HETEROATOM DERIVATIVES OF AZIRIDINE

VIII.* ORGANOSILICON DERIVATIVES OF 2-AMINOETHANETHIOL

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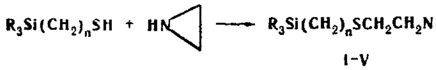
N-Trialkylsilyl- and N-trialkoxysilyl-2-aminoethanethiols were obtained by reaction of aziridine with trialkylsilyl- and trialkoxysilylalkanethiols or 1-(2-trialkylsilylethyl)aziridines with aliphatic and aromatic thiols.

Organosilicon derivatives of aminoalkyl sulfides have been synthesized on the basis of reactions of aminoalkanethiols with Si-substituted aminosilanes, vinylsilanes, and chloroalkylsilanes [2]. Mannich reaction between trialkylsilylalkanethiols and alkenylamines or amines [3] is also a convenient method for their preparation. The bacteriostatic activity of some organosilicon derivatives of aminoalkylsulfides has been studied [3].

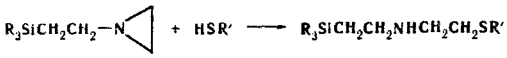
In order to obtain new types of biologically active organosilicon compounds we found new methods for the synthesis of N-trialkylsilyl and N-trialkoxysilyl derivatives of 2-aminoethanethiol (Table 1). Aziridine reacts readily with trialkylsilyl- and trialkoxysilylalkanethiols in methanol at 55-60 deg C.



I-V

I $n=1$, $R=C_2H_5$; II $n=2$, $R=C_2H_5$; III $n=3$, $R=CH_3$;
IV $n=1$, $R=CH_3O$; V $n=3$, $R=CH_3O$

More severe conditions (120 deg C for 15 h) are necessary to open the aziridine ring in 1-(2-trialkylsilylethyl)aziridines by aliphatic and aromatic thiols.



VI-IX

VI $R=C_2H_5$, $R'=n\text{-}C_3H_7$; VII $R=C_2H_5$, $R'=n\text{-}C_4H_9$; VIII $R=C_2H_5$, $R'=C_6H_5$;
IX $R=n\text{-}C_3H_7$, $R'=C_6H_5$

Methyl iodide reacts with trialkyl[(2-aminoethylthio)alkyl]silanes I and III in ether to give hydriodides of the corresponding secondary amines (X, XI).

Trimethoxy[(2-aminoethylthio)methyl]silane (IV) reacts with triethylamine in the same way as organyltrialkoxysilanes [4] to give the previously unknown 1-[(2-aminoethylthio)methyl]silatrane (XII):

$$N(CH_2CH_2OH)_3 + (CH_3O)_3SiCH_2SCH_2CH_2NH_2 \longrightarrow \underset{XII}{N(CH_2CH_2O)_3SiCH_2SCH_2CH_2NH_2}$$

EXPERIMENTAL

The PMR spectra of CCl_4 (for I-VI and IX), D_2O (for X and XI), and dimethyl sulfoxide (DMSO) (for XII) solutions were obtained with a Tesla BS 487C spectrometer (80 MHz). The chemical shifts are presented on the δ scale with respect to tetramethylsilane.

Triethyl[(2-aminoethylthio)methyl]silane (I). A mixture of 2.41 g (0.015 mole) of triethylsilylmethanethiol and 0.65 g (0.015 mole) of aziridine in 40 ml of methanol was heated at 55-60 deg C for 4 h, after which the solvent was removed by distillation, and the residue was fractionated in vacuo to give 1.0 g (33%) of silane I with bp 127-128 deg C (3 mm) [5]. Compounds II-V were similarly obtained (Table 1).

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*See [1] for communication VII.

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TABLE 1. Organosilicon Derivatives of 2-Aminoethanethiol

