

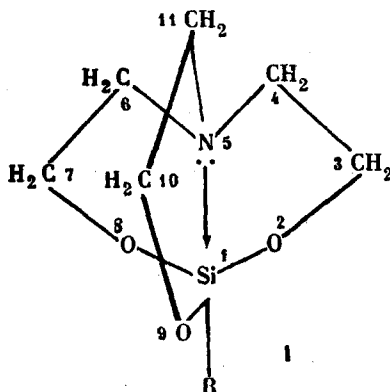
ATRANES. V*. PROTON MAGNETIC RESONANCE SPECTRA OF ORGANYL
AND ORGANOXYSIATRANES*

A. N. Egorochkin, V. A. Pestunovich, M. G. Voronkov, and G. I. Zelchan

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 300-303, 1965

The proton magnetic resonance spectra of eight organyl- and organoxysilatrane, $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ ($\text{R} = \text{CH}_3$, C_2H_5 , $i\text{-C}_3\text{H}_7$, $\text{CH}_2=\text{CH}$, C_6H_5 , CH_3O , $\text{C}_2\text{H}_5\text{O}$, $n\text{-C}_3\text{H}_7\text{O}$) are investigated. The PMR resonance signals are interpreted, taking into account magnetic anisotropy of substituents and $d_\pi\text{-}p_\pi$ interaction effects.

The present communication gives results of proton magnetic resonance (PMR) studies of organyl- and organoxysilatrane (I). The table shows the compounds studied and the chemical shifts of the magneto-equivalent groups of protons in their spectra (see figure).



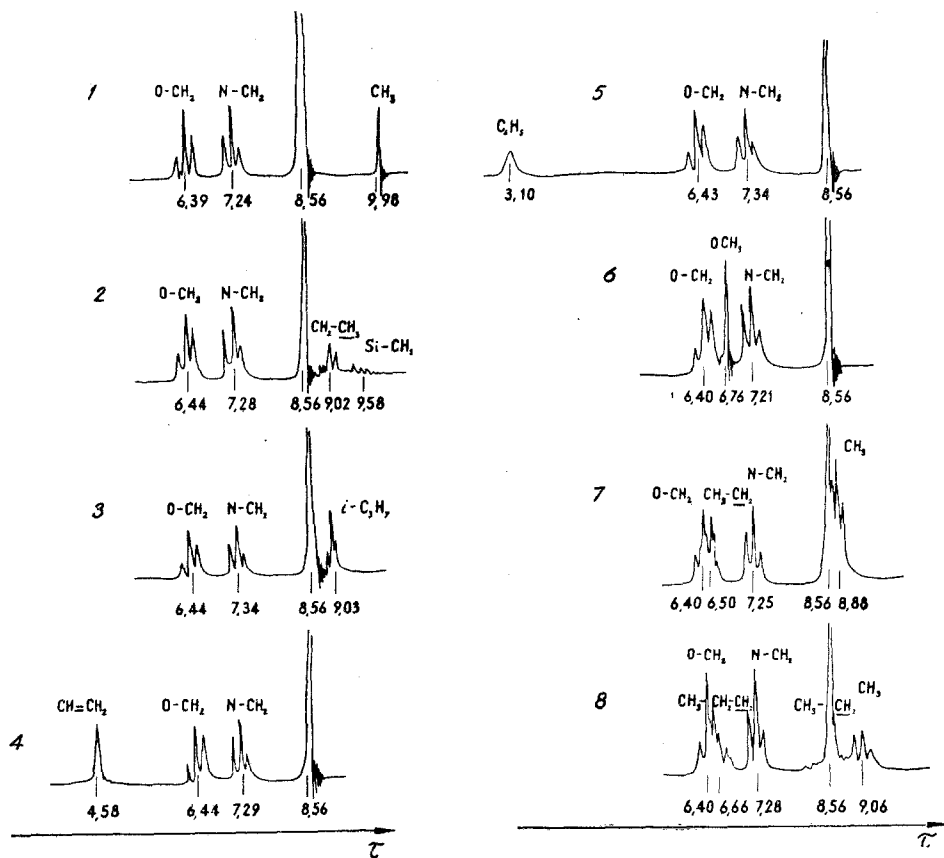
The proton spectrum of the $\text{O}-\text{CH}_2-\text{CH}_2-\text{N}$ part of the silatrane molecules is an A_2B_2 system, whose chemical shifts are determined directly from an experimental spectrum. There is no difficulty in relating the rest of the spectra signals.

