PAPER

Synthesis of non-substituted phthalocyanines by standard and non-standard techniques. Influence of solvent nature in phthalocyanine preparation at low temperature by UV-treatment of the reaction system

B. I. Kharisov,* U. Ortiz Méndez, J. L. Almaraz Garza and J. R. Almaguer Rodríguez

*Universidad Autónoma de Nuevo León, Monterrey, México. E-mail: bkhariss@ccr.dsi.uanl.mx*

Several synthetic techniques for metal-free phthalocyanines (Pc) and d- and f-metal phthalocyaninates ("PcM") starting from different precursors (phthalonitrile, urea and phthalic anhydride, phthalimide, phthalic acid, *etc.*) are reviewed. Conventional methods are presented, as well as some less well-known techniques such as those using ultrasound, laser, microwaves, or nuclear transformation. Special attention is paid to phthalocyanine formation at relatively low temperatures (0–60 °C). Experimental results on Pc formation using UV-irradiation of the reaction system are presented.

Brief revision of the main techniques for phthalocyanine preparation

Precursors and techniques

The well-known metal-free phthalocyanine (Pc or PcH_2) and its numerous metal complexes ("PcM", metal phthalocyanines or, more exactly phthalocyaninates) have been intensively studied since the early thirties[1–4] and are widely used in the pigment industry. Pc can be obtained by the classic template reactions starting from diverse precursors, such as phthalonitrile (PN), *o*-cyanobenzamide, 1,3-diiminoisoindoline (1,3-D), phthalimide (PM), phthalic acid, *etc.*, generally in high-boiling non-aqueous solvents at elevated temperatures,[5,6] or electrochemically from phthalonitrile.[7] In the case of PN use, CH_3O-Na (sodium methoxide, SM) and other strong bases are used in order to perform a nucleophilic attack at the cyano group of phthalonitrile:

Phthalocyanine precursors

Phthalonitrile
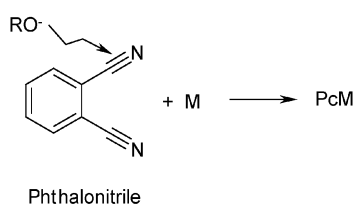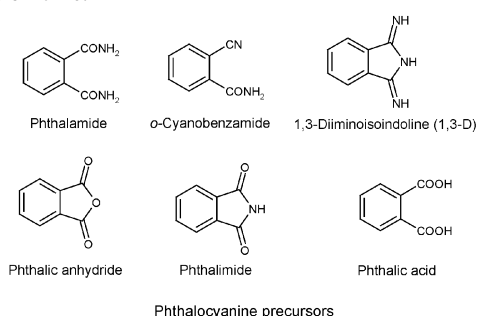
M = elemental Fe, Co, Ni, Cu, Zn, Cd, Sn or their salts

Metal-free phthalocyanine forms metal complexes with "strong" (for example, Fe, Cu, Ni) or "weak" (Mg, Sb) metals (according to their resistance to elimination from the product)

which can be synthesized: (a) *chemically* from metals or their salts[2–4] or (b) *electrochemically* from the bulk metals or their salts.[7] The first type (a) of reactions employs elemental metals or their salts, the above precursors and non-aqueous solvent. High-boiling substances as nitrobenzene, *o*-dichloro- and trichloro-benzene, ethyleneglycol, α-methylnaphthalene, quinoline, *etc.*, are usually used as solvents, although some alcohols or benzene have been successfully applied using PN as a precursor of Pc. The yields of these reactions are in the order of 90–100%.[5]

The electrochemical route, as well as less common techniques (use of laser, ultrasonic, and microwave treatment, see Table 1), is not often used for Pc preparation. The feasibility of the electrosynthesis of PcM was first reported by C. H. Yang,[7] who obtained "PcM" of Cu, Ni, Co, Mg, and Pb using metal salts or elemental Fe and Cu as a source for the central atom. Furthermore, Petit's research group[8] studied the electrosynthesis of PcCu by electroreduction of Pc with a copper sheet or an electrodeposited layer of copper on platinum as an anode. Among reported "non-standard" techniques for metal phthalocyanine production, microwave irradiation under solvent free conditions has been used for obtaining phthalocyanine derivatives of Ru, Rh, Pt, and Pt,[9] Zn, Mg, Co, and Cu[10] or Si.[11] Ultrasonic treatment is used as for synthetic purposes (Table 1) as for phthalocyanine destruction.[12]

As well as a variety of metal-free and d-metal phthalocyanines,[5,6] actinide phthalocyanines should be especially mentioned. In addition to classic synthetic techniques from Pc precursors and corresponding metal salts, sometimes they are obtained by element transformation processes. Thus, protactinium-233 and neptunium-239 di-phthalocyanines were prepared from the corresponding thorium-232 and uranium-238 di-phthalocyanines this way.[6] The existence of Pa and Np di-Pcs in reaction products is proven by repeated sublimation of the irradiated parent compounds using platinum gauze to retain the impurities. Np di-Pc is also synthesized on the trace scale from irradiated uranium metal, using the normal synthetic method for uranium di-Pc.[6] Actinide phthalocyanine structures, as well as those of 200 metal phthalocyanines and their derivatives, are classified in ref. 13. The lanthanides form, in particular, "super-complexes" (triple-decker) Ln_2Pc_3,[6] among others.

