

REACTIONS OF TRIETHYLSILANETHIOL AND THE RELATED COMPOUNDS WITH TRIETHYLALUMINUM, -GALLIUM AND -INDIUM

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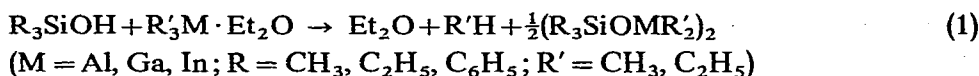
SUMMARY

Stepwise cleavage of carbon-aluminum bonds was observed in the reaction of triethylsilanethiol, $(C_2H_5)_3SiSH$, with triethylaluminum in hexane. Colourless crystalline associates $[(C_2H_5)_3SiAl(C_2H_5)_2]_2$, $\{[(C_2H_5)_3Si]_2AlC_2H_5\}_{1.4}$ or $[(C_2H_5)_3SiSAIS]_x$ were formed respectively by the reaction of $(C_2H_5)_3Al$ with one, two or three moles of silanethiol. The first two complexes were found to be thermally unstable disproportionating into $[C_2H_5AIS]_x$, $[(C_2H_5)_3Si]_2S$ and $(C_2H_5)_3Al$ and $[C_2H_5AIS]_x$ and $[(C_2H_5)_3Si]_2S$, respectively.

Triethylsilaneselenol and -tellurol react analogously with triethylaluminum, -gallium and -indium.

INTRODUCTION

The etherates of trialkylaluminum, -gallium and -indium undergo a selective heterolytic cleavage of the metal-carbon bond with an equimolar quantity of triorganosilanol¹⁻⁴ providing the cyclic heterosiloxanes $[R_3SiOMR'_2]_2$ ($M=Al, Ga, In$).



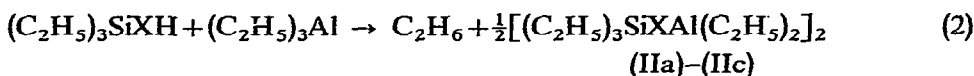
Similarly, heterogermoxanes $[(C_6H_5)_3GeOGa(C_6H_5)_2]_2$ and $[(C_6H_5)_3GeOGa(CH_3)_2]_2$ have been obtained⁵. However, it was not mentioned whether the derivatives of the type $(R_3SiO)_2MR'$, where $M=Al, Ga, In$, can be obtained in an analogous way. The known compounds of this series $[(CH_3)_3SiO]_2MCH_3$ have been prepared by the reaction of CH_3MCl_2 with two equivalents of $(CH_3)_3SiONa$ ⁶.

Also compounds of the type $(R_3SiXAIR_2)_2$ ($X=S, Se, Te$) have not been obtained. But accounting for decreasing donor ability $O > S > Se > Te$ ⁷, one may expect that the said associates and oxygen-containing analogous should have different physical and chemical properties.

RESULTS AND DISCUSSION

Interaction of unsolvated triethylaluminum with an equimolar amount of triethylsilanol in hexane at 0-10° affords ethane and diethyl(triethylsiloxy)aluminum

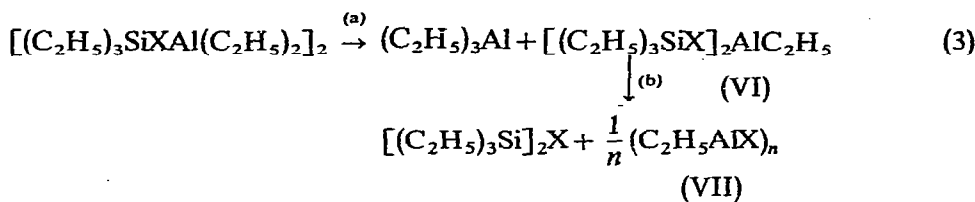
(I) (cf. ref. 3) in almost quantitative yield. Under the comparable conditions the reaction of triethylaluminum with triethylsilanethiol, -selenol or -tellurol gave ethane and corresponding derivative with Si-X-Al grouping (X=S, Se, Te) via selective scission of the C-Al bond.



