

SYNTHESIS OF PHTHALOCYANINES FROM PHTHALONITRILE WITH ORGANIC STRONG BASES

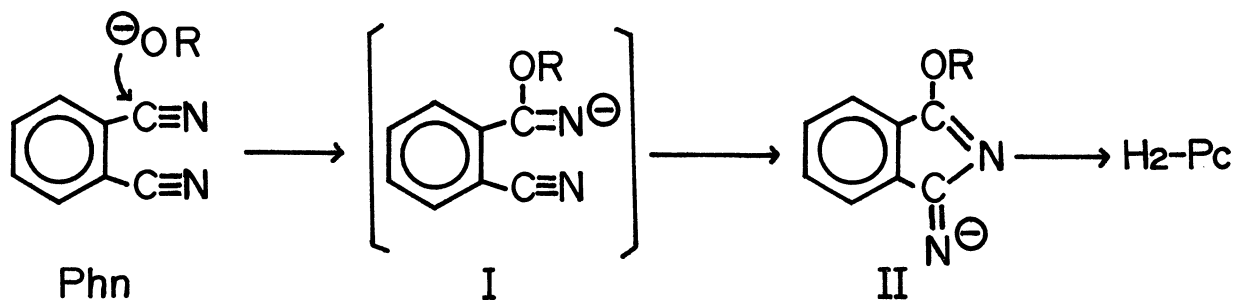
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In the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene or 1,5-diazabicyclo[4.3.0]non-5-ene, metal-free phthalocyanine was obtained by heating phthalonitrile in alcohols. Addition of a copper(II) salt in the reaction gave copper phthalocyanine in a good yield.

There are two usual methods for the synthesis of metal-free phthalocyanine (H_2 -Pc) from phthalonitrile (Phn). One is to heat Phn at high temperature in a basic solvent with a high boiling point, such as quinoline or pyridine.^{1,2)} The other is to heat it in an alcohol with an alkali metal alkoxide.³⁾ The authors reported that UV irradiation of an alcoholic solution of Phn in the presence of a catalytic amount of sodium alkoxide gave H_2 -Pc even at room temperature.⁴⁾

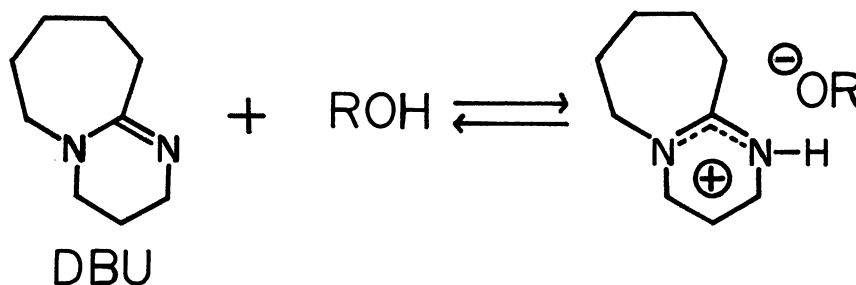
Baumann et al.⁵⁾ and Borodkin⁶⁾ studied the formation of H_2 -Pc with an alkoxide and suggested that the alkoxide anion performed a nucleophilic attack at the cyano group of Phn to form a 1-alkoxy-3-iminoisoindolenine intermediate (II), as shown in Scheme 1.



Baumann et al.⁵⁾ speculated that the addition-elimination of four molecules of the

intermediate II and the subsequent reduction and cyclization occur in the formation of H_2 -Pc.

An organic strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) is expected to act as a proton acceptor. An equilibrium such as shown in Scheme 2 may exist. Thus, we attempted the reaction using some organic strong bases in place of the alkali metal alkoxide, and succeeded in preparing H_2 -Pc from Phn. Moreover, we found that the addition of copper(II) salt in the reaction led to the formation of copper phthalocyanine (Cu-Pc) in a good yield.



Scheme 2

A mixture of Phn (2.56 g, 20 mmol) and DBU[or DBN] (20 mmol) in ethanol (50 cm³) was heated to reflux. As the reaction proceeded, H_2 -Pc gradually deposited as blue precipitates, which were collected by filtration, washed with ethanol, and purified by an extraction technique with ethanol. The product was identified by IR, UV, and elemental analyses.

Fig. 1 shows that the yield of H_2 -Pc increased with increasing reaction time, but leveled off after 18 h. DBN was more than twice as effective as DBU in the yield. The yield of H_2 -Pc by this new method was better than that by the sodium alkoxide method under similar conditions.

