A Rapid and Convenient Synthesis of Acylals from Aldehydes and Acetic Anhydrides Catalyzed by $SnCl_4/SiO_2$

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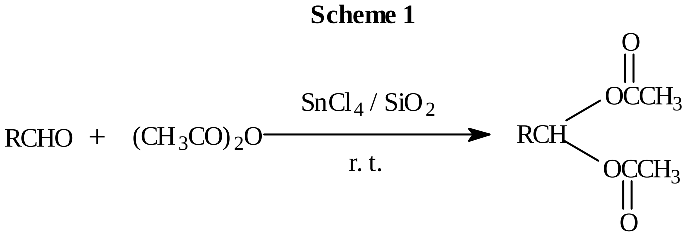
Abstract: A variety of aldehydes were converted into acylals in excellent yields with acetic anhydride in the presence of a catalytic amount of tin (IV) chloride supported on silica gel at room temperature.

Keywords: Acylals, tin (IV) chloride supported on silica gel.

Acylals (1, 1-diacetates) are efficient protecting groups for aldehydes as they are stable in neutral and basic media[1]. Usually, the acylals are prepared from aldehydes and acetic anhydride in the presence of strong protonic acids such as sulfuric acid[2], phosphoric acid[2], or methanesulfonic acid[2], and Lewis acids such as anhydrous zinc chloride[3], phosphorus(III) chloride[4], and anhydrous ferric(III) chloride[5]. Recently the use of montmorillonite clay[7], TMCS-NaI[8], Sc $(OTf)_3$[9], Cu $(OTf)_2$[10] as catalysts have also been reported.

Supported reagents have recently found favor in organic synthesis in view of their higher selectivity, milder reaction conditions and easier work-up. We herein reported that tin (IV) chloride supported on silica gel is an effective reagent for the rapid conversion of various aldehydes to acylals in high yields at room temperature (**Scheme 1**).

Scheme 1



1 **2**

The synthesis of acylals was performed at room temperature in the presence of catalytic amounts of $SnCl_4/SiO_2$ and the desired products were obtained in excellent yields. The results are listed in the **Table 1**.

Table 1 Conversation of aldehydes to the corresponding acylals catalyzed by $SnCl_4/SiO_2$

Aldehydes (**1**) R	Acylals[a] (**2**) R	Time (min)	Yield[b] (%)	mp (°C) Found	mp (°C) Reported
CH_3 (**1a**)	CH_3 (**2a**)	10	83	oil	none
$CH_3(CH_2)_2$ (**1b**)	$CH_3(CH_2)_2$ (**2b**)	10	88	oil	none
CH_2=CH (**1c**)	CH_2=CH (**2c**)	10	85	oil	none
(E)-PhCH=CH (**1d**)	(E)-PhCH=CH (**2d**)	10	95	84-86	83.5-84.5[7]
4-MeO-C_6H_5 (**1e**)	4-MeO-C_6H_5 (**2e**)	20	94	64-65	64-65[2]
4-Me-C_6H_5 (**1f**)	4-Me-C_6H_5 (**2f**)	20	96	81-82	81-82[2]
1-Nathphyl (**1g**)	1-Nathphyl (**2g**)	25	97	105-106	105-106[2]
2-Nathphyl (**1h**)	2-Nathphyl (**2h**)	25	94	99-100	99-100[2]
C_6H_5 (**1i**)	C_6H_5 (**2i**)	20	95	44-46	44-45[2]
4-ClC_6H_5 (**1j**)	4-ClC_6H_5 (**2j**)	15	92	79-81	79-80[2]
4-BrC_6H_5 (**1k**)	4-BrC_6H_5 (**2k**)	15	93	93-95	91-92[2]
2-$NO_2C_6H_5$ (**1l**)	2-$NO_2C_6H_5$ (**2l**)	15	88	85-86	85.5-86.5[2]
4-$NO_2C_6H_5$ (**1m**)	4-$NO_2C_6H_5$ (**2m**)	15	91	125-126	124-125[2]

[a]All the products gave satisfactory spectral analysis for IR, NMR and MS.
[b]Isolated yield.

