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Synthesis and Diels–Alder reactions of 2-(buta-1,3-dien-2-yl)-5,10,15,20-tetraphenylporphyrin

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Abstract

A new method for the introduction of a buta-1,3-dien-2-yl group in a β-position of a porphyrin is described. The new β-dienic porphyrin was used in Diels–Alder reactions with several dienophiles giving the corresponding adducts in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: porphyrins; extrusion reactions; dienes; Diels–Alder reactions; Heck reactions.

Synthesis and functionalization of porphyrins are scientific matters which, in recent years, have received much attention. This has been mainly due to the use of these compounds in catalysis,[1] photodynamic therapy of cancer cells,[2] as materials with novel electrical properties[3] and as biomimetic model systems of the primary processes of natural photosynthesis.[4] The introduction of adequate substituents might improve the macrocycle properties such that new applications can be found. Recently, we have been developing new methodologies for the functionalization of porphyrins.[5] In this communication we report a new method for the introduction of a buta-1,3-dien-2-yl group in a β-position of a porphyrin and the use of the obtained derivative in Diels–Alder reactions with several dienophiles.

Our synthetic pathway for the synthesis of the β-butadienyl porphyrin **4** is shown in Scheme 1. Porphyrin **3** was obtained by our approach to the synthesis of β-alkenyl substituted *meso*-tetraphenylporphyrins, based on the Heck reaction of porphyrinic diazonium salts.[5c] Diazotization of nickel(II) β-amino-*meso*-tetraphenylporphyrin **1**,[5d] with sodium nitrite and sulphuric acid, followed by the in situ addition of 3-sulfolene and palladium(II) acetate afforded, after work-up and preparative chromatography, compound **3** in 67% yield. The structure of **3** was unambiguously established by spectroscopic data[6], namely ^{1}H, ^{13}C and 2D COSY ($^{1}H-^{1}H$) NMR, HRMS and

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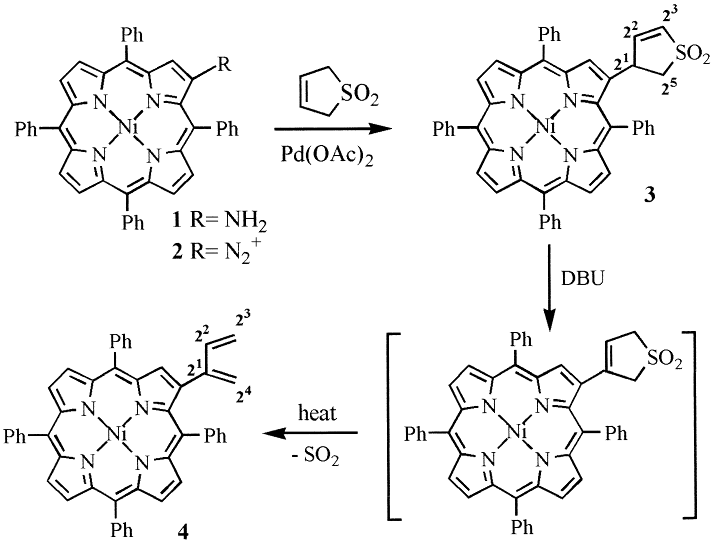
UV–vis (in many cases the visible absorption features of porphyrin derivatives can be considered as a proof of product formation; in this case, compound **3** absorbs at 420 and 532 nm while its precursor **1** absorbs at 412, 533 and 585 nm). Isomerization of porphyrin **3** with DBU, followed by the thermal extrusion of sulfur dioxide in refluxing *o*-dichlorobenzene afforded the expected porphyrin **4** in 83% yield. The structure of this new dienic porphyrin was fully established.[7] From the analysis of its ^{1}H NMR spectrum it was possible to assign the proton resonances of the butadienyl group: H-2^2 appears as a double doublet at δ 6.32 ppm (*J* 17.2 and 10.4 Hz), one of the H-2^3 protons appears as a doublet at δ 4.71 ppm (*J* 17.2 Hz) and the other proton as another doublet at 4.94 ppm (*J* 10.4 Hz); H-2^4 protons appear as broad singlets at δ 4.96 and 5.10 ppm.

