Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 74 (2007) 279–282
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Microwave assisted synthesis of metal-free phthalocyanine and metallophthalocyanines

A. Shaabani*, R. Maleki-Moghaddam, A. Maleki, A.H. Rezayan

Department of Chemistry, Shahid Beheshti University, P.O. Box 19839-4716, Tehran, Iran

Received 19 August 2005; received in revised form 22 January 2006; accepted 7 February 2006
Available online 31 March 2006

Abstract

The metal-free phthalocyanine and metallophthalocyanine complexes of Cu, Co, Ni, Fe, Zn, Pd, Pt and Ru are easily prepared upon exposure to microwave irradiation and reaction times are reduced from several hours to a few minutes.

Keywords: Phthalocyanine; Metallophthalocyanine; Microwave irradiation; Synthesis

1. Introduction

Phthalocyanines (Pcs) constitute a remarkably versatile class of compounds with diverse technological applications [1–5]. The metallophthalocyanines (MPcs) are usually prepared by cyclotetramerization of phthalonitrile (PN) or phthalic acid analogues such as phthalimide (PI), phthalic anhydride (PA) and phthaloacetic acid (PAA) at high temperature (about 200 °C) and reaction times of several hours (10–24 h) are needed [6–10]. The PN process is generally a cleaner reaction, a phenomenon that is understandable in view of the fact that the PN molecules provide the parent structure of the phthalocyanine ring. The phthalic acid analogue methods are favored in industry due to the cheaper precursor, but requires source of nitrogen such as urea or ammonium chloride as a co-reagent. All of the reactions are helped by the template effect afforded by a suitable metal ion.

In such conventional synthesis of metallophthalocyanines, which need longer reaction times and high temperature, yield is often low and a mixture of products is often generated. In addition, the pure metallophthalocyanines may be difficult to obtain under these hard conditions. Furthermore, in the synthesis of the most of the MPcs from phthalic anhydride, ammonium molybdate is used as a catalyst and usually products may be contaminated with MoPc.

Very recently, "Toru" has reported [11] a convenient route for the synthesis of metal-free phthalocyanine (H_2Pc) from phthalonitrile and metallophthalocyanines from phthalonitrile, phthalimide and phthalic anhydride using hexamethyldisilazane (HMDS). In spite of the potential utility of this approach, reaction times necessary for these reactions are very long at relatively high temperature. For example, the reaction times are 10–24 h at 100–150 °C when metal-free phthalocyanine is synthesized from phthalonitrile, in the case of metallophthalocyanines from phthalimide or phthalic anhydride 10–48 h at 150 °C and 10–12 h at 100–125 °C in the case of phthalonitrile.

Therefore, one of the main purposes for the synthesis of metal-free and metallophthalocyanines has been to decrease the reaction times as well as the temperature.

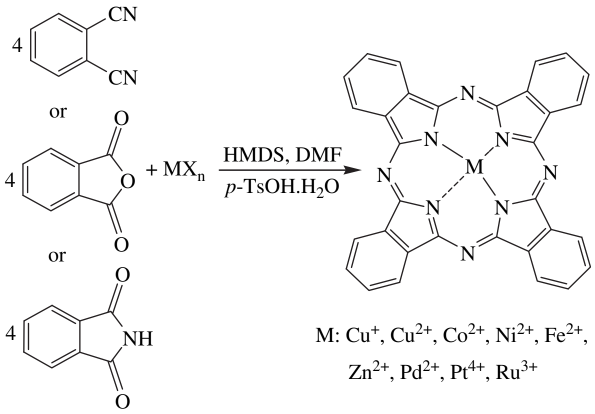
Microwave-promoted organic reactions are well known as environmentally benign methods that can accelerate a great number of chemical processes. In particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [12].

In continuation of our study to develop a fast and effective procedure for the synthesis of metallophthalocyanines [13], we herein wish to study the possibility of synthesis of metal-free

---

* Corresponding author. Fax: +98 21 2403041.
E-mail address: a-shaabani@cc.sbu.ac.ir (A. Shaabani).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.02.005



Scheme 1.

phthalocyanine and metallophthalocyanines from phthalonitrile, phthalimide and phthalic anhydride upon treatment with hexamethyldisilazane using microwave irradiation (Scheme 1).

