Easy Preparation of Enoxysilanes from Aldehydes and Ketones Catalyzed by Samarium Diiodide

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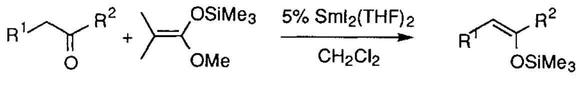
Ketones and α-substituted aldehydes are converted to trimethylsilyl enol ethers by reaction with the trimethylsilyl ketene acetal of methyl isobutyrate in dichloromethane in presence of a catalytic amount of samarium diiodide.

Enoxysilanes are useful intermediates for various chemical transformations and their preparations have been reviewed.[1] Two main methods have been described for the conversion of aldehydes and ketones into silyl enol ethers: (i) reaction of chlorosilanes with carbonyl compounds in the presence of amines: (ii) addition of chlorosilanes to the preformed lithium or potassium enolates.[2] The major products obtained by these methods are thermodynamic and kinetic isomers, respectively. The nature of the solvent has been shown to influence the *E*/*Z* ratio in the preparation of *tert*-butyldimethylsilyl ethers in THF/hexane mixtures.[3] Regio- and stereoselectivities in the formation of enol ethers have been controlled by the use of manganese enolates.[4] When ethyl trimethylsilylacetate is employed as a silylating agent high selectivities for the formation of the *Z* isomer are also observed.[5] Silyl triflates in the presence of amines yield enoxysilanes, especially in the case of sterically hindered ketones.[6] Other methods of preparation, such as the reaction of iodotrimethylsilane prepared in situ, in acetonitrile, with carbonyl compounds,[7] or electrochemical process synthesis,[8] have been reported. Most of these preparations involve either the formation of enolates at low temperature and in the presence of HMPA, or the separation of moisture sensitive compounds from ammonium salts, and need cautious workup for the reactions and the isolation of the silyl enol ethers.

We recently disclosed that $SmI_2(THF)_2$ in CH_2Cl_2 is a very efficient Lewis acid catalyst for various reactions such as aldolization, Michael and Diels–Alder reactions or ring opening of epoxides by nucleophiles.[9] In the presence of 5 % $SmI_2(THF)_2$, the trimethylsilyl ketene acetal derived from methyl isobutyrate (1-methoxy-2-methyl-1-trimethylsilyloxypropene) reacts with aromatic aldehydes, linear aliphatic aldehydes and acetophenone to give addition products as silylated ethers in good yield. With aliphatic ketones or bulky aldehydes the trimethylsilyl enol ethers of the carbonyl compounds are obtained instead of the aldolization products. We wish to report now an easy method of preparation of enoxysilanes, using the trimethylsilyl ketene acetal of methyl isobutyrate (KSA) as a silylating agent, and $SmI_2(THF)_2$ as a catalyst.

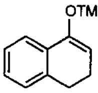
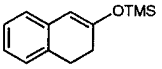
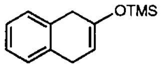
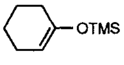
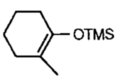
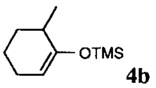
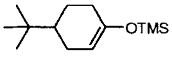
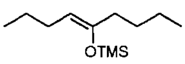
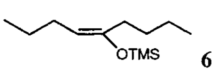
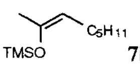
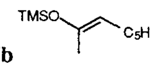
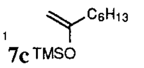
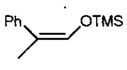
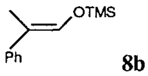
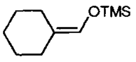
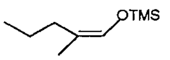
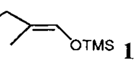
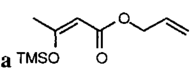
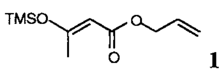
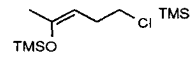
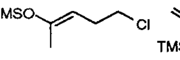
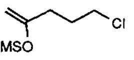
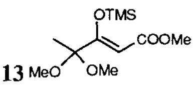


