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SULFATED ZIRCONIA: AN EFFICIENT CATALYST FOR SOLVENT-FREE SYNTHESIS OF SILYL ETHERS UNDER MILD CONDITIONS

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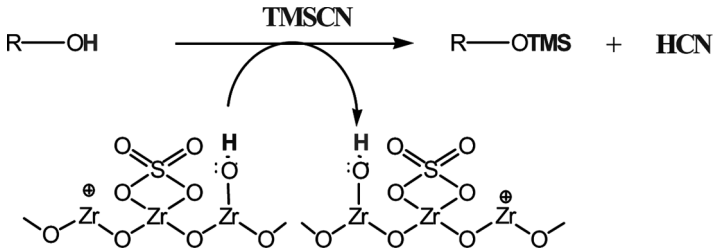
GRAPHICAL ABSTRACT



Abstract *Oximes, allylic, aliphatic, aromatic, cyclic, acyclic, and hetero alcohols are silylated in short reaction times with good yields in the midst of a catalytic amount of sulfated zirconia solid acid catalyst and trimethylsilyl cyanide under nonbasic, solvent-free, and ambient temperature conditions. Selectivity toward O-silyl ether rather than N-silyl ether has been observed. This simple experimental procedure, combined with easy recovery and reusability of the catalyst, is expected to contribute to the development of a clean and environmentally friendly strategy for the synthesis of O-silyl ethers.*

Keywords Heterogeneous catalyst; silylation of alcohols; solid acid; solvent-free; sulfated zirconia

INTRODUCTION

Reliable, selective, and environmentally friendly chemical transformations are crucial to the development of new therapeutics and the design of novel materials. Heterogeneous catalysts that can be easily prepared and used to obtain organic molecules selectivity are important to modern chemical synthesis. The development of protecting groups that shield reactive functionalities has also proved indispensable in the preparation of complex biologically active molecules.[1] Recently, several

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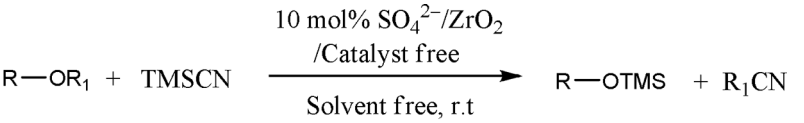
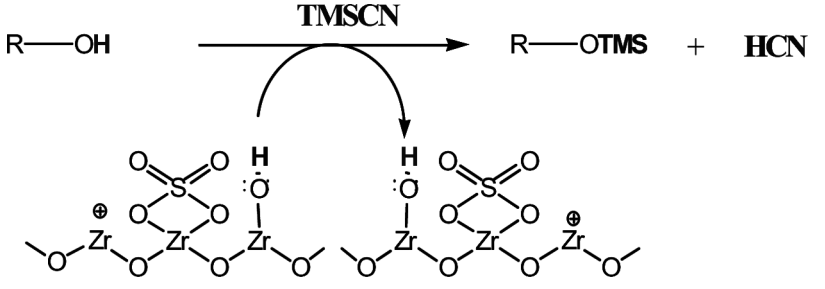


Scheme 1. Efficient and solvent-free O-silylation of alcohols.

groups synthesized an anticancer drug NCX 4040 by selective silylation of 4-hydroxy benzyl alcohol as a starting material.[2] Moreover, the protection of hydroxy groups by silylation is imperative in peptide synthesis and as lipophilicity modifiers for the peptides.[3] A variety of O-silylation methods for the preparation of silyl ether compounds from alcohols have been developed. These methods utilized many silylating agents, such as chlorotrimethylsilane,[4,5] trimethylsilyl azide,[6] triethylsilyl chloride,[7] allylsilane,[8] triethylsilyl hydride,[9] and hexamethyldisilazane[10] for the introduction of a silyl group onto a variety of alcohols. Hexamethyldisilazane (HMDS) is a cheap and commercially available compound that can be used for the preparation of trimethylsilyl ethers from hydroxy compounds. All these methods frequently suffer from drawbacks such as lack of reactivity and difficult removal of ammonium salts. The poor silylating power of HMDS is also the main drawback to its application. Therefore, a variety of catalysts have been employed for activating this reagent, which include sulfuric acid,[11] $ZrCl_4$,[12] nitrogen–ligand complexes of metal chlorides,[13] montmorillonite,[10a] iodine,[14] $H_3PW_{12}O_{40}$,[10c] $LiClO_4$,[15] and $CuSO_4/5H_2O$.[16] Although several of these procedures are useful, most of them suffer from the use of homogeneous[17,18] and often corrosive catalysts, which are usually nonrecoverable and thus potentially polluting,[13,10c] tedious workups, and/or long reaction times. Consequently, new procedures that address these downsides are desirable.

