A New, Simple *in Situ* Preparation of Trimethylsilyl Trifluoromethanesulfonate[1]

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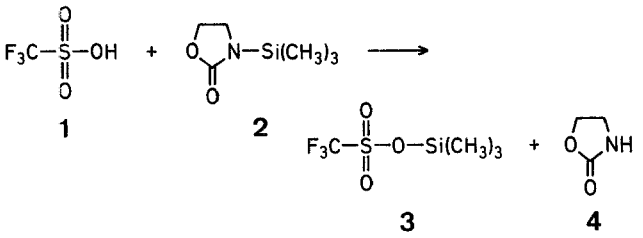
Trimethylsilyl trifluoromethanesulfonate (**3**; trimethylsilyl triflate), is a commercial product with important synthetic applications such as the silyl enol ether and silyl enol acetal preparations[2,3,4]. However, interest in the *in situ* formation of **3** by methods which yield only inert by-products has been shown[6,7]. Although a number of methods were described and elegant procedures for the virtually quantitative conversion of trifluoromethanesulfonic acid (**1**) into **3** at room temperature using allyltrimethylsilane[6] or tetramethylsilane[7], were developed, the requirements for an optimal formation of the relevant reagent were not studied. In all cases, the reaction takes place with substantial emission of dangerous flammable gases.

Other silylating agents such as hexamethyldisilazane, *N,O*-bis[trimethylsilyl]acetamide, or 1,3-bis[trimethylsilyl]urea, have been used for the conversion of **1** into **3**, with unsatisfactory results (0%, 20%, or 30% yields of **3**, respectively). This was expected since a complex, adduct-type system is formed similar to that resulting from **3** and tertiary amides and amines[3]. The formation of **3** from **1** and hexamethyldisilazane in acetonitrile was reported[8]. The formation of ammonium chloride and the anhydrous condition required constitute some disadvantages of the method. In a similar way, *N*-trimethylsilylimidazole and *N*-trimethylsilyldiethylamine would also form the respective hydrochlorides; the latter form salts with **1** which do not yield **3** at room temperature.

All the formation reactions described for **3** are further limited with regard to the requirements of: (a) isolation of the triflate, (b) its use in stoichiometric amounts, and (c) its use as catalyst. The procedures we describe below circumvent these peculiarities and are easy to perform on a preparative scale.

To be expected was the reaction of the acid **1** with 3-trimethylsilyl-2-oxazolidinone (**2**) to yield **3** and 2-oxazolidinone (**4**). These results were foreseeable since the reactivity of **2** with numerous carboxylic and sulfonic acids was already known[9]. Thus, trifluoroacetic, methanesulfonic, and chlorosulfonic acids react with **2** in strongly exothermic reaction to give the respective trimethylsilyl derivatives.



The reaction of **1** with **2** is rapid on mixing the components at room temperature (temperature of the mixture reaches 90 °C) and can be monitored by ^{1}H-N.M.R. spectrometry (signal at $\delta = 0.40$ ppm).

The oxazolidinone moiety in **2** is an excellent nucleofugial group and the product **4** is inert towards **3** in mixtures. These properties are valuable for the *in situ* generation and use of reagent **3** from **1** and **2**.

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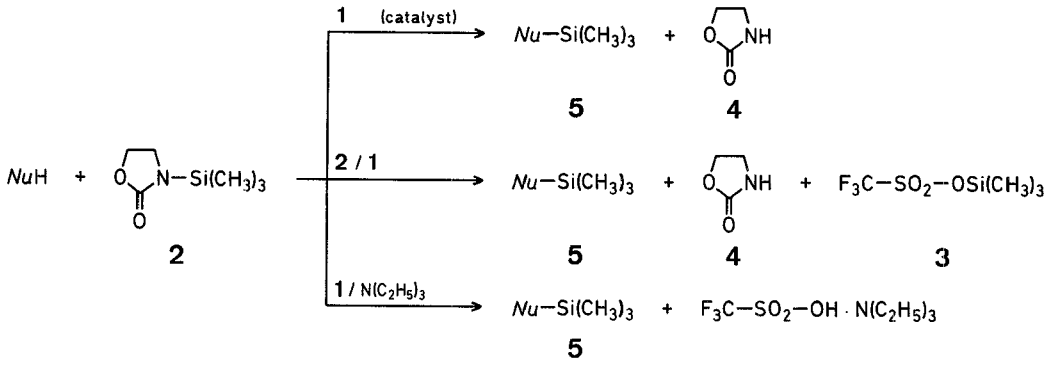

