

## Synthesis of 2,7,12,17-Tetra-arylporphyrins, New Sterically Hindered Porphyrins

Noboru Ono,\* Hisayuki Kawamura, Masahiro Bougauchi, and Kazuhiro Maruyama\*

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

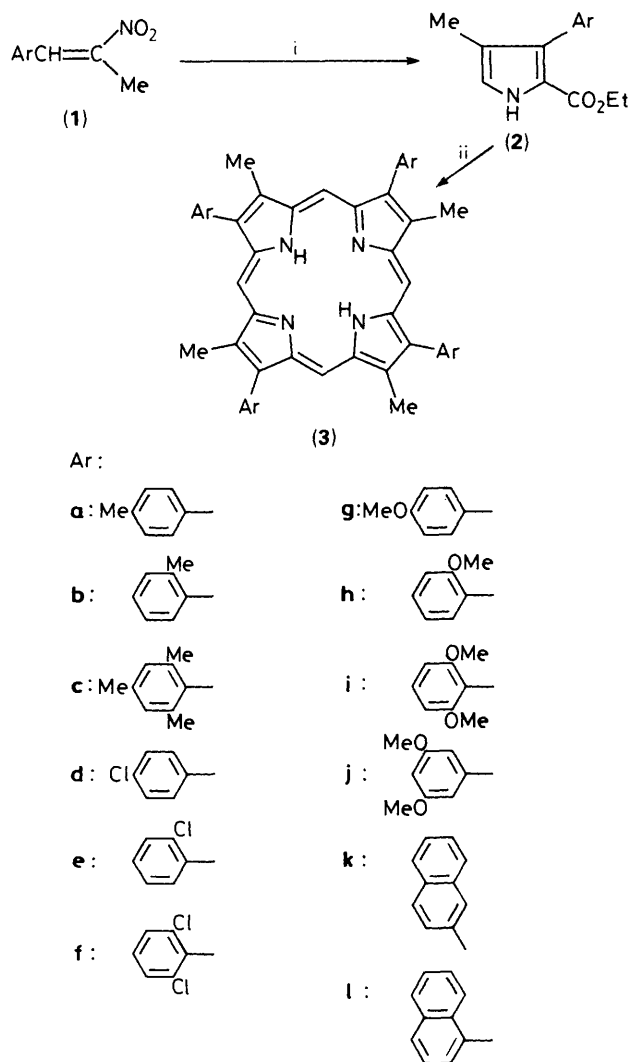
Sterically hindered porphyrins with four bulky aryl groups in the  $\beta$ -positions are prepared by the reduction of ethyl 3-aryl-4-alkylpyrrole-2-carboxylate with  $\text{LiAlH}_4$  followed by treatment with an acid and an oxidizing agent.

Recently sterically hindered tetra-aryl porphyrins have become the principal species used not only to model bimimetic transformations but also to investigate catalytic oxygen transfer and solar energy conversion by synthetic metalloporphyrins.<sup>1</sup> Steric blocking in the porphyrin ring inhibits dimerization and various bimolecular decomposition reactions. Thus, hindered porphyrins are more stable to intramolecular oxidative decomposition than unhindered porphyrins. Unfortunately, hindered porphyrins are generally obtained in low yields,<sup>2</sup> and furthermore most known hindered porphyrins have the bulky aryl groups in the *meso* positions, which causes deviations from planarity of the

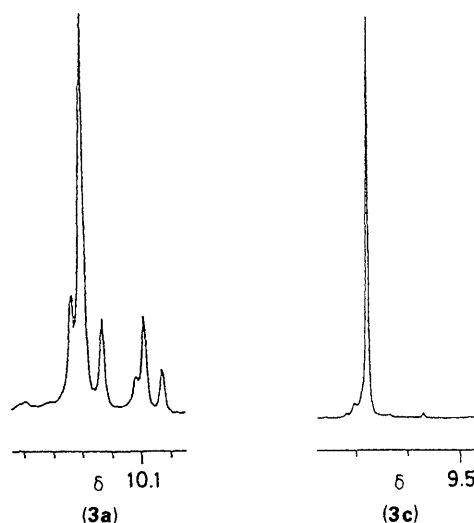
porphyrin ring. Such porphyrins behave in an unusual manner compared with naturally occurring porphyrins and the usual model compounds with  $\beta$ -substituents.<sup>3</sup>

