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ORGANIC SYNTHESIS BY MEANS OF METAL COMPLEXES. XVI.[1)]

EFFICIENT CATALYTIC OXIDATION REACTIONS OF o-PHENYLENEDIAMINE, DIHYDRAZONES OF α-DIKETONES, AND HYDRAZIDES OF CARBOXYLIC ACIDS USING COPPER SALTS

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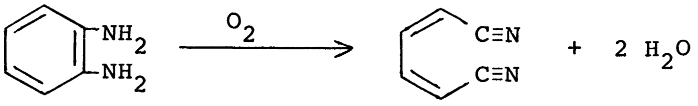
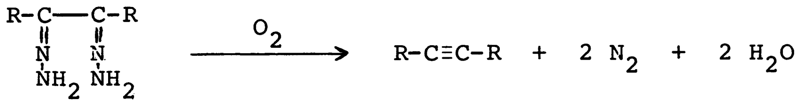
Oxidations of o-phenylenediamine to cis,cis-mucononitrile, dihydrazones of α-diketones to acetylenes, and hydrazides of carboxylic acids to the corresponding acids can be carried out smoothly at room temperature and under atmospheric pressure of oxygen by using a catalytic amount of copper salts.

In previous papers, we have shown that oxygen-treated Cu_2Cl_2 in pyridine is a useful system for efficient oxidation of various nitrogen compounds under very mild conditions. Oxidative cleavage of o-phenylenediamine gives cis,cis-mucononitrile in a high yield.[2)] Dihydrazones of α-diketones can be converted into acetylenes.[3)] Also hydrazides of carboxylic acids are transformed to corresponding acids, esters and amides by using Cu_2Cl_2 or $Cu(OAc)_2$ as an oxidizing agent.[1)] These reactions are useful for organic synthesis, because usually they are carried out by using more expensive and toxic mercury[4)] or lead[5)] compounds as the oxidizing agents. In these reactions, it is assumed that the real oxidizing agent is cupric state generated in situ from cuprous state by absorbing oxygen, and stoichiometric amounts of the copper salts were used for the oxidation. In order to make the reactions the more useful, we attempted to carry out the oxidation as a catalytic process with regard to the copper salts by taking advantage of the fact that cuprous state can be converted to cupric state by oxygen under selected conditions. In this communication, the attempted catalytic processes of the above reactions are presented.

A pyridine solution of Cu_2Cl_2 (9.9 g, 0.05 mol in 200ml) was prepared in a flask and treated with oxygen until no more absorption was observed. o-Phenylenediamine (27.0 g, 0.25 mol) dissolved in 300 ml of pyridine was added slowly into the flask with efficient stirring under oxygen atmosphere at room temperature in 5 hr. After the reaction, pyridine was evaporated and the residue was treated with dichloromethane and dilute hydrochloric acid. From the organic layer, mucononitrile was obtained as crystals (24.4 g, 94%). When the addition of phenylenediamine was too fast, the yield decreased drastically. Also with 16:1 mol ratio of the diamine to Cu_2Cl_2, the nitrile was obtained in 90% yield by adding the diamine in 20 hr. Cupric salts can not be used.



The oxidation of dihydrazone of 6,7-dodecanedione was carried out similarly. A pyridine solution of Cu_2Cl_2 (0.08 g, 0.4 mmol in 10 ml) was prepared and treated with oxygen. The dihydrazone (0.453 g, 2 mmol) in pyridine (17 ml) was added in 3 hr. During the reaction, oxygen was passed into the stirred solution. The reaction mixture was treated in the same manner as shown above. Crude oily 6-dodecyne was purified by passing through a silica gel column to give 0.238 g (71.5%) of the product which showed one spot on a thin layer chromatogram. Oxidation of dihydrazone of benzil was carried out more conveniently in methanol using $Cu(OAc)_2$ as a catalyst. At first we confirmed that the dihydrazone (1.19 g, 5 mmol) was oxidized with 4 equivalents of $Cu(OAc)_2 \cdot H_2O$ (4.0 g, 20 mmol) with evolution of ca. 250 ml of nitrogen in 12 min to give diphenylacetylene in 94% yield under nitrogen atmosphere. Then, $Cu(OAc)_2 \cdot H_2O$ (0.2 g, 1 mmol, 0.05 equiv.) was dissolved in methanol (20 ml). The dihydrazone (1.19 g, 5 mmol) dissolved in a mixture of benzene (15 ml) and methanol (10 ml) was added in 10 min, and the solution was stirred with constant bubbling of oxygen for one and a half hr. After the usual work-up, crude crystals of diphenylacetylene were obtained and purified by passing a silica gel column to give 0.69 g (78%) of pure product (m.p. 59-61°C).



$$R\text{-}C(=N\text{-}NH_2)\text{-}C(=N\text{-}NH_2)\text{-}R \xrightarrow{O_2} R\text{-}C{\equiv}C\text{-}R + 2\,N_2 + 2\,H_2O$$

Hydrazide of benzoic acid (0.68 g, 5mmol) in methanol (20 ml) was added dropwise into a methanolic solution of $Cu(OAc)_2$ (0.2 g, 1 mmol, 0.1 equiv. to the hydrazide) in 1 hr. Oxygen was bubbled into the stirred solution for one hr. Methanol was evaporated and the residue was treated with dichloromethane and dilute hydrochloric acid. The organic layer was extracted with aqueous sodium carbonate solution, which was acidified with hydrochloric acid. The precipitated benzoic acid was collected (0.42 g, 69%). When 2.5 mmol (0.25 equiv.) of $Cu(OAc)_2$ was used, benzoic acid was obtained in 82% yield. Although the reaction was carried out in methanol, only a negligible amount of methyl benzoate was formed.

$$PhCONHNH_2 \xrightarrow{O_2} PhCOOH + N_2 + H_2O$$

The above shown successful catalytic processes are very practical and markedly enhance the synthetic usefulness of the oxidation reactions.

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