The concept of electrophile activation by Lewis acids has long been the core of catalysis by transition metal complexes. Whereas Me_3SiNu activation remains as an important issue in the development of most effective and highly selective methods for carrying out addition reactions, a new trend based on the simultaneous activation of the Me_3SiNu and the electrophile has been gaining importance. Electrophile activation requires the application of a Lewis acid, and this role is usually played by various transition metal salts and complexes.



Scheme 2. Plausible reaction mechanism for O-silylation of alcohols.

On the other hand, sulfated zirconia (SO_4^{2-}/ZrO_2) is a popular solid superacid catalyst exhibiting the highest acid strength ($H_0 \leq -16.04$).[19] Treatment of a variety of alcohols and phenols with dihydropyrimidinones (DHP) in the presence of a catalytic amount of sulfated zirconia provided the corresponding tetrahydropyrane (THP) ethers in good yields. This procedure could also be efficiently applied to highly acid-sensitive alcohols such as allyl and propargyl alcohols.[20] This solid catalyst was also utilized for the tetrahydropyranylation of hydroquinone protected with benzyl ether.[21] The present investigation was undertaken against this background.

RESULTS AND DISCUSSION

During the itinerary of our investigation on Strecker synthesis, 1,3-asymmetric induction for optically pure α-aminonitrile synthesis,[22] and cyanosilylation of aldehydes,[23] we found that trimethylsilyl cyanide (TMSCN) is activated by promoted zirconia solid acid catalysts. Subsequently, we have initiated our exploration by direct cyanation of secondary alcohols by using sulfated zirconia catalyst and TMSCN. To our surprise, this expected reaction did not work well for the cyanation of alcohols, but silylation of alcohols was accomplished within 2 min. Further, we have reported previously the tetrahydropyranylation of alcohols and phenols under solvent-free conditions by employing sulfated zirconia,[21] and other work on sulfated zirconia catalyst.[24] We therefore commenced the reaction of TMSCN with a wide variety of proton changeable compounds such as alcohols (primary, secondary, tertiary, aliphatic, aromatic, cyclic, acyclic, and allylic), oximes, phenols, carboxylic acids, amines, and thiols. Indeed, the reaction proceeds so fast that within a few minutes, the products were readily isolated either by recrystallization or by column chromatography.

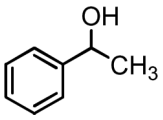
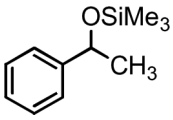
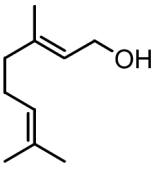
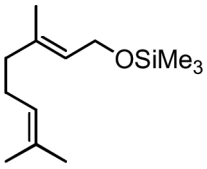
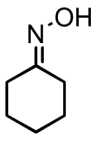
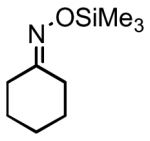
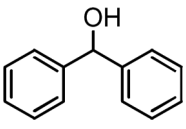
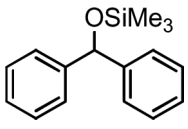
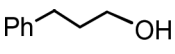
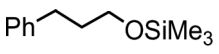
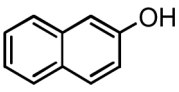
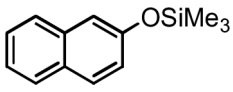
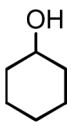
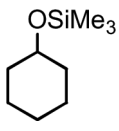
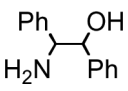
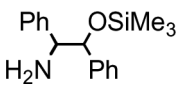
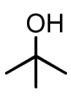
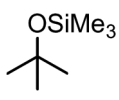
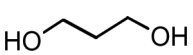
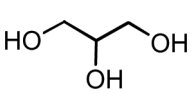
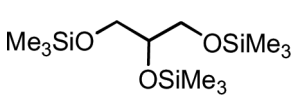
Initially, we instigated our exploration with the screening of various solvents by making use of sulfated zirconia catalyst for O-silylation. Preliminary experiments in various solvents confirmed that the reaction progresses very well under solvent-free conditions (Table 1) in comparison to different solvents. In addition, the reaction is selectively applicable to sterically hindered alcohols, facilitating selective O-silylation rather than N-silylation in the case of 2-amino-1,2-diphenylethanol (entry 8, Table 2) and selective hydroxyl silylation more favorably than addition reactions (entry 2, Table 2). Allylic alcohols proceeded somewhat slower, and O-silylation of citronellol has taken long reaction time, resulting in less yield of product under catalyst-free

Table 1. Screening of solvents for O-silylation of alcohols

Entry	Amount of SO_4^{2-}/ZrO_2 catalyst (mg)	Solvent	Time (min)	Yield (%)[a]
1	50	Dichloro methane	15	82
2	50	Methanol	20	75
3	50	Toluene	60	54
4	50	Benzene	80	72
5	50	Acetonitrile	15	65
6	50	Neat	02	96
7	—	Neat	10	90

[a]Isolated yields of the pure product.

