

The Addition of Some Mercapto Compounds to α,β -Unsaturated Silanes

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This paper deals with the addition of different mercapto compounds to trimethylvinylsilane in the presence of a catalytic amount of peroxide that gives the two possible isomers. The addition has also been studied with base catalysis, but here only the β -addition product has been isolated. For identification, the addition products have been compared with model compounds using gas chromatography, infra-red spectrophotometry and NMR-spectrometry.

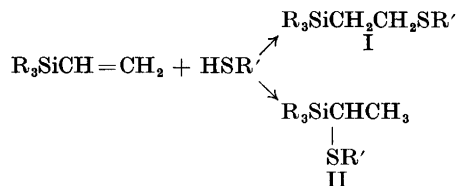
The addition of different compounds to olefins, including vinylsilanes, are described in detail in the literature. The direction of addition in the free radical reaction is commonly referred to as anti-Markownikoff. The purpose of this investigation is to establish if the addition of mercapto compounds to vinylsilanes goes in one direction only or if the two possible isomers are formed.

Sommer *et al.*¹ have studied the addition of hydrogen bromide to trimethylvinylsilane, and they found that, in the presence of benzoyl peroxide, hydrogen bromide was almost quantitatively absorbed with the formation of β -bromoethyltrimethylsilane. Hey and Waters,² and Kharasch, Engelmann and Mayo³ have proposed a mechanism for the peroxide catalyzed addition. The initial attack of the bromine atom can theoretically take place either at the α - or β -carbon atom of the vinyl group. The attack at the β -carbon atom indicates that this has the highest value of the free valence. Other factors influencing the course of the addition can be steric effects, the relative stability of the two possible radicals formed after the addition of the bromine atom, and the delocalization of the unpaired electron at the α -carbon atom into the vacant d-orbitals of silicon. According to Seyferth,⁴ the last effect is small for radicals from vinylsilanes.

The addition of mercapto compounds to vinylsilanes in the presence of peroxide can be supposed to be analogous to that described for the addition of

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hydrogen bromide to vinylsilanes. Theoretically, two isomeric compounds can be formed.



Larsson⁵ added thioglycolic acid to triethylvinylsilane in the presence of peroxide and found a product of type I. Burkhard,⁶ in a similar manner, added thioglycolic acid to trimethylvinylsilane and also got a product of type I.

The results of the earlier investigations were that only the β -addition products were formed. It is possible that the α -compounds have also been formed, but in such small quantities that these were missed by older identification methods. For this work thioglycolic acid, β -mercapto propionic acid, thiophenol, and benzyl mercaptan have been added to trimethylvinylsilane. The reaction mixture was fractionated and the distillates investigated by gas chromatography. Two compounds were shown to be present. The two components could not be separated by further fractional distillations. In order to identify these components the compounds of type II were prepared. By the gas chromatographic investigation it was found that the retention times for these agreed with the corresponding retention times of those compounds formed in the smallest amount at the additions. Different column materials and column combinations have been used, but the above results have been confirmed in all cases. The investigation shows that the two possible isomers are formed at the addition of mercapto compounds to trimethylvinylsilane in the presence of peroxide, but the addition anti-Markownikoff is the dominating. The relative yields of the two isomers are listed in Table 1. (The yields are determined from the gas chromatograms by means of a planimeter.) At the addition of thiophenol to trimethylvinylsilane, the yields of the crude and the distilled products were determined and these confirmed that there was no separation of the isomers at the distillation.

The infra-red spectra of the addition products and of the compounds of type II have been compared. When the addition products only hold 3–7 %

Table 1. Relative yields of the two isomers at the peroxide catalyzed addition reactions.

