

Tetrahedron Letters 39 (1998) 9841-9844

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

Stefan Smeets and Wim Dehaen*

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee (Leuven)

Received 11 September 1998; accepted 19 October 1998

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. © 1998 Elsevier Science Ltd. All rights reserved.

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 pyrrole³ or in the McDonald type condensation with dipyrromethanes.⁴ Alternatively, *meso*-haloporphyrins can be coupled with monosubstituted alkynes⁵, 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}

* E-mail: wim.dehaen@chem.kuleuven.ac.be

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 procedure² (ratio 2:1). This yielded, apart from the symmetrical A₄ porphyrin (12% yield), three fractions containing the A₃B porphyrin 3 (15% yield), and the two possible A₂B₂ 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 ¹H NMR spectrum shows the disappearance of the thiadiazole peak at $\delta = 9.09$ ppm, and a new peak appearing at $\delta = 4.20$ ppm. In the ¹³C NMR spectrum, the two acetylene carbons were observed at $\delta = 85.87$ 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).



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 ¹H NMR (at 400 MHz) and ¹³C NMR (at 100 MHz) spectroscopies, and by ESMS.



Scheme 2

Acknowledgement

We thank the Ministerie voor Wetenschapsbeleid, the FWO-Vlaanderen and the Katholieke Universiteit Leuven for their financial support. S.S. thanks the IWT for a predoctoral fellowship.

References

- A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, J. Org. Chem, 1967, 32, 476; A.M. d'A. Rocha Gonsalves, J.M.T.B. Varejao and M.M. Pereira, J. Heterocycl. Chem., 1991, 28, 635.
- (a) J.S. Lindsey, I.C. Schrieman, H.C. Hsu, P.C. Kearny and A.M. Marguerettaz, J. Org. Chem., 1987, 52, 827; (b) J.S. Lindsey and R.W. Wagner, J. Org. Chem., 1989, 54, 828.
- (a) H.L. Anderson, A.P. Wylie and K. Prout, J. Chem. Soc., Perkin Trans. 1, 1998, 1607; (b) H.L. Anderson, Tetrahedron Lett. 1992, 33, 1101; (c) L.R. Milgrom and G. Yahioglu, *ibid.*, 1995, 36, 1995; (d) H.L. Anderson, S.J. Martin and D.D.C. Bradley, Angew. Chem. Int. Ed. Engl., 1994, 33, 655.
- (a) G. S. Wilson and H. L. Anderson, Synlett 1996, 1039; (b) B. Jiang, S.-W. Yang, D.C. Barbini and W. E. Jones, J. Chem. Soc., Chem. Commun., 1998, 213; see also reference 3b.
- See for instance : (a) S.M. Lecours, H.-W. Guan, S.G. DiMagno, C.H. Wang and M.J. Therien, J. Am. Chem. Soc., 1996, 118, 1497; (b) V.S.-Y. Lin, S.G. DiMagno and M. J. Therien, Science, 1994, 264, 1105.
- 6. (a) D.P. Arnold and L.S. Nitschinsk, Tetrahedron Lett., 1992, 33, 8781; (b) ibid., 1993, 34, 693.
- 7. L.R. Milgrom, R. D. Rees and G. Yahioglu, Tetrahedron Lett., 1997, 38, 4905.
- 8. G. L'abbé, M. Verbeke, W. Dehaen and S. Toppet, J. Chem. Soc., Perkin Trans. 1, 1993, 1719.
- 9. R. Raap and R. G. Micetich, Can. J. Chem., 1968, 46, 1057.
- 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 MgSO₄, evaporated and the residue was chromatographed (SiO₂, 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 ; ¹H NMR (CDCl₃, 400 MHz, ppm): $\delta = 9.74$ (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_{para}), 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); ¹³C NMR (CDCl₃, 100 MHz, ppm) $\delta = 148.92$, 148.76, 133-129 (broad, C_β), 129.78, 129.54, 123.62, 122.33, 121.19, 97.02 (porphyrin C₅, 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⁺)
- 11. R.G. Micetich, Org. Prep. Proc. Int. 1971, 3, 163.

9844