Tetrahedron Letters, Vol. 34, No. 52, pp. 8531-8534, 1993
Printed in Great Britain

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

The Synthesis of Butadiene-bridged Porphyrin Dimers and Styryl Porphyrins Using a Porphyrin-derived Wittig Reagent

Edia E. Bonfantini and David L. Officer*

Department of Chemistry and Biochemistry, Massey University, Palmerston North, New Zealand.

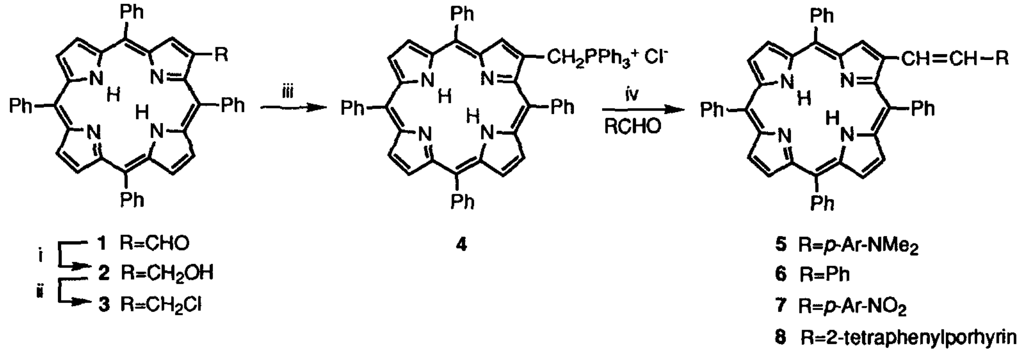
Abstract: The synthesis of 2-tetraphenylporphyrinylmethyltriphenylphosphonium chloride and its use in Wittig reactions is described, providing an efficient and versatile method for the syntheses of styryltetraphenylporphyrins as well as the hitherto unknown free base and heterometallated butadiene porphyrin dimers.

The syntheses of conjugatively-substituted porphyrin dimers are being vigorously pursued[1-7] at the present time as models for the study of electron transfer processes[8] and there is a growing interest in their potential for use in molecular devices[9]. The dimers are linked by a variety of olefinic or aromatic bridging groups and generally have the same porphyrinyl end groups. They are commonly prepared by a dimerisation process which limits the type of dimer that can be made; the synthesis of unsymmetrical dimers is difficult, the bridging group is symmetrical and there is limited scope in such methods for the preparation of variably metallated and heterometallated derivatives.

The availability of a porphyrin-derived Wittig reagent would allow the rapid construction of a whole variety of new symmetrical dimers, limited only by the availability of the bridging group dialdehydes. Mixed porphyrin dimers could also be easily synthesised providing novel materials with redox gradients, one porphyrin end-group being more easily oxidised or reduced than the other. Of marked significance is the fact that such a reagent could offer a versatile synthesis of heterometallated dimers, leading to compounds with interesting electrochemical, redox and spectroscopic properties.

This synthetic approach could also provide a useful addition to the current limited methodology for the direct substitution of porphyrins. Wittig reactions of a porphyrin-derived phosphonium salt with aliphatic and aromatic aldehydes and subsequent transformations could afford a number of new and interesting substituted porphyrins. In this paper, we demonstrate the power and simplicity of this approach with the efficient syntheses of some new styryl derivatives and hitherto unknown butadiene porphyrin dimers. The facile synthesis of a heterometallated dimer demonstrates the great potential of this methodology.

The synthesis of the porphyrin phosphonium chloride **4** appeared straightforward (Scheme 1)[10], but it was not readily achieved. Although the chloride could be obtained cleanly (94%) after a number of attempts were made to halogenate the known hydroxymethyl porphyrin **2**[11], it was found to be unstable to chromatography. The phosphonium salt **4** did not form using standard reaction conditions (1-2 mol. equiv. PPh_3 in refluxing solvent). However, it was recently reported that a large excess of triphenylphosphine (8 mol. equiv.) can be used to effect salt formation[12]. In this way, gram quantities of the pure salt could be obtained in 76% overall yield from 2-formyltetraphenylporphyrin **1**[13].



i) $NaBH_4$, THF/H_2O, 15 min; ii) $SOCl_2$, pyridine, Et_2O, 15 min; iii) 10 mol. eq. PPh_3, $CHCl_3$, 8 h reflux; iv) 25-40% aq. NaOH, CH_2Cl_2.

