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Novel and Mild Route to Phthalocyanines and 3-Iminoisoindolin-1-ones *via N,N*-Diethylhydroxylamine-Promoted Conversion of Phthalonitriles and a Dramatic Solvent-Dependence of the Reaction

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Abstract: Refluxing a mixture of phthalonitrile $C_6R^1R^2R^3R^4(CN)_2$ **1** (R^1–R^4 = H), or its substituted derivatives **2** (R^1, R^3, R^4 = H, R^2 = Me), or **3** (R^1, R^4 = H, R^2, R^3 = Cl) (1 equiv.) and *N,N*-diethylhydroxylamine, Et_2NOH, (4 equivs.) in *methanol* for 4 h results (**Route A**) in precipitation of the symmetrical (**6** and **8**) and an isomeric mixture of unsymmetrical (**7**) phthalocyanines, isolated in good (55–65%) yields. The reaction of phthalonitriles **1**, **2**, or **4** (R^1, R^3, R^4 = H, R^2 = NO_2) (4 equivs.) with Et_2NOH (8 equivs.) in the presence of a metal salt MCl_2 (M = Zn, Cd, Co, Ni) (1 equiv.) in *n*-BuOH or without solvent results in the formation of metallated phthalocyanine species (**9**–**17**). Upon refluxing in freshly distilled dry *chloroform*, phthalonitrile **1** or its substituted analogues **2**, **3** or **5** (R^1–R^4 = F) (1 equiv.) react with *N,N*-diethylhydroxylamine (2 equivs.) affording 3-iminoisoindolin-1-ones **18**–**21** (**Route B**) isolated in good yields (55–80%). All the prepared compounds were characterized with C, H, and N elemental analyses, ESI-MS, IR, and compounds **18**–**21** also by 1D (^{1}H, ^{13}C{^{1}H}), and 2D (^{1}H,^{15}N-HMBC and ^{1}H,^{13}C-HMQC, ^{1}H,^{13}C-HMBC) NMR spectroscopy.

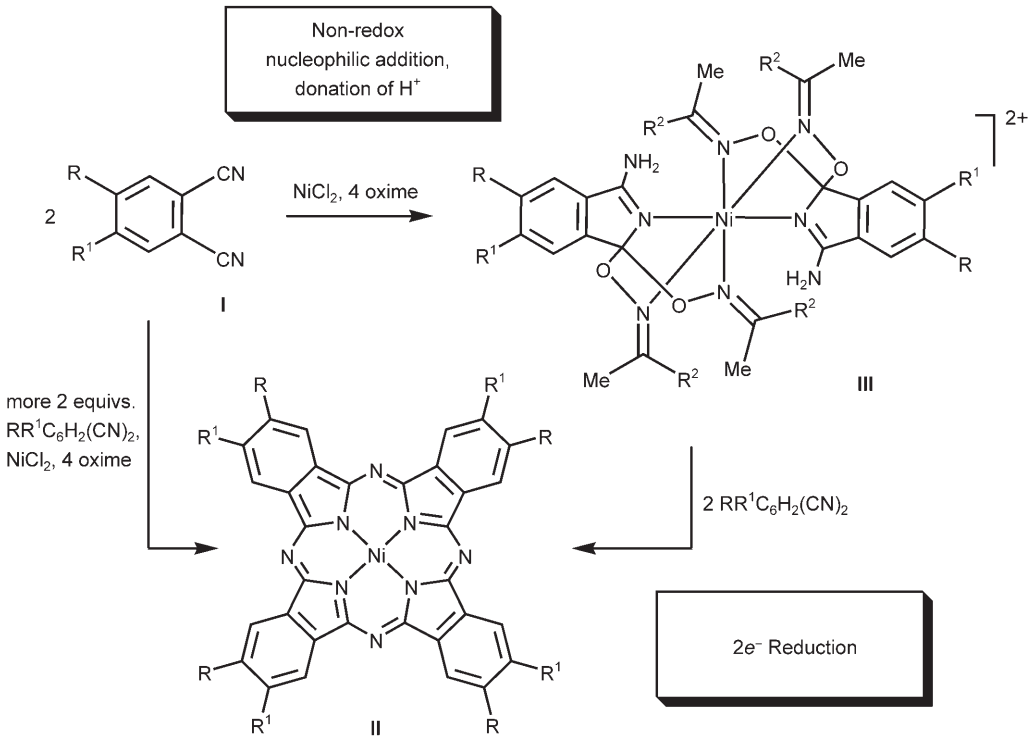
Keywords: *N,N*-diethylhydroxylamine; 3-iminoisoindolin-1-ones; metal-free phthalocyanines; metallated phthalocyanines; phthalonitriles; solvent dependence

