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Copper-Catalyzed Oxidative Coupling of Diphenylmethanimine Promoted by Some Monodentate Pyridines[1]

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Aerial oxidation of diphenylmethanimine to benzophenone azine was carried out at room temperature in the presence of cuprous chloride and a monodentate pyridine, such as pyridine, γ-picoline, isoquinoline, or quinoline. Cupric chloride, hydroxide, and nitrate were inactive in the reaction, whereas $CuCl_2$–KOH and $Cu(OH)_2$–HCl were active in the presence of excess pyridine. Bidentate ligands, such as ethylenediamine and monoethanolamine, inhibited the oxidative coupling of imine. Using isoquinoline for the direct synthesis of azine from benzophenone, ammonia and molecular oxygen, the reaction temperature can be lowered and the catalysts recycled.

INTRODUCTION

Benzophenone is selectively converted to diphenylmethanimine ($Ph_2C{=}NH$) by dehydrative condensation with ammonia over thoria (*1*) or thoria–silica (*2*) catalyst. Benzophenone azine($Ph_2C{=}N{-}N{=}CPh_2$), which yields hydrazine quantitatively on acid hydrolysis (*3*), is prepared by aerial oxidation of diphenylmethanimine in a liquid phase (*4, 5*). A continuous process for hydrazine synthesis from benzophenone, ammonia, and oxygen via the azine with recycling of benzophenone is possible (*6*).

$$\rightarrow Ph_2C{=}O + \boxed{NH_3}$$
$$\rightarrow Ph_2C{=}NH + H_2O \quad (1)$$
$$2Ph_2C{=}NH + \tfrac{1}{2}O_2 \rightarrow Ph_2C{=}N{-}N{=}CPh_2 + H_2O \quad (2)$$
$$Ph_2C{=}N{-}N{=}CPh_2 + 2H_2O \rightarrow 2Ph_2C{=}O + \boxed{NH_2NH_2} \quad (3)$$

[1] Ammonia–Hydrazine Conversion Processes. VIII. The previous paper (Part VII) is Ref. (*8*).

Diphenylmethanimine forms complexes with copper chlorides, $CuCl\cdot Ph_2C{=}NH$ [1], $CuCl\cdot 2Ph_2C{=}NH$ [2], $CuCl_2\cdot Ph_2C{=}NH$ [3] and $CuCl_2\cdot 2Ph_2C{=}NH$ [4], and these complexes can all catalyze the oxidative coupling of diphenylmethanimine (*5, 7*). However, in all cases the formation of azine probably proceeds through complex [1], because complexes [2]–[4] are interchangeable with [1] under suitable conditions (*5*). Complex [1] absorbs ¼ mol of oxygen in solution to form an oxygen-containing copper(II) complex, $CuCl_2\cdot 2Ph_2C{=}NH\cdot CuO$ [5], which is converted to azine above 120°C with reduction of copper(II) to copper(I) (*8*).

Similar reactions are observed in the oxidative coupling of anilines (*9, 10*) and phenols (*11–13*), and these reactions are usually carried out at room temperature in the presence of cuprous chloride and excess pyridine. No azo compounds are formed in the absence of pyridine (*10*).

It seemed likely that the redox cycle of copper in the formation of azine could be

promoted by pyridine and/or related compounds at a lower temperature. In the present work, the oxidative coupling of diphenylmethanimine in the presence of various copper-coordinating nitrogen bases, such as pyridine, γ-picoline, isoquinoline, quinoline, ethylenediamine, and monoethanolamine, was studied. It was found that monodentate pyridines *promoted* the oxidative coupling of imine, while bidentate ligands *inhibited* it. Using isoquinoline for the direct synthesis of azine from benzophenone, ammonia, and oxygen in the presence of zinc chloride and cuprous chloride, the reaction temperature could be lowered and the catalysts recycled.

EXPERIMENTAL

Apparatus and procedure. The oxidation of diphenylmethanimine was carried out at 27–110°C and atmospheric pressure under oxygen. A mixture of cuprous chloride and nitrogen base was allowed to absorb oxygen and then diphenylmethanimine was added. The absorbed oxygen was measured volumetrically. The direct synthesis of azine was carried out at 150°C under 5 atm pressure in the presence of isoquinoline. Benzophenone azine separated as needle-like crystals when the reaction mixture was diluted with aqueous ethanol.