Table 2. Catalyst-free and SO_4^{2-}/ZrO_2-catalyzed O-silylation of alcohols

Entry	Substrate	Product	Time (min)	Yield (%)[a]
1.			02[b]; 10[c]	96[b]; 90[c]
2.			15[b]; 180[c]	90[b]; 63[c]
3.			03[b]; 20[c]	89[b]; 76[c]
4.			03[b]; 08[c]	92[b]; 86[c]
5.			02[b]; 15[c]	92[b]; 88[c]
6.			15[b]; 45[c]	68[b]; 70[c]
7.			02[b]; 10[c]	87[b]; 80[c]
8.			05[b]; —[c]	95[b]; —[c]
9.			30[b]; 30[c]	Traces
10.			02[b]; 08[c]	92[b]; 90[c]
11.			05[b]; 15[c]	85[b]; 76[c]

[a]Yields of isolated products after column chromatography otherwise mentioned.
[b]Reaction with SO_4^{2-}/ZrO_2.
[c]Reaction without catalyst.

condition (entry 2, yield 63%, time 3 h, Table 2). However, this reaction proceeded smoothly in the presence of sulfated zirconia catalyst (entry 2, yield 92%, time 15 min, Table 2). We also observed that TMSCN is inactive in case of tertiary alcohols (not included in the table) and amines toward N-silylation (entry 8, Table 2, also for aniline). Therefore, this might provide access to selective O-silylation more easily than N-silylation and addition reactions.

EXPERIMENTAL

Preparation of Catalyst

Zirconium hydroxide was prepared first from zirconium oxychloride by hydrolysis with dilute aqueous ammonia solution. For this purpose, the requisite quantity of $ZrOCl_2 \cdot 8H_2O$ (Loba Chime, GR grade) was dissolved in doubly distilled water, and aqueous NH_3 was added dropwise with vigorous stirring to this clear solution until the pH of the solution reached 8. The obtained precipitate was washed thoroughly with hot distilled water several times until free from chloride ions and dried at 393 K for 24 h. On the resulting hydrous zirconium hydroxide, sulfate promoter was deposited by a wet impregnation method. To incorporate the promoter, sulfuric acid (Aldrich, analytical reagent grade) was used as the precursor. Detailed procedures for the preparation of this catalyst and its characterization can be found elsewhere.[25,26] In particular, the X-ray powder diffraction and other characterization results revealed the presence of ZrO_2 tetragonal phase. The preferential formation and subsequent stabilization of tetragonal zirconia has been mainly attributed to high acidity and activity of promoted zirconia solid acid catalysts.

Representative Experimental Procedure

A glass reactor was charged under nitrogen atmosphere with the substrate (1.0 mmol), TMSCN (1.2 mmol) (2.2 mmol in case of 1,3 propane diol, 3.2 mmol in case of glycerol reactions), and SO_4^{2-}/ZrO_2 catalyst (50 mg, 10 mol%) and stirred at room temperature for an appropriate time. *Caution*: TMSCN must be used in a well-ventilated hood because of its toxicity and moisture-sensitive nature. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was filtered off and washed with ethyl acetate (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum to yield the corresponding product (column chromatography was performed whenever required). The wet catalyst was used for recycling, and no appreciable change in the activity was noted. NMR and mass spectrometric techniques were utilized for the analysis of products. All products were identified by comparing their spectral data with literature. The spectral data for some selected representative compounds are given.

Selected Data

Trimethyl(1-phenylethoxy)silane (Table 2, Entry 1). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9 H), 1.50 (d, $J = 6.446$ Hz, 3H), 4.88–4.93

(q, $J = 6.446$ Hz, 1H), 7.24–7.29 (m, 1H), 7.31–7.37 (m, 4H); IR (neat) ν 3448, 3030, 2966, 1605, 1450, 1367, 1253, 1096, 958, 944, 755, 698 cm^{-1}; EIMS: m/z 194 (M^+), 193 [$M^+ - H$], 179 [$M^+ - CH_3$], 149 [$M^+ - (CH_3)_3$], 105 [$M^+ - OSi(CH_3)_3$].

(E)-(3,7-Dimethylocta-2,6-dienyloxy)trimethylsilane (Table 2, Entry 2). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.69 (s, 3H), 1.76 (s, 6H), 2.02–2.26 (m, 4H), 4.20 (d, $J = 6.043$ Hz, 2H), 5.15 (t, $J = 6.798$ Hz, 1H), 5.37 (t, $J = 6.798$ Hz, 1H); IR (neat): ν 3453, 3028, 2956, 1947, 1600, 1493, 1450, 1252, 1103, 1058, 967, 889, 746, 695 cm^{-1}; EIMS: m/z 226.

