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Reaction of isoindole, benzaldehyde and zinc acetate at 400°C has been shown to be a useful synthesis of zinc meso-tetraphenyltetrabenzporphyrin. We have repeated this reaction using mesitaldehyde (2,4,6-trimethylbenzaldehyde) in place of benzaldehyde. Proton NMR analysis of the product indicates that only partial substitution of mesityl groups in the meso positions has occurred. This is contrasted with the reaction of pyrrole and mesitaldehyde in the presence of boron trifluoride etherate followed by treatment with chloranil to yield meso-tetramesitylporphyrin. Attempts to extend this synthesis to the tetrabenzporphyrins by using isoindole in place of pyrrole were unsuccessful. <i>Keywords</i>					
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PREFACE

The work described in this report was authorized under work unit number 1L161102AH5201019 entitled Energy Absorption and Dissipation Mechanisms in Organic Materials and covers the period from May 1987 to August 1987. The report describes the progress that was made on the synthesis and characterization of some facially hindered meso-substituted metallotetrabenzoporphyrins during this time period. The authors wish to express their gratitude to Ms. Gretchen Richard of the Science and Advanced Technology Directorate, U.S. Army Natick Research, Development and Engineering Center for NMR data, to Ms. Eileen Sullivan of Worcester Polytechnic Institute (W.P.I.) for NMR data and for much of the synthetic work on porphyrins and to Dr. Stephen Weininger of W.P.I. for valuable discussions.



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PROGRESS ON THE SYNTHESIS OF FACIALLY HINDERED METALLOBENZPORPHYRINS

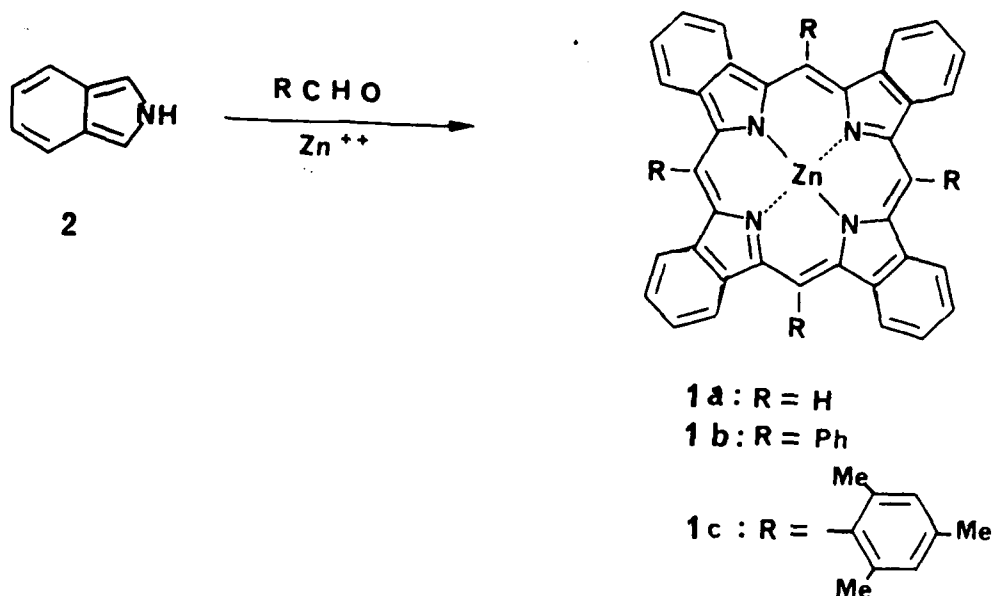
INTRODUCTION

The porphyrins and their metal complexes are of primary importance in biological systems. One area of great interest is the interaction of metalloporphyrin systems such as hemoglobin, myoglobin, chlorophyll and the cytochromes with oxygen. These biomolecules either reversibly bind oxygen to transport it¹ or complex oxygen in such a way that it is activated to react with organic molecules. An example of this latter process is the cytochrome P-450 catalyzed oxidations seen in metabolism.²

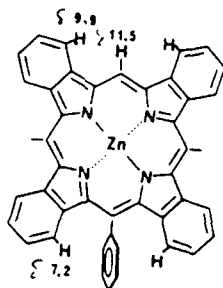
There has been much interest in preparing simple metalloporphyrins that can mimic the reactivity of the active site of these naturally occurring systems. J.P. Collman³ has prepared and characterized "picket fence porphyrins", facially hindered iron (II) porphyrins that reversibly bind O₂. Of great interest in these laboratories is the development of systems that could catalytically oxidize substances such as chemical warfare agents so as to inactivate them. Facially hindered metallobenzporphyrins should have properties that make them excellent candidates to be catalytic oxidizing agents under the appropriate conditions.