Materials. Diphenylmethanimine was prepared by thermal decomposition of benzophenone oxime (*14*). A preparation containing 30% diphenylmethanimine and 70% benzophenone was used. Other materials were obtained commercially.

RESULTS AND DISCUSSION

Oxidation of Cuprous Chloride in the Presence of Coordinating Ligands

The oxidation of cuprous chloride in water is represented by Eq. (4) (*11*).

$$6CuCl + \tfrac{3}{2}O_2 + 3H_2O \rightarrow CuCl_2 \cdot 3Cu(OH)_2 + 2CuCl_2 \quad (4)$$

Cuprous chloride is, however, inert toward oxygen in benzene, toluene, or xylene, and in these solvents the absorption of oxygen is observed only in the presence of a coordinating ligand. The reactions in benzene–pyridine are represented by Eq. (5) in the absence of water and by Eq. (6) in the presence of water (*11*).

$$4CuCl + O_2 \xrightarrow{Py} 2CuCl_2 \cdot 2CuO \cdot n\text{Py} \quad (5)$$

$$4CuCl + O_2 + 2H_2O \xrightarrow{Py} 2CuCl_2 \cdot 2Cu(OH)_2 \cdot n\text{Py} \quad (6)$$

Stoichiometrically ¼ mol of oxygen is required for the oxidation of cuprous chloride, though the reactions involved are not simple as shown by Eq. (4)–(6).

The oxygen absorptions by systems of cuprous chloride and various nitrogen bases at room temperature are shown in Fig. 1. The results may be classified into two groups. One includes the absorptions with pyridine, γ-picoline, and isoquinoline, where oxygen uptake did not exceed ¼ mol per mol of CuCl, showing that the absorptions are due to oxidation of cuprous chloride only. Much more oxygen was absorbed in the presence of quinoline, ethylenediamine, or ethanolamine, showing that these absorptions are due to oxidation of the solvent as well as of the cuprous chloride.

The oxygen uptake was also found to be about ¼ mol per mol of pyridine, γ-picoline, and isoquinoline in the presence of excess cuprous chloride suspended in xylene, showing that a (1:1)-complex was formed. However, in the reaction with pyridine at 80–110°C, about 1.5 times more oxygen was absorbed than that expected for a (1:1)-complex. Thus at a higher temperature, coordinated pyridine must be liberated and used repeatedly to oxidize cuprous chloride.

Promotion of Oxidative Coupling of Diphenylmethanimine by Monodentate Pyridines

A temperature of above 120°C is required for oxidation of diphenylmethan-

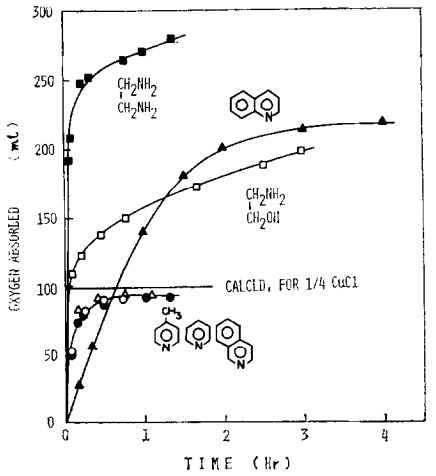

FIG. 1. Oxygen absorptions by systems of cuprous chloride and various nitrogen bases. Temperature, 27°C; CuCl, 1.75 g; nitrogen base, 50 ml.

imine to azine in the absence of copper-coordinating ligands, as reported previously (*5*, *8*). In the present work attempts were made to obtain benzophenone azine at a lower temperature in the presence of monodentate pyridines. When diphenylmethanimine was added to a solution of cuprous chloride in excess pyridine, γ-picoline, or isoquinoline after absorption of oxygen at room temperature, oxygen was absorbed as shown in Fig. 2, and benzophenone azine was formed. The amount of oxygen absorbed agreed well with the stoichiometric amount required for the