Introduction

Since their discovery, metal-free (**Pcs**) and metallated phthalocyanines (**M-Pcs**) have become compounds of a great importance with a wide range of applications in industry, laboratory, and medicine,[1,2] e.g., as dyes/pigments,[1,2] molecular and photoconductors,[3] liquid crystalline mesophases,[3] oxidation catalysts,[2] and agents in anticancer photodynamic therapy.[4]

Pcs are commonly the parent compounds for a series of phthalocyanine species and from a *synthetic viewpoint* they are even more important than **M-Pcs**. Indeed, **Pcs** are employed for the preparation of **M-Pcs**, especially those which are not directly accessible *via* template synthesis (e.g., yields of lanthanide-**Pcs** obtained from **Pcs** and an Ln compound[5] are by an order of magnitude higher than in the template synthesis[6]). In addition, the reaction between **Pcs** and metal sources to afford **M-Pcs** proceeds under much milder conditions in comparison with the conventional template synthesis; the former is particularly useful for the preparation of thermally unstable **M-Pcs**.

The synthetic routes to metal-free **Pcs** have not changed substantially since the early works by Linstead,[7] and usually involve cyclotetramerization of the so-called phthalogenes (1,2-disubstituted benzenes),[1] e.g., 1,3-diiminoisoindoline, *o*-cyanobenzamide or phthalonitrile (**Pn**). The reaction of **Pns** occurs upon reflux in C_3–C_8 alcohols, 2-(*N,N*-dimethylamino)ethanol or without solvent at 100–300 °C for



Scheme 1.

prolonged time and requires the presence of a nucleophile, e.g., OR^- or DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene).[1,2]

Another route to **Pcs** is the demetallization of **M-Pcs**, obtained by template synthesis, on their heating in concentrated H_2SO_4.[1,2] Thus, the majority of methods for the preparation of **Pcs** are typically performed at elevated temperatures, are energy- and/or time-consuming, involve moisture-sensitive or dangerous reagents (e.g., Na or Li) and dry solvents or require demetallization.

Recently, within our ongoing project on metal-mediated and/or metal-catalyzed reactions of RCN (the topic surveyed in a number of articles and reviews[8–10] including those written by some of us[8,10]), we have discovered a novel method for the synthesis of **M-Pcs** starting from **Pns**,[11,12] which employs oximes (R_2C=NOH) as highly efficient promoting agents. This reaction proceeds *via* the formation of an intermediate complex (**III**) (generated by the double nucleophilic addition to a cyano-carbon), which in turn reacts further with 2 equivs. of *o*-phthalonitriles to form **NiPcs** (Scheme 1).

However, when this method is applied to the preparation of metal-free **Pcs**, it becomes much less effective insofar as it requires prolonged heating (8–24 h) followed by purification of the target compounds. Moreover, the method is not applicable to **Pns** with donor substituents (e.g., R = Me).

It is clear from Scheme 1 that the cyclotetramerization of **Pns** (**I**) to yield **Pcs** (**II**) involves the donation of two protons from the oxime and a $2e^-$ reduction. In addition, the promoter should exhibit nucleophilic properties to lower the kinetic barrier toward cyclotetramerization by forming intermediate **III**. All this means that the search for novel efficient promoters should include H^+ donors exhibiting higher nucleophilic/reducing properties.

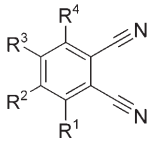
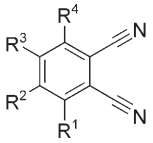
Recently we found that, in the addition to metal-activated nitriles, dialkyl-substituted hydroxylamines are *ca.* 10^4 times better protic nucleophiles than the corresponding oximes.[13] Taking into account the known higher reducing abilities of hydroxylamines *vs.* oximes,[14] we have decided to investigate the promoting ability of the former species in the conversion of **Pns** to **Pcs** and observed that a dialkylhydroxylamine, *viz.*, *N*,*N*-diethylhydroxylamine (Et_2NOH), can so greatly enhance the cyclotetramerization of **Pns** in alcohols that this reaction could even proceed without a metal source. We have found that this reaction provides a mild and expedient protocol for the facile preparation of metal-free **Pcs** in MeOH, while in $CHCl_3$ it proceeds in another direction furnishing 3-iminoisoindolin-1-ones and all this study is reported herein.

