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Highly Efficient and Chemoselective Thioacetalization of Carbonyl Compounds Catalyzed with Aluminum Trifluromethanesulfonate [AI(OTf)₃]

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ABSTRACT

Aluminum trifluromethanesulfonate $[Al(OTf)_3]$ is a highly efficient and chemoselective catalyst for the thioacetalization of carbonyl compounds.

Key Words: Aluminum trifluromethanesulfonate; Carbonyl compounds; Catalyst; Chemoselective; Solvent-free; Thioacetalization.

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INTRODUCTION

Dithioacetals have long been used as protection groups for the carbonyl functions, while the carbanion forming capacity of cyclic dithioacetals have brought out numbers of useful applications in organic synthesis as the nucleophilic acyl equivalents.^[1,2] In addition, they often serve as intermediates for the conversion of carbonyl compounds to parent hydrocarbons. Dithioacetalization of carbonyl compounds is usually catalyzed by Lewis acids,^[3] protic and solid acids.^[4] We have recently reported efficient thioacetalization reactions catalyzed by molecular iodine,^[5a] trichloroisocyanoric acid^[5b] and heteropoly acids.^[5c] Preparation of dithioacetals has been reviewed recently.^[5d] Now in this report, we wish to introduce aluminum trifluromethanesulfonate $[Al(OTf)_3]^{[6]}$ as a stable, easily prepared compound which is weakly hygroscopic in comparison with AlCl₃, can be used in catalytic amounts as an efficient catalyst for the highly chemoselective dithioacetalization of aryl aldehydes and ketones in solution and also under solvent-free conditions (Sch. 1).

RESULTS AND DISCUSSION

Various types of aromatic and aliphatic aldehydes were efficiently converted to the corresponding dithianes in the presence of equimolar amounts of 1,3-propanedithiol and Al(OTf)₃ (5 mol%) under solventfree conditions. In the absence of solvent, aliphatic and aromatic ketones were also converted to their corresponding dithianes in high yield in the presence of Al(OTf)₃ (5–20 mol%) with short reaction times (Table 1).



Scheme 1.

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Table 1. Thioacetalization of carbonyl compounds with 1,3-propanedithiol and $Al(OTf)_3$ at room temperature in solution or under non-solvent conditions.

Entry	R^1	R^2	Solvent	Sub./Thiol/Al(OTf) ₃	Time (min)	Yield (%) ^a
1	Ph	Н	None	1/1.1/0.05	5	97 ^b
2	$4-(CH_3)C_6H_4$	Н	None	1/1.1/0.05	5	95 ^b
3	$2-(Cl)C_6H_4$	Н	None	1/1.1/0.05	10	98 ^b
4	3-(CH ₃ O)C ₆ H ₄	Н	None	1/1.1/0.05	5	95 ^b
5	PhCH=CH	Н	None	1/1.1/0.05	5	94 ^b
6	$CH_3(CH_2)_5$	Н	None	1/1.1/0.05	10	92 ^b
7	PhCH ₂ CH ₂	CH_3	None	1/1.5/0.15	60	93 ^b
8	Ph	CH_3	None	1/1.5/0.15	3 h	95 ^{b,c}
9	Ph	Ph	None	1/1.7/0.2	4 h	94 ^{b,c}
10			None	1/1.2/0.1	25	96 ^b
11			None	1/2/0.2	14 h	50 ^{b,c}
12			None	1/2/0.2	2 h	85 ^b
13	Ph	Н	ClCH ₂ CH ₂ Cl	1/1.1/0.05	15	95
14	PhCH=CH	Н	ClCH ₂ CH ₂ Cl	1/1.1/0.05	20	94
15	PhCH ₂ CH ₂	CH ₃	ClCH ₂ CH ₂ Cl	1/1.5/0.15	7 h	85
16	Ph	CH_3	ClCH ₂ CH ₂ Cl	1/1.7/0.15	24 h	
17			ClCH ₂ CH ₂ Cl	1/1.2/0.1	45	95

^aIsolated yields.

^bUnder neat conditions.

^cNMR yield.

