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REACTIONS OF TRIORGANOSILYLSULFENYL HALIDES WITH SOME NUCLEOPHILES

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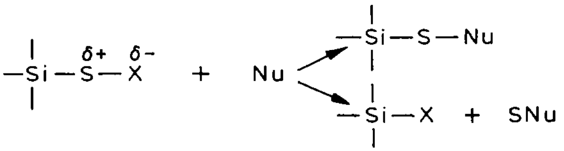
Summary

The reaction of triorganosilylsulfenyl halides R_3SiSX (R = Ph, Et; X = Cl, Br) with carbon–carbon double bonds, trialkyl phosphites, and organometallic reagents have been studied. With the first two nucleophiles the course of the reactions differed from that with organosulfenyl chlorides because of nucleophilic attack of halide ion on silyl group.

Introduction

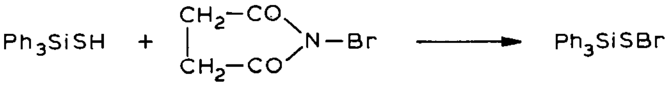
Organic sulfenyl halides are well known as very effective reagents used for introducing sulfur groups into chemical compounds. Organometallic sulfenyl halides were obtained some years ago by Fukuyama [1] but, to our knowledge, the reactions of such compounds have not been investigated.

We expected that triorganosilylsulfenyl halides might be an efficient electrophilic sulfurization agent capable of introducing sulfur or silyl-protected sulfur groups into organic compounds containing a nucleophilic site, according to the scheme:



Results and discussion

For synthesis of the triorganosilylsulfenyl halides we used the method proposed by Fukuyama, e.g. reaction of the respective thiols with *N*-halosuccinimide:



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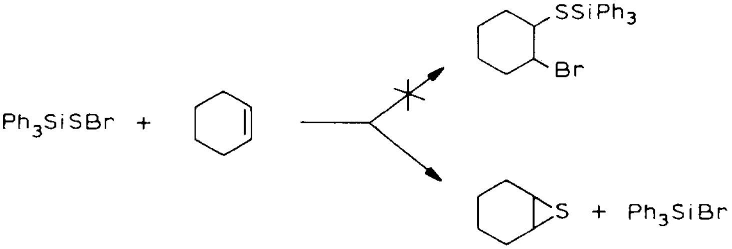
These compounds are formed also by treatment of disilathianes with sulfuryl chloride [2]:

$$Et_3SiSSiEt_3 + SO_2Cl_2 \xrightarrow[CH_2Cl_2\ r.t.]{} Et_3SiSCl + Et_3SiCl + SO_2$$

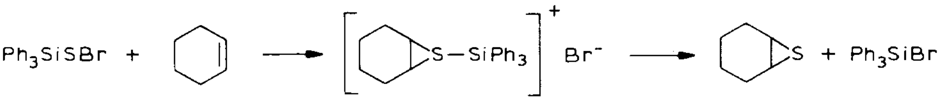
This method is less convenient for in situ use, since the chlorosilane and SO_2 may react with the nucleophile.

In organic chemistry, electrophilic addition of organic sulfenyl halides to carbon–carbon double bond as well as to trialkyl phosphites is well known. We have examined the corresponding reactions using triorganosilylsulfenyl halides. The reaction of triphenylsilylsulfenyl bromide with cyclohexene does not give a product analogous to that formed from an organic sulfenyl chloride. Instead, addition of sulfur occurs, and cyclohexyl thiirane is formed.



The yield from the reaction of Ph_3SiSCl with cyclohexene under the same conditions was much lower. We also used vinyltrimethylsilane, proposed by Magnus [3] as an ethylene equivalent in electrophilic substitution reactions with organic sulfenyl chlorides, but failed to obtain the desired product.

It is possible that the reaction involves the formation of a sulfonium salt intermediate:

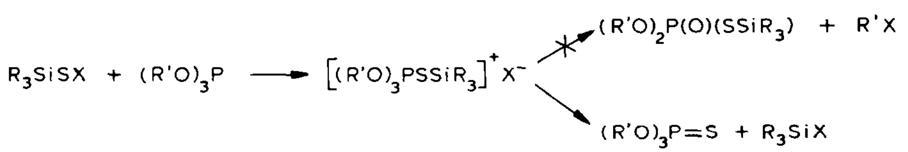


The greater electrophilicity of silicon than of carbon accounts for the different course of the reaction.

It is noteworthy that the formation of thiirane was recently postulated as the first step of the reaction of triphenylmethylsulfenyl chloride with some compounds containing the olefinic function [4].

The reaction of silylsulfenyl halides with phosphites was slightly exothermic in every case. The ^{31}P NMR spectra show that the reaction proceeds almost quantitatively to phosphorothionates; e.g. triethyl phosphite reacts with triphenylsilylsulfenyl to give triethyl phosphorothionate.

The course of this reaction is different from that of the reaction of organosulfenyl chloride with trialkyl phosphites, which gives *O,O*-bisalkyl, *S*-organophosphorothiolates [5]:



X = Br

R = Ph R' = Et(δ(^{31}P) 137 ppm R = Ph R' = Et(δ(^{31}P) 67 ppm

R = Et R' = Me_3Si(δ(^{31}P) 113 ppm R = Et R' = Me_3Si(δ(^{31}P) 31 ppm

In the light of the observations, an ionic mechanism may be proposed involving nucleophilic displacement by phosphite at the sulfur atom of the silylsulfenyl halide. The intermediate complex may be broken down by nucleophilic attack of a halide ion on the silyl group, leading to phosphorothionate.