We have provide a simple, rapid and high-yielding method for the preparation of acylals.

Experimental

Melting points were uncorrected. Infrared spectra were recorded on a Perkin-Elmer 16PC spectrometer using KBr pellet. ^{1}H NMR spectra were recorded on a Bruker ARX 300 (300MHz) instrument in $CDCl_3$ with TMS as an internal standard. Mass spectra were obtained on a Finnigan Mat TSQ7000 spectrometer.

Preparation of $SnCl_4/SiO_2$ reagent

Silica gel (20 g) was stirred with a solution of commercially available $SnCl_4 \cdot 5H_2O$ (5 g, 14 mmoL) in ethanol (100 mL) for 10 min. Then the excess ethanol was removed under reduced pressure and supported $SnCl_4 \cdot 5H_2O$ on SiO_2 was obtained as white powder, which can be kept for several months in air at room temperature without losing its activity.

General procedure for the preparation of acyalals

A mixture of the aldehyde (10 mmoL), acetic anhydride (10 mL) and $SnCl_4/SiO_2$ (1.0 g, Sn^{4+} content 0.56 mmoL) was stirred at room temperature for the length of the time indicated in **Table 1**. The progress of the reaction was monitored by TLC or GC. After completion of the reaction, the catalyst was filtered off and washed with ethyl acetate (10×3 mL). The filtrate was washed with brine and then dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure afforded the corresponding product which was purified by chromatography or by crystallization from cyclohexane to give pure acyalals.