Results and Discussions

Reaction of Phthalonitriles and *N,N*-Diethylhydroxylamine in Methanol

For this work we addressed, on one hand, phthalonitriles (**1–5**; Table 1) bearing a substituent with various donor/acceptor properties to investigate their influence on proceeding reactions and, on the other hand, the most common and cheap dialkyl-substituted hydroxylamine, i.e., *N,N*-diethylhydroxylamine (available under the commercial name PENNSTOP®).

Table 1. Phthalonitriles employed as starting materials.

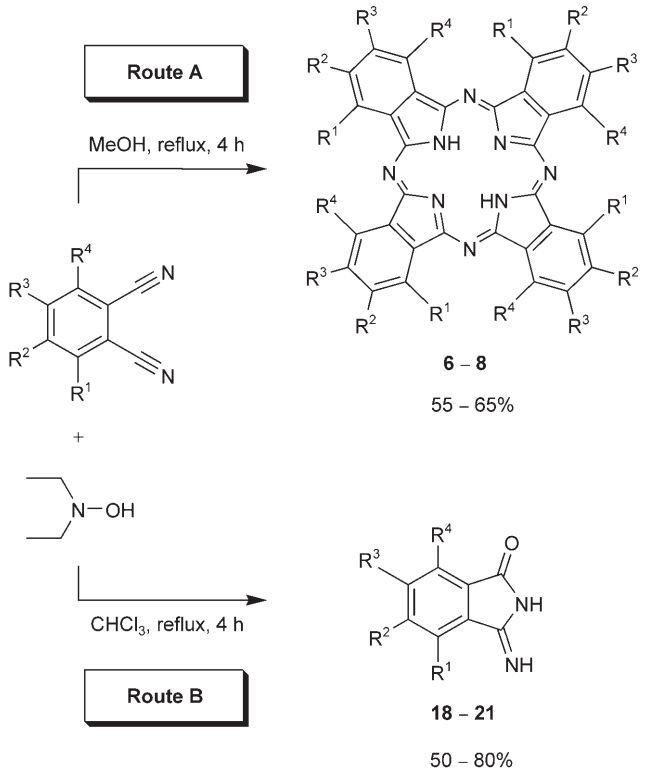
1	R^1 to R^4 = H	**4**	R^1 = R^3 = R^4 = H, R^2 = NO_2
2	R^1 = R^3 = R^4 = H, R^2 = Me	**5**	R^1 to R^4 = F
3	R^1 = R^4 = H, R^2 = R^3 = Cl		

Refluxing a mixture of **1–3** (1 equiv.) and *N,N*-diethylhydroxylamine (4 equivs.) in methanol for 4 h results (Route A, Scheme 2) in precipitation of the symmetrical (**6** and **8**) and an isomeric mixture of the unsymmetrical (**7**) **Pcs** which were isolated in good yields (60% for **6**, 65% for **7** and 55% for **8**). The formulations of **6–8** (see Experimental Section) are based on elemental analyses (C, H, N), electrospray ionization mass-spectrometry (ESI-MS), IR, and ^{1}H NMR spectroscopy. In addition, **6** was identified by comparison with a sample commercially available from Aldrich.

The increase of reaction time (up to 24 h) does not affect the yield but results in significant contamination of **6–8** with some by-products. The reactions with **Pns** containing strong electron-acceptor groups, for example, $C_6F_4(CN)_2$ **5** or $(NO_2)C_6H_3(CN)_2$ **4**, does not afford **Pcs**; the first reaction leads to 3-iminoisondolin-1-one species (see later), while the later case results in the known oxidation of Et_2NOH by the NO_2 group.[14,15]

For **1–3**, the best results were obtained with a **Pn**:Et_2NOH ratio of 1:4; with lower amounts of Et_2NOH the yields of **Pcs** strongly decreased, while the change of the **Pn**:Et_2NOH molar ratio to 1:8 does not significantly affect the reaction. In chlorinated solvents, e.g., $CHCl_3$, the interaction between the **Pcs** and Et_2NOH proceeds in another direction to yield 3-iminoisoindolin-1-ones (Route B, Scheme 2). The replacement of methanol by ethanol decreases drastically the yields, and only traces of **7** were isolated along with unreacted **2** and 3-iminoisoindolin-1-one **19** (Scheme 2), while in the cases of **1** and **3** the reaction does not proceed at all. All these observations together demonstrate the dramatic role of the solvent in the Et_2NOH-promoted conversions of **Pcs**.

