CHEMISTRY LETTERS, pp. 313-316, 1983.

SYNTHESIS OF METALLOPHTHALOCYANINES FROM PHTHALONITRILE WITH STRONG ORGANIC BASES

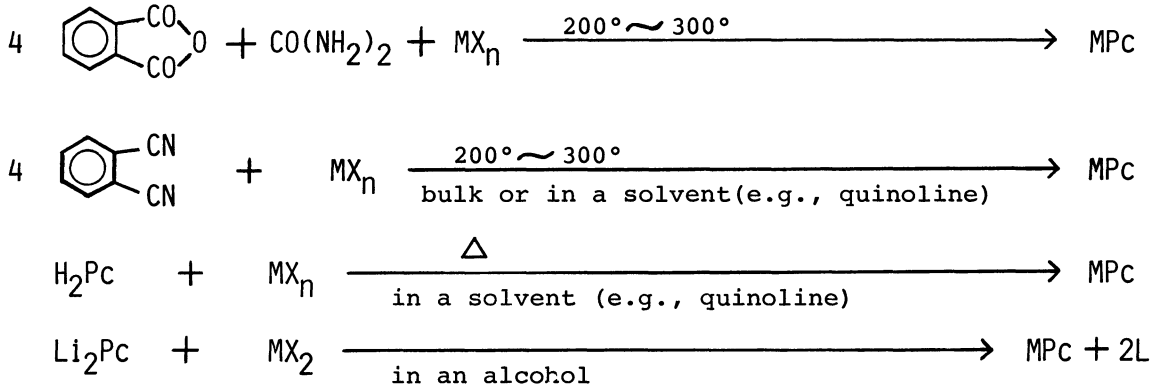
Haruhiko TOMODA*, Shojiro SAITO,and Shinsaku SHIRAISHI†

Department of Industrial Chemistry, Shibaura Institute of Technology, Shibaura, Minato-ku, Tokyo 108

†Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

Several metallophthalocyanines (MPc: M=Ni(II), Co(II), Zn(II), Pb(II), Fe(II), Sn(II), Cd(II), Mg(II), and Mn(III)) were obtained by heating phthalonitrile with metal salts in alcohols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. Metal acetylacetonates as well as metal halides were available as metal sources for preparation of metallophthalocyanines by this method.

A large number of metallophthalocyanines (MPc) are known.[1)2)3)] MPc's have important uses not only as commercial pigments but also as optical and electrical materials and as catalysts. There are several methods for the preparation of MPc's, as shown in the following equations. The reactions are usually carried out under rather severe conditions, especially at high temperatures.



However, MPc's prepared by the methods exemplified above are usually contaminated with intractable impurities, and the technique of purification or exploitation of an improved or a novel synthetic process is a matter of immediate importance.

We have reported that metal-free phthalocyanine (H_2Pc) was obtained by heating phthalonitrile (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) and also that the incorporation of copper(II) chloride in the reaction gave copper phthalocyanine (CuPc) in a good yield.[4] H_2Pc and CuPc prepared by the method are of adequate purity, and the purification procedure is rather simple. In this paper, we wish to report the synthesis of various MPc's under mild conditions with strong organic bases such as DBU or DBN.

A typical experimental procedure is as follows: a mixture of Phn (1.28 g 10 mmol) and a metal salt (2.5 mmol) in the presence of DBU [or DBN] (10 mmol) was heated to reflux in a primary alcohol such as 1-pentanol. As the reaction proceeded, blue or greenish blue powder gradually precipitated. The precipitate was collected by filtration, washed with 3% HCl solution, water, and then ethanol, and purified by an extraction technique with chloroform. The product was identified by IR and UV-Vis spectra, X-ray diffraction patterns, and elemental analyses. IR spectra in the 700-1350 cm^{-1} region were especially useful for the identification of MPc's.

Table I shows the yield of CuPc obtained by the use of various copper salts. Copper(I or II) halides gave a better yield of CuPc than cyanide or hydroxide. CuPc was also obtained by the use of copper(II) acetylacetonate ($Cu(acac)_2$) in a fairly good yield. The yield of CuPc was always better when DBU was used as a base than when DBN was used. Therefore, DBU was employed as catalyst in the synthesis of other MPc's.

Table I Formation of CuPc with various Copper Salts

Copper salt	Yield (%) DBU	DBN
CuCl	85	79
CuBr	83	71
CuI	82	69
CuCN	67	49
$CuCl_2$	80	73
$Cu(OH)_2$	63	49
$Cu(acac)_2$	70	55

Conditions: Phn 10 mmol, Copper salt 2.5 mmol, Base 10 mmol, $n\text{-}C_5H_{11}OH$ 40 cm^3, Time 6 h.

The yields of MPc's under various conditions are shown in table II. Most copper salts are soluble in alcohol, but other metal salts such as $NiCl_2$, $CoCl_2$, SnI_2 are only slightly soluble in alcohol. The syntheses of MPc's were conducted using not only metal halides but also metal acetylacetonates ($M(acac)_2$). When M=Ni(II), Co(II), Zn(II), Pb(II), Fe(II), Sn(II), Cd(II), Mg(II),

