

Synthesis of *meso*-Tetravinyl Porphyrins through 1-Selenoallyl Cationic Species

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The highly regioselective reaction of postulated 1-methylseleno-allyl cations with pyrrole permits the one-pot synthesis of a series of novel porphyrins; alternatively, β -methylcrotonaldehyde gives (**5a**).

Selenium stabilized carbenium ions have been described recently in some detail.¹ These species allow a number of useful synthetic transformations,² in particular 1- and 2-selenoallyl cations react with electron rich (hetero)aromatic compounds to give substitution and not cycloaddition products.³ Furthermore, we have shown⁴ that a high degree of regioselectivity can be achieved in the reaction of 1-selenoallyl cations with *N*-methylpyrrole when appropriate cation precursors and reaction conditions are used (Scheme 1).

Cation precursors leading to an overall regioselectivity of

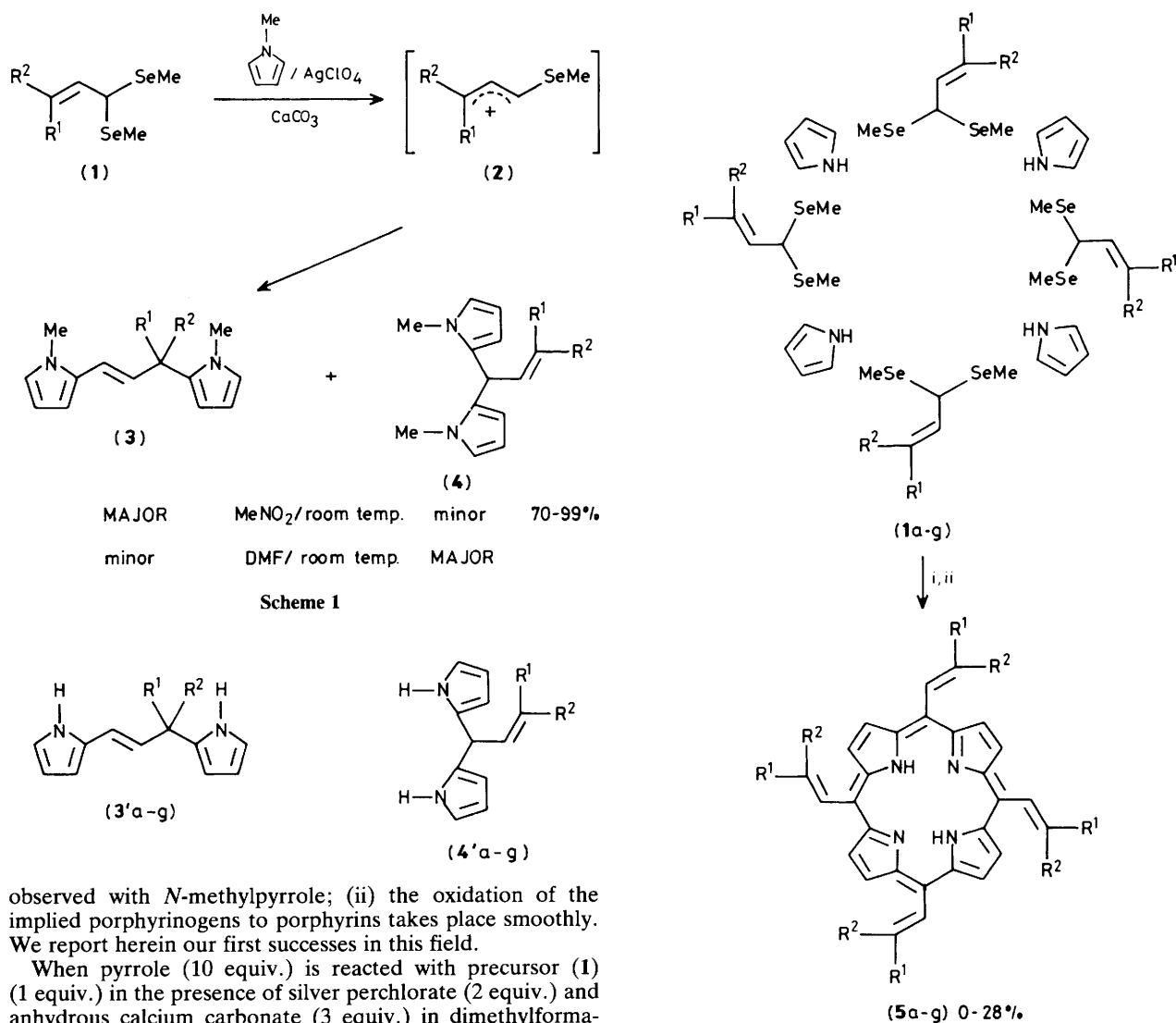
$\geq 90\%$ include (**1a**) $R^1 = R^2 = \text{Me}$; (**1b**) $R^1 = R^2 = \text{Et}$; (**1c**) $R^1 = R^2 = \text{Pri}$; (**1d**) $R^1 = R^2 = \text{Ph}$;⁵ (**1e**) $R^1 = \text{Me}$, $R^2 = \text{Ph}$;⁵ (**1f**) $R^1 = \text{H}$, $R^2 = \text{Ph}$;⁵ and (**1g**) $R^1 = \text{H}$, $R^2 = o\text{-NO}_2\text{C}_6\text{H}_4$.⁵

Since the most frequently used porphyrin syntheses proceed through dipyrrolyl methanes of type (**4'**) the above mentioned observation should permit a straightforward synthesis of porphyrins (**5**) bearing vinyl substituents at the four *meso* positions. The essential requirements are that (i) the reaction of the postulated intermediate 1-selenoallyl cations (**2**) with pyrrole will exhibit the same or similar regioselectivity to that

Table 1. U.v.-visible data for compounds (5).

