Novel Synthesis of Metal-Free Phthalocyanines from Phthalimides and Phthalic Anhydrides with Hexamethyldisilazane

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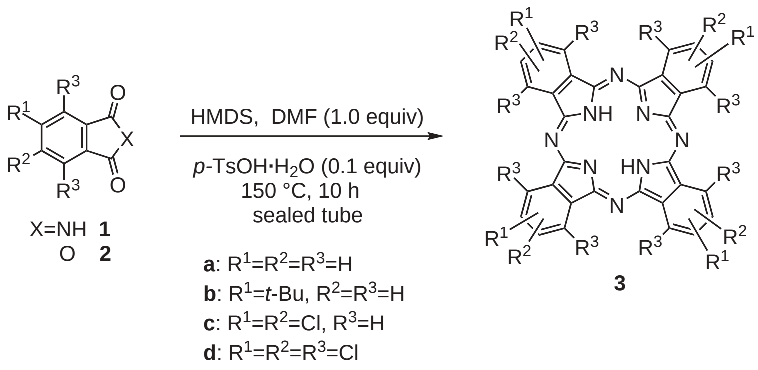
Abstract: Metal-free phthalocyanines and their peripherally substituted derivatives have been synthesized from unsubstituted and substituted phthalimides, phthalic anhydrides, and naphthalimide on heating with hexamethyldisilazane under mild conditions.

Key words: phthalocyanine, naphthalocyanine, phthalimide, phthalic anhydride, hexamethyldisilazane

The development of new synthetic methods for the preparation of phthalocyanines are important in view of their many important applications.[1] The usual synthesis of metallophthalocyanines has been based on classically established methods, starting from phthalonitriles,[2] phthalimides and phthalic anhydrides on treatment with urea[3] under harsh reaction conditions. In particular, metal-free phthalocyanines, which can serve as precursors of various metallophthalocyanines, have only a limited synthetic route.[1] The most common methods for the preparation of metal-free phthalocyanines are reactions starting from phthalonitriles under rather harsh reaction conditions; the heating at high temperature[1a] or treatment with a strong base such as metal alkoxides,[4] DBN or DBU.[5] Preparation of metal-free phthalocyanines from phthalonitriles under mild conditions with benztellurate[6] and $CeCl_3$[7] has been reported. The reaction of 1,3-diiminoisoindolines under reflux in alcohols provides a method under mild conditions,[8] although 1,3-diiminoisoindolines should be prepared from phthalonitriles.[1] Dimethylaminoethanol effects the cyclization to metal-free phthalocyanines from both phthalonitriles and 1,3-diiminoisoindolines.[9] Despite more than a few decades of intensive research on phthalocyanines, chemists still have no new methods available for the synthesis of metal-free phthalocyanines from easily obtainable phthalimides or phthalic anhydrides. Formation of a trace amount of metal-free hexadecachlorophthalocyanine has been observed as a side product in the preparation of Co-hexadecachlorophthalocyanine on treatment of tetrachlorophthalic anhydride with urea and cobalt in 1-chloronaphthalene at 263 °C.[10] Recently, we found a convenient method for the preparation of metallophthalocyanines from phthalimides.[11] We wish to report herein a new synthetic method for the preparation of metal-free phthalocyanines starting from phthalimides and phthalic anhydrides with hexamethyldisilazane (HMDS).

We first examined the reaction of phthalimide **1a**. After examination of the reaction under various conditions, phthalimide **1a** was found to give metal-free phthalocyanine **3a**[12] in 58% yield[13] by heating **1a** in a sealed tube for 10 hours at 150 °C in the presence of 4.0 equivalents of HMDS, 1.0 equivalent of DMF and a catalytic amount of *p*-TsOH·H_2O (Scheme 1).[14] The results are shown in Table 1.

Under similar reaction conditions, *tert*-butyl-, 4,5-dichloro- and 3,4,5,6-tetrachlorophthalimides gave the corresponding phthalocyanines in good to moderate yields. Crude metal-free phthalocyanines were purified as follows: For **3a**, **3c**,[15] and **3d**[10] the reaction mixture