2. Results and discussion

2.1. Metal-free phthalocyanine

Metal-free phthalocyanines are an important class of phthalocyanines, which are usually prepared from phthalonitriles in the presence of basic catalyst [14], $CeCl_3$ [15], Na_2S [16] and HMDS [11a] at high temperature and very long reaction times. As indicated in Scheme 2, application of microwave technology to this reaction decreased the time required to obtain good yields by a factor of about 240. For example, the time required for the conversion of phthalonitrile to metal-free phthalocyanine (72%), at 140–160 °C after 1440 min is reduced to 5–6 min when microwave irradiation is used.

Optimization of reaction conditions, the yields and necessary times for the syntheses of H_2Pc were indicated in Table 1. It was found that the molar ratio of the reactants influenced the conversion as well as yields, and the best results were obtained when 1:2:0.1:1 mole ratio of phthalonitrile, HMDS, $(NH_4)_2SO_4$ and DMF, respectively, were used.

It is important to note that in the absence of each of the reagents, the reaction is completely stopped (Table 1, experiments 2, 4 and 7).

We also repeated the experiments in the presence of $Na_2S \cdot xH_2O$ under MW irradiation and classical heating conditions. As can be seen from Scheme 3, phthalonitrile is efficiently converted into the H_2Pc in relatively high yields using MW irradiation, however, attempt for the synthesis of H_2Pc under classical heating conditions at 160–170 °C after 180 min is not so successful.

As indicated in Table 2, the optimized amount of reagents is 4:0.3:6.0 mole ratio of phthalonitrile, $Na_2S \cdot xH_2O$ and 1,2-propylene glycol (PG), respectively. Thus, the reaction is not carried out in the absence of $Na_2S \cdot xH_2O$ or PG. (Entries 1 and 2 in Table 2.)

2.2. Metallophthalocyanines

The reaction conditions were optimized with CuCl or/and with various raw materials such as PN, PA and PI. We found that the molar ratio of 1:4:4:1:0.41 of CuCl:phthalonitrile:HMDS:DMF:p-TsOH$\cdot H_2O$ obtained the best results.

In a typical experiment, the reaction was carried out by the mixing of PN, PA or PI with HMDS, MX_n, p-TsOH and DMF in a glass tube and the reaction mixture was stirred at room temperature for 20 min under a nitrogen atmosphere. Then, the tube was sealed and the mixture was irradiated for 10–15 min in the microwave oven.

To explore the scope and limitations of this reaction further, we extended the procedure to various raw materials and to different metal salts such as $Cu(OAc)_2 \cdot H_2O$, $CuCl_2 \cdot 2H_2O$, $CoCl_2$, $NiCl_2$, $FeCl_2 \cdot 4H_2O$, $ZnCl_2$, $PdCl_2$, $PtCl_4$ and $RuCl_3$.

As can be seen from Table 3, the different starting materials such as PN, PA and PI are converted to MPcs with good yields after several minutes. In general these results showed the PN to produce the best yield.

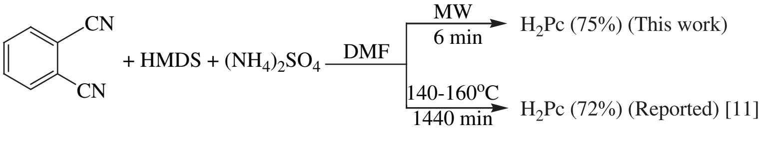
It is important to note that the yield of the reaction in the absence of HMDS and p-TsOH$\cdot H_2O$ as a catalyst intensively decreased and in the case of the PN the reaction is completely stopped. In addition, the reaction in the absence of DMF with each of the raw materials has not occurred.

It is important to note that the MPcs of two expensive metals such as Pt and Ru are prepared efficiently from PN. However, synthesis of these compounds from PA or PI was not successful and yields of the reaction were very low or reaction was completely stopped (entries 9 and 10).

