

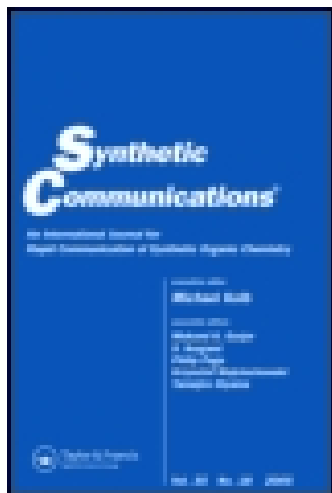
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One-Step Conversion of Formate Esters to O-Silyl Ethers by Means of Samarium Diiodide in the Presence of Chlorosilane Reagents

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**ONE-STEP CONVERSION OF FORMATE ESTERS TO *O*-SILYL
ETHERS BY MEANS OF SAMARIUM DIODIDE
IN THE PRESENCE OF CHLOROSILANE REAGENTS**

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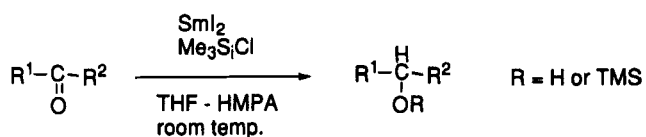
Abstract: One-step conversion of various types of formate esters into the corresponding *O*-silyl ethers under neutral reaction conditions was established by employing samarium diiodide in the presence of chlorosilane reagents.

O-Formyl group is often employed as a protecting group of a number of alcohols in organic synthesis, since such protecting group can generally be cleaved selectively under weakly basic condition in the presence of the other types of ester groups, such as acetate and benzoate.¹ Silyl ethers are also useful protecting

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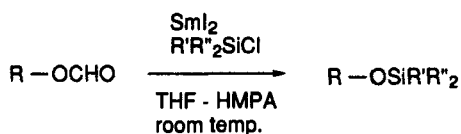
groups for a variety of alcohols, and this types of protecting groups can be removed under either acidic or basic conditions.¹ In the synthesis of structurally complex compounds including natural products having poly-hydroxy functions in the molecules, a manipulation of hydroxy protecting groups are sometimes required to accomplish the synthetic sequences. We are, therefore, interested in searching a convenient method for the conversion of formate esters into the corresponding silyl ethers under mild reaction conditions.

Recently we have published the trimethylsilyl chloride-accelerated reduction of carbonyl compounds by using samarium diiodide.² (Scheme 1)



Scheme 1.

We applied this strategy to the conversion of the formate esters to the corresponding silyl ethers as follows, since this reaction can be carried out under neutral reaction conditions. (Scheme 2)



R = alkyl, aryl, allyl
 R'R''₂ = Et₃, *tert*-BuMe₂

Scheme 2.

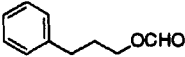
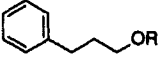
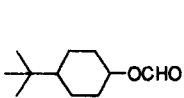

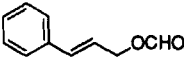
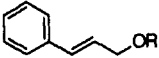
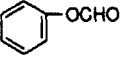

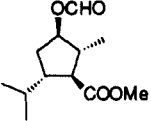
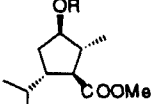
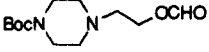
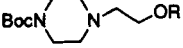
Reaction of the formate ester of 3-phenyl-1-propanol with 2.5 equiv. of samarium diiodide in THF - HMPA (20:1, v/v) in the presence of 2.5 equiv. of triethylsilyl chloride at room temperature for 5 min afforded the corresponding triethylsilyl ether in 97.2% yield. When this reaction was carried out under the similar reaction condition in the absence of triethylsilyl chloride, the alcohol was obtained in quantitative yield. The results obtained were summarized in the Table. Based on the results shown in the Table, it will be figured out that this protecting group-exchange reaction can be applicable to the wide variety of alcohols. The formates³ of the primary (runs 1, 3, and 6) and secondary alcohols (runs 2 and 5) can easily be converted to the silyl ethers. The formate of the allyl alcohol derivative (run 3) can also be transformed into the corresponding silyl ether in good yield. Moreover, the reaction of *O*-formylphenol afforded triethylsilyl ether of phenol as expected in 88% yield (run 4). It should be noted that this reaction can be carried out with remaining of other functional groups, such as alkyl ester and amide groups, intact. Other silylating agents, such as trimethylsilyl chloride and *tert*-butyldimethylsilyl chloride could also be employed in this reaction to give the corresponding silyl ethers. However, desilylated alcohols were sometimes isolated during the work up, when trimethylsilyl chloride was used as the silylating reagent, because of the instability of trimethylsilyl ethers.

