## ADDITION OF ISOCYANATES AND ISOTHIOCYANATES

## TO 2-AMINO-3-PHENYLCARBAMOYLAZIRINES

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When investigating the addition of isocyanates and isothiocyanates to 2-amino-3-phenylcarbamoyl-1-azirine (I) in [1] we established that nitriles of N-acylaminomalonic acid (II, III) (60-70% yield) and 2,5-diaminothiazoles (V, VI) (~60% yield), respectively were formed.



II, V R =  $CH_3$ ; III, IV, VI R =  $C_6H_5$ 

The results of the experiments with isocyanates differed from the literature data as to the final products of the reaction of isocyanates with 2-dialkylamino- and 2,3-alkylaryl-l- azirines in which both imidazolidines, oxazolines, and acylamidines [2, 3], and substituted perhydrothiazines, carbodiimides, zwitterionic 1,1- and 1,2-adducts [4-7] were formed.

Compounds, yield, and mp were (II) 63%, 203°C; (III), 70%, 243°C; (V), 58%, 205°C; (VI), 60%, 176°C.

Bands were observed in the IR spectra (Nujol) of compounds (II) and (III) (mp 203°C and 243°C, respectively) for the stretching vibrations of the C=O (1550-1680), C=N (2260), and NH (3300, 3360 cm<sup>-1</sup>) groups. The data of the IR spectra of compounds (V) and (VI) (mp 205°C and 176°C, respectively) indicated the presence of NH2 and NH (3280-3380) and also C=0 (1540-1670 cm<sup>-1</sup>) groups. In the PMR spectra (DMSO-D<sub>6</sub>) of amides (II) and (III) doublet signals appeared for the protons of COCHNH (5.6 ppm, J = 8 Hz) and NHCH (7.6 ppm, J = 8 Hz) groups in comparison with the spectrum of azirine (I). In the spectrum of amide (II) there were in addition signals of the protons of NHCH<sub>3</sub> (6.35 ppm, 1 H, br q and 2.6 ppm, 3H, d, J = 4 Hz). Similar signals of protons of the NHCH<sub>3</sub> group (6.90 ppm, 1H, br q, 2.90 ppm, 3H, d, J = 4 Hz) were also observed in the PMR spectra of diaminothiazole (V). Signals were also recorded for protons of NHPh at 9.1 ppm in the PMR spectra of compounds (III) and (VI). On comparing the <sup>13</sup>C NMR spectra of amides (II) and (III) with the spectra of azirine (I), signals for the carbon atom of a CEN bond at 117.1 ppm and for the carbon of a carbonyl group (156.9 ppm) appeared, and in the analogous spectra of diaminothiazoles (V) and (VI) there were signals for the carbon atoms of a C=C bond at 120.6 and 146.6 ppm and of a C=N bond (150.4 ppm). The structures of the nitriles of N-acylaminomalonic acids (II) and (III) were confirmed by hydrolysis of the latter under the action of boron trifluoride etherate to the amide (IV) known from [1]. The data of elemental analysis corresponded to calculated values.

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## FIRST SYNTHESIS OF ETHYLENEBISPORPHYRINS

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The study of bisporphyrins is one of the main modern directions of the chemical and physicochemical investigations in the area of prophyrins. These compounds have proven to be convenient models for the clarification of processes of energy transfer in photosynthesis and for the study of various catalytic systems (see review in [1]).

While studying the chemical properties of ethanebisporphyrins, the synthesis of which will be described in a separate communication, we discovered that compounds (Ia-c) are converted in acetic acid at 70°C after 20 min in a yield close to quantitative into new substances having significantly higher chromatographic mobilities on silica gel in comparison with the initial porphyrins.

Analysis of PMR and mass spectral data of the isolated compounds made it possible unambiguously to ascribe to them the structure of the previously unknown ethylenebisporphyrins (IIa-c).

I A = CH<sub>2</sub>-CH<sub>2</sub>; II A = CH=CH; I, II a R<sup>1</sup> = Me, R<sup>2</sup> = Et; b R<sup>1</sup> = R<sup>2</sup> = Et; c R<sup>1</sup> = R<sup>2</sup> = Pr

There were intense peaks for the molecular ions in the electron impact mass spectra of compounds (IIa-c) reaching 100% for the metal complexes which indicated their high stability in comparison with ethanebisporphyrins [m/z (relative intensity, %): IIa 980 (M<sup>+</sup>, 100), 492 (65), 490 (83), 488 (95), 478 (92); IIb 1092 (M<sup>+</sup>, 41), 560 (31), 558 (33), 548 (51), 546 (51), 534 (100); IIc 1316-1319 (100), 672 (13), 658 (50), 646 (17)].

A singlet signal was observed in the PMR spectra of the ethylenebisporphyrins in the region of 8.5 ppm for the bridge protons which on protonation of the porphyrins is shifted to the region of meso-proton signals. For example, the PMR spectrum of compound (IIb) (CDCl<sub>3</sub>) was  $\delta$  10.12 and 9.93 (4H and 2H, two s, meso-H), 8.56 (2H, s, CH=CH), 4.13, 4.11, 4.08, and 3.89 [(latter not resolved) all to  $\alpha$ -CH<sub>2</sub>], 1.98, 1.96, 1.93, and 1.0 (all t,  $\beta$ -CH<sub>3</sub>), -2.72 ppm (s, NH); (CDCl<sub>3</sub> + 1% CF<sub>3</sub>COOH),  $\delta$ : 10.26 (2H, s, CH=CH), 10.19 and 9.92 (4H and 2H, two s, meso-H), -0.43 and -2.03 ppm (two s, NH).

The presence of an immensely broadened Soret band in the electronic spectra was a characteristic of the ethylenebisporphyrins (IIa-c). The band partially masked the four band spectra in the visible spectrum, which is traditional for porphyrins, but a splitting of the

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