In this paper we report the synthesis of a new type of sterically hindered porphyrins with  $\beta$ -aryl substituents which may be expected to be more suitable models than *meso*-tetra-arylporphyrins. Twelve new porphyrins (**3a**–**3l**) were prepared by the procedure in Scheme 1.<sup>†</sup>

The nitroalkenes (**1**) were prepared in 60–80% yield by refluxing a mixture of the aldehyde, nitroethane, methylamine hydrochloride, potassium acetate, and methyl orthoformate in MeOH.<sup>4</sup> Such hindered aldehydes as mesitaldehyde and 2,6-dichlorobenzaldehyde gave (**1**) in good yield by this procedure. The reaction of (**1**) with ethyl isocyanoacetate gave (**2**) in 70–80% yield.<sup>5</sup> Here again steric hindrance has no effect on the transformation. The reduction of (**2**) with  $\text{LiAlH}_4$  followed by tetramerization with *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$  and oxidation with chloranil gave the porphyrins (**3**) in 50–70% yield.<sup>6</sup> In general, tetramerization of monopyrroles with an acid induces the rearrangement of substituents to give four possible isomers of porphyrins.<sup>3</sup> However, we have found that this type of rearrangement is not serious if the aryl groups are sterically hindered. Namely, type I porphyrins were selectively formed in the preparation of (**3b**), (**3c**), (**3e**), (**3f**), and (**3j**), and a



**Scheme 1.** Reagents and conditions: i,  $\text{CNCH}_2\text{CO}_2\text{Et}$ , 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in tetrahydrofuran (THF) at 25°C, for 24 h; ii,  $\text{LiAlH}_4$  in THF at 5°C for 2 h; *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$  in  $\text{CH}_2\text{Cl}_2$  at 25°C for 24 h; chloranil in  $\text{CH}_2\text{Cl}_2$  at 25°C for 5 h.



**Figure 1.** *meso*-H resonances for (**3a**) and (**3c**).

<sup>†</sup> Preparation of (**3f**) as a typical procedure. To a stirred mixture of  $\text{LiAlH}_4$  (5.2 mmol) in tetrahydrofuran (THF) (30 ml) was added (**2f**) (3.4 mmol) in THF (5 ml) at 5°C. The mixture was stirred for 2 h at 5°C under  $\text{N}_2$  then poured into saturated  $\text{NH}_4\text{Cl}$ , and extracted with  $\text{CH}_2\text{Cl}_2$  (100 ml  $\times$  3). The extracts were combined and dried ( $\text{MgSO}_4$ ). To the dried  $\text{CH}_2\text{Cl}_2$  solution was added *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$  (0.02 g); the resulting solution was stirred for 12 h at 25°C and then chloranil (0.4 g) was added. The mixture was stirred for 8 h and washed with 5%  $\text{NaHCO}_3$ , and the organic layer dried ( $\text{MgSO}_4$ ). After evaporation, flash chromatography of the residue (silica gel/ $\text{CHCl}_3$ ) gave (**3f**) (0.57 g, 70% yield);  $m/z$  (f.a.b.) 947 ( $M^+ + 1$ ).

