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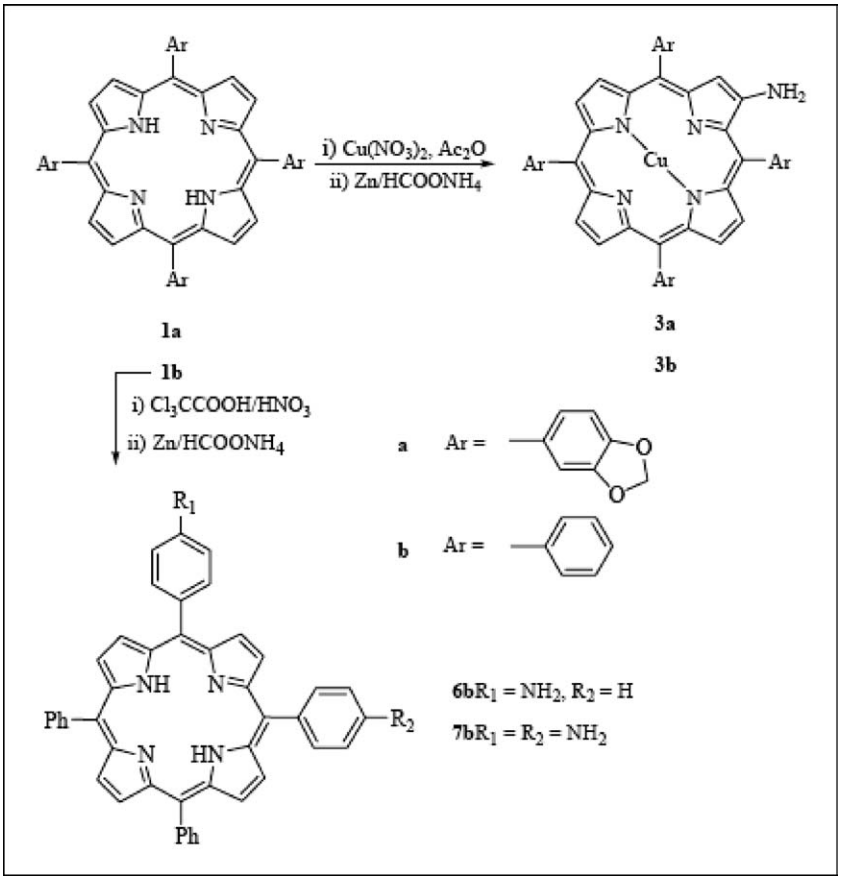

Modified nitration of tetraphenylporphyrin at para of phenyl with HNO_3/Cl_3CCOOH and one-pot nitration of free tetraarylporphyrins to metalized 2-nitroporphyrin in high yield are described. A novel reducer of $Zn/HCOONH_4$ has been developed for above nitro of porphyrin into amino effectively.

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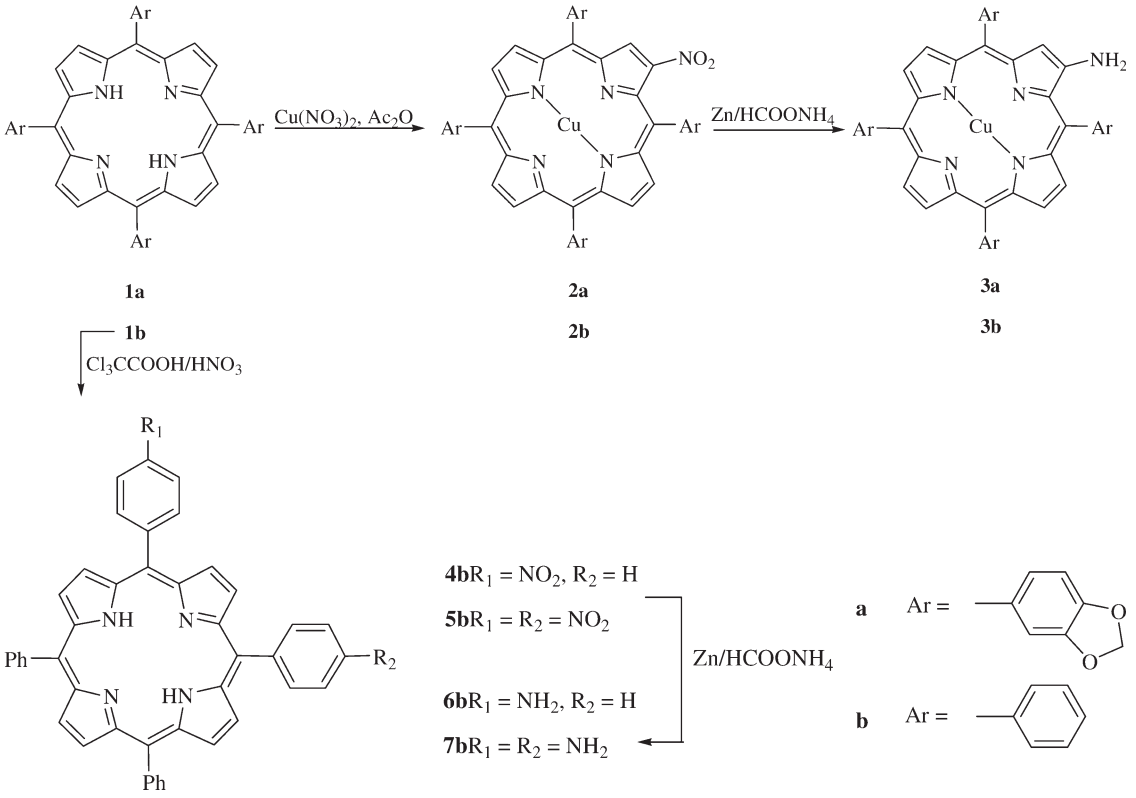
INTRODUCTION

