Reduction of Acetals with Samarium Diiodide in Acetonitrile in the Presence of Lewis Acids

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Transformation of acetals into ethers by partial reduction using a samarium diiodide–Lewis acids–acetonitrile system is described. The reaction with aromatic acetals occurred in good yields in the presence of aluminum chloride (2 eq) whereas the corresponding aliphatic, vinylic, and alkynyl derivatives did not afford ethers under the same conditions. β-Elimination to give an enol ether becomes predominant when aliphatic acetals that possess a hydrogen at the 2-position are treated with iodotrimethylsilane in the presence of SmI_2 or SmI_3.

Key words samarium diiodide; reduction; dealkoxylation; acetal; ether

Partial reduction of acetals constitutes an important transformation of ketones or aldehydes into ethers.[1] Among various methods, reaction using the powerful reducing agent samarium diiodide (SmI_2)[2] is very limited because acetals have been recognized as stable to SmI_2 in the absence of additives. Studer and Curran first reported that reduction of dimethyl acetals to methyl ethers proceeded using SmI_2/tetrahydrofuran (THF) in the presence of trifluoroacetic acid or water.[3] Independently, we found that partial reduction of diallyl acetals occurred without additives by simple refluxing in acetonitrile giving α-allyloxy carbanions, which underwent [2,3]-Wittig rearrangement leading to the formation of homoallyl alcohols.[4] We also showed the first example of reduction of dithioacetals to sulfides with SmI_2 in a related reaction.[5] We report here our efforts towards reductive dealkoxylation of acetals with SmI_2 in acetonitrile in the presence of Lewis acids.

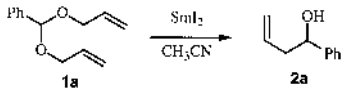
Results and Discussion

In previous work, we found that acetonitrile (CH_3CN) as a solvent is more effective than THF or benzene–hexamethylphosphoric triamide (HMPA) for reduction of diallyl acetals.[4] In addition, reactions in CH_3CN are completely suppressed by addition of HMPA, a well known activator for SmI_2. Therefore, we proposed that the SmI_2-induced [2,3]-Wittig rearrangement, initiated by reductive cleavage of diallyl acetals, could proceed by the mechanism illustrated in Chart 1, in which activation of acetals by complexation with a di- or trivalent samarium ion to generate **3** could be more important than increasing the reducing potential of SmI_2. Because of the strong coordinating ability of HMPA to samarium ions, the formation of complex **3** could be prevented by HMPA, therefore no reaction takes place. THF might also have coordinating ability sufficient to inhibit the complexation, but the ability of CH_3CN might be insufficient. This assumption is supported by the order of the donor number as follows: HMPA (38.8)>THF (20.0)>CH_3CN (14.1).[6]

Based on this consideration, we expected that addition of Lewis acids stronger than samarium ions could activate the acetals. Thus, various Lewis acids as additives were examined to facilitate the transformation of diallyl acetal **1a** into homoallyl alcohol **2a** *via* [2,3]-Wittig rearrangement (Table 1). Reactions were conducted until either **1a** or the purple color of SmI_2 disappeared. Since SmI_2 was consumed independent of the disappearance of **1a** in some cases, excess SmI_2 (5 eq) was used to obtain good yields. Although all Lewis acids afforded yields lower than those observed in their absence, $AlCl_3$ and BF_3-Et_2O allowed the reaction to occur at room temperature.

We next attempted transformation of simple dialkyl acetal **6a** into ether **7a** as shown in Table 2. Surprisingly, the yield of **7a** was much lower (13%) than that of **2a** under the same conditions (refluxing in CH_3CN: Table 2, run 1 *vs*. Table 1, run 1). However, the observed solvent effect was similar to

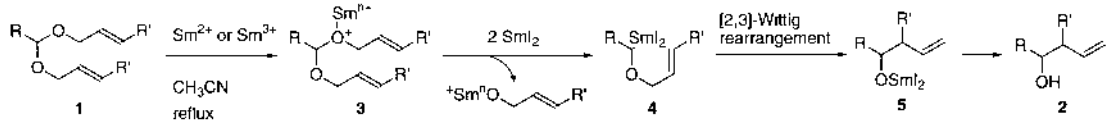
Table 1. Activation of Diallyl Acetal by Lewis Acids



1a 2a

Run	Eq of SmI_2	Additive (eq)	Conditions	Yield (%)[a] of **2a**
1	3	None	Reflux, 2 h	72
2	3	SmI_3 (1)	Reflux, 40 min	64
3	5	TMSCl (2)	Reflux, 30 min	52
4	3	TMSI (1)	Reflux, 15 min	34
5	5	$AlCl_3$ (2)	r.t., 10 min	50
6	5	$BF_3 \cdot Et_2O$ (2)	r.t., 10 min	36
7	3	$ZnCl_2$ (2)	Reflux, 2 h	18
8	3	$SnOTf_2$ (2)	Reflux, 15 min	<2
9	3	$SnCl_2$ (2)	Reflux, 30 min	0
10	3	$MgCl_2$ (2)	Reflux, 30 min	0
11	3	$TiCl_4$ (2)	Reflux, 30 min	0

a) Isolated yield.



