SYNTHESIS OF TETRAPHENYLPORPHINS WITH ACTIVE GROUPS IN THE PHENYL RINGS.

2.* PREPARATION OF TETRAKIS(HYDROXYPHENYL)PORPHINS

A. S. Semeikin, O. I. Koifman,
B. D. Berezin, and S. A. Syrbu

UDC 547.979.733.0.7:543.422.6

The corresponding tetrakis(hydroxyphenyl)porphins were obtained by demethylation of tetrakis(methoxyphenyl)porphins with aniline hydrochloride or 60% HBr.

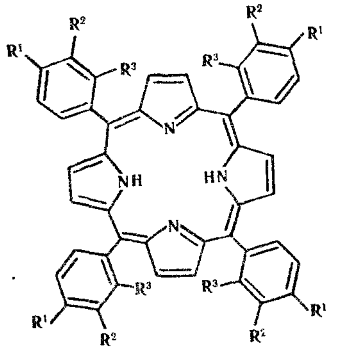
In a continuation of our research [1] on the synthesis of tetraphenylporphins that contain active groups in the phenyl rings by changing the substituents that are already present, in the present paper we describe the synthesis of tetrakis(hydroxyphenyl)porphins, which was realized by demethylation of the corresponding tetrakis(methoxyphenyl)porphins. There are several methods for the synthesis of tetrakis(hydroxyphenyl)porphins: tetrakis-(3-hydroxyphenyl)porphin from m-hydroxybenzaldehyde and pyrrole [2], tetrakis(4-hydroxyphenyl)porphin from tetrakis(4-acetoxyphenyl)porphin by hydrolysis with alcoholic alkali [tetrakis(4-acetoxyphenyl)porphin was obtained from pyrrole and the corresponding aldehyde] [3], and tetrakis(2-hydroxyphenyl)porphin by hydrolysis of tetrakis(2-methoxyphenyl)porphin with HBr [4] or pyridinium hydrochloride [5]. However, the conditions and yields were not presented in the last two cases, and it is therefore difficult to form a judgment regarding their effectiveness. The preparation of tetrakis(2,5-dihydroxyphenyl)porphin by hydrolysis of tetrakis(2,5-dimethoxyphenyl)porphin in the presence of boron tribromide is mentioned in [6], also without indications of the conditions and yields.

Tetrakis(methoxyphenyl)porphins are obtained in high yields by condensation of pyrrole with the corresponding aldehydes (Table 1), whereas tetrakis(hydroxyphenyl)porphins are formed in low yields, and the products in this case contain large amounts of impurities that are difficult to remove. A porphyrin is not formed at all when salicylaldehyde is used. The demethylation of tetrakis(methoxyphenyl)porphins with 48% hydrobromic acid is less effective. The use of anhydrous $AlCl_3$ in refluxing chlorobenzene as the demethylating agent [7] also did not give satisfactory results. Because of partial decomposition, the yields of tetrakis(hydroxyphenyl)porphins do not exceed 30%. Acceptable results are obtained when aniline hydrochloride or pyridinium hydrochloride is used. However, this method is less applicable for the synthesis of tetrakis(2-hydroxyphenyl)porphin (Table 2). The reaction with 60% hydrobromic acid is more suitable in this case.

---

*See [1] for communication 1.

TABLE 1. Yields of Tetrakis(methoxyphenyl)porphins



R¹	R²	R³	Yield, %
OCH_3	H	H	38
H	OCH_3	H	20
H	H	OCH_3	16
OCH_3	OCH_3	H	30
H	OCH_3	OCH_3	14

Ivanovo Institute of Chemical Technology, Ivanovo 153460. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1359-1361, October, 1983. Original article submitted January 4, 1983; revision submitted April 11, 1983.

