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IDENTIFICATION OF RANDOMERS OF TETRA(tert-BUTYL)PORPHYRAZINE

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UDC 547.979.733:541.621:543.422.25'51

Randomers of tetra(tert-butyl)porphyrazine, the assignment of which was made on the basis of data from mass spectrometry and high-resolution PMR spectroscopy, were isolated by high-performance liquid column chromatography.

One of the important problems of the structural chemistry of macroheterocyclic compounds, particularly porphyrins and their aza and areno analogs, is the identification of the isomers with respect to the location of the substituents in the macroring (randomers) [1, 2]. This is associated with the fact that the common methods for the synthesis of such compounds, which are based on the template tetramerization of unsymmetrical porphyrinogens, lead to a mixture of randomers, the number of which is close to the number of possible connections of the fragments. The separation of the randomers is facilitated in the case of polar substituents. Thus they can be separated by paper or adsorption chromatography etc. and identified by spectral methods.

The identification of structures with alkyl or phenyl substituents is difficult and requires specific approaches.

We have investigated the possibility of the separation and identification of randomers of tetra(tert-butyl)porphyrazine obtained by tetramerization of tert-butylmaleonitrile in the presence of magnesium ethoxide with subsequent treatment of the intermediate complex of tetra(tert-butyl)porphyrazine with magnesium with boiling acetic acid [3]. Theoretically, one might expect the formation of four randomers, which, in conformity with the nomenclature of porphyrins [4, p. 101], can be assigned to the I-IV types (see scheme on following page).

High-performance liquid chromatography (HPLC) of this mixture revealed the presence in it of three randomers with identical electronic absorption spectra (λ_{max} 621, 547, and 334 nm). Calculation of the column efficiency with respect to each of the three peaks (~20,000 theoretical plates) shows that these compounds are individual. The yields of the randomers are 58.4% (fraction A), 25.2% (fraction B), and 16.4% (fraction C). The retention times of the isolated fractions differ markedly. Fraction A is eluted virtually with the free volume of the column ($K_A^1 = 0$), whereas capacity coefficients K_B^1 and K_C^1 for fractions B and C are 1.14 and 1.31, respectively. The retention of the isomer of fraction A under the investigated chromatographic conditions is characteristic for aromatic systems that do not contain strongly sorbed functional groups. On the basis of this we assumed

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1261-1263, September, 1988. Original article submitted April 1, 1987.

0009-3122/88/2409-1043$12.50

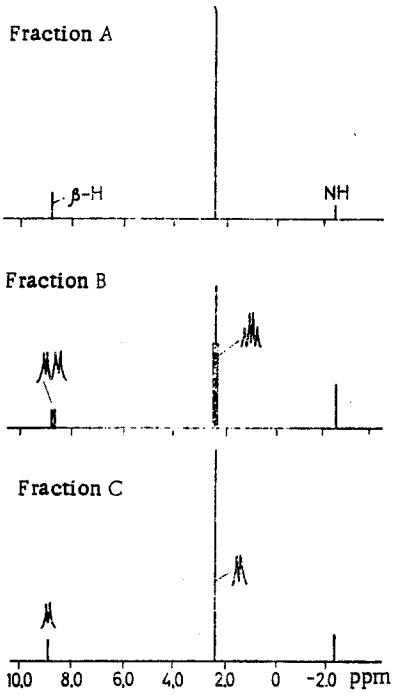
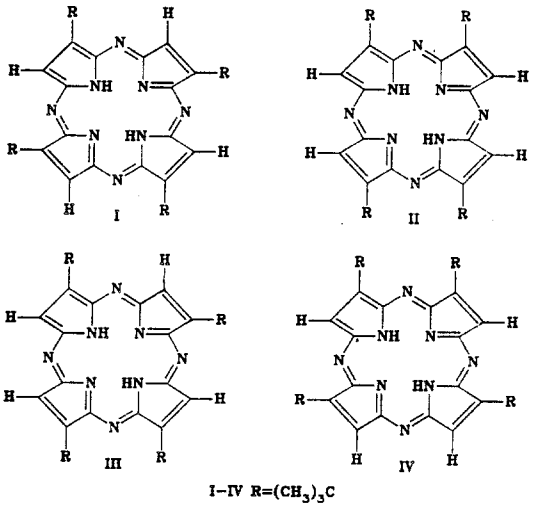


Fig. 1. PMR spectra of randomers of tetra(tert-butyl)porphyrazine (in $CDCl_3$).



