SYNTHESIS OF 10,15,20-TRIPROPYLCYCLOPENTAPORPHYRIN AND THE STRUCTURE OF ITS NH TAUTOMERS

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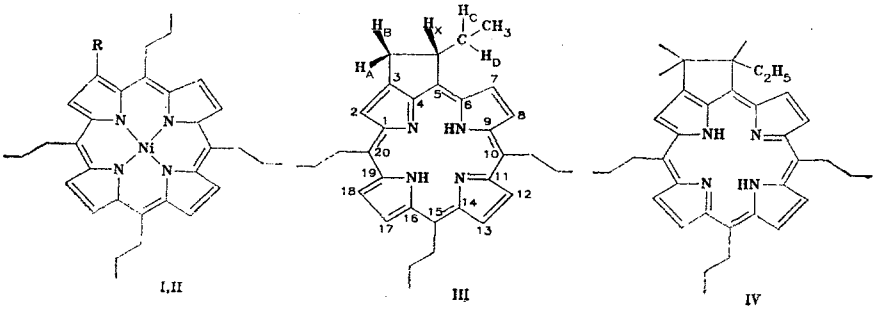
UDC 547.749:543.422

In a study of the spectroluminescent properties of previously synthesied prophyrins with a cyclopentane ring [1, 2] (joint work with É. I. Zen'kevich, A. V. Chernookii, and G. P. Gurinovich), we discovered a dependence of the fluorescence spectra of these compounds on the wavelength of the incident light due to the capacity of the cyclopentaneporphyrins to exist as a mixture of two NH tautomers both at low and room temperature and not to prophyrin impurities. In some cases, the spectral dispersal of the S_0–S_1 transition reaches 15 nm and a fifth band displaced toward the red region is observed in the absorption spectrum in the visible region in addition to the four known bands. In this case, the "short-wavelength" tautomer is more stable than the "long-wavelength" tautomer. However, it was not possible to assign the position of the NH protons to a given tautomeric structure by such methods. In addition, the cyclopentaneporphyrins reported have all contained alkyl substituents in the pyrrole rings, which makes it impossible to determine the PMR coupling constants with the NH protons. We have synthesized a new class of cyclopentaneporphyrins with substituents in the meso positions and unsubstituted pyrrole rings. For this purpose, we prepared the intermediate "phosphorus" complex [3] by treatment of 0.6 g Ni-meso-tetrapropylprophyrin with a mixture of 9.5 ml $POCl_3$ and 8.5 ml DMF in 350 ml dichloroethane for 8-9 h at 52-53°C. The reaction of this complex with methylamine in chloroform at room temperature for three days leads to Shiff base I, which gives formylporphyrin II upon heating. The Schiff base was subjected to thermolysis after crystallization from hexane since it is completely converted to aldehyde II upon chromatography on aluminuma or silica gel.



I, II III IV

I R=CH=NCH$_3$; II R=CHO

The thermolysis of I (0.25 g) was carried out at 300-305°C at 10^{-2} mm over 10 min. Chromatography on a silica gel column (40/100 μ) was carried initially with 1:1.5 $CHCl_3$–CCl_4 as the solvent and then with CCl_4 led to separation of the leading red-brown zone. The solvent was removed and the residue was treated with concentrated sulfuric acid. Extraction and chromatography on silica gel with 4:1 benzene–chloroform as eluent gave 77 mg (36%) of a mixture of tautomers III and IV. Absorption spectrum in $CHCl_3$, λ_{max} ($\varepsilon \cdot 10^{-3}$): 4.6 (351), 518 (12), 556 (14), 590 (5), 643 (3), 567 (1). Mass spectrum, m/z (relative intensity, %): 490 (M^+, 100), 461 (80), 432 (9), 403 (10). The PMR spectrum was taken on a Bruker WM-360 spectrometer and shows only signals for the stable tautomer III, δ: 9.55 and 9.46 (17- and 18-H), 9.52 and 9.33 (8- and 7-H), all d.d. due to proton nonequivalence (J = 5.1 Hz) and coupling with the NH protons (J = 1.8 Hz), 9.51 (d, 13-H), 9.49 (d, 12-H, J = 5.1 Hz), 8.89 (5, 2-H, J = 1.5 Hz), 5.75 (m, H_X), 5.02, 4.95, 4.83 (all t, 15^{α}-, 10^{α}-, 20^{α}-CH_2), 4.31 (m, H_A, J_{AB} = 17.8 Hz, J_{AX} = 6.7 Hz, J_{AH-2} = 1.7 Hz), 3.82 (H_B, J_{BX} = J_{BH-2} = 1.7 Hz), 2.90 and 2.46 (m, H_C, H_D, J_{CD} = 14.3 Hz, J_{CX} = 3 Hz, J_{DX} = 8.5 Hz), 2.53-2.58 (m, 10^{β}-, 15^{β}-, 20^{β}-CH_2), 1.36, 1.33, 1.31 (t, 10^{γ}-, 15^{γ}-, 20^{γ}-CH_3), 1.11 (t, 5^{β}-CH_3), −1.85 (s, 24-H), −2.72 (s, 22-H). The signals were assigned using double resonance and the nuclear Overharuser effect. Comparison of the spectroluminescent and PMR data shows that the lifetime of tautomer IV is considerably shorter than for III and the PMR spectrum of IV cannot be recorded. The common nature of the