Dithioacetalization of hindered ketones such as benzophenone is a low yield and a time-consuming process. However, with the present method, benzophenone can easily be converted to its corresponding dithioacetal in 95% yield within 4 h at room temperature. The catalytic activity of $Al(OTf)_3$ for dithioacetalization in solution has also been studied. 1,2-Dichloroethane (ClCH₂CH₂Cl) is a good solvent for this purpose and the

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protection of aldehydes and aliphatic ketones proceeded well and their corresponding dithianes were obtained in high yields. Sterically hindered ketones, in solution, resist towards protection by this catalyst (Entry 16; Table 1).

The selectivity of the present method is demonstrated by competition experiments using structurally differing carbonyl compounds in the absence of solvent and also in solution. Our observation shows that selectivity of the catalyst is more pronounced in solution (Table 2) than in the absence of the solvent (Table 3).

Table 2.Selective dithioacetalization of carbonyl compounds catalyzed with
 $Al(OTf)_3$ in 1,2-dichloroethane.

Entry	Substrate	Sub. 1/Sub. 2/ Thiol/Cat	Product	Time (min)	Yield (%) ^a
1	С)-сно	1/1/1.1/0.05		15	100
	$\langle \bigcirc \prec \rangle$		$() \rightarrow s_s$		0
2	СНО ОСНО	1/1/1.1/0.05	$\overline{\mathbb{S}}$	15	95
			$\langle O \rangle \langle s \rangle$		5
3	О-сно	1/1/1.1/0.05	$\langle O \rangle + \langle S \rangle$	15	80
	 o		$\langle \rangle^{s}$		20
4	MI	1/1/1.2/0.1	$\langle \gamma \rangle \rangle$	45	35
			$\langle \rangle^{s} \rangle$		65
5		1/1/1.2/0.1	$\langle \gamma_{s} \rangle$	45	80
	$\widetilde{\bigcirc} \not\prec \overset{\circ}{\sim}$		$\$		20

^aYields based on GC and NMR.

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Table 3.	Selective	dithioacetalization	of carbonyl	compounds	catalyzed	with	
$Al(OTf)_3$ in the absence of solvent.							

Entry	Substrate	Sub. 1/Sub. 2/ Thiol/Cat	Product	Time (min)	Yield (%) ^a
1	О-сно	1/1/1.1/0.05		5	98
	\sim		$\overline{\mathbb{S}}$		2
2	СНО	1/1/1.1/0.05	$\overline{\mathbf{S}}$	5	70
	<−o		$\left(\right)_{s}^{s}$		30
3	() ML	1/1/1.5/0.15	$\langle \mathcal{M}_{s}^{s} \rangle$	60	70
	$\widetilde{\bigcirc}$		$\overline{\bigcirc}$		30
4	Сно	1/1/1.1/0.05		5	92
			$\langle \mathcal{A}_{s} \rangle$		8

^aYields based on GC and NMR.

In conclusion, Al(OTf)₃ which is a weakly hygroscopic compound in comparison with AlCl₃ and its handling is also easier, can be used in catalytic amounts for selective protection of carbonyl groups in the absence of solvent and also in solution. Efficient protection of hindered ketones proceeded well with Al(OTf)₃ whereas, the other recently reported catalysts such as WCl₆,^[3i] LiBr,^[3i] and LiOTf^[31] completely failed or the reaction proceeded very sluggishly.

General Procedure

To a mixture of carbonyl compound (5 mmol) and 1,3-propanedithiol (5.5–10 mmol) was added Al(OTf)₃ (0.25–1 mmol), and the resulting mixture was magnetically agitated at room temperature. The progress HIH

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of the reaction was monitored by TLC or GC. After completion of the reaction, a cold aqueous solution of NaOH (10%, 25 mL) was added to the mixture and stirred for a few minutes. The resulting mixture was extracted with Et₂O (3×40 mL) and the etheral solution was washed with water (20 mL) and dried over anhydrous Na₂SO₄. Evaporation of the solvent gave almost pure product(s). Further purification, if necessary, was proceeded by column chromatography by an appropriate solvent. Procedure for the reactions in solution is similar to non-solvent procedure.

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