1 3 4 5 2

Chart 1

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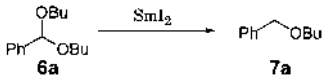
Table 2. Acetal Reduction with SmI_2 under Various Conditions



Run	SmI_2 (eq)	Additive (2eq)	Solvent	Conditions		Yield (%)[a]	Recovery (%)[a]
				Temp.	Time		
1	3	None	CH_3CN	Reflux	30 min	13	24
2	5	None	CH_3CN	r.t.	24 h	0	91
3	3	None	THF	Reflux	2 h	8	76
4	3	None	CH_3CN–HMPA	Reflux	2 h	0	84
5	5	None	PhH–HMPA	Reflux	2 h	0	93
6	5	$AlCl_3$	CH_3CN	r.t.	30 min	80	0
7	5	$AlCl_3$ (1eq)	CH_3CN	r.t.	10 min	14	—[b]
8	5	$AlCl_3$	THF	r.t.	20 min	41	33
9	5	$AlCl_3$	PhH–HMPA	r.t.	24 h	0	92
10	5	$BF_3 \cdot Et_2O$	CH_3CN	Reflux	10 min	72	0
11	5	TMSI	CH_3CN	r.t.	15 min	6	3
12	5	TMSI	CH_3CN	−20 °C	15 min	62	17[c]
13	5	TMSI (1eq)	CH_3CN	−20 °C	2 h	15	71
14	5	CF_3CO_2H	CH_3CN	Reflux	15 min	52	0
15	5	CH_3CO_2H	CH_3CN	Reflux	10 min	43	0
16	5	TsOH	CH_3CN	r.t.	30 min	20	7
17	5	HCl (35%)	CH_3CN	Reflux	4 min	30	0

a) Isolated yield. *b*) Not determined. *c*) Benzaldehyde (18%) was obtained.

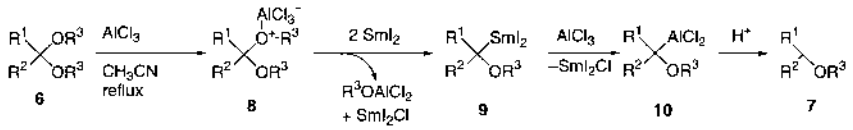


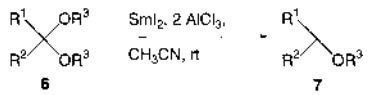
Chart 2

that using diallyl acetals **1**. Reactions conducted in the presence of HMPA (CH_3CN–HMPA or PhH–HMPA) resulted in 0% yield (runs 4, 5). Addition of 2 eq of $AlCl_3$ successfully promoted the reaction to give **7a** in 80% yield whereas decreasing the amount of $AlCl_3$ to 1 eq resulted in 14% yield. When THF or benzen–HMPA (9 : 1) was used as a solvent, the yields were decreased to 41% and 0%, respectively. BF_3-Et_2O was also effective to give a 72% yield of **7a**. Interestingly, iodotrimethylsilane (TMSI; 2 eq) was found effective at low temperature (−20 °C) affording **7a** in 62% yield whereas it was ineffective at room temperature (6%). Brønsted acids promoted the reaction moderately.

Table 3 shows the scope of the reaction using the $AlCl_3$–SmI_2–CH_3CN system. Dialkyl acetals of aromatic aldehydes or ketones underwent reduction to give the corresponding ethers in good yields whereas those derived from aliphatic, alkenyl, and alkynyl aldehydes afforded poor results.

As illustrated in Chart 2, the reduction of acetals may proceed by a mechanism similar to that for diallyl acetals. A net two-electron transfer from SmI_2 to the complex **8** with the liberation of an aluminum alkoxide followed by protonation would give **7**. The observed lower yield of **7a** compared to **2a** can be attributed to the facile decomposition of alkylsamarium intermediates **9a** under reflux conditions.[7] Alkylsamariums possessing an α-allyloxy group such as **4** undergo [2,3]-sigmatropic rearrangement faster than decomposition and product **2** was obtained in good yields. In the presence of $AlCl_3$, the reduction of **6** giving **9** might be completed rapidly at room temperature before the decomposition of **9**.