In the preparation of H_2 -Pc, 2,4,6-tris(o-cyanophenyl)-1,3,5-triazine was formed as a by-product in a considerable yield. This result suggests that the triazine was formed by an intermolecular reaction of the intermediate I with Phn or with another I.

The formation of H_2 -Pc occurred also in other alcohols besides ethanol, such as

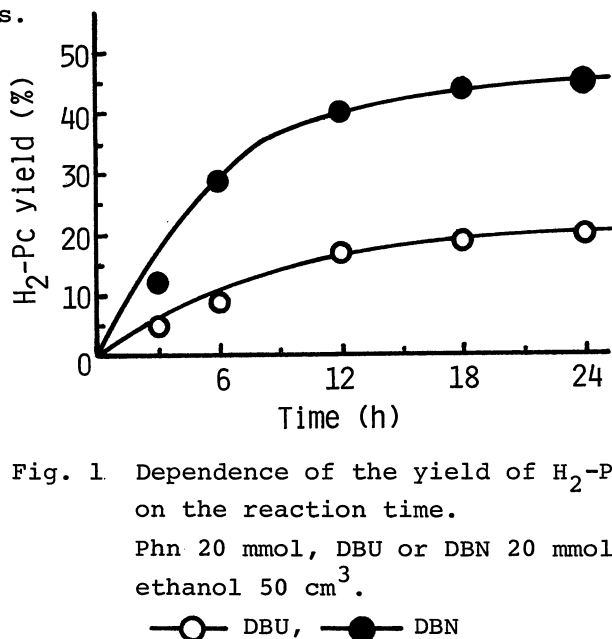


Fig. 1. Dependence of the yield of H_2 -Pc on the reaction time. Phn 20 mmol, DBU or DBN 20 mmol, ethanol 50 cm³.
 —○— DBU, —●— DBN

methanol and 1-propanol. In the absence of alcohol, however, no formation of H_2 -Pc was observed at all (in benzene); thus the starting material, Phn, was recovered unchanged in the reaction. This result shows that the alkoxide anion participates in the formation of H_2 -Pc. Neither pyridine nor 1,4-diazabicyclo[2.2.2]octane effected the formation of H_2 -Pc in ethanol.⁷⁾

The preparation of Cu-Pc was effected successfully by heating a mixture of Phn (1.28 g, 10 mmol), $CuCl_2$ (0.337 g, 2.5 mmol), and DBU (or DBN) in ethanol (50 cm³). Fig. 2 shows the yield of Cu-Pc under six-hour-long refluxing with varying molar ratios of DBU or DBN to Phn. The yield of Cu-Pc increased with increasing molar ratio of DBU or DBN to Phn. At a high molar ratio, the yield of Cu-Pc with DBN was better than that with DBU. The formation of Cu-Pc was not observed at all, when the molar ratio was less than 0.25 (equimolar amount to $CuCl_2$). This suggests that the formation of ethoxide anion did not occur at any concentration of the amines lower than that of $CuCl_2$, owing to predominant complexation of the amines used with $CuCl_2$. The yield of Cu-Pc increased with increasing reaction time, as shown in Fig. 3. Furthermore, Fig. 3 shows that DBN affords a better yield than DBU in prolonged reactions (over 24 h). The yields of Cu-Pc were about seven times better than those of H_2 -Pc under similar reaction conditions. In the presence of $CuCl_2$, neither the triazine nor H_2 -Pc was formed as a by-product. This new method is useful for the preparation of Cu-Pc in a better yield under milder reaction conditions.

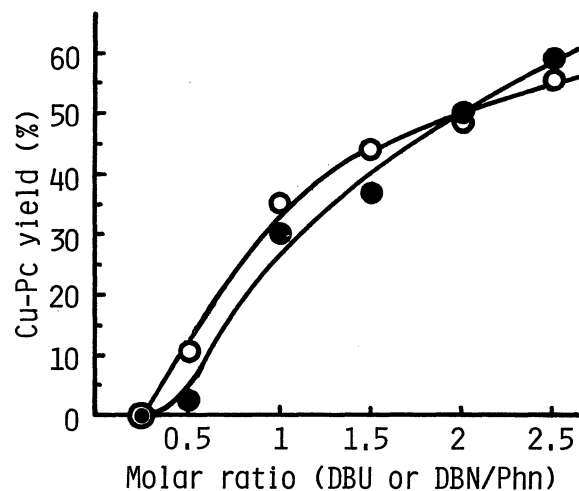


Fig. 2 Effect of molar ratios of DBU or DBN to Phn on the yield of Cu-Pc. Phn 10 mmol, $CuCl_2$ 2.5 mmol, ethanol 50 cm³, reflux time 6 h.
 ○ DBU, ● DBN