(5)	R ¹	R ²	Yield (%)	λ_{\max}/nm (ϵ_{\max})(C ₆ H ₆)
a	Me	Me	9	423 (266 100); ~494 (sh., ~3 400); 523 (10 700); 561 (9 800); 600 (3 600); 661 (2 900)
b	Et	Et	15	421 (270 500); ~491 (sh., ~3 200); 521 (10 700); 559 (9 800); 596 (3 700); 657 (2 500)
c	Pr ⁱ	Pr ⁱ	20	421 (275 300); 488 (4 000); 520 (11 300); 556 (9 800); 596 (3 600); 657 (3 000)
d	Ph	Ph	28	448 (304 400); ~513 (sh. ~7 700); 548 (12 800); 593 (24 700); 686 (10 000)
e	Me	Ph	28	429 (291 600); ~497 (sh. ~3 700); 528 (10 300); 570 (15 000); ~600 (sh. ~5 300); 663 (4 100)
f	H	Ph	0	—
g	H	<i>o</i> -NO ₂ C ₆ H ₄	trace	— ^a

^a The low yield of this compound prevented us from obtaining exact data.



observed with *N*-methylpyrrole; (ii) the oxidation of the implied porphyrinogens to porphyrins takes place smoothly. We report herein our first successes in this field.

When pyrrole (10 equiv.) is reacted with precursor (1) (1 equiv.) in the presence of silver perchlorate (2 equiv.) and anhydrous calcium carbonate (3 equiv.) in dimethylformamide (DMF) solution at ambient temperature the starting materials (1) are consumed within a few minutes. Although contaminated with various by-products,[†] the main reaction products are assumed (on the basis of ¹H n.m.r. spectra of the

[†] Probably small amounts of (3') as well as 'oligomers' corresponding to compounds (8) and (10) quoted in ref. 4.

Scheme 2. Reagents: i, AgClO₄, CaCO₃, DMF, room temp., 5 min.; ii, DDQ, room temp., 0.5 h.

crude products) to be dipyrromethanes (4'). These compounds however have been found to be much less stable than the corresponding *N*-methyl derivatives⁴ (4), therefore they could not be purified and characterized.

At this point we attempted to synthesize the title compounds directly by reacting equimolar amounts of pyrrole and unsaturated selenoacetals (**1**) under the same conditions as above ($\text{AgClO}_4/\text{CaCO}_3/\text{DMF}/\text{room temp.}$), but followed by an oxidation step (Scheme 2). It was again observed that starting selenoacetals (**1**) reacted quite fast (≤ 5 min) and that the most efficient oxidizing agent was dichlorodicyanoquinone (DDQ, 0.5 equiv., room temp., 0.5 h). From the apparently black reaction mixture obtained in this way porphyrins (**5**) could be isolated in 0–28% yield (Table 1) by t.l.c. (SiO_2 , diethyl ether–pentane eluant) purification.

As shown in Table 1 all the disubstituted precursors (**1a–e**) lead to porphyrins (**5a–e**) bearing disubstituted vinyl groups in their *meso* positions. Although the yields are not very high, they are comparable to those often observed in one-pot porphyrin syntheses.⁶ Thus we feel that the ease of access⁷ of precursors (**1**) as well as the rapidity and mildness of our synthesis make it competitive with regard to other methods. The validity of our approach to the hitherto unknown class of title porphyrins is further illustrated by control experiments we carried out with a view to preparing (**5a**) from β -methylcrotonaldehyde.

Refluxing this aldehyde with pyrrole in acetic acid led only to intractable products containing no trace of porphyrin. However, when equimolar amounts of the aldehyde and pyrrole were treated with toluene-*p*-sulphonic acid (1 equiv., DMF, room temp.) for twelve hours followed by oxidation with DDQ, porphyrin (**5a**) could be isolated in *ca.* 10% yield.

Although the regioselectivities and solvent effects on the reactions of (**1f**) and (**1g**) with *N*-methylpyrrole were very much the same as for the other precursors (**1a–e**), the synthesis of (**5f**) failed completely and (**5g**) was obtained in trace amounts. The reasons for these failures are not clear at present.

Porphyrins (**5a–c**) were also transformed to the corresponding metallo-porphyrins (metal = Cu or Zn) by treating a diethyl ether–methanol (1:1) solution of (**5a–c**) with the metal acetates at room temperature for two hours. Alternatively, the copper porphyrin derived from (**5c**) was prepared directly in 20% yield by reacting 1 equiv. of pyrrole and 1 equiv. of (**1c**) with an excess of $\text{Cu}(\text{OAc})_2$ in DMF solution at 60°C for 5 minutes.

IRSIA (Institut pour l'encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture) is gratefully acknowledged for a predoctoral fellowship to M. R.

Received, 7th July 1986; Com. 935

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