A characteristic peculiarity of the chemical shifts of the silatrane PMR spectra is the lack of manifest dependence of chemical shifts of CH_2 group protons in the portion $\text{O}-\text{CH}_2-\text{CH}_2-\text{N}$ on the inductive effect of substituent R. This is not unexpected, if it is borne in mind that all substituents except alkyl are capable of $d_\pi\text{-}p_\pi$ interaction with the silicon atom. The stated effect acts in a direction the reverse of that of the inductive $-I$ effect of substituents R. In the case of 1-phenylsilatrane, apart from the previously mentioned two effects (inductive and $d_\pi\text{-}p_\pi$ interaction), the effect of magnetic anisotropy, due to circulation of the π electrons of phenyl groups, must be added to the actual contribution of the chemical shifts of the protons of the methylene groups. Furthermore, evidently participation of lone electron pairs of oxygen atoms of the actual silatrane group $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ for $d_\pi\text{-}p_\pi$ has a major role in the preservation of

relative constancy of the chemical shifts of $\text{O}-\text{CH}_2$ protons with change of substituent at the central silicon atom. Participation of lone nitrogen electron pairs in the formation of a transannular dipolar coordination bond with silicon, on account of the vacant 3d orbitals of the latter [1-4] is a quite striking feature of the structure of silatrane. It is considered that this characteristic of the electronic structure of silatrane molecules, confirmed by their high dipole moments (5-7D) [2], is also manifest in their PMR spectra. In fact, for 1-vinyl- and 1-alkylsilatrane, the chemical shifts of the methylene group protons in the fragment $\text{Si}-\text{O}-\text{CH}_2$ are 6.39-6.44 ppm on the τ scale. At the same time, the protons of the methylene groups in the molecules of vinyl- and alkyltriethoxysilanes are less shielded ($\tau = 6.18\text{-}6.20$ ppm according to present measurements and literature data [5]). Chemical shifts of protons of substituents R in molecules of 1-methyl-, 1-ethyl-, and 1-vinylsilatrane are observed in stronger fields than with the molecules of the corresponding substituted

*For part IV see [1].

triethoxysilanes $\text{RSi}(\text{OCH}_2\text{CH}_3)_3$. This indicates a higher electron density at the silicon atom in silatrane molecules.



Proton magnetic resonance spectra of the silatranes, $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$.

R = (1) CH_3 , (2) C_2H_5 , (3) $i\text{-C}_3\text{H}_7$, (4) $\text{CH}_2 = \text{CH}$, (5) C_6H_5 , (6) CH_3O , (7) $\text{C}_2\text{H}_5\text{O}$, (8) $n\text{-C}_3\text{H}_7\text{O}$.

Comparing the chemical shifts of the CH_2 protons in the $\text{Si}\leftarrow\text{N}-\text{CH}_2$ portion of silatranes with those of the protons of $\text{N}-\text{CH}_2$ in triethanolamine and N -dimethylethanolamine ($\tau = 7.48$ and 7.55 ppm from present, and other data given in the literature [5]), it can be concluded that the nitrogen atom in silatrane molecules is less screened than in β -hydroxyethylamines.

Chemical shifts in PMR spectra of silatranes (I)

R	$\tau_{\text{Si}-\text{O}-\text{CH}_2}$	$\tau_{\text{Si}\leftarrow\text{N}-\text{CH}_2}$	τ_{R}
CH_3	6.39	7.24	9.98
C_2H_5	6.44	7.28	9.02 ^a 9.58 ^b
$i\text{-C}_3\text{H}_7$	6.44	7.34	9.03
$\text{CH}_2=\text{CH}$	6.44	7.29	4.58 ^c
C_6H_5	6.43	7.34	3.10
CH_3O	6.40	7.21	6.76
$\text{C}_2\text{H}_5\text{O}$	6.40	7.25	6.50 ^d 8.88 ^e
$n\text{-C}_3\text{H}_7\text{O}$	6.40	7.28	—

