NEW SYNTHESES 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.