	Compound	bp, °C (mm)	n_D^{20}	Found, %					Empirical formula	Calc., %					Yield, %
				C	H	N	S	Si		C	H	N	S	Si	
I	$(C_2H_5)_3SiCH_2SCH_2CH_2NH_2$	127—128 (3)	1,4998	52,7	11,3	6,5	14,7	13,4	$C_9H_{23}NSSi$	52,6	11,3	6,8	15,6	13,7	33
II	$(C_2H_5)_3SiCH_2CH_2SCH_2CH_2NH_2$	135—137 (1)	1,4932	54,9	11,8	6,5	14,3	13,0	$C_{10}H_{25}NSSi$	54,7	11,5	6,4	14,6	12,8	30
III	$(CH_3)_3SiCH_2CH_2CH_2SCH_2CH_2NH_2$	88—90 (2)	1,4812	50.3	10,6	6,9	16,6	14,2	$C_8H_{21}NSSi$	50,2	11,1	7,3	16,8	14,7	45
IV	$(CH_3O)_3SiCH_2SCH_2CH_2NH_2$	75—76 (0,1)	1,4703	34,1	8,3	6,3	14,8	12,9	$C_6H_{17}NO_3SSi$	34,1	8,1	6,6	15,2	13,3	30
V	$(CH_3O)_3SiCH_2CH_2CH_2SCH_2CH_2NH_2$	89—91 (0,01)	1,4685	39,9	8,7	5,5	13,2	11,6	$C_8H_{21}NO_3SSi$	40,1	8,9	5,8	13,4	11,7	40
VI	$(C_2H_5)_3SiCH_2CH_2NHCH_2CH_2SC_3H_7$	145—146 (4)	1,4730	59,4	11,7	5,5	11,8	10,6	$C_{13}H_{31}NSSi$	59,7	12,0	5,4	12,3	10,7	50
VII	$(C_2H_5)_3SiCH_2CH_2NHCH_2CH_2SC_4H_9$	180—182 (5)	1,4809	61,5	11,8	4,9	11,2	10,2	$C_{14}H_{33}NSSi$	61,0	12,1	5,1	11,6	10,2	55
VIII	$(C_2H_5)_3SiCH_2CH_2NHCH_2CH_2SC_6H_5$	130—131 (0,01)	1,5433	64,6	9,6	5,3	11,3	10,4	$C_{16}H_{29}NSSi$	65,0	9,9	4,7	10,8	9,5	72
IX	$(C_3H_7)_3SiCH_2CH_2NHCH_2CH_2SC_6H_5$	194—196 (4)	1,5285	67,7	10,4	4,2	9,5	8,1	$C_{19}H_{35}NSSi$	67,6	10,4	4,2	9,5	8,3	65

TABLE 2. Parameters of the PMR Spectra of Organosilicon Derivatives of 2-Aminoethanethiol (δ, ppm)

Compound	R_3Si		$SiCH_2$	$Si—C—CH_2$	CH_2S	CH_2N	$NH_2(NH)$	SC_3H_7, SC_6H_5
	CH_2	$CH_3(OCH_3)$						
I	0,63 (m)	0,92 (m)	1,75 (s)	—	2,55 (m)	2,80 (m)	1,42 (s)	
II	0,67 (m)	0,94 (m)	0,67 (m)	2,62 (m)	2,65 (m)	2,80 (m)	1,35 (s)	
III	—	0,05 (s)	0,67 (m)	1,70 (m)	2,45—2,58 (m)	2,86 (m)	1,35 (s)	
IV	—	3,53 (s)	1,77 (s)	—	2,59 (m)	2,79 (m)	1,65 (s)	
V	—	3,50 (s)	0,74 (m)	1,61 (m)	2,50 (m)	2,75 (m)	1,25 (s)	
VI	0,57 (m)	0,93 (m)	0,57 (m)	2,65 (m)	2,44 (m)	2,65 (m)	1,84 (s)	2,44 (t); 1,54 (t); 0,93 (t)
IX	0,50; 1,28 (m)	0,93 (m)	0,60 (m)	2,75 (m)	2,50 (m)	2,75 (m)	—	7,12 (m)

Propyl 2-[2-(Triethylsilyl)ethylamino]ethyl Sulfide (VI). A mixture of 1.60 g (8 mmole) of triethyl(2-aziridinoethyl)silane and 0.90 g (12 mmole) of propanethiol was heated in a sealed ampul at 120 deg C for 15 h, after which sulfide VI was removed by vacuum distillation to give 1.12 g (50%) of a product with bp 145-146 deg C (4 mm). Compounds VII-IX were similarly synthesized (Table 1).

2-Methylaminoethyl Triethylsilylmethyl Sulfide Hydriodide (X). A 0.20-g (1.4 mmole) sample of methyl iodide was added to a solution of 0.30 g (1.4 mmole) of aminosilane I in 15 ml of absolute ether, and the crystalline precipitate that formed in the course of 30 min was removed by filtration, washed with absolute ether, and dried in vacuo to give 0.20 g (40%) of a product with mp 203-204 deg C. PMR spectrum: 0.63 (6H, m, CH_2), 0.92 (9H, m, CH_3), 1.98 (2H, m, $SiCH_2$), 2.95 (2H, m, SCH_2), 3.17 (3H, s, $\overset{+}{N}CH_3$), and 3.46 ppm (2H, m, NCH_2). Found: S 8.9%. $C_{10}H_{25}NSSi \cdot HI$. Calculated: S 9.2%.

