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REDUCTIVE SILYLATION REACTIONS OF SULFIDES. A FACILE CONVERSION OF CARBON-SULFUR LINKAGES INTO CARBON-SILICON ONES

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It has been found that various phenyl sulfides undergo reductive silylation to afford the corresponding alkyltrimethylsilanes in good yield.

Since several characteristic features of trialkylsilyl groups have been utilized for organic synthesis in various aspects,[1] much attentions have been focused on the preparation of organosilicon compounds. Among the various methods reported hitherto, reductive silylation of the unsaturated systems with alkali metal-chlorotrimethylsilane is one of the most versatile procedures.[2]

In the present paper, we wish to describe the reductive silylation reaction of sulfides, which provides an efficient method for new carbon-silicon bond formation. It is well known that various sulfides undergo facile C-S bond cleavage with alkali metals to generate the corresponding carbanions, which are effectively converted into the corresponding hydrocarbons in the presence of proton source, e.g., primary amines.[3] We have examined reactions of sulfides with metallic sodium in the presence of chlorotrimethylsilane with the expectation that the chlorosilane would trap the anion generated to give the corresponding organosilicon compounds. Such an expectation is realized in efficient manner as shown in the following example. To a refluxing THF (50 ml) solution suspended with sodium dispersion (4.50 g, 0.196 mol) was added a THF (20 ml) solution of decyl phenyl sulfide (10.00 g, 40 mmol) and chlorotrimethylsilane (17.36 g, 160 mmol) during 30 min. After it was heated to reflux for additional 4 hr, the deposited materials were filtered off and the filtrate was washed with aq NaOH and then with water. Removal of the solvent followed by distillation afforded decyltrimethylsilane (96-97°C/3.2 Torr.,7.28 g, 85%) along with an appreciable amount of trimethylphenylsilane.[4]

$$\text{Alkyl-S-C}_6\text{H}_5 \xrightarrow{\text{Na, Me}_3\text{SiCl}} \text{Alkyl-SiMe}_3 + \text{C}_6\text{H}_5\text{SiMe}_3$$

The reaction usually proceeds cleanly for n-alkyl phenyl sulfides to afford the corresponding alkyltrimethylsilanes in good yield along with trimethylphenylsilane and thiophenol. Prolonged heating appears to be necessary for complete conversion of phenylthio group into trimethylphenylsilane.

On the other hand, the reaction with sec-alkyl phenyl sulfides is not so effective in tetrahydrofuran or 1,2-dimethoxyethane as the case with primary one and affords the corresponding sec-alkyltrimethylsilanes in only moderate yield, accompanied with substantial formation of non-silylated hydrocarbons. This is probably attributable to the strong tendency of sec-carbanion generated to abstract protons from the solvent[5] or the starting sulfides. Such kind of side-reaction can not be reduced to give the sec-alkyltrimethylsilane in much less amount even if benzene is employed as the solvent.

On contrary to the facile cleavage of alkyl phenyl sulfides, the reaction with dialkyl sulfides proceeds only sluggishly and most of the starting sulfides are usually recovered even after prolonged reaction period.[6] Employment of potassium-sodium alloy as the reducing agent does not improve such a situation.[6]

Diphenyl dithioacetal can also be converted into the corresponding gem-bis(trimethylsilyl)alkane similarly, while diethyl dithioacetal is not appropriate for such a transformation based on the similar reason with dialkyl sulfides.[7]

$$R^1R^2C(SC_6H_5)_2 \xrightarrow{Na,\ Me_3SiCl} R^1R^2C(SiMe_3)_2$$

Further, 1,1,1-tris(trimethylsilyl)alkane can be obtained in good yield through a similar procedure from 1-trimethylsilyl-1,1-bis(phenylthio)alkane prepared easily by treating the corresponding lithiated dithioacetal[8] with chlorotrimethylsilane, as shown in the following equation.

$$RCLi(SC_6H_5)_2 \xrightarrow{Me_3SiCl} \underset{\displaystyle SiMe_3}{\overset{\displaystyle |}{RC(SC_6H_5)_2}} \xrightarrow{Na,\ Me_3SiCl} RC(SiMe_3)_3$$

This type of product appears to be useful especially for the preparation of vinylsilanes,[9] versatile intermediates in organic synthesis.[10]

