Reactions of Group IV Organometallic Compounds. Part XI.† Some Insertion Reactions of Alkylsilyl and Alkylstannyl Sulphides

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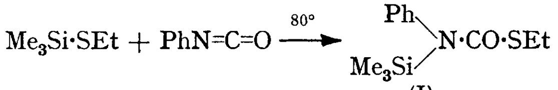
Reaction of trimethylsilyl sulphide with phenyl isocyanate gives a 1 : 1 insertion product, but subsequent insertion of phenyl isocyanate takes place readily in the case of trialkylstannyl sulphide, to produce triphenyl isocyanurate. When chloral is used as a reactant for trialkyltin sulphides, substitution of all three chlorine atoms occurs, to afford trialkyltin chloride and $(RS)_3C{\cdot}CHO$, although a simple insertion product was obtained in the case of trialkylsilyl sulphide. Alkyl–oxygen bond cleavage of β-propiolactone has been carried out selectively for the reaction with Si–S compounds.

ALTHOUGH the chemistry of Group IV organometallic sulphides was recently reviewed,[1] no study had been made of their insertion reactions, probably because of their low reactivity. We now describe the different behaviour of some silyl and stannyl sulphides in their reactions with phenyl isocyanate, chloral, and β-propiolactone. Simple insertion in polar double bonds of common types[2] arose for organosilyl sulphides, but further insertion or substitution reactions were induced in the case of organotin sulphides.

Phenyl isocyanate, which has been considered[2] an effective acceptor, gave a simple **1 : 1** addition product (I) with (ethylthio)trimethylsilane under relatively drastic conditions (80° for 80 hours). Based on infrared and n.m.r. spectra, C=N addition by phenyl isocyanate, which is a mode of addition known to be general,[2] is suggested.

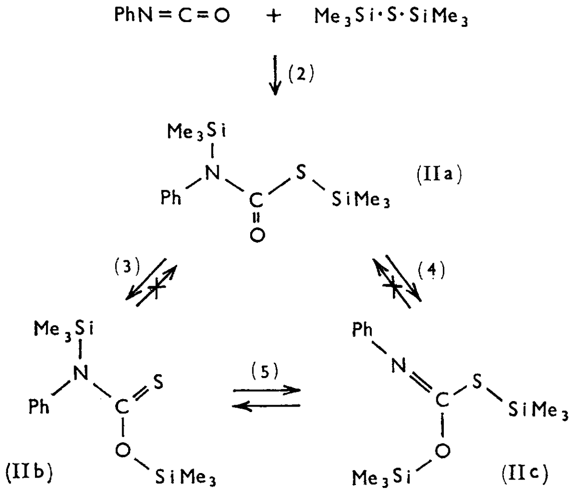


$$Me_3Si{\cdot}SEt + PhN{=}C{=}O \xrightarrow{80^\circ} \begin{matrix}Ph\\ Me_3Si\end{matrix}{>}N{\cdot}CO{\cdot}SEt \qquad (1)$$

(I)

Either treatment of an excess of isocyanate with (ethylthio)trimethylsilane, or reaction of the isolated amide (I) with isocyanate yielded the cyclic trimer, triphenyl isocyanurate, and (ethylthio)trimethylsilane was recovered. This suggests two further insertions of phenyl isocyanate into the new Si–N bond in (I), and final cyclization in the same way as for trialkyltin alkoxides or oxides.[3]

Surprisingly, the insertion product with bistrimethylsilyl sulphide showed no infrared carbonyl stretching absorption, which should appear around 1600—1700 cm.$^{-1}$ [$\nu_{max.}$ for the adduct (I) was at 1646 cm.$^{-1}$]. Strong absorptions which might be assigned to the C=S bond were observed at 1340 and 1328 cm.$^{-1}$, in positions quite similar to that of the absorption for thiocarbanilide at 1344 cm.$^{-1}$.[4] This anomalous behaviour can be explained on the basis of a 1,3-transfer of a trimethylsilyl group from a sulphur to an oxygen atom in the initially formed C=N insertion product [reaction (1)]; (IIa) would thus give (IIb). Such a 1,3-transfer of a trimethylsilyl group was predicted[5] in the case of some bistrimethylsilyl amides, from a nitrogen to an oxygen atom.



