

Chemoselective Protection of Carbonyl Compounds as Dithioacetals Using Polystyrene and Silica Gel Supported AlCl_3

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ABSTRACT

Cross-linked polystyrene supported AlCl_3 and FeCl_3 and silica gel supported AlCl_3 have shown to be mild and chemoselective heterogeneous catalysts for dithioacetalization of carbonyl compounds. 1,3-Dithiolanes are obtained in excellent yields in the presence of Ps-AlCl_3 , Ps-FeCl_3 and $\text{SiO}_2\text{-AlCl}_3$ from various aldehydes and ketones containing electron donating and withdrawing groups. The chemoselectivity of these catalysts toward aldehydes and ketones is successfully employed in the chemoselective dithioacetalization. The results show that these catalysts are able to discriminate between aldehydes and ketones, and aliphatic and aromatic ketones. The order of catalytic activities of these catalysts was $\text{SiO}_2\text{-AlCl}_3 > \text{Ps-AlCl}_3 > \text{Ps-FeCl}_3$. These polymeric catalysts are stable (as a bench top catalyst) and can be easily regenerated and used.

Key Words:

polymer supported Lewis acids;
dithioacetalization;
carbonyl compound;
aluminium chloride;
iron(III) chloride.

INTRODUCTION

As an important kind of functional polymers, polymeric catalysts have unique features and functions [1,2]. Chemists have been enamoured with the idea of anchoring transition metal catalysts to organic polymers. Such studies have sought to produce

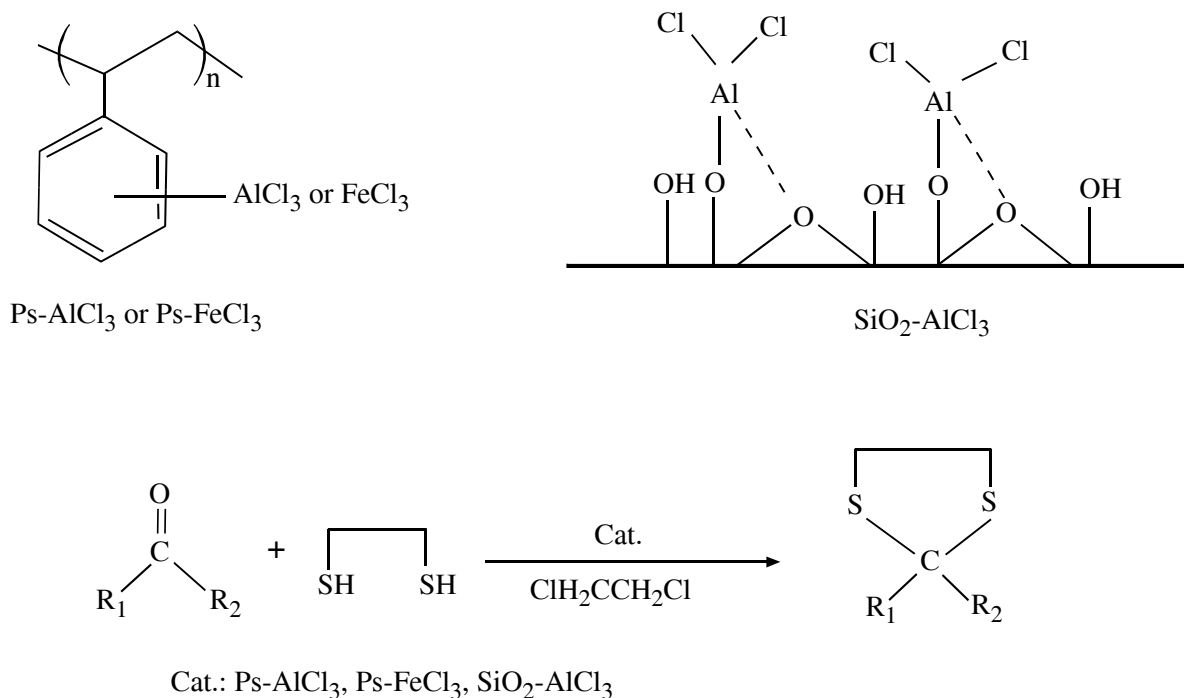
heterogenized catalyst systems that are as active and selective as their homogeneous counterparts while having the distinguishing characteristic of being easily separable from the reaction media [3-7]. Such metal complexes are no longer volatile and