2-Methylaminoethyl 3-(Trimethylsilyl)propyl Sulfide Hydriodide (XI). This compound was similarly obtained from 0.60 g (3.0 mmole) of aminosilane III and 0.43 g (3.0 mmole) of methyl iodide after 6 h. Workup gave 0.29 g (28%) of a product with mp 177-178 deg C. PMR spectrum: 0.05 [9H, s, $(CH_3)_3Si$], 0.65 (2H, m, SCH_2), 1.61 (2H, m, CH_2), 2.70-2.98 (4H, m, CH_2SCH_2), 3.20 (3H, s, $\overset{+}{N}CH_3$), and 3.62 ppm. (2H, m, NCH_2). Found: S 9.4%. $C_9H_{23}NSSi \cdot HI$. Calculated: S 9.6%.

1-[(2-Aminoethylthio)methyl]silatrane (XII). A mixture of 0.80 g (3.8 mmole) of aminosilane IV, 0.60 g (3.8 mmole) of triethanolamine, and 0.1 g of KOH in 50 ml of dry toleuene was heated, during which the resulting methanol was removed by distillation. The mixture was then cooled, and the crystals of XII that precipitated were recrystallized from chloroform to give 0.65 g (61%) of a product with mp 161-162 deg C. PMR spectrum: 1.36 (2H, s, $SiCH_2S$), 2.81 (6H, m, NCH_2), 3.40 (2H, m, NH_2), and 3.62 ppm (6H, m, OCH_2). Found: C 41.0; H 7.8; N 10.0; Si 10.3%. $C_9H_{20}N_2O_3SSi$. Calculated: C 40.9; H 7.6; N 10.6; Si 10.6%.

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HETARYLATION OF INDOLIZINES

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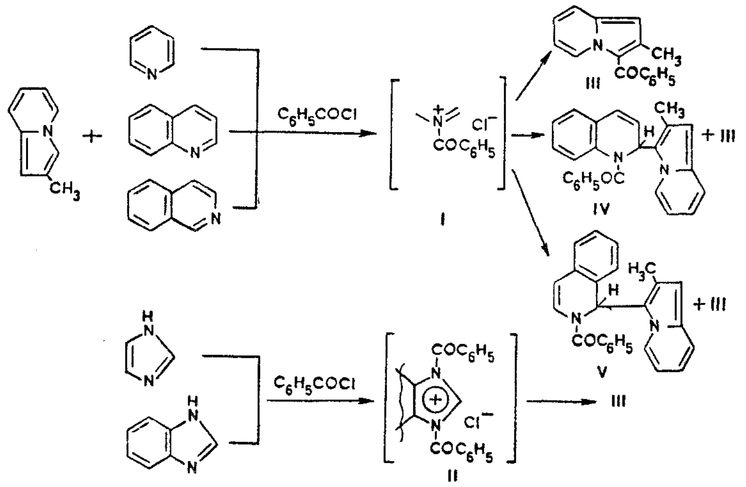
The direct incorporation of quinoline, isoquinoline, acridine, imidazole, and benzimidazole residues in the indolizine ring was accomplished by reaction of N-heteroaromatic compounds with indolizine derivatives in the presence of acylating agents.

Indolizine readily undergoes electrophilic substitution reactions, during which the 1 and 3 positions, the relative reactivities of which in these reactions are determined by the 1 : 3 isomer ratio, undergo electrophilic attack [1].

We have found that 2-methylindolizine may undergo both hetarylation [2] and acylation on reaction with N-heteroaromatic systems in the presence of acyl halides. Heterocyclic derivatives of the IV and V type are formed in the hetarylation of 2-methylindolizine, whereas 2-methyl-3-acylindolizines III are obtained in the case of acylation:



The relative amounts of acylation and hetarylation products depend on many factors but mainly on the nature of the N-heteroaromatic cation.

Thus only acylation of the indolizine ring with the quantitative formation of III occurs when N-acyl pyridinium salts I in situ and N,N'-diacylimidazolium and benzimidazolium chlorides II are used. The more stable N-acyl quinolinium and isoquinolinium cations form both types of reaction products, during which the formation of 2-methyl-3-acylindolizine III proceeds to a greater extent with quinoline than with isoquinoline. Characteristic $\nu_{C=O}$ bands at 1660-1680 cm^{-1} and $\nu_{C=C}$ bands at 1610-1620 cm^{-1} are observed in the IR spectra of hetarylation products IV and V; this, taken together with the set of mass spectrometric data – the presence in the spectra of a molecular ion, C$_6$H$_5$CO fragments, and fragments of quinoline, isoquinoline, and indolizine residues – confirms their structure [3].

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