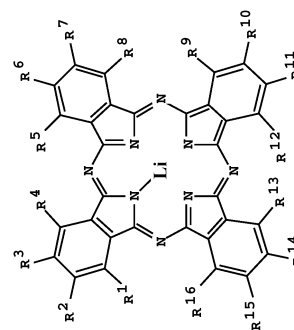**Table 1** Synthetic methods for phthalocyanine preparation

Metal or its salt	System	Product(s)	Conditions	Ref.
Traditional techniques				
Salts of various transition metals	(a) Phthalonitrile, CH$_3$ONa, solvent; (b) 1,3-diiminoisoindoline, solvent	Metal phthalocyanine	80–140 °C. In the case of absence of metals or their salts, free phthalocyanine PcH$_2$ is formed.	1–6
Transition metals in elemental state				
Salts of various transition metals	Urea and phthalic anhydride, inert high-boiling solvent, ammonium molybdate (catalyst), tetramethylurea (promoter)	Metal phthalocyanine	120–250 °C. Other phthalocyanine precursors can be used. Industrial process. PcH$_2$ is formed in absence of metal.	1–6
Microwave irradiation				
Metal (Zn, Mg, Co, Cu) chlorides or acetates	Metal-free phthalocyanines	Metal tetra-*tert*-butylphthalocyanine, (un)substituted phthalocyanines	Absence of any organic solvent. Sandwiched-type MPc$_2$ (such as LuPc$_2$) can be produced only through metal replacement from a metal-free phthalocyanine by microwave irradiation.	14,15
Rare earth elements and Hf and Zr salts	Phthalic and 4-*tert*-butylphthalic acid derivatives.	Bisphthalocyanines	—	16
Ru, Rh, Pt, Pd, Cu, Co, Ni, Fe and Zn salts	Phthalic anhydride	Phthalocyanines	Under solvent free conditions	9,17
	1,2-Bis(hydroxymethyl)benzene and 4-nitrophthalodinitrile	1,2-**Bis**(3,4-dicyanophenoxymethyl)benzene; its tetramerization with Zn(OAc)$_2 \cdot$2H$_2$O gives a binuclear Zn phthalocyanine of a new type, containing four *o*-phenylidene bridges	—	18
CuCl	Urea, phthalic anhydride, catalysts.	CuPc	The rate increased with increased microwave power	19–21
Mg, Zn, Cd, Ti, Zr, V, Mo, Mn, Fe, Ru, Ni, Pd, Pt, Co, Rh, Eu, U, La, Cr, and Ce salts	Phthalonitrile or tetrachlorophthalic anhydride	Metal phthalocyanines	Allows reproducible synthesis of large quantities of phthalocyanines	22
MCl$_2$, M = Si, Ge, Sn	Phthalonitriles or diiminoisoindolines in quinoline	Octaalkoxy-substituted metallophthalocyanines	—	23
Ultrasonic treatment				
CuCl	Phthalonitrile, solvent	Cu phthalocyanine	Sonication reactions were carried out *under room temperature conditions* extending from 1 min to 8 h in length	24
	Dichlorosilicon phthalocyanine monomer, a sodium chalcogenide	Cofacially stacked poly(phthalocyanato) siloxane polymer [Si(Pc)O]$_n$		25
Ge(Pc)Cl$_2$	Molecular oxygen or moisture	A coaxially stacked polymeric [Ge(Pc)O]$_n$	The synthesis was conducted in the presence of Na$_2$Te at room temperature	26
	α-Form of metal-free phthalocyanine.	X-form		27
Electrosynthesis				
LiCl	Phthalonitrile, ethanol	LiPc$^\bullet$ radical (see also *Phthalocyanine radicals*)		28–32
Cu, Fe, Mg, Sb	Phthalonitrile; or urea + phthalic anhydride; or phthalimide	Metal phthalocyanines or metal-free phthalocyanines	Influence of solvent on the reaction course is examined	33
Fe, Co, Ni, and Cu	Phthalonitrile	MPc	A facile, 1-stage, room-temperature preparation of MPc	34
	Phthalonitrile, PrOH	Metal-free phthalocyanine.		35
Cu, Ni, Co, Mg, and Pb salts	The catholyte (100 mL) contained 0.2 M Bu$_4$NClO$_4$ or Na xylenesulfonate and 0.2 M phthalonitrile, and the anolyte (100 mL) contained the respective metal salts in an alcohol solution		Electrolysis was carried out at −1.6 V *vs.* SCE and 60–100 mA for 3–5 h at room temperature Cu, Ni, Co, and Mg complexes were prepared using MeOH and the Pb-phthalocyanine complex was prepared using EtOH. Attempts using UO$_2^{2+}$ and Pb^{2+} in MeOH and UO$_2^{2+}$ in DMF failed to produce the corresponding complex but instead produced phthalocyanine.	7
Synthesis at relatively low temperatures (<100 °C) (see also Electrosynthesis)				
Ln, Nd, Pr, Sm	Phthalonitrile, solvent	M$_2$Pc$_3$		36
NiCl$_2$, CoCl$_2$	Phthalonitrile with DBU as a catalyst in BuOCH$_2$CH$_2$OH.	A polymorphic CoPc, NiPc	100 °C	37,38
	A mixture of 20 mmol phthalonitrile, 20 mmol of 1,8-diazabicyclo[5.4.0]undec-7-ene, and 50 mL ethanol	Metal-free phthalocyanine	Reflux	39

