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LETTER

Preparation of unsymmetrical phthalocyanine by means of a ring expansion of subphthalocyanine

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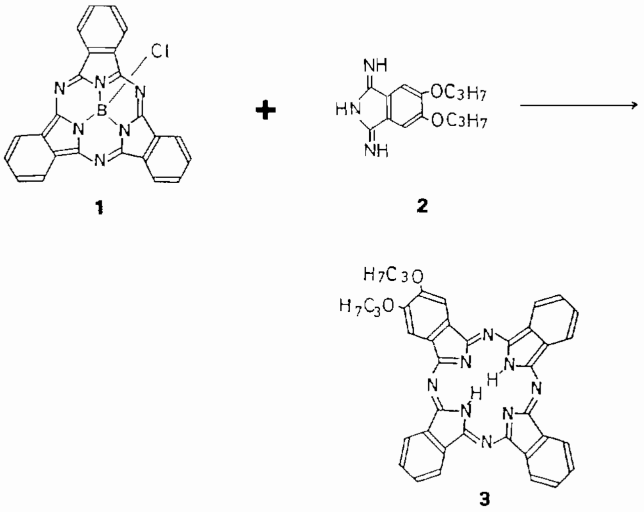
Phthalocyanine derivatives having substituents on the phthalocyanine ring have been prepared in order to increase their solubility, and also to study the effect of the substituent on the electronic structure of the ring [1]. For further detailed studies of their properties, it is necessary to introduce the substituents at a particular position on the ring. However, it is difficult to prepare mono-substituted phthalocyanine using statistical condensation reactions of two different *ortho*-dinitriles of aromatic compounds due to the formation of a mixture of products [1].

Recently, it has been reported that subphthalocyanine (shown in Scheme 1) changes to phthalocyanine by the addition of a few 1,3-diiminoisoindoline derivatives [2, 3]. Therefore, the ring-expansion reaction could be an attractive method for preparing unsymmetrical phthalocyanine derivatives having substituents at a particular position on the ring. We report here some factors affecting the ring-expansion reaction of subphthalocyanine.

Chloro(subphthalocyaninato)boron(III) (**1**) was prepared in similar way to that reported by Meller and Ossko [4]. 1,3-Diiminoisoindoline and its dipropoxy derivative (**2**) were prepared by refluxing a methanol solution of the corresponding 1,2-dicyanobenzene under bubbling of ammonia gas through the solution [5]. The dipropoxy derivative of phthalocyanine (**3**) was prepared as follows: 10 mg (0.3 mmol) of compound **1** and 120 mg (0.45 mmol) of compound **2** were dissolved in a solvent mixture of dimethyl sulfoxide (DMSO) and 1-chloronaphthalene (CNP) (1:2, vol./vol.); subsequently the solution was allowed to stand at *c*. 90 °C overnight. By addition of adequate amounts of methanol to the reaction mixture, the precipitates were obtained. Then, a chloroform solution of the crude products was poured onto a silica gel column. Using chloroform as eluent, a green solution was eluted out (yield 12 mg). Mass spectrometry measurements showed a parent peak at 630 in agreement with the formula of compound **3**.



Scheme 1.

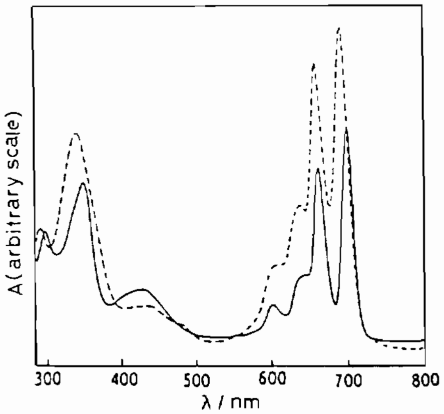


Fig. 1. Absorption spectra of the phthalocyanine derivatives in chloroform: ——, octa-substituted phthalocyanine; – – –, compound 3.

Octapropoxy-substituted phthalocyanine was prepared according to the method described in the literature [6]. The Q and B bands of compound **3** are somewhat shifted to a shorter wavelength compared with those of the octapropoxy-substituted phthalocyanine (Fig. 1).

Upon heating the solvent mixture of DMSO and CNP (1:2, vol./vol.) of compounds **1** and **2** at 90 °C, the Q band of compound **1** decreased, but the Q bands

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of compound **3** appeared at 662 and 684 nm (Fig. 2). This shows that unsymmetrical phthalocyanine was formed by the ring-expansion reaction of subphthalocyanine.

The formation of compound **3** upon heating largely depends on the kind of solvents used in the reaction. In DMSO solution, the Q-band intensity of compound **1** largely decreased, but the Q bands of compound **3** scarcely appeared. That is, the decomposition of compound **1** mainly occurred in the DMSO solution. In CNP solution, on the other hand, the Q-band intensity at 571 nm scarcely changed, but the Q bands of the phthalocyanine derivative appeared, showing the direct formation of phthalocyanine from 5,6-dipropoxy-1,3-diiminoisoindoline. In the solvent mixture of DMSO and CNP (3:1 ~ 1:3, vol./vol.), according to the decrease of the Q-band intensity of compound **1**, those of the phthalocyanine derivative increased. The polarity of the solvents seems to be an important factor for the ring-expansion reaction of subphthalocyanine.

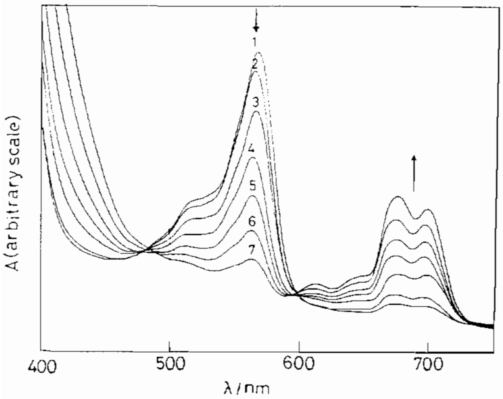

Fig. 2. Spectral changes during the reaction of compounds **1** and **2** in the solvent mixture of DMSO and CNP (1:2, vol./vol.) at 90 °C; [compound **1**] = 1.0×10^{-4} M, [compound **2**] = 1.0×10^{-2} M: (1) 5 min, (2) 10 min, (3) 35 min, (4) 65 min, (5) 105 min, (6) 170 min, (7) 250 min, after the reaction.

The pseudo first-order rate plots showed that the reaction was first order with respect to compound **1** in the 1:2 solvent mixture*. From the slopes of the plots, values of the pseudo first-order rate constants were obtained: 3.5×10^{-3} min^{-1} for 5,6-dipropoxy-1,3-diiminoisoindoline and 2.1×10^{-3} min^{-1} for 1,3-diiminoisoindoline. The electron-donating substituents might increase the ring-expansion reaction. Furthermore, phthalocyanine was not formed from compound **1** by the addition of 1,2-dicyanobenzene in the 1:2 solvent mixture.

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*The reaction rate was measured by following the absorbance change of the unsymmetrical phthalocyanine derivatives at 662 nm in a 1:2 solvent mixture at 90 °C: [compound **1**] = 1.0×10^{-4} M, [1,3-diiminoisoindoline derivatives] = 1.0×10^{-2} M.