In conclusion, we have developed a convenient and rapid procedure for the synthesis of H_2Pc and MPcs using microwave irradiation within a few minutes. Investigation toward extension of this procedure to other derivatives is in progress.

3. Experimental

The microwave oven was a domestic (max. 900 W) National model NN-6653 with five select power levels (two



Scheme 2.

Table 1
Optimization of reaction conditions and yield for the synthesis of H_2Pc from phthalonitrile

Entry	Molar ratio of raw materials (mmol)				Yield (%)/ time (min)	Literature[a]
	PN	HMDS	$(NH_4)_2SO_4$	DMF		
1	1.0	2.0	0.1	0.5	64(6)	
2	1.0	2.0	0.1	0.0	0(7)	
3	1.0	1.0	0.1	1.0	64(8)	
4	1.0	0.0	0.1	1.0	0(6)	
5	1.0	3.0	0.1	1.0	63(6)	
6	1.0	4.0	0.1	0.5	65(6)	
7	1.0	2.0	0.0	0.5	0(10)	
8	1.0	2.0	0.2	1.0	65(6)	
9	1.0	0.1	0.1	0.5	8(10)	
10	1.0	2.0	0.1	1.0	75(6)	72[b]
11	2.0	2.0	0.1	1.0	68(7)	
12	3.0	2.0	0.1	1.0	68(6)	

[a] Ref. [11a].

[b] PN (2.34 mmol), $(NH_4)_2SO_4$ (0.234 mmol), HMDS (4.69 mmol) and DMF (2.33 mmol) after heating at 150 °C for 24 h.

Table 2
The synthesis of H_2Pc from PN in the presence of $Na_2S \cdot xH_2O$ and 1,2-propylene glycol using microwave irradiation

Entry	Molar ratio (mmol)			Yield (%)/ time (min)	Literature[a]
	PN	$Na_2S \cdot xH_2O$	PG		
1	4.0	–	4.0	0(5)	–
2	4.0	0.3	–	0(5)	–
3	4.0	0.3	0.5	40(5)	–
4	4.0	0.2	1.0	60(5)	–
5	4.0	0.3	2.0	65(5)	–
6	4.0	0.3	3.0	70(5)	86.5[b]
7	4.0	0.2	3.0	60(5)	–
8	4.0	0.1	3.0	45(5)	–
9	4.0	0.3	6.0	72(5)	–

[a] Ref. [16].

[b] After heating at 140–150 °C for about 7 h.

of this was used for this experiment; high 100% Wattage, medium 70% Wattage). IR and UV–vis spectra were recorded with a Shimadzu IR-470 spectrometer and UV–vis Shimadzu 2100, respectively.

3.1. Procedure for the synthesis of H_2Pc

A mixture of PN (0.128 g, 1 mmol), HMDS (0.414 cm^3, 2 mmol), $(NH_4)_2SO_4$ (0.139 g, 0.1 mmol) and DMF (0.077 cm^3, 1 mmol) was irradiated in a glass sealed tube in the domestic microwave oven. As the reaction proceeded, dark purple solid gradually appeared. After completion of the reaction, the mixture was cooled and filtered. The solid was washed with methanol and dissolved in concentrated sulfuric acid (5 cm^3), and then the solution was poured into water (200 cm^3) to give a blue precipitate. The precipitate was filtered and washed successively with distilled water and dried in an oven. The solid was further purified by soxhlet extractor with methanol to give 0.096 g (75%) of H_2Pc.

3.2. Typical procedure for the synthesis of CuPc

A glass tube was charged with PN (0.512 g, 4 mmol) and CuCl (0.1 g, 1 mmol), HMDS (0.828 cm^3, 4 mmol), p-TsOH·H_2O (0.078 g, 0.41 mmol) and DMF (0.077 cm^3, 1 mmol) and stirred under a nitrogen atmosphere at room temperature for 20 min. The tube was sealed and irradiated in the domestic microwave oven for 7 min. As the reaction proceeded blue solid gradually appeared. The crude product was washed successively with cold water, acetone and then was dried. Next the product was dissolved in the concentrated H_2SO_4, precipitated from distilled water, filtrated off and washed with water and dried to give 0.449 g (78%) of CuPc.

