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HETEROATOMIC DERIVATIVES OF AZIRIDINE.

15.* REACTION OF 1-(TRIETHYLSILYL)- AND 1-[2-(TRIALKYLSILYL)ETHYL]-AZIRIDINES WITH THIOLS

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The reaction of 1-(triethylsilyl)aziridine with alkanethiols proceeds with splitting out of aziridine and the formation of (alkylthio)triethylsilanes. The reaction of 1-(triethylsilyl)aziridine with 2-mercaptoethanol leads to 2-(triethylsilyloxy)ethanethiol; the same reaction in a closed system leads to [2-(2-aminoethylthiol)ethoxy]triethylsilane. 1-[2-(Trialkylsilyl)ethyl]aziridines react with 2-mercaptoethanol and with mercapto carboyxlic acids with opening of the aziridine ring.

Carbofunctional derivatives of organosilicon amines have a broad spectrum of biological activity. Their antiinflammatory, antispasmodic, and soporofic activity has been studied. These compounds are effective tranquilizers and agents for protection against radiation.

One of the methods for the synthesis of carbofunctional organosilicon amines is based on the reaction of (trialkylsilyl)- or (trialkoxysilyl) alkanethiols with aziridine, as well as on the reaction of 1-[(2-trialkylsilyl)ethyl]aziridines with thiols or thiophenols [3].

In order to obtain new types of biologically active organosilicon compounds, monomers for the synthesis of silicon-containing polymers, and complexones that are active with respect to transition metal ions we studied the reaction of 1-(triethylsilyl)aziridine (I) with alkanethiols and 2-mercaptoethanol and also accomplished the reaction of 1-[2-(trialkylsilyl)-ethyl]aziridines with 2-mercaptoethanol and mercaptosuccinic and 2-mercaptobenzoic acids.

Heating an equimolar mixture of 1-(triethylsilyl)aziridine (I) with propanethiol or butanethiol to 70°C with removal of the resulting aziridine by distillation leads to (alkylthio)triethylsilanes II and III in 60-65% yields. Thus cleavage of the Si—N bond rather than opening of the aziridine ring occurs in this case.

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*See [1] for Communication 14.

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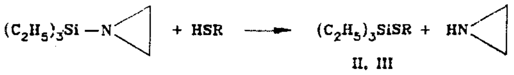
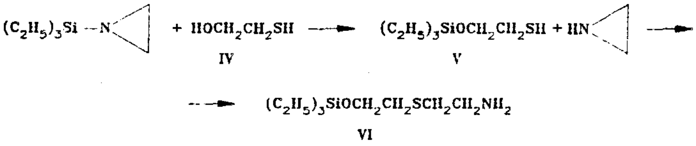
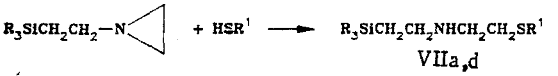


II $R=C_3H_7$; III $R=C_4H_9$

1-Triethylsilyl)aziridine (I) also reacts with 2-mercaptoethanol (IV) in THF at 55°C with splitting out of aziridine to give 2-(triethylsilyloxy)ethanethiol (V). The reaction between the same reagents in a sealed ampul at 100°C leads to [2-(2-aminoethylthio)ethoxy]-triethylsilane (VI) in 60% yield.



The reaction of 1-[2-(triethylsilyl)ethyl]aziridine with 2-mercaptoethanol (IV) proceeds with opening of the aziridine ring and the formation of amino sulfide VIIa in 45% yield. 1-[2-(Triethylsilyl)ethyl]aziridine and 1-[2-(tripropylsilyl)ethyl]aziridine react with 2-mercaptobenzoic or mercaptosuccinic acid via a similar scheme.



VII a $R=C_2H_5$, $R^1=CH_2CH_2OH$; b $R=C_2H_5$, $R^1=C_6H_4COOH$-2; c $R=C_3H_7$, $R^1=C_6H_4COOH$-2; d $R=C_2H_5$, $R^1=CH(COOH)CH_2COOH$

Absorption bands corresponding to Si–Alk vibrations (1010, 1250 cm^{-1}) are present in the IR spectra of II, III, and V–VIIa-d. In the spectra of II and III the frequencies of Si–S vibrations are found at 490-510 cm^{-1}. Vibrations of an Si–O bond are observed at 1056-1060 cm^{-1} in the spectra of V and VI. The frequencies of the vibrations of a sulfide group in the spectra of VI and VIIa-d are observed at 715-730 cm^{-1}, while the ν_{NH_2} band in the spectrum of VI is found at 3380 cm^{-1}. The spectrum of VIIa contains a broad absorption band at 3300-3400 cm^{-1}, which corresponds to the vibrations of associated NH and OH groups. A betaine structure should be assigned to VIIb-d, since their spectra contain NH_2^+ absorption bands at 3070, 1645, and 1560 cm^{-1}. The ionized carboxy group of these compounds absorbs at 1590 and 1375 cm^{-1}.

EXPERIMENTAL

The IR spectra were obtained with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Tesla BS-487-C spectrometer (80 MHz).

