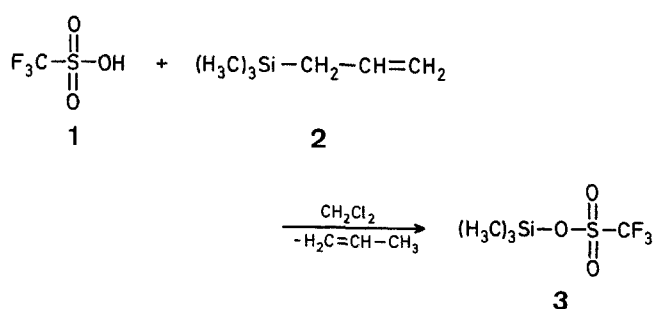


sis of α -methylidene- γ -lactones⁶ and nucleosides^{7,8,9}. Noyori et al. have reported the use of **3** for converting oxiranes into the allylic alcohols, its effectiveness as a catalyst for the reaction of acetals with allyltrimethylsilane or trialkylsilanes, a stereospecific aldol-type condensation of enol silyl ethers, and acetalization of carbonyl compounds¹⁰. The reaction of carboxylic acid *t*-butyl esters with **3** gave the corresponding trimethylsilyl esters and free acids under non-acidic conditions¹¹.

Trimethylsilyl trifluoromethanesulfonate (**3**) fumes in air and is extremely sensitive to atmospheric moisture. The synthetic route to **3** involving chlorotrimethylsilane and expensive silver salt of trifluoromethanesulfonic acid (**1**) in benzene at 80°C for 12 h provides the silyl ester **3** in a moderate yield¹². The preparation of **3** from excess chlorotrimethylsilane and **1** requires prolonged heating of the reaction mixture at 120°C for 24 h to drive off the evolved hydrogen chloride¹³. Häbich and Effenberger reported a new method for preparing **3** from phenyltrimethylsilane and **1** under mild conditions¹⁴.

More recently, we have found allyltrimethylsilane to be an effective silylating agent for alcohols and carboxylic acids¹⁵. The silylation proceeds at 70–80°C in the presence of a catalytic amount of *p*-toluenesulfonic acid in acetonitrile. The new synthetic route to trialkylsilylated derivatives using allylsilanes possesses several advantages such as the availability and stability of the reagent, the lack of by-products, and the high yield of products. In an extension of our silylating method, we planed to apply it to a convenient preparation of **3**.

When allyltrimethylsilane (**2**)¹⁶ was added to trifluoromethanesulfonic acid (**1**) in acetonitrile at 20–25°C within 1 h, an exothermic reaction occurred rapidly and propene was evolved¹⁷. A direct distillation of the reaction mixture gave the corresponding silyl ester (**3**) in 36–41% yield, accompanied by a considerable amount of distillation residue. Using dichloromethane as a solvent in place of acetonitrile, the ester (**3**) was easily prepared in 85% yield and residue hardly remained in the distillation flask. The ¹H-N.M.R. spectrum of a dichloromethane solution of **1** and **2** shows *in situ* formation of **3**.



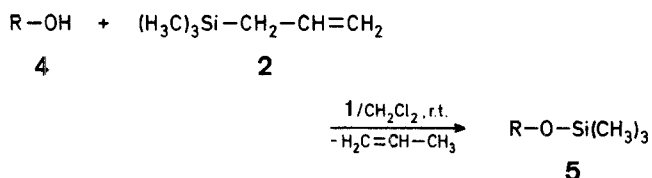
A Simple and Efficient Preparation of Silyl Esters and Ethers Using Allyltrimethylsilane/Trifluoromethanesulfonic Acid

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In recent years, trimethylsilyl trifluoromethanesulfonate¹ (**3**) has been demonstrated to be an excellent reagent for the preparation of enol silyl ethers^{2,3}, α -silylnitriles, *C*-silylated esters⁴, and *N*-silylenamines⁵. It was also applied to the synthe-

