Conversion of 1,2,5-Selenadiazoloporphyrin to Diformamidoporphyrin

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Attempt to obtain imidazoporphyrin by treatment of formic acid on “diaminoporphyrazine” formed in situ by deselenation of hexaphenyl substituted (1,2,5-selenadiazoloporphyrin in the presence of H\textsubscript{2}S and pyridine unexpectedly led to diformamidoporphyrin. It is suggested that formation of imidazoporphyrin is hindered by steric strain appearing in the case when two 5-membered heterocycles – pyrrole and imidazole are fused together.

Introduction

It is known that reductive opening of the 1,2,5-selenadiazole ring leads to the vicinal diaminospecies\(^{[1]}\) and H\textsubscript{2}S has been reported\(^{[2-3]}\) as a convenient reducing agent. This reaction has been used for the peripheral modification of porphyrazines with annulated 1,2,5-selenadiazole rings.\(^{[4,5]}\) In a common procedure H\textsubscript{2}S was bubbled through the pyridine solution of 1,2,5-selenadiazoloporphyrines until the characteristic colour change and following treatment of the reaction mixture with \(\alpha\)-diketones led to pyrazinoporphyrazines.\(^{[6]}\) When aromatic aldehydes were used the Schiff-base porphyrazines were obtained.\(^{[6]}\) The \textit{in situ} formation of the intermediate vicinal aminoporphyrazine species was postulated.\(^{[6]}\) Recently it was reported that only its N-alkylated derivatives can react in mixed co-condensation with substituted phthalodinitriles affording low symmetry (N-alkylimidazo)tribenzoporphyrazines.\(^{[8,9]}\) However, commercially available 4,5-dicyanoimidazole failed to form corresponding tetra(imidazoporphyrin) in analogous template tetramerization procedure.\(^{[10]}\) It was reported that only its N-alkylated derivatives can react in mixed co-condensation with substituted phthalodinitriles affording low symmetry (N-alkylimidazo)tribenzoporphyrazines.\(^{[11]}\) In present work we have made an attempt to obtain imidazo annulated porphyrazine [H\textsubscript{2}\{1M\textsubscript{H}PAPh\}] (4) by deselenation of 1,2,5-selenadiazoloporphyrin [H\textsubscript{2}\{SeN\textsubscript{2}\}PAPh\textsubscript{6}] (1) under action of H\textsubscript{2}S followed by treatment of the resulting reaction mixture containing diphosphinoporphyrazine [H\textsubscript{2}PA\{NH\textsubscript{2}\textsubscript{2}PPh\textsubscript{6}] (2) with formic acid (Scheme 1). However instead of the expected imidazoporphyrin 4 we have observed the formation of diformamidoporphyrazine [H\textsubscript{2}PA\{NHCOH\\textsubscript{2}PPh\textsubscript{6}] (3).

Scheme 1.
Experimental

UV-vis spectra were recorded using Hitachi U-2000 spectrophotometer. MALDI-TOF spectra were measured on Ultraflex Brucker Daltonics mass-spectrometer without matrix or with CCA matrix.

Reagents and solvents for synthesis, chromatography and spectroscopic characterization of compounds were pure chemicals (Fluka, Aldrich). 4,5-Dicyanimidazole was prepared following the known procedure[12] and was identical with the commercial product (Aldrich). 7,8,12,13,17,18-Hexaphenyl[1,2,5]selenadiazolo[3,4-β]porphyrazine, [H₂[SeN₆]²⁺PAPh₈] (1) was prepared as described in our recent works[7,13].

2,3-Diformamido-7,8,12,13,17,18-hexaphenylporphyrazine, [H₂PA[NHC(OH)]₈] (3); H₂S was bubbled through solution of [H₂[SeN₆]²⁺PAPh₈] (1) (20 mg, 0.023 mmol) in pyridine-chloroform mixture (1:4, 5 ml) for 1 min until colour was changed from green to dark blue. Then formic acid (20 ml) was added and solution was refluxed for 1 hour. After vacuum distillation of solvents residue was dissolved in chloroform and chromatographed on silica gel. The first fraction was collected and after evaporation of the solvent 15.7 mg (81 %) of compound II was obtained.

MS (MALDI-TOF): m/z = 858 (100 %)[M+H]⁺, calc m/z = 857. UV-vis λmax (CHCl₃) nm (ε/με): 361(1.00), 448(0.51), 589(0.51), 671(0.88).

Results and Discussions

We have attempted to prepare imidazoporphyrazine [H₂[ImH]²⁺PAPh₈] (4) using two approaches - (i) by direct synthesis from two dinitrile precursors and (ii) by peripheral modification of porphyrazine macrocycle. Mixed co-cyclotetramerization (i) of diphenylfuramorodinitrile taken in excess with 4,5-dicyanimidazole (4:1 molar ratio) in the presence of Mg⁷⁺ butoxide in n-butanol under reflux led exclusively to Mg⁷⁺ complex of symmetrical octaphenyloporphyrin [MgPAPh₈] and no formation of 4 or other low-symmetry imidazo-anneulated porphyrines was observed. This is in contrast with successful use of this procedure for preparation of Mg⁶⁺ complexes of 1,2,5-thiadiazolato-, 1,2,5-selenadiazolo- and benzoxanucleated -phenylsubstituted porphyrines from diphenylfuramorodinitrile and corresponding heterocyclic dinitrile or phthalodinitrile.[7,13]