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far less hygroscopic. As an important kind of polymeric catalysts, Lewis acids have been immobilized on polymers via coordinate or covalent bonds. The most frequently used polymeric support for this purpose is polystyrene; its hydrophobic nature protects the water-sensitive Lewis acids from hydrolysis by atmospheric moisture until it is placed in an appropriate solvents where it can be used in a chemical reaction [7-16]. In addition, silica-supported heterogeneous catalysts are also used for the synthesis of many organic compounds. The silica support is generally thought of as a carrier for the catalytically active phase. The support serves to maximize the active-phase surface area to allow greater contact of the catalyst with the substrates [17-21].

Dithioacetal has long been used as a protecting group for the carbonyl function, while the carbanion forming capacity of cyclic dithioacetals have also brought out number of useful applications in organic synthesis as the nucleophilic acyl equivalent [22,23]. Dithioacetalization is usually catalyzed by Lewis acids such as AlCl_3 [24], LaCl_3 [25], BiX_3 (X:Cl,Br,I) [26], WCl_6 [27], $\text{Li}(\text{OTf})$ [28], $\text{Sc}(\text{OTf})_3$ [29] and some sophisticated reagents such as polyphosphoric acid trimethylsilyl ester [30] and 2-chloro-1,3,2-dithioborolane [31]. Among many of the recently

developed catalysts, solid supported catalysts are of the choice for this purpose due to easier handling, mildness of the reaction conditions, and simple work-up procedure. Recently supported catalysts such as, anhydrous $\text{SOCl}_2\text{-SiO}_2$ [32], $\text{FeCl}_3/\text{SiO}_2$ [33], $\text{Cu}(\text{OTf})_2\text{-SiO}_2$ [34], Nafion-H catalyst [35], Amberlyst-15 catalyst [36], modified clays such as, Ce-Mont [37] and Natural Kaolinitic Clay [38] have been reported for efficient thioacetalization. A large number of these methods involve harsh reaction conditions. Also, literature survey shows that only a few methods are available for selective thioacetalization of aldehydes in the presence of ketones specially by using a heterogeneous catalyst [32,36,38]. Furthermore, some of these methods suffer from a few drawbacks. For example, Hojo [32] reported utilization of thionyl chloride impregnated silica gel as a chemoselective catalyst for thioacetalization but large amount of HCl and SO_2 were released upon mixing thionyl chloride and silica gel, and in addition its handling is difficult. Amberlyst-15 catalyst has also been reported by Perni [36] for thioacetalization but reaction times were long and due to acidic nature of the catalyst, it may be incompatible for acid sensitive substrates. Thus, it seems that convenient and general methods for thioacetalization using heterogeneous catalysts are still being demanded. In this paper we



Scheme I

describe the preparation and use of polystyrene supported AlCl_3 , FeCl_3 and silica gel supported AlCl_3 as a stable, and highly chemoselective catalysts in dithioacetalization of carbonyl compounds (Scheme I).

EXPERIMENTAL

General

Substrates were either prepared in our laboratory or were purchased from Fluka AG and Merck Co. Polystyrene (8% divinylbenzene) was obtained from Iran Polymer and Petrochemical Institute (prepared via suspension polymerization, polyvinylpyrrolidone 90 K as suspension agent, grain size range (95%): 0.25-0.6 mm). Products were characterized by comparison of their physical data with those of known samples. Melting points were determined in open capillaries on Buchi 510 apparatus. Progress of the reactions was followed by T.L.C or by G.L.C on a Shimadzu model-GC-8A instrument with a flame ionization detector and using a column of 15% carbowax 20 M on chromosorb-w acid washed 60-80 mesh. IR Spectra were recorded on Perkin-Elmer 781 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX FT 250 MHz instrument. Mass spectra were recorded on a Shimadzu Gc MS-QP 1000EX.