Thus, we could disclose a convenient protecting group-exchange reaction of various types of alcohols by means of samarium diiodide and this procedure might be useful in the synthesis of structurally complex poly-hydroxylated compounds.

EXPERIMENTAL SECTION

Products obtained were characterized by comparison of their physicochemical properties (IR, NMR, and MS) with those of the authentic sample. Infrared spectra were recorded for thin films on a JASCO FT/IR-200 Fourier transform

Table. Conversion of the formate esters into the silyl ethers

run	Starting Material	Reaction Conditions	Product	Yield (%)
1		A B C	 R = SiEt ₃ R = H R = TBS	97.2 quant. 99.7
2		A B C	 R = SiEt ₃ R = H R = TBS	quant. quant. 88.5
3		A B	 R = SiEt ₃ R = H	98.2 97.7
4		A B	 R = SiEt ₃ R = H	88.0 99.3
5		A B	 R = SiEt ₃ R = H	92.2 95.8
6		A B	 R = SiEt ₃ R = H	86.1 87.0

Reaction conditions: A : SmI₂ (2.5 eq.), TESCO (2.5 eq.), THF-HMPA (20:1); B: SmI₂ (2.5 eq.), THF-HMPA (20:1); C: SmI₂ (2.5 eq.), TBSCl (2.5 eq.), THF-HMPA (20:1);

infrared spectrophotometer. ^1H and ^{13}C NMR spectra were obtained for solutions in CDCl_3 on a JEOL GSX-270. Mass spectra were measured with a JEOL HMS D-300 spectrometer. Elemental analyses were measured with Yanako MT-5.

General Procedure for the preparation of the formate esters.

To a stirred solution of the alcohol (10 mmol) in chloroform (30 ml) were added formic acid (18 mmol) and DCC (20 mmol) at 0°C under argon, and the resulting mixture was allowed to warm up to room temperature and stirred for further 3 h. After addition of 0.1N hydrochloric acid (20 ml), the mixture was filtered through the pad of Celite and the filtrate was washed with water. The organic layer was dried over Na_2SO_4 . Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel.

General Procedure for the conversion of formate esters to *O*-silyl ethers.

To a stirred solution of the formate ester (1 mmol) in dry THF (30 ml) was added a solution of SmI_2 (2.5 mmol) and TESCl (or TBSCl) (2.5 mmol) in dry THF-HMPA (20:1, 5 ml) at ambient temperature under argon. After the stirring had been continued for 5 min, saturated sodium hydrogen carbonate (20 ml), Celite (20 g) and diethyl ether (50 ml) were added to the solution. The mixture was filtered to remove the insoluble materials and the filtrate was washed with water, and dried over Na_2SO_4 . Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel.

General Procedure for the cleavage of formate esters.

The cleavage of the formate esters was carried out employing the essentially same

procedure as for the conversion into the silyl ethers in the absence of the silylating agent.

Acknowledgements. This work was supported by the Ministry of Educations, Science, Sports and Culture of Japan.

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2. Honda, T. and Katoh, M. *J. Chem. Soc., Chem. Commun.*, 1997, 369.
3. The formate esters (runs 1, 2, 3, 4, and 6) were prepared from the corresponding commercially available alcohols by formylation described in Experimental Section. The formate ester in run 5 was obtained from the corresponding alcohol.⁴
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