Since the silicon atom is known to possess 'hard' character[6] (Class a),[7] and would accordingly prefer an oxygen to a sulphur atom, the above migration of a trimethylsilyl group would be reasonable. Furthermore, the Si–O bond formed in (IIb) [or (IIc)] acquires high stability due to $p\pi \longrightarrow d\pi$ donation. The n.m.r. spectrum of the adduct predicted the existence of two kinds of trimethylsilyl group, having a sharp singlet at τ 9·83 and a broad singlet at 9·62. The former signal may be attributed to the trimethylsilyloxy-group, because 1,3-transfer of a trimethylsilyl group was prohibited in the case of O ⟶ S migration [(IIb) ⟶ (IIa)] or O ⟶ N migration [(IIc) ⟶ (IIa)]. The appearance of the lower-field signal as a broad singlet can be explained in two ways: (1) the occurrence of a 1,3-transfer equilibrium between a nitrogen and a sulphur atom, (IIb) $\rightleftarrows$ (IIc), at a moderate rate; (2)

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† Part X. K. Itoh, Y. Kato, and Y. Ishii, *J. Org. Chem.*, in the press.

[1] E. W. Abel and D. A. Armitage, *Adv. Organometallic Chem.*, 1967, **5**, 1.

[2] M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, 1967, **5**, 225.

[3] A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 1965, 6858.

[4] L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1958, p. 356.

[5] J. Pump and E. G. Rochow, *Chem. Ber.*, 1964, **97**, 627.

[6] (*a*) R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3433; (*b*) R. G. Pearson and J. Songstad, *ibid.*, 1967, **79**, 1827.

[7] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

restricted rotation in the *N*-(trimethylsilyl)thioamide structure in the case of (IIb). Generally, restricted rotation about the carbon–nitrogen bond in thioamides does not occur at room temperature, in contrast to the occurrence in the corresponding amides,[8] so explanation (2) would thus be invalid. The fact that the broad singlet became sharper above 50° at τ 9·67, and at 2° at τ 9·60, suggests also the existence of 1,3-transfer between the nitrogen and the sulphur atom.

Although much heat was evolved in the reaction of (alkylthio)trimethyltin with phenyl isocyanate, the isolated product was only triphenyl isocyanurate which is the cyclic trimer of phenyl isocyanate. Also, the original (alkylthio)trialkyltin was recovered. Since the Sn–N bond in the 1 : 1 insertion product, $Me_3Sn\cdot NPh\cdot CO\cdot SMe$, showed much greater reactivity towards phenyl isocyanate than the original Sn–S compounds because of low stability due to $p\pi$–$d\pi$ overlap compared with that in the Si–N bond, successive insertions of phenyl isocyanate to give a 1 : 3 insertion product, and subsequent cyclization through elimination of the original (alkylthio)trialkyltin, were readily induced. Consequently, the attempted isolation of a 1 : 1 adduct, as in the case of the similar (alkylthio)trimethylsilane, was unsuccessful, and (alkylthio)trialkyltin compounds were found to act as a catalyst for the trimerization [3] of isocyanate.

TABLE 1

Insertion of chloral in (ethylthio)trimethyl- and bis(ethylthio)dimethyl-silane

Reactant	Product [a]	B.p./mm.	Found (%)		Required (%)		Yield (%)
			C	H	C	H	
$Me_3Si\cdot SEt$	$Me_3Si\cdot O\cdot CH(CCl_3)\cdot SEt$ (III)	61/0·5	29·7	5·25	29·8	5·45	77
$Me_2Si(SEt)_2$	$Me_2Si(SEt)\cdot O\cdot CH(CCl_3)\cdot SEt$ (IV)	89/1·0	29·75	5·05	29·3	5·25	31 [b]
	$Me_2Si[O\cdot CH(CCl_3)\cdot SEt]_2$ (V)	141/1·0	25·4	3·85	25·25	3·8	91

[a] Reaction was performed at 80° for 36—43 hr. [b] Mixed also with 44% of the 1:2 adduct (V) from the equimolar reaction.