Silane	Mercapto compound HSR'	$(\text{CH}_3)_3\text{SiCH}_2\text{-CH}_2\text{SR}'$ $(\text{CH}_3)_3\text{SiCH}$ <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> $\begin{array}{l} \text{SR}' \\ \text{CH}_3 \end{array}$ </div>	
		%	%
$(\text{CH}_3)_3\text{SiCH}=\text{CH}_2$	HSCH ₂ COOH	94	6
»	HS(CH ₂) ₂ COOH	94	6
»	HSC ₆ H ₅	97	3
»	HSCH ₂ C ₆ H ₅	95	5

of the compounds of type II, the infra-red spectra of the addition products can be presumed to be characteristic for the compounds of type I. A comparison of the infra-red spectra of the compounds of type I and II showed differences in the CH-stretching vibration range around 3000 cm^{-1} . Thus, compounds of type I had absorption bands at 2955 and 2910 cm^{-1} ; compounds of type II at 2955 , 2920 , 2895 , and 2860 cm^{-1} . An interpretation of these absorption bands has not been made as the material is too small for such a determination, and the positions of the bands not are quite in accordance with those given in the literature for pure hydrocarbons. Probably the positions and the intensities of the CH-stretching vibrations can be influenced by the silicon and sulphur atoms in the molecule. In spectra of compounds of type II absorption bands were registered at 1370 cm^{-1} . These bands, which could not be found in the spectra from the addition products, could be the symmetrical CH-deformation vibrations of the CCH_3 groups. The infra-red spectra were recorded by a Perkin Elmer model 221 spectrophotometer equipped with prism-grating, in 5 % solution of carbon tetrachloride.

The infra-red spectroscopic investigations support the theory that compounds of type I are the main products at the additions. When the differences in the infra-red spectra of compounds of type I and II are relatively small, a NMR-spectrometric investigation of the compounds has been made in order to definitely confirm the structures of the main addition products.

Table 2. Chemical shifts of the compounds of type I and II in ppm. referred to tetramethylsilane as standard. The figures in brackets show the number of protons in each group calculated from the integration curves. The NMR-spectra were recorded by a Varian A-60 spectrometer in 20 % solutions of carbontetrachloride.

$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{COOH}$	0.0 (9)	0.4 (2)	1.3 (2)	1.6 (2)	6.0 (1)
$(\text{CH}_3)_3\text{SiCH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{SCH}_2\text{COOH} \end{array}$	0.0 (9)	0.7 (3)	1.1 (1)	1.6 (2)	5.8 (1)
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{COOH}$	0.0 (9)	0.4 (2)	1.2 (2)	1.3 (4)	5.8 (1)
$(\text{CH}_3)_3\text{SiCH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{SCH}_2\text{CH}_2\text{COOH} \end{array}$	0.0 (9)	0.6 (3)	1.0 (1)	1.3 (4)	5.8 (1)
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{SC}_6\text{H}_5$	0.0 (9)	0.9 (2)	2.8 (2)	7.1 (5)	
$(\text{CH}_3)_3\text{SiCH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{SC}_6\text{H}_5 \end{array}$	0.1 (9)	1.2 (3)	2.4 (1)	7.1 (5)	
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$	0.0 (9)	0.8 (2)	2.4 (2)	3.6 (2)	7.2 (5)
$(\text{CH}_3)_3\text{SiCH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{SCH}_2\text{C}_6\text{H}_5 \end{array}$	0.0 (9)	1.2 (3)	1.7 (1)	3.6 (2)	7.2 (5)

Analyses of the NMR-spectra showed that the main products at the additions must have a structure of type I; see Table 2.

The positive inductive effect of the $(\text{CH}_3)_3\text{Si}$ -group is greater than that of the $(\text{CH}_3)_3\text{C}$ -group. In trimethylvinylsilane the β -carbon atom of the vinyl group should therefore be activated for electrophilic reagents. In trimethylvinylsilane the positive inductive effect of the $(\text{CH}_3)_3\text{Si}$ -group is opposed by a $-\tau$ effect that is by d_π - p_π bonding between the π -electrons of the double bond and the vacant d-orbitals of silicon. Thus, one must calculate with contribution from a structure such as $(\text{CH}_3)_3\text{Si}^- = \text{CH}^+ - \text{CH}_2$. The $-\tau$ effect must be stronger than the positive inductive effect as the addition goes anti-Markownikoff.