For peripheral modification (ii) we have chosen [H₂[SeN₆]²⁺PAPh₈] (1) and studied first its behaviour in the presence of H₂S. Bubbling of H₂S into the solution of [H₂[SeN₆]²⁺PAPh₈] (1) in pure chloroform did not produce any changes in the UV-vis spectra. However, in the presence of pyridine additions (10-20%) the colour of the solution saturated with H₂S was rapidly changed from green to dark blue. In the UV-vis spectra two characteristic Q-bands (576 and 694 nm) of the initial 1,2,5-selenadiazoloporphyrinate 1 disappeared and the broad absorption band with maximum at 578 nm appeared (Figure 1, spectra a and b). Such broad Q-band is characteristic feature of the UV-vis spectra of aminosubstituted porphyrines.[14] In the MALDI-TOF spectra of the reaction product the peak corresponding to the molecular ion [M+H]⁺ of danimoporphyrinate [H₂PA[NH₂]₂P₈] (2) was observed at m/z = 801. The mass-spectrum contains also the peak at m/z = 827 which can be assigned to 1,2,5-thiadiazoloporphyrinate [H₂[SN₆]²⁺PAPh₈]. However, in the UV-vis spectrum of the reaction mixture no indication can be seen presence of [H₂[SN₆]²⁺PAPh₈] which have Q-bands at 574 and 679 nm.[13] Taking into account previous observations made for the Fe⁷⁺ complex [P₈Fe²⁺[SeN₆]²⁺PAPh₈], we can conclude that also in the case of the free base [H₂[SeN₆]²⁺PAPh₈] the reaction mixture after treatment with H₂S contains along with imidazoporphyrazine [H₂PA[NH₂]₂P₈] (2) some amount of its precursors with the S,Se-substituted diazine and diazepine rings [H₂[SeN₆]²⁺PAPh₈] (X = SSe, S₂, S₃). One can suppose that upon evaporation of the solvent before and/or during mass-spectral measurements these species are transformed to the more stable 1,2,5-thiadiazole derivative [H₂[SN₆]²⁺PAPh₈].

We have tried to convert [H₂PA[NH₂]₂P₈] (2) and its precursors [H₂[(NH₂)₂X]²⁺PAPh₈] (X = SSe, S₂, S₃) into imidazoporphyrazine [H₂[ImH]²⁺PAPh₈] (4) by treatment of the reaction mixture with formic acid. The UV-vis spectrum of the reaction product obtained after chromatography is shown in Figure 1 (c). It contains two narrow Q-bands in the visible region which is typical for porphyrazine having C₂v symmetry of the π-chromophore. The maxima of the long-wave Q₁-component is shifted bathochromically and Q₂-component bathochromically and the splitting of the Q-band is reduced from 2950 cm⁻¹ to 2075 cm⁻¹ as compared with the initial [H₂[SeN₆]²⁺PAPh₈]. Such spectrum might be characteristic for imidazoporphyrazine 4. However in the MALDI-TOF mass-spectrum of this species (Figure 2) no peak which can be assigned to the molecular ion of imidazov derivative [H₂[ImH]²⁺PAPh₈] (calculated m/z=811 for [M⁺]) is present. Instead the spectrum contains the intense peak at m/z=858 which shows no defragmentation but is accompanied by two less intense peaks at 1061 and 1264 having the difference of 203 mass units. The presence of these peaks evidences that under the used reaction conditions formic acid is not condensed with two vicinal amino groups of [H₂PA[NH₂]₂P₈] (2) with closure of imidazole ring, but formylate them with formation of diformamidoporphyrinate (3). The peak at m/z=858 corresponds to [M+H]⁺ and at 1061 and 1264 to the daughter ions [M+H+203]⁺ and [M+H+2·203]⁺.

Figure 1. UV-vis spectra of 1 (a), 2 (b) and 3 (c) in chloroform.
Deselenation of 1,2,5-Selenadiazoloporphyrazine

Unsuccessful efforts of synthesis of imidazoporphyrazine both by direct template cyclotetramerization of two dinitrile precursors and by peripheral modification of vicinal dianinoporphyrazine can be understood if one takes into account that in both cases formation of imidazo[4,5-b]pyrrole involves closure of 5-membered ring fused to another 5-membered ring (pyrrole to imidazole or imidazoporphyrazine involves closure of 5-membered ring into account that in both cases formation of vicinal diaminoporphyrazine can be understood if one takes into account that in both cases formation of imidazo[4,5-b]pyrrole). According to results of AM1 calculations demonstrate that the obtained structure of bisformamidoporphyrazine derivative 3 can be additionally stabilized by formation of hydrogen bonds, and formylamino groups adopt conformation which is close to planarity (Figure 3). This enables their conjugation with porphyrazine chromophore and agrees with the character of UV-vis spectra.

Conclusion

In summary, we have investigated the reaction of deselenation of 1,2,5-selenadiazoloporphyrazine and reaction of intermediate “diaminoporphyrazines” with formic acid. The closure of imidazole ring is hindered by steric strain and did not occur under condition used. Instead new diformamidoporphyrazine was obtained and characterized by mass-spectrometry and UV-vis data.

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References