Table 1 (*continued*)

Metal or its salt	System	Product(s)	Conditions	Ref.
CuCl	Phthalonitrile		95 °C	40
CuCl₂ on Cu metal	$3,4\text{-}(NC)_2C_6H_3O(CH_2)_nOC_6H_3(CN)_2\text{-}3,4$ ($n = 3, 6, 10, 12$)	Alkylenedioxy-bridged polymeric phthalocyanines	Compared with other tetracarbonitriles, the reactions applying $3,4\text{-}(NC)_2C_6H_3O(CH_2)_nOC_6H_3(CN)_2\text{-}3,4$ ($n = 3, 6, 10, 12$), which contain a flexible alkylene chain, run at relatively low temperatures leading to good yields of polymers with a high degree of formation of phthalocyanine rings	41
Cu phthalocyaninetrisulfonyl chloride	Ethylenediamine and aniline-4-β-sulfatoethyl sulfone, then 2,4,6-trichloro-5-cyanopyrimidine	$Pc(SO_3H)_a(SO_2NR^1AX)_b(SO_2YZ)_c$ [Pc = (metal-containing) phthalocyanine residue; $R^1 = H$, Me, Et; A = (un)substituted phenylene, naphthylene; X = $SO_2CH{=}CH_2$, $SO_2CH_2CH_2W$; W = alkali-releasable group; Y = $NR_2(CH_2)_nNR_3$; R^2, $R^3 = H$, Me, Et; $n = 0$–6; Z = pyrimidinyl containing ≥ 2 Cl and containing no F; $a = 0$–2; b, $c = 1$–3; $a + b + c \leq 4$	At 30 °C	42
Mg, Zn, Fe or Cu powder	Phthalonitriles	Metal phthalocyanines	Room temperature	43
Li 1-octanolate Ni(CO)₄	Phthalonitrile, NaY zeolite matrix	Ni phthalocyanine	Template synthesis with Ni(CO)₄ began at 70–80 °C, *i.e.* milder conditions than previously reported template syntheses of Ni phthalocyaninate	44
Irradiation (UV or visible light)				
Li salts	Phthalonitrile in various alcohols, CH₃ONa	PcH₂	Room temperature processes	45,46
	Quaternary ammonium phthalocyaninates(2−)	LiPc˙	See also *Electrosynthesis and Synthesis of phthalocyanine radicals*	47
Zn salts	Phthalocyanine, CBr₄ as an electron acceptor	π-Cation-radical species of ZnPc, $Zn(Pc^-)^{\bullet+}$	Quantitative yield	48
Laser irradiation				
Cu target	Li₂Pc or 1,3-diiminoisoindoline	CuPc	CuPc was prepared by the implantation of laser-ablated copper atoms onto a thin film of 1,3-diiminoisoindoline	49
Phthalocyanine complexes of radioactive elements (or radioactive isotopes of stable elements)				
Am acetate	Phthalonitrile	Am phthalocyanine	DTA data indicate that Am phthalocyanine decomposes at 650 °C. In DMF–N₂H₄·H₂O, the complex exists in the form of [Pc₂Am]⁻, where Pc is the phthalocyanine dianion. In the solid phase Am phthalocyanine is found in the oxidized form as PcAmPcₒₓ, where Pcₒₓ is the 1-electron oxidized form of the phthalocyanine dianion.	50
U	1,2-Dicyanobenzene under a stream of I₂	UPc₂I₂		51
UO₂, U hydride	Neutron bombardment	Np, Pu phthalocyaninates	Irradiated UO₂ was oxidized by air and sometimes reduced by EtOH vapor; the resulting oxide was treated with acetylacetone vapor, which removed some Np and some Ru. The oxide samples were also treated with C₆H₄(CN)₂ vapor, with molten C₆H₄(CN)₂, or with mixed C₆H₄(CN)₂-phthalocyanine melt, in order to form in each case the phthalocyanine complexes.	52,53
Dioxocyclopentakis(1-iminoisoindolinato)uranium(VI), UO₂(SPc)	PBu₃, DMF, PhSH, 2-mercaptoethanol, CuCl₂, FeCl₃, ZnCl₂ and Th(NO₃)₄·6H₂O	Phthalocyanine (H₂Pc) or MPc (M = Fe, Zn or Cu) or UPcL_m (L = PBu₃, DMF or 2-mercaptoethanol; m unknown)	The mechanism involves the initial reduction of UO₂(SPc) by either PBu₃, DMF or 2-mercaptoethanol	54
UO₂(NO₃)₂·6H₂O		UO₂Pc	UO₂Pc was prepared *via* a Lewis base complex	55

Table 1 (*continued*)

