

NEW SYNTHESSES OF PHTHALOCYANINES

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Metal-free and metal phthalocyanines were obtained by the new methods, Photochemical reactions with alkali metal alkoxides and thermal reactions with strong organic bases. UV irradiation of 1-pentanol solution of phthalocyanine(Phn) in the presence of a catalytic amount of alkali metal alkoxides gave metal-free phthalocyanine (H_2Pc). Alkali metals used were Li, Na, and K. The dark thermal reactions were also carried out and compared with photochemical ones. The Yield of H_2Pc in the photochemical reaction was far better than that in the corresponding dark reaction. In the dark reaction, the yield of H_2Pc decreased with the alkali metals, K, Na, Li in the order. In the photochemical reaction, however, the yields of H_2Pc were almost unchanged with the alkali metals used. H_2Pc was also obtained by heating Phn in ethanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). Incorporation of copper(II) chloride in the reaction gave copper phthalocyanine (CuPc) in a good yield. The formation of H_2Pc and CuPc was also studied with various amines. Amines used were n-dodecylamine, triethylamine, 2-(dimethylamino)-ethanol, N,N,N',N'-tetramethyl-1,3-diaminopropane, 1,4-diazabicyclo[2.2.2]octane, N-methylimidazole, benzimidazole, pyridine, 4-aminopyridine, and 4-(dimethylamino)-pyridine. Organic strong bases, DBU and DBN, were far more effective for H_2Pc and MPc formation than the other amines. They were also shown to be effective for the formation of various MPc, such as Fe(II), Fe(III), Ni(II), Co(II), Zn(II), Pb(II), Mn(III) phthalocyanines.