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HETEROATOMIC DERIVATIVES OF AZIRIDINE.

11.* REACTION OF AZIRIDINE WITH TRIALKYLSILANETHIOLS

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The reaction of aziridine with trialkylsilanethiols in dry tetrahydrofuran (THF) at 55-60°C, which leads to the formation of mixtures of substances [according to the data from the IR and PMR spectra, hexalkyldisilyl sulfides, 2-mercaptoethylamine, trialkyl(2-aminoethylthio)silanes, and 1-trialkylsilylamino-2-trialkylsilylthio-ethanes], was studied. 2-Mercaptoethylamine and 1-trialkylsilylamino-2-trialkyl-silylthioethanes, the structures of which were established on the basis of the IR and PMR spectra, were isolated in pure form.

We have previously obtained N-trialkylsilyl and N-trialkoxysilyl derivatives of 2aminoethanethiol by the reaction of aziridine with trialkylsilyl- and trialkoxysilylalkanethiols [2]. In order to obtain new types of biologically active organosilicon compounds we accomplished the synthesis of 1-trialkylsilylamino-2-trialkylsilylthioethanes (VIIa-c) by the reaction of aziridine with trialkylsilanethiols.

The reaction of aziridine with trialkylsilanethiols Ia-c proceeds in dry tetrahydrofuran (THF) at 55-60°C in 4 h.



1. 11, 1V VII **a** $R = R' = R'' - C_2 H_5$; **b** $R = C_2 H_5$, $R' = R'' = n - C_3 H_7$; **c** $R = C_2 H_5$, $R' = R'' = i - C_4 H_9$

*See [1] for communication 10.

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The intermediate formation of trialkyl(aziridino)silanes VIa-c is evidently the result of nucleophilic attack by the aziridine molecule on the coordination-unsaturated silicon atom of silanethiols Ia-c, which leads to four-center complexes Va-c, the decomposition of which gives VIa-c and hydrogen sulfide. The absence in the reaction mixture of aziridinosilanes VIa-c and the products of their reaction with H_2S , viz., the hypothetical N-trialkylsilyl-2-aminoethanethiols, indicates that the hydrogen sulfide may react with aziridinosilanes VIa-c without opening of the aziridine ring to give again trialkylsilanethiols Ia-c. At the same time, trialkylsilanethiols Ia-c, which have heightened nucleophilicity as compared with hydrogen sulfide, react with aziridinosilanes VIa-c with opening of the aziridine ring and the formation of 1-trialkylsilylamino-2-trialkylsilylthioethanes (VIIa-c). In order to confirm this assumption, we studied the reaction of triethylsilanethiol with triethyl(aziridino)silane in dry THF at 55-60°C for 4 h. 1-Triethylsilylamino-2-triethylsilylthioethane (VIIa) was obtained in 65% yield.

Trialkyl(2-aminoethylthio)silanes (IVa-c) are formed in the first step of the reaction of aziridine with silanethiols Ia-c, but they subsequently react with a second molecule of silanethiols Ia-c to give 1-trialkylsilylamino-2-trialkylsilylthioethanes (VIIa-c). We were unable to isolate trialkyl(2-aminoethylthio)silanes IVa-c in pure form because of the presence of a difficult-to-remove admixture of the corresponding hexaalkyldisilyl sulfides IIa-c.

EXPERIMENTAL

The IR spectra of the compounds were obtained with a UR-20 spectrometer. The PMR spectra of solutions in CCl₄ were recorded with a Tesla BS487C spectrometer (80 MHz). The chemical shifts are presented on the δ scale with respect to tetramethylsilane.

Triethylsilanethiol (Ia) was obtained by the method in [3]. The previously unknown ethyl(di-n-propyl)silanethiol [Ib, bp 112-115°C (20 mm) and n_D^2 ° 1.4610] and ethyl(disobutyl)-silanethiol [Ic, bp 95°C (8 mm) and n_D^2 ° 1.4630] were similarly obtained by reaction of the corresponding trialkylsilanes with sulfur at 240°C.