Metal or its salt	System	Product(s)	Conditions	Ref.
	DMF, Li$_2$Pc $\quad$ H$_2$Pc = phthalocyanine, H$_2$Pc(SO$_3$H)$_4$ = phthalocyanine-tetrasulfonic acid)			
ThCl$_4$·2Et$_3$N	Phthalocyanine	ThPc$_2$	240 or 530 °C, in case of MI$_4$ use.	56
Th; ThI$_4$ or UI$_4$	Phthalonitrile	MPc$_2$	^{239}NpPc$_2$ was also chemically synthesized on the trace scale from irradiated U metal (U + ^{239}Np) using the normal synthetic method for UPc$_2$, yielding (UPc$_2$ + ^{239}NpPc$_2$)	57,58
MPc$_2$ (M = Th, U)	Element transformations (n,γ) of ^{232}Th and (β$^-$) of ^{238}U, respectively.	MPc$_2$ (M = ^{233}Pa, ^{239}Np)		59
PaI$_4$·4MeCN	*o*-Phthalic acid dinitrile in 1-chloronaphthalene	PaPc$_2$	A product almost completely free of H$_2$Pc impurity which is known to be present in previously reported complexes of the type AnPc$_2$	60
Tc salts	NH$_4$$^+$ salts, phthalonitrile	Tc phthalocyanine		61
Mixture of Mo or W (or its oxide)	Cu phthalocyanine, (d, xn) reactions. The synthesis of Tc and Re phthalocyanines was undertaken by recoil implantation of isotopes generated by (d, xn) reactions in mixture of Mo or W (or its oxide) with Cu phthalocyanine.	Tc and Re phthalocyanines	The most probable valence state of Tc and Re in the complex seems to be +4	62
Radioactive ions of In$^+$, InCl$^+$, and InCl$_2$$^+$	Cu phthalocyanine or metal-free phthalocyanine	Indium phthalocyanine complexes	Ion-implantation was used to synthesize radioactive In phthalocyanine complexes. Radioactive ions of In$^+$, InCl$^+$, and InCl$_2$$^+$ gave definite complex yields after bombarding Cu phthalocyanine or metal-free phthalocyanine. The yield varied with the conditions of implantation and increased with an increase of total ion current in most cases.	63
Synthesis of phthalocyanine radicals (see also Electrosynthesis and Irradiation)				
Dichloro(phthalocyaninato)antimony(v) hexachloroantimonate	An electrolyte soln. of 170 mg Bu$_4$NClO$_4$ in 100 mL CH$_2$Cl$_2$ (concentration 1 × 10^{-4} mol L^{-1}) and electrolyzed at −200 mV	A phthalocyanine radical anion	A phthalocyanine radical anion which is stable against air oxidation in the atmosphere, is prepared by one electron-reduction of dihalo(phthalocyaninato)antimony(v) cation salt. The phthalocyanine radical anion is useful for n-type org semiconductors.	64
Di-Li phthalocyanine	Electronic oxidation	Li phthalocyanine radical (R$^{1-16}$) = H, D		65

In Table 1, we present a brief generalization of the most important techniques for metal-free and metal phthalocyanines preparation. The experimental results on the synthesis of phthalocyanines at relatively low temperatures (0–60 °C) using phthalonitrile as a precursor in the conditions of UV-irradiation of the reaction system will be described below. The reviewed techniques are generally "non-standard"; according to some of them, the yield of metallophthalocyanines is increased relative to that obtained by conventional methods and the reaction time is usually shorter.

As can be seen, various routes can yield PcH_2 or PcM at low temperature, in particular direct electrochemical procedures with use of sacrificial metal anodes or metal salts,[66,67] use of strong bases, and by UV-irradiation of the reaction system. In this respect, two recent articles[43,68] should be especially mentioned, in which very mild conditions for Pc synthesis were offered. In ref. 68 room-temperature synthesis of substituted and non-substituted PcM was carried out from phthalonitriles in the presence of *solid* sodium methoxide in THF; several important advantages of this approach were reported. It was considered that the Pc core formation probably occurs on the surface of solid CH_3ONa. A series of primary alcohols and elemental metals were used for the condensation of phthalonitriles at room temperature.[43] Leznoff[43] proposed that more activated forms of some metals are required. In this respect, at low temperatures an additional "impulse" is needed for the cyclization process; precisely, surface energy of strong base (solid CH_3ONa)[68] or extra energy of defects in the surface of elemental metals[43] could serve as such an impulse to reach the energetic barrier. So, any source of additional energy could be useful for successful synthesis at low temperatures. To serve as such sources, the metals in activated form (in particular, Rieke metals[69]) could be extremely useful. The peculiarity of their surface is a high concentration of imperfections, which render them much more active in comparison with the same metals in their "standard" form (sheet, wire or non-active powder). Additionally, zeolites and other microporous materials can be also used for obtaining phthalocyanine from phthalonitrile in cavities.[70–72]

According to the considerations above for optimizing the low-temperature preparation of phthalocyanines, six routes are being developed in our laboratory: (1) UV-irradiation of the reaction system (without use of metals)[45] and use of radical-forming compounds; (2) use of elemental metals[43] in the form of active finely divided pyrophoric metal powders[73] and *Rieke* metals[69] as "matrices" for phthalonitrile cyclization and Pc core formation; (3) direct electrochemical synthesis using sacrificial anodes and even cathodes;[7,8,32,33,36,66,67] (4) use of zeolites and other microporous materials,[70–72] (5) use of so-called "supported metals"[69] and (6) search of active (or non-stable) complexes or organic bases[68] for the first cyclization reaction step. In this publication, we present the experimental results of the first technique.