When chloral was taken as an acceptor molecule for (ethylthio)trimethylsilane or bis(ethylthio)dimethylsilane, simple insertion products, (III) and (IV), were isolated by distillation, and their structure was established with elemental analysis and infrared and n.m.r. spectra. Results are summarized in Table 1.

$$Me_3Si\cdot SEt + Cl_3C\cdot CHO \xrightarrow{80^\circ} \underset{\text{(III)}}{Me_3Si\cdot O\cdot CH(CCl_3)\cdot SEt} \quad (6)$$

Further insertion of a second molecule of chloral in the silicon–oxygen bond in adduct (III) could not occur owing to strong $p\pi \longrightarrow d\pi$ donation.

The n.m.r. spectrum of a 1 : 1 mixture of (methylthio)-trimethyltin and chloral (although addition proceeded exothermically at room temperature) showed, in addition to the two singlets ascribed to reactant, (methylthio)-trimethyltin, at τ 9·60 and 8·02, three singlets which were explained as due to the 1 : 1 adduct (VI), which is similar to (III), at τ 9·45 (9H), 7·79 (3H), and 5·00 (1H). Thus, the insertion reaction was not complete. The absence of complete addition was also indicated by the residual infrared absorption characteristic of chloral ($\nu_{max.}$ 1780 cm.$^{-1}$).

$$Me_3Sn\cdot SMe + Cl_3C\cdot CHO \underset{\text{distd.}}{\rightleftharpoons} \underset{\text{(VI)}}{Me_3Sn\cdot O\cdot CH(CCl_3)\cdot SMe} \quad (7)$$

Distillation of the above reaction mixture yielded both reactants quantitatively, and thus the existence of an equilibrium such as (7) was apparent. From peak areas at τ 9·60 and 9·45, or τ 8·02 and 7·79 (SCH_3), the ratio of (VI) to $Me_3Sn\cdot SMe$ was estimated as 0·7 at 20° in carbon tetrachloride. The low stability of this insertion product obtained from (alkylthio)trialkyltin was attributed to the lower stability of the Sn–O bond in (VI) due to $p\pi \longrightarrow d\pi$ donation than that of the stable Si–O bond in (III).

When the reaction mixture was heated in order to complete the reaction, elimination of trimethyltin chloride was observed. Treatment of a three-fold excess of chloral with (alkylthio)trialkyltin at 80° caused, surprisingly, substitution of all three chlorine atoms of chloral, to give trialkylthioacetaldehyde (VII), identified by elemental analysis and infrared ($\nu_{max.}$ 1710 cm.$^{-1}$) and n.m.r. spectra, together with trialkyltin chloride.

$$3R_3Sn\cdot SR' + Cl_3C\cdot CHO \longrightarrow 3R_3SnCl + \underset{\text{(VII)}}{(R'S)_3C\cdot CHO} \quad (8)$$

$$R = Me, Et;\ R' = Me, Et$$

Recently, β-elimination of trichloromethyltrialkyltin was observed for Sn–O [9] and Sn–N [10] compounds in the reaction with chloral. However, the fact that reaction (7) exists as an equilibrium, and that no 7,7-dichloronorcarane was detected with cyclohexene as scavenger, suggests that elimination of trialkyltin chloride did not proceed through the intermediate formation of trialkyltin trichloromethide but was obtained through a four-centre transition state. When one chlorine atom is replaced by an RS group, the mesomeric effect in the latter

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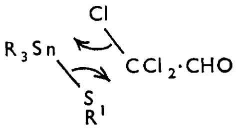
[8] T. M. Valega, *J. Org. Chem.*, 1966, **31**, 1150.

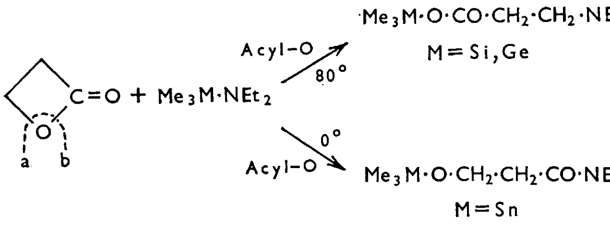
[9] A. G. Davies and W. R. Symes, *J. Organometallic Chem.*, 1966, **5**, 394.

[10] Part IX. K. Itoh, M. Fukui, and Y. Ishii, *Tetrahedron Letters*, 1968, 3867.

group greatly favours elimination of a further chlorine atom, so intermediates such as (RS)Cl_2C·CHO or $(RS)_2$ClC·CHO could not be isolated.



