65 ml (~1.0 mole) of acetic acid was boiled for 2 hr, cooled, made alkaline, and extracted with benzene. The benzene extracts were dried with magnesium sulfate, the benzene was driven off, and the mixture was distilled in vacuum. In the range from 150 to 160° C (6 mm) 10.0 g of a distillate crystallizing during distillation was collected.

1.4 g of the distillate was triturated with 10 ml of petroleum ether. The insoluble fraction was filtered off and the filtrate was evaporated, giving 1.1 g of a crystalline mass with mp 69° C (from hexane) forming a picrate with mp 199–200° C (from ethanol). The substances obtained melted without depression in admixture with authentic samples of sym-octahydroacridine and its picrate. The fraction insoluble in petroleum ether (0.2 g) was washed repeatedly with boiling water and the residue was recrystallized from ethanol, mp 191–192° C. It gave no depression of the melting point with an authentic sample of 12-hydroxy-Δ^{10}-dodecahydroacridine (IV). The aqueous extracts were evaporated to dryness. The residue (about 0.1 g) had 157–158° C (from acetone or dioxane) and gave no depression of the mp with an authentic sample of 5-azabicyclo[8, 4, 0]tetradecane-6, 11-dione (V).

The reaction in an atmosphere of argon was carried out similarly and with the same amounts of substances. After heating for 2 hr, the mixture was made alkaline and extracted with benzene, the benzene extract was dried with magnesium sulfate, the benzene was driven off, and the residue was distilled in vacuum. The operations of drying, eliminating the benzene, and vacuum distillation were also carried out in an atmosphere of argon. 11.7 g of distillate was collected in the range from 120–135° C (0.2 mm). It consisted of a viscous liquid partially crystallizing on standing in a sealed vessel.

A solution of 1.55 g of the distillate in 10 ml of heptane was oxidized with molecular oxygen. In 2 hr, 58 ml of O_2 was absorbed, 38 ml of this having been absorbed in the first 10 min. The precipitate of hydroperoxide that had deposited was filtered off and dried at 0° C over paraffin wax, giving 0.5 g of the hydroperoxide of Δ^{10}-dodecahydroacridine (VII), mp 96° C, showing no depression on fusion with an authentic sample. After the removal of the hydroperoxide, the filtrate was evaporated to dryness, giving 0.9 g of sym-octahydroacridine (III), mp 69° C (from hexane).

REFERENCES

1. V. A. Kaminskii and M. N. Tilichenko, KhGS [Chemistry of Heterocyclic Compounds], 3, 708, 1967.
2. M. Weiss, J. Am. Chem. Soc., 74, 200, 1952.
3. F. Chubb, A. S. Hay, and R. B. Sandin, J. Am. Chem. Soc., 75, 6042, 1953.
4. J. Colonge, J. Dreux, and H. Delplace, Bull. Soc., chim. France, 447, 1957.
5. M. N. Tilichenko and V. G. Kharchenko, ZhOKh, 30, 2283, 1960.
6. V. A. Kaminskii, V. I. Vysotskii, and M. N. Tilichenko, KhGS [Chemistry of Heterocyclic Compounds], 5, 373, 1969.

3 July 1967

Far Eastern State University,
Vladivostok

ELECTRONIC INTERACTION BETWEEN THE NITROGEN, OXYGEN, AND SILICON ATOMS IN THE MOLECULES OF α-AZIRIDIN-1-YLALKOXY(TRIETHYL)SILANES

V. A. Pestunovich, M. G. Voronkov, V. N. Perchenko, Yu. Yu. Popel,
L. G. Batalova, and N. S. Nametkin

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 4, pp. 753–755, 1969

UDC 546.287

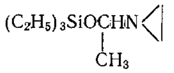
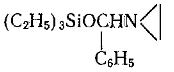
By the PMR method we have established the existence of a high frequency of the inversion of the nitrogen atom in the molecules of α-aziridin-1-ylalkoxysilanes. This is due to the fact that the high (because of $p_\pi - d_\pi$ bonding with the silicon atom) electronegativity of the oxygen atom in the Si—O—C—N system makes possible an interaction between the unshared electron pair of the nitrogen atom and the antibonding orbital of the C—O bond. The latter, in its turn, increases the degree of $p_\pi - d_\pi$ bonding between the oxygen and silicon atoms (in these compounds the order of the Si—O bond is greater than in the alkoxysilanes).

The α-aziridin-1-ylalkoxy(triethyl)silanes (I and II) which we were the first to study by the PMR method are, at the present time, the only synthetically accessible class of aminoalkoxysilanes containing a nitrogen atom in the α position with respect to the oxygen atom.

It might have been expected that in the molecules of these compounds the electronic interaction between the silicon, oxygen, and nitrogen atoms would have an extremely peculiar nature because of the possibility of the delocalization of the unshared electron pair of the nitrogen on the antibonding orbital of the C—O bond.