Experimental

Synthesis of metal-free phthalocyanines at relatively low temperatures (0–60 °C) by UV-treatment of the reaction system

Materials and equipment. Phthalonitrile, DBU, 30% solution of CH_3ONa in CH_3OH, and PcH_2 (Aldrich) were used as supplied. Solvents (from Aldrich and Fisher) were distilled by standard methods before use. The photochemical reactor (Fig. 1, mercury lamp of 1200 W) was used for irradiation of samples. Although the mercury lamp was cooled by water flow, it caused a rapid heating of the reactor space. So, in order to maintain the necessary constant temperature, the quartz tubes with sample solutions were partially immersed in a bath, connected to a thermostat outside the reactor. The temperature inside the bath and in the thermostat was controlled by thermometers. The distance of the samples from light source
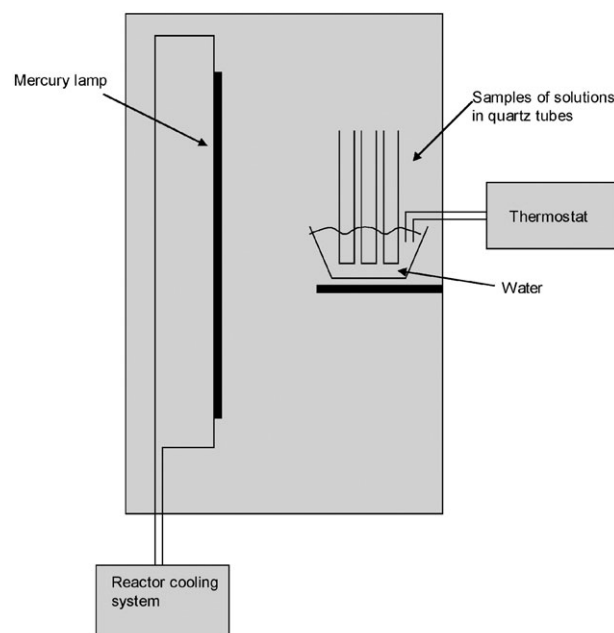

Fig. 1 Scheme of the UV-reactor.

was about 20 cm; the samples were located in the vertical middle of the reactor.

Organic microanalyser (Perkin-Elmer) was used for C, H and N content determination. Infrared and UV/visible (in pyridine) spectra were recorded on Perkin-Elmer and Lambda 12, respectively.

UV-Irradiation of the reaction system. The solutions, in a series of solvents, contained phthalonitrile as Pc-precursor and CH_3ONa (or DBU, 1,8-diazabicyclo[5.4.0]undecene-7-ene) as a nucleophilic reagent, were irradiated for 3 h in a photochemical reactor at 0–60 °C. The following alcohols were used: methanol, ethanol, isobutanol, *tert*-butanol, cyclohexanol, 2-octanol, ethyleneglycol, ethoxyethanol, and DMEA (dimethylethanolamine). Parallel experiments were carried out without any nucleophilic reagent in the same conditions. Each solution in quartz tube contained 0.5–1 g of phthalonitrile, depending on the solubility of phthalonitrile in a solvent, 5–10 mL of the solvent and 2 drops of DBU or 30% solution of CH_3ONa in CH_3OH.

Purification and identification of the products. Phthalocyanines formed were purified by washing with hot ethanol in a Soxhlet equipment and dried in air. According to elemental analysis data, a composition of the obtained products corresponds to typical phthalocyanine (metal-free PcH_2). Some variations of composition (0.05–0.30%) were observed in different experiments. The IR spectra (KBr pellet) of the phthalocyanine contain the following main bands (cm^{-1}), among others: 3500–3380(vs, w), 2815(m), 2504(m) {ν(C–H)}; 2300–2280(s), 1730(vs), 1607(s), 1524(m) {ν(C–C) of benzene rings}; 1448(m) {ν(C–C) of pyrrole rings}; 1385(v.s.), 1365(s) (pyrrole nuclei-*meso* atoms of N); 1320(m), 1309 (m), 1150(s) {γ(C–H)}, 720, 690, 675 and 622. UV/vis data (nm) of PcH_2 in pyridine are the following: 692–693, 659–660 (Q-band), 640, 602–604.

Results and discussion

Observations

It was observed that in ethyleneglycol the product is formed in all the range 0–60 °C with yields from traces to quantitative (Table 2). In case of ethyleneglycol, due to the high viscosity of this solvent it was difficult to evaluate exactly a real yield.

