

Trisil[®], trimethylchlorosilane, and hexamethyldisilazane were purchased from Pierce Chemical Company, Rockford, Illinois.

Preparation of derivatives The epoxides were derivatised in the following way with pure trimethylchlorosilane or Trisil[®] (trimethylchlorosilane-hexamethyldisilazane in pyridine). Mixtures of 25 μ l of the epoxide and 0.2 ml of trimethylchlorosilane (or 1 ml of Trisil[®]) were kept in sealed glass tubes at 100 °C for different time intervals. The tube was then cooled and opened, and the reaction mixture was transferred to a micro round flask and the volatile components were removed under vacuum. Dry pentane (2 ml) was added and solid by-products were separated by centrifugation. The clear pentane solution was concentrated under vacuum and the oily residue was directly used for GLC and MS analysis.

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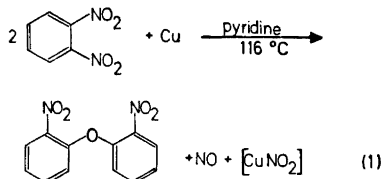
Nitrodiphenyl Ethers from 1,2- or 1,4-Dinitrobenzenes and Copper in Pyridine

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Copper and copper salts have been used in a variety of organic reactions, including Ullmann's biaryl and diaryl ether syntheses¹⁻³ and various copper-promoted arylations.^{3,4}

Symmetrical dinitrophenyl ethers are formed when 1,2- or 1,4-dinitrobenzenes are treated with copper in boiling pyridine [Reaction (1)].



1,2-Dinitrobenzene gave bis(2-nitrophenyl) ether (*1*) (65 %), and 1,4-dinitrobenzene bis(4-nitrophenyl) ether (77 %). Some 2-nitrophenol (*2*) or 4-nitrophenol, respectively, was also obtained.

Various copper compounds were tried (Table 1). Copper(0) was found to be most suitable. Both copper and copper(I) oxide dissolved during the reactions. The molar ratio of copper to 1,2-dinitrobenzene in reaction 1 was varied from 0.5 to 5. The yields of *1* and *2* were essentially the same in all cases. We believe the stoichiometric ratio to be 0.5 (*cf.* Scheme 1). A lower ratio gave lower yields and longer reaction times. Reaction 1 can be carried out in the presence of glacial acetic acid or water with essentially unchanged yields.

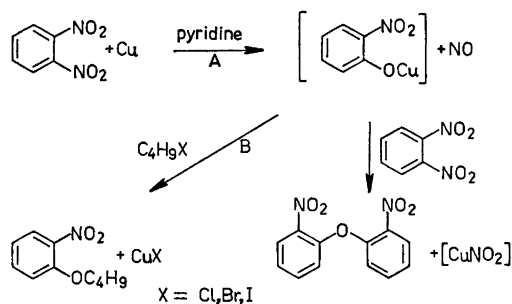
Table 1. Yields of products from reaction 1 with different copper sources.

Copper compound	1/%	2/%
Cu	65	19
Cu ₂ O	25	38
CuO	0	9
None	0	8

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Apparently, pyridine is essential for the reaction. No ether could be detected when the reaction was carried out in quinoline or diglyme or without a solvent. In the presence of triphenylphosphine the yield of *1* was reduced to 10%. Triphenylphosphine oxide was also formed.

When 1 mol of 1,2-dinitrobenzene reacted with copper in boiling pyridine, about 0.5 mol of nitric oxide (NO) was evolved. This led us to consider that the reaction proceeds *via* an intermediate resembling 2-nitrophenoxycopper(I), *cf.* Scheme 1. A pyridine solution of 2-nitrophenoxycopper(I) was therefore prepared from methylcopper(I) and 2-nitrophenol according to the method given by Whitesides *et al.*⁵ To this solution 1,2-dinitrobenzene was added and the mixture heated to 116 °C for 2 h. A high yield of *1* was obtained.