Over the last three decades, functionalization of porphyrins has received considerable attention for introducing functions into porphyrins could varied the properties of porphyrins and afford availability of diverse porphyrin architecture by arising a energetic bond for further functionalization [1]. Therefore, fairish efforts were underway in various laboratories to explore novel and available approach to modify porphyrins [2]. *meso*-Tetraarylporphyrin (TAP) including tetraphenylporphyrin (TPP) is one of the most readily available synthetic porphyrin [3], so modifying its porphyrin macrocycle or aryl around was an available way to get various novel porphyrins [4]. The nitration modification has been investigated in detail by many reagents [5]. The sort of porphyrin containing amino function has wide use in the architecture of porphyrins with extended π-system, chlorines, porphyrin assembly, supermolecule propertie [6].

We have afforded access to nitro TPP by nitration of para of phenyl, which was transformed into widely useful amino function for subsequent modification [7].

Scheme 1. Synthesis of amino porphyrin via nitration and reduction.



Herein, we report the synthesis of TAP by modified Alder–Longo method condensing pyrrole with acid sensitive 3,4-methylenndioxyphenylaldehyde, sequent modified nitration of phenyl, as well as one-pot nitration of porphyrin periphery. A rapid and efficient process for reduction of nitro group at phenyl or β of porphyrin into amino has been developed.

RESULTS AND DISCUSSION

On account of the fact that *meso*-TPP **1b** was particularly readily prepared, it should be a handy way to achieve a variety of substituted porphyrins by introducing suitable group to TPP, especially at the phenyl rings. A few workers reported phenyl para nitration of TPP with fuming nitric acid, or $NaNO_2$/TFA (trifluoroacetic acid). As shown in Scheme 1, condensation of pyrrole with aromatic aldehyde in refluxing xylene under *meta*-nitrobenzoic acid provided porphyrin **1a** and **1b** in moderate yield of somewhat 50%. The starting porphyrin TPP was subjected to nitration to afford porphyrin containing mono and bis-nitro phenyl. Instead of TFA/$NaNO_2$, which was used in the Smith's method, the solid trichloroacetic acid and concentrated nitric acid was found to be effect, preferable control for this reaction. In chloroform, TPP was translated into porphyrins **4b** and **5b** at room temperature under air condition with total yield 81%.

In the molecule of TAP, β-site of pyrrolic is another active site as well as para-site of phenyl, and nitration at this site with various reagents and the further reduction had been investigated in detail by many researchers [8]. The earlier works showed that there were two steps, including metallization of free porphyrins with chloride or acetate and nitration using nitrate salt. Cuprous ion was found to readily insert into core of free porphyrins during treatment with cuprous ion, implying that metallization and nitration both could be likely conducted by sole cuprous nitrate. The previous nitration through two steps may be pieced together. The attempt to ''one-pot'' nitration with acetic anhydride and cuprous nitrate was successful in excellent yield. Nitration of free base porphyrins **1a** and **1b** by $Cu(NO_3)_2$ and Ac_2O for 2 h resulted in **2a** and **2b** with nitro group at β-site.

Nitrobenzenes were successfully converted into corresponding azoaryl by Zn/$HCOONH_4$ [9], similarly, we would prepare azoaryl porphyrin [10] from nitro compound. As shown in Scheme 1, an unpredicted amino porphyrin was achieved starting with **4b** under similar conditions. No azoaryl products came into being no matter how we regulated the reaction conditions, such as

temperature, stoichiometry of reagent, solvent, and reaction times. Treatment of nitro porphyrins **4b** and **5b** at room temperature in $CHCl_3$ with large excess Zn/$HCOONH_4$ gave rapidly corresponding amino porphyrins over a few minutes in yield up to 90%. As alike as **4b** and **5b** with *para*-nitrophenyl porphyrin, easy reduction of **2a** and **2b** with nitro at β-site produced **3a** and **3b** in high yield.

Most reductions of nitro were actualized by $SnCl_2$/HCl or hydrogenation with Pd/C. However, many functions were sensitive to strong acid, as well as the hardness of separating inorganic objects was trying. Although Pd/C is high efficient, it is somewhat inconstant. An attempt of reduction was unsuccessful, the great mass of material spared when crude nitration product from TPP was performed with Pd/C. The value of here process is nevertheless very obvious: milder conditions, simpler experimental procedure.