Table 2 Phthalocyanine yields at different temperatures under UV-irradiation

Solvent/base	Yield (%)										
	Temperature/°C/										
	0–5	5–10	10–15	15–20	20–25	25–30	30–35	35–40	40–45	45–50	50–55
Ethyleneglycol	0	0	0	0	0	0	0	0	0	0	0
Ethyleneglycol/DBU	Traces	Traces	Traces	<5	17–20	35–40	50–55	100	100	100	100
Ethyleneglycol/CH$_3$ONa	Traces	Traces	Traces	<7	20–25	32–36	40	60	80	100	100
Ethanol	0	0	0	0	0	0	0	0	0	0	0
Ethanol/DBU	0	0	Traces	Traces	15–20	38–40	45–50	100	100	100	100
Ethanol/CH$_3$ONa	0	Traces	Traces	15–22	50–55	70–75	100	100	100	100	100
Methanol	0	0	0	0	0	0	0	0	0	0	0
Methanol/DBU	Traces	Traces	<10	20–25	45–55	65–73	100	100	100	100	100
Methanol/CH$_3$ONa	Traces	Traces	10–15	25–30	50–55	70–75	100	100	100	100	100
DMEA	0	0	0	0	0	0	0	0	0	0	0
DMEA/DBU	0	0	0	0	0	0	0	Traces	Traces	80–85	100
DMEA/CH$_3$ONa	0	0	0	0	0	0	<10	50–60	75–80	100	100
Ethoxyethanol	0	0	0	0	0	0	0	0	0	0	0
Ethoxyethanol/DBU	0	0	0	0	0	0	0	Traces	Traces	75–80	100
Ethoxyethanol/CH$_3$ONa	0	0	0	0	0	0	Traces	45–50	65–75	75–80	100

Among the other solvents used, methanol and ethanol were the best, in which media quantitative yields were registered at 30–60 °C and smaller at 0–25 °C. Ethoxyethanol and DMEA also appeared to be good solvents for Pc formation by UV-irradiation, although the yields were lower. It was also confirmed by higher Pc yields that CH$_3$ONa is a stronger nucleophilic agent in comparison with DBU. In some cases, the Pc formation was not immediate: in 3–48 h after finishing UV-irradiation. In the parallel experiments, when no nucleophilic reagent was used, no phthalocyanine formation was observed. In other alcoholic media, no Pc formation was detected.

UV irradiation effect on Pc formation

Tomoda and co-workers reported[45] that PcH$_2$ could be produced from phthalonitrile at room temperature in different alcoholic solvents. The authors concluded that the UV treatment is effective only at the initial stage of the reaction because of an absence of the product after heating the reaction mixture in the dark and further exposure to UV light.[45] In our previous investigation,[33] it was established that, starting from 1,3-di-iminoisoindoline (1,3-D), PcH$_2$ formation takes place even at 5–7 °C in N,N-dimethylethanolamine exposing 1,3-D solution at UV light.

When phthalonitrile is used as a precursor, free RO$^\bullet$ radicals appear due to UV irradiation of the alcohol solutions of phthalonitrile, contributing to the nucleophilic attack on the carbon atom of the CN group together with the action of CH$_3$ONa or DBU. Probably, this is a cause of PcH$_2$ formation at room temperature under the conditions of UV-irradiation. In case of use of N,N-dimethylethanolamine, the formation of free radicals (CH$_3$)$_2$NCH$_2$CH$_2$O$^\bullet$ takes place; additionally, the electron lone pair of the nitrogen atom could take part in nucleophilic attack on the carbon atom of the CN group.

It was noted that the yields in ethyleneglycol seem to be higher in comparison with other alcohols having only one OH group. Unfortunately, as was mentioned earlier, it is difficult to evaluate a real yield due to the difficulties in isolation of the product from this solvent. Evidently, an increase in the number of OH groups leads to an increase in the quantity of free radicals. The experiments in glycerine gave the similar results, but it was absolutely impossible to isolate the product from this solvent, so real yields in glycerine are unknown.

Conclusions

Phthalocyanines can be obtained from phthalonitrile as a precursor under mild conditions at room temperature in the conditions of additional activation of the reaction system (UV irradiation, direct electrochemical procedure, use of strong solid bases or elemental metals, etc.). Non-substituted phthalocyanine can be obtained from phthalonitrile under mild conditions (0–60 °C) in various alcohols under UV-irradiation of the reaction system.