As shown in our previous paper¹⁵, the silylation of alcohols and carboxylic acids with allylsilanes catalyzed by *p*-toluenesulfonic acid is slower in dichloromethane or chloroform than in acetonitrile. Recently, Hosomi and Sakurai described the silylation of alcohols and carboxylic acids using allylsilanes catalyzed by iodine or iodotrimethylsilane in chlorinated hydrocarbons¹⁸. We have now found that **1** is the most effective catalyst for this type of silylation using **2**. When the reactions of alcohols **4** with **2** were carried out in the presence of **1** (0.02 equiv.) in dichloromethane at room temperature within 30 min, the corresponding alkyl trimethylsilyl ethers **5** were obtained in 92–96% yields (Table).



Treatment of carboxylic acids **6** with this reagent under the same conditions afforded trimethylsilyl carboxylates **7** in 91–95% yields (Table).

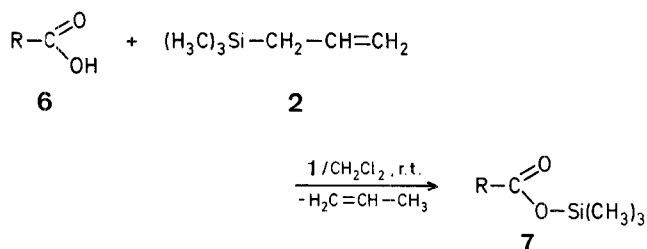


Table. Silylation of Alcohols **4** and Carboxylic Acids **6** with Allylsilane **2** Catalyzed by Trifluoromethanesulfonic Acid **1**

Substrate 4 or 6	Reaction time [h]	Yield [%] ^a	b.p. [°C]/torr	
			observed	Ref. ¹⁵
<i>n</i> -C ₇ H ₁₅ -OH	0.5	96	88–90°/25	83–85°/21
<i>c</i> -C ₆ H ₁₁ -OH	0.5	93	66–68°/23	68–70°/26
1-menthol	1	93	91–93°/10	87–88°/8
borneol	1	92	85–86°/10	92–93°/12
C ₆ H ₅ -CH ₂ -OH	0.5	96	74–75°/10	96–97°/24
C ₆ H ₅ -OH	0.5	94	75–76°/19	78–79°/22
<i>n</i> -C ₈ H ₁₇ -COOH	0.5	95	80–81°/20	75–76°/15
C ₆ H ₅ -COOH	0.5	91	97–98°/10	97–99°/10

^a Yield of product isolated by distillation. Their purities (≥98%) were checked by G.L.C. (5% Silicone OV-17 on Chromosorb W, 3 mm × 3 m, 140°C).

Trimethylsilyl Trifluoromethanesulfonate (**3**):

To a solution of trifluoromethanesulfonic acid (**1**; 1.5 g, 10 mmol) in dry dichloromethane (8 ml), allyltrimethylsilane (**2**; 1.6 g, 14 mmol) is added dropwise with stirring. The reaction temperature is maintained between 15–20°C for 1 h. The resulting mixture is directly transferred to a distillation apparatus. Distillation under reduced pressure gives **3** as a colorless liquid; yield: 1.9 g (85%); b.p. 52–53°C/31 torr (Lit.¹², b.p. 36.5°C/10 torr).

¹H-N.M.R. (CDCl₃): δ = 0.50 ppm.

Silylation of Alcohols **4** or Carboxylic Acids **6**; General Procedure:

A mixture of alcohol **4** (10 mmol) or carboxylic acid **6** (10 mmol), allyltrimethylsilane (**2**; 1.4 g, 12 mmol), and trifluoromethanesulfonic acid (**1**; 0.03 g, 0.2 mmol) in dry dichloromethane (10 ml) is stirred at room temperature for 0.5–1 h. The reaction is monitored by G.L.C.

(5% Silicone OV-17 on Chromosorb W, 3 mm × 3 m, 140°C). After the reaction is complete, triethylamine (0.02 g, 0.2 mmol) is added to the solution to neutralize the catalyst. Then direct distillation of the resulting solution gives **5** or **7** (Table).

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