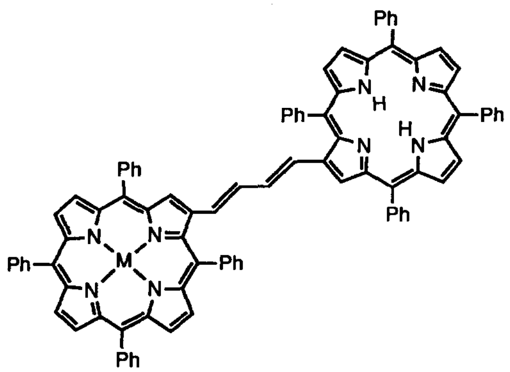
Scheme 1

Wittig reactions of **4** with aryl aldehydes were carried out to test the efficacy of the reagent. The reactions took place with extraordinary facility under liquid-liquid phase transfer conditions giving excellent yields after chromatography[10]. With dimethylaminobenzaldehyde, 65% of the pure (*E*)-isomer of **5** was isolated whereas the phenyl derivative **6** was obtained (88%) as a two component mixture (95% (*E*)). As a result of the extensive signal overlap in the ^1H nmr spectrum, the second porphyrin product could not be positively identified as the (*Z*)-isomer nor could it be isolated by chromatography or crystallisation. In marked contrast, a 7:3 mixture (87%) of the (*E*):(*Z*)-isomers of *p*-nitrostyryl derivative **7** was obtained. Although the two isomers could not be chromatographically separated, the presence of a *cis*-double bond in the minor component was clearly evident in the ^1H nmr spectrum. This was confirmed by iodine-catalysed isomerisation of the mixture which provided the pure (*E*)-*p*-nitrostyryltetraphenylporphyrin in 81% overall.

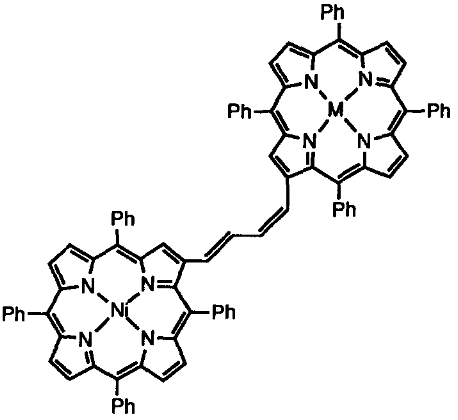
The stereochemistry of these reactions was intriguing. The preference for (*E*)-stereochemistry was predictable given the bulk of the phosphonium salt **4**. However, the formation of a significant amount of (*Z*)-*p*-nitrostyrylporphyrin suggested that, in this case, a second effect was influencing the stereochemical course of the reaction. Molecular modelling[14] showed that hydrogen-bonding of one of the porphyrinyl NH protons to the nitro group of *p*-nitrobenzaldehyde could lead to the required *cis*-configuration. A π–π interaction may have also been involved but cannot have been the sole influence in this reaction.

It is worthy of note that ring protonation of the dimethylamino derivative **5** and metallation of the *p*-nitrostyrylporphyrin **7** could lead to two new donor/acceptor molecules. Further study of these molecules and the stereochemical features of their formation is currently being undertaken.

The syntheses of porphyrin dimers[10] using this approach provided some fascinating results. Although the reaction of **4** with 2-formyltetraphenylporphyrin failed to provide the known dimer **8** presumably due to steric effects, the first 2-substituted free base porphyrinylbutadiene dimer **9** (62% after chromatography, 95% (*E,E*)) was readily obtained from 2-tetraphenylporphyrinylacrolein[15]. As a result of the poor solubility of **9**, the pure (*E,E*)-isomer could not be isolated and attempts to isomerise the mixture failed. The 500 MHz ^1H nmr spectrum displayed AA'BB' olefinic multiplets (δ 6.22 and 6.81) typical of an



9 M=2H
11 M=Ni



10 M=2H
12 M=Zn

(*E,E*)-1,4-disubstitutedbutadiene and the simple, uncluttered appearance of the aromatic resonances indicated there was some symmetry in the molecule. There was no evidence[2] of porphyrin chromophore interaction in the electronic absorption spectrum suggesting an out-of-plane butadiene moiety.

In order to test the viability of using this procedure for the synthesis of mono-metallated and bis-heterometallated porphyrin dimers, the reaction of the phosphonium chloride **4** with nickel porphyrinylacrolein[15] was investigated. The nickel porphyrin dimer was indeed formed (80% after chromatography) but surprisingly, it was found to be the pure (*E,Z*)-isomer **10**, clearly identified from its 500 MHz ^{1}H and COSY nmr spectra (δ 5.88, apparent t, $^3J_{\text{cis}}$ = 11.2 Hz, ^3J = 11.4 Hz; δ 6.15, d, $^3J_{\text{cis}}$ = 11.2 Hz; δ 6.26, d, $^3J_{\text{trans}}$ = 15.5 Hz; δ 7.61, dd, $^3J_{\text{trans}}$ = 15.4 Hz, ^3J = 11.2 Hz). This is only the second example of a *cis*-dimer[7]. A second porphyrin product was isolated which was identified as the (*E,E*)-isomer **11** (6%, δ 6.11 and 6.18, 2xd, $^3J_{\text{trans}}$=14.3 Hz; δ 6.61 and 6.71, 2xdd, $^3J_{\text{trans}}$ = 14 Hz, ^3J = 11 Hz). These characterisations were confirmed by conversion of the (*E,Z*)-isomer **10** into the (*E,E*)-isomer **11** by iodine-catalysed isomerisation, albeit in poor yield, and demetallation of **11** gave as the major product, the free base (*E,E*)-isomer **9**, identified in the ^{1}H nmr spectrum of the reaction mixture.