References

1 R. P. Linstead, *J. Chem. Soc.*, 1934, 1016.
2 G. T. Byrne, R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1934, 1017.
3 R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1934, 1022.
4 C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1934, 1027.
5 (*a*) *Phthalocyanines Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publ. Inc., New York., Vol. 1, 1990; (*b*) *Phthalocyanines Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publ. Inc., New York., Vol. 2, 1992; (*c*) *Phthalocyanines Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publ. Inc., New York., Vol. 3, 1993; (*d*) *Phthalocyanines Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publ. Inc., New York., Vol. 4, 1996.
6 A. L. Thomas, *Phthalocyanines. Research and Application*, CRC Press, Boca Raton, 1990.
7 C. H. Yang, S. F. Lin, H. L. Chen and C. T. Chang, *Inorg. Chem.*, 1980, **19**, 3541.
8 M. A. Petit, V. Plichon and H. Belkacemi, *New J. Chem.*, 1989, **13**, 459.
9 A. Shaabani, F. Bahadoran and N. Safari, *Indian J. Chem. A*, 2001, **40**(2), 195.
10 L.-C. Liu, C.-C. Lee and A. T. Hu, *J. Porphyrins Phthalocyanines*, 2001, **5**(11), 806.
11 D. A. Davies, C. Schnik, J. Silver, J. L. Sosa-Sánchez and P. G. Riby, *J. Porphyrins Phthalocyanines*, 2001, **5**(4), 376.
12 Shin Pin Tu, Daeik Kim and The Fu Yen, *J. Environ. Eng. Sci.*, 2002, **1**, 237.
13 M. K. Engel, *Report Kawamura Inst. Chem. Res. 1996*, 1997, **8**, 11–54 (*Chem. Abs.*, 1998, **127**, 313213).
14 Hu, Andrew Teh, Tseng, Tsai-Wie, Hwu, Herng-Dar, Liu, Lung-Chang, Lee, Chung-Chun, Lee, Ming-Chia, Chen and Jun-Rong, *US Pat*., 2002, 5 pp., US 6491796 B1 20021210.
15 Liu, Lung-Chang, Lee, Chung-Chun, Hu and Andrew Teh, *J. Porphyrins Phthalocyanines*, 2001, **5**(11), 806–807.
16 E. G. Kogan, A. V. Ivanov, L. G. Tomilova and N. S. Zefirov, *Mendeleev Commun.*, 20022), 54–55.

17 (*a*) A. Shaabani, F. Bahadoran, A. Bazgir and N. Safari, *Iran. J. Chem. Chem. Eng.*, 1999, **18**(2), 104–107; (*b*) A. Shaabani, *J. Chem. Res.*, 1998, **10**, 672–673.

18 A. Yu, Tolbin, A. V. Ivanov, L. G. Tomilova and N. S. Zefirov, *Mendeleev Commun.*, 2002, **12**(3), 96–97.

19 He, Xiao-mei, Lu, Jian-bo, Lu, Jian-mei and Zhu, Xiu-lin, *Hecheng Huaxue*, 2002, **10**(1), 87–90.

20 Jung, Ki Suck, Ro, Ji Young, Lee, Jong Young and Park, Seong Soo, *J. Mater. Sci. Lett.*, 2001, **20**(24), 2203–2205.

21 Park Seong Soo, Jung Ki Suck, Lee Jong Young, Park Jin Hwan, Lee Gun Dae and Suh Cha Soo, *Kongop Hwahak*, 2001, **12**(7), 750–754.

22 D. Villemin, M. Hammadi, M. Hachemi and N. Bar, *Molecules*, 2001, **6**(10), 831–844, http://www.mdpi.org/molecules/papers/61000831.pdf.

23 C. P. Ungurenasu, *Síntesis*, 199910), 1729–1730.

24 B. B. Khanukaev and N. S. Khanukaeva, *Zh. Fiz. Khim.*, 1998, **72**(9), 1607–1611.

25 B. J. Exsted and M. W. Urban, *Adv. Chem. Series 236 (Structure-Property Relations in Polymers)*, 1993, 791–809.

26 M. D. Hohol and M. W. Urban, *Polymer*, 1993, **34**(9), 1995–2002.

27 P. Gregory and P. M. Mistry, *Br. Pat. Appl.*, 1989, 4 pp., GB 2214922 A1 19890913.

28 G. Ilangovan, J. L. Zweier and P. Kuppusamy, *J. Phys. Chem. B*, 2000, **104**(40), 9404–9410.

29 G. Ilangovan, J. L. Zweier and P. Kuppusamy, *J. Phys. Chem. B*, 2000, **104**, 4047.

30 M. A. Petit, T. Thami and R. Even, *J. Chem. Soc., Chem. Commun.*, 198915), 1059–1060.

31 P. Turek, J. J. Andre, A. Giraudeau and J. Simon, *Chem. Phys. Lett.*, 1987, **134**(5), 471–476.

32 M. A. Petit, T. Thami, C. Sirlin and D. Lelievre, *New J. Chem.*, 1991, **15**(1), 71–74.

33 Kharisov, B. I. Blanco, L. M. Torres-Martinez and L. M. Garcia-Luna, *Ind. Eng. Chem. Res.*, 1999, **38**(8), 2880–2887.