All of the products are known compounds and their purities were confirmed by comparison with the literature.

$C_{32}H_{18}N_8$: IR (KBr): υ (cm^{-1}) 422, 688, 730, 735, 760, 869, 999, 1087, 1111, 1151, 1180, 1245, 1278, 1297, 1320, 1327, 1399, 1430, 1468, 1490, 1520, 3040, 3055, 3400, 3420. UV–vis ($CHCl_3$): λ_{max} (nm) 693, 656, 637, 594.

$C_{32}H_{16}CuN_8$: IR (KBr): υ (cm^{-1}) 724, 752, 775, 799, 871, 897, 1067, 1085, 1166, 1282, 1328, 1415, 1457, 1500, 1602. UV–vis (H_2SO_4): λ_{max} (nm) 791, 699, 440.

$C_{32}H_{16}CoN_8$: IR (KBr): υ (cm^{-1}) 729, 756, 778, 871, 911, 948, 1024, 1085, 1115, 1153, 1284, 1326, 1420, 1484, 1517, 1604. UV–vis (H_2SO_4): λ_{max} (nm) 784, 697, 425.

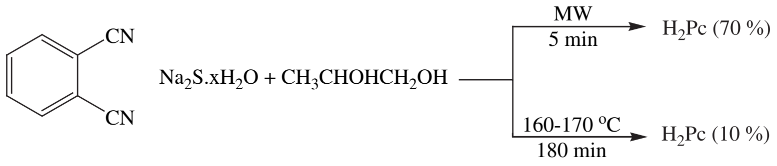
$C_{32}H_{16}NiN_8$: IR (KBr): υ (cm^{-1}) 724, 758, 770, 886, 911, 1086, 1114, 1158, 1287, 1327, 1421, 1455, 1538. UV–vis (H_2SO_4): λ_{max} (nm) 775, 683.

$C_{32}H_{16}FeN_8$: IR (KBr): υ (cm^{-1}) 724, 749, 775, 884, 1087, 1112, 1150, 1279, 1327, 1404, 1448, 1478, 1601. UV–vis (H_2SO_4): λ_{max} (nm) 796, 698.

$C_{32}H_{16}ZnN_8$: IR (KBr): υ (cm^{-1}) 726, 751, 775, 864, 948, 1065, 1112, 1158, 1282, 1325, 1415, 1462, 1600. UV–vis (H_2SO_4): λ_{max} (nm) 786, 697, 418.

$C_{32}H_{16}PdN_8$: IR (KBr): υ (cm^{-1}) 720, 752, 767, 807, 885, 911, 940, 1076, 1101, 1116, 1164, 1287, 1126, 1346, 1415, 1460, 1588. UV–vis (H_2SO_4): λ_{max} (nm) 797, 692.

$C_{32}H_{16}PtN_8$: IR (KBr): υ (cm^{-1}) 724, 765, 771, 915, 938, 998, 1071, 1119, 1164, 1325, 1417, 1456, 1588. UV–vis (H_2SO_4): λ_{max} (nm) 784, 693, 426.



Scheme 3.

Table 3
Synthesis of MPc by the reaction of PN, PI or PA under microwave irradiation

Entry	MX_n	Yield (%)/time (min)			
		PN	PI	PA	Literature[a]
1	CuCl	78(7)	75(7)	50(8)	–
2	$Cu(OAc)_2 \cdot H_2O$	55(7)	68(8)	35(8)	–
3	$CuCl_2 \cdot 2H_2O$	88(7)	50(8)	62(8)	63(10 h)[b]
4	$CoCl_2$	86(7)	48(9)	48(8)	51(10 h)[b]
5	$NiCl_2$	50(7)	45(9)	30(8)	53(4 h)[b]
6	$FeCl_2 \cdot 4H_2O$	78(7)	44(9)	40(8)	–
7	$ZnCl_2$	69(7)	40(10)	33(8)	47(10 h)[b]
8	$PdCl_2$	87(7)	68(9)	72(8)	–
9	$PtCl_4$	76(15)	0 (15)	17(12)	–
10	$RuCl_3$	65(15)	18(12)	0(12)	–

[a] Refs. [11b] and [11c].
[b] At 150 °C.