Scheme 1.

Samples were withdrawn at intervals from a boiling mixture of pyridine, copper and 1,2-dinitrobenzene and hydrolysed and analysed by GLC. The formation of *2*, which might be a hydrolytic product of 2-nitrophenoxycopper(I), starts earlier than the formation of *1*. However, some *2* could arise from the attack of nitrite ion on 1,2-dinitrobenzene.⁶ Effecting reaction *1* in the presence of sodium nitrite doubled the yield of *2*.

Butyl 2-nitrophenyl ether, *3*, was formed together with *1* when the reaction was carried out in the presence of 1-halobutanes (see Table 2). The yields of *3* do not differ much for the three butyl halides but the rate of disappearance of 1,2-dinitrobenzene varies with the halogen (I ~ Br > Cl). This indicates that paths A and B in Scheme 1 may not be mutually independent and that Scheme 1 may give a simplified picture of the reaction paths. No *3* was observed in the absence of copper, or after an attempted reaction of 2-nitrophenol and butyl bromide in pyridine.

An intermediate such as 2-nitrophenoxycopper(I) may be important in the reactions leading to both symmetrical and unsymmetrical

Table 2. Yields of products from reactions between 1,2-dinitrobenzene, copper and 1-halobutanes (C₄H₉X) in pyridine.

X	<i>3</i>	<i>1</i>	<i>2</i>	<i>t</i> _½ (h) ^a
I	16	15	47	0.4
Br	22	17	41	0.6
Cl	23	31	31	5
Br	50(37) ^b	2	7	

^a *t*_½ = time for 50 % reaction; see Experimental.
^b Isolated yield. Three mol of butyl bromide.

ethers (*cf.* Scheme 1). Copper(I) phenolates react with organic halides in diglyme at 120 °C to give moderate yields of ethers^{5,7}. It has been suggested that aryloxy copper(I) compounds are intermediates in the Ullman diaryl ether synthesis⁸ and in oxidative couplings of phenols catalysed by copper(I) chloride.⁹ The first step on the route from 1,2-dinitrobenzene and copper to an intermediate resembling 2-nitrophenoxycopper(I) might be the formation of a dinitrophenyl anion radical and copper(I), *cf.* Saegusa *et al.*¹⁰ Once formed, the phenoxycopper(I) complex attacks a molecule of dinitrobenzene. One of the nitro groups then leaves as a nitrite anion. The reaction between 1,2- or 1,4-dinitrobenzenes and potassium cyanide gives a small yield of symmetrical

Table 3. Isolated yields of products from reactions of dinitrobenzenes, copper and phenols in boiling pyridine. A, unsymmetrical diaryl ether; B, symmetrical diaryl ether; C, 2-nitrophenol.

Substituent on the phenol	A	B	C
1,2-Dinitrobenzene			
None	67	0.5	22
4-Methyl-2-nitro-	63	6 ^a	12
4-Nitro-	73	2 ^a	15
2,4,5-Trinitro-	0	62	
4-Bromo-	74	0	18
2-Bromo-	72	0.5	18
4-Iodo-	92 ^b	0	2
1,4-Dinitrobenzene			
None	86	0	0
4-Iodo-	87 ^c	0	0

^a Isolated as a mixture of diphenyl ethers. Relative amounts determined by GLC. ^b 75 °C, 2.3 h, 20 % excess iodophenol. ^c 80 °C 2.5 h, 20 % excess iodophenol.

diphenyl ethers,¹¹ perhaps by a related reaction path.

Unsymmetrical nitrophenyl ethers were formed when 1,2- or 1,4-dinitrobenzenes were treated with copper and phenols in pyridine. The results are summarized in Table 3. Apparently, reactions with phenols proceed faster than the one leading to symmetrical ethers. About ten times more of the unsymmetrical product was obtained from 1,2-dinitrobenzene and 2-nitro-4-methylphenol, as shown in Table 3. More strongly nucleophilic phenols yielded larger amounts of unsymmetrical diphenyl ethers. In the absence of copper, about 9% of 2,4'-dinitrophenyl ether was formed from 1,2-dinitrobenzene and 4-nitrophenol after prolonged boiling with pyridine.