I–IV R=$(CH_3)_3C$

that the structure of the randomer of fraction A is a planar unstrained structure. This structure is unfavorable for adsorption of the imino group on the surface of silica gel, and this randomer is virtually not retained on this sorbent. On the other hand, in the case of the randomers of fractions B and C the planar porphyrazine structure is evidently disrupted; this ensures participation of the nitrogen atoms of the pyrrole and pyrrolenine fragments in the retention mechanism. This, in turn, leads to an increase in the capacity coefficients. Disruption of the coplanarity of the macroring in a number of porphyrins that simultaneously contain substituents in the pyrrole rings and in the methine bridges was noted by Woodward and Skaric [5]. However, the conversion of the macroring in the case of the randomers in fractions B and C is so slight that it does not affect the electronic absorption spectra.

The electron-impact mass spectra of fractions A-C are basically similar. The peak of the molecular ion M^+ 538, which corresponds to the proposed empirical formula $C_{32}H_{42}N_8$, is the most intense peak in the spectra of fractions A-C. The successive loss by the molecular ion of four methyl groups (ions at 523, 508, 493, and 478*) constitutes evidence that the methyl groups in the starting molecule are bonded to sp^3-hybridized carbon atoms. Ions

*Here and subsequently, the m/z values are presented.

TABLE 1. Chemical Shifts in the PMR Spectra of Randomers I, III, and IV (in $CDCl_3$)

Randomer	δ, ppm		
	β-protons	Protons of the $(CH_3)_3C$ groups	NH protons
I	8,92	2,23	−2,48
III	8,94	2,23	−2,45
	8,93	2,22	
	8,90	2,20	
	8,89	2,15	
IV	8,95	2,24	−2,45
	8,90	2,22	

due to cleavage of the bonds in the macrocyclic ring are not formed. However, there are some differences in the spectra of fractions A-C. Thus groups of peaks in the region of mass numbers 442, 427, and 411, which are absent in the spectra of the other two fractions, are observed in the spectrum of fraction A. Groups of ions with mass numbers 463-466, 449-453, and 435-439, which are absent in the spectrum of fraction A, are formed in the fragmentation of the molecular ions of fractions B and C. These differences make it possible to assume that the mutual orientation of the tert-butyl groups in fraction A is more ordered. This assumption is also confirmed by the higher intensities of the peaks of the characteristic $[M - CH_3]^+$ and $[M - C_4H_9]^+$ ions in fractions B and C.

The PMR spectra of fractions A-C (Fig. 1) are characteristic for the macrocyclic conjugated system of porphyrins. Owing to the ring currents [6], the peripheral β protons undergo a significant shift to weak field (by 3-4 ppm as compared with pyrrole), while the protons of the NH groups within the ring are shielded and show up at unusually strong field (at −2.45 ppm). The chemical shifts of the protons of the randomers of fractions A-C are presented in Table 1.

Proceeding from the number of signals of the β protons and protons of the tert-butyl groups of tetra(tert-butyl)porphyrazine fractions B and C can be readily assigned to structures of the III and IV type, respectively, with respect to the type of substitution (Fig. 1). It is apparent from the structural formula that the β protons and the protons of the tert-butyl groups in IV are equivalent in pairs. Two signals at 8.9 and 2.2 ppm are observed in the PMR spectrum. In the case of the less symmetrical structure (fraction B) all of the positions are nonequivalent, and each of the β protons shows up in the spectrum in the form of a separate signal. In principle, the spectrum of the randomer of fraction A satisfies structures of the I and II type. However, the noncoincidence of the chemical shifts of this randomer as compared with the randomer of fraction C constitutes evidence in favor of the formation of a randomer of the I type; this is confirmed by data from the mass spectrum and HPLC.