[(a), X=S; (b), X=Se; (c), X=Te]

An analogous reaction with triethylgermaneselenol, $(C_2H_5)_3GeSeH$, gives $[(C_2H_5)_3GeSeAl(C_2H_5)_2]_{1.7}$ (III); the reactions of triethylsilaneselenol with triethylgallium and -indium lead respectively to $[(C_2H_5)_3SiSeGa(C_2H_5)_2]_2$ (IV) and $[(C_2H_5)_3SiSeIn(C_2H_5)_2]_2$ (V). The cryoscopic molecular weight determination shows that in benzene the compounds (I), (IIa), (IIb), (III), (IV) and (V) are associates. We failed to determine the molecular weight of (IIc) owing to its thermal instability.

All the associates prepared may be isolated as colourless crystalline solids by crystallization at low temperature from the reaction mixtures in hexane. However, the complexes (I) and (V) are liquids at room temperature. All these compounds have been found to be hydrolytically unstable and susceptible to oxidation. Unlike heterosiloxane (I) which is thermally stable and does not decompose during vacuum distillation, its analogues containing the Si-S-Al, Si-Se-Al and Si-Te-Al groupings undergo disproportionation according to the scheme:

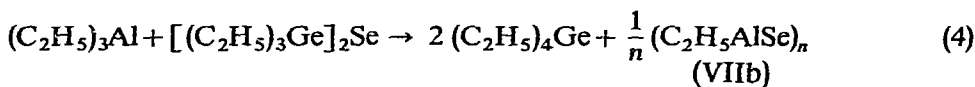


[(a), X=S; (b), X=Se; (c), X=Te]

The selenium and tellurium derivatives were found to be unstable in the solid state and in solution even at room temperature. It is very likely that reactions (3) proceed via $[(C_2H_5)_3SiX]_2AlC_2H_5$ (VI) as an intermediate. The view is further supported by the fact that disproportionation of bis(triethylsilylthio)ethylaluminum (VIa) at 80° proceeds to give bis(triethylsilyl) sulfide and ethylaluminum sulfide (VIIa), i.e. according to eqn. (3b) [see also eqn. (5b)].

A quantitative yield of the virtually insoluble ethylaluminum selenide (VIIb) allows to conclude that diethyl(triethylgermylseleno)aluminum (III) disproportionates analogously to eqn. (3). But fractionation of the liquid from the reaction mixture gives tetraethylgermane and an additional amount of (VIIb).

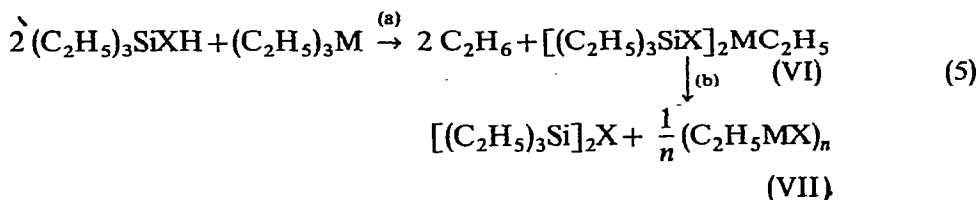
However separate experiments showed that triethylaluminum can react with bis(triethylgermyl) selenide at 130° ($\frac{1}{2}$ h), to produce tetraethylgermane and (VIIb).



Compared with other associates, the gallium and indium complexes (IV) and (V) are more stable. The gallium complex disproportionates only at 220° according

to eqn. (3). A pure sample of (V) decomposed completely after 1 h at 170° *in vacuo* in a sealed tube. Relatively large quantities of bis(triethylsilyl) selenide and tetraethylsilane were identified amongst the decomposition products.