Direct preparation of vinylsilanes was also attempted, starting from phenyl vinyl sulfides. However, the reaction was quite slow and the corresponding vinylsilane was obtained in only low yield (ca. 30% from 1-decenyl phenyl sulfide). Prolonged heating or use of large excess amount of metallic sodium accompanied complex side reactions, without any improvement of the yield of vinylsilane. On treatment with this reductive silylating system, phenyl-sulfur linkage of phenyl vinyl sulfide appears to be cleaved preferentially to yield the corresponding trimethylvinylthiosilane as the initial product. Indeed, such kind of product derived from phenyl-sulfur bond cleavage could be isolated in

certain case, as shown in the following equation. This might be a reason why the reaction becomes so complex.

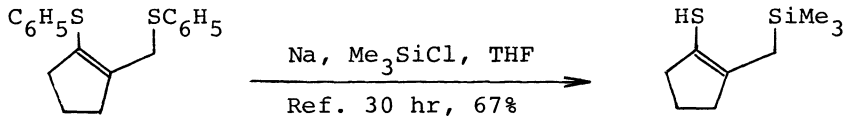

Table. Reductive Silylation of Sulfides with Na-Me_3SiCl

Substrate	Product[a] (B.p., °C/Torr)	Yield (%)
$C_{10}H_{21}SC_6H_5$	$C_{10}H_{21}SiMe_3$ (96-97/3.2)	(85%[b], 96%[c])
$C_6H_5CH_2CH_2CH_2SC_6H_5$	$C_6H_5CH_2CH_2CH_2SiMe_3$ (125-127/37)	(88%[b])
$C_7H_{15}CH(C_2H_5)SC_6H_5$	$C_7H_{15}CH(C_2H_5)SiMe_3$ (110-115/24)	(43%[c,d])
$C_9H_{19}CH(SC_6H_5)_2$	$C_9H_{19}CH(SiMe_3)_2$ (111-115/1.7)	(86%[e])
$C_6H_5CH_2CH_2CH(SC_6H_5)_2$	$C_6H_5CH_2CH_2CH(SiMe_3)_2$ (101-105/1)	(82%[e])
$C_6H_{13}C(SC_6H_5)_2CH_3$	$C_6H_{13}C(SiMe_3)_2CH_3$ (108-112/5)	(75%[e])
$C_5H_{11}C(SC_6H_5)_2SiMe_3$	$C_5H_{11}C(SiMe_3)_3$ (112-117/5)	(84%[e])
$C_6H_5CH_2CH_2C(SC_6H_5)_2SiMe_3$	$C_6H_5CH_2CH_2C(SiMe_3)_3$ (125-130/0.7)	(88%[e])

a) All of the products gave satisfactory analytical and spectral data. They showed characteristic IR absorption bands at ca. 1250, 860, and 840 cm^{-1}. b) The reaction was carried out in THF by heating for 3-4 hr with Na(4.4 eq) and Me_3SiCl(4.0 eq). c) The reaction was carried out under the same condition with b). Glpc yield. d) n-Decane was also formed in 45% yield. e) The reaction was carried out in THF by heating for 4-6 hr with Na(8.8 eq) and Me_3SiCl(8.0 eq). All of these products exhibited characteristic IR absorption band at 980 cm^{-1} attributable to $C(SiMe_3)_2$ functionality.

We are currently studying this type of reaction in more details and exploring synthetic utilities of the organosilicon compounds prepared through these procedures.

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References and Notes

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4) Formation of trimethylphenylsilane could not be excluded completely, which sometimes made it difficult to separate the desired alkyltrimethylsilanes from phenyl derivative by simple distillation.
5) R. B. Bates, L. M. Kroposki, and D. E. Potter, J. Org. Chem., 37, 560 (1972).
6) On treatment of decyl octyl sulfide with Na(8.8 eq) and Me_3SiCl(8.0 eq) for 19 hr under refluxing in THF, decyl- and octyl-trimethylsilanes were obtained in 14 and 17% yields, respectively. On the similar treatment with Na-K(8.8 eq) and Me_3SiCl(8.0 eq) for 10 hr, they were obtained in 7 and 9% yields, respectively.
7) 1,1-Bis(ethylthio)decane afforded the corresponding bis silylated product in 57% yield when it was heated with Na(30 eq) and Me_3SiCl(24 eq) for 10 hr in THF.
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