The presence of three randomers rather than the four theoretically possible randomers in the reaction products is fully explainable, since the fourth randomer, which was assigned to a structure of the II type, is probably not formed because of great steric hindrance.

Thus it was established that in the case of tert-butyl-substituted porphyrazines the ratio of the randomers formed (I:III:IV = 58.4:25.2:16.4) is regulated to a greater extent by steric factors than by statistical factors (I:II:III:IV = 1:1:4:2).

EXPERIMENTAL

High-performance liquid chromatography (HPLC) was carried out with a Waters chromatograph (USA) with a model 481 spectrophotometric detector and a U6K injector. Detection was accomplished at 620 nm. The stainless-steel column was 25-cm long, had an inner diameter of 4.5 mm, and was packed with Silasorb 600-5 μm sorbent (the column efficiency was 20,000 theoretical plates, and the pressure was 10 MPa). The mobile phase was a mixture of methylene chloride and hexane (7:3), and the flow rates were 1 ml/min and 1 cm/min; a 3-μl sample of a solution of the mixture to be analyzed in methylene chloride was introduced into the chromatograph.

The electronic absorption spectra were recorded with a Pye–Unicam 8800 spectrophotometer. The mass spectra were recorded with a Varian MAT CH-6 spectrometer with direct introduction of the samples at an electron-ionization energy of 70 eV and a sample-vaporization temperature of 150-200°C. The high resolution PMR spectra of solutions in $CDCl_3$ (10^{-3} M) were recorded with a Bruker WM-360 spectrometer (360 MHz) with tetramethylsilane as the internal standard. The signals were accumulated using a 90° pulse (7 μsec) into a memory of 16K at a scan width of 6024 Hz.

The mixture of randomers of tetra(tert-butyl)porphyrazine was obtained in accordance with [3], whereas the samples of the individual randomers for the PMR and mass spectra were obtained by micropreparative HPLC.

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CONDENSED THIOLANE 1,1-DIOXIDE SYSTEMS.

2.* BROMINATED cis-PERHYDROTHIENO[3,4-d]OXAZOLES AND IMIDAZOLES

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UDC 547.787.3'783'495.3:542.944:541.634

Bromocyclization of 2-bromo-4-ureido-2-thiolene 1,1-dioxide has given perhydrothieno[3,4-d]oxazol-2-imino 5,5-dioxide, in which hydrogen atoms are absent from one of the α-methylene groups. In weakly basic media, this undergoes conversion into the corresponding aminooxazoline. Treatment of an aqueous solution of 2-bromo-4-ureido-2-thiolene 1,1-dioxide with bases gives a mixture of perhydrothieno[3,4-d]imidazol-2-one 5,5-dioxides in which the bromine atoms have the exo- and endo-orientations. In all the bicyclic compounds, the two rings are cis-fused.

Derivatives of thiolan 1,1-dioxide containing a substituent bonded to the heterocyclic ring via an oxygen atom are cleaved in dilute solutions of caustic alkali [2]. Thiolan 1,1-dioxides which do not bear a good leaving group or which cannot form an α-sulfonylcarbanion are more stable to bases [3]. The aim of the present investigation was to synthesize such compounds from the readily accessible 4-ureido-2-thiolene 1,1-dioxides (I).

In order to avoid the possible formation of an α-sulfonylcarbanion in the β-position to the good leaving group, we decided to replace both hydrogen atoms in this position by bromine. Such compounds have not previously been described. Ellis and Sammes [4] synthesized a compound with one bromine atom by bromocyclizing (I) in acetic acid. They showed that, as would be expected, the oxazolidine (II) was readily cleaved to the urea (III) on basification. We have repeated these reactions, and found that the yields from both

*For Communication 1, see [1].

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1264-1268, September, 1988. Original article submitted September 18, 1987.

0009-3122/88/2409-1046$12.50