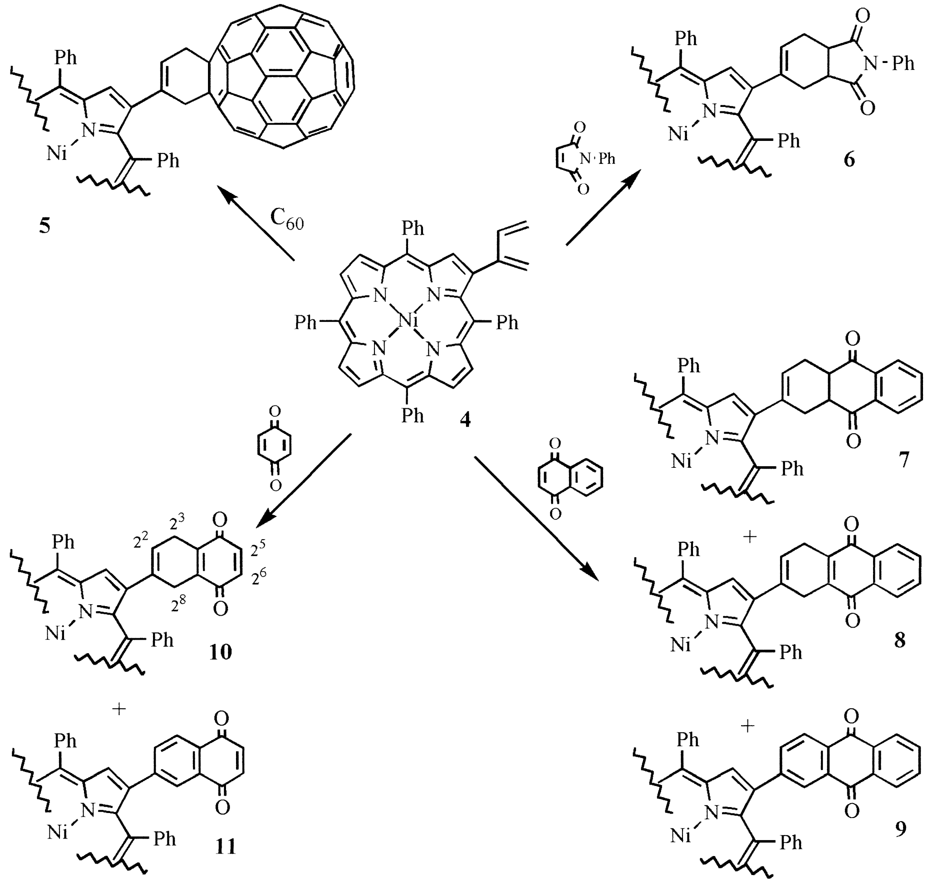


Scheme 1.

The reactivity of diene **4** in Diels–Alder reactions was tested by using a range of dienophiles: [60]fullerene, *N*-phenylmaleimide, 1,4-benzoquinone and 1,4-naphthoquinone. The reactions were performed by heating porphyrin **4** with an excess of the dienophile (between 1.5 and 3 equiv.) in refluxing toluene. The reactions were controlled by TLC and took place until porphyrin **4** was completely consumed.[8]

When the Diels–Alder reactions were carried out with fullerene or *N*-phenylmaleimide, the expected adducts **5** (95%) and **6** (97%) were obtained in high yields (Scheme 2). The structures of both compounds were unambiguously established by spectroscopic data, namely ^{1}H and ^{13}C NMR, UV–vis and MS.

When these studies were extended to 1,4-naphthoquinone, three new compounds were obtained after the usual work-up and purification by preparative chromatography (Scheme 2). Based on their ^{1}H, ^{13}C NMR and mass spectra we were able to identify the compound with the smaller R_f as the Diels–Alder adduct **7** (22%) and the other two as the dehydrogenated adducts **8** (28%) and **9** (32%). When the cycloaddition reaction was carried out with 1,4-benzoquinone, only the dehydrogenated adducts **10** and **11** were obtained. These two products were characterized by UV–vis, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.[9,10]



Scheme 2.

These results show that the novel (and stable) β-dienic porphyrin **4** can be successfully used as a precursor of a range of new porphyrin derivatives with various types of substituents in the β-position of the porphyrin macrocycle.

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References

1. Meunier, B. *Chem. Rev.* **1992**, *92*, 1411–1456.
2. (a) Sternberg, E. D.; Dolphin, D. *Tetrahedron* **1998**, *54*, 4151–4202; (b) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19–33.
3. (a) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759–9760; (b) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135–137.

