DIELS-ALDER REACTION OF Ni(II) β -VINYL-*meso*-TETRAPHENYLPORPHYRIN WITH DIMETHYL ACETYLENEDICARBOXYLATE AND *N*-PHENYL MALEIMIDE †

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Abstract : Ni(II) β -vinyl-*meso*-tetraphenylporphyrin underwent Diels-Alder reaction with the title dienophiles to give the corresponding porphyrins *via* 1,3-hydrogen shift of the initial adducts in good to moderate yields.

Porphyrins and their synthetic analogues (1) have been extensively investigated because of their increasingly diverse applications in fields ranging from catalysis (2) to biomedical science (3). One of the most general methods for modification of the porphyrin core would be attachment of additional moieties by the Diels-Alder reaction of vinyl porphyrins with electron-deficient dienophiles. Indeed, the Diels-Alder reaction of vinyl porphyrins and divinyl porphyrins with electron-deficient dienophiles has been used for the synthesis of chlorin (4), bacteriochlorins, and isobacteriochlorins (5). Previously, Diels-Alder reaction of Ni(II) β -vinyl-*meso*-tetraphenylporphyrin with tetracyanoethylene has been reported by Cavaleiro *et al.* to give, as a thermodynamically stable product, the [2+2] adduct containing a cyclobutane

Scheme 1

ring via rearrangement of the [4+2] adduct as shown Scheme 1 (4f). In the course of our studies on the scope and limitations of the Diels-Alder reaction of vinyl porphyrins with a variety of dienophiles, this was not the case with dimethyl acetylenedicarboxylate and *N*-phenyl maleimide. This is a subject of the present communication.

Reaction of Ni(II) β -vinyl-meso-tetraphenylporphyrin **1** with DMAD in refluxing toluene for two days, after chromatography on silica gel afforded purple solids, which has been proven to have the structure **2** (Scheme 2), based upon its MS and NMR analyses (6). The ^1H NMR spectrum of the adduct **2** displays four protons (H at C-a and C-b) as a multiplet at δ 2.65-2.80, three protons (H at C-f) at 2.98 as a singlet, and three protons (H at C-h) at 3.87 as a singlet (Scheme 3, **2A**). There were no side products. No vinylporphyrin **1** is recovered under the conditions described in the note. When the reaction with *N*-phenyl maleimide was carried out (Scheme 3), the porphyrin-type adduct **3** has been obtained in 81% yield according to the result of NMR structure analysis, e.g. the ^1H NMR spectrum of the adduct displays two protons (H at C-b) as a multiplet at δ 2.0-2.3, one proton (H at C-c) at 3.39-3.43 as a multiplet, and one proton (H at C-d) at 4.25 as a doublet (Scheme 3, **3B**). That the strong absorption at around 650-700 nm, a characteristic of chlorin, was not found and that the solution color was red-purple also supported this structure. The formation of the porphyrins **2** and **3** are explained by Diels-Alder reaction of **1** with dienophiles to form an initial adduct such as the chlorin **4**, followed by 1,3-hydrogen shift. In the present cases, no chlorin was able to be isolated in our hands.

In conclusion, it has proven that, contrary to the previous results of the reaction with tetracyanoethylene, Diels-Alder reaction of the title vinyl porphyrin affords the corresponding porphyrins *via* 1,3-hydrogen shift of the initial adducts. Further work on application of the present reaction for the synthesis of supramolecular porphyrins is in progress.

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 6. The assignments were based upon the NMR methods (DEPT, COSY, NOESY, and CHSHF). Typical experimental procedure: A mixture of **1** (0.212 mmol) and DMAD (0.732 mmol) in toluene (15 ml) was refluxed for 2 days. After evaporation of the solvent, the residue was subjected to silica gel chromatography, eluting with hexane/triethylamine=100/1 and hexane/toluene/triethylamine=25/75/1. The purple fraction was collected, the solvent being evaporated, and the residue was recrystallized from dichloromethane/methanol, giving the purple crystals **2** in 57 % yield.