<u>1-Triethylsilylamino-2-triethylsilylthioethane (VIIa).</u> A) A solution of 1.2 g (28 mmole) of aziridine in 10 ml of dry THF was added to a solution of 4.0 g (28 mmole) of triethylsilanethiol (Ia) in 40 ml of dry THF, and the mixture was heated at 55-60°C for 4 h. The solvent was then removed by distillation, and the precipitated 2-mercaptoethylamine (III) was removed by filtration and recrystallized from ethanol to give 0.47 g of a product with mp 98-99°C [4]. Vacuum distillation of the filtrate gave a mixture of hexaethyldisilyl sulfide (IIa) and triethyl(2-aminoethylthio)silane (IVa) [0.55 g; bp 100-105°C (3 mm). PMR spectrum: 0.71 (18H, q, SiCH₂), 1.03 (27H, m, CH₃), 2.66 (2H, t, SCH₂), and 2.93 ppm (2H, m, NCH₂)], as well as 1.35 g (33%) of VIIa with bp 143-145°C (3 mm) and n_2^{22} 1.4838. IR spectrum: 3370 (NH), 1010 and 1245 [(C₂H₅)₃Si], and 490-510 cm⁻¹ (Si-S). PMR spectrum: 0.55 (12H, q, SiCH₂), 0.93 (18H, t, CH₃), 2.41 (2H, t, -SCH₂), and 2.80 ppm (2H, m, -NCH₂). Found: C 55.2; H 11.6; N 4.9; S 10.3; Si 17.2%. C₁₄H₃₅NSSi₂. Calculated: C 55.1; H 11.5; N 4.6; S 10.5; Si 18.3%.

B) A mixture of 2.0 g (13.5 mmole) of triethylsilanethiol and 2.1 g (13.5 mmole) of triethyl(aziridino)silane in 30 ml of dry THF was heated at 55-60°C for 4 h, after which the solvent was removed by distillation, and the residue was distilled in vacuo to give 2.7 g (65%) of VIIa with bp $142-145^{\circ}$ C (3 mm) and $n_{D}^{2^{\circ}}$ 1.4824.

<u>1-Ethyl(di-n-propyl)silylamino-2-ethyl(di-n-propyl)silylthioethane (VIIb)</u>. This compound was similarly obtained from 6.2 g (35 mmole) of silanethiol Ib and 1.5 g (35 mmole) of aziridine. The product [2.4 g (38%)] had bp 160-162°C (2 mm) and $n_{\rm H}^{2^2}$ 1.4760. IR spectrum: 3380 (NH), 1010 and 1205 [C₂H₅(n-C₃H₇)₂Si], and 490-510 cm⁻¹ (Si-S). PMR spectrum: 0.60 (12H, m, SiCH₂), 1.33 (8H, m, Si-C-CH₂), 0.90 (18H, t, CH₃), 2.40 (2H, t, SCH₂), and 2.79 ppm (2H, m, NCH₂). Found: C 59.9; H 12.1; N 3.9; S 9.5; Si 15.8%. C₁₈H₄₃NSSi₂. Calculated: C 59.7; H 12.0; N 3.8; S 8.9; Si 15.5%.

<u>1-Ethyl(diisobutyl)silylamino-2-ethyl(diisobutyl)silylthioethane (VIIc).</u> This compound was similarly obtained from 5.5 g (27 mmole) of silanethiol Ic and 1.16 g (27 mmole) of aziridine. The product [2.1 g (38%)] had bp 185-188°C (2 mm) and $n_D^{2^\circ}$ 1.4812. IR spectrum: 3360 (NH), 1010 and 1205 [C₂H₅(iso-C₄H₉)₂Si], and 490-510 cm⁻¹ (Si-S). PMR spectrum: 0.68 (12H, m, SiCH₂), 1.0 (4H, m, Si-C-CH), 0.90 (30H, m, CH₃), 2.48 (2H, t, SCH₂), and

2.81 ppm (2H, m, NCH₂). Found: C 63.0; H 11.9; N 3.1; S 8.0; Si 12.7%. C_{22H₅₁NSSi₂. Calculated: C 63.2; H 12.3; N 3.3; S 7.7; Si 13.4%.}

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SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF 5-ACETYL-SUBSTITUTED INDOLINOSPIROCHROMENES

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Four photochromic 5-acetyl-substituted indolinospirochromenes were synthesized. The introduction of an acetyl group does not change the spectral characteristics of the merocyanine form but leads to a decrease in the efficiency of photocoloring.

The photocoloring of indolinospirochromenes can be sensitized in a number of cases by aromatic ketones, particularly acetophenone derivatives [1, 2]. The existence of triplet—triplet transfer of energy between the two halves of the spirochromene molecule makes it possible to assume that the indoline part is an internal sensitizer with respect to the chromene part, in which the photoreaction occurs [3]. In this connection, it seemed of interest to synthesize and study the properteis of 5-acetyl-substituted indolinospirochromenes, the indoline part of which can be regarded as a 4-aminoacetophenone derivative.

By exhaustive methylation of 5-acetylindole [4] by the action of methyl iodide in an autoclave and subsequent treatment of the resulting 1,2,3,3-tetramethyl-5-acetylindoleninium iodide with alkali we obtained 1,3,3-trimethyl-5-acetyl-2-methyleneindoline, which reacted readily with substituted nitrosalicylaldehydes to give indolinospirochromenes Ia-d:



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