

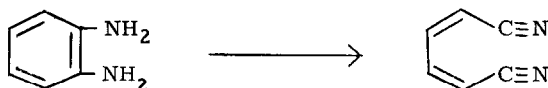
ORGANIC SYNTHESIS BY MEANS OF METAL COMPLEXES. XII¹
COPPER CATALYZED OXIDATION OF DIHYDRAZONES TO ACETYLENES

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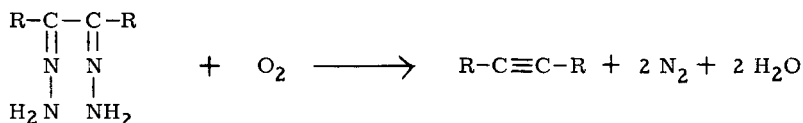
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A smooth oxidation of *o*-phenylenediamine catalyzed by cuprous chloride in pyridine at room temperature to form *cis*, *cis*-mucononitrile in a high yield has been reported.² Cuprous chloride in pyridine is an extremely efficient catalyst system under very mild conditions.



This paper describes further successful application of this catalyst system to the oxidation of hydrazones.

The oxidation of dihydrazones of α -diketones was attempted under similar conditions as those of the *o*-phenylenediamine oxidation and the reaction took place smoothly to give acetylenes in a high yield. The following is a typical example.



Cuprous chloride (1.0 g) was added to pyridine (25 ml) in a flask connected to a gas buret filled with oxygen. Oxygen was introduced to the catalyst solution with vigorous stirring. Rapid absorption of oxygen (about 50 ml) stopped after 15 minutes. Then a solution of benzil dihydrazone (1.19 g) in pyridine (20 ml) was added dropwise in 15 minutes at room temperature with stirring. Exothermic reaction proceeded rapidly with nitrogen evolution. The stirring was continued for one hour under the oxygen atmosphere to ensure the completion of the oxidation. A large portion of pyridine was

removed under reduced pressure and the residue was added to cold dilute hydrochloric acid. The solution was extracted with ether. The ethereal solution was dried and evaporated to give crude diphenylacetylene, which was recrystallized from ethanol to give 0.86 g (96.6 %) of crystals and identified by mixed melting point determination (59~60 °C). Similarly acetylenes substituted with aliphatic groups are prepared.

For example, 4-octyne was obtained from dihydrazone of 4,5-octanedione in 89.1% yield.

The oxidation of dihydrazones to acetylenes is a well known reaction, which is carried out by using various strong oxidizing agents, such as mercuric oxide,³ silver trifluoroacetate,⁴ and lead tetraacetate.⁵ In comparison, the oxidation with cuprous chloride reported in this paper is superior to these methods in that the reaction proceeds under mild conditions in high yields by using the cheaper reagent.

By the similar procedure, monohydrazone of benzil (2.24 g) was oxidized with oxygen catalyzed by cuprous chloride (1.98 g) to give red yellow crystals of azibenzil (2.20 g, m. p. 67~67.5 °C) in an almost quantitative yield.



These reactions show clearly that cuprous chloride in pyridine is a very good catalyst system for oxidation of various amine derivatives.

References

1. Part XI. Y. Mori and J. Tsuji, *Tetrahedron*, **29**, 827 (1973).
2. H. Takahashi, T. Kajimoto, and J. Tsuji, *Synth. Commun.*, **2**, 181 (1972).
3. A. C. Cope, D. S. Smith, and R. J. Cotler, *Org. Synth.*, Coll. Vol. **4**, 377 (1963).
4. M. S. Newman and D. E. Reid, *J. Org. Chem.*, **23**, 665 (1958).
5. H. Krebs, *Tetrahedron Letters*, 4511 (1968).