The most common and so far the most useful method for the preparation of metal-free phthalocyanines is based on the heating of phthalogens in the presence of such organic bases as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or DBN (1,5-diazabicyclo[4.3.0]non-5-ene) and it requires a prolonged reflux of a phthalonitrile and the base in EtOH to furnish metal-free **Pcs** in low/moderate yields [20% (DBU) or 42% (DBN) after 18 h].[16] Hence, our method has at least triple benefits, i.e., it requires a lower temperature, it is less time-consuming, and gives metal-free **Pcs** in better yields.



Scheme 2.

Reaction of Phthalonitriles and *N,N*-Diethylhydroxylamine in Chloroform

Phthalonitrile (**1**) or its substituted analogues (**2**, **3**, **5**) react with *N,N*-diethylhydroxylamine in refluxing freshly distilled dry chloroform (the distillation is needed to remove EtOH added to commercially available chloroform as a stabilizer), giving precipitates of **18–21** (Scheme 2; compound **19** is obtained as an isomeric mixture) isolated in good yields (65, 50,

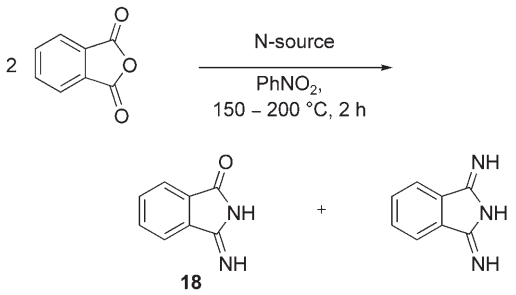
80, 51%, respectively). In the presence of added water, the yield of the reaction decreases (e.g., 50% for **18**). In non-distilled commercially available $CHCl_3$, the 3-iminoisoindolin-1-one product is strongly contaminated with phthalocyanines. The substitution of $CHCl_3$ with CH_2Cl_2 decreases the yield (e.g., to 20% for **18** upon reflux from 4 to 8 h), while in acetone or acetonitrile the formation of **18** has been detected but its high solubility in these solvents complicates the isolation and purification. The replacement of $CHCl_3$ by CH_2ClCH_2Cl decreases drastically the selectivity and the yield and only traces of **18** were detected by TLC upon reflux in 1,2-dichloroethane for 8 h.

The best results were obtained with a phthalonitrile:$HONEt_2$ molar ratio of 1:2; with lower amounts of $HONEt_2$, e.g., 1:0.5, the yields of the target compounds strongly decreased, while the change of the phthalonitrile:$HONEt_2$ molar ratio to 1:3 did not significantly affect the reaction.

The 3-iminoisoindolin-1-ones (**18**–**21**) precipitate from the reaction mixture in a pure form and they do not require further recrystallization. They give satisfactory C, H, and N elemental analyses and the ESI-MS of **18**–**21** display molecular ion peaks. In the IR spectra, **18**–**21** show no bands in the interval between 2200 and 2300 cm^{-1} specific for ν(C≡N) stretching vibrations, but display two (**21**) or three (**18**–**20**) medium intensity bands in the range of 1730–1630 cm^{-1} assigned to ν(C=O) and ν(C=N) of the newly formed carbonyl and imino groups. The 1D (^1H, $^{13}C\{^1H\}$), 2D (^1H,^{15}N-HMBC and ^1H,^{13}C-HMQC, ^1H,^{13}C-HMBC) NMR spectra of **18**–**21** are in good agreement with the proposed structures.