At the base catalyzed addition of thiophenol to trimethylvinylsilane, the anion formed from the mercapto compound is added to the β -carbon atom of the vinyl group, and the new anion adds a proton from the mercapto compound and gives a saturated sulphide. The addition has been made in the presence of trimethylbenzylammonium hydroxide. As the peroxide catalyzed additions also give β -addition products precautions must be taken to avoid a radical catalyzed reaction. The components were shaken with hydroquinone and placed in an ampoule of thick walled glass together with the base and hydroquinone. The ampoule was sealed and placed in a steel bomb and heated in darkness. The addition product was isolated and identified by gas chromatography and infra-red spectra. It was found that the yield was considerably lower at the base catalyzed addition than at the corresponding peroxide catalyzed reaction, and that only the β -addition product was formed. Experiments have been made with only silane, mercapto compound, and hydroquinone, but no addition product could be found.

EXPERIMENTAL

Addition of thioglycolic acid to trimethylvinylsilane. In an ampoule of thick walled glass were introduced 8.0 g (0.08 mole) trimethylvinylsilane,⁷ 7.2 g (0.08 mole) thioglycolic acid and 0.3 g di-*tert*-butylperoxide. The reagents used were dried and fractionated in a glass-helix packed column of about ten theoretical plates. The ampoule was sealed and placed in a steel bomb and heated at 100° for 15 h. The reaction mixture was fractionated in a semi-micro-column *in vacuo*, b.p. 94–95°/0.1 mm. The yield was 10.0 g (66 %); see Table 1. (Found: C 43.6; H 8.4; Si 14.6; equiv.wt. 192.1. Calc. for $\text{C}_7\text{H}_{16}\text{O}_2\text{SSi}$: C 43.7; H 8.4; Si 14.6; equiv.wt. 192.4).

(α -Trimethylsilyl-ethyl)-sulphide acetic acid. To 9.2 g (0.1 mole) thioglycolic acid was added a solution of 10.0 g (0.25 mole) sodium hydroxide in 100 ml of water followed by a solution of 13.7 g (0.1 mole) trimethyl- α -chloroethylsilane⁸ in 150 ml ethanol. The reaction mixture was heated at reflux temperature for 1 h. The ethanol was evaporated and the water solution acidified with sulphuric acid and extracted with ether. The ether solution was dried with anhydrous magnesium sulphate, the ether was distilled off, and the residue distilled in a semi-micro-column. B.p. 88–89°/0.1 mm. Yield 12.1 g (63 %), n_D^{25} 1.4783, d_4^{25} 1.0144. (Found: C 43.5; H 8.3; Si 14.5; equiv.wt. 192.1. Calc. for $\text{C}_7\text{H}_{16}\text{O}_2\text{SSi}$: C 43.7; H 8.4; Si 14.6; equiv.wt. 192.4).

Addition of β -mercapto propionic acid to trimethylvinylsilane. 4.0 g (0.04 mole) trimethylvinylsilane, 4.2 g (0.04 mole) β -mercaptopropionic acid and 0.2 g di-*tert*-butylperoxide were heated in an ampoule at 100° for 12 h. The reaction mixture was distilled *in vacuo*, b.p. 139–140°/2 mm. The yield was 7.1 g (87 %); see Table 1. (Found: C 46.4; H 8.7; Si 13.5; equiv.wt. 206.3. Calc. for $\text{C}_8\text{H}_{18}\text{O}_2\text{SSi}$: C 46.6; H 8.8; Si 13.6; equiv.wt. 206.4).