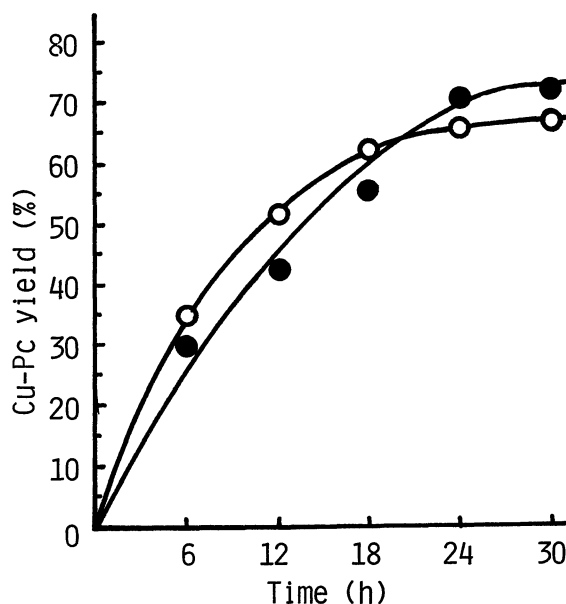


Fig. 3 Dependence of the yield of Cu-Pc on the reaction time. Phn 10 mmol, $CuCl_2$ 2.5 mmol, DBU or DBN 10 mmol, ethanol 50 cm³.
 ○ DBU, ● DBN

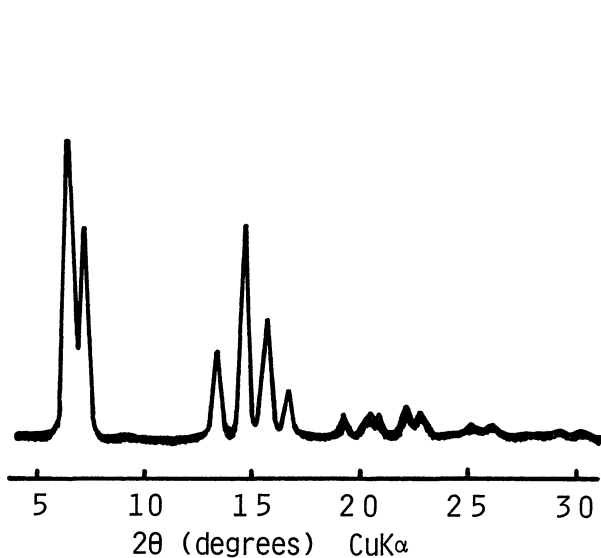


Fig. 4 X-ray diffraction pattern of H_2 -Pc.

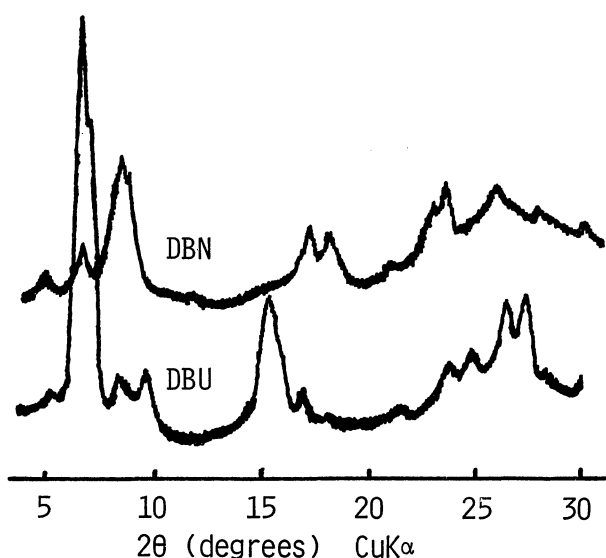


Fig. 5 X-ray diffraction patterns of Cu-Pc.

It is known that phthalocyanines have several polymorphic forms. However, the X-ray diffraction patterns of H_2 -Pc and Cu-Pc formed by the new method did not agree with those of the well-known α , β , or γ forms. The crystal form of H_2 -Pc obtained by the new method was the same as that of the photoproduct already reported (see Fig. 4),⁸⁾ while the crystal form of Cu-Pc was thought to be amorphous from its X-ray diffraction pattern (see Fig. 5).

References and Note

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