0009-3122/83/1910-1082$07.50

TABLE 2. Yields, Results of Elementary Analysis, and Some Properties of Tetrakis(hydroxyphenyl)porphins

Substituents			UV spectra in pyridine, λ_{max}, nm (log ε)					Found, %; calc., %			R_f[a]	Yield, %		
R^1	R^2	R^3	I	II	III	IV	soret	C	H	N		A	B	C
OH	H	H	656 (3,81)	598 (3,67)	561 (4,11)	521 (4,16)	426 (5,64)	78,0; 77,9	4,1; 4,4	8,5; 8,3	0,33 (E)	92	78	72
H	OH	H	649 (3,57)	593 (3,72)	552 (3,87)	517 (4,26)	423 (5,65)	77,5; 77,9	4,4; 4,4	8,0; 8,3	0,21 (E—B, 2 : 1)	84[b]	85	42
H	H	OH	651 (3,36)	594 (3,53)	550 (3,63)	516 (4,04)	423 (5,39)	77,5; 77,9	4,0; 4,4	8,6; 8,3	0,09; 0,42; 0,61; 0,69 (E—B, 2 : 1)[c]	35[b]	73	—
OH	OH	H	657 (3,92)	595 (3,99)	564 (4,23)	523 (4,31)	431 (5,42)	71,5; 71,2	4,5; 4,1	7,2; 7,5	0,56 (A – C 2 : 1)	75	82	—
H	OH	OH	654 (3,91)	593 (3,99)	553 (4,09)	518 (4,42)	426 (5,60)	71,8; 71,2	4,0; 4,1	7,3; 7,5	0,42; 0,53; 0,59 (A—B, 1 : 1)[c]	—	53	—

---

[a] Eluents: E is ether, B is benzene, A is acetone, and C is chloroform. [b] The reaction time was decreased to 15 min. [c] Separation to give atropo isomers occurs.

Tetrakis(4-hydroxyphenyl)- and tetrakis(3-hydroxyphenyl)porphins can also be obtained in 72% and 42% yields, respectively, by hydrolysis of diazotized tetrakis(aminophenyl)-porphins.

EXPERIMENTAL

The electronic spectra were recorded with a Specord UV-vis spectrophotometer. The individuality of the compounds was established by thin-layer chromatography (TLC) on Silufol.

A) Demethylation with Aniline Hydrochloride. A 1-g sample of tetrakis(methoxyphenyl) porphin was added with stirring to 20 g of refluxing aniline hydrochloride, and the mixture was stirred for 30 min. It was then cooled and dissolved in hot water, and the precipitated porphyrin was removed by filtration, washed with water, and dissolved in 5% NaOH. The solution was filtered, and the tetrakis(hydroxyphenyl)porphin was precipitated with concentrated HCl with subsequent neutralization of the excess acid with ammonia. The precipitate was removed by filtration, washed with water, and dried. For purification, the porphyrin obtained was dissolved in ether and chromatographed on silica gel.

B) Demethylation with 60% Hydrobromic Acid. A 1-g sample of tetrakis(methoxyphenyl)-porphin was refluxed in 50 ml of 60% HBr for 2 h, after which the mixture was cooled and filtered. The precipitate was dissolved in 5% NaOH, the solution was filtered, and the tetrakis(hydroxyphenyl)porphin was precipitated by means of concentrated HCl with subsequent neutralization with ammonia. The precipitate was removed by filtration, washed with water, and dried.

C) Hydrolysis of Diazotized Tetrakis(aminophenyl)porphins. A 1-g (0.148 mmole) sample of tetrakis(aminophenyl)porphin was dissolved in 50 ml of 5% HCl, and a solution of 0.04 g (0.59 mmole) of $NaNO_2$ in 1 ml of water was added with stirring at 5°C. The resulting solution of the diazonium salt was heated on a water bath until nitrogen evolution ceased, and the precipitated tetrakis(hydroxyphenyl)porphin was removed by filtration. It was then reprecipitated from solution in NaOH, and the precipitate was removed by filtration and dried.

LITERATURE CITED

1. A. S. Semeikin, O. I. Koifman, and B. D. Berezin, Khim. Geterotsikl. Soedin., No. 10, 1354 (1982).
2. A. Treibs and N. Haberle, Ann. Chem., 718, 183 (1968).
3. R. G. Little, J. A. Anton, P. A. Loach, and J. A. Ibers, J. Heterocycl. Chem., 12, 343 (1975).
4. L. K. Gottwald and E. F. Ullman, Tetrahedron Lett., No. 36, 3071 (1969).
5. M. Momenteau and B. Loock, J. Mol. Catal., 7, 315 (1980).
6. J. Dalton and L. Milgram, Chem. Commun., No. 14, 609 (1979).
7. Weygand-Hilgetag, Experimental Methods in Organic Chemistry [Russian translation], Khimiya, Moscow (1968), p. 361.