Scheme 1

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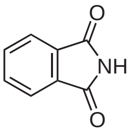
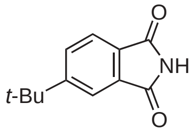
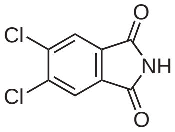
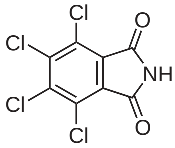
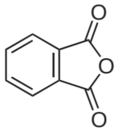
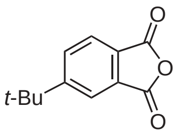
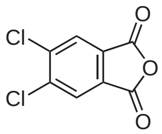
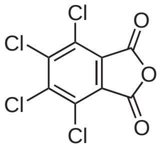
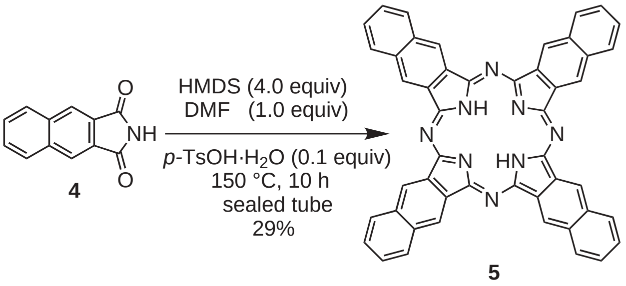
Table 1 Preparation of Unsubstituted and Peripherally Substituted Metal-Free Phthalocyanines **3** by Treatment of Phthalimides or Phthalic Anhydrides with HMDS, DMF, and *p*-TsOH·H_2O[a]

Entry	Phthalimide or phthalic anhydride		HMDS (equiv)	Product	Yield (%)
1		**1a**	4	**3a**	58
2		**1b**	4	**3b**	42[b]
3		**1c**	4	**3c**	62
4		**1d**	4	**3d**	20
5		**2a**	5	**3a**	42
6		**2b**	5	**3b**	38[b]
7		**2c**	5	**3c**	23
8		**2d**	5	**3d**	25

[a] The reaction mixture of **1** or **2**, 4.0 or 5.0 equiv of HMDS, 1.0 equiv of DMF, and 0.1 equiv of *p*-TsOH·H_2O was heated for 10 h at 150 °C.
[b] Peripherally substituted metal-free phthalocyanines were obtained as a mixture of regioisomers, which were not separated.

obtained was dissolved in conc. H_2SO_4 and the resulting solution was poured into cold water. The precipitates were collected, washed with water thoroughly, and further purified by soxhlet extractor with methanol. For **3b**,[16] purification was carried out by column chromatography (silica gel, toluene/THF 9:1).

The reaction starting with phthalic anhydride **2a** also gave metal-free phthalocyanine **3a**. Better yield of **3a** was obtained in the reaction with 5.0 equivalents of HMDS in comparison with that using 4.0 equivalents of HMDS apparently because **2a** requires one more nitrogen per molecule than **1a** to form the phthalocyanine skeleton. Substituted phthalocyanines **3b**, **3c**, and **3d** were also obtained from **2b**, **2c**, and **2d**, respectively. The metal-free naphthalocyanine **5**[17] was also prepared in the reaction of 2,3-naphthalimide **4** (Scheme 2).



Scheme 2

It is rather surprising that the present reaction conditions afford metal-free phthalocyanines from phthalimides or phthalic anhydrides even in the absence of templates such as metal halides.[18] Such metal templates are supposed to be requisite for the formation of metallophthalocyanines in the reaction of phthalimides or phthalic anhydrides on heating with urea. HMDS is not only a source of nitrogen atoms but also a good dehydrating agent. These specific properties of HMDS realized hitherto unknown procedure for the direct formation of metal-free phthalocyanines.

In conclusion, we have developed a new and efficient protocol for the production of unsubstituted and substituted metal-free phthalocyanines, which can be performed under substantially neutral and mild conditions.

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(13) **Typical Procedure for the Preparation of 3a.** A glass tube was charged with phthalimide (100 mg, 0.68 mmol), *p*-$TsOH\cdot H_2O$ (13 mg, 0.07 mmol), HMDS (560 μL, 438 mg, 2.7 mmol) and DMF (50 μL, 0.68 mmol) under argon atmosphere. Then the tube was sealed. The mixture was heated at 150 °C, when a dark purple solid immediately appeared. After heating for 10 h, the mixture was cooled and filtered. The solid was washed with MeOH, and then dissolved in conc. H_2SO_4 (5.0 mL). The resulting solution was poured into H_2O (100 mL) and the blue precipitates were filtered and washed with H_2O. The solid was further purified by extraction by soxhlet extractor with methanol to give 62 mg (58%) of **3a** as a blue solid.

(14) Metal-free phthalocyanines are not formed in the absence of either *p*-TsOH or DMF. *p*-TsOH probably plays a role to activate HMDS as a silylating agent as well as phthalimides and DMF is requisite for dissolving substrates, although the role of these reagents is not clear enough.

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(18) We also found that metal-free phthalocyanines were obtainable from phthalonitriles by the action of HMDS. The results will be reported in due course.