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An Unexpected Wittig Reaction of Dimethyl 3,3`-(3-formyl-2,7,12,18-tetramethyl-21H, 23H-porphyrin-13,17-diyl)-dipropionate

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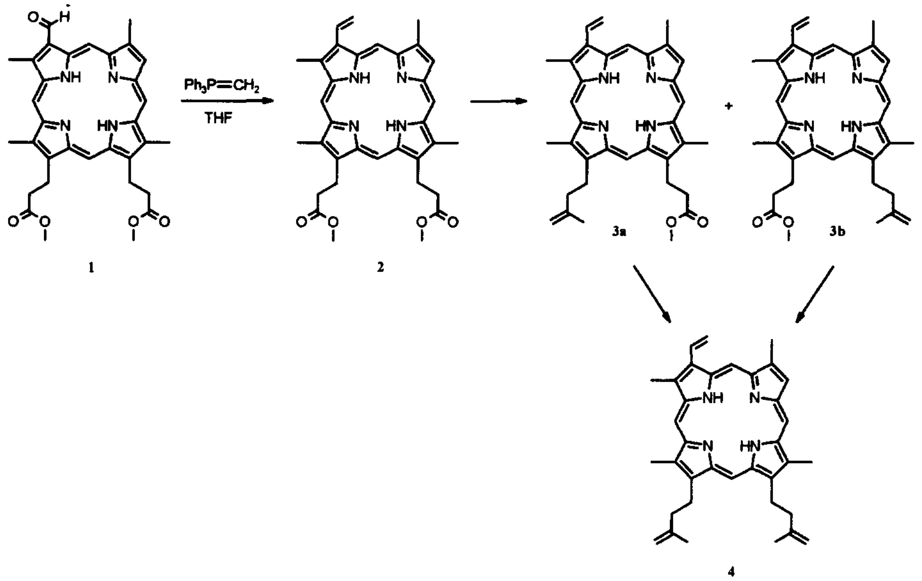
Abstract: Transformation of one or both of the methoxycarbonyl groups of dimethyl 3,3`-(3-formyl-2,7,12,18-tetramethyl-21H,23H-porphyrin-13,17-diyl)-dipropionate (**1**) to isopropenyl groups was observed when an excess of ylide was used in the Wittig reaction. © 1997 Elsevier Science Ltd.

The Wittig reaction is one of the most often used syntheses in organic chemistry. Chlorin syntheses have been accomplished using the Wittig reaction for linking formyl groups of two pyrochlorophyllide *a* derivatives to yield bis(pyrochlorophyllide *a*).[1] In porphyrin syntheses, the Wittig reaction has been used for the olefination of an oxo or a formyl group.[2] Usually the Wittig reaction is selective to an aldehyde or a ketone in the presence of an ester or a carboxylic acid, because the reaction of phosphorus ylides with an ester or acid carbonyl is much slower than with a formyl or an oxo group.[3] There exist some examples in the literature[4] where esters have been treated with phosphorus ylides and after hydrolysis converted into isopropenyl derivatives. The possible mechanism is discussed in the literature.[5]

We were interested in this kind of transformation in the case of porphyrins. Thus, the Wittig reaction was performed with dimethyl 3,3`-(3-formyl-2,7,12,18-tetramethyl-21H, 23H-porphyrin-13,17-diyl)-dipropioniate (**1**) in the presence of an excess of phosphorus ylide, yielding only compounds **4**, **3a** and its constitutional isomer **3b** but not any of the expected compound **2**. Our experimental procedure was as follows. The phosphorus ylide was prepared by refluxing methyltriphenylphosphonium bromide (1.05 eq. relative to the base) and sodium bis(trimethylsilyl)amide in dry THF (20 ml) under nitrogen for 3 h, providing an orange suspension. Porphyrin **1** (59 mg) was dissolved in the ylide suspension (10 ml). The excess of methyltriphenylphosphonium bromide relative to porphyrin was 86 equivalents. The reaction mixture was stirred at ambient temperature for 1 h under nitrogen. Then the solution was diluted with water (150 ml), extracted with chloroform (2 × 50 ml) and the extract was washed with water. The total yield of porphyrins **3a, 3b** and **4** was 58 %. Compound **4**[6] (33%) was separated from the product mixture by chromatography on a silica gel column (eluent: CCl_4 - acetone, 40:1, v/v) and crystallized from $CHCl_3$-light petroleum. The compounds obtained were characterized by EI-MS[7] and ^1H NMR.[6]



1 2 3a 3b 4

Normally the product of the Wittig reaction would be compound **2**. In our case the large excess of the Wittig reagent is the propable reason for the formation of the new-type porphyrins **3a**, **3b** and **4**. In the literature, it is mentioned that already three equivalents of phosphorus ylide is enough to transform alkoxycarbonyl groups into isopropenyl groups.[4,5] The reaction observed seems to be rather convenient for converting the formyl groups of porphyrins into vinyl groups and the carboxylic acid ester groups into isopropenyl groups. The yield of porphyrin **4** can be increased by lengthening the reaction time.

References and Notes

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6. ^{1}H NMR (360 MHz, CDCl$_3$) of compound **4**: δ -3.86 (s, 2H, 21-NH, 23-NH), 2.05, 2.06 (s, 6H, $13^{3'}$-, $17^{3'}$-CH$_3$), 2.92 (m, 4H, 13^2-, 17^2-CH$_2$), 3.55, 3.56, 3.68, 3.72 (s, 12H, 2^1-,7^1-, 12^1-, 18^1-CH$_3$), 4.09 (m, 4H, 13^4-,17^4-CH$_2$), 4.94, 5.01 (m, 4H, 13^1-,17^1-CH$_2$), 6.17, 6.35 (dd, 2H, 3^2-CH$_2$), 8.28 (dd, 1H, 3^1-CH), 9.06 (s, 1H, 8-CH), 9.91, 9.96, 10.02, 10.18 (s, 4H, 5-, 10-, 15-, 20-CH).
7. EI-MS of compound **4**: 528 $[M]^+$, 473 $[M - CH_2C(CH_2)CH_3]^+$, 418 $[M - 2 \times CH_2C(CH_2)CH_3]^+$, EI-MS of mixture of compounds **3a** and **3b**: 546 $[M]^+$, 491 $[M - CH_2C(CH_2)CH_3]^+$, 418 $[M-(CH_2C(CH_2)CH_3 + CH_2COOCH_3]^+$.

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