- a - CH_3 protons of the ethyl group.
- b - CH_2 protons of the ethyl group.
- c - Singlet, readily spread peak.
- d - CH_2 protons of the ethoxyl group, quadruplet.
- e - CH_3 protons of the ethoxyl group, triplet

The results stated above can be attributed to a shift of electrons from the nitrogen to the silicon atom, due to the formation of an intramolecular coordination link $\text{Si}\leftarrow\text{N}$ in the silatrane molecules. The existence of such a link is also indicated by the fact that a change in the nature of the substituent at the silicon atom in the compounds under consideration brings about a large change of chemical shifts of the protons of methylene groups attached to a nitrogen atom. In the opposite case (absence of the coordinate link $\text{Si}\leftarrow\text{N}$), starting from the law of decrease (damping) of the inductive effect, the chemical shift of $\beta\text{-CH}_2$ groups must be less sensitive to the effect of substituents at the silicon atom than the magnitude of the electronic screening of the protons of α -methylene groups.

Finally, it must be said that the data and their interpretation are of a preliminary nature, because of the possibility of intermolecular action with the solvent. More detailed results will be published soon.

Experimental

The 1-organyl- and 1-organoxysilatrane were synthesized and purified as described previously [1-4]. The melting points and analytical data were the same as previously recorded.

The spectra were determined with an INM-3 spectrophotometer working at 40 Mc. Saturated solutions of silatrane in chloroform were used for measuring the PMR spectra. Cyclohexane was used as the internal standard. The chemical shifts τ were measured as ppm (millionths) relative to the reference signal from C_6H_{12} protons, whose chemical shift was taken as 8.56 ppm on the τ scale. The side band method was used to determine the positions of the resonance signals in the spectra to an accuracy of $\pm 0.01-0.03$ ppm, using the arithmetic mean of not less than four measurements.

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29 October 1964

Scientific Research Institute of Chemistry,
Lobachevskii Gor'kii State University,
Institute of Organic Synthesis
AS Latvian SSR, Riga.

UDC 547.78+542.95

ALKYLATION OF AMINOTHIAZOLES; IV* . ALKYLATION OF 2-AMINO-4, 5-DIMETHYLTHIAZOLE

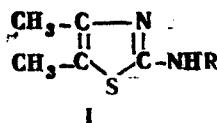
V. A. Krasovskii, and S. I. Burmistrov

Khimiya Geterotsiklicheskih Soedinenii, Vol. 1, No. 2, pp. 303-305, 1965

Alkylation of 2-amino-4, 5-dimethylthiazole with isopropanol and cyclohexanol in 85% sulfuric acid gives good yields of isopropylamino- and 2-cyclohexylamino-4, 5-dimethylthiazole. The structures of the products are demonstrated by reverse synthesis from 3-chlorobutanone and substituted thioureas.

Previous papers described the alkylation of 2-amino-4-methylthiazole and 2-aminothiazole with secondary and tertiary alcohols and 80-85% sulfuric acid, which in all of the cases examined gave up to 98% yields of 2-alkylaminothiazoles, i. e. alkylation took place at the nitrogen atom outside the ring. The present communication describes experiments on alkylating 2-amino-4, 5-dimethylthiazole with cyclohexanol and isopropanol.

Related compounds (I) were obtained in up to 85% yields at an alcohol : aminothiazole ratio of 1.5 : 1.



The structures of the alkylation products (I) were demonstrated by synthesis from 3-chlorobutan-2-one and the appropriate thiourea [3].

Experimental

2-Amino-4, 5-dimethylthiazole was prepared from 3-chlorobutan-2-one and thiourea. B. p 120°/ 3-4 mm, m. p. 80-82° (the literature [4] gives m. p. 82-83°).

Alkylation was effected by the following standard method: 0.075 mole of the anhydrous secondary alcohol was added dropwise, with stirring, to 0.05 mole (6.4 g) 2-amino-4, 5-dimethylthiazole which had been dissolved with cooling in 100 ml 85% sulfuric acid and then heated to 60-90°. When addition was complete, the mixture was stirred at this temperature for 5-7 hr, cooled, and poured onto 200 g ice, then neutralized, while cooling, with concentrated aqueous ammonia. The solid was separated and washed with water. If the amine came out as an oil, it was extracted with benzene, the benzene layer dried with anhydrous sodium sulfate, and then vacuum-distilled.

*For Part III see [1].