To examine the reactions of triethylsilylsulfenyl halides with organometallic compounds we used n-BuLi and Grignard reagents. The reaction with n-butyl lithium gave a mixture of products:

$$Et_3SiSX \xrightarrow{BuLi} BuSBu + Et_3SiSSiEt_3 + BuSSBu + BuSSiEt_3 + Et_3SiX$$

The total yield of all products was about 50–60%, the contributions of the first two thioethers being ca. 30–40%, with only ca. 10% of triethyl(butylthio)silane. The presence of the first three sulfur compounds indicates that the reaction is complex. These thioethers are probably formed in consecutive reactions:

$$Et_3SiSBu + Et_3SiSX \rightarrow Et_3SiSSBu + Et_3SiX$$

$$Et_3SiSBu + Et_3SiSSBu \rightarrow Et_3SiSSiEt_3 + BuSSBu$$

$$Et_3SiSBu + BuSSBu \rightarrow BuSBu + Et_3SiSSBu$$

The mixed silyl alkyl disulfide is probably very unstable [2] and could not be detected in the reaction system.

The reactions with Grignard reagents take a simpler course, and give triethyl(organothio)silanes as the main products in 60–70% yields.

$$Et_3SiSBr + RMgBr \rightarrow RSSiEt_3 \qquad (R = Et, Ph)$$

It is possible that the reaction is fast enough to prevent the formation of the symmetric products in subsequent reactions involving the silylsulfenyl substrate.

The organothiosilanes undergo fast hydrolytic or alcoholic cleavage under mild conditions to give organic thiols. This method may be used to introduce thiol groups into organic compounds via Grignard reagents.

Experimental

All the syntheses were carried out under argon. Solvents were purified prior to use by standard techniques. The reactions were monitored by GLC or, in the case of phosphorus-containing reagents, by ^{31}P NMR spectroscopy. Nuclear magnetic resonance spectra were taken on JEOL JNM-Fx-60-FT instrument at 24.2 MHz, and the products were identified with an LKB Model 2091 gas chromatograph-mass spectrometer.

The organosilylsulfenyl halides were prepared as described by Fukuyama [1] on a millimol scale at room temperature using benzene, toluene, or ether as solvent. A nucleophile was added to the reaction medium after 0.1–1 h, with or without removal by filtration of the succinimide formed in the first steps.

Some examples of the reactions are given below.

Reaction with cyclohexene

Cyclohexene (2 g, 0.024 mol) was added to the solution obtained from reaction of 1.8 g (0.01 mol) of *N*-bromosuccinimide and 2.9 g (0.01 mol) of triphenylsilanethiole in 25 ml benzene. After 3 h GLC showed the presence of about 20% of a substance which was identified by GC/MS as cyclohexene sulfide. Attempts to isolate the pure product were unsuccessful.

Reaction with triethyl phosphite

Triethyl phosphite (3.3 g, 0.02 mol) was added dropwise to the solution obtained from 3.6 g (0.02 mol) of *N*-bromosuccinimide and 5.8 g (0.02 mol) of triphenylsilanethiole in 50 ml benzene. The reaction was slightly exothermic and the colour of sulfenyl bromide disappeared during the addition. The ^{31}P NMR spectrum after 1 h showed that the reaction was complete. After filtration of the solution and evaporation of the solvent, a product was obtained by distillation (3.7 g, 93%) at 100°C/16 mmHg and identified by GC/MS and ^{31}P NMR spectroscopy as triethyl phosphorothionate.

Reaction with phenylmagnesium bromide

The solution obtained by reaction of 3.6 g (0.02 mol) *N*-bromosuccinimide with 2.6 ml (0.02 mol) triethylsilanethiol in 30 ml benzene was filtered and added dropwise to the Grignard reagent obtained from 0.48 g (0.02 mol) Mg and 3.3 g (0.022 mol) bromobenzene in 30 ml diethyl ether. After 12 h the mixture was filtered, and the filtrate was shaken with cold water, dried over $CaCl_2$, and evaporated. The residue was distilled at 98–103°C/3 mmHg, (lit. 95°C/2 mmHg [6]) to give 2.8 g of triethyl(phenylthio)silane (yield 62%).

Reaction with ethylmagnesium bromide

The solution of 1.8 g obtained by treatment (0.01 mol) of *N*-bromosuccinimide with 1.48 g (0.01 mol) of triethylsilanethiol in 25 ml diethyl ether was filtered and then added dropwise to the Grignard reagent obtained from 0.24 g (0.01 mol) Mg and 1.50 g (0.011 mol) n-butyl bromide in 15 ml diethyl ether. After 12 h the mixture was filtered, and the filtrate was washed with cold water, dried over $CaCl_2$ and evaporated. The residue was distilled at 115°C/20 mmHg (lit 110°C/15 mmHg [6]) to give 1.4 g of triethyl(butylthio)silane (yield 70%).

Reaction with n-butyllithium

n-Butyllithium (5 ml, 15% in n-hexane) was added at $-50°C$ to a solution mixture of 1.8 g (0.01 mol) of *N*-bromosuccinimide and 1.48 g (0.01 mol) of triethylsilanethiole in a mixture of 25 ml diethyl ether and 5 ml benzene. After the mixture had been allowed to warm to room temperature, GLC analysis showed the presence of the following products (which were identified by GC/MS): BuSBu, $Et_3SiSSiEt_3$, BuSSBu, $BuSSiEt_3$ and Et_3SiX (yields ca. 20, 20, 5, 10 and 60%, respectively).

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