RESULTS AND DISCUSSION

Although several syntheses have been reported^{4,5} for the parent tetrabenzporphyrin (TBP), 1a (R=H), there are few reported routes to meso-substituted TBPs. In 1983 D. Remy reported⁶ that the reaction of isoindole, 2,⁷ benzaldehyde, and zinc acetate at 400°C produces a meso-substituted TBP, zinc 5,10,15,20-tetraphenyltetrabenzporphyrin, 1b, (R = C₆H₅).

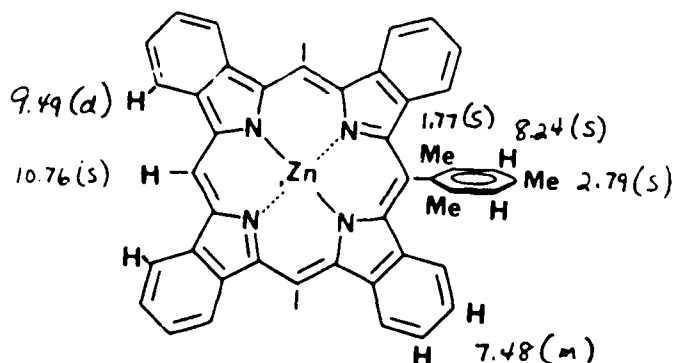


In 1985 we reported⁸ the preparation of a number of other zinc meso-tetraaryl TBPs from isoindole, zinc acetate, and the appropriate aromatic aldehyde. We observed that there were several TBP bands when these compounds were subjected to high performance liquid chromatography (HPLC) or thin layer chromatography (TLC). Several explanations for these multiple bands were considered and discussed: photodegradation of TBPs, aggregation of TBPs, apical ligand exchange, and lack of complete meso substitution. We wish to report that 1b undergoes thermal degradation on heating at 400°C for 24 hr in vacuo to give partial loss of phenyl groups from the meso-position. Evidence for this is seen in the ¹H-NMR of the material after it was heated. Several peaks appeared in the region 11.3–11.5 ppm, which were assigned to the meso hydrogens.⁶ In addition, there is a multiplet at 9.9 ppm, which is assigned to the protons nearest the meso hydrogens on the benzo rings (positions 1,4, 6,9,11,14,16, and 19). In the parent TBP 1a these protons appear at 9.80 ppm. In the meso-tetraphenyl TBP 1b they are shifted upfield to 7.22 ppm indicating that they are in the shielding region of the benzene ring, which is known to be orthogonal to the porphyrin ring.



To obviate the problems of lack of complete meso-substitution, we attempted to prepare the tetraphenyl TBP 1b by using benzophenone in place of benzaldehyde. If the problem is caused by competitive loss of phenyl or hydrogen from a tetrahedral intermediate (e.g. by radical cleavage), the use of benzophenone should give 1b cleanly. However, we were unable to isolate any 1b from the reaction. Interestingly, we were able to isolate the unsubstituted TBP 1a in very low yield. We cannot explain this result at this time.

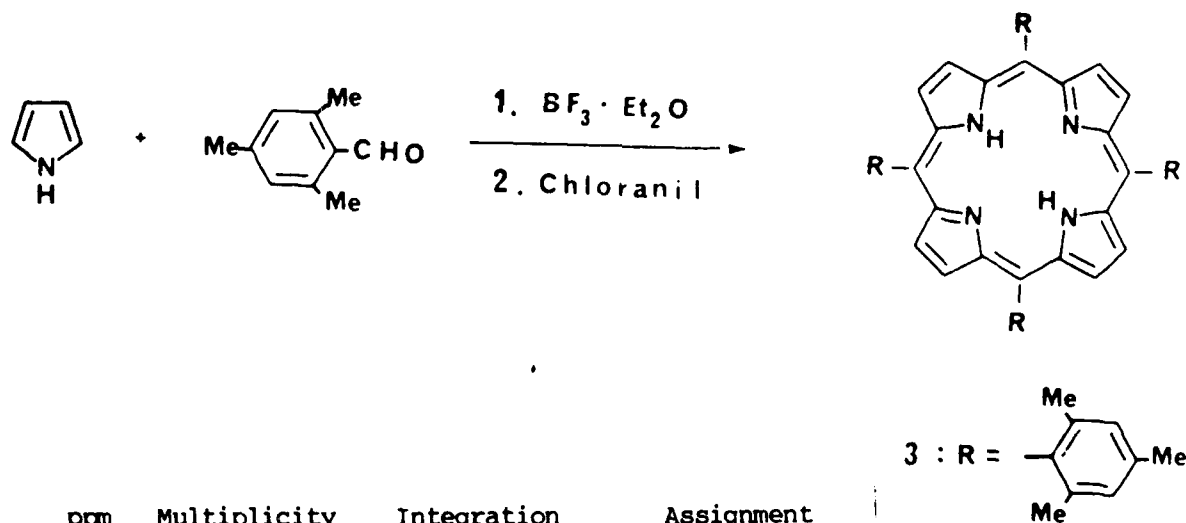
In an attempt to prepare the facially hindered porphyrin, zinc meso-tetramesityl TBP 1c, isoindole was allowed to react with zinc acetate and mesitaldehyde (2,4,6-trimethylbenzaldehyde) at 400°C. After flash chromatography of the crude reaction mixture on silica gel, a blue-green solid was isolated in about 2% yield. A proton NMR spectrum (CDCl₃) indicated that the product was partially mesitylated Zn TBP. Tentative NMR assignments are given below:



That the product is at least partially mesitylated in the meso-positions is seen by the chemical shift of the methyl groups. In mesitaldehyde the two methyls ortho to the aldehyde group absorb at 2.54 ppm, and the para methyl group at 2.28 ppm.

In the product the ortho methyls are shifted significantly upfield to 1.77 ppm, indicating that they are sitting above and below the plane of the porphyrin ring. The para methyl group, which should be in the same plane as the porphyrin ring, is shifted downfield somewhat to 2.79 ppm. That the product is not completely mesitylated in the meso positions is shown by the presence of meso hydrogens at 10.76 ppm and the corresponding benzo hydrogens at 9.49 ppm. Attempts were made to purify the product by preparative thin layer chromatography on diphenyl reverse phase silica gel plates, but the recovery was low and the NMR spectrum indicated that the material had degraded.

While this work was in progress, Wagner, Lawrence, and Lindsey⁹ reported that meso-tetramesitylporphyrin 3 can be prepared by the reaction of pyrrole and mesitaldehyde in the presence of BF_3 -etherate at room temperature, followed by addition of p-chloranil and refluxing in chloroform. We repeated their procedure and obtained a 28% crude yield of 3. This product was purified by recrystallization from chloroform/methanol to give an intensely purple solid (15% yield). The structure of 3 was confirmed by its proton NMR spectrum in $\text{CF}_3\text{CO}_2\text{D}$ (in the diprotonated form).



ppm	Multiplicity	Integration	Assignment
10.46	s	-	N-H
8.95	s	8H	meta-H
7.50	s	8H	pyrrole-H
2.69	s	12H	para-CH ₃
2.00	s	24H	ortho-CH ₃

We next attempted to adapt the procedure of Wagner et al. to the preparation of the tetrabenzoporphyrin lc. To a solution of isoindole (prepared in the usual manner⁸) in ether was added a solution containing benzaldehyde and BF₃-etherate. After addition of chloranil and refluxing, an insoluble black solid was obtained. This solid has not been identified, but it is not a porphyrin. It may be polyisoindole since isoindole is known to be unstable and to polymerize on warming.⁷ The addition of zinc acetate to the isoindole did not appear to change the course of the reaction.

CONCLUSIONS

The reaction of isoindole, zinc acetate, and benzaldehyde at high temperatures (400°C) is a useful preparative route to zinc meso-tetraphenyl-tetrabenzoporphyrin, lb. In an attempt to prepare the facially hindered metallobenzoporphyrin lc, we repeated the reaction using the bulky mesitaldehyde in place of benzaldehyde. We were able to demonstrate by NMR the formation of a metallobenzoporphyrin that was only partially mesitylated. One reason for the failure to achieve complete meso-substitution may be the thermal instability of the very hindered zinc meso-tetramesityl TBP, lc. We have shown that the even less sterically hindered zinc meso-tetraphenyl TBP, lb, on extended heating at 400°C, suffers partial loss of the meso-phenyls.

The novel room temperature synthesis of Wagner et al. affords meso-tetramesitylporphyrin in moderate yield. We were unable to extend this route to prepare the benzoporphyrin lc.

This document reports research undertaken at the US Army Natick Research, Development and Engineering Center and has been assigned No. NATICK/TR-88/062 in the series of reports approved for publication.

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