This remarkable inversion of stereochemical preference in the formation of **10** must result from some interaction strong enough to overcome the significant steric control apparently dominant in such reactions. The most appropriate candidate for this would appear to be a porphyrin-porphyrin interaction. Hunter and Sanders[16] have predicted the optimum geometry for free base and metallated porphyrin-porphyrin interactions. Molecular modelling[14] showed that a *cis*-double bond could have formed if the porphyrin rings of the phosphonium salt and nickel aldehyde had interacted with this geometry during the Wittig reaction. Since this preference for *cis*-geometry was not observed in the formation of **9**, the presence of the nickel atom must have been the controlling factor. Further work is underway to attempt to shed some light on this phenomenon. However, to the best of our knowledge, this is the first example of a metal porphyrin-porphyrin interaction controlling the stereochemical outcome of a reaction.

Conversion of the nickel dimer **10** into the mixed-metal nickel-zinc dimer **12** proceeded quantitatively. Not surprisingly, the ^{1}H nmr spectrum of **12** was very similar to that of the nickel dimer **10** although its visible spectrum (λ_{max} 420, 554, 599 nm) was simpler than that of **10** (λ_{max} 418, 523, 597, 649sh nm), reflecting the metallation of the second porphyrin ring. None of these spectra provided any evidence for intramolecular electronic interaction as observed by Ponomarev *et al.*[7] for a *cis*-vinyl dimer. The ease of formation of **12** highlights the potential of this methodology for the synthesis of a variety of mixed-metal dimers.

In summary, we believe that this approach to porphyrin dimers and other conjugatively-substituted porphyrins will provide rapid access to a number of new areas of porphyrin chemistry. We have already exploited this methodology for the synthesis of potential porphyrin-derived molecular electronic devices[17]. We are currently exploring using this methodology for the synthesis of mixed-porphyrin porphyrin dimers, extended chain dimers and porphyrin arrays which have the potential to act as light harvesting devices.

Acknowledgements: We thank the New Zealand Universities Grants Committee for a Post-doctoral Fellowship (E.E.B.), Dr Max Crossley (University of Sydney) for a generous gift of 2-formyltetraphenylporphyrin and discussions on some aspects of this work,. and Dr Herbert Wong (Industrial Research Ltd., Gracefield) for 500 MHz nmr spectra.

References and Notes

1. Graça, M.; Vicente, H.; Smith, K. M. *J. Org. Chem.*, **1991**, *56*, 4407.
2. Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron*, **1992**, *48*, 8781.
3. Osuka, A.; Ikawa, Y.; Maruyama, K. *Bull. Chem. Soc. Jpn.*, **1992**, *65*, 3322.
4. Ono, N.; Tomita, H.; Maruyama, K. *J. C. S. Perkin Trans. I*, **1992**, 2453.
5. Pandey, R. K.; Forsyth, T. P.; Gerzevske, K. R.; Lin, J. J.; Smith, K. M. *Tetrahedron Lett.*, **1992**, *33*, 5315.
6. Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron Lett.*, **1993**, *34*, 693.
7. Ponomarev, G. V.; Borovkov, V. V.; Sugiura, K.; Sakata, Y.; Shul'ga, A. M. *Tetrahedron Lett.*, **1993**, *34*, 2153.
8. Wasielewski, M. R.; *Chem. Rev.*, **1992**, *92*, 435 and references cited therein.
9. Crossley, M. J.; Burn, P. L. *J. C. S. Chem. Commun.*, **1991**, 1569.
10. All compounds gave satisfactory ^{1}H nmr, uv-vis and high resolution ms data.
11. Crossley, M. J.; Harding, M. M.; Sternhell, S. J. *J. Am. Chem. Soc.*, **1986**, *108*, 3608.
12. Hanekamp, J. C.; Rookhuizen, R. B.; Bos, H. J. T.; Brandsma, L. *Tetrahedron*, **1992**, *48*, 5151.
13. Crossley, M. J. unpublished synthesis, personal communication.
14. Molecular modelling was carried out using Macromodel on a Silicon Graphics workstation.
15. The free base and nickel 2-porphyrinylacroleins were synthesised from the appropriate 2-formyltetraphenylporphyrin and will be reported in due course.
16. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.*, **1990**, *112*, 5525.
17. Bonfantini, E. E.; Officer, D. L. submitted for publication.

(Received in UK 20 August 1993; accepted 22 October 1993)