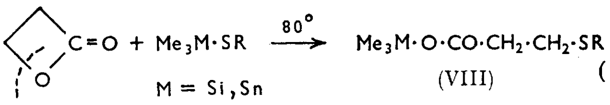
Previous work in this laboratory[11] made clear the occurrence of two types of ring-opening in β-propiolactone for various Group IV organometallic compounds. In particular, very different mechanisms occurred for germanium compared with tin in reaction with trimethylmetal(IV) amines,[11a,b] as shown in reactions (9).



(9)

On reaction of β-propiolactone with (ethylthio)-trimethylsilane, at 80° for 40 hours, the characteristic β-lactone ring absorption at 1835 cm.$^{-1}$ vanished and an insertion product was isolated by distillation. The existence of a strong carbonyl stretching frequency at 1723 cm.$^{-1}$ and a trimethylsilyl signal at τ 9·74, as well as no alkoxy-protons below τ 7·0, suggested that the 1 : 1 insertion product obtained was selectively induced through the alkyl–oxygen bond fission of β-propiolactone, giving trimethylsilyl β-(ethylthio)propionate (VIII).

The reaction of β-propiolactone with (methylthio)-trimethyltin proceeded also by this mode of cleavage;[11e]



(VIII) (10)

no variation of bond fission in the M(IV)–N compounds was observed as above [reactions (9)] for the tin atom.

TABLE 2

Methylsilyl β-(ethylthio)propionate by the ring-opening reaction of β-propiolactone with (ethylthio)methylsilane

Reactant	Product	Temp. (°c)	B.p./mm.	Yield (%)	$\nu_{C=O}$ (cm.$^{-1}$)	Found (%)		Required (%)	
						C	H	C	H
$Me_3Si·SEt$	$Me_3Si·O·CO·CH_2·CH_2·SEt$	80°	51/0·2	70	1723	46·7	8·8	45·55	8·8
$Me_2Si(SEt)_2$	$Me_2Si(SEt)·O·CO·CH_2·CH_2·SEt$	80	84/0·5	35	1725	42·8	7·85	42·8	8·0
	$Me_2Si(O·CO·CH_2·CH_2·SEt)_2$	80	125/0·5	77	1725	44·4	7·3	44·3	7·45
$(Me_3Si)_2S$	$Me_3Si·O·CO·CH_2·CH_2·S·SiMe_3$	20	62/0·04	79	1720	43·15	8·7	43·15	8·2

Table 2 summarizes the results for the reaction of β-propiolactone with (ethylthio)methylsilanes.

EXPERIMENTAL

All reactions were carried out in an argon atmosphere. Infrared and n.m.r. spectra were recorded with a Nippon Bunko model IR-S and a Japan Electron Optics C-60 spectrometer, respectively.

(Ethylthio)methylsilanes, bistrimethylsilyl sulphide, and (alkylthio)trialkyltin were prepared by the procedure proposed by Abel *et al.*,[12] and purified by distillation.

Reaction of Phenyl Isocyanate with (*Ethylthio*)*trimethylsilane*.—(*a*) (Ethylthio)trimethylsilane (2·68 g., 20 mmoles) and phenyl isocyanate (2·38 g., 20 mmoles) were mixed at room temperature and kept at 80° for 80 hr. Distillation of the mixture under reduced pressure gave the ethyl N-*phenyl*-N-*trimethylsilylthiocarbamate* (I), b.p. 94—95°/2 mm. (86%) (Found: C, 57·35; H, 7·55; N, 5·9. $C_{12}H_{19}NOSSi$ requires C, 56·85; H, 7·55; N, 5·55%), $\nu_{C=O}$ (CCl_4) 1646 cm.$^{-1}$; n.m.r.: τ 9·80 (s, 9H, CH_3Si), 8·82 (t, 3H, CH_3CH_2), 7·31 (q, 2H, CH_2S), and 2·7—3·1 (m, 5H, C_6H_5). Compound (I) was extremely unstable to moisture, and ethyl *N*-phenylcarbamate was obtained quantitatively through hydrolysis, m.p. 69·5—70·0° (Found: C, 59·45; H, 5·95; N, 7·75. Calc. for $C_9H_{11}NOS$: C, 59·65; H, 6·1; N, 7·7%).