$C_{32}H_{16}RuN_8$: IR (KBr): υ (cm^{-1}) 730, 756, 775, 886, 903, 935, 998, 1052, 1113, 1179, 1283, 1318, 1408, 1435, 1460, 3040. UV–vis (H_2SO_4): λ_{max} (nm) 764, 680.

Acknowledgement

We gratefully acknowledge the financial support from the Research Council of Shahid Beheshti University.

References

[1] McKeown NB. Phthalocyanine materials: structure, synthesis and function. Cambridge: Cambridge University Press; 1998. 200 pp and references therein.

[2] Leznoff CC, Lever ABP. Phthalocyanines: properties and applications, vol. 1. New York: VCH; 1989. 1993 (vols. 2 and 3), 1996 (vol. 4).

[3] McKeown NB. Phthalocyanines. In: Comprehensive coordination chemistry. 2nd ed., vol. 1. Amsterdam: Elsevier; 2003 [chapter 1.24] p. 507–14 and references therein.

[4] De la Torre G, Claessens CG, Torres T. Eur J Org Chem 2000:2821. and references therein.

[5] Moser FH, Thomas AL. The phthalocyanines. Boca Raton: CRC Press; 1983.

[6] Moser FH, Thomas AL. Phthalocyanine compounds. New York: Reinhold; 1963.

[7] (a) Brit Patent; 1962: 909375;
(b) Swiss Patent; 1967: 428046;
(c) Brit Patent; 1965: 991419.

[8] (a) Shigemitsu M. Bull Chem Soc Jpn 1959;32:691;
(b) Shurvell HF, Pinzuti L. Can J Chem 1966;44:125–36.

[9] Turker L, Oker L. Dyes Pigments 1990;13:81–92.

[10] Calderazzo F, Pampaloni G, Vitali D. J Chem Soc Dalton Trans 1980:1965.

[11] (a) Uchida H, Yoshiyama H, Reddy PY, Nakamura S, Toru T. Bull Chem Soc Jpn 2004;77:1401–4;
(b) Uchida H, Reddy PY, Nakamura S, Toru T. J Org Chem 2003;68:8736;
(c) Uchida H, Tanaka H, Yoshiyama H, Reddy PY, Nakamura S, Toru T. Synlett 2002:1649;
(d) Uchida H, Tanaka H, Yoshiyama H, Reddy PY, Nakamura S, Toru T. Synlett 2003:2083.

[12] Loupy A. Microwave in organic synthesis. Weinheim: Wiley-VCH; 2002.

[13] (a) Shaabani AJ. Chem Res Synop 1998:672–3;
(b) Shaabani A, Bahadoran F, Bazgir A, Safari N. Iran J Chem Chem Eng 1999;18:104–7;
(c) Shaabani A, Safari N, Bahadoran F, Bazgir A, Sharifi N, Jamaat PR. Synth Commun 2003;33:1717–25;
(d) Safari N, Jamaat PR, Pirouzmand M, Shaabani A. J Porphyrins Phthalocyanines 2004;8:1209–13;
(e) Shaabani A, Bahadoran F, Safari N. Ind J Chem 2001;40A:195–7.

[14] (a) Tomoda H, Saito S, Ogawa S, Shiraishi S. Chem Lett 1980:1277;
(b) Tomoda H, Saito H, Shiraishi S. Chem Lett 1983:313;
(c) Wohrl D, Schnurpfeil G, Knothe G. Dyes Pigments 1992;18:91;
(d) Kitahara K, Asano T, Tokita S, Nishi H. J Heterocycl Chem 1989;26:1887;
(e) Brach PJ, Grammatica SJ, Ossana OA, Weinberger L. J Heterocycl Chem 1970;7:1403;
(f) Kobayashi N, Laver ABP. J Am Chem Soc 1987;109:7433.

[15] Lee CH, Ng DKP. Tetrahedron Lett 2002;43:4211.

[16] Seha Z. US Patent; 1976. 3,998,839 [Chem Abst. 82: 18624 j].