Preparation of Ps- AlCl_3 [8,9]

Anhydrous AlCl_3 (4.5 g) was added to polystyrene (8% divinylbenzene) (3.5g) in carbon disulphide (25 mL). The mixture was stirred under reflux condition for 50 min, cooled, and then water (40 mL) was cautiously added to hydrolyze the excess AlCl_3 . The mixture was stirred until the deep orange colour disappeared and the polymer became light yellow. The polymer beads were then filtered and washed with water (350 mL) and then with ether, acetone and ether. The polymer was dried in a vacuum oven overnight. Complex formation was demonstrated by the increased colour of the polymer and by a new band at 1650 cm^{-1} in the IR spectrum of the polymer. The capacity of the polymeric catalyst based on its chloride determination [39] was $0.4\text{ mmol AlCl}_3/\text{g}$.

Preparation of Ps- FeCl_3 [10]

Anhydrous FeCl_3 (4.5 g) was added to polystyrene (8%

divinylbenzene) (3.0 g) in chloroform (30 mL). The mixture was stirred under reflux condition for 2 h and cooled. The polymer beads were then filtered and washed with chloroform (100 mL) and ethyl ether (100 mL). The polymer was dried in a vacuum oven overnight. The capacity of the polymeric catalyst based on its chloride determination [39] was $0.3\text{ FeCl}_3/\text{g mmol}$.

Preparation of $\text{SiO}_2\text{-AlCl}_3$ [17-19]

Anhydrous AlCl_3 (5.1 g) was added to silica gel (10.2 g, Merck grade 60, 230-400, washed with 1M HCl and dried under vacuum at 80°C for 72 h) in carbon tetrachloride (30 mL). The mixture was stirred under reflux condition for two days under N_2 atmosphere and then filtered and washed with 50 mL of dry CCl_4 and dried under vacuum at 60°C for 3 h. The loading of aluminium chloride determined was 1.3 mmol/g [39].

Dithioacetalization Procedure

Typical Procedure for Thioacetalization of 4-Tolylaldehyde (Entry 2)

To a mixture of 4-tolylaldehyde (0.12 g, 1 mmol), 1,2-ethanedithiol (1.1-1.2 mmol) in 1,2-dichloroethane (10 mL) was added Ps- AlCl_3 (0.4 mmol) and the resulting mixture was magnetically stirred under reflux condition. Progress of the reaction was monitored by TLC (n-hexane/ethylacetate) and GC. After completion of the reaction, the polymeric catalyst was filtered off and washed with dichloromethane (25 mL). The combined filtrates were treated with an aqueous NaOH solution (10%, 25 mL) and the mixture was extracted with dichloromethane (25 mL). The organic layer was washed with water and dried over anhydrous (Na_2SO_4). Evaporation of the solvent gave the 2-(4-tolyl)-1,3-dithiolane (98%). (white needles) which crystallized from petroleum ether, mp $56\text{-}58^\circ\text{C}$. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 2.38$ (s, 3H), 3.28-3.45 (m, 4H), 5.60 (s, 1H), 7.11 (d, 2H), 7.40 (d, 2H); ^{13}C NMR (CDCl_3 , 63 MHz): $\delta = 21.09, 40.16, 56.11, 127.79, 129.12, 137.10, 137.78$; MS (20 eV) m/z (relative intensity) 196 (M^+ , 68.9), 168 (M^+ , $\text{CH}_2 = \text{CH}_2$, 25.4), 153 (100), 135 (83.6), 91 (57.5), 45 (99.3).

Regeneration of Catalysts

Ps- AlCl_3 or Ps- FeCl_3 were reactivated by leaving the


polymer overnight in 1M HCl. It was then filtered and dried. The regenerated catalyst showed almost the same capacity and activity as its original form and could be used with the same results. For SiO₂-AlCl₃, after each reaction the catalyst was washed with ethyl ether and used again without further drying.

RESULTS AND DISCUSSION

Ps-AlCl₃ and Ps-FeCl₃ were prepared by addition of AlCl₃ and FeCl₃ to polystyrene (8% divinylbenzene) in carbon disulphide and chloroform, respectively, under reflux condition. SiO₂-AlCl₃ was prepared by treating