Table 3. Reduction of Acetals Using the SmI_2–$AlCl_3$–CH_3CN System



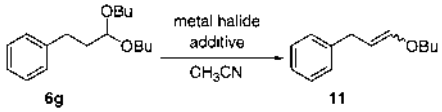
	6			SmI_2	Time	Yield of **7** (%)[a]	Recovery of **6** (%)[a]
	R^1	R^2	R^3				
b	Ph	H	Me	5	40 min	85[b]	0
c		H	Bu	5	30 min	88	3
		H	Bu	3	15 min	80	0
d		H	Bu	5	30 min	84	0
e	Ph	Me	Me	5	4 h	72[b]	0
f	$PhCH_2$	H	Me	5	2 h	0	7
g	$Ph(CH_2)_2$	H	Bu	5	2 h	11	16
h		H	Bu	5	1 h	0	0
i		H	Et	5	2 h	0	79

a) Isolated yield. *b*) Determined by GC.

Alternatively, metal-metal exchange between samarium ion and aluminum ion would generate an alkylaluminum intermediates **10**, which may be stable during the reaction. When 1 eq of $AlCl_3$ was used, exclusive complexation of a liberated alkoxy anion with aluminum ion may prevent the formation of **10**, and therefore, may be responsible for the low yield.

To achieve reduction of aliphatic acetals, we examined the effects of Lewis acids on the reduction of **6g** under several conditions. Unfortunately, we could not find good conditions,

Table 4. Elimination of Aliphatic Acetals Possessing β-Hydrogen



6g 11

Run	Metal halide	Additive	Temp.	Time	Yield (%)	*E*/*Z*	Recovery (%)[a]	Aldehyde (%)[a]
1	$3SmI_2$	2TMSI	r.t.	4 h	20	30/70	4	—[b]
2	$3SmI_2$	5TMSI	r.t.	45 min	60	27/73	14	21
3	—	2TMSI	r.t.	2.5 h	0	—	8	75
4	—	5TMSI	r.t.	25 min	0	—	8	48
5	$5SmI_2$	2TMSI	−20°C	4 h	0	—	83	6
6	$3SmI_3$	5TMSI	r.t.	20 min	64	34/66	8	10
7	$3SmCl_3$	5TMSI	r.t.	45 min	0	—	11	65
8	$3SmCl_3$+30LiI	5TMSI	r.t.	30 min	0	—	16	68
9	9LiI	5TMSI	r.t.	30 min	0	—	2	88
10	$3SmI_2$	5TMSCl	r.t.	75 min	37	30/70	7	33
11	$3SmI_2$+12HMPA	5TMSI	r.t.	1 h	0	—	96	—[b]
12	$5SmI_2$	$2AlCl_3$	r.t.	2 h	0	—	16	14
13	$5SmI_2$	$2AlCl_3$	Reflux	2 h	30	35/65	21	—[b]

a) Isolated yield. *b*) Not determined.

but the formation of enol ether **11** was found to take place when TMSI was used (Table 4). As Jung *et al.* reported that the reaction of acetals with TMSI gives ketones or aldehydes under non-aqueous conditions,[8] 3-phenylpropionaldehyde was obtained without any detectable formation of **11** when the reaction was conducted in the absence of SmI_2. SmI_3 in place of SmI_2 was found to be useful, but $SmCl_3$, LiI, and SmI_2–HMPA did not produce **11** at all. Chlorotrimethysilane (TMSCl), which could generate TMSI in the reaction media, was found to be effective. Miller and McKean reported that β-elimination to give enol ether became predominant when hexamethyldisilazane (HMDS) as a base was added to the reaction of acetals and TMSI.[9] In comparison with their results, it should be noted that our reaction enables the same transformation under non-basic conditions. The stereoselectivity, in which the Z-isomer is major, is similar to that observed in the TMSI-HMDS system.

Experimental

Acetals **1a**, **6a**, **6c**, **6d**, and **6g** were prepared from the corresponding aldehydes according to a method in the literature.[10] Other acetals and chemicals were obtained from commercial sources and used as received unless otherwise noted. CH_3CN and HMPA were distilled from calcium hydride prior to use. Benzene and THF were distilled from sodium/benzophenone prior to use. 1,2-Diiodoethane was purified by treating with $Na_2S_2O_3$. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded in ppm (δ) downfield from tetramethylsilane as an internal standard using a Brüker DPX 400 spectrometer. Infrared spectra were recorded on a JEOL JIR-100 FT-IR spectrometer. Preparative thin-layer chromatography was performed on Merck precoated silica gel plates. GLC analysis was performed on a Hitachi 263-50 Gas Chromatograph with 10% Silicone SE-30 on a Chromosorb WAS DMCS (3 mm×1 m).