(*b*) When an excess of phenyl isocyanate was used (1·59 g., 13·2 mmoles) with (ethylthio)trimethylsilane (0·59 g., 4·4 mmoles), triphenyl isocyanurate appeared as a precipitate after 5 days at 80°. The solid part was recrystallized from aqueous ethanol, to give triphenyl isocyanurate (86%), m.p. 292° (Found: C, 69·6; H, 4·3; N, 11·35. Calc. for $C_{21}H_{15}N_3O_3$: C, 69·6; H, 4·25; N, 11·75%), $\nu_{C=O}$ ($CHCl_3$) 1710 cm.$^{-1}$. (Ethylthio)trimethylsilane was recovered (74%) from distillation of the liquid part.

Triphenyl isocyanurate was also obtained from the reaction of compound (I) with phenyl isocyanate at 80° for 10 days.

Reaction of Bistrimethylsilyl Sulphide with Phenyl Isocyanate.—A mixture of bistrimethylsilyl sulphide (1·30 g., 7·5 mmoles) and phenyl isocyanate (0·87 g., 7·3 mmoles) was heated in a sealed tube at 80° for 24 hr. The characteristic absorption of isocyanate at 2280 cm.$^{-1}$ had vanished completely, and the reaction mixture solidified on cooling to room temperature. Recrystallization from n-hexane gave colourless hygroscopic *needles* (79%), m.p. 54° (Found: C, 52·3; H, 7·6. $C_{12}H_{23}NOSSi_2$ requires C, 52·45; H, 7·8%), $\nu_{max.}$ (CCl_4) 1328 and 1340 cm.$^{-1}$, τ 9·83 (s) and 9·62br (s).

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[11] K. Itoh, S. Sakai, and Y. Ishii, (*a*) *J. Org. Chem.*, 1966, **31**, 3948; (*b*) *Tetrahedron Letters*, 1966, 4941; (*c*) *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1967, **70**, 935; preliminary account, *Chem. Comm.*, 1967, 36; (*d*) K. Itoh, S. Kobayashi, S. Sakai, and Y. Ishii, *J. Organometallic Chem.*, 1967, **10**, 451; (*e*) K. Itoh, Y. Kato, and Y. Ishii, Ann. Meeting Chem. Soc. Japan, Tokyo, 1967, Preprint, p. 386.

[12] E. W. Abel *et al.*, *J. Chem. Soc.*, **1965, 1192**; **1960, 4406**; 1961, 4933.

Trimerization of Phenyl Isocyanate with (Alkylthio)-trialkyltin.—When equimolar amounts of phenyl isocyanate and (alkylthio)trialkyltin were mixed at room temperature, reaction proceeded exothermically. After the reaction mixture was kept at 80° or at room temperature, triphenyl isocyanurate, identified by infrared and n.m.r. spectra and mixed m.p., precipitated as white crystals. The liquid part was identified as the original (alkylthio)-trialkyltin compounds, which were recovered by distillation. Triphenyl isocyanurate was washed twice with n-hexane and recrystallized from aqueous ethanol (Table 3).

TABLE 3

Trimerization of isocyanate, RNCO, by (alkylthio)-trialkyltin

(Alkylthio)-trialkyltin	R	Time (hr.)	Temp. (°c)	Yield of trimer (%)	Re-covered Sn–S compds. (%)
$Me_3Sn{\cdot}SMe$	Ph	28	20°	89	86
$Me_3Sn{\cdot}SBu^t$	Ph	110	20	80	79
$Et_3Sn{\cdot}SEt$	Ph	110	80	90	71
$(Me_3Sn)_2S$	Ph	120	20	90	74
$Me_3Sn{\cdot}SMe$	Me	17	20	87 *	80

* Trimethyl isocyanurate, m.p. 174—175° (lit.,[3] 175°); $\nu_{C=O}$ 1689 cm.$^{-1}$.

Insertion of Chloral into (Ethylthio)trimethylsilane.—A mixture of the silane (1·38 g., 10·3 mmoles) and chloral (1·51 g., 10·3 mmoles) was heated at 80° for 43 hr. Distillation under reduced pressure afforded (trichloroethylthiomethoxy)trimethylsilane (III) which was a simple insertion product (see Table 1). Mol. Wt., (Found: *M*, 278. Reqd., 281); n.m.r.: τ 9·71 (s, 9H, CH_3Si), 8·62 (t, 3H, CH_3CH_2), 7·04 (q, 2H,CH_2), and 4·92 (s, 1H,CH).