Cyclohexanone O-trimethylsilyl oxime (Table 2, Entry 3). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.55–1.79 (m, 6H), 2.23 (t, $J = 6.798$ Hz, Hz, 2H), 2.50 (t, $J = 6.798$ Hz, 2H); IR (neat) ν 3320, 2933, 2858, 1635, 1447, 1250, 989, 913, 844, 752, 648 cm^{-1}; EIMS: m/z 186 (M + 1) (M^+), 169, 141, 115, 106, 92, 77, 51.

Benzhydryloxytrimethylsilane (Table 2, Entry 4). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 5.84 (s, 1H), 7.27–7.32 (m, 2H), 7.35–7.45 (m, 8H); IR (neat): ν 3029, 2957, 2863, 1949, 1597, 1450, 1253, 1186, 1065, 882, 745, 698, 605 cm^{-1}; EIMS: m/z 258 [M + 1] (M^+), 242 [$M^+ - CH_3$].

Trimethyl(3-phenylpropoxy)silane (Table 2, Entry 5). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.87–1.96 (m, 2H), 2.75 (t, $J = 7.365$ Hz, 2H), 3.66 (t, $J = 6.23$ Hz, 2H), 7.19–7.24 (m, 3H), 7.29–7.34 (m, 2H); IR (neat): ν 3027, 2952, 2862, 1603, 1452, 1615, 1251, 1099, 963, 869, 840, 744, 697 cm^{-1}; EIMS: m/z 209 [M + 1] (M^+), 193[$M^+ - CH_3$], 134, 119, 105, 91, 56.

Trimethyl(naphthalen-2-yloxy)silane (Table 2, Entry 6). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 6.87–6.91 (dd, $J = 6.798$ Hz, $J = 2.266$ Hz, 1H), 7.00 (s, 1H), 7.15 (t, $J = 6.798$ Hz, 1H), 7.24 (t, $J = 6.798$ Hz, 1H), 7.50–7.59 (m, 3H); IR (neat): ν 3056, 2959, 1630, 1597, 1467, 1355, 1260, 1173, 970, 928, 855, 747, 471 cm^{-1}; EIMS: m/z 216 (M^+), 181, 131.

Cyclohexyloxytrimethylsilane (Table 2, Entry 7). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.25–1.46 (m, 5H), 1.54–1.66 (m, 1H), 1.75–1.88 (m, 4H), 3.61–3.68 (m, 1H); IR (neat): ν 3393, 2935, 2860, 1720, 1602, 1504, 1450, 1253, 1180, 1096, 845, 750, 693 cm^{-1}; EIMS: m/z 172 (M^+), 158, 143.

1,2-Diphenyl-2-(trimethylsilyloxy)ethanamine (Table 2, Entry 8). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 9H), 2.54 (s, 2H), 4.37 (d, $J = 6.798$ Hz, 1H), 4.95 (d, $J = 6.798$ Hz, 1H) 7.57–7.64 (m, 10H); IR (neat): ν 3380, 3331, 3276, 3062, 3030, 2956, 2885, 1949, 1598, 1493, 1453, 1251, 1092, 1066, 885, 842, 755, 699, 535 cm^{-1}; EIMS: m/z 286 [M + 1], 196 [$M^+ - OSi(CH_3)_3$].

2,2,8,8-Tetramethyl-3,7-dioxa-2,8-disilanonane (Table 2, Entry 10). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.013 (s, 9H), 1.60 (q, $J = 6.043$ Hz, 2H), 3.54 (t, $J = 12.086$ Hz, 4H); IR (neat): ν 3394, 2956, 1655, 1395, 1253, 1091, 975, 841, 753, 689 cm^{-1}; EIMS: m/z 220 (M^+), 221 (M + 1), 149, 131, 73.

2,2,8,8-Tetramethyl-5-(trimethylsilyloxy)-3,7-dioxa-2,8-disilanonane (Table 2, Entry 11). Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 18H),

0.21 (s, 9H), 3.50–3.55 (dd, $J = 6.043$, $J = 5.288$ Hz, 2H), 3.61–3.66 (dd, $J = 6.043$, $J = 5.288$ Hz, 2H), 3.68–3.80 (m, 1H); IR (neat) ν 3404, 2958, 1638, 1404, 1253, 1147, 1100, 988, 841, 752 cm^{-1}. EIMS: m/z 308 (M^+), 309 (M + 1), 237, 219, 165, 147, 131, 117, 105, 103.

CONCLUSION

In conclusion, we have developed a novel protocol with short reaction times under solvent-free conditions without the requirement of a base for silylation of different types of alcohols and oximes with a simple reaction procedure by using sulfated zirconia and trimethysilyl cyanide for the synthesis of trimethylsilyl ethers in excellent yields.

ACKNOWLEDGMENTS

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