SYNTHESIS OF TETRAPHENYLPORPHINES WITH ACTIVE GROUPS IN THE PHENYL RINGS

6.* SYNTHESIS OF MONOSUBSTITUTED TETRAPHENYLPORPHINES BY DIAZOTIZATION

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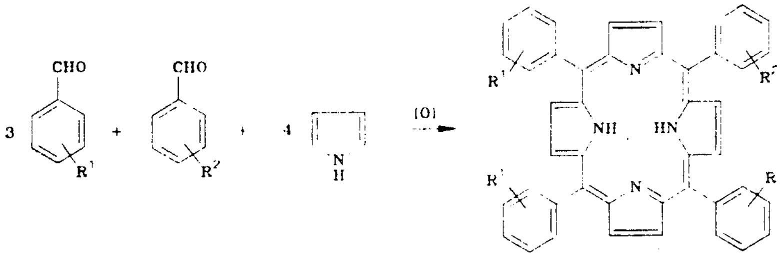
Monoaminophenyltriphenylporphines are diazotized and then used to produce monohalosubstituted tetraphenylporphines. Isomeric mono(p-hydroxyphenylazo)phenyltriphenylporphines are synthesized by replacing the azo group of diazonium salts of monosubstituted porphines with phenol.

Porphyrins and metalloporphyrins are used as catalysts [2], models of natural biologically active systems [3], medicinal preparations [4], etc. Tetraphenylporphines substituted on the phenyl rings are especially interesting. They are readily available and are formed in high yield by condensation of pyrrole and benzaldehyde [5]. However, the symmetric substitution system of many tetraphenylporphines prohibits their application to many practical problems.



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The purpose of the present work was to develop simple methods for synthesis of unsymmetrically substituted tetraphenylporphins I. These porphines can be prepared by condensation of pyrrole with a mixture of benzaldehydes [6]. The mixture of mono-, di-, tri-, and tetraphenylporphines formed can only be separated with strongly polar substituents. Porphyrins containing slightly polar substituents have similar chromatographic mobilities. Therefore, it is difficult or impossible to prepare and separate them by this method. These difficulties can be overcome by changing the functional groups of the tetraphenylporphines.

We diazotized monoaminophenyltriphenylporphines IIa-c and converted the products into the monohalo- and mono-p-hydroxyphenylazosubstituted tetraphenylporphines (see scheme on following page).

The starting monoaminophenyltriphenylporphines were synthesized by reduction of the mononitrophenyltriphenylporphines analogously to [7]. The latter were obtained by the methods of [8].

Using sodium nitrite as the diazotizing agent in aqueous acid solutions analogously to [9] did not give positive results since monoaminoporphines are insoluble in these media. It was found that monoaminophenyltriphenylporphines are readily diazotized by isoamylnitrite in a mixture of $CHCl_3$–CH_3COOH, 1:2.5. The solutions of diazonium salts III obtained are rather stable. They decompose noticeably with evolution of N_2 only above 25°C. Like tetraaminophenylporphines [9], diazotized 2-aminophenyltriphenylporphine is unstable and is oxidized on heating to nonporphyrin compounds. Therefore, por-

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*See [1] for Communication-5.

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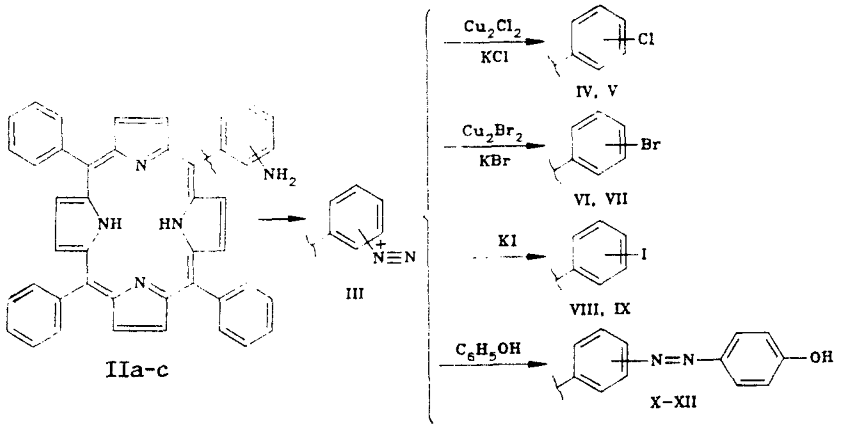

II-XIII: a) NH_2 in the 4-position; b) NH_2 in the 3-position; c) NH_2 in the 2-position.

phyrins are prepared from 2-aminophenyltriphenylporphine in low yield and with a large amount of difficulty separated impurities. Salts of 3- and 4-substituted mono(diazophenyl)triphenylporphines readily undergo the Sandmeyer reaction, forming monohalosubstituted tetraphenylporphines IV-IX, which are difficult to prepare by other routes.

Regarding the possibility of preparing compounds with two chromophores (porphyrin and azodye), the linking of the azo group of diazonium salts of monosubstituted porphyrins with phenol is interesting. The reaction is carried out in an organic solvent, in contrast to [8]. Triethylamine was used as base to adjust the basicity to the required value (pH 8-9).

The electronic absorption spectra of the monohalosubstituted porphyrins IV-IX are very similar (Table 1). The small bathochromic shift of the absorption bands of para-substituted porphyrins IV, VI, and VIII is probably due to partial conjugation of the substituents with the π–π system of the porphyrin macrocycle.