It is worth noting that the preparation of iminoisoindolinones is an area of avid attention owing to their great utility in versatile chemical transformations, including industrial applications. Various heterocyclic compounds containing the iminoisoindolinone skeleton exhibit important biological properties, such as antihypertensive, antipsychotic, anti-inflammatory, anesthetic, antiulcer, vasodilatory, antiviral, antileukemic, cytotoxic, and hypolipidemic activities.[17] Moreover, 3-iminoisoindolin-1-one (**18**), as the parent compound of the series, is a common precursor for the synthesis of other heterocycles and it is also useful for the manufacture of pigments (e.g., phthalocyanines), heat-sensitive colorants, some components for thermal-recording sheets, charge-controlling agents for electrophotographic toners, stabilizers for plastics, pharmaceuticals, and cosmetics.[1,18]

Despite the interest in alternative syntheses of **18**, the most recognized and *industrially* used method, which is based on a reaction between phthalic anhydride or phthalamide and a nitrogen source such as urea or ammonia (Scheme 3), is not free from a number of disadvantages. The reaction is usually performed at elevated temperatures (130–200 °C), reached by the use of high boiling point solvents (e.g., $PhNO_2$[19a,b]) and in some methods requires toxic and environmentally dangerous gaseous NH_3.[19a,b] The synthesis proceeds in a moderate yield (30–45%), it is not selective and typically results in formation of a mixture of **18** (30–40%) and isoindoline-1,3-diimine (Scheme 3; up to 60% yield) and some unidentified heterocyclic species. Consequently, this method requires separation and purification of **18**. A high-yield *laboratory* method for the conversion of phthalamide into **18** is also known[19c] but it is based on the hazardous Pinner synthesis utilizing great amounts of toxic HCl.

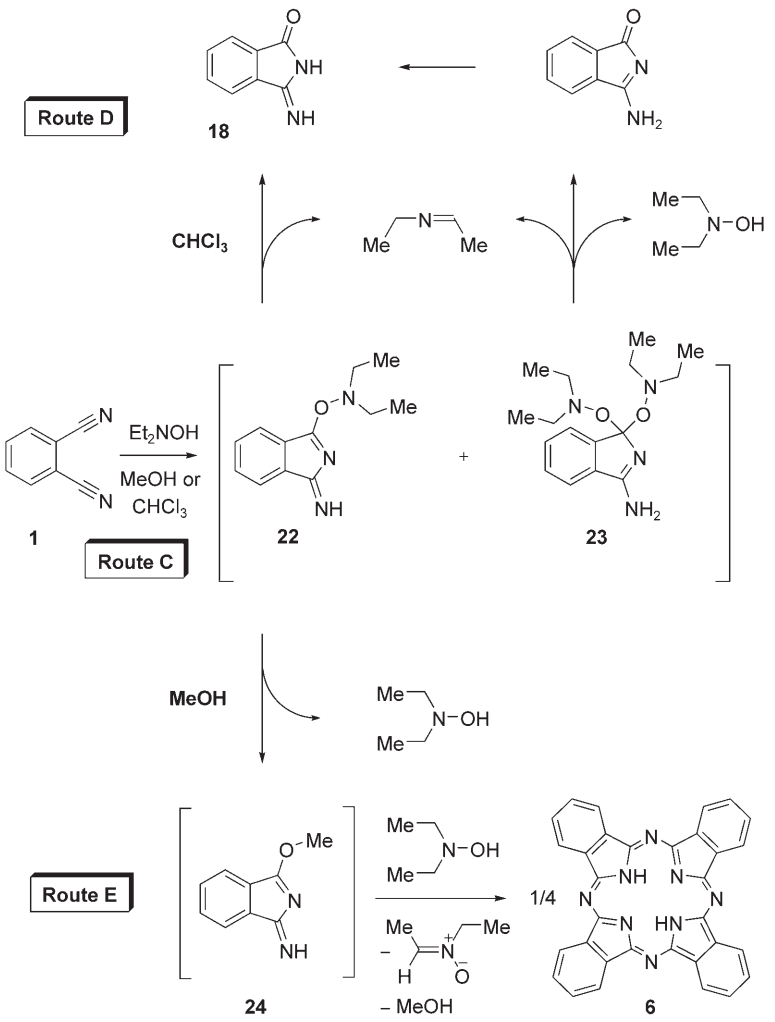


Scheme 3.

Thus, we have now found that **Pns** can be effectively transformed to **18** and relevant substituted 3-iminoisoindolin-1-ones (**19**–**21**) in $CHCl_3$ *via* a novel process (Route B, Scheme 2), involving *N,N*-diethylhydroxylamine. We also should note that a synthesis of **18** was described in a Japanese patent application[20a]: the reaction between **Pn**, water, hydrogen peroxide, and ammonia or amines led to 3-iminoisoindolin-1-one. We believe that there is a similarity between this method and that found by us and it might be anticipated that, in the former case, hydroxylamines are generated *in situ* from the amines and hydrogen peroxide.

