CHEMISTRY LETTERS,pp. 981-982, 1977. Published by the Chemical Society of Japan

COPPER-CATALYZED OXIDATIVE COUPLING OF DIPHENYLMETHANIMINE PROMOTED BY BICYCLOAMIDINES[1]

Hiromu HAYASHI, Toshikazu TANAKA,
Naoya SHIGEMOTO, and Tatsuya OKAZAKI
Department of Chemical Engineering, Tokushima University,
Minamijosanjima, Tokushima 770

Benzophenone azine was obtained in a high yield by copper-catalyzed oxidative coupling of diphenylmethanimine in the presence of bicycloamidines, 1,8-diazabicyclo[5.4.0]-undecene-7(DBU) or 1,5-diazabicyclo[4.3.0]nonene-5(DBN) in tetrahydrofuran or 1,4-dioxane as a solvent.

Copper-catalyzed oxidative coupling of diphenylmethanimine yields benzophenone azine,[2] which gives hydrazine quantitatively on acid-hydrolysis.[3,4] The oxidation required a higher temperature above 120°C in benzophenone as a solvent.[5] The azine was, however, obtained in a high yield even at room temperature in the presence of an excess of monodentate pyridines, such as pyridine, γ-picoline or isoquinoline.[6]

In the present work, it has been found that bicycloamidines, 1,8-diazabicyclo-[5.4.0]undecene-7(DBU), and 1,5-diazabicyclo[4.3.0]nonene-5(DBN), also promote the oxidative coupling of diphenylmethanimine. With a suitable solvent, a catalytic amount of amidines was sufficient, while it required a large excess of pyridines[6] to give the azine in a high yield. Cuprous chloride was used as a catalyst. Oxidation of diphenylmethanimine was carried out at 50°C for 3 hr under oxygen with vigorous stirring, where cuprous chloride was previously oxidized in a given solvent containing DBU or DBN at the same temperature and then the imine was added.

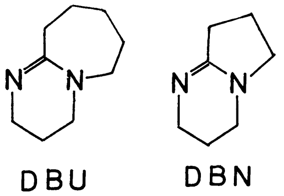

Table 1 shows yields of benzophenone azine in various solvents. The molar ratio of amidine/CuCl was 1/1. The results with pyridine[6] are also given in comparison. A dark-green oily complex precipitated on the bottom in toluene. In other solvents, homogeneous dark-green solutions were obtained. Tetrahydrofuran and 1,4-dioxane were suitable solvents. Oxidation of cuprous chloride in methanol gives $Cu^{II}OCH_3Cl$, which was a superior catalyst to cuprous chloride itself in the oxidative coupling

Table 1. Yields of benzophenone azine in copper-catalyzed oxidative coupling of diphenylmethanimine in the presence of bicycloamidines in various solvents[a]

Solvents / Additives	Toluene	THF	Dioxane	D/E[b]	EtOH	MeOH	Pyridine
	Yield of benzophenone azine (%)[c]						
DBU	46.8	94.7	88.3	18.9	8.4	0.0[d]	--
DBN	61.0	83.5	74.2	--	20.3	--	--
Pyridine[e]	22.4[f]	--	--	--	--	--	87.0[g]

*a)*Conditions; $Ph_2C{=}NH$:17.7 mmol, CuCl:4.4 mmol, amidine/CuCl=1/1(by mol), 50°C, 3 hr, solvent:50 m*l*. *b)*Dioxane/EtOH=1/1(by vol). *c)*Based on charged $Ph_2C{=}NH$ and on stoichiometry of eq.(1). *d)*DBU/CuCl=4/1(by mol). *e)*Results obtained at 27°C for 6 hr.[6] Other conditions were same as *a)*, except pyridine/CuCl ratio. *f)*Pyridine/CuCl=16/1(by mol). *g)*Pyridine/CuCl=142/1(by mol).

of diphenylmethanimine in pyridine.[7] However, the results of the oxidation carried out in alcohols were disappointing as shown in Table 1.

Oxygen-uptake for stoichiometry,

$$2\ Ph_2C{=}NH + 1/2\ O_2 \rightarrow Ph_2C{=}N{-}N{=}CPh_2 + H_2O \quad (1),$$

and the yield of azine agreed well at a lower DBU/CuCl ratio, but some abnormal oxygen absorptions were observed in the presence of excess DBU in toluene as shown in Fig. 1. Similar behavior was also observed for DBU in dioxane and DBN in toluene, where the maximum yield of azine was obtained at DBU/CuCl=1/1 and DBN/CuCl=2/1, respectively. There are no informations for the abnormal oxygen-uptake, whether it comes from the oxidation of solvent or amidine.

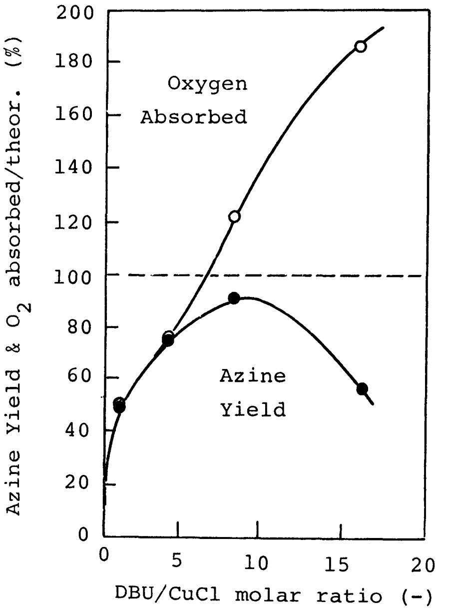

Fig. 1. Abnormal oxygen-uptake at a higher DBU/CuCl ratio.

$Ph_2C{=}NH$:17.7 mmol, CuCl:4.4 mmol, 50°C, 3 hr, solvent: toluene.

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(Received June 18, 1977)