Institute of Physics, Academy of Sciences of the Belorussian SSR, Minsk 220602. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 132-133, January, 1985. Original article submitted June 12, 1984.

 0009-3122/85/2101-0110$09.50

the spectral characteristics indicates that this NH-tautomer structure is characteristic for cyclopentaneporphyrins with alkyl groups on the pyrrole rings.

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ASYMMETRIC METHYLATION OF 1-[(S)-α-PHENYLETHYL]-2-AZETIDINONE

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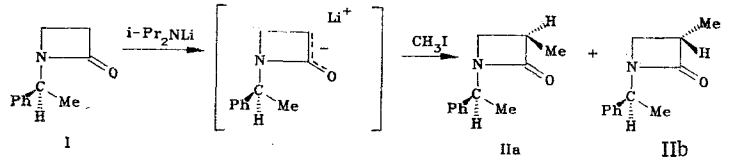
UDC 547.718.323.5:541.632

Monocyclic 2-azetidinones (β-lactams) have attracted the considerable attention and chemists and the medical profession since the discovery of nocardicine and monolactam antibiotics. Since the biological activity of these compounds depends stongly on the absolute configuration of the chiral centers of the β-lactam ring, special interest is found in the asymmetric of these compounds.

We have reported the asymmetric synthesis of 2-azetidinones upon alkylation of their metallated derivatives [1].

The methylation of the lithium derivative of 1-[(S)-α-phenylethyl]-2-azetidinone (I) by methyl iodide in THF at −78°C in an argon atmosphere gives of mixtures of diastereomers IIa and IIb in 33% yield.



Thin-layer chromatographic separation on silica gel gave the pure diastereomers IIa (with greater R_f value) and IIb (with smaller R_f value) with a 35% diastereomeric excess of IIb. The structures of the chromatographically pure isomers IIa and IIb was shown by spectral data [2] and the diastereomeric purity was 98%.

The action of sodium on pure diastereomers IIa and IIb in liquid ammonia gave enantiomeric-3-methyl-2-azetidinones, as indicated by the different configurations for C-3 in IIa and IIb.

Methylation of racemic 1-(α-phenylethyl)-2-azetidinone under the same conditions leads to a 1:4 mixture of racemic 3-methylated isomers IIa and IIb in 39% yield (60% diastereomeric excess).

A sample of 2 mmoles 1-[(S)-α-phenylethyl]-2-azetidinone in 10 ml THF was added dropwise with stirring at −78°C in an argon atmosphere to 2.3 mmoles lithium diisopropylamide obtained from 2.3 mmole diisopropylamine in 10 ml THF and 2.4 ml (2.3 mmoles) 0.99 N butyllithium in hexane. After 30 min, 4 mmoles CH_3I in 10 ml THF was added dropwise and stirred for 45 min at 78°C. The reaction mixture was poured into 50 ml saturated aqueous NaCl and extracted with five 20-ml portions of ether. The extract was dired over $MgSO_4$. After removal of ether, the residue was subjected to chromatography on a column packed with silica gel L 40/100 using 2:1 benzene—ethyl acetate as the solvent to give 40.7 mg (32%) isomer IIa (R_f 0.37) and 83.7 mg (68%) isomer IIb (R_f 0.32 on Silufol-254 plates with 2:1 benzene—ethyl acetate as the eluent). All the physicochemical indices for IIa and IIb were identical to those previously described for these diastereomers [2].

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Translated from Khimiya Geterotsiklicheksikh Soedinenii, No. 1, p. 134, January, 1985. Original article submitted July 12, 1984.