4. (a) Nakano, A.; Osuka, A.; Yamazaki, I.; Yamazaki, T.; Nishimura, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3023–3027; (b) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849–866; (c) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435–461.
5. (a) Tomé, A. C.; Lacerda, P. S. S.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **1997**, 1199–1120; (b) Silva, A. M. G.; Tomé, A. C.; Neves, M. G. P. M. S.; Silva, A. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **1999**, 1767–1768; (c) Ludtke, K.; Alonso, C. M.; Neves, M. G. P. M. S.; Silva, A. M. S.; Cavaleiro, J. A. S. *Heterocycl. Commun.* **1997**, *3*, 503–506; (d) Alonso, C. M. A.; Neves, M. G. P. M. S.; Silva, A. M. S.; Cavaleiro, J. A. S.; Hombrecher, H. K. *Tetrahedron Lett.* **1997**, *38*, 2757–2758.
6. Selected data for compound **3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.19–3.31 (m, 2H, H-2^5), 4.52–4.58 (m, 1H, H-2^1), 6.71 (dd, 1H, H-2^3, J 2.4 and 6.6 Hz), 6.86 (dd, 1H, H-2^2, J 3.0 and 6.6 Hz), 7.63–8.06 (m, 20H, $4\times C_6H_5$), 8.58 (s, 1H, H-3), 8.64–8.74 (m, 6H, H-7,8,12,13,17,18); ^{13}C NMR ($CDCl_3$) δ (ppm) 39.5 (C-2^1), 56.9 (C-2^5), 117.3, 118.7, 119.1, 119.4, 127.0, 127.1, 127.5, 127.6, 127.9, 128.0, 129.1, 131.0 (C-2^3), 132.1, 132.4, 132.6, 132.65, 132.7, 132.8, 132.9, 133.1, 133.6, 137.7, 140.0, 140.1, 140.3, 142.1 (C-2^2), 142.5, 142.56, 142.6, 142.9, 143.1, 143.2; UV–vis ($CHCl_3$) λ_{max}/nm (log ε), 420 (5.37), 532 (4.15); HRMS (FAB) m/z calculated for $C_{48}H_{32}N_4O_2SNi$ ($M^{+\cdot}$) 786.1599; found 786.1568.
7. Selected data for compound **4**: m.p. > 300°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.71 (d, 1H, H-2^3, J 17.2 Hz), 4.94 (d, 1H, H-2^3, J 10.4 Hz), 4.96 (br s, 1H, H-2^4), 5.10 (br s, 1H, H-2^4), 6.32 (dd, 1H, H-2^2, J 10.4 and 17.2 Hz), 7.37–8.01 (m, 20H, $4\times C_6H_5$), 8.56 (s, 1H, H-3), 8.57–8.74 (m, 6H, H-7,8,12,13,17,18); ^{13}C NMR ($CDCl_3$) δ (ppm) 116.5, 118.1, 118.7, 119.1, 119.4, 120.5, 125.8, 126.9, 127.6, 127.7, 127.8, 131.6, 132.1, 132.2, 132.3, 132.4, 132.9, 133.7, 134.8, 134.9, 139.8, 140.1, 140.4, 140.6, 140.7, 142.2, 142.3, 142.4, 142.5, 142.6, 143.7, 143.9, 144.4; UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 418 (5.25), 531 (4.12); HRMS (FAB) m/z calculated for $C_{46}H_{32}N_4Ni$ ($M^{+\cdot}$) 722.1980; found 722.1975.
8. The reaction with C_{60} is completed in 2 h while it requires ca. 2 days with the other dienophiles.
9. Selected data for compound **10**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.93–2.99 (m, 2H, H-2^3), 3.32–3.37 (m, 2H, H-2^8), 5.55 (br s, 1H, H-2^2), 6.77 (s, 2H, H-2^5 and H-2^6), 7.36–8.01 (m, 20H, Ph-H), 8.48 (d, 1H, β-H, J 5.0 Hz), 8.54 (s, 1H, β-H), 8.64 (d, 1H, β-H, J 5.0 Hz), 8.70–8.74 (m, 4H, β-H); ^{13}C NMR ($CDCl_3$) δ (ppm) 25.2, 29.6, 118.1, 118.8, 118.9, 119.3, 125.2, 126.1, 126.9, 127.3, 127.8, 131.1, 131.7, 132.1, 132.3, 132.4, 132.5, 132.6, 132.7, 133.6, 133.7, 134.0, 136.2, 138.5, 138.9, 139.2, 140.5, 140.6, 142.4, 142.6, 142.7, 143.8, 147.4, 186.7, 186.8; UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 418 (5.27), 535 (4.14); HRMS (FAB) m/z calculated for $C_{54}H_{36}N_4O_2Ni$ $(M+2H)^+$ 830.2192; found, 830.2194.
10. Selected data for compound **11**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.95 and 6.99 (AB, 2H, H-2^5 and H-2^6, J 11.6 Hz), 7.06–7.12 (m, 2H, Ph-H), 7.59 (dd, 1H, H-2^2, J 1.9 and 8.0 Hz), 7.63–7.73 (m, 12H, Ph-H), 7.80 (d, 1H, H-2^8, J 1.9 Hz), 7.81 (d, 1H, H-2^3, J 8.0 Hz), 7.99–8.01 (m, 6H, Ph-H), 8.45 (d, 1H, β-H, J 5.0 Hz), 8.64 (d, 1H, β-H, J 5.0 Hz), 8.70–8.76 (m, 5H, β-H); ^{13}C NMR ($CDCl_3$) δ (ppm) 118.6, 119.0, 119.3, 125.6, 126.3, 126.9, 127.0, 127.2, 127.8, 127.9, 128.8, 130.5, 131.9, 132.4, 132.6, 133.0, 133.6, 133.7, 134.4, 134.6, 138.4, 138.6, 138.8, 139.4, 140.1, 140.4, 142.3, 142.7, 142.9, 143.1, 143.8, 144.8, 145.0, 184.9, 185.0; UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 419 (5.23), 536 (4.14); HRMS (FAB) m/z calculated for $C_{54}H_{32}N_4O_2Ni$ ($M^{+\cdot}$) 826.1879, found, 826.1911.