Detection of Intermediates and Plausible Mechanism for the Reaction between Pns and *N,N*-Diethylhydroxylamine

The study of solvent-dependence of the reactions depicted in Scheme 2 and the detection of some intermediates were done by NMR and ESI-MS. Thus, phthalonitrile **1** reacts with *N,N*-diethylhydroxylamine in methanol or chloroform giving a mixture of imino species **22** and **23** (Route C, Scheme 4), derived from the nucleophilic addition, with concomitant heterocyclization, of 1 or 2 equivs. of Et_2NOH to **Pn**; although the latter species are unstable, they were detected in ESI^+-MS. If the reaction is performed in $CDCl_3$ or purified $CHCl_3$, both **22** and **23** are subject to further transformations (Route D) to furnish 3-imi-



Scheme 4.

noisoindolin-1-ones **18** and the known[21] imine $MeCH_2N=C(H)Me$ as well as the starting Et_2NOH which thus is regenerated. The imine has been detected by ESI (found $m/z=93$ [M + Na]; calcd.: $m/z=93$) and 2D TOCSY and $^1H,^{13}C$- and $^1H,^{15}N$-HMBC NMR.

In the case of **23**, its conversion proceeds *via* the amino tautomer of isoindolinone, which then undergoes the known tautomerization[22] to the more stable imino form **18**. The double addition of a nucleophile at a single cyano group is very rare[11,23] but it has been ascertained in our previous study[11] on the conversion of phthalonitriles into phthalocyanines mediated by an oxime (also an HON nucleophile).

In the case of the formation of **19**, the reaction was followed directly in the NMR tube. Besides the two isomers of the isoindolinone (ratio nearly 1:1) with R^2 or R^3 being a methyl group, one equivalent of $MeCH_2N=C(H)Me$ was released and unequivocally identified by NMR spectroscopy *via* 2D TOCSY, $^1H,^{13}C$-, and $^1H,^{15}N$-HMBC NMR measurements (Figure 1). In the TOCSY NMR spectrum, shift correlation signals of the CH proton (quartet in the typical region at 6.82 ppm) to both methyl protons (2.02 and 1.48 ppm) as well as to the CH_2 protons (3.83 ppm) could be detected. ^{13}C NMR signals were found at 13.1 (CH*Me*), 13.7 (*Me*CH_2), 60.3 (Me*CH*$_2$) and 134.0 ppm (N=*CH*), respectively. Furthermore, long-range coupling of both CH_3 protons and the CH proton to the same nitrogen atom at 269 ppm (measured relative to NH_4Cl, which is equivalent to −84 ppm relative to nitromethane) finally unequivocally proved the release of $MeCH_2N=C(H)Me$.

In methanol, the Route D is not dominant and the reaction proceeds mostly *via* Route E, furnishing **6** through the intermediate formation (with regeneration of Et_2NOH) of **24**, which was also detected by ESI^+-MS (found $m/z=183$ [M + Na]; calcd.: $m/z=183$). Furthermore, **24** is subject to cyclotetramerization with regeneration of MeOH; this $2e^-/2H^+$ process requires a protic reducing agent, and Et_2NOH,

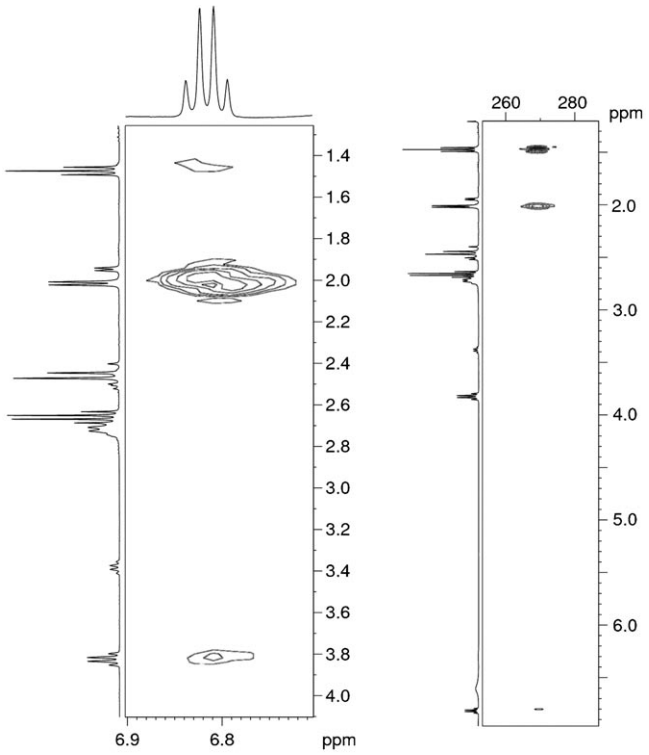


Figure 1. Selected regions of the TOCSY (*left*) and the long-range $^{1}H,^{15}N$-HMBC (optimized at 10 Hz, *right*) NMR spectra.