2: mp>300°C. UV-Vis(CH₂Cl₂): λ_{max}(ε) 307(19500), 430(204000), 545(16800), 573(7460) nm. IR(KBr): ν(C=O)1724 cm⁻¹. ¹H NMR(500MHz, CDCl₃): δ 2.65-2.80 (4H, m, H at C-a and C-b), 2.98(3H, s, H at C-f), 3.87(3H, s, H at C-h), 7.52~8.18(20H, m, H at C-Ph), 8.51(2H, d, J=4.9Hz, H at C-β), 8.58(2H, d, J=4.9Hz, H at C-β), 8.62(2H, d, J=4.9Hz, H at C-β), 8.70(2H, d, J=4.9Hz, H at C-β), 8.74(2H, d,

$J=4.9\text{Hz}$, H at C- β), 8.78(2H, d, $J=4.9\text{Hz}$, H at C- β). ^{13}C NMR(500MHz, CDCl_3): δ 25.3(C-a), 28.3(C-b), 51.4(C-f), 52.2(C-h), 117.5, 118.1, 119.0, 119.3, 127.0, 127.2, 127.5, 127.8, 128.3, 128.3, 129.9, 131.8, 132.0, 132.4, 132.5, 133.0, 133.2, 133.7, 133.8, 135.8, 136.2, 138.3, 138.5, 139.9, 140.1, 140.2, 140.3, 142.3, 142.3, 142.6, 143.0, 144.5, 146.0, 164.1(C-e), 170.0(C-g). MALDI-TOF Mass(gentisic acid/toluene): $m/z=839$ (M^+). *Anal.* Calcd for $\text{C}_{52}\text{H}_{36}\text{N}_4\text{O}_4\text{Ni} \cdot \text{H}_2\text{O}$: C, 72.83; H, 4.23; N, 6.53. Found: C, 73.11; H, 4.25; N, 6.47.

3: 81 %; mp>300 $^\circ\text{C}$.; IR(KBr): $\nu(\text{C}=\text{O})$ 1716 cm^{-1} ; UV-Vis(CH_2Cl_2): $\lambda_{\text{max}}(\epsilon)=300(10800)$, 420(214000), 535(12300) nm. ^1H NMR(500 MHz, CDCl_3) 2.00-2.07 (1H, m, H at C-b), 2.27-2.33 (1H, m, H at C-b), 2.53-2.65 (2H, m, H at C-a), 3.39-3.43 (1H, m, H at C-c), 4.25 (1H, d, J 9.2, H at C-d), 7.01-8.20 (25H, m, H at Ph), 8.55 (1H, d, J 4.9, H at C- β), 8.61 (1H, d, J 4.9, H at C- β), 8.63 (1H, d, J 4.9, H at C- β), 8.63 (1H, d, J 4.9, H at C- β), 8.65 (1H, d, J 4.9, H at C- β), 8.68 (1H, d, J 4.9, H at C-b); ^{13}C NMR(125 MHz, CDCl_3) 23.6 (C-a), 25.5 (C-b), 41.0 (C-c), 41.1 (C-d), 117.5, 117.6, 119.1, 119.1, 126.2, 126.5, 126.6, 127.0, 127.4, 127.8, 128.2, 128.3, 128.9, 131.9, 132.0, 132.1, 132.2, 132.4, 132.5, 133.0, 133.4, 133.7, 134.9, 135.0, 137.7, 139.1, 140.2, 140.4, 140.5, 140.6, 142.2, 142.4, 142.4, 142.8, 143.0, 144.9, 174.7 (C-e), 178.4 (C-f). MALDI-TOF Mass(gentisic acid/toluene): $m/z=870$ (M^+). *Anal.* Calcd for $\text{C}_{56}\text{H}_{37}\text{N}_5\text{O}_2\text{Ni}$: C, 77.26; H, 4.28; N, 8.04. Found: C, 76.87; H, 4.35; N, 8.35%.

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