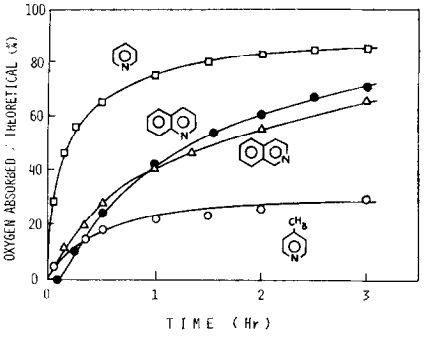

FIG. 2. Oxidative coupling of diphenylmethanimine in the presence of cuprous chloride and some monodentate pyridines. Temperature, 27°C; Ph_2C = NH, 3.2 g; CuCl, 1.75 g (CuCl/imine = 1/1); pyridines, 50 ml.

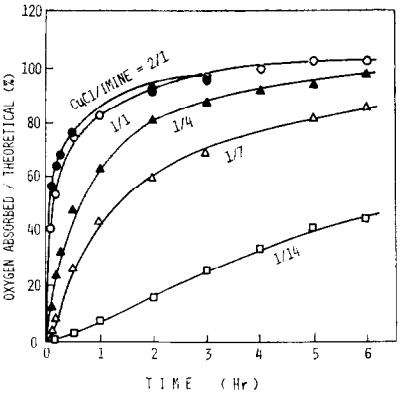

FIG. 3. Effect of the concentration of cuprous chloride on the oxidative coupling of diphenylmethanimine in the presence of pyridine. Temperature, 27°C; Ph_2C = NH, 3.2 g, pyridine, 50 ml.

oxidation of imine (Eq. (2)). Formation of azine was also observed in the presence of quinoline, but there was a discrepancy between the consumption of oxygen and the yield of azine (about 140% for azine).

Figure 3 shows that the oxidation of imine proceeded in the presence of a catalytic amount of cuprous chloride with excess pyridine, indicating that the reaction involved a redox cycle of the copper. Pyridine is weakly coordinated, but in excess it may promote the elimination of coordinated imine, where the product would be azine, not imine. In fact pyridine must be in excess to promote the oxidation of imine, as shown in Fig. 4.

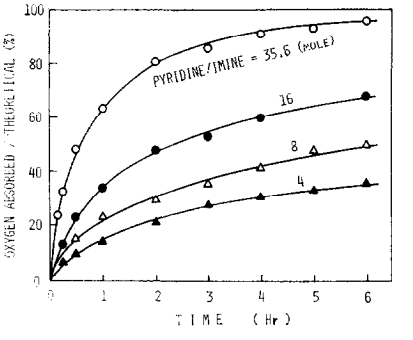

FIG. 4. Effect of the concentration of pyridine on the oxidative coupling of diphenylmethanimine. Temperature, 27°C; Ph_2C = NH, 3.2 g; CuCl, 0.44 g (CuCl/imine = 1/4); diluent, toluene.

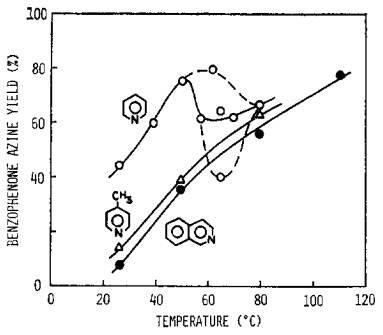

FIG. 5. Effect of temperature on the oxidative coupling of diphenylmethanimine in the presence of cuprous chloride and excess pyridine, γ-picoline, or isoquinoline. CuCl, 0.25 g; $Ph_2C = NH$, 3.2 g; (CuCl/imine = 1/7); pyridines, 50 ml.

The amount of diphenylmethanimine decreased to a copper/imine ratio of unity immediately after adding excess imine to a solution of cuprous chloride in a large excess of pyridine saturated by oxygen and then a slow decrease in the amount of free imine accompanied by oxygen uptake was observed. The results show that the copper–pyridine complex is easily converted to a copper–imine complex by ligand exchange.

