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A facile synthesis of fluorinated alkoxytrimethylsilanes using 1-methylimidazole as an acid scavenger

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Abstract

Fluorinated alkoxytrimethylsilanes ($R_fCH_2OSiMe_3$), potential candidates for the third-generation cleaning agents, were synthesized in high yields over 95% from the reaction of chlorotrimethylsilane and fluorinated alcohol (R_fCH_2OH) in the presence of 1-methylimidazole. Elemental and ^1H NMR spectroscopic analysis showed that the reaction proceeds through the formation of an intermediate, 3-methyl-1-trimethylsilylimidazolium chloride.

Keywords: Chlorofluorohydocarbons; Fluorinated alkoxytrimethylsilanes; CFC alternatives; 1-Methylimidazolium chloride; Ionic liquids

1. Introduction

Chlorine-containing cleaning agents such as CFC-11 ($CFCl_3$), CFC-113 ($CClF_2CCl_2F$), 1,1,1-trichloroethane (CH_3CCl_3), and methylene chloride (CH_2Cl_2) have been widely used in chemical, mechanical, and semiconductor industries because of their excellent solvent property, thermal and chemical stability, and relatively low harmlessness in contact. However, chlorine-containing molecules are recognized as the causes not only for contaminating water but for destroying the stratospheric ozone layer once they are released to the air [1–4]. According to the Montreal Protocol on Substances that Deplete the Ozone Layer, these chemicals are internationally requested to be phased out, and new alternative chemicals, such as HCFC-141b (CH_3CCl_2F), HCFC-225ca/cb ($C_3HCl_2F_5$), and HFC-4310 ($C_5H_2F_{10}$) which have less or no chlorine, have been proposed. However, because HCFCs still contain chlorine atom or atoms and HFCs generally have long atmospheric lifetimes and high global warming potentials, these are accepted only as interim alternatives, namely the second-generation CFCs [5–7].

Fluorinated alkoxytrimethylsilanes ($R_fCH_2OSiMe_3$) containing both oxygen and silicon atoms in the molecular backbone are currently considered as plausible candidates for the third-generation cleaning agent, because they are zero ozone depleting, low global warming, thermally stable, and highly capable of cleaning the surfaces of metals, plastics, and elastomers without any damage.

Besides the application as cleaning agents, fluorinated alkoxytrialkylsilanes can also be used in diverse areas including chemical reaction media, lubricants, foam-blowing agents, polymer modifying agents and insulating agents, due to their excellent physical and chemical properties [8,9].

Fluorinated alkoxytrialkylsilane can be synthesized by the reaction of chlorotrialkylsilane and fluorine-containing alcohol, where hydrochloric acid, inevitably produced as a by-product, is apt to cause the corrosion of facilities [10]. Or it can be prepared from the reaction between hexamethyldisilazane and fluorine-containing alcohol [9]. However, the process suffers from the relatively high cost of raw material, hexamethyldisilazane, and low product yield even at elevated temperatures and a longer reaction time. Furthermore, ammonia, a by-product, is also highly corrosive. Fluorinated alkoxytrialkylsilane was also obtained from the reaction of alkylsilane with fluorinated olefin

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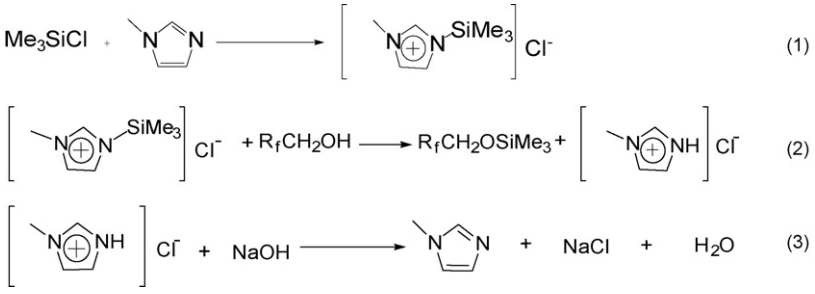

Scheme 1. Pathway to the formation of fluorinated alkoxytrimethylsilane.

in the presence of a peroxide, but the process has some drawbacks such as high cost of fluorinated olefin and difficulty in handling of the explosive peroxide [11].

Recently, BASF developed an elegant process called BASIL (Biphasic Acid Scavenging using Ionic Liquids) using 1-methylimidazole as a HCl scavenger [12–14]. The BASIL process yields a photo-initiating precursor alkoxyphenylphosphine and the ionic liquid 1-methylimidazolium chloride from the reaction of dichlorophenylphosphine and an alcohol in the presence of 1-methylimidazole. The ionic liquid formed in the bottom layer is separated by simple decantation, and then washed with sodium hydroxide to recycle the 1-methylimidazole.

Being motivated by this, we present here a convenient method for synthesizing alkoxytrimethylsilanes by adopting 1-methylimidazole as a HCl scavenger and a reaction promoter, thereby enhancing the product yield and reducing the corrosion problem.