β -(α -Trimethylsilyl-ethyl)-sulphide propionic acid. 10.6 g (0.1 mole) β -mercapto propionic acid was added to a solution of 10.0 g (0.25 mole) sodium hydroxide in 100 ml water. Then 13.7 g (0.1 mole) trimethyl- α -chloroethylsilane in 100 ml ethanol was added. The reaction mixture was heated and worked up in the same manner as described for (α -trimethylsilyl-ethyl)-sulphide acetic acid, b.p. 125–126°/1.5 mm. The yield was 6.3 g (31 %). n_D^{25} 1.4787, d_4^{25} 1.0028. (Found: C 46.6; H 8.9; Si 13.5; equiv.wt. 206.8. Calc. for $C_8H_{18}O_2SSi$: C 46.6; H 8.8; Si 13.6; equiv.wt 206.4).

Addition of thiophenol to trimethylvinylsilane. This synthesis was carried out in exactly the same way as earlier described for the addition of β -mercapto propionic acid to trimethylvinylsilane, from 4.0 g (0.04 mole) trimethylvinylsilane, 4.4 g (0.04 mole) thiophenol and 0.2 g di-*tert*-butylperoxide. The fraction with b.p. 89–91°/1.2 mm was taken. The yield was 7.5 g (89 %); see Table 1. (Found: C 62.7; H 8.8; Si 13.3. Calc. for $C_{11}H_{18}SSi$: C 62.8; H 8.6; Si 13.4).

(α -Trimethylsilyl-ethyl)-phenyl sulphide. To 11.0 g (0.1 mole) thiophenol in 75 ml ethanol was added 4.0 g (0.1 mole) sodium hydroxide in 125 ml water. 13.7 g (0.1 mole) trimethyl- α -chloroethylsilane in 225 ml ethanol was added, and the reaction mixture was heated for 2 h at reflux temperature and worked up as earlier described. The fraction with b.p. 88–89°/1.7 mm was taken and the yield was 14.5 g (69 %). n_D^{25} 1.5318, d_4^{25} 0.9569. (Found: C 62.6; H 8.7; Si 13.2. Calc. for $C_{11}H_{18}SSi$: C 62.8; H 8.6; Si 13.4).

Addition of benzyl mercaptan to trimethylvinylsilane. 4.0 g (0.04 mole) trimethylvinylsilane, 5.0 g (0.04 mole) benzyl mercaptan and 0.2 g di-*tert*-butylperoxide were reacted in the way earlier described for the addition of β -mercapto propionic acid to trimethylvinylsilane. The fraction with b.p. 101–103°/1.8 mm was taken and the yield was 8.1 g (90 %); see Table 1. (Found: C 64.1; H 9.0; Si 12.5. Calc. for $C_{12}H_{20}SSi$: C 64.2; H 9.0; Si 12.5).

(α -Trimethylsilyl-ethyl)-benzyl sulphide. 12.4 g (0.1 mole) benzyl mercaptan in 150 ml ethanol and 4.0 g (0.1 mole) sodium hydroxide in 100 ml water were reacted, and 13.7 g (0.1 mole) trimethyl- α -chloroethylsilane in 150 ml ethanol was added. The reaction mixture was heated at reflux temperature for 4 h and worked up as earlier described. The distillation gave 16.4 g (73 %), b.p. 97–98°/1.6 mm. n_D^{25} 1.5214, d_4^{25} 0.9455. (Found: C 64.2; H 8.9; Si 12.4. Calc. for $C_{12}H_{20}SSi$: C 64.2; H 9.0; Si 12.5).

Addition of thiophenol to trimethylvinylsilane. 2.0 g (0.02 mole) trimethylvinylsilane, 2.2 g (0.02 mole) thiophenol, 0.2 g hydroquinone and 0.2 g trimethylbenzylammonium hydroxide were placed in an ampoule and heated at 110° for 14 h. The reaction mixture was poured into water and extracted with benzene. The benzene solution was dried with anhydrous magnesium sulphate and the benzene evaporated. The residue was distilled in a semi-micro-column and the fraction with b.p. 95–96°/1.7 mm was taken. The yield was 0.6 g (14 %). Gas chromatographic investigation and infra-red spectra showed that the product was (β -trimethylsilyl-ethyl)-phenyl sulphide.

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