Pyridine was much more effective than γ-picoline or isoquinoline for the oxidative coupling of imine at room temperature. As shown in Fig. 5, with the latter two monodentate pyridines, the rate of formation of azine increased with increase in temperature. However, with pyridine the yield of azine decreased at 50–80°C, although the reproducibility was not good in this temperature range. As a result, the activities with these three compounds were of the same order of magnitude above 80°C. At higher temperatures near the boiling point of pyridine, the copper–pyridine complex may be unstable, as previously suggested for the case of oxidation of cuprous chloride in pyridine.

Other Catalysts than Cuprous Chloride with Absorbed Oxygen

Cupric chloride catalyzes the oxidative coupling of diphenylmethanimine at 120°C,

TABLE 1

Oxidative Coupling of Diphenylmethanimine in the Presence of Various Copper Salts and Excess Pyridine[a]

Catalyst	Benzophenone azine yield (%)
O_2 preabsorbed CuCl	84.7
$CuCl_2$	0
$CuCl_2$ + KOH	73.1
$CuCl_2$ + 2KOH	1.1
$Cu(OH)_2$	0
$Cu(OH)_2$ + HCl	52.9
$Cu(NO_3)_2 \cdot 3H_2O$	0

[a] $Ph_2C{=}NH$, 3.2 g; Cu/imine, 1/7; pyridine, 50 ml. Oxygen was absorbed for 3 hr at 50°C.

as described in a previous paper (*5*). It was expected that azine would be formed at a lower temperature in the presence of cupric chloride and excess pyridine, as in the case of cuprous chloride, but no azine was obtained.[2] Cupric hydroxide and cupric nitrate were also inactive as catalysts, as shown in Table 1. However, it is interesting that cupric chloride and cupric hydroxide were active in the presence of an equimolar amount of potassium hydroxide and hydrochloric acid, respectively, as shown in Table 1.

Similar behaviors are observed in the oxidative coupling of phenols (*11, 12, 15*) and anilines (*9, 10*) in the presence of pyridine, where basic copper(II) chloride, Cu(OH)Cl [6], is suggested as an active intermediate (*15*).

$$4CuCl + O_2 + 2H_2O \rightarrow 4Cu(OH)Cl \quad (7)$$

$$CuCl_2 + KOH \rightarrow Cu(OH)Cl + KCl \quad (8)$$

$$Cu(OH)_2 + HCl \rightarrow Cu(OH)Cl + H_2O \quad (9)$$

It is difficult to isolate the intermediate

[2] Cupric chloride forms complexes, [3] and [4], with diphenylmethanimine (*5*). These copper (II) complexes are converted to the copper (I) complex [1] at higher temperatures (*5,7*). The formation of azine at 120°C in the absence of pyridine can be attributed to formation of the active intermediate [1].

[6], but Finkbeiner *et al.* (*11*) obtained an analogous complex, $CuOCH_3Cl$ [7], by the reaction of cupric chloride with sodium methoxide in methanol (cf. Eq. (8)).

$$CuCl_2 + NaOCH_3 \rightarrow CuOCH_3Cl + NaCl \quad (10)$$

Subsequent reaction of [7] with pyridine gives a copper(II) complex, $PyCuOCH_3Cl$ [8], for which a chlorine-bridged, binuclear structure was suggested (*11*).

In the oxidative coupling of diphenylmethanimine in the presence of excess pyridine, the effectiveness of catalysts is in the order $CuCl$–O_2 > $CuCl_2$–KOH > $Cu(OH)_2$–HCl, as shown in Table 1. This difference in activities with the same intermediate [6] is difficult to understand. Moreover, it should be noticed that in the system of $CuCl$–O_2–Py the reaction was carried out in the absence of water, which is necessary for formation of [6] as shown in Eq. (7).