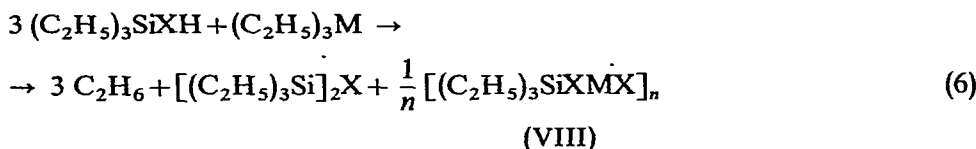
In the reaction of triethylaluminum with two equivalents of $(C_2H_5)_3SiXH$ ($X=S, Se$) in hexane only one mole of ethane was evolved during the course of exothermic reaction. The second mole of ethane was evolved only after leaving the reaction mixture for a long time at room temperature or heating to 65° (20–30 min). The disubstituted product formed, $[(C_2H_5)_3SiX]_2AlC_2H_5$, can be isolated only when $X=S$. Its selenium analogue (VIb) cleaves under the reaction conditions according to eqn. (5b). Attempts to prepare bis(triethylsilylseleno)ethylgallium (VIc) and -indium (VIe) were also unsuccessful. These compounds immediately decompose to give the products of disproportionation.



[(a), $X=S, M=Al$; (b), $X=Se, M=Al$; (d), $X=Se, M=Ga$; (e), $X=Se, M=In$]

The compounds (VIIa)–(VIIe) are probably coordination polymers. These have high decomposition points and are insoluble in non-donor solvents, but moderately soluble in tetrahydrofuran and pyridine.

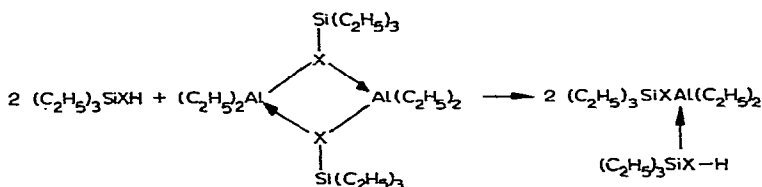
The reaction of triethylaluminum and -indium with three equivalents of $(C_2H_5)_3SiXH$ ($X=S, Se$) can be represented by the following equation:



[(a), $X=S, M=Al$; (b), $X=Se, M=Al$; (c), $X=Se, M=In$]

Again in these reactions the replacement of a second or third ethyl group requires more vigorous conditions. The compounds (VIIIa)–(VIIIc) are colourless virtually insoluble crystalline solids with high decomposition points.

It may be assumed that in the reactions (2), (5) and (6) a heterolytic fission of the C–Al (respectively C–Ga and C–In) bond is preceded by formation of the donor–acceptor complex between the cleaving agent and organometallic compound. In such a case the necessity to employ the more vigorous conditions for preparing the



disubstituted products (VI) [see eqn. (5)] is explained by the fact that the heterolytic cleavage of the second C–M bond should be preceded by dissociation of the two coordination bonds X–M in the cyclic associates generating in reaction (2). As for a heterolytic fission of the C–M bond, apparently, this involves the four-center transition state and a simultaneous nucleophilic attack at the atom M and electrophilic attack at the α -carbon of the ethyl group.

EXPERIMENTAL

All the reactions were carried out in an evacuated sealed ampoule or under an atmosphere of dry argon. GLC analyses of bis(triethylsilyl) sulfide and its analogues

