Tetrahedron Letters, Vol.33, No.2, pp. 269-272, 1992
Printed in Great Britain

0040-4039/92 $3.00 + .00
Pergamon Press plc

Synthesis of meso-Tetraalkynyl Porphyrins Using 1-Seleno-2-alkynyl Cation Precursors

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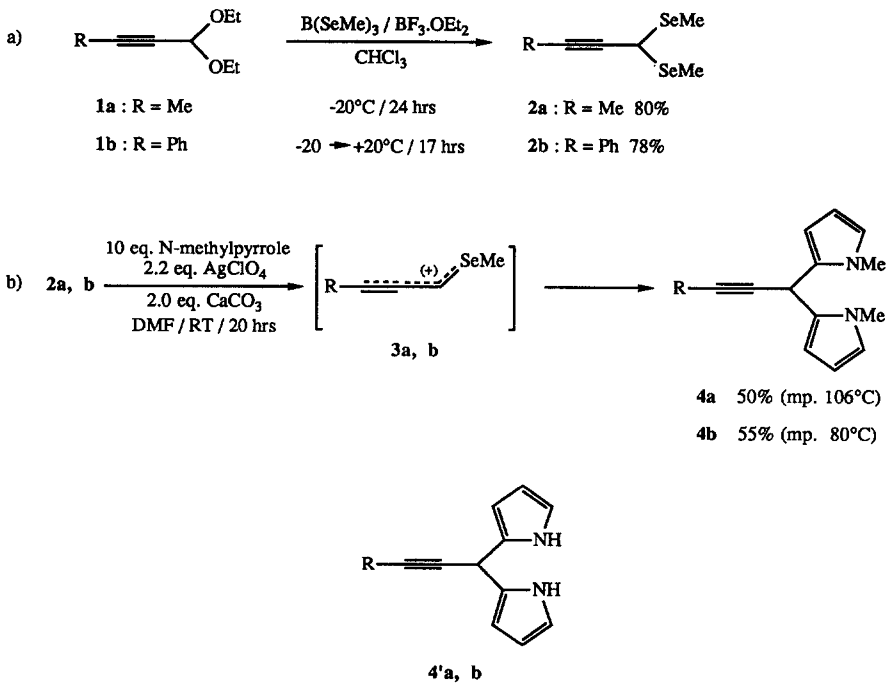
Abstract : *The strongly regioselective reaction of the silver perchlorate activated selenoacetals derived from 2-butynal and 3-phenylpropynal with pyrrole allows for a straightforward synthesis of the corresponding title compounds but the yields are low.*

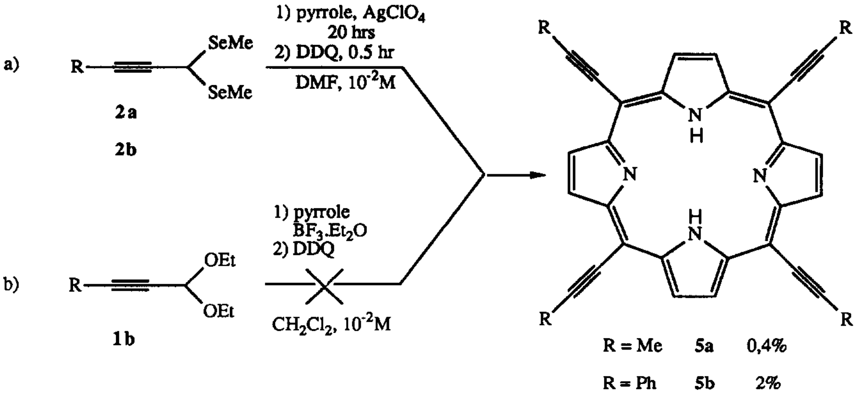
It has been established that selenium (especially alkylseleno) moieties provide considerable stabilisation of a carbocationic center [1], and that such species can be used to effect a variety of C-C bond forming reactions [2]. Of particular relevance to our present purpose are the findings that β,γ-unsaturated selenoacetals generate, when treated with Lewis acids, 1-selenoallyl cation type intermediates which react efficiently with carbon nucleophiles [3]. We have reported on the possible application of the latter type of reaction to the synthesis of meso-tetravinylporphyrins [4], and the process has now been generalised [5]. It was therefore attractive to test the above methodology in the case of the "propargylic" selenoacetals **2** ; we present herein our preliminary successful results.

Although quite unstable [6], the hitherto unknown selenoacetals **2a** and **2b** could be prepared in good yields according to Scheme 1a by transacetalisation of **1a**, **b** using $B(SeMe)_3$ as methaneselenol equivalent [7].

Scheme 1



Scheme 2



As in the case of allylic selenoacetals [4], our proposed porphyrin synthesis crucially relies upon the next step, i. e. conversion of **2a, b** into dipyrrylmethanes **4'a, b** on reaction with pyrrole. Our previous studies [3a, 4] have shown that N,N-dimethylformamide (DMF) as solvent allows for the desired and highly regioselective reaction of 1-selenoallyl cations with pyrroles. That the same sort of regioselectivity is induced by DMF for the reaction of the putative 1-selenopropargylic cations **3a, b** is convincingly demonstrated in Scheme 1b. Dipyrrylmethanes **4a, b** were found to decompose extensively on attempted chromatographic (SiO_2) purification, they however could be isolated (by crystallisation from pentane as light brown solids) sufficiently pure for spectroscopic (IR, ^1H NMR) identification [8].

