Tetrahedron Letters, Vol. 34, No. 32, pp. 5125-5126, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Synthesis of Monoquinonyl Porphyrins via Benzannulation of Fischer Carbene Complexes and Palladium Catalysed Cross Coupling Reactions.

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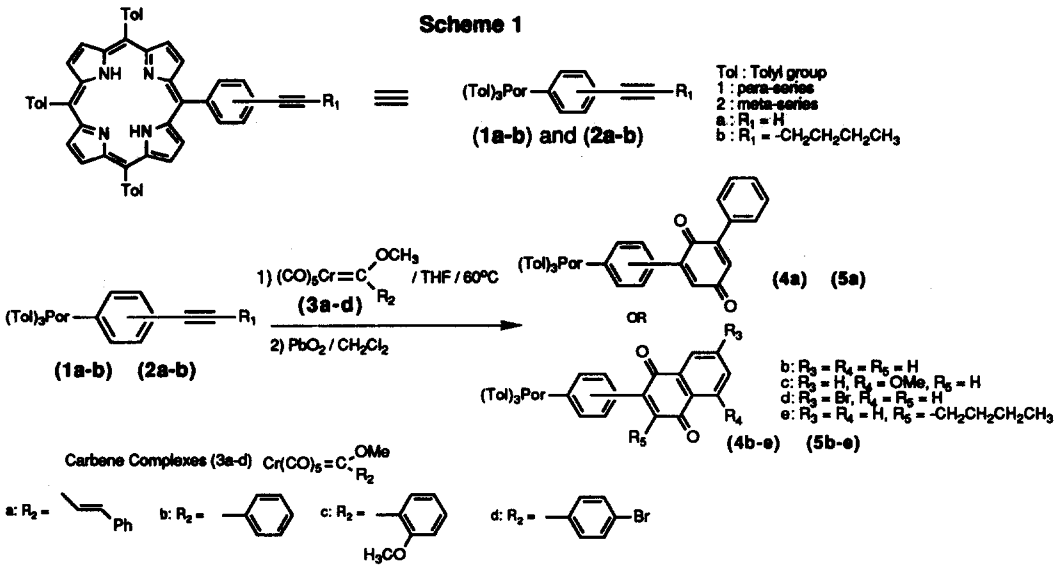
Abstract: *Meso*-para- and *meso*-meta-monoquinonyl porphyrins were prepared in good yields by bennzannulation of chromium carbene complexes with unsymmetrical alkynyl porphyrins, and palladium-catalysed cross-coupling reaction of 2,5-dimethoxyphenyl boronic acid with unsymmetrical porphyrin aryl triflates, followed by oxidation.

Covalently-linked porphyrin quinones have been used as models for the studies of the primary electron transfer of photosynthesis,[1] and the synthesis of these porphyrin-quinones bearing different redox potentials provide an opportunity for the detailed studies of the electron transfer step. We now report two synthetic approaches for the preparation of monoquinonyl porphyrins based on the benzannulation of Fischer carbene complexes[2,3] and palladium catalysed cross coupling reactions.[6] Both of these methods take advantages of the high chemical yields, ease of operation, and a short synthetic sequence. For the benzannulation reaction, the (alkynyl)phenyl porphyrins **1a-b**, **2a-b**[5] underwent smooth benzannulation with chromium carbene complexes **3a-b**[3] in tetrahydrofuran at 60 °C to produce porphyrin-quinones **4a-e**, **5a-e**[6] (Scheme 1), after oxidative work up with PbO_2, in good overall yields (Table 1). The reaction is highly regioselective. Both alkenyl and aryl carbene complexes can be employed to produce porphyrin-quinone derivatives with different redox potentials.

Alternatively, the mono(benzoquinonyl)phenyl porphyrins were also prepared via Suzuki cross-coupling reaction of 2,5-dimethoxyphenyl boronic acid **6**[6] with porphyrin aryl triflates **7a-b**[5] (Scheme 2),[4] using a catalytic quantity of $Pd(PPh_3)_4$ (10 mol %), K_2CO_3 (2 eq). The desired mono(dimethoxyphenyl) aryl porphyrins **8a-b**[6] were isolated in 74-76% yield, which were converted to porphyrin-quinones **9a-b** by treatment with BBr_3 at low temperature and then oxidized with PbO_2 in methylene chloride to give the corresponding quinonyl porphyrins **9a-b**[6,7]. The overall yield of the synthesis of the mono(benzoquinonyl)phenyl porphyrins **9a-b** from the porphyrin aryl triflates **7a-b** were about 57%. Work is continued on the synthesis of tetraquinonyl porphyrins by using the above methods.

Acknowledgement:

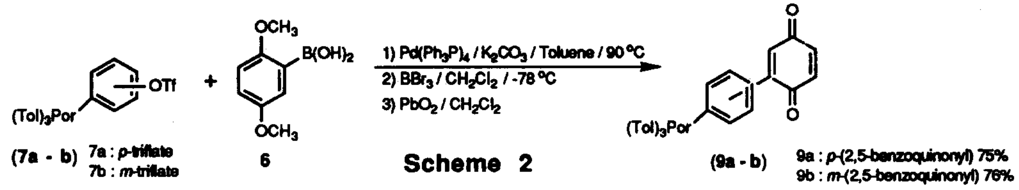
We thank the Research Grants Council (RGC) of Hong Kong (A/C 221600050) for financial support.



Scheme 1

Table 1. Synthesis of mono-quinone linked porphyrins from the bennzannulation.

Porphyrin	Carbene complex	Product	Yield (%)
1a	3a	4a	73
1a	3b	4b	72
1a	3c	4c	75
1a	3d	4d	76
1b	3b	4e	75
2a	3a	5a	71
2a	3b	5b	74
2a	3c	5c	74
2b	3b	5e	73



Scheme 2

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(Received in Japan 3 April 1993; accepted 11 June 1993)