Reaction of Bis(ethylthio)dimethylsilane with Chloral.—(*a*) A mixture of bis(ethylthio)dimethylsilane (1·22 g., 6·8 mmoles) and chloral (1·00 g., 6·8 mmoles), kept at 80° for 36 hr., gave the following three fractions: recovered bis-(ethylthio)dimethylsilane (21%); ethylthio-(trichloroethylthiomethoxy)dimethylsilane, $Me_2Si(SEt){\cdot}O{\cdot}CH(CCl_3){\cdot}SEt)$ (see Table 1), (Found: *M*, 324. Reqd., 327); bis-(trichloroethylthiomethoxy)dimethylsilane, $Me_2Si[O{\cdot}CH(CCl_3){\cdot}SEt]_2$ (see Table 1), (Found: *M*, 481. Reqd., 474).

(*b*) Distillation of the reaction mixture from bis(ethylthio)dimethylsilane (0·81 g., 4·5 mmoles) and chloral (1·32 g., 9 mmoles) which had been kept for 43 hr., afforded a pale yellow oily 1 : 2 adduct, bis-(trichloroethylthiomethoxy)dimethylsilane (1·93 g., 91%).

Reaction of Chloral with (Alkylthio)trialkyltin.—(*a*) *Equimolar reaction.* Chloral and (methylthio)trimethyltin reacted exothermically, but the reaction mixture showed $\nu_{C=O}$ at 1780 cm.$^{-1}$ which is characteristic of chloral. The n.m.r. spectrum of this reaction mixture showed two singlets, ascribed to the remaining (methylthio)trimethyltin, at τ 9·60 and 8·02, and three singlets, at τ 9·45 (9H, CH_3Sn) with two satellites at 7·79 (3H,CH_3S) and 5·00 (1H,CH); the latter three singlets might be due to the unstable 1 : 1 adduct (V). Distillation of this mixture under reduced pressure below 80° (above 80°, elimination of trimethyltin chloride arose), gave chloral and (methylthio)trimethyltin nearly quantitatively, both of which were identified by comparison with pure materials.

(*b*) (Methylthio)trimethyltin (3·08 g., 14·7 mmoles) and chloral (0·73 g., 4·9 mmoles) were heated at 80° for 4 hr. A new carbonyl stretching frequency at 1710 cm.$^{-1}$ appeared, and the absorption ascribed to chloral vanished completely after 20 hr. From the brown mixture were isolated trimethyltin chloride (2·34 g., 80%) and trimethylthioacetaldehyde (0·67 g., 75%), b.p. 74—75°/0·5 mm. (Found: C, 32·65; H, 5·4%; *M*, 178. Calc. for $C_5H_{10}OS_3$: C, 32·94; H, 5·53%; *M*, 182), $\nu_{C=O}$ (CCl_4) 1710 cm.$^{-1}$; n.m.r.: τ 7·94 (s, 9H, CH_3S) and 1·03 (1H, aldehyde H). Trimethylthioacetaldehyde was isolated (67%) from the reaction of (methylthio)triethyltin (80° for 72 hr.).

(*c*) (Ethylthio)trimethyltin reacted similarly with chloral (80° for 6 hr.) and gave trimethyltin chloride (91%) and triethylthioacetaldehyde (63%), b.p. 84°/0·5 mm. (Found: C, 42·45; H, 7·1. Calc. for $C_8H_{16}OS_3$: C, 42·8; H, 7·2%), $\nu_{C=O}$ (CCl_4) 1710 cm.$^{-1}$; n.m.r.: τ 8·70 (t, 9H, CH_3), 7·33 (t, 6H,CH_2), and 1·08 (1H, aldehyde H).

Reaction of β-*Propiolactone with (Ethylthio)methylsilanes.*—(Ethylthio)trimethylsilane (1·02 g., 7·5 mmoles) and β-propiolactone (0·54 g., 7·5 mmoles) were treated at 80° for 40 hr. Distillation under reduced pressure gave trimethylsilyl β-(ethylthio)propionate (1·09 g., 70%) as a colourless oily liquid. Reaction of β-propiolactone with bis(ethylthio)dimethylsilane and with bis(trimethylsilyl) sulphide were carried out in an analogous way, and the results, including elemental analyses and infrared carbonyl stretching vibrations, are in Table 2.

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