The oxidative coupling of diphenylmethanimine proceeds via an oxygen-containing copper(II) complex [5], which requires somewhat higher temperatures for conversion to azine in the absence of pyridine (*5, 8*). Although benzophenone azine was obtained at room temperature in the presence of excess pyridine, complex [5] should be an intermediate in the oxidative coupling of diphenylmethanimine whether pyridine is present or not, since it was found that the copper–pyridine complex is easily converted to the copper–imine complex by ligand exchange. Complex [5] has an N–H bond of coordinated imine but no absorption due to an O–H bond was detected in the ir spectrum (*8*). Therefore, the most probable intermediate might be the dehydrated dimer of [6] coordinated imine rather than [6]. The chemical composition of this dehydrated dimer is the same as that of [5] described in a previous paper (*8*). Unlike phenols and anilines, diphenylmethanimine is easily hydrolyzed in the presence of water so that a catalyst system which forms water is less active. The system with $Cu(OH)_2$–HCl forms $\frac{3}{2}$ mol of water, that with $CuCl_2$–KOH forms $\frac{1}{2}$ mol and that with $CuCl$–O_2 forms none, and the activities given in Table 1 are in the expected order.

Inhibition of Oxidative Coupling by Bidentate Ligands

Cuprous chloride is readily soluble in both ethylenediamine and ethanolamine giving blue solutions which both absorb oxygen, as shown in Fig. 1. However, no azine was obtained when diphenylmethanimine was added to these solutions after absorption of oxygen. Cupric ion forms chelate complexes with ethylenediamine (*16*) and ethanolamine (*17*), and these complexes are usually isolated as perchlorates, nitrates, or sulfates. The anions in these copper(II) complexes of bidentate ligands may exchange so that copper is not necessarily in the chloride form. Oxidations by cupric ions are known to proceed by both electron and ligand transfer: The former predominates with oxy salts and the latter with halides (*18*). Thus the inhibition of the oxidative coupling of imine could be explained as due to formation of a stable chelate complex of cupric ion with the bidentate ligand rather than the chlorine-bridged complex coordinating imine.

Use of Isoquinoline for Synthesis of Benzophenone Azine in a Single Stage

Zinc chloride (*19*) and ammonium chloride (*20*) catalyze dehydrative condensation of benzophenone with ammonia in a liquid phase. Therefore, we tried to obtain benzophenone azine in a single stage by passing an equimolar mixture of ammonia and oxygen through benzophenone at 200°C in the presence of $ZnCl_2$–CuCl or NH_4Cl–CuCl (*19, 20*). The direct process involves reaction (1) and the *in situ* oxidative coupling of imine (2). The finding

TABLE 2

Application of Isoquinoline for Synthesis of Benzophenone Azine in a Single Stage[a]

Isoquinoline added (ml)	Time (hr)	Yield (%)	
		Imine	Azine
0	3	6	0
5	3	6	29
50	1.5	8	36
50	3	8	44

[a] $Ph_2C{=}O$, 18.2 g; $ZnCl_2$, 1.0 g; CuCl, 0.5 g; temperature, 150°C; pressure, 5 atm; flow rate, 10 liters/hr (NTP); NH_3/O_2 = 9/1.

in the present work, that the copper-catalyzed oxidative coupling of diphenylmethanimine occurs at room temperature in the presence of monodentate pyridines, was applied to lower the reaction temperature in the direct synthesis of azine. Reaction (1) requires a somewhat higher temperature, and isoquinoline was used as a coordinating ligand. No azine was formed without a coordinating ligand at 150°C, whereas good yields were obtained in the presence of isoquinoline, as shown in Table 2.

Cuprous chloride is expensive and so its recovery for recycle use is an important problem in developing this direct method for industrial use. It was found that isoquinoline was useful for this purpose, as shown in the following example.

A mixture of ammonia and oxygen (NH_3/O_2=4/1) was passed through a mixture containing 18.2 g of benzophenone, 1.0 g of zinc chloride, 0.5 g of cuprous chloride and 50 ml of isoquinoline at 150°C under 5 atm pressure at a rate of 10 liters/hr for 2 hr. Then the reaction mixture was diluted with 250 ml of ethanol to obtain azine. The ethanol was evaporated off from the filtrate under vacuum, and further benzophenone was added to make up for loss. The procedure was repeated three times and 17.1 g of benzophenone azine were obtained for a total of 32.8 g of benzophenone (overall yield, 52%).

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