To a dark blue suspension of $SmI_2(THF)_2$ in dichloromethane are successively added KSA and the carbonyl compound (see Table 1). With aldehydes and cyclic ketones, using 5 % catalyst and 1.1 equiv KSA, the reaction is complete within half an hour, while linear ketones need a longer reaction time (24 h for nonan-5-one, octan-2-one or 3-chloropentan-2-one, entries 6, 7 and 12). Addition of hexane to the reaction mixture allows the precipitation of samarium salts, which are easily filtered off. After evaporation of the solvents, the enoxysilanes prepared from ketones are obtained with a purity over 95 %, as shown by their NMR spectra. The aldolization products are formed in small amounts only in the reactions involving aldehydes with a substituent in the α-position to the carbonyl (entries 8–10). The reaction tolerates the presence of different functional groups: enoxysilanes can be prepared from a β-oxo ester (entry 11) or 5-chloropentan-2-one (entry 12). Using a β-oxo ester with an acetal in the α-position the formation of the enoxysilane was observed, but the reaction is much slower than with other substrates, probably due to the presence of several oxygen atoms (entry 13). Silyl ethers were obtained preferentially to the enoxysilanes on reaction of α- or β-hydroxy ketones with one equivalent of KSA. With very bulky ketones, such as camphor or norcamphor, enoxysilanes are not formed. The transformation of carbonyl compounds into enoxysilanes is much slower in THF than in dichloromethane and the yield is low (33 % of enoxysilanes **2** are obtained after 24 h in THF).

For the carbonyl compounds which can yield several regioisomers, the thermodynamic isomer is formed preferentially (entries 2, 4, 7, 12). The reaction of 2-methylcyclohexanone with KSA has been performed at −78 °C and gave the same ratio of regioisomers as at room temperature, **4a**/**4b** 90:10. This result allows a mechanism to be discarded involving a samarium enolate or a naked enolate which should lead to the kinetic isomer at low temperature.[2] Moreover various studies have shown that samarium enolates do not rapidly react with chlorotrimethylsilanes.[10] With linear ketones such as nonan-5-one, octan-2-one, or 5-chloropentan-2-one *Z* isomers (**6a**, **7a** and **12a**) are the major ones as well as with α-substituted aldehydes such as 2-phenylpropanal or 2-methylpentanal (entries 8 and 10).

We had previously observed that various lanthanide iodides are active catalysts for reactions such as aldolization or the ring opening of epoxides.[9] We have tested presently their activity for the formation of the trimethylsilyl ether of nonan-5-one which needs a longer reaction time than for other substrates. The results reported in Table 2 show that the oxidation state of the catalyst has no dramatic effect on its activity, since samarium diiodide and samarium triiodide give similar results (entries 1 and 2). The

Table 1. Synthesis of Enoxysilanes from Ketones and Aldehydes

Entry	Carbonyl compound	Enoxysilane	Yield (%)[a]	Regioselectivity[g]	Ratio (*Z*/*E*)[g]
1	α-tetralone	 **1**	88[b]		
2	β-tetralone	 **2a**  **2b**	70[b]	**2a**/**2b** 98:02	
3	cyclohexanone	 **3**	70[b]		
4	2-methylcyclohexanone	 **4a**  **4b**	74[b]	**4a**/**4b** 90:10	
5	4-*tert*-butylcyclohexanone	 **5**	77[b]		
6	nonan-5-one[d]	 **6a**  **6b**	60[c]		82:18
7	octan-2-one	 **7a**  **7b**  **7c**	65[c]	**7a** + **7b**/**7c** 89:11	75:25
8	2-phenylpropanal[e]	 **8a**  **8b**	72[b]		90:10
9	cyclohexanecarbaldehyde[e]	 **9**	73[b]		
10	2-methylpentanal[f]	 **10a**  **10b**	78[b]		70:30
11	allyl 3-oxobutanoate	 **11a**  **11b**	80[c]		82:18
12	5-chloropentan-2-one[d]	 **12a**  **12b**  **12c**	75[c]	**12a** + **12b**/**12c** 90:10	78:22
13	methyl 4,4-dimethoxy-3-oxopentanoate	 **13**	93[h]		100:0

