Monatshefte für Chemie 135, 509–511 (2004)
DOI 10.1007/s00706-003-0134-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Mono-*meso*-*tert*-butylporphyrin

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Received October 10, 2003; accepted (revised) October 14, 2003

Summary. Treatment of *meso*-tetra(*tert*-butyl)porphyrin with sulfuric acid/*n*-butanol affords a mixture of porphyrin and mono-*tert*-butylporphyrin in relatively high yield.

Keywords. Porphyrin; Mono-*meso*-*tert*-butylporphyrin; NMR spectra; ESI-MS spectra.

Introduction

Synthesis of unsubstituted porphyrin (**2**) has been a rather difficult task due to low reaction yields rather than synthesis itself [1]. *Neya et al.* obtained **2** in larger amounts, but this was due to reaction scale-up rather then yield itself [2]. In 2002 the same authors described an elegant method of porphyrin synthesis *via* de-*tert*-butylation of much more easily obtained *meso*-tetra-*tert*-butylporphyrin **1** [3]. *Senge et al.* described a synthesis of **3** by condensing dipyrromethane, pyrrole-2-carbaldehyde, and pivaloyl aldehyde (7%) [4], by reacting *tert*-butyllithium and **1** (4%) or by condensing tripyrrane, pyrrole, and pivaloyl aldehyde (6%) [5]. An efficient synthesis will be described in the present paper.

Results and Discussion

During the synthesis of **2** carried out according to Ref. [3], a porphyrin-like by-product was washed out with methanol. We investigated this by-product by ESI-MS and it turned out to be almost pure **3**. Occasionally, it was admixed with negligible amounts of di-*tert*-butylporphyrin, which, however, could not be obtained with a yield sufficient to determine which isomer it was (5,10- or 5,15-). Our studies on de-*tert*-butylation of **1** were performed under various experimental conditions (heating temperature from 90°C to refluxing, heating periods from 15 min to 2 h). We always obtained **3** in amounts considerably larger than expected (appr. 70% of **3** and 30% of **2**). We purified **3** contained in methanol washings on a silica gel column. Because silica very strongly adsorbs **1**, it cannot be eluted with

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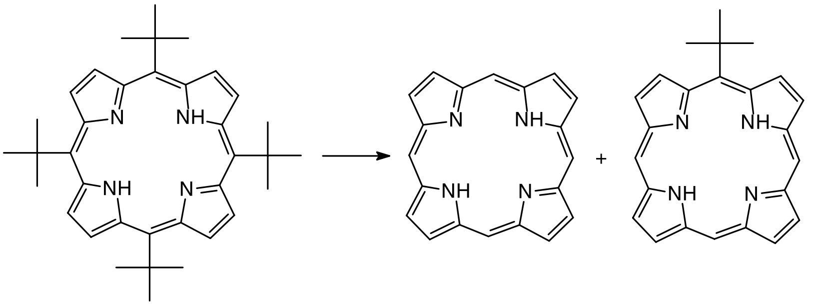

1 **2** **3**

Scheme 1

methanol. Changing the eluent to chloroform allows **2** to be eluted from the column. However, some amount of **3** was found also in chloroform fraction. Use of different stationary phases (aluminum oxide or cellulose) did not improve separation conditions. The mono-*tert*-butyl derivative **3** owing to its structure (non-planar porphyrin ring) appears interesting for spectroscopic (and future crystallographic) studies.

Porphyrin **3** has D_2 symmetry. The ^{1}H NMR spectrum shows four β-pyrrolic doublets ($\delta = 9.91$ and 9.26 ppm, $J = 4.8$ Hz, and $\delta = 9.36$ and 9.33 ppm, $J = 4.5$ Hz). The signals of three *meso* protons appear as two singlets at $\delta = 10.12$ ppm (2H) and 10.04 ppm (1H). Also two NH protons appear as two broad singlets at $\delta = -2.7$ and -2.65 ppm. The extent of the NH proton signal shift suggests a considerably greater planarity of the central porphyrin ring of **3** as compared to **1** ($\delta = +1.58$ ppm). The *tert*-butyl group signal appears at $\delta = 2.60$ ppm. The planarity of **3** may be comparable with that of *meso-tetra*-phenylporphyrin.

The UV-Vis spectra point to a slight departure from planarity of the central ring of **3**. The difference of the *Soret* band shifts between **2** and **3** is minimal (393 *vs.* 396 nm), compared to the value for **1** (446 nm). The extent of this band shift characterizes the planarity of the central porphyrin ring [6].

ESI MS of the porphyrins obtained show characteristic peaks of molecular ions augmented by hydrogen ion ($m/z = 535$ for **1**, 367 for **3**, and 311 for **1**). The ESI spectrum of **2** shows a characteristic cluster peak ($m/z = 621$, 2M + H) absent from spectra of **1** and **3**. Formation of such ions may be facilitated by lack of spatial hindrance as well as by planarity of the compounds in question. The MS–MS of **3** molecular ions' disintegration reveals the presence of ions with $m/z = 311$ (molecular ion **2**) and with $m/z = 352$ the latter forming *via* CH_2 fragment split-off from molecular ion **3**. The MS–MS of molecular ion **1** ($m/z = 535$) leads to ions with $m/z = 505$ (M-2×CH_3), 478 (M-*tert*-butyl or M-3×CH_2–CH_3), 463 (M-*tert*-butyl-CH_2 or M-4×CH_2–CH_3), and a cluster of peaks with $m/z = 421$ (M-2×*tert*-butyl or M-6×CH_2-2×CH_3).

In conclusion we found that de-*tert*-butylation of tetra-*tert*-butylporphyrin can be an alternative method of obtaining the mono-*tert*-butyl derivative of porphyrin.

Experimental

All materials were of commercial reagent grade (Aldrich). UV-Vis spectra were recorded in CH_2Cl_2 using a JASCO V-530 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ using *TMS* as internal standard on a Varian Unity INOVA-300 spectrometer (300 MHz). ESI MS spectra were recorded for $CHCl_3$/methanol solutions on a Finnigan Quatro spectrometer.

Compound **1** was obtained according to Ref. [7]. Compounds **2** and **3** were obtained according to a method described in Ref. [3]. Compound **3** was isolated from the methanolic solutions used to wash **2** according to an original procedure described in Ref. [3]. Purification of **3** was performed on a silica gel column, using methanol as the eluent. Similarly, **3** was obtained by separation (by methanol washing) of a mixture left over from de-*tert*-butylation of **1**. Total yield of **3** from the de-*tert*-butylation process was appr. 45%.

Spectroscopic data for **1** and **2** are identical with those listed earlier in the literature [3, 7].

meso-tert-Butylporphyrin (**3**, $C_{24}H_{22}N_4$)

^1H NMR: $\delta = 10.12$ (s, 2H), 10.04 (s, 1H), 9.36, 9.33 (2d, 4H, J = 4.5 Hz), 9.91, 9.26 (2d, 4H, J = 4.8 Hz), 2.60 (s, 9H), −2.65 (bs, 1H), −2.70 (bs, 1H) ppm; UV-Vis (CH_2Cl_2): λ_{max} (rel. int.) = 396.5 (27.1), 498 (1.94), 535.5 (0.84), 560.5 (sh, 0.82), 574.5 (1), 635.5 (0.26) nm; ESI MS: m/z (%) = 367 ($[M+H]^+$, 100).

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