In summary, we have shown an effective nitration at para of phenyl of tetraphenylporphyirn with HNO_3/Cl_3CCOOH, and ''one-pot'' nitration of free TAPs by $Cu(NO_3)_2$/$(CH_3CO)_2O$ excellently. The process for reduction of nitro at above porphyrins into amino using Zn/$HCOONH_4$ was rapid, convenient, and excellent. Further transformation for application of amino porpyrins is underway.

EXPERIMENTAL

General. Pyrrole was purchased from Aldrich and distilled under reduced pressure immediately before use. All other reagents and solvents were used as received from Aldrich. Solvents were reagent grade unless otherwise specified and were dried and distilled by standard method. The UV-visible spectra were obtained on a Perkin-Elmer LS-5B spectrofluroimeter. ^1H NMR spectra were recorded on BRUKER AVANCE DMX 500 spectrometer. Elementary analyses were obtained on a Carlo Erba 1106 Elemental Analyzer.

Porphyrins **1b**, **1a** were synthesized by literature methods [7]. Spectra of porphyrins **1b–7b** were agreement with literature.

5,10,15,20-Tetra (3,4-methylendioxy)phenylporphyrin (1a). Porphyrin **1a** was synthesized in yield 48%. ^1H NMR (deuterichloroform): δ 8.92–8.80 (8H, m, β -pyrrole), 7.70–7.63 (m, 8H), 7.24–7.17 (m, 8H), 6.25 (s, 4H), −2.73 (s, 2H). UV λ_{max}: 419.0, 516.0, 554.0, 597.0, 648.0 nm. *Anal*. Calcd. for $C_{48}H_{30}N_4O_8$: C, 72.90; H, 3.82; N, 7.09. Found: C, 72.73; H, 3.91; N, 7.17.

5-(4-Nitrophenyl)-10,15,20-triphenyl-porphyrin (4b) and 5,10-di(4-nitrophenyl)-15,20-diphenyl-porphyrin (5b). To a solution of porphyrin **1b** (1 g, 1.6 mmol) and trichloroacetic acid (30 g) in chloroform (100 mL) was slowly added HNO_3 (6.0 mL, 75%, 15.5 mmol) over 2 min with fierce stir at room temperature under atmosphere. The mixture was stirred for 5 min. Reaction was quenched with water, and the mixture was neutralized with ammonium hydroxide aqueous solution to pH = 7. Chloroform (100 mL) was added, and the organic layer was washed with water (4 × 150 mL), and dried over magnesium sulfate. Solvent was removed with evaporation under reduced pressure. The crude product was purified by column chromatography to provide **4b** (370 mg, 36%) and **5b** (506 mg, 45%).

General procedure for nitration of β at porphyrin. To a solution of porphyrins in Ac_2O and chloroform, $Cu(NO_3)_2$ was added. The mixture was heated to reflux, kept for 2 h. Solvent was evaporated in a vacuum. Purification on silica gel gave nitro porphyrins in yields of about 90%.

(2-nitro-5,10,15,20- tetra (3,4-methylendioxy)phenylporphyrinato)copper-II (2a). Porphyrin **1a** (500 mg, 0.8 mmol) in Ac_2O (20 mL, 0.2 mol) by $Cu(NO_3)_2 \bullet 3H_2O$ (800 mg, 3.3 mmol) gave porphyrin **2a** in yield 86%. IR: NO_2 1508, 1345 cm^{-1}. UV: λ_{max} 432, 552.5, 595.5 nm. *Anal*. Calcd. for $C_{48}H_{27}CuN_5O_{10}$: C, 64.25; H, 3.03; N, 7.80. Found: C, 64.33; H, 3.09; N, 7.65.

General procedure for reduction of nitro function to amino function. To a solution of nitro porphyrins in $CHCl_3$, Zn powder, and $HCOONH_4$ was added with fierce stirring. The mixture was kept at room temperature for a little of 5 min. The solid inorganic was removed by filtration. Solution of porphyrin was washed by water, followed by drying with magnesium sulfate. Solvent was evaporated in a vacuum. The crude product was purified on a silica gel column, providing amino porphyrins in yield of 82–90%.

(2-Amino-5,10,15,20-tetra (3,4-methylendioxy)phenylporphyrinato)copper-II (3a). Porphyrin **2a** (200 mg, 0.8 mmol) in $CHCl_3$ (50 mL) with Zn powder (5.0 g, 0.1 mol) and $HCOONH_4$ (8.0 g, 0.1 mol) gave porphyrin **3a** in yield 86%. IR: NH_2, 3475, 1483, 1247, 1036 cm^{-1}. UV: λ_{max} 419, 547, 596nm. *Anal*. Calcd. for $C_{48}H_{29}CuN_5O_8$: C, 66.47; H, 3.37; N, 8.07. Found: C, 66.32; H, 3.43; N, 8.16.

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