Benzaldehyde Diallyl Acetal (**1a**)[11]: A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 4.06 (4H, dt, J=5.5, 1.7 Hz), 5.18 (2H, dq, J=10.4, 1.7 Hz), 5.31 (2H, dq, J=17.2, 1.7 Hz), 5.64 (1H, s), 5.94 (2H, ddt, J=17.2, 10.4, 5.5 Hz), 7.29—7.40 (3H, m), 7.47—7.52 (2H, m). IR (film) cm^{-1}: 3081, 2867, 1646, 1095, 1074, 1041. MS *m*/*z*: 204 (M^+).

Benzaldehyde Dibutyl Acetal (**6a**)[12]: A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (6H, t, J=7.4 Hz), 1.35—1.46 (4H, m), 1.54—1.64 (4H, m), 3.53 (2H, dt, J=9.4, 6.6 Hz), 3.47 (2H, dt, J=9.4, 6.6 Hz), 5.50 (1H, s), 7.27—7.38 (3H, m), 7.44—7.49 (2H, m). IR (film) cm^{-1}: 3070, 3035, 2960, 2935, 2873, 1103, 1068, 1039. MS *m*/*z*: 236 (M^+). *Anal.* Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.09; H, 10.37.

4-Biphenylcarboxaldehyde Dibutyl Acetal (**6c**): A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (6H, t, J=7.4 Hz), 1.37—1.48 (4H, m), 1.57—1.66 (4H, m), 3.50 (2H, dt, J=9.4, 6.6 Hz), 3.58 (2H, dt, J=9.4, 6.6 Hz), 3.54 (1H, s), 7.31—7.37 (1H, m), 7.40—7.46 (2H, m), 7.51—7.55 (2H, m), 7.56—7.62 (4H, m). ^{13}C-NMR ($CDCl_3$) δ: 14.0, 19.5, 32.0, 65.3, 101.5, 127.0, 127.2 (2C), 127.3, 128.8, 138.3, 141.0, 141.1. IR (film) cm^{-1}: 3058, 3031, 2958, 2931, 2873, 1101, 1068, 1041, 1008. *Anal.* Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.96; H, 9.12.

2-Naphthaldehyde Dibutyl Acetal (**6d**): A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.92 (6H, t, J=7.4 Hz), 1.36—1.48 (4H, m), 1.58—1.67 (4H, m), 3.51 (2H, dt, J=9.4, 6.6 Hz), 3.58 (2H, dt, J=9.4, 6.6 Hz), 5.65 (1H, s), 7.43—7.51 (2H, m), 7.55—7.60 (1H, m), 7.80—7.89 (3H, m), 7.94 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 14.0, 19.5, 32.0, 65.3, 101.7, 124.6, 125.9, 126.0, 126.1, 127.7, 128.0, 128.3, 133.1, 133.4, 136.7. IR (film) cm^{-1}: 3060, 2958, 2933, 2871, 1170, 1126, 1099, 1066, 1043. *Anal.* Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.66; H, 9.28.

Phenylpropionaldehyde Dibutyl Acetal (**6g**): A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (6H, t, J=7.4 Hz), 1.34—1.45 (4H, m), 1.52—1.61 (4H, m), 1.90—1.98 (2H, m), 2.65—2.72 (2H, m), 3.42 (2H, dt, J=9.3, 6.6 Hz), 3.58 (2H, dt, J=9.3, 6.6 Hz), 4.47 (1H, t, J=5.7 Hz), 7.14—7.22 (3H, m), 7.24—7.30 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 13.9, 19.5, 31.1, 32.1, 35.1, 65.4, 102.4, 125.8, 128.4, 128.4, 141.9. IR (film) cm^{-1}: 3033, 2958, 2871, 1128, 1043. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.26; H, 10.40.

