Indian Journal Chemistry
Vol. 36B, August 1997, pp. 637 - 638

Rapid Communication

Preparation of *meso*-tetra(4-benzenesulfonylphenyl) - porphyrin by the method of phase transfer catalysis[†]

Yu-Feng He, Rong-Min Wang*, Yun-Pu Wang,
ZI-Qiang Lei, & Li Zhang

Department of Chemistry, Northwest Normal University,
Lanzhou 730070, P.R.China

Received 2 July 1997; accepted 21 July 1997

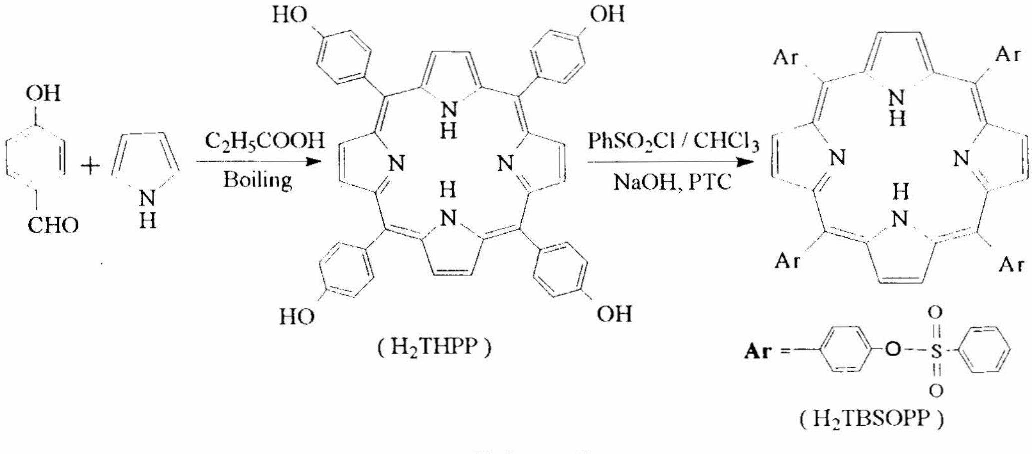
A new synthetic method for the preparation of *meso*-tetra(4-benzenesulfonyl)phenylporphyrin using phase transfer catalysis is reported. The product has been characterized on the basis of electronic, IR and ^{1}HNMR spectra.

The porphyrins lie at the focal points of different fields of research, including solar energy conversion, catalysis, spectroscopy, etc. , and the 5, 10, 15, 20-tetraphenylporphyrin derivatives have been widely used as models for the the preparation of naturally occurring porphyins[1,2] because of their easy preparation. The typical synthetic methods for tetraaryl have been improved and refined through many investigations[3,4] by improving the reaction conditions, such as solvent, catalyst, oxidation or substrate. In this communication, we report the title compound which has been synthesized using phase transfer catalysis.

The *meso*-tetra(4-benzenesulfonyl)phenylporphyrin (H_2TBSOPP) was synthesized as shown in Scheme I.

Pyrrole and propionic acid were freshly distilled before using. Chloroform was dried and distilled before use. All other reagents used were of accepted grades of purity. Contrary to the original method[5], *meso*-tetra(4-hydroxylphenyl)porphyrin (H_2THPP) was directly prepared[6] from pyrrole and *p*-hydroxylbenzaldehyde.

The H_2THPP (0.3 mmole) was dissolved in 10 mL of aqueous 5% NaOH (free from Na_2CO_3) by stirring, 15 mg of the phase transfer catalyst (hexadecyltrimethylammonium bromide) added to it, and then whole mixture stirred for 15 min. To the solution was added dropwise a solution (4mL) of benzenesulfonyl chloride (31 mmoles) in dry chloroform with vigorous stirring. The colour of the solution changed to red brown from deep green, and the mixture stirred for 10 min in order to complete the reaction. Water (20 mL) was added and the chloroform phase separated. The water phase was extracted with chloroform (3×10 mL). All the chloroform solutions were pooled and poured into Et_2O, (three times the volume of $CHCl_3$). The crude



Scheme I

[†] Work supported by the National Natural Science Foundation of China.

product which crystallized immediately was isolated by filtration, dried in air and purified by chromatography over neutral alumina column using chloroform as eluant. After drying under vacuum, the *meso*-tetra(4-benzenesulfonyl)phenylporphyrin (H_2TBSOPP) was obtained in 76% yield.

The H_2TBSOPP was characterized by electronic, vibration, and nuclear magnetic resonance spectra. The electronic spectrum was measured on a Hitachi U-3400 spectrophotometer using chloroform as solvent. The electronic spectrum exhibited Soret band at 418.9 (log ε =5.58), Qx(0-0) band at 646.1 (log ε=3.49), Qx(1-0) band at 590.1 (log ε=3.70), Qy(0-0) band in 550.1 (log ε=3.82), and Qy(1-0) band at 512.3 nm (log ε=4.38). It is a typical UV-Vis spectrum of porphyrins.

The vibration spectrum was recorded in KBr on an Alpha-centauri FT-IR spectrophotometer. It exhibited bands at 1372 due to S=O vibrations, a weak νNH at 3314, δNH at 966 and C=C and C=N stretching vibrations at 1596, 1583, 1561, 1497 and 1475 cm^{-1}.

The ^{1}H NMR spectrum was recorded on a Bruker AM-400 instrument. It showed signals at δ 2.92 (pyrrol NH), 8.74(pyrrol CH) and 7.25-8.50 (phenyl CH).

References

1 Dolphin D, *The porphyrins*, Vol. 1-7 (Academic Press, New York) **1978**.

2 Montanari F & Casella L, *Metalloporphyrins catalyzed oxidations* (Kluwer Academic Publishers, Dordrecht) **1994**.

3 Lindzey T S, Schreiman I C, Hzu H C, Kearney P C, & Marguerettaz A M, *J Org Chem* , 52,**1989**, 827.

4 Kuroda Y, Murase H, Suzuki Y, Ogoshi H, *Tetrahedron Lett*,30, **1989**, 2411.

5 Little R G, Anton J A, Loach P A & Ibers J A, *J Heterocyclic Chem*, 12, **1975**, 343.

6 WANG Rong-Min, WANG Yun-Pu, *J Northwest Nor. University (Natural Science)*, 30, **1994**, 98.