With this information at hand, we next attempted one-pot syntheses of the title compounds by reacting unmethylated pyrrole with **2a** or **2b** in equimolar amounts, and under very much the same conditions as in Scheme 1b. When no more precursor **2** was present in the reaction mixture, the oxidant, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was introduced and allowed to react for 0.5 hr. On work-up of the reaction mixtures we were pleased to find that they contained the expected porphyrins **5a, b** (Scheme 2a) [9]. In view of the excellent regioselectivities and moderately good efficencies of the model reactions (Scheme 1b), the low yields in porphyrins **5a,b** may appear somewhat disappointing. Since oxidation of the intermediate porphyrinogens into porphyrins is usually a facile reaction, we suspect that the yield-limiting step should be the formation and cyclisation of the linear tetrapyrrole precursor of the porphyrinogen. It is probably significant in this regard to note that in the present porphyrin forming reactions (Scheme 2a) the first step (i.e. formation of dipyrrylmethanes **4'a, b**) is rather slow, since it requires ~20 hrs. to consume the starting materials **2a, b**. Considering the very limited stability of **4'a,b** (as inferred from that of **4a, b**, see above), they may not survive long enough to react further with **2a, b** and another molecule of **4'a, b**.

Inspite of the low yields, formation of the meso-tetraalkynyl porphyrins **5a, b** is gratifying for at least two reasons : i) these derivatives cannot at all be obtained from the (O,O)-acetals **1a, b** even under conditions considered as best [10] (Scheme 2b), ii) we believe this type of compounds should be valuable building blocks for sophisticated porphyrin-based organic materials.

Work is being continued to check this latter perspective, as well as to increase yields in **5** and to generalise the synthesis.

I. R. S. I. A (Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture) is gratefully acknowledged for predoctoral fellowships to one of us (G. P.).

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5) G. Proess, Dissertation Doctorale, Facultés Universitaires N-D de la Paix, Namur, 1991.

6) Some decomposition occurs during preparative thin layer chromatography (basic Al_2O_3, and the so obtained pale yellow liquids further decompose on storage at -18°C.
Spectral data of **2a, b** :
2a : ^{1}H NMR (CCl_4, δ) : 1.92 (3H, d, J = 2 Hz, CH_3-C≡C) ; 2.10 (6H, s, $SeCH_3$) ; 4.43 (1H, q, J = 2 Hz, ≡C-CH<)
IR (liq. film) : 2995, 2920, 2846, 2812, 2225, ...
Mass (m / e) : 243 $(M + 1)^+$; 148 $(M - SeCH_3)^+$; 95 $(CH_3Se)^+$
2b : ^{1}H NMR (CCl_4, δ) : 2.22 (6H, s, $SeCH_3$) ; 4.75 (1H, s, ≡C-CH<) ; 7.12-7.53 (5H, m, aromatics)
IR (liq. film) : 3081, 3061, 3033, 3020, 2926, 2193, 1597
Mass (m / e) : 304 (M) ; 209 $(M - SeCH_3)^+$; 95 $(CH_3Se)^+$; 77 $(C_6H_5^+)$

7) $B(SeMe)_3$ / acid is a known reagent for selenoacetalisation of carbonyl compounds :
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8) Spectral data of **4a, b** :
4a : ^{1}H NMR (CCl_4, δ) : 1.83 (3H, d, J = 2 Hz, CH_3-C≡) ; 3.52 (6H, s, N-CH_3) ; 4.97 (1H, q, J = 2 Hz, ≡C-CH<) ; 5.98 (4H, m, pyrrole) ; 6.52 (2H, m, pyrrole)
IR (KBr pellet) : 3122, 3101, 2938, 2916, 2878, 2806, 2228
GC / MS (m / e) : 212 (M) ; 197 $(M - CH_3)^+$; 132 (M - N-methylpyrryl)$^+$; 80 (N-methylpyrryl)$^+$
4b : ^{1}H NMR (CCl_4, δ) : 3.50 (6H, s, NCH_3) ; 5.17 (1H, s, ≡C-CH<) ; 5.87 (4H, m, pyrrole) ; 6.33 (2H, m, pyrrole) ; 7.03-7.47 (5H, m, phenyl)
IR (KBr pellet) : 3097, 3052, 2945, 2229, 1597
GC / MS (m / e) : 274 (M) ; 194 (M - N-methylpyrryl)$^+$; 197 $(M - C_6H_5)^+$; 77 $(C_6H_5^+)$

9) Spectral data of **5a, b** :
5a : FAB / MS (m / e) : 463 (MH^+) ; 402 $(MH^+ - 4\ CH_3)$; 385 $(MH^+ - 2\ CH_3\text{-}C{\equiv}C)$
UV-VIS (CH_2Cl_2, λ, log ε) : 446 (4.81) ; 517 (2.90) ; 563 (3.30) ; 602 (3.87) ; 647 (2.93) ; 708 (3.32)
5b : FAB / MS-MS (m / e) : 711 (MH^+) ; 634 $(MH^+ - C_6H_5)$; 557 $(MH^+ - 2\ C_6H_5)$
UV-VIS (CH_2Cl_2, λ) : 455, 560 (sh), 607, 699

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(Received in UK 18 October 1991)