being oxidized to the known nitrone $Me(H)C{=}N^{+}(CH_2Me)O^{-}$ (detected in ESI-MS),[21] plays this role.

It should be mentioned that (i) both **Pns** (**6**–**8**) and 3-iminoisoindolin-1-ones (**18**–**21**) are stable in methanol; (ii) pure 3-iminoisoindolin-1-ones do not transform to **Pcs** in the presence Et_2NOH under the reaction conditions employed although they can be converted to **Pcs** *via* cyclotetramerization in the presence of strong bases or DBU and urea.[1,2] Based on these observations and those described above we believe that the function of *N*,*N*-diethylhydroxylamine is dual and it includes lowering the kinetic barrier toward addition of MeOH (thus acting as a catalyst) and reduction with concomitant H^{+} donation when phthalogene **24** cyclotetramerizes to the corresponding **Pc**.

Reaction of Phthalonitriles and *N*,*N*-Diethylhydroxylamine in the Presence of a Metal Source

In the presence of a metal center, the reaction does not show the above solvent-dependence and the formation of **M-Pcs** (Table 2) in the reaction of various **Pns** (**1**, **2**, **4**) with Et_2NOH and MCl_2 (M = Zn, Cd, Co, Ni) is observed in *n*-BuOH or without solvent. When methanol is used as the solvent the reaction does not occur, while in chloroform a mixture of 3-iminoisoindolin-1-one with yet unidentified products was obtained.

Table 2. Reaction of phthalonitriles with *N*,*N*-diethylhydroxylamine in the presence of a metal source.[a]

M	M source	Phthalonitrile	Solvent	T [°C]	Yield [%]	**M-Pc**
Zn	$ZnCl_2$	**1**	-	80	45	**9**
Zn	$ZnCl_2$	**2**	-	120	55	**10**
Cd	$CdCl_2$	**1**	*n*-BuOH	reflux	50	**11**
Co	$CoCl_2$	**1**	*n*-BuOH	reflux	55	**12**
Co	$CoCl_2$	**2**	-	80	65	**13**
Co	$CoCl_2$	**4**	-	120	65	**14**
Ni	$NiCl_2$	**1**	*n*-BuOH	reflux	40	**15**
Ni	$NiCl_2$	**2**	-	120	45	**16**
Ni	$NiCl_2$	**4**	-	120	45	**17**

[a] In all cases Et_2NOH is used as promoter and the reaction time is 15 min.

All the reactions involving the metal salts proceed for *ca.* 15–30 min and the highest yields (45–65%) were obtained under the conditions depicted in Table 2. The compounds were isolated by filtration and purified by washing with organic solvents and 5 M hydrochloric acid (see Experimental Section), while some of them were purified by sublimation (**9**, **10**, **15**) under *ca.* 10 mm vacuum at 200–300 °C.

Thus, our fast and relatively low-temperature protocol for the preparation of **9**–**17** is among the most advantageous methods for the synthesis of **M-Pcs** and gives well-comparable yields with those known for other methods.[1]

Conclusions

The results from this study can be considered from three perspectives. First, we found a novel and efficient method for the preparation of metal-free **Pcs** with both donor and moderate acceptor R substituents, which starts from low-cost reagents, such as **Pns** in MeOH, and is promoted by the widely comercially available and industrially employed (for other purposes) *N*,*N*-diethylhydroxylamine, operates at low temperatures, requires only a short reaction time and does not need purification of the **Pcs** products. The employment of Et_2NOH as an HON nucleophile alternative to an oxime[11,12] (Scheme 1) enhances the reactivity of **Pns** to such a degree that the tetramerization proceeds fast in a single pot and the intermediate similar to **III** (Scheme 1) could not be detected.

Second, a protocol identical to that for generation of metal-free **Pcs** further provides a convenient method for the synthesis of metallated phthalocyanines (**M-Pcs**), when the reactions of the corresponding **Pns** with Et_2NOH are performed in the presence of a metal source.

