Tetrahedron Letters Vol. 21, pp 767-768
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0040-4039/80/0215-0767$02.00/0

# SILYLATION WITH A PERFLUORINATED RESINSULFONIC ACID TRIMETHYLSILYL ESTER[1]

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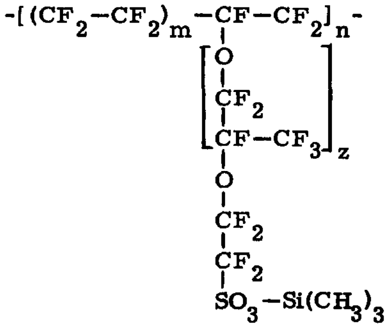
Summary: A new polymer-supported silylating agent, Nafion-TMS, is introduced.

Trimethylsilyl trifluoromethanesulfonate is an efficient silylating agent. Reported herein is the immobilization of the silyl ester on a resin,[2] which allows easy silylation of organic compounds.

We chose Nafion,[3] a perfluorinated resinsulfonic acid, as the supporting framework. The potassium salt of Nafion 511 (35—62 mesh) was converted to the $H^+$ form according to the standard procedure.[4] Then the resin was heated with chlorotrimethylsilane (1 ml/g of resin) and a drop of conc sulfuric acid at refluxing temperature (bath temp 80 °C) for 5 h. The mixture was washed with petroleum ether and then dichloromethane, and evacuated (1 mmHg, 30 °C, 1 h) to afford the desired trimethylsilyl ester I (for which we suggest the name, Nafion-TMS). Through such procedure the incorporation of 0.8 mmol of the silyl group per gram of the resin[5] was obtained. Trimethylsilyl trifluoromethanesulfonate fumes upon exposure to air, but the reagent I does not.



$$-[(CF_2-CF_2)_m-\underset{\substack{|\\ [O-CF_2-CF(CF_3)]_z\\ |\\ O-CF_2-CF_2-SO_3-Si(CH_3)_3}}{CF}-CF_2]_n-$$

I

The polymer-bound reagent thus obtained has reasonable stability and sufficient chemical reactivity. A variety of compounds possessing an active hydrogen atom can be silylated by this reagent. A 1:1:1.2 mixture of a protic substrate, I, and triethylamine (if necessary) in dichloromethane (4.1 ml/g of I) was shaken vigorously at room temperature. The reaction mixture was filtered and the resin was washed thoroughly with dichloromethane. The combined organic solutions were analyzed by GLC or NMR using an internal standard technique. Some examples are given in Table I.

Table I. Silylation by Nafion-TMS

| substrate | base | conditions<br>temp, °C | time, h | product (% yield)[a] |
|---|---|---|---|---|
| $C_2H_5OH$ | none | 29 | 12 | $C_2H_5OSi(CH_3)_3$ (100)[b] |
| $C_6H_5OH$ | $(C_2H_5)_3N$ | 23 | 18 | $C_6H_5OSi(CH_3)_3$ (86) |
| $CH_3COOH$ | $(C_2H_5)_3N$ | 25 | 3 | $CH_3COOSi(CH_3)_3$ (54) |
| $C_2H_5SH$ | $(C_2H_5)_3N$ | 29 | 2 | $C_2H_5SSi(CH_3)_3$ (91) |
| $(C_2H_5)_2NH$[c] | none | 28 | 6 | $(C_2H_5)_2NSi(CH_3)_3$ (94) |

[a] Determined by GLC analysis. [b] Determined by NMR analysis. [c] Substrate/I = 2.4:1.

Acknowledgement. We thank Mitsui Fluorochemicals Co. for generous supply of the potassium salt of Nafion 511.

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(Received in Japan 26 November 1979)