**Table 1.** Spectral data for the hindered porphyrins (**3**).<sup>a</sup>

	N.m.r., $\delta$			$\lambda_{\max}/\text{nm}$ ( $\text{CH}_2\text{Cl}_2$ )
	NH	$\text{CH}_3$	<i>meso</i> -H	
( <b>3a</b> )	-3.45	3.60	10.15	418, 506, 540, 572, 626
( <b>3b</b> ) <sup>b</sup>	-3.34	3.47	9.80	410, 501, 536, 568, 622
( <b>3c</b> )	-3.38	3.24	9.60	403, 499, 531, 565, 620
( <b>3d</b> )	-3.46	3.60	10.08	418, 506, 540, 572, 626
( <b>3e</b> ) <sup>b</sup>	-3.38	3.41	9.85	406, 500, 535, 568, 621
( <b>3f</b> )	-3.35	3.37	9.71	404, 500, 533, 566, 621
( <b>3g</b> )	-3.35	3.70	10.15	416, 507, 542, 573, 626
( <b>3h</b> ) <sup>b</sup>	-3.34	3.40	9.97	409, 505, 540, 573, 624
( <b>3i</b> )	-3.25	3.30	9.77	407, 504, 539, 572, 624
( <b>3j</b> )	-3.44	3.62	10.22	417, 505, 540, 573, 626
( <b>3k</b> ) <sup>b</sup>	-3.27	3.50	10.23	411, 507, 542, 573, 627
( <b>3l</b> ) <sup>b</sup>	-3.22	3.20	9.55	409, 504, 538, 571, 624

<sup>a</sup> N.m.r. spectra were recorded in  $\text{CDCl}_3$  ( $5 \times 10^{-3} \text{ M}$ ) at 400 MHz at ambient temperature with  $\text{Me}_4\text{Si}$  internal reference. <sup>b</sup> A mixture of stereoisomers was formed, but they could not be separated.

mixture of four isomers was produced in other cases. As a typical example, the partial n.m.r. spectra of the products in the preparation of (**3a**) and (**3c**) are shown in Figure 1, where the *meso* protons appear as a sharp singlet in the case of (**3c**). Thus, sterically hindered porphyrins with four  $\beta$ -aryl groups are readily prepared in a selective way.

Spectral data for the porphyrins (**3**) are summarized in Table 1. The NH chemical shifts are not much affected by the aryl groups, but  $\beta$ - $\text{CH}_3$  and *meso*-H resonances are shifted to

higher field as the aryl groups become large. The u.v.-visible absorption maxima are also blue shifted with more bulky aryl groups. The absorption maxima of (**3c**) are very close to those of octaethylporphyrin. These data show that the out-of-plane rotation angles of the aryl groups in (**3**) change with the increasing steric bulk and approach  $90^\circ$  in porphyrin (**3c**). However, the planarity of the porphyrin ring is maintained in these hindered porphyrins, because the NH resonances all appear in the range  $\delta -3.3$  to  $-3.5$ .

Received, 15th June 1989; Com. 9/02525A

## References

- 1 Some of the many references concerning sterically hindered porphyrins are as follows: J. P. Collman, *Acc. Chem. Res.*, 1977, **10**, 265; M. Momenteau, *Pure Appl. Chem.*, 1986, **58**, 1493; B. Meunier, *Bull. Soc. Chim. Fr.*, 1986, 758; K. S. Suslick and T. J. Reinert, and K. S. Suslick, *J. Am. Chem. Soc.*, 1986, **108**, 7281; J. Davila, A. Harriman, M. C. Richoux, and L. R. Milgrom, *J. Chem. Soc., Chem. Commun.*, 1987, 525; S. Banfi, F. Montanari, and S. Quici, *J. Org. Chem.*, 1988, **53**, 2863; 1989, **54**, 1850; H. Volz and T. Barth, *Leibigs Ann. Chem.*, 1989, 171; R. Belal, M. Momenteau, and B. Meunier, *J. Chem. Soc., Chem. Commun.*, 1989, 412.
- 2 T. J. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 6243; O. Bortolini, M. Ricci, B. Meunier, P. Friant, L. Ascone, and J. Goulon, *Nouv. J. Chim.*, 1986, **10**, 39; J. S. Lindsey and R. W. Wagner, *J. Org. Chem.*, 1989, **54**, 828, and references cited therein.
- 3 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975.
- 4 E. McDonald and R. T. Martin, *Tetrahedron Lett.*, 1977, 1317.
- 5 D. H. R. Barton and S. Z. Zard, *J. Chem. Soc., Chem. Commun.*, 1985, 1098.