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE COMPOUNDS OBTAINED

No.	Compound	Yield (%)	M.p. (°C)	Mol.wt. found (calcd.)	Analysis found (calcd.) (%)	
					C	H
(I)	$[(C_2H_5)_3SiOAl(C_2H_5)_2]_2$	30.7	26–27 ^a	412 (216.38)		
(IIa)	$[(C_2H_5)_3SiSAl(C_2H_5)_2]_2$	43.2	33–35	445 (232.43)	51.47 (51.67)	10.80 (10.84)
(IIb)	$[(C_2H_5)_3SiSeAl(C_2H_5)_2]_{1.7}$	83.4	54–55	470 (279.33)	43.17 (42.99)	9.09 (9.02)
(IIc)	$(C_2H_5)_3SiTeAl(C_2H_5)_2$	35.5	33–34(decompn.)		36.05 (36.62)	7.77 (7.68)
(III)	$[(C_2H_5)_3GeSeAl(C_2H_5)_2]_{1.7}$	62.1	53	550 (323.83)	37.01 (37.09)	7.95 (7.78)
(IV)	$[(C_2H_5)_3SiSeGa(C_2H_5)_2]_2$	35.2	47	709 (322.07)	37.01 (37.29)	8.12 (7.82)
(V)	$[(C_2H_5)_3SiSeIn(C_2H_5)_2]_2$	17.5	–55––54	658 (367.17)	33.02 (32.71)	7.25 (6.86)
(VIa)	$\{[(C_2H_5)_3SiS]_2AlC_2H_5\}_{1.4}$	97.4	^b	492 (350.72)	47.86 (47.95)	10.07 (10.06)
(VIIa)	$(C_2H_5AlS)_n$	99.3 ^c	480(decompn.)		27.87 (27.97)	5.94 (5.72)
(VIIb)	$(C_2H_5AlSe)_n$	82.5 ^d	376		17.95 (17.79)	3.45 (3.73)
(VIIc)	$(C_2H_5AlTe)_n$	98.6 ^d	352(decompn.)		12.59 (13.08)	3.18 (2.74)
(VIId)	$(C_2H_5GaSe)_n$	95.0 ^{c,e}	360–410(decompn.)		11.51	2.42
(VIIe)	$(C_2H_5InSe)_n$	87.2 ^c	280(decompn.)		(10.78)	(2.26)
(VIIIa)	$[(C_2H_5)_3SiSAlS]_n$	82.5	350(decompn.)		34.98 (34.92)	7.53 (7.33)
(VIIIb)	$[(C_2H_5)_3SiSeAlSe]_n$	63.9	432–436(decompn.)		23.02 (24.00)	4.86 (5.03)
(VIIIc)	$[(C_2H_5)_3SiSeInSe]_n$	96.5	110(decompn.)		18.82 (18.57)	3.87 (3.89)

^a B.p. 136–140° (1 mm), n_D^{20} 1.4683. Reported⁸ b.p. 193–197° (16 mm). Found: Al, 12.33. $C_{10}H_{22}AlOSi$ calcd.: Al, 12.45%. ^b Undistillable liquid, n_D^{20} 1.5210, d_4^{20} 0.964. ^c Yield was calculated from eqn. (5). ^d Yield was calculated from eqn. (3). ^e Found: Ga, 39.21%. C_2H_5GaSe calcd.: Ga, 39.23%.

were carried out on a Tsvet-1 chromatograph with a thermoconductivity detector using an 100×0.4 cm column packed with Apiezon L (20%) on chromosorb W and helium as the carrier gas. Melting points were determined using sealed evacuated capillaries. The properties of the new compounds obtained are listed in Table 1.

Reaction of triethylgermaneselenol with triethylaluminum (ratio 1/1)

1.38 g (12.1 mmoles) of triethylaluminum in 6 ml of hexane was placed in an ampoule connected with a gas burette through a reflux condenser. Triethylgermaneselenol (2.93 g, 12.2 mmoles) was added dropwise to the solution at ca. 0° . The temperature of the mixture went up to 10° due to the exothermic reaction with evolution of 250 ml (95%) of ethane. The resulting mixture was filtered and the filtrate was chilled at ca. -78° . The white crystalline product obtained was recrystallized twice from hexane at -78° . Yield of diethyl(triethylgermylseleno)aluminum (III) was 2.30 g (62.2%). The compounds (I), (IIa)–(IIc), (IV) and (V) were prepared analogously.

Disproportionation of diethyl(triethylsilylseleno)aluminum (IIb)

A hexane solution of (IIb) prepared as described above from 2.04 g (17.9 mmoles) of triethylaluminum and 3.54 g (18.1 mmoles) of triethylsilaneselenol was allowed to stand overnight at room temperature. The liquid phase was decanted off and the solid was extracted with hexane and dried *in vacuo*. 1.01 g (82.5%) of (VIIb) was obtained, m.p. 376° , subliming at 360° (1 mm). Distillation of the liquid phase and hexane extract gave 0.80 g (78.5%) of triethylaluminum, b.p. $65-70^\circ$ (2 mm); lit.⁹ b.p. $63-64^\circ$ (1 mm). The product was identified by GLC. The fractionation also gave 1.52 g (55.0%) of $[(C_2H_5)_3Si]_2Se$, b.p. $116-118^\circ$ (4 mm), n_D^{20} 1.5068; lit.¹⁰ b.p. $114-118^\circ$ (4 mm), n_D^{20} 1.5072.

