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Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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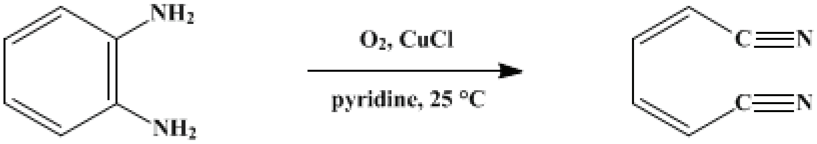
CUPROUS ION-CATALYZED OXIDATIVE CLEAVAGE OF AROMATIC *o*-DIAMINES BY OXYGEN: (*Z,Z*)-2,4-HEXADIENEDINITRILE



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1. Procedure

Caution! Benzene has been identified as a carcinogen. OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A 1-l. three-necked, round-bottomed flask equipped with a mechanical stirrer, a gas-inlet tube, and a dropping funnel is charged with 200 ml. of pyridine (Note 1) and 9.9 g. (0.10 mole) of copper(I) chloride (Note 2) which partially dissolves in pyridine, forming a yellow suspension (Note 3). Oxygen is bubbled into the suspension rapidly for 10 minutes; the suspension changes into a deep-green turbid solution (Note 4). A solution of 27 g. (0.25 mole) of 1,2-benzenediamine (Note 5) in 300 ml. of pyridine is added slowly from the dropping funnel during 2 hours, while vigorous stirring and bubbling of oxygen are continued (Note 6), (Note 7). The reaction mixture is transferred to a 1-l., round-bottomed flask, and pyridine is removed under reduced pressure (20 mm.) using a rotary evaporator until a deep-green solid residue is obtained, to which 400 ml. of 6 *N* hydrochloric acid and 400 ml. of dichloromethane are added. The mixture is shaken until the solid is dissolved, and the lower layer is separated (Note 8). The upper layer is extracted with three 100-ml. portions of dichloromethane. The combined dichloromethane solution is washed with 100 ml. of 5% aqueous sodium hydrogen carbonate, dried over anhydrous sodium sulfate, and evaporated. The brown residue is dissolved in 600 ml. of warm benzene, and the solution is filtered through filter paper. When the benzene is evaporated, 23–24 g. (88–93%) of crude product is obtained as a brownish solid, which is recrystallized twice from methanol (7 ml. for 1 g. of the crude material), yielding 19–20 g. (73–77%) of (*Z,Z*)-2,4-hexadienedinitrile as colorless needles, m.p. 128–129° (Note 9).

2. Notes

1. Commercial pyridine dried over potassium hydroxide pellets is satisfactory.
2. Reagent grade copper(I) chloride was obtained from Wako Pure Chemical Co., Osaka, Japan.
3. Powdered cuprous chloride should be added in small portions with efficient stirring in order to prevent coagulation.
4. When oxygen is bubbled too long, the solution becomes viscous and separation of solid mass occurs, but the mass dissolves with addition of 1,2-benzenediamine.
5. Reagent grade 1,2-benzenediamine was obtained from Wako Pure Chemical Co., Osaka, Japan.
6. The moment a drop of the diamine solution hits the reaction mixture, a spot becomes violet then turns to deep-green again. The addition should be slow, so that the violet color does not persist. The yeild of (*Z,Z*)-2,4-hexadienedinitrile decreases drastically if the addition is too fast.
7. The reaction is slightly exothermic, but no precaution is necessary for a small-scale experiment. It is advisable to cool the flask in a water bath when a large-scale synthesis is carried out.
8. As both layers are black and the interface is not easy to distinguish, careful separation is necessary. In addition, black amorphous material forms at the interface, making the separation difficult. It can be

coagulated by standing or removed by filtration.

9. The IR spectrum ($CHCl_3$) shows bands at 2230 (medium strong), 1348, and 940 (medium) cm.$^{-1}$. The ^{1}H NMR spectrum ($CDCl_3$) shows absorption at δ 5.73 and 7.33 (AA'XX' pattern).

3. Discussion

A practical method of synthesizing (*Z,Z*)-2,4-hexadienedinitrile is the oxidative cleavage of 1,2-benzenediamine. Various oxidizing agents such as nickel peroxide,[2] lead tetraäcetate,[3] and silver oxide[4] are used in more than stoichiometric amounts, but the yields are below 50%. In comparison, the present method described by Takahashi, Kajimoto, and Tsuji[5] gives a very high yield and requires less than a stoichiometric quantity of copper(I) chloride. This procedure can also be applied satisfactorily to the preparation of mucononitrile derivatives from 1,2-benzenediamines substituted with an electron-donating group, but no reaction takes place with the derivatives substituted with an electron-withdrawing group.

References and Notes

1. Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan.
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3. K. Nakagawa and H. Onoue, *Chem. Commun.*, 396 (1965).
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5. H. Takahashi, T. Kajimoto, and J. Tsuji, *Synth. Commun.*, 181 (1972); T. Kajimoto, H. Takahashi, and J. Tsuji, *J. Org. Chem.*, **41**, 1389 (1976).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

sodium hydrogen carbonate (144-55-8)

silver oxide (20667-12-3)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

cuprous chloride,
copper(I) chloride (7758-89-6)

dichloromethane (75-09-2)

1,2-benzenediamine (95-54-5)

nickel peroxide

(Z,Z)-2,4-Hexadienedinitrile (1557-59-1)