixed and stirred in a nitrogen atmosphere; this excluded the possibility of oxidation of I by air. 2-Hydroxyquinoxaline was unreactive toward cupric chloride. However, if II was treated with cupric chloride in the presence of a reducing agent like zinc foil (4), complex formation was observed.

The complex was stable to hot acid or water (*vide* Experimental). Though I and III yielded II on treatment with cupric nitrate, it did not give any of the complex; this could be due to the fact that cuprous nitrate was too unstable and therefore could not form the complex.

The uv spectrum of the complex in aqueous acidic solution showed λ_{max} at 249, 286 and 341 nm which are characteristic of II; the slight hypochromic shift was due to change of solvent. The N-H and C=O stretching vibrations of the complex were observed at 3320 (m) and 1660 (s) cm^{-1} , respectively, which were at a slightly higher region than the reported value for II (8). The sodium salt of II did not react with cuprous chloride. This could mean that the complex was more easily formed with the keto form of II (rather than enol form). The mass spectrum of the complex (taken at 255°) showed M^+ at 146 corresponding to II. The next lower peak was at 118. No peak was observed at 129 ($\text{M}^+ - \text{OH}$; present in the mass spectrum of II), thereby indicating perhaps that the complex has a higher contribution from the keto form of II (than in II itself).

The difference in the reactivity of keto and enol form (*i.e.*, the Na Salt) toward cuprous chloride and the spectral data indicated that the amide nitrogen was involved in the complex formation and the keto form was more reactive (toward cuprous chloride) because of the stronger electron donating ability of the SP^3 nitrogen over the SP^2 nitrogen atom. The common coordination number adopted by Cu^+ is four but the coordination number of two (linear) is also known (9); the complex appears to be of later type.

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EXPERIMENTAL

The ir (potassium bromide pellets) data were recorded on a 237-B Perkin-Elmer spectrophotometer. The DTA curves were recorded on a Paulik-Paulik-Erdey System MOM derivatograph. The uv spectrum was recorded on a Beckmann DU2 and mass spectral analysis was carried on AEI MS-30 mass spectrometer.

Preparation of 2-Hydroxyquinoxaline-Cuprous Chloride Complex.

To a warm and well stirred solution of 2-keto-1,2,3,4-tetrahydroquinoxaline (10) (14.8 g., 0.1 mole) was added an alcoholic solution of cupric chloride dihydrate (17.0 g., 0.1 mole). The neutral solution became dark immediately and on refluxing a brickcoloured precipitate gradually started to settle out. After two hours the reaction mixture was cooled and filtered, leaving a highly acidic filtrate. The brick red solid (13.7 g.) decomposed slowly above 250°, was insoluble in water and alcohol but soluble in hot acetonitrile giving a reddish yellow solution.

The complex could be recovered unchanged after refluxing with water for one hour, or with concentrated hydrochloric acid for 0.5 hour. On shaking with 10% sodium hydroxide for ten minutes, the complex went into solution precipitating copper in the form of the hydroxide and the filtrate on neutralisation yielded 2-hydroxyquinoxaline (II) having a superimposable ir spectrum with an authentic sample.

Anal. Calcd. for $C_8H_6N_2O \cdot CuCl$: Cu, 25.5; Cl, 14.4. Found: Cu, 25.2; Cl, 14.5.

Reaction of 2-Hydroxyquinoxaline II with Cuprous Chloride.

A suspension of II in alcohol and white cuprous chloride in alcohol, on mixing and shaking readily gave a brick red complex which was found identical with the complex obtained from I and cupric chloride, by ir and DTA.

Reaction of Quinalphos with Cupric Chloride.

An alcoholic solution of quinalphos (12) was mixed with an alcoholic solution of cupric chloride dihydrate and warmed when the red complex

started appearing slowly. This complex was found identical with the complex from I and cupric chloride by superimposable ir and DTA. Acknowledgement.

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