A similar interaction in the N—C—X system has recently been considered within the framework of the MO LCAO theory [1,2]. It was found that in this system the interaction should be enhanced to a considerable extent by an increase in the electronegativity of the X-atom. Furthermore, the delocalization of the unshared pair of electrons of the nitrogen atom on the antibonding orbital of the C—X bond is facilitated with a planar arrangement of the valence bonds of the N-atom. This is due to the fact that the orbital of the unshared pair of the nitrogen is closer to the 2p type, facilitating its maximum overlapping with the corresponding orbital of the C—X bond.

Chemical Shifts in the PMR Spectra of the α-Aziridin-1-ylalkoxysilanes and of Ethoxytriethylsilane in CCl_4 Solution

Compound	Formula	Chemical shifts (τ, ppm)					
		τ_{CH_2-Si}	$\tau_{CH_3(Si)}$	τ_{CH_3}	τ_{CH_2}	τ_{CH}	$\tau_{C_6H_5}$
I	 $(C_2H_5)_3SiOCH(CH_3)N(CH_2)_2$	9.49	9.13	8.86	8.71	5.92	—
II	 $(C_2H_5)_3SiOCH(C_6H_5)N(CH_2)_2$	9.49	9.13	—	8.53	5.13	2.74
III	$(C_2H_5)_3SiOC_2H_5$	9.30	9.04	8.86	6.38	—	—

The results of calculation have been used to explain the anomalously high rate of inversion of the nitrogen atom in the molecules of the aziridin-1-ylmethanols [2]. In these molecules, the above-mentioned interaction proves to be sufficiently great to decrease the energy of the planar state of the nitrogen atom during its inversion. In addition to this, replacing the hydrogen atom ($\sigma^* = 0.49$) by more highly electron-donating substituents—benzyl ($\sigma^* = 0.21$) or methyl ($\sigma^* = 0.00$) groups—leading to a decrease in the electronegativity of the oxygen atom with respect to the aziridinyl radical, markedly lowers the rate of inversion of the nitrogen atom in compounds of the type of $|\rangle N-CH_2OR$.

In the light of this information, in the Si—O—C—N system that we studied the silicon atom, the formal electronegativity of which is considerably lower than that of the carbon atom ($\varkappa_{Si} = 1.89$ and $\varkappa_C = 2.43$ [3]) should weaken the interaction of the unshared pair of electrons of the nitrogen atom with the antibonding orbital of the C—O bond.

We have shown that in the PMR spectra of α-azirindin-1-ylethoxy(triethyl)silane (I) and [aziridin-1-yl(phenyl)methoxy]triethylsilane (II), the signal of the methylene protons of the heterocycle is singlet, both at room temperature and when the sample is cooled to −80° C. This shows the extremely high rate of inversion of the nitrogen atom in these systems, which is observed in spite of the comparatively low electronegativity of the silicon atom.

In addition, the spectra of the compounds mentioned differ from the spectrum of ethoxytriethylsilane (III) by the relatively high values of the chemical shifts of the protons of the ethyl groups attached to the silicon atom (see table), which shows the high electron density on the latter.

Here we apparently encounter the mutual strengthening of the two types of interactions with an increase in the number of participating atoms. In actual fact, as shown previously [4], the silicon atom in the Si—O—C system is capable, to a large extent, of raising the electronegativity of the oxygen atom with respect to the carbon atom because of $p_\pi - d_\pi$ interaction. This increase in electronegativity apparently leads to a considerable delocalization of the unshared pair of the nitrogen atom on the antibonding orbitals of the C—O bond in the molecules of I and II which also explains the high frequency of inversion of the heterocycle even at low temperatures.

In addition to this, a partial increase in the electron density of the C—O bond permits the oxygen atom to participate in $p_\pi - d_\pi$ interaction with the silicon atom to a greater extent than in the molecules of the alkoxysilanes. In the final account, the over-all effect of the two types of interaction leads to a considerable transfer of charge from one part of the molecule (heterocycle) to the other (silicon atom).

EXPERIMENTAL

The methods for synthesizing and purifying the compounds I and II studied, and their physicochemical constants and analytical data have been given previously [5].

The PMR spectra were obtained on a YaMR-5535 TsLA spectrometer with a working frequency of 40 MHz. The compounds were studied in the form of solutions in carbon tetrachloride or, at low temperatures, in dichloromethane (10–20 mole-%). Tetramethylsilane was used as internal standard. The spectra were calibrated by the side-band method. The values of the chemical shifts were averaged from the results of not less than five measurements. The deviation did not exceed ± 0.02 ppm.

REFERENCES

1. E. A. C. Lucken, J. Chem. Soc., 2954, 1959.
2. V. F. Bystrov, R. G. Kostyanovskii, O. A. Pan'shin, A. U. Stepanyants, and O. Yu. Yuzhakova, Opt. i spektr., 19, 217, 1965.
3. M. G. Voronkov and I. F. Kovalev, Izv. AN LatvSSR, ser. khim., 158, 1965.
4. H. A. Brune, Chem. Ber., 97, 2829, 1964.
5. N. S. Nametkin, L. G. Batalova, V. N. Perchenko, and N. I. Ter-Asaturova, KhGS [Chemistry of Heterocyclic Compounds], 3, 106, 1967.

3 May 1967

Institute of Organic Synthesis
AS LatvSSR, Riga