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[a] Reactions are performed with 5% $SmI_2(THF)_2$, isolated yield (%) after distillation.
[b] Time of reaction of 30 min.
[c] Time of reaction of 24 h.
[d] 10% $SmI_2(THF)_2$ are used.
[e] 10% Aldol is obtained in the crude mixture (measured by GC and NMR).
[f] 5% Aldol is obtained in the crude mixture (measured by GC and NMR).
[g] Isomer ratios are measured by NMR.
[h] Time of reaction of five days, yield in crude product.

reaction is faster with samarium diiodide, samarium triiodide and lanthanum triiodide than with the other catalysts. The nature of the metal and of the ligands also influences the stereochemistry of the product formed: a bulky ligand such as *tert*-butyloxy brings a decrease in the selectivity in the *Z* isomer (entry 3), while the best results (**6a**/**6b** 90:10) are obtained with lanthanum, europium and ytterbium iodides (entries 4–6). This *Z*/*E* ratio is similar to values reported with other methods.[4] Amongst lanthanide iodides, $LaI_3(DME)_2$ is the best catalyst for the preparation of compound **6** in terms of activity and stereoselectivity.[11]

Table 2. Influence of the Catalyst on the Formation of Enoxysilane **6**

Entry	Catalyst	Yield (%)[a]	Ratio **6a**/**6b**[b]
1	$SmI_2(THF)_2$	90	82:18
2	$SmI_3(THF)_3$	88	78:22
3	$SmI_2OtBu(THF)_3$	78	75:25
4	$LaI_3(DME)_2$	95	90:10
5	$EuI_2(THF)_2$	60	88:12
6	$YbI_3(DME)_2$	84	90:10

[a] Yields measured by GC and NMR after 24 h and using 10% catalyst.

[b] The ratio of isomers **6a**/**6b** are measured by GC and NMR.

In order to determine the influence of the bulk of the ketene acetal on the *Z*/*E* selectivity of enoxysilane, we examined reaction of nonan-5-one with trimethylsilyl ketene acetal derived from methyl propionate and *tert*-butyldimethylsilyl ketene acetal derived from ethyl acetate catalyzed by 10% $SmI_2(THF)_2$. The *Z*/*E* ratios were respectively 69:31 and 74:26. In the latter case only 60% enoxysilane was formed after 48 h reaction time and in both cases the *Z* selectivity was lower than that obtained with the dimethyl-substituted silyl ketene acetal (Table 2, entry 1).

The formation of trimethylsilyl enol ethers from various ketones and α-substituted aldehydes via the transfer of