Disproportionation of (IIc) was carried out analogously. The compounds (IIa), (IV) and (V) were decomposed by heating at 225° , 220° and 170° , respectively, for 1–4 h.

Reaction of triethylsilanethiol with triethylaluminum (ratio 2/1)

3.60 g (24.6 mmoles) of $(C_2H_5)_3SiSH$ was added to a solution of 1.41 g (12.4 mmoles) of triethylaluminum in 10 ml of hexane. 300 ml of ethane was evolved during the course of exothermic reaction. The yield, [based on amount calculated from eqn. (5)] was 55%. Heating the mixture at 65° for 0.5 h gave additional 220 ml (41%) of ethane. The mixture was then filtrated. The solvent and the volatile products were removed by trap-to-trap distillation of the filtrate at 0.05 mm (pot temperature $\sim 20^\circ$). 4.15 g (97.4%) of ethylbis(triethylsilylthio)aluminum (VIa) was obtained as a colourless liquid, n_D^{20} 1.5210, d_4^{20} 0.964.

Disproportionation of bis(triethylsilylthio)ethylaluminum (VIa)

2.88 g (8.6 mmoles) of (VIa) was heated at 80° for 5 h in an evacuated sealed ampoule. Ethylaluminum sulfide (VIIa) precipitated out. The normal procedure gave 0.72 g (99.3%) of (VIIa), m.p. 480° and 1.53 g (71.0%) of bis(triethylsilyl)sulfide, b.p. $130-132^\circ$ (10 mm), n_D^{20} 1.4885; lit.¹¹ b.p. $130-132^\circ$ (10 mm), n_D^{20} 1.4865. In this reaction no triethylaluminum was formed.

Reaction of triethylsilaneselenol with triethylindium (ratio 2/1)

Using the general procedure described above, 1.55 g (7.9 mmoles) of triethyl-

silaneselenol was allowed to react with 0.88 g (4.3 mmoles) of triethylindium in 7 ml of hexane. 84 ml (43%) of ethane was evolved at 0–20° for 10 min. Heating the mixture at 65° for 20 min gave additional 93 ml (48%) of ethane. Ethylindium selenide (VIIe) precipitated out. The reaction mixture after work up gave 0.75 g (87.2%) of (VIIe) and 0.80 g (67.5%) of bis(triethylsilyl) selenide identified by GLC.

The reactions of $(C_2H_5)_3SiSeH$ with triethylaluminum and -gallium were carried out analogously.

Reaction of triethylsilaneselenol with triethylindium (ratio 3/1)

Triethylsilaneselenol (4.17 g, 21.4 mmoles) was slowly added to a solution of 1.46 g (7.2 mmoles) of triethylindium in 6 ml dry hexane at ca. 0°. During the course of exothermic reaction 290 ml of ethane was evolved. The yield [based on amount calculated from eqn. (6)] was 60%. Additional 190 ml (40%) of ethane was obtained by heating the mixture on a boiling water bath. The precipitate was filtered off extracted with hexane and dried *in vacuo*. 2.51 g (96.5%) of (triethylsilyl)seleno)indium selenide (VIIIc) was obtained. On heating the compound in a sealed evacuated capillary its decomposition appears to start at 110° followed by complete destruction and blackening at 260°. Distillation of the filtrate gave 1.72 g (83.6%) of bis(triethylsilyl) selenide b.p. 112–114° (4 mm), n_D^{20} 1.5060.

The compounds (VIIIa) and (VIIIb) were obtained analogously.

Reaction of triethylaluminum with bis(triethylgermyl) selenide

A mixture of 1.01 g (8.8 mmoles) of triethylaluminum and 2.76 g (7.0 mmoles) of bis(triethylgermyl) selenide was heated in a sealed ampoule at 130° for 0.5 h. The precipitated ethylaluminum selenide (VIIb) was filtered off extracted with hexane and dried *in vacuo*, m.p. 372–374°. Yield 0.94 g (100%). The yield of tetraethylgermane, determined by GLC, was 23%.

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