Table II Formation of Various MPc's with DBU

Metal salt	(mmol)	Alcohol	(cm^3)	Time (h)	Product	MPc Yield (%)
$NiBr_2$	3	$CH_3OCH_2CH_2OH$	30	6	NiPc	75
$Ni(acac)_2$	2.5	$n\text{-}C_5H_{11}OH$	40	6	NiPc	59
$CoBr_2$	2.5	$n\text{-}C_5H_{11}OH$	40	6	CoPc	60
$Co(acac)_2$	2.5	$n\text{-}C_5H_{11}OH$	40	6	CoPc	53
$ZnCl_2$	2.5	$n\text{-}C_5H_{11}OH$	40	6	ZnPc	74
$Zn(acac)_2$	2.5	$n\text{-}C_5H_{11}OH$	40	6	ZnPc	58
$PbCl_2$	2.5	$n\text{-}C_5H_{11}OH$	40	6	PbPc	77
$FeCl_2$	3	$C_2H_5OCH_2CH_2OH$	25	6	FePc	57
$SnCl_2$	3	$C_2H_5OCH_2CH_2OH$	25	6	SnPc	50[a]
$CdCl_2$	3	$C_2H_5OCH_2CH_2OH$	25	6	CdPc	64[a]
$MgCl_2$	3	$n\text{-}C_5H_{11}OH$	25	6	$MgPc\cdot H_2O$	53[b]
$MnCl_2$	2.5	$n\text{-}C_5H_{11}OH$	40	6	Mn(OH)Pc	74
$Mn(acac)_2$	2.5	$n\text{-}C_5H_{11}OH$	30	6	Mn(OH)Pc	49
$MoO_2(acac)_2$	2.5	$n\text{-}C_4H_9OH$	40	24	MoOPc	2

Conditions: Phn 10 mmol, DBU 10 mmol, Under reflux.
a) Not treated with dil. HCl. b) The product was washed only with benzene.

MPc's were obtained selectively, i.e. without the contamination of H_2Pc.[5] The manganese complex obtained either from $MnCl_2$ or $Mn(acac)_2$ was identified to be Mn-(OH)Pc by comparing its UV-Vis spectrum with that of the literature.[6] Possibly this is due to the after-treatment with dil. HCl and water. MgPc was identified to be $MgPc\cdot H_2O$ by its UV-Vis spectrum.[7] The Pc derivative of Mo was also obtained, though in a low yield, and identified to be MoOPc by comparison with the reported IR spectrum.[8] The Pc derivative from $FeCl_2$ was identified to be FePc. However, the structure of the products from $FeCl_3$ and $Fe(acac)_3$ was not definitely determined to be FePc or Fe(III)Pc. Mössbauer spectrometry suggests that the product may be a mixture of them. This problem is now receiving detailed investigation. CuPc, NiPc, ZnPc, and PbPc were obtained in fairly good yields by the use of metal chlorides. The yields of MPc from $M(acac)_2$ were not generally better than those from metal halides. In concern to the yields of the products, this process can not be said to be better than other conventional processes but leave some room for optimization. In the preparation of FePc and CdPc, care must be taken to dissolve the metal

components sufficiently. Unless this was done, H_2Pc was apt to contaminate as a by-product. TiPc and PdPc were also obtained, but always accompanied with the contamination of H_2Pc. The presence of a band at 1002 cm^{-1} indicated the presence of H_2Pc in TiPc and PdPc.[9] In the cases of the preparation of TiPc and PdPc using $TiCl_3$ and $PdCl_2$, respectively, the yields of TiPc and PdPc were about 60% and the contamination of H_2Pc was about 5 to 10%. The formation of H_2Pc in the preparation of TiPc may be due to the alcoholysis of $TiCl_3$ prior to TiPc formation. $PdCl_2$ is not sufficiently soluble in the alcohol used. Attempted synthesis of AlPc with $Al(acac)_3$ resulted in the formation of H_2Pc as the main product, with a small amount of an unidentified AlPc derivative. When $AlCl_3$ was used, neither AlClPc nor H_2Pc was obtained. The attempts to prepare ZrPc and CrPc using $Zr(acac)_4$ and $Cr(acac)_3$ by this method have not been successful and only H_2Pc were obtained in 52% and 40% yields, respectively. The crystal forms of the MPc's obtained with DBU were mostly β forms; this was determined X-ray diffraction patterns.

From the preliminary investigation on the syntheses of various kinds of MPc's with strong organic bases described above, the following observations were obtained. Good results were obtained: 1) when the starting metal components were soluble in alcohol, or when soluble metal-amine complexes were formed in the reaction mixture, and 2) when the MPc's formed were stable enough under the reaction conditions.

Further investigations on the syntheses of other MPc's and on the optimization of the reactions are now in progress. The authors are grateful to the San Avott Co. for 1,8-diazabicyclo[5.4.0]undec-7-ene.

References

1) F. H. Moser and A. L. Thomas, Phthalocyanine compound, Reinhold Publishing Corp., New York (1963), Chap. 3.
2) A. B. P. Lever, Adv. Inorg. Radiochem., 7, 28 (1965).
3) G. Booth, The Chemistry of Synthetic Dyes, ed by K. Venkataraman, Academic Press, New York and London (1971), Vol. 5, Chap. 4.
4) H. Tomoda, S. Saito, S. Ogawa, and S. Shiraishi, Chem. Lett., 1980, 1277.
5) The IR and UV-Vis spectra of NiPc, CoPc and ZnPc synthesized here were identical with those of the literature.[1] PbPc, FePc, SnPc, and CdPc gave satisfactory elemental analyses for C, H, and N.
6) G. Engelsma, A. Yamamoto, E.Markham, and M. Calvin, J. Phys. Chem., 66, 2517 (1962).
7) M. Whalley, J. Chem. Soc., 1961, 866.
8) H. A. O. Hill and M. M. Norgett, J. Chem. Soc. (A), 1966, 1476.
9) M. P. Sammes, J. Chem. Soc. Perkin II, 1972, 160.

(Received December 15, 1982)