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REACTION OF PHENYLBORIC ANHYDRIDE WITH HEXAMETHYLCYCLOTRISILAZANE

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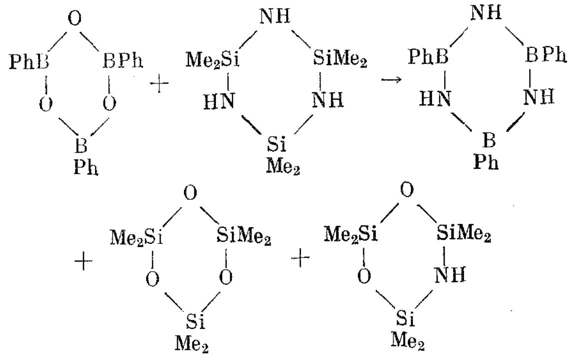
The synthesis of borazines, as a rule, is based on the reaction of halogen-containing boron compounds with organic and organosilicon amines [1, 2] and cyclosilazanes [3]. The use of esters of organoboron acids for the synthesis of borazines presupposes their initial conversion to amino derivatives with subsequent heating at 280-295°C [4].

We selected phenylboric anhydride (PBA), which is a relatively stable and readily available anhydride, as the starting compound. A studied was carried out on the reaction of PBA with hexamethylcyclotrisilazane in the presence of 1% KOH, starting at 180°C and raising the temperature gradually over 4 h to 280°C.



(I)

Up to 40% triphenylborazine was isolated from the solid products by recrystallization from heptane. Methane, benzene, hexamethylcyclotrisiloxane, and the mixed silazasiloxane ring (I) were found in the liquid and gaseous reaction products.

Thus, this reaction proceeds with cleavage of the B–O and Si–N bonds, such that an oxygen atom in PBA is replaced by an NH group of the silazane with the formation of borazine, siloxane and silazaoxane rings. In addition, a side-reaction occurs, in which a B–C bond is broken, as indicated by the finding of benzene in the reaction products.

EXPERIMENTAL

A mixture of 2.19 g (0.01 mole) hexamethylcyclotrisilazane, 3.12 g (0.01 mole) PBA and 0.05 g (1%) KOH was heated for 4 h at from 180 to 280°C, collecting the liquid and gaseous products. We obtained 65 ml (30 mole %) CH_4 and 0.6 ml of a liquid containing hexamethylcyclotrisiloxane, benzene (30 mole %) and mixed silazasiloxane as indicated by gas-liquid chromatography on an LKhM-8MD chromatography using a 3 m × 4 mm column packed with 5% SE-30 on Inertone AW-HMDS with 0.2-0.25 particles using a 30 ml/min helium gas carrier flow rate and katharometer detector. The residue was extracted with benzene. The solvent was removed and the residue was recrystallized from heptane to give 1.2 g (40%) triphenylborazine with mp

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177-178°C [5]. Found: C, 70.48; H, 6.06; B, 9.94; N, 13.10%; m/z 309 M^+. Calculated for $C_{18}H_{18}B_3N_3$: C, 70.01, H, 5.89; B, 10.49; N, 13.61%; molecular mass 309. IR spectrum (ν, cm^{-1}): 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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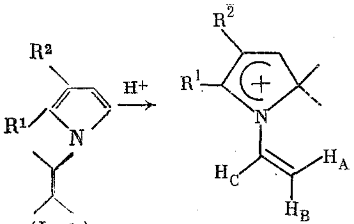
The electrophilic reactions of pyrrole derivatives hold both considerable theoretical and practical interest [1]. N-vinylpyrroles containing three probable sites for electrophilic attack (the α and β positions of the heterocycle and the β position of the vinyl group (VG)) significantly expand the range of 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 α-protonated species (II) with retention of the double bond.



(Ia,b) (IIa,b)

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 σ-complex formed in strongly acidic media.

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