Comparison of the absorption spectra of compounds X-XII (in $CHCl_3$) shows that a bathochromic shift and a broadening of the bands is characteristic for the 2- and 4-isomers. These changes do not occur for the 3-isomer. This is probably due to conjugation of the π–π systems of the azodye and macrocycle.

We did not record the PMR spectra since the signals for protons of the substituted phenyl rings are completely overlapped by those of the unsubstituted rings.

TABLE 1. Yield and Certain Properties of Monosubstituted Tetraphenylporphines IV-IX

Porphyrin	Empirical formula	R_f	Yield, %	Electronic, absorption spectra, λ, nm (log ε)				
				I	II	III	IV	Cope
IV	$C_{44}H_{29}ClN_4$	0,93	36	645 (3,65)	590 (3,81)	550 (3,94)	515 (4,31)	419 (5,68)
V	$C_{44}H_{29}ClN_4$	0,90	87	645 (3,82)	589 (3,95)	550 (4,06)	515 (4,40)	418 (5,80)
VI	$C_{44}H_{29}BrN_4$	0,91	82	648 (3,63)	590 (3,77)	551 (3,91)	516 (4,26)	419 (5,64)
VII	$C_{44}H_{29}BrN_4$	0,87	90	647 (3,67)	590 (3,80)	549 (3,97)	515 (4,30)	419 (5,67)
VIII	$C_{44}H_{29}IN_4$	0,88	60	647 (3,80)	592 (3,86)	551 (3,91)	516 (4,26)	419 (5,64)
IX	$C_{44}H_{29}IN_4$	0,90	85	647 (3,86)	590 (3,82)	550 (3,90)	515 (4,30)	420 (5,67)
X	$C_{50}H_{34}N_6O$	0,13	38	647 (3,85)	592 (3,92)	552 (4,14)	517 (4,38)	421 (5,65)
XI	$C_{50}H_{34}N_6O$	0,15	57	647 (3,77)	590 (3,87)	550 (3,99)	515 (4,35)	419 (5,68)
XII	$C_{50}H_{34}N_6O$	0,11	31	648 (3,65)	592 (3,65)	554 (3,82)	518 (3,93)	422 (5,52)

EXPERIMENTAL

Electronic absorption spectra were recorded on a Specord M 40 spectrophotometer. The identity and purity of the compounds was established by TLC on Silufol using benzene.

The elemental analyses for C, H, and N for compounds IV-XII agree with those calculated.

4-Chlorophenyltriphenylporphine (IV). To a solution cooled to 5°C of 100 mg (0.16 mmole) monoaminophenyltriphenylporphine in 35 ml $CHCl_3$–CH_3COOH (1:2.5) were added dropwise with stirring 20 mg (19 mmoles) isoamylnitrite in 3 ml $CHCl_3$. To the solution of diazonium salt obtained was added at once a solution of 0.5 g (2.53 mmoles) Cu_2Cl_2 in 5 ml HCl (d = 1.36 g/ml). The mixture was heated on a water bath until N_2 evolution ceased. It was diluted with 50 ml water. Porphyrin IV was extracted with 30 ml $CHCl_3$. The $CHCl_3$ extract was washed with 5% Na_2CO_3 solution and then water. It was chromatographed on a L 100/250 silica gel column (2 × 60 cm) using $CHCl_3$ as eluent. The effluent was evaporated to 5 ml. Porphyrin IV was precipitated by adding 30 ml CH_3OH. Yield or porphyrin IV, 30 mg.

3-Chlorophenyltriphenylporphine (V). This was prepared similarly to (IV). Yield 90 mg.

4-Bromophenyltriphenylporphine (VI) and 3-Bromophenyltriphenylporphine (VII). These were prepared analogously using a solution of 2 g (6.70 mmoles) Cu_2Br_2 and 0.5 g (4.20 mmoles) KBr in 10 ml HBr (48%) to decompose the diazonium salts instead of Cu_2Cl_2 solution. Yield of VI, 90 mg; VII, 100 mg.

4-Iodophenyltriphenylporphine (VIII) and 3-Iodophenyltriphenylporphine (IX). These were prepared analogously to VI and VII using a solution of 0.5 g (3.01 mmoles) KI. Yield of VIII, 70 mg; IX, 100 mg.

4-(p-Hydroxyphenylazo)phenyltriphenylporphine (X-XII). To a solution cooled to 5°C of 100 mg (0.16 mmole) monoaminophenyltriphenylporphine in 25 ml $CHCl_3$ and 1 ml CH_3COOH were added dropwise with stirring 20 mg (19 mmoles) isoamylnitrite in 3 ml $CHCl_3$. To the diazonium salt solution obtained was added dropwise a mixture of 0.1 g (1.06 mmoles) phenol and 3 ml triethylamine in 15 ml $CHCl_3$. The mixture was stirred for 1 h, neutralized with HCl (d = 1.18) to pH 7, and chromatographed on a L 100/250 silica gel column (2 × 60 cm) using $CHCl_3$ eluent. The effluent was evaporated to 5 ml. Porphyrin X was precipitated by 30 ml hexane. Yield of X, 40 mg.

3-(p-Hydroxyphenylazo)phenyltriphenylporphine and 2-(p-Hydroxyphenylazo)phenyltriphenylporphine (XII). These were prepared analogously. Yield of the former, 60 mg; of the latter, 16 mg.

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