Third, we also discovered that the conversion of the **Pns** promoted by *N,N*-diethylhydroxylamine shows a dramatic solvent dependence and in $CHCl_3$ leads to various 3-iminoisoindolin-1-ones instead of **Pcs**. The latter route for the preparation of 3-iminoisoindolin-1-ones, taking into account its simplicity, low-cost of Et_2NOH and purity of the final products, may have a broad application both in laboratory and in industry.

Experimental Section

All starting materials and solvents were obtained from commercial sources and used as received, besides chloroform and methanol that were purified by conventional methods over calcium hydride and activated magnesium, respectively. Spectroscopic and analytical data for the compounds made are available in the electronic Supporting Information file.

Reaction of Phthalonitriles and *N,N*-Diethylhydroxylamine in MeOH; General Procedure for the Synthesis of Metal-Free Pcs (6–8)

A mixture of phthalonitrile **1** (0.010 mol) or any of the corresponding substituted phthalonitriles (**2**, **3**) and Et_2NOH (0.040 mol, 1.80 g) in methanol (7 mL) was placed in a round-bottom flask equipped with a magnetic stirrer and reflux condenser and refluxed for 4 h. On heating, the solid phthalonitrile dissolved, and the color of the solution changed from slightly yellow to dark green followed by precipitation of a dark blue solid. The reaction mixture was cooled to 20–25 °C, stirred additionally for *ca.* 1 h, the precipitate was filtered off, washed with five 5-mL portions of methanol, and with five 5-mL portions of acetone. The yields are 60 % (for **6**), 65 % (for **7**) and 55 % (for **8**).

Reaction of Phthalonitriles and *N,N*-Diethylhydroxylamine in $CHCl_3$; General Procedure for the Synthesis of 3-Iminoisoindolin-1-ones (18–21)

A mixture of phthalonitrile **1** (0.010 mol) or any of the corresponding substituted phthalonitriles (**2**, **3**, **5**) and Et_2NOH (0.020 mol, 1.80 g) in freshly distilled dry $CHCl_3$ (7 mL) was placed in a round-bottom flask equipped with a magnetic stirrer and reflux condenser and refluxed for 4 h. On heating, the solid phthalonitrile dissolved, and the color of the solution changed from slightly yellow to orange-green in the case of **1**, or to dark yellow in the case of **2** and **3**, and **5**, followed by precipitation of an almost colorless slightly greenish solid. The reaction mixture was cooled to 20–25 °C, stirred additionally for *ca.* 1 h, the precipitate was filtered off, washed with five 5-mL portions of cold (10 °C) chloroform. An additional quantity of 1.8–2.0 g (*ca.* 15 %) was obtained upon evaporation of the filtrate to dryness. Treatment of the residue with a 1:1 mixture of diethyl ether and chloroform (20 mL) resulted in precipitation of the 3-iminoisoindolin-1-ones (**18–21**), which are separated by filtration and washed with five 5-mL portions of cold (10 °C) chloroform. Both fractions of **18–21** were combined and dried in air at room temperature. Overall yields are 50–80 %.

Reaction of Phthalonitriles and *N,N*-Diethylhydroxylamine in the Presence of a Metal Source; General Procedure for the Synthesis of Metallated Pcs (9–17)

All starting **Pns** (**1**, **2**, and **4**) and the corresponding **M-Pcs** are shown in Table 2. A mixture of phthalonitrile **1** (4 mmol) or its corresponding substituted derivative (**2**, **4**) and MCl_2 (1 mmol; M = Zn, Co, Cd, Ni), and Et_2NOH (8 mmol, 0.75 g) was placed in a round-bottom flask equipped with a magnetic stirrer and, if required, a reflux condenser and stirred at room temperature for *ca.* 10 min. In the case of **Pn** = **1** and M = Cd, Co and Ni, *n*-BuOH was added (10 mL), while in all other cases the reaction proceeded without solvent. The mixture was heated at temperatures shown in Table 2, or upon reflux of the solvent for *ca.* 15 min. The reaction mixture was then cooled to 20–25 °C, stirred additionally for *ca.* 10 min, the precipitate was filtered off, washed with five 5-mL portions of methanol, two 5-mL portions of warm 5 M hydrochloric acid, and with five 5-mL portions of acetone. The yields of **9**–**17** are 40–65 %.

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