Table 3. Spectroscopic Data for Compounds **1**–**13**

Product	IR ν_{COTMS} (cm^{-1})	MS *m*/*z* (%)	^1H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
1	1638	218 (M^+, 74), 203 (36), 190 (24), 128 (24), 115 (19), 73 (100), 45 (15)	7.42–7.07 (m, 4H), 5.17 (t, 1H, *J* = 4.6, CH), 2.75 (t, 2H, *J* = 8.2, CH_2), 2.31 (m, 2H, CH_2), 0.22 [s, 9H, $Si(CH_3)_3$]	150.82, 144.49, 133.39, 132.61, 128.77, 127.17, 126.63, 105.32, 29.71, 23.28, 0.20
2a	1638	218 (M^+, 98), 203 (6), 201 (17), 128 (11), 115 (11), 73 (100), 45 (13)	7.30–7.01 (m, 4H), 5.69 (s, 1H, CH), 2.89 (t, 2H, *J* = 10, CH_2), 2.35 (t, 2H, *J* = 10, CH_2), 0.27 [s, 9H, $Si(CH_3)_3$]	149.04, 135.64, 131.95, 126.91, 126.41, 124.70, 124.62, 105.95, 29.20, 28.85, 0.32
3	1670	170 (M^+, 30), 155 (34), 127 (28), 75 (100), 73 (75)	4.75 (m, 1H), 1.85 (m, 4H, 2 × CH_2), 1.65 (m, 2H), 1.45 (m, 2H), 0.10 [s, 9H, $Si(CH_3)_3$]	150.24, 104.22, 29.85, 23.77, 23.13, 22.29, 0.30
4a	1688	184 (M^+, 33), 169 (63), 155 (14), 141 (37), 77 (11), 73 (100), 45 (28)	2.2–1.8 (m, 4H, 2 × CH_2), 1.8–1.2 (m, 5H, CH_3 + CH_2), 0.2 [s, 9H, $Si(CH_3)_3$]	142.88, 111.80, 56.52, 30.27, 30.11, 23.79, 23.03, 0.09
4b	1662	184 (M^+, 32), 169 (43), 155 (8), 142 (24), 127 (25), 77 (11), 73 (100), 45 (28)	4.7 (t, 1H, *J* = 6, CH), 2.2–1.8 (m, 2H, CH_2), 1.8–1.2 (m, 5H), 0.98 (d, 3H, *J* = 7, CH_3), 0.10 [s, 9H, $Si(CH_3)_3$]	
5	1678	226 (M^+, 10), 211 (45), 169 (18), 142 (28), 128 (11), 127 (94), 73 (100)	4.81 (m, 1H), 1.99 (m, 3H, CH_2 + CH), 1.77 (m, 2H), 1.20 (m, 2H), 0.84 (s, 9H, *t*-Bu), 0.15 [s, 9H, $Si(CH_3)_3$]	150.23, 103.97, 43.95, 32.11, 30.95, 27.34, 25.05, 24.36, 0.31
6a	1672	214 (M^+, 9), 199 (5), 185 (43), 130 (27), 73 (100)	4.58 (t, 1H, *J* = 10, CH), 1.94 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 1.30 (m, 6H, 3 × CH_2), 0.87 (t, 6H, *J* = 8, CH_3), 0.15 [s, 9H, $Si(CH_3)_3$]	150.21, 108.22, 42.51, 36.3, 29.15, 27.41, 23.03, 22.21, 13.90, 0.58
6b			4.42 (t, 1H, *J* = 10, CH)	
7a	1677	200 (M^+, 9), 143 (56), 75 (23), 73 (100). HRMS calcd for $C_{12}H_{26}OSi$ 214.1752, found: 214.1744	4.41 (t, 1H, *J* = 7.5, CH), 1.92 (m, 2H, CH_2), 1.73 (s, 3H, CH_3), 1.25 (m, 6H, 3 × CH_2), 0.86 (t, 3H, *J* = 6.3, CH_3), 0.16 [s, 9H, $Si(CH_3)_3$]	146.25, 109.22, 31.69, 29.57, 25.33, 22.67, 22.60, 14.11, 0.65
7b		200 (M^+, 9), 143 (46), 75 (26), 73 (100)	4.63 (t, 1H, *J* = 7.5, CH), 1.92 (m, 2H, CH_2), 1.69 (s, 3H, CH_3), 1.25 (m, 6H, 3 × CH_2), 0.86 (t, 3H, *J* = 6.3, CH_3), 0.16 [s, 9H, $Si(CH_3)_3$]	
7c		200 (M^+, 9), 185 (8), 143 (40), 130 (23), 115 (34), 75 (64), 73 (100)	4.01 (s, 2H, CH_2)	
8a	1685	206 (M^+, 100), 191 (38), 175 (35), 173 (10), 117 (12), 73 (82), 45 (44)	7.51–7.16 (m, 5H, Ph), 6.68 (s, 1H, CH), 2.01 (s, 3H, CH_3), 0.25 [s, 9H, $Si(CH_3)_3$]	136.93, 132.97, 128.55, 128.28, 128.24, 127.72, 125.90, 125.19, 12.18, −0.38
9	1677	184 (M^+, 33), 169 (23), 155 (11), 94 (17), 79 (25), 75 (100), 73 (96), 45 (15)	5.96 (s, 1H, CH), 2.14 (br s, 2H, CH_2), 1.91 (br s, 2H, CH_2), 1.55 (m, 2H, CH_2), 1.47 (m, 4H, 2 × CH_2), 0.137 [s, 9H, $Si(CH_3)_3$]	130.1, 122.6, 30.6, 28.5, 27.1, 25.4, 0.40
10a	1677	172 (M^+, 6), 143 (36), 73 (100), 45 (12) HRMS calcd for $C_9H_{20}OSi$ 172.1283, found: 172.1291	6.01 (d, 1H, *J* = 1.4, CH), 1.79 (t, 2H, *J* = 7.5, CH_2), 1.54 (d, 3H, *J* = 1.4, CH_3), 1.43–1.28 (m, 2H, CH_2), 0.82 (t, 3H, *J* = 7.2, CH_3), 0.13 [s, 9H, $Si(CH_3)_3$]	133.22, 117.81, 35.83, 21.01, 13.92, 12.5, −0.52
10b	1677	172 (M^+, 6), 143 (38), 73 (100), 45 (12)	6.01 (d, 1H, *J* = 1.4, CH), 2.02 (t, 2H, *J* = 7, CH_2), 1.48 (d, 3H, *J* = 1.4, CH_3), 1.43–1.28 (m, 2H, CH_2), 0.86 (t, 3H, *J* = 7.2, CH_3), 0.12 [s, 9H, $Si(CH_3)_3$]	132.91, 118.14, 30.50, 20.43, 14.12, 13.52, −0.01