The reactions given in Table 3 could be of synthetic use since they occur under mild conditions and permit the presence of bromo and iodo substituents in the substrates.

Experimental. A finely powdered copper of electrolytic purity was used. Products were identified by spectral methods and melting points. A general procedure for similar reactions has been reported earlier.⁴

Bis(2-nitrophenyl) ether (1). A mixture of 1,2-dinitrobenzene (5 mmol), copper (25–2.5 mmol) and pyridine (25 ml) was boiled (116 °C) under nitrogen for 2 h to yield **1**, 0.42 g (65%) and 2-nitrophenol, 0.13 g (19%).

The gas evolved from the reaction mixture was collected (56 ml corresponding to a molar ratio of 0.47 between gas and 1,2-dinitrobenzene) and injected into a GLC-MS equipped with a Linde Molecular Sieve 5A column (80 °C). The MS (70 eV) showed the gas to be almost pure nitric oxide (except for nitrogen).

Reaction with 2-nitrophenoxycopper(I). Dry pyridine (4 ml) was added to methylcopper(I)⁵ (about 1.2 mmol) under N₂ and at 0 °C followed by a solution of 2-nitrophenol (1.2 mmol) in pyridine (2 ml). The solution became reddish brown and gas evolved. After 3 h at 0 °C 1,2-dinitrobenzene (1.2 mmol) in a little dry pyridine was injected through a septum and the solution was heated to 116 °C for 2 h. After workup ⁴ 2-nitrobiphenyl was added as an internal standard. The yield of **1** (76%, based on 2-nitrophenol or 1,2-dinitrobenzene) was determined by GLC.

Bis(4-nitrophenyl) ether. 1,4-Dinitrobenzene (5 mmol) and copper (5 mmol) were boiled in pyridine (25 ml) for 10 h. Yield after recrystallisation from ethanol 0.50 g (77%). 4-Nitrophenol 0.02 g (3%) was also isolated.

Reactions with 1-halobutanes. A mixture of distilled 1-halobutane (6 mmol), 1,2-dinitrobenzene (5 mmol), copper (25 mmol) and pyridine (20 ml) was stirred under N₂ at 75 °C. 2-Nitrobiphenyl was added as an internal standard and samples withdrawn at intervals were analysed by GLC. The results were plotted and times when 50% of the 1,2-dinitrobenzene remained were determined.

Reactions of 1,2- and 1,4-dinitrobenzene with phenols. A dinitrobenzene (5 mmol), copper (10 mmol) and a phenol (5 mmol) were boiled in pyridine (25 ml) for 0.5–2 h. Yields based on dinitrobenzene were determined by GLC using an internal standard and have been optimized only in the reactions with 4-iodophenol. Most of the diphenyl ethers were purified by dissolving in dichloromethane or dichloromethane:tetrachloromethane 1:1 and filtering under suction through a 6×2.5 cm column of silica gel moistened with solvent. Fresh solvent was added until the diphenyl ether had passed into the suction flask. Evaporation of the solvent gave the diphenyl ether, now free of more polar impurities. Since the reactions were terminated when no dinitrobenzenes remained, this purification was usually adequate.

2-Nitro-4'-iododiphenyl ether from 1,2-dinitrobenzene (5 mmol) and 4-iodophenol (6 mmol) at 75 °C. Reaction time 2.3 h. Yield 1.57 g, 92%. A higher reaction temperature or a longer time results in the formation of nitrobenzene and 2-nitrodiphenyl ether together with the title compound. Excess 4-iodophenol is needed as otherwise a little **1** will be formed.

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