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A Novel Synthesis of Phenylthiomethyl(PTM) Ethers and Esters by Anodic Oxidation of Phenyl Trimethylsilylmethyl Sulfide[1)]

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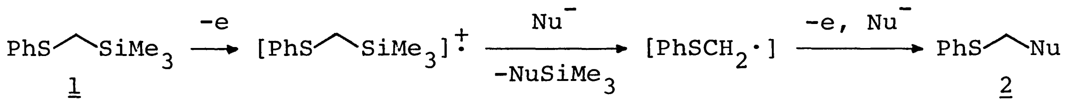
It was found that anodic oxidation of phenyl trimethylsilylmethyl sulfide in the presence of alcohols and carboxylic acids afforded various kinds of PTM ethers and esters, respectively, in good to reasonable yields.

Phenylthiomethyl(PTM) ethers($PhSCH_2OR$) are versatile synthetic reagents for C_1 homologation[2)] and the protection of phenols as PTM ethers has been shown to be a useful technique in organic synthesis.[3)] However, it is not so easy to obtain various desired PTM ethers except for methyl and aryl PTM ethers.[3)]

It is known that α-methoxylated sulfides can be also obtained by anodic methoxylation of sulfides.[4)] But an electron-withdrawing group is necessary for the successful methoxylation. The key step of the reaction may be deprotonation from cation radicals of sulfides generated by one-electron oxidation. Hence, electron-withdrawing groups seem to accelerate the deprotonation to result in methoxylation of the sulfides.

On the other hand, a silyl group is well known to be a good leaving one as a cationic species, in fact, we have shown successful anodic substitution of allyl- and benzylsilanes with oxygen-nucleophiles.[5)]

From these viewpoints, anodic alkoxylation and acyloxylation of phenyl sulfide bearing a trimethylsilyl group at its α-position have been attempted to give a wide variety of PTM ethers and esters, respectively, as shown in Scheme 1.

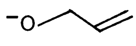
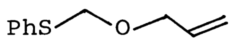
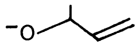
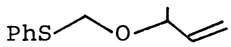


(Scheme 1)

A typical procedure is as follows. An undivided cell was employed, and graphite and platinum plates were used as an anode and a cathode, respectively. The anodic oxidation of 1(2.5 mmol) was carried out at a constant current (1.0 A dm^{-2}) in 0.6 mol dm^{-3} Et_4NOTs/CH_3CN(15 cm^3) containing alcohols(50 mmol) or carboxylic acids(50 mmol) below 5 °C. After 2 x 96485 C mol^{-1} of electricity based on 1 were passed, usual work-up followed by column chromatography on silica gel (hexane-chloroform, 4:1) provided 2 in yields shown in Table 1.

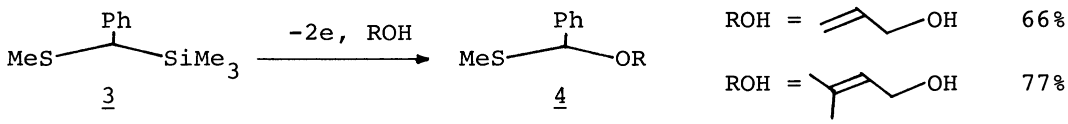
Expectedly, anodic substitution took place and the corresponding PTM ethers and esters were obtained in good to reasonable yields. It is known that readily available chloromethyl phenyl sulfide does not give any corresponding PTM ethers

Table 1. Synthesis of PTM Ethers and Esters from 1

Run	Nucleophile(Nu^-)	Product(2)	Yield[b)]/%
1[a)]	$^-$OMe	PhS⌒OMe	66[c)]
2			60
3			52
4	$^-$OPr^i	PhS⌒OPr^i	49
5	$^-$OBu^t	PhS⌒OBu^t	25
6	$^-$OAc	PhS⌒OAc	66
7	$^-$OCOCHMe$_2$	PhS⌒OCOCHMe$_2$	61

a) Electrolysis was carried out in 0.6 mol dm^{-3} Et_4NOTs/CH_3OH (35 cm^3) containing 2.5 mmol of 1. b) Isolated yield. c) Yield was determined by GLC.

by the reaction with aliphatic alkoxides, e.g., *t*-butoxide generates phenylthiocarbene(PhS$\ddot{C}$H).[6,7] Contrarily, *t*-butyl PTM ether could be obtained by the electrochemical technique (Run 5), although the yield was not satisfactory. It is also noteworthy that various kinds of allyl alkoxides could be used as nucleophiles in this reaction (Runs 2 and 3, and Scheme 2), although they have considerably low oxidation potentials. This is rationalized as due to the fact that the silyl group makes the oxidation potential of 1 lower as observed in the case of allyl- and benzylsilanes.[8)]



(Scheme 2)

Since the allyloxylated products thus formed seem to be useful intermediates for organic synthesis, their utilization is currently under investigation.

References

1) A part of this study has been presented: T. Koizumi, T. Fuchigami, and T. Nonaka, '86 National Meeting of Electrochem. Soc. Jpn., Tokyo, 1986, Abstr. p. 17. 2) J. Otera, J. Synth. Org. Chem. Soc. Jpn., 44, 459 (1986). 3) R. A. Holton and R. V. Nelson, Synth. Commun., 10, 911 (1980). 4) T. Fuchigami, Y. Nakagawa, and T. Nonaka, Tetrahedron Lett., 27, 3896 (1986) and references cited therein. 5) T. Koizumi, T. Fuchigami, and T. Nonaka, Chem. Express, 1, 355 (1986). 6) R. H. Rynbrandt and F. E. Dutton, J. Org. Chem. Soc., 40, 2282 (1975). 7) Recently the alkoxylation under acidic conditions has been reported, but it requires the use of $SnCl_2$ and $AgClO_4$ more than stoichiometric amounts: T. Mukaiyama, T. Sugaya, S. Marui, and T. Nakatsuka, Chem. Lett., 1982, 1555. 8) The oxidation potential of 1 was found to be lower by 0.13 V than that of the parent sulfide($PhSCH_3$).

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