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A novel way of preparing *meso*-substituted ethynylporphyrins and their derivatives by using 1,2,3-thiadiazole as a protecting group

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Abstract: *Meso*-(1,2,3-thiadiazol-4-yl) porphyrins are smoothly transformed to the corresponding ethynyl derivatives using potassium *tert*-butoxide as base. Some metal-catalyzed coupling reactions of these acetylenes are described.

Keywords : porphyrins, alkynes, 1,2,3-thiadiazoles, coupling reactions

Introduction

Meso-tetraaryl- and tetraalkylporphyrins[1,2] are prepared with relative ease and have been known for a long time. However, the corresponding alkynylporphyrins were only described in the last decade. A number of these compounds have been prepared with varying efficiency, using 3-substituted alkynals either in the Rothemund condensation with pyrrole[3], or in the McDonald type condensation with dipyrromethanes.[4] Alternatively, *meso*-haloporphyrins can be coupled with monosubstituted alkynes[5], or porphyrin-5-aldehydes can be converted in a number of steps to ethynylporphyrins.[6] Recently, improved yields of alkynylporphyrins have been obtained by protection of the alkynal with dicobalt octacarbonyl, prior to the porphyrin condensation, and oxidative deprotection.[7]

The alkynylporphyrins are of potential use as conjugated electronic materials,[4b,5a] compounds with NLO activity,[3d] and in light harvesting.[5b]

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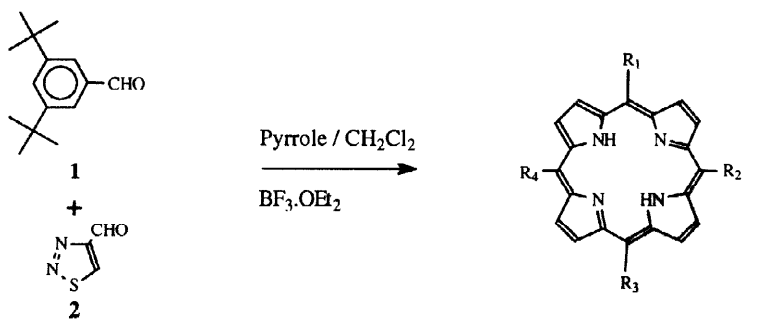
Results

As part of a project to evaluate the use of 1,2,3-thiadiazoles in organic synthesis, and in particular their conversion to alkynethiolates, we carried out a mixed Rothemund condensation of 3,5-bis(*tert.*-butyl)benzaldehyde **1** and 4-formylthiadiazole **2**[8] using the Lindsey procedure[2] (ratio 2:1). This yielded, apart from the symmetrical A_4 porphyrin (12% yield), three fractions containing the A_3B porphyrin **3** (15% yield), and the two possible A_2B_2 porphyrins **4** (11% yield) and **5** (9% yield). To our knowledge, **3-5** are the first *meso*-substituted (1,2,3-thiadiazol-4-yl)porphyrins. We now attempted to convert **3** to the corresponding alkynethiolate **6** by treating it with excess potassium *tert.*-butoxide. This base normally abstracts the proton at C-5 of the thiadiazole, followed by ring cleavage to the alkynethiolate.[9] We had thought to use **6** as a nucleophile in combination with alkylating agents, forming alkynesulfides **7**, or to carry out the dimerization of **6** to the dithiafulvene **8** by adding water. To our surprise, we isolated ethynylporphyrin **9** in good yield (73 %).[10] The NMR data of **9** allowed unambiguous assignment of the structure. The ^{1}H NMR spectrum shows the disappearance of the thiadiazole peak at δ = 9.09 ppm, and a new peak appearing at δ = 4.20 ppm. In the ^{13}C NMR spectrum, the two acetylene carbons were observed at δ = 85.87 ppm ($^2J_{CH}$ = 50 Hz) and 83.60 ppm ($^1J_{CH}$ = 250 Hz). Furthermore, the UV spectrum shows the expected[3c] shifted values for the Soret and Q bands (see Scheme 1).



3 $R_1 = R_2 = R_3$ = 3,5-bis(t-butyl)phenyl — R_4 = 4-(1,2,3-thiadiazolyl)

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5 $R_1 = R_3$ = 3,5-bis(t-butyl)phenyl — $R_2 = R_4$ = 4-(1,2,3-thiadiazolyl)

6 $R_1 = R_2 = R_3$ = 3,5-bis(t-butyl)phenyl — $R_4 = -C{\equiv}C-S^{\ominus}$

7 $R_1 = R_2 = R_3$ = 3,5-bis(t-butyl)phenyl — $R_4 = -C{\equiv}C-SMe$

9 $R_1 = R_2 = R_3$ = 3,5-bis(t-butyl)phenyl — $R_4 = -C{\equiv}C-H$

12 $R_1 = R_2$ = 3,5-bis(t-butyl)phenyl — $R_3 = R_4 = -C{\equiv}C-H$

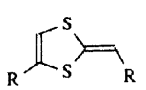
13 $R_1 = R_3$ = 3,5-bis(t-butyl)phenyl — $R_2 = R_4 = -C{\equiv}C-H$