The use of **3** as a catalyst for carbon-carbon, carbon-oxygen, or carbon-nitrogen forming bonds seems promising[2]. This and other properties suggest its use for the silylation of nucleophiles. The alternative procedures involving stoichiometric amounts of a nucleophile (*Nu*—H) and 3-trimethylsilyl-2-oxazolidinone **(2)** are illustrated above.

However, it has been reported that **3** generated *in situ* does not function as a catalyst for silyl enol ether formation[6]. This is due to the fact that trimethylsilyl group transfer does not proceed between **2** and the triethylammonium triflate, consequently, for the preparation of **5** according to the above scheme, stoichiometric amounts of **3** and a tertiary organic base will be necessary. The base is both involved in the reaction mechanism and acts as a neutralizing agent for the possibly aggressive behaviour of the acid **1**.

The ^{1}H-N.M.R. spectra were recorded on a Perkin-Elmer R-12 spectrometer and the mass spectra on a Hewlett-Packard 5930A instrument. The refractive indexes were determined with an Abbe Kyowa 302 model refractometer.

Trimethylsilyl Trifluoromethanesulfonate (3; Trimethylsilyl Triflate):
Trifluoromethanesulfonic acid (**1**; 37.5 g, 0.25 mol) is added gradually to 3-trimethylsilyl-2-oxazolidinone (**2**; 50.8 g, 0.32 mol) while stirring and cooling with ice; the temperature of the reaction is controlled at 40–50 °C. Stirring is continued for 15 min at 40 °C and thereafter the mixture is distilled at reduced pressure; all systems being protected from atmospheric moisture. The product **3** is isolated as a colourless liquid which fumes in air; yield: 54.4 g (98%); b.p. 23–24 °C/3 torr (Ref.[7], b.p. 40 °C/11 torr); d_4^{20}: 1.225; $n_D^{20.5}$: 1.3604.

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 0.50$ ppm (Ref.[7], $\delta = 0.50$ ppm).

M.S. (70 eV): $m/e = 222$ (M^+), 207, 147, 77, 73, 69.

3-Trimethylsilyl-2-oxazolidinone (2)[9]:
In the above isolation of **3**, after distilling there remains a liquid mixture composed of **4** ($\approx$22 g) and excess **2**. Hexamethyldisilazane (35 ml) is added and the mixture refluxed with stirring. When the emission of ammonia has practically finished, the resulting solution is distilled at reduced pressure through a Vigreux column to give **2**; yield: 43.0 g (90%); b.p. 32–34 °C/26–28 torr; $n_D^{21.0}$: 1.45344 (Ref.[9], n_D^{24}: 1.45339).

Trimethylsilyl Triflate (3) Solutions; General Procedures:

Method A: The liquid mixture resulting from the **3** (15 mmol) preparation reaction is cooled, and **4** crystallizes. The chosen solvent (5 ml) is added; when tetrachloromethane is used, the 2-oxazolidinone **(4)** accumulates on the solution surface.

Method B: The acid **1** (0.88 ml, 10 mmol) is gradually added to a solution of **2** (2.4 ml, 15.4 mmol) in the selected solvent (5 ml), while stirring and cooling with a water/ice bath, resulting in virtually quantitative formation of **3**. Homogeneous solutions are obtained using 1,2-dichloroethane, dichloromethane, or acetonitrile as solvent and separation of liquid phases is observed with diethyl ether, methyl *t*-butyl ether, 1,4-dioxan, tetrachloromethane, or benzene in lower proportions.

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