Table 3. (continued)

Product	IR ν_{COTMS} (cm^{-1})	MS m/z (%)	^{1}H NMR (CDCl$_3$) δ, J (Hz)	^{13}C NMR (CDCl$_3$) δ
11a	1624	214 (M$^+$, 2), 157 (26), 115 (26), 73 (100) HRMS calcd for $C_{10}H_{18}O_3Si$ 214.1025, found: 214.1027	6.0–5.8 (m, 1 H, CH), 5.4–5.2 (m, 2 H, CH), 5.15 (s, 1 H, CH), 4.64 (d, J = 4.8, 2 H, CH$_2$), 2.26 (s, 3 H, CH$_3$), 0.25 [s, 9 H, Si(CH$_3$)$_3$]	167.51, 133.30, 117.58, 99.21, 64.13, 20.72, 0.14
11b			6.0–5.8 (m, 1 H, CH), 5.4–5.2 (m, 2 H, CH), 5.15 (s, 1 H, CH), 4.56 (d, J = 5.5, 2 H, CH$_2$), 2.27 (s, 3 H, CH$_3$), 0.09 [s, 9 H, Si(CH$_3$)$_3$]	170.47, 132.89, 118.88, 99.89, 61.30, 30.12, −0.57
12a	1676	194 (M$^+$, 2), 192 (M$^+$, 5), 143 (46), 95 (12), 93 (28), 75 (11), 73 (100) HRMS calcd for $C_8H_{17}OSiCl$ 192.0737, found: 192.0740	4.46 (t, 1 H, J = 8, CH), 3.44 (t, 2 H, J = 9, CH$_2$), 2.42 (m, 2 H, CH$_2$), 1.77 (s, 3 H, CH$_3$), 0.18 [s, 9 H, Si(CH$_3$)$_3$]	149.16, 103.99, 44.52, 29.74, 22.54, 0.62
12b		194 (M$^+$, 2), 192 (M$^+$, 4), 142 (45), 95 (10), 93 (25), 75 (12), 73 (100) HRMS calcd for $C_8H_{17}OSiCl$ 192.0737, found: 192.0736	4.62 (t, 1 H, J = 8, CH), 3.44 (t, 2 H, J = 9, CH$_2$), 2.42 (m, 2 H, CH$_2$), 1.76 (s, 3 H, CH$_3$), 0.17 [s, 9 H, Si(CH$_3$)$_3$]	
12c		192 (M$^+$, 4), 143 (26), 130 (89), 115 (83), 95 (41), 93 (78), 75 (55), 73 (100)	4.05 (br s, 2 H, CH$_2$)	
13	1628	262 (M$^+$, 0.3), 247 (0.7), 231 (3), 89 (100), 73 (13) HRMS calcd for $C_{11}H_{22}O_5Si$ 262.1240, found: 262.1247	5.44 (s, 1 H, CH), 3.44 (s, 3 H, CH$_3$), 3.00 (s, 6 H, CH$_3$), 1.18 (s, 3 H, CH$_3$), 0.09 [s, 9 H, Si(CH$_3$)$_3$]	166.25, 100.35, 99.23, 52.15, 49.13, 19.48, 0.82