34 L. Griffiths, B. P. Straughan and D. J. Gardiner, *J. Chem. Soc., Dalton Trans.*, 19836), 1193.

35 H. Distler, W. Habermann, J. Kranz and R. Widder, *Ger. Offen.*, 1980, 17 pp., DE 2849065 19800522.

36 B. I. Kharisov, L. M. Blanco-Jerez and A. Garcia-Luna, *Rev. Soc. Quím. Méx.*, 1999, **43**(2), 50–53.

37 T. Enokida and R. Hirohashi, *Chem. Mater.*, 1991, **3**(5), 918–921.

38 T. Enokida and R. Hirohashi, *Chem. Lett.*, 1991, **12**, 2155–2158.

39 H. Tomota, *Jpn. Kokai Tokkyo Koho*, 1983, 5 pp., JP 58023854 A2 19830212.

40 S. Horiguchi, Y. Abe and T. Hosoda, *Jpn. Tokkyo Koho*, 1970, 4 pp., JP 45006708 19700307.

41 D. Woehrle and B. Schulte, *Makromol. Chem.*, 1988, **189**(6), 1229–1238.

42 T. Hibara and Y. Shimizu, *Jpn. Kokai Tokkyo Koho*, 1995, 6 pp., JP 07316453 A2 19951205.

43 C. C. Leznoff, A. M. D'Ascanio and S. Z. Yildiz, *J. Porphyrins Phthalocyanines*, 2000, **4**(1), 103–111.

44 A. N. Zakharov, *Kinet. Katal.*, 1991, **32**(6), 1377–1384.

45 H. Tomoda, E. Hibiya, T. Nakamura, H. Ito and S. Saito, *Chem. Lett.*, 1976, **9**, 1003–1006.

46 K. Uosaki and Ueda, *Chemistry of Functional Dyes, Proceedings of the 2nd International Symposium*, (Meeting date August, 1992), Mita Press, Japan, 1993, pp. 270–275.

47 H. Homborg and W. Z. Kalz, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1978, **33B**(10), 1067–1971.

48 T. Nyokong, Z. Gasyna and M. J. Stillman, *Inorg. Chem.*, 1987, **26**(4), 548–553.

49 H. Sato, S. Nishio and M. Tani, *Appl. Phys. A: Mater. Sci. Proc.*, 1999, **69**(Suppl.), S775–S777.

50 P. N. Moskalev and G. N. Shapkin, *Radiokhimiya*, 1977, **19**(3), 356–9.

51 J. Janczak, R. Kubiak, I. Svoboda, A. Jezierski and H. Fuess, *Inorg. Chim. Acta*, 2000, **304**(1), 150–155.

52 F. Ammentorp-Schmidt, Avail. Gmelin. AEC Access. Nos. (1965), (AED-Diss. 65-361), p. 76. From: *Nucl. Sci. Abstr.*, 1966, **20**(23), 43153.

53 F. Lux and F. Ammentorp-Schmidt, *Radiochim. Acta*, 1965, **4**(2), 112–13.

54 J. Silver and Q. A. A. Jassim, *Inorg. Chim. Acta*, 1988, **144**(2), 281–8.

55 N. A. Frigerio, *US Pat.*, 1962, 5 pp., US 3027391 19620327.

56 I. S. Kirin and A. B. Kolyadin, *Zh. Neorgan. Khim.*, 1973, **18**(11), 3140–1.

57 K. Endo and M. Sakanoue, *Radiochem. Radioanal. Lett.*, 1972, **9**(4), 255–61.

58 F. Lux, D. Dempf and D. Graw, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**(10), 819–820.

59 F. Lux, F. Ammentorp-Schmidt, D. Dempf, D. Graw and W. Hagenberg, *Radiochim. Acta*, 1970, **14**(2), 57–61.

60 F. Lux, O. F. Beck, H. Krauss, D. Brown and T. C. Tso, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1980, **35B**(5), 564–567.

61 S. Rummel, M. Herrmann and K. Schmidt, *Ger. Offen.*, 1985, 5 pp., DD 219486 A1 19850306.

62 K. Yoshihara, G. K. Wolf and F. Baumgaertner, *Radiochim. Acta*, 1974, **21**(1–2), 96–100.

63 K. Yoshihara, M. Kishimoto, M. Takahashi, S. Suzuki and T. Shiokawa, *Radiochim. Acta*, 1974, **21**(3–4), 148–150.

64 H. Isago, Y. Kagaya and M. H. Zahir, *Kokai Tokkyo Koho*, 2000, 3 pp., JP 2000095782 A2 20000404.

65 M. Moussavi (Commissariat a l'Energie Atomique, Fr.), *Eur. Pat. Appl.*, 1992, 13 pp., EP 467747 A1 19920122.

66 *Direct Synthesis of Coordination & Organometallic Compounds*, ed. A. D. Garnovskii and B. I. Kharisov, Elsevier Science, Amsterdam, 1999, p. 244.

67 *Synthetic Coordination & Organometallic Chemistry*, ed. A. D. Garnovskii and B. I. Kharisov, Marcel Dekker, New York, 2003, p. 513.

68 V. N. Nemykin, N. Kobayashi, V. M. Mytsyk and S. V. Volkov, *Chem. Lett.*, 2000, 546.

69 *Active Metals. Preparation Characterization. Applications*, ed. A. Furstner, VCH, Weinheim, 1996, p. 465.

70 P. Prochnow, G. Schulz-Ekloff, D. Wohrle, A. Zukal, J. Rathousky, M. Borowski and M. Wark, *Microporous Mesoporous Mater.*, 2002, **56**(2), 131.

71 S. Seelan, A. K. Sincha, D. Srinivas and S. J. Sivasanker, *Mol. Catal., A: Chem.*, 2000, **157**(1–2), 163.

72 M. Wark, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Elsevier Science, USA, 2003, vol. 17, pp. 247–283.

73 B. I. Kharisov, C. E. Cantú Coronado, K. P. Coronado Cerda, U. Ortiz Méndez, J. A. Jacobo Guzmán and L. A. Ramírez Patlán, *Inorg. Chem. Commun.*, 2004, **7**(12), 1269–1272.