(Propylthio)triethylsilane (II). A mixture of 1.73 g (11 mmole) of aziridine I and 0.84 g (11 mmole) of propanethiol was heated to 70°C with removal of the aziridine formed in the reaction by distillation. The residue was removed by distillation in vacuo to give 1.26 g (60%) of II with bp 80-81°C (13 mm). Found: C 56.2; H 11.3; S 16.5; Si 14.4%. $C_9H_{22}SSi$. Calculated: C 56.6; H 11.6; S 16.8; Si 14.7%.

1-(Butylthio)triethylsilane (III). This compound was similarly obtained in 65% yield and had bp 110°C (15 mm) [bp 109-110°C (15 mm) [4]. Found: C 58.3; H 11.6; S 15.2; Si 13.4%. $C_{10}H_{24}SSi$. Calculated: C 58.7; H 11.8; S 15.7; Si 13.7%.

2-(Triethylsilyloxy)ethanethiol (V). A 1.56-g (20 mmole) sample of 2-mercaptoethanol (IV) in 30 ml of dry THF was added to a solution of 3.14 g (20 mmole) of aziridine I in 60 ml of dry THF, and the mixture was heated for 5 h at 55°C. The solvent was removed by distillation, and the residue was distilled in vacuo to give 1.52 g (40%) of V with bp 62-64°C (2 mm). PMR spectrum: 0.50, 0.90 [m, $(C_2H_5)_3Si$], 2.67 (m, CH_2S), 3.60 ppm (m, CH_2O). Found: C 49.5; H 10.2; S 16.2; Si 14.3%. $C_8H_{20}OSSi$. Calculated: C 49.9; H 10.4; S 16.6; Si 14.6%.

[2-(2-Aminoethylthio)ethoxy]triethylsilane (VI). A mixture of 2.0 g (13 mmole) of aziridine I and 1.1 g (13 mmole) of 2-mercaptoethanol was heated in a sealed ampul at 100°C for 16 h, after which it was distilled in vacuo to give 1.8 g (60%) of VI with bp 135°C (1 mm). PMR spectrum: 0.62, 0.90 [m, $(C_2H_5)_3Si$], 2.77 (m, CH_2N, CH_2S), 3.80 ppm (m, CH_2O). Found: C 49.6; H 10.4; N 5.6; S 13.2; Si 11.7%. $C_{10}H_{25}NOSSi$. Calculated: C 51.0; H 10.7; N 6.0; S 13.6; Si 11.9%.

2-[2-[2-(Triethylsilyl)ethylamino]ethylthio]ethanol (VIIa). A solution of 0.93 g (12 mmole) of 2-mercaptoethanol in 20 ml of propyl alcohol was added to a solution of 2.2 g (12 mmole) of 1-[2-(triethylsilyl)ethyl]aziridine in 50 ml of propyl alcohol, after which the mixture was heated for 5 h at 90°C. The solvent was removed by distillation, and the residue was distilled in vacuo to give 1.4 g (45%) of VIIa with bp 159-160°C (0.5 mm). PMR spectrum: 0.60, 0.90 [m, $(C_2H_5)_3Si$], 2.70 (m, CH_2S), 3.20 (m, CH_2N), 3.80 ppm (m, CH_2O). Found: C 54.4; H 11.1; N 5.1; S 12.6; Si 11.2%. $C_{12}H_{29}ONSSi$. Calculated: C 54.7; H 11.1; N 5.3; S 12.2; Si 10.7%.

2-[2-[2-(Triethylsilyl)ethylamino]ethylthio]benzoic Acid (VIIb). [5]. A solution of 1.0 g (53 mmole) of 1-[2-(triethylsilyl)ethyl]aziridine in 5 ml of methanol was added at room temperature to a solution of 0.82 g (53 mmole) of 2-mercaptobenzoic acid in 20 ml of methanol, and the resulting precipitate was separated, washed with methanol, and recrystallized from DMSO to give 1.63 g (89%) of a product with mp 260°C. Found: C 59.3; H 8.6; N 4.0; S 9.4; S 8.6%. $C_{17}H_{29}NO_2SSi$. Calculated: C 60.1; H 8.6; N 4.2; S 9.4; Si 8.3%.

2-[2-[2-(Tripropylsilyl)ethylamino]ethylthio]benzoic Acid (VIIc). This compound was similarly obtained in 85% yield and had mp 218-219°C. Found: C 63.2; 8.9; 3.5; S 7.8; Si 7.6%. $C_{20}H_{35}NO_2SSi$. Calculated: C 62.9; H 9.3; N 3.7; S 8.4; Si 7.4%.

2-[2-[2-(Triethylsilyl)ethylamino]ethylthio]succinic Acid (VIId). This compound was similarly obtained in 70% yield in the form of a thick oil. Found: C 49.5; H 9.0; N 3.7; S 9.9; Si 8.8%. $C_{14}H_{29}NO_4SSi$. Calculated: C 50.1; H 8.7; N 4.2; S 9.5; Si 8.4%.

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