177-178°C [5]. Found: C, 70.48; H, 6.06; B, 9.94; N, 13.10%; m/z 309 M<sup>+</sup>. Calculated for C<sub>18</sub>H<sub>18</sub>B<sub>3</sub>N<sub>3</sub>: C, 70.01, H, 5.89; B, 10.49; N, 13.61%; molecular mass 309. IR spectrum (v, cm<sup>-1</sup>): 1450 (BPh), 1472 (BN), 3450 (NH).

#### CONCLUSION

The reaction of phenylboric anhydride with hexamethylcyclotrisilazane gives triphenylborazine, cyclosiloxane, cyclosilazaoxane, benzene and methane.

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# FEATURES OF THE PROTONATION OF N-VINYLPYRROLES

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The electrophilic reactions of pyrrole derivatives hold both considerable theoretical and practical interest [1]. N-vinylpyrroles containing three probable sites for electrophilic attack (the  $\alpha$  and  $\beta$  positions of the heterocycle and the  $\beta$  position of the vinyl group (VG)) significantly expand the range  $\uparrow$ f possible transformations which may hold preparative interest [2]. One of the simplest electrophilic reactions is protonation. In the presence of traces of acid, N-vinylpyrroles polymerize [3] or dimerize with the involvement of the pyrrole ring (PR) and VG [4]. Acid hydrolysis leads to complex oligomeric products [5]. However, the structure of the primary cations in these transformations is still unknown.

In the present work, NMR spectroscopy was used to study the protonation of 2,3-diorganyl-1-vinylpyrroles (I) by trifluoroacetic and fluorosulfonic acids in order to understand the effect of the nature of the acid and substitution in the PR on the structure and stability of the cations formed.

The effect of excess  $HSO_3F$  on pyrroles (I) in  $CD_2Cl_2$  from -40 to -80°C leads to the formation of the  $\alpha$ -protonated species (II) with retention of the double bond.



 $R^1 = Me$ ,  $R^2 = Et(a)$ ;  $R^1 = Ph$ ,  $R^2 = i - Pr(b)$ .

Warming the sample in the probe of an NMR spectrometer up to 0°C does not affect the shape of the spectrum, which indicates the significant stability of the  $\sigma$ -complex formed in strongly acidic media.

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Under analogous conditions, the reaction of 2-methyl-3-ethyl-1-vinylpyrrole (Ia) with excess  $CF_3CO_2H$  in  $CD_2Cl_2$  at -60°C gives the same cation. Warming the sample to -20°C leads to the conversion of (IIa) to a cation over 10-15 min. PMR spectroscopy indicates structure (IIIa), which is the protonated form of the dimer by analogy to that described previously [4]:



In the case of (Ib), this conversion in the presence of  $CF_3CO_2H$  is very rapid and only cation (IIIb) is observed in the reaction mixture. Even traces of the adduct of  $CF_3CO_2H$  to the vinyl group are not found for both pyrroles. These results indicate that the following equilibrium exists:



Cation (IV), which is present in lower concentrations (and is not detected by NMR spectroscopy) and is less stable but more reactive, attacks an unprotonated pyrrole molecule to form dimeric cation (V), which is then converted to the more stable cation (III).



The significantly greater reaction rate for the 2-phenyl derivatives indicates the greater stability of cation (IIIb) due to additional delocalization of the charge



The PMR spectra of the dimeric cations display an interesting feature, namely, anisochronicity of the protons of the 5-CH<sub>2</sub> group in the protonated pyrrole ring. This is especially pronounced in the spectrum of (IIIb) ( $\Delta\delta = 0.64$  ppm, <sup>2</sup>J = 27.0 Hz). To our knowledge, this is the first example of inequivalence of protons of this type in arenonium and heteroarenonium ions. This anisochronicity is attributed to the presence of asymmetric carbon atom and its significant magnitude is apparently related to hindrance to rotation about the C(Me)H-N bond at the protonated pyrrole ring and the anisotropic effect of the neighboring groups.



The reaction of (Ia) with  $CF_3CO_2D$  stops at the first step. In this case, the intensity of the signal for the H<sup>4</sup> proton in the spectrum of (IIa) is reduced, indicating its partial replacement by deuterium in accord with the data given by Jones and Bean [1] concerning the greater rate of protonation of the  $\beta$ -position of the pyrrole ring. Maintaining the sample up to 1 h at -20°C leads only to a reduction in the intensity of the signal for the 5-CHD group. On the other hand, a dimer is formed in the reaction with phenyl derivative (Ib) although, as previously, the intermediate  $\alpha$ -protonated form could not be observed. Thus, the dimerization in this case is also high. There are no signals for the 5-CH<sub>2</sub> protons in the spectrum of the dimeric cation obtained due to rapid H-D exchange.

# EXPERIMENTAL

The PMR spectra were obtained on Tesla BS-567A and Bruker WH-90 spectrometers. The rections of the vinylpyrroles with  $HSO_3F$  and  $CF_3CO_2H(D)$  was carried out at -60°C by mixing 0.02 g (I) with a 5-10-fold molar excess of the acid in equal 0.25-ml volumes of  $CD_2Cl_2$  in an NMR ampul.

PMR spectrum of (IIa) ( $\delta$ , ppm, in CF<sub>3</sub>CO<sub>2</sub>H): 7.52 s (H<sup>4</sup>), 7.18 q (H<sub>C</sub>), 5.83 q (H<sub>A</sub>), 5.58 q (H<sub>B</sub>), 5.11 br (5-CH<sub>2</sub>), 2.68 t (2-CH<sub>3</sub>), 2.46 q and 1.28 t (C<sub>2</sub>H<sub>5</sub>). <sup>2</sup>J<sub>H<sub>A</sub>,H<sub>B</sub> = 3.0, J<sub>2</sub>-CH<sub>3</sub>,5-CH<sub>2</sub> = 2.5 Hz.</sub>

PMR spectrum of (IIb) ( $\delta$ , ppm, in HSO<sub>3</sub>F): 7.0-7.5 m (C<sub>6</sub>H<sub>5</sub>,H<sup>4</sup>), 6.86 q (H<sub>C</sub>), 5.55 q (H<sub>A</sub>), 5.28 q (H<sub>B</sub>), 5.06 br (5-CH<sub>2</sub>), 2.88 m (3-CH), 1.12 d (3-(CH<sub>3</sub>)<sub>2</sub>).

PMR spectrum of (IIIb) ( $\delta$ , ppm): 7.82 s (H<sup>4</sup>), 7.2-7.7 m (C<sub>6</sub>H<sub>5</sub>), 6.63 s (H<sup>4</sup>), 6.08 q (H<sub>C</sub>), 5.76 s (CH), 5.04 d and 4.40 d (5-CH<sub>2</sub>), 4.70 d (H<sub>B</sub>), 4.55 d (H<sub>A</sub>), 2.74 m (3-CH, 3'-CH) 2.05 d (CH<sub>3</sub>), 1.25 d and 1.19 d (3'-(CH<sub>3</sub>)<sub>2</sub>), 1.02 d and 0.81 d (3-(CH<sub>3</sub>)<sub>2</sub>).

#### CONCLUSIONS

The protonation of N-vinylpyrroles by fluorosulfonic and trifluoroacetic acids occurs at the  $\alpha$ -carbon atom of the pyrrole ring. Dimerization of the cation formed takes place in CF<sub>3</sub>CO<sub>2</sub>H. The rate of this process is much higher for the 2-phenyl derivative than for the 2-alkylvinylpyrrole derivative.

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