2. Results and discussion

Fluorinated alkoxytrimethylsilanes were synthesized by the reaction of fluorinated alcohol and chlorotrimethylsilane in the presence of 1-methylimidazole as a HCl scavenger as well as a reaction mediator as shown in Scheme 1.

The reaction mixture forms two liquid layers at around 60 °C: upper product layer and lower ionic liquid (1-methylimidazolium chloride) layer. NMR and GC-mass analysis of both layers showed the product, fluorinated alkoxy trimethylsilane was present only in the upper layer. As can be seen in Table 1, fluorinated alkoxytrimethylsilanes were produced in high yields over 95%, irrespective of the types of alcohol and chlorotrimethylsilane, but small amount of disiloxane was always produced as a by-product. The formation of disiloxanes is most likely to be ascribed to water initially present in the reactant mixtures. In fact, the yield of hexamethyldisiloxane was confirmed to increase significantly from 1.7% to 13.2% when chlorotrimethylsilane was reacted with the solution containing 2,2,2-trifluoroethanol, 1-methylimidazole, and water (molar ratio = 1.0/1.1/0.1).

Table 1
Reaction of chlorotrimethylsilane (TMSCl) and fluorinated alcohol

Entry	R_fCH_2OH	Conversion (%)	Selectivity (%)	
			$R_fCH_2OSiMe_3$	Disiloxane
1	CF_3CH_2OH	100.0	98.3	1.7
2	$CF_3CF_2CH_2OH$	100.0	96.4	3.6
3	CH_2FCH_2OH	100.0	97.1	2.9
4	$CF_3CF_2CF_2CH_2OH$	98.4	95.2	4.8
5[a]	CF_3CH_2OH	66.8	98.7	1.3

Molar ratio of TMSCl/R_fCH_2OH/1-methylimidazole = 1/1/1.1.
[a] Reaction was carried out in the absence of 1-methylimidazole.

Fluorinated alkoxytrimethylsilane was also produced from the direct reaction of chlorotrimethylsilane with a fluorinated alcohol even in the absence of 1-methylimidazole, but at a much slower rate. It seems due to the reverse reaction of fluorinated alkoxytrimethylsilane with HCl formed and dissolved in the reaction medium. However, the formation of 2,2,2-trifluoroethyltrimethylsilane was greatly increased when 1-methylimidazole was added to the above reaction mixture after the reaction performed in the absence of 1-methylimidazole.

In order to have a better understanding of the role of 1-methylimidazole, a separate experiment was conducted. When chlorotrimethylsilane was mixed with 1-methylimidazole, a rather unstable compound was produced, which was transformed into 2,2,2-trifluoroethoxytrimethylsilane and 1-methylimidazolium chloride upon contacting with 2,2,2-trifluoroethanol. ^{1}H NMR spectrum of the unstable compound showed a characteristic peak of imidazolium salt at 8.50 ppm, strongly indicating the formation of 3-methyl-1-trimethylsilylimidazolium chloride. It is well known that 1-methylimidazole reacts with alkyl halide to produce 1-alkyl-3-methylimidazolium halide [15]. Likewise, the formation of 3-methyl-1-trimethylsilylimidazolium chloride can be easily expected from the reaction of 1-methylimidazole with chlorotrimethylsilane. Based on these results, 1-methylimidazole seems to function as both a reaction mediator or a promoter and a HCl scavenger.

In addition, the ionic liquids are low melting and immiscible with silicon-containing organic products, the products can be easily recovered by a simple layer separation, where the upper phase mainly contains the products and the lower layer mostly consists of 1-methylimidazolium chloride, which could be converted to 1-methylimidazole by treating with 40 wt.% NaOH aqueous solution at a room temperature.

3. Conclusions

Fluorinated alkoxytrimethylsilanes ($R_fCH_2OSiMe_3$) were obtained in high yields and selectivities from the reaction of

chlorotrimethylsilane and fluorinated alcohol (R_fCH_2OH) using 1-methylimidazole as a HCl scavenger and a reaction mediator. The reaction was found to proceed through the formation of an intermediate, 3-methyl-1-trimethylsilylimidazolium chloride, which was quantitatively converted to alkoxytrimethylsilane and 1-methylimidazolium chloride upon contact with a fluorinated alcohol. 1-Methylimidazole was successfully recovered from 1-methylimidazolum chloride by reacting with 40 wt.% NaOH aqueous solution.

4. Experimental

4.1. Method and materials

All manipulations were carried out under nitrogen atmosphere unless otherwise stated. Fluorinated alcohols, 1-methylimidazole, and NaOH were purchased from Aldrich Chemical Co. and used as received. Cholorotrimethylsilane (98+%) was obtained from Aldrich Chemical Co. and freshly distilled before use according to the literature procedure.