Typical Procedure for [2,3]-Wittig Rearrangement in the Presence of Lewis Acids Benzaldehyde diallyl acetal **1a** (0.196 mmol) was added to a solution of SmI_2 (0.099 M, 0.979 mmol) and $AlCl_3$ (0.392 mmol) in CH_3CN at room temperature. After 10 min, the reaction mixture was poured into aqueous K_2CO_3, and extracted with ether. The organic layer was washed with water and brine and dried over $MgSO_4$. After evaporation, the residue was purified by preparative TLC (hexane/AcOEt=8 : 2) to give **2a**[4] as a colorless oil (yield 50%). ^{1}H-NMR ($CDCl_3$) δ: 2.09 (1H, br s), 2.45—2.58 (2H, m), 4.73 (1H, dd, J=7.6, 5.3 Hz), 5.11—5.19 (2H, m), 5.74—5.86 (1H, m), 7.24—7.37 (5H, m). IR (film) cm^{-1}: 3380, 3080, 3040, 2940, 2920, 1640, 1500, 1460, 1320, 1200, 1050. HRMS Calcd for $C_{10}H_{12}O$ *m*/*z*: 148.0888. Found *m*/*z*: 148.0895.

General Procedure for Reduction of Dialkyl Acetals by the SmI_2–$AlCl_3$–CH_3CN System Benzaldehyde dibutyl acetal **6a** (0.169 mmol) was added to a solution of SmI_2 (0.108 M, 0.846 mmol) in CH_3CN followed by addition of a solution of $AlCl_3$ (0.338 mmol) in CH_3CN at room temperature. After 30 min, the reaction mixture was poured into aqueous K_2CO_3, and extracted with ether. The organic layer was washed with water and brine and dried over $MgSO_4$. After evaporation, the residue was purified by preparative TLC (hexane/AcOEt=9 : 1) to give **7a** as a colorless oil (yield 80%).[13] ^{1}H-NMR ($CDCl_3$) δ: 0.92 (3H, t, J=7.4 Hz), 1.34—1.46 (2H, m), 1.56—1.65 (2H, m), 3.47 (2H, t, J=6.6 Hz), 4.50 (2H, s), 7.24—7.36 (5H, m). IR (film) cm^{-1}: 3029, 2958, 2933, 2863, 1101.

Butyl 4-Biphenylmethyl Ether (**7c**): A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.92 (3H, t, J=7.4 Hz), 1.35—1.47 (2H, m), 1.57—1.66 (2H, m), 3.50 (2H, t, J=6.6 Hz), 4.53 (2H, s), 7.29—7.36 (1H, m), 7.37—7.46 (4H, m), 7.53—7.64 (4H, m). ^{13}C-NMR ($CDCl_3$) δ: 14.0, 19.5, 31.9, 70.4, 72.6, 127.1,

127.2, 127.3, 128.1, 128.8, 137.9, 140.5, 141.1. IR (film) cm^{-1}: 3023, 2958, 2861, 1097. *Anal.* Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.24; H, 8.63.

Butyl 2-Naphthylmethyl Ether (**7d**): A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (3H, t, J=7.4 Hz), 1.36—1.47 (2H, m), 1.58—1.67 (2H, m), 3.52 (3H, t, J=6.6 Hz), 4.66 (2H, s), 7.42—7.50 (3H, m), 7.77 (1H, s), 7.79—7.85 (3H, m). IR (film) cm^{-1}: 2927, 2854, 1054. *Anal.* Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.84; H, 8.58.

Butyl Phenylpropyl Ether (**7g**)[14]: A colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (3H, t, J=7.4 Hz), 1.33—1.44 (2H, m), 1.52—1.61 (2H, m), 1.85—1.94 (2H, m), 2.69 (2H, t, J=7.7 Hz), 3.41 (2H, t, J=6.6 Hz), 3.41 (2H, t, J=6.4 Hz), 7.14—7.21 (3H, m), 7.24—7.30 (2H, m). IR (film) cm^{-1}: 3027, 2935, 2863, 1114. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.27; H, 10.65.

Butyl 3-Phenyl-1-Propenyl Ether (**11**): A colorless oil. ^{1}H-NMR ($CDCl_3$) for *E* isomer: δ: 0.93 (3H, t, J=7.4 Hz), 1.34—1.47 (2H, m), 1.58—1.67 (2H, m), 3.26 (2H, d, J=7.3 Hz), 3.66 (2H, t, J=6.6 Hz), 4.92 (1H, dt, J=12.6, 7.3 Hz), 6.34 (1H, d, J=12.6 Hz), 7.14—7.31 (5H, m). for *Z* isomer: δ: 0.94 (3H, t, J=7.4 Hz), 1.34—1.47 (2H, m), 1.58—1.67 (2H, m), 3.43 (2H, d, J=7.4 Hz), 3.77 (2H, t, J=6.6 Hz), 4.55 (1H, td, J=7.4, 6.2 Hz), 6.06 (1H, dt, J=6.2, 1.4 Hz), 7.14—7.31 (5H, m). IR (*E*/*Z* mixture) (film) cm^{-1}: 3027, 2960, 2933, 2873, 1664, 1110. MS *m*/*z*: 190 (M^+).

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