the silyl group of the trimethylsilyl ketene acetal of methyl isobutyrate catalyzed by SmI$_2$(THF)$_2$ and other lanthanide iodides is performed under mild conditions and high yield. The scope of the reaction is broader than that of other nonbasic systems which allow only the direct conversion of ketones[5] or cyclic ketones[13] into enol ethers. Owing to the good selectivities and simplicity of this room temperature procedure which requires nonaqueous workup, and as the products may be used without further purification in the majority of cases, it compares well with previously described methods.

Bruker AM 200 and AM 250 NMR spectrometers operating at 200 and 250 MHz for ^{1}H and 50.4 and 63 MHz for ^{13}C were used for determining spectra. IR spectra were recorded neat in KBr plates on a Perkin-Elmer 883 spectrometer. GC analyses were performed with 25 m BP 1 capillary column connected with a computing integrator. Mass spectra (MS) (70 eV) data were determined on a Ribermag R-10 GC/MS.

SmI$_2$ was prepared by the published procedure.[14] Silyl ketene acetals were purchased from Aldrich or prepared according to Tamura's method.[15]

Known products have spectral data in agreement with those previously reported.[2,7] Satisfactory HRMS were obtained for other enoxysilanes.

2-Trimethylsilyloxy-3,4-dihydronaphthalene (2); Typical Procedure: A solution of SmI$_2$ in THF (0.1 M, 10 mL, 1.0 mmol) was evaporated in a Schlenk tube using a vacuum line before addition under argon of CH$_2$Cl$_2$ (40 mL, distilled from P$_2$O$_5$). SmI$_2$(THF)$_2$ was insoluble in CH$_2$Cl$_2$ and gave a blue suspension. The trimethylsilyl ketene acetal of methyl isobutyrate (4.5 mL, 22 mmol) was added by a syringe followed by β-tetralone (2.6 mL, 19.6 mmol). After the addition of the carbonyl compound the mixture turned yellow and was stirred under argon for 30 min. The Schlenk tube was then opened, hexane (150 mL) was added and the mixture was stirred in contact with air for 15 min which induced the precipitation of samarium salts. After filtration on Celite the solvents were evaporated and enoxysilane **2** was obtained as a colorless liquid (3.95 g, 92 % yield).

Trimethylsilyloxymethylenecyclohexane (9); Typical Procedure: The same procedure as above was followed with a solution of SmI$_2$ (0.1 M, 5 mL, 0.5 mmol) in CH$_2$Cl$_2$ (20 mL), KSA (2.24 mL, 12.0 mmol) and cyclohexanecarbaldehyde (1.20 mL, 10 mmol). After 30 min, hexane (60 mL) was added, the samarium salts were filtered off and the solvent was evaporated. The crude product containing 10 % of silyl ether of aldol was distilled (bp 105 °C/150 mbar) to give pure enoxysilane (1.504 g, 81 % yield).

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