Scheme 1

This reaction bears some analogy to the decomposition of 4,5-diphenyl-1,2,3-thiadiazole to diphenylacetylene.[11] However, this is the first documented example where a 4-monosubstituted 1,2,3-thiadiazole reacts in this way. One possible explanation is that the porphyrinyl substituent, which under these circumstances is the dianion, is releasing electrons into the thiadiazole ring. Thus, the acidity at C-5 is drastically lowered, making the alternative process starting with the attack at sulfur more plausible. Alternatively, the alkynethiolate **6** could be unstable and desulfurize with base. However, we were not able to trap any alkynethiolate formed with either methyl iodide or carbon disulfide.

This serendipitous discovery opens the possibility to introduce a porphyrin moiety in a given molecule through coupling at the alkyne function of **9**.[6b] As a first experiment, we carried out a copper(II) catalyzed Glaser dimerization of [Zn]**9** to obtain the bis(porphyrinyl) diacetylene **10** in a satisfactory yield of 90 %. The Hagihara coupling of 1,4-diodobenzene with [Zn]**9** also afforded the bisporphyrin **11** in excellent yield (94 %, Scheme 2).

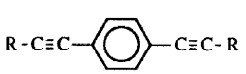
The bis(alkynyl)porphyrins **12** and **13** (Scheme 1) were obtained similarly in fair yields, starting respectively from **4** (35 % yield) and **5** (29 % yield). An alternative synthetic pathway towards **12** and **13**, using a mixed condensation with 3,5-bis(t-butyl)benzaldehyde and 2-(trimethylsilyl)propynal as adapted from the literature,[3] gave a mixture from which the expected products could not be isolated. These compounds **12** and **13** are of obvious interest as building blocks to prepare porphyrin arrays, using the coupling strategies as for [Zn]**9** above (see Scheme 2). The new products **3-5** and **9-13** were fully characterized by ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100 MHz) spectroscopies, and by ESMS.



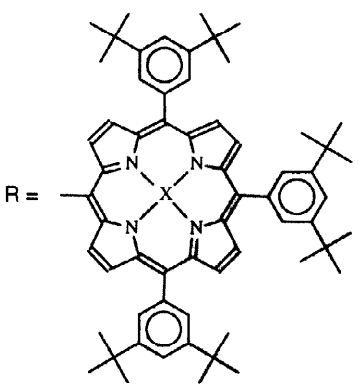
8

R-C≡C-C≡C-R

10



11



X = H, Zn

Scheme 2

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10. ***Procedure*** : A stirred solution of the thiadiazole **6** (0.193 g, 0.20 mmol) in dry diethyl ether (25 mL), while kept under a nitrogen atmosphere at ambient temperature, was treated with potassium *tert.*-butoxide (0.27 g, 2.4 mmol). The resulting green reaction mixture was stirred for 10 minutes, and then worked up with water (20 ml). The organic layer was washed with water (2 x 20 ml), dried over $MgSO_4$, evaporated and the residue was chromatographed (SiO_2, eluent petroleum ether/diethyl ether 17/3). This gave the product in 73 % yield, mp >300°C (decomposition), UV (diethyl ether): λ_{max} 427, 527, 564, 601, 658 nm ; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 9.74 (d, 2 H, J = 4.8 Hz, β-pyrrole), 9.00 (d, 2 H, J = 4.8 Hz, β-pyrrole), 8.89 (s, 4 H, β-pyrrole), 8.13 (d, 4 H, J = 1.2 Hz, H_{ortho}), 8.09 (d, 2 H, J = 1.2 Hz, H_{ortho}), 7.87 (t, 2 H, J = 1.2 Hz, H_{para}), 7.84 (t, 1 H, J = 1.2 Hz, H_{para}), 4.20 (s, 1 H, acetylene H), 1.59 (s, 36 H, *tert.*-butyl), 1.56 (s, 18 H, *tert.*-butyl), -2.30 (s, 2 H, N-H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 148.92, 148.76, 133-129 (broad, C_β), 129.78, 129.54, 123.62, 122.33, 121.19, 97.02 (porphyrin C_5, ^3J = 4.2 Hz), 85.87 (acetylene C, ^2J = 50 Hz), 83.60 (acetylene CH, ^1J = 250 Hz), 35.09, 35.05, 31.77, 31.74; ESMS; *m/z*: 899.4 (MH^+)
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