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11. **2a:** ^{1}H NMR($CDCl_3$) δ ppm: 1.47 (d, 3H, J=5.40Hz, CH_3), 2.08 (s, 6H, 2CH_3), 6.78 (q, 1H, J=5.46Hz, CH); IR(KBr) cm^{-1}: 2945, 1748, 1376, 1248, 1217, 1078; MS(CI): 148 (M^+ +2).
2b: ^{1}H NMR($CDCl_3$) δ ppm: 0.94 (t, 3H, J=3.48Hz, CH_3), 1.41-1.44 (m, 2H, CH_2), 1.76-1.78 (m, 2H, CH_2), 2.09 (s, 6H, 2CH_3), 6.81(t, 1H, J=5.61Hz, CH); IR(KBr) cm^{-1}: 2966, 2878, 1764, 1638, 1376, 1248, 1208; MS(CI): 174 (M^+).
2c: ^{1}H NMR($CDCl_3$) δ ppm: 2.11 (s, 6H, 2CH_3), 5.42 (d, 1H, J=10.44Hz, CH=), 5.57 (d, 1H, J=17.31Hz, CH=), 5.84-5.95 (m, 1H, CH=), 7.14 (d, 1H, J=5.64Hz, CH); IR(KBr) cm^{-1}: 2980, 2930, 1750, 1425, 1360, 1230; MS(CI): 159 (M^++1).
2d: ^{1}H NMR($CDCl_3$) δ ppm: 2.14 (s, 6H, 2CH_3), 6.25 (dd, 1H, J=16.02Hz, J=9.54Hz, CH=), 6.89 (d, 1H, J=16.05Hz, CH=), 7.31-7.43 (m, 5H-Ar + CH,); IR(KBr) cm^{-1}: 2938, 1760, 1602, 1496, 1372, 1242, 1202, 1138, 1062, 1008, 944, 752, 696; MS(CI): 234 (M^+).
2e: ^{1}H NMR($CDCl_3$) δ ppm: 2.10 (s, 6H, 2CH_3), 3.80 (s, 3H, CH_3), 6.75 (d, 2H, J=9.0Hz, Ar-H), 7.35 (d, 2H, J=9.0Hz, Ar-H), 7.40 (s, 1H, CH); IR(KBr) cm^{-1}: 1763, 1614, 1519, 1372, 1241, 1204; MS(CI): 238 (M^+).
2f: ^{1}H NMR($CDCl_3$) δ ppm 2.15 (s, 6H, 2 CH_3), 2.37 (s, 3H, CH_3), 7.21 (d, 2H, J=7.98Hz, Ar-H), 7.41(d, 2H, J=8.08Hz, Ar-H), 7.64 (s, 1H, CH); IR(KBr) cm^{-1}: 2928, 2867, 1770, 1750, 1368, 1244, 1206, 1068, 1004, 960, 930, 856, 814; MS(CI): 207 (M^+-Me).
2g: ^{1}H NMR($CDCl_3$) δ ppm: 2.13 (s, 6H, 2 CH_3), 7.47-7.57 (m, 3H, Ar-H), 7.74-7.75 (m, 1H, Ar-H), 7.89-7.93 (m, 2H, Ar-H), 8.19-8.28 (m, 1H, Ar-H), 8.24 (s, 1H, CH); IR(KBr) cm^{-1}: 2927, 1762, 1743, 1512, 1372, 1238, 1201, 938, 920, 808, 776, 738; MS(CI): 258 (M^+).
2h: ^{1}H NMR($CDCl_3$) δ ppm: 2.12 (s, 6H, 2CH_3), 7.50-7.54 (m, 2H, Ar-H), 7.60-7.64 (m, 1H, Ar-H), 7.85-7.91 (m, 4H, Ar-H), 8.00 (s, 1H, CH); IR(KBr) cm^{-1}: 2937, 1751, 1372, 1245, 1209, 1066, 1043, 969, 935, 848, 735; MS(CI): 258 (M^+).
2i: ^{1}H NMR($CDCl_3$) δ ppm: 2.12 (s, 6H, 2CH_3), 7.39-7.41 (m, 3H, Ar-H), 7.51-7.54 (m, 2H, Ar-H), 7.69 (s, 1H, CH); IR(KBr) cm^{-1}: 1758, 1516, 1432, 1374, 1262, 1210, 1012, 948, 762, 702; MS(CI): 209 (M^++1).
2j: ^{1}H NMR($CDCl_3$) δ ppm: 2.13 (s, 6H, 2CH_3), 7.37-7.39 (m, 2H, Ar-H), 7.45-7.48 (m, 2H, Ar-H), 7.64 (s, 1H, CH); IR(KBr) cm^{-1}: 2986, 1758, 1600, 1380, 1246, 1202, 1066, 1010, 978, 940, 914; MS(CI): 244 (M^++1).
2k: ^{1}H NMR($CDCl_3$) δ ppm: 2.14 (s, 6H, 2CH_3), 7.40-7.42 (m, 2H, Ar-H), 7.54-7.57 (m, 2H, Ar-H), 7.64 (s, 1H, CH); IR(KBr) cm^{-1}: 2998, 1756, 1594, 1372, 1208, 1062, 1012, 908, 848, 828; MS(CI): 287 (M^+-1).

2l: ^{1}H NMR($CDCl_3$) δ ppm: 2.16 (s, 6H, 2CH_3), 7.57-7.63 (m, 1H, Ar-H), 7.62-7.68 (m, 2H, Ar-H), 8.05-8.08 (m, 1H, Ar-H), 8.21 (s, 1H, CH); IR(KBr) cm^{-1}: 2938, 2872, 1766, 1591, 1528, 1364, 1257, 1202, 1016, 972, 912; MS(CI): 253 (M^+).
2m: ^{1}H NMR($CDCl_3$) δ ppm: 2.17 (s, 6H, 2CH_3), 7.71 (d, 2H, J=8.73Hz, Ar-H), 7.74 (s, 1H, CH), 8.28 (d, 2H, J=8.76Hz, Ar-H); IR(KBr) cm^{-1}: 1764, 1610, 1530, 1350, 1234, 1204, 1062, 1012, 978, 994; MS(CI): 251 (M^+-2).

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