Gas chromatographic analyses of the product mixture were made on an Agilent 6890 gas chromatography equipped with a flame ionization detector and a HP-5 capillary column (0.32 μm × 50 m). The identity of reaction products was confirmed by Agilent 6890-5973 MSD GC-Mass spectrometer. ^{1}H NMR spectra were recorded on a Brucker 400 spectrometer. Elemental analysis was carried out using a Perkin-Elmer 2400 CHNS analyzer. Silicon and F content were analyzed using an ICP-AES (Thermo Polyscan 61E) and Metrohm ion chromatography, respectively, after appropriate treatments.

4.2. Preparation of fluorinated alkoxytrimethylsilanes

4.2.1. Synthesis of 2,2,2-trifluoroethoxy trimethylsilane [16–17]

A 100 mL, three-necked, round-bottomed flask was equipped with an internal thermocouple adaptor, a dropping funnel, and a reflux condenser with a nitrogen inlet adaptor. The flask was flushed with nitrogen, charged with 2,2,2-trifluoroethanol (8.00 g, 80 mmol), 1-methylimidazole (7.22 g, 88 mmol), and *m*-xylene as an internal standard and cooled to 0 °C using an ice bath. To this solution, chlorotrimethylsilane (8.70 g, 80 mmol) in the dropping funnel was added dropwise over a period of 1 h. The resulting solution was then heated to 60 °C and reacted at the temperature for 1 h to complete the reaction.

After the reaction, the product in the upper layer was separated by a decantation and analyzed by GC and GC-Mass (Yield: 98.3%). Elemental analysis calcd. (%) for $C_5H_{11}F_3OSi$: C, 34.87; H, 6.44; F, 33.09; O, 9.29; Si, 16.31. Found: C, 35.22; H, 6.48; F, 33.16; Si, 16.53. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.8 (2H, *q*, J = 8.8 Hz, CF_3CH_2), 0.11 (9H, s, Si–CH_3).

The ionic liquid, 1-methylimidazolium chloride in the bottom layer was treated with 40 wt.% sodium hydroxide (solution) to recycle 1-methylimidazole.

Other fluorinated alkoxytrimethylsilanes were prepared in a similar manner to that employed in synthesizing the above 2,2,2-trifluoroethoxytrimethylsilane but by replacing the fluoroalcohol. All the fluorinated alkoxytrimethylsilanes show the characteristic fragmentation peaks of 77 $[FSi(CH_3)_2]^+$ and $[M\text{-}CH_3]^+$ in the GC-Mass spectra.

4.2.2. 2,2,3,3,3-Pentafluoropropoxy trimethylsilane [18,19]

Yield: 96.4%. Elemental analysis calcd. (%) for $C_6H_{11}F_5OSi$: C, 32.43; H, 4.99; F, 42.75; O, 7.20; Si, 12.63. Found: C, 32.73; H, 5.02; F, 42.26; Si, 12.94. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.02 (2H, *t*, J = 12.4 Hz, CH_2), 0.15 (9H, s, Si–CH_3).

4.2.3. 2-Fluoroethoxy trimethylsilane [20–22]

Yield: 97.1%. Elemental analysis calcd. (%) for $C_5H_{13}FOSi$: C, 44.08; H, 9.62; F, 13.94; O, 11.74; Si, 20.61. Found: C, 45.00; H, 9.82; F, 13.46; Si, 20.21. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.32 (2H, *dt*, J_1 = 48.0 Hz, J_2 = 4.4 Hz, CH_2F), 3.70 (2H, *dt*, J_1 = 28.4 Hz, J_2 = 4.4 Hz, CH_2), 0.02 (9H, s, Si–CH_3).

4.2.4. 2,2,3,3,4,4,4-Heptafluorobutoxy trimethylsilane [18,19,23]

Yield: 95.2%. Elemental analysis calcd. (%) for $C_7H_{11}F_7OSi$: C, 30.88; H, 4.07; F, 48.85; O, 5.88; Si, 10.32. Found: C, 30.12; H, 3.99; F, 49.26; Si, 10.65. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.03 (2H, *t*, J = 12.2 Hz, CH_2), 0.17 (9H, s, Si–CH_3).

4.2.5. Synthesis of 3-methyl-1-trimethylsilylimidazolium chloride [24]

A 100 mL, three-necked, round-bottomed flask was charged with 1-methylimidazole and cooled to 0 °C. To this flask, chlorotrimethylsilane (8.70 g, 80 mmol) was added dropwise over a period of 30 min to produce white precipitates. Yield: 99.3%. Elemental analysis calcd. (%) for $C_7H_{15}N_2SiCl$: C, 44.08; H, 7.93; N, 14.69; Si, 14.72. Found: C, 43.88; H, 7.81; N, 14.35; Si, 14.91. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.50 (1H, s, 2-CH), 7.26 (1H, s, CH), 7.06 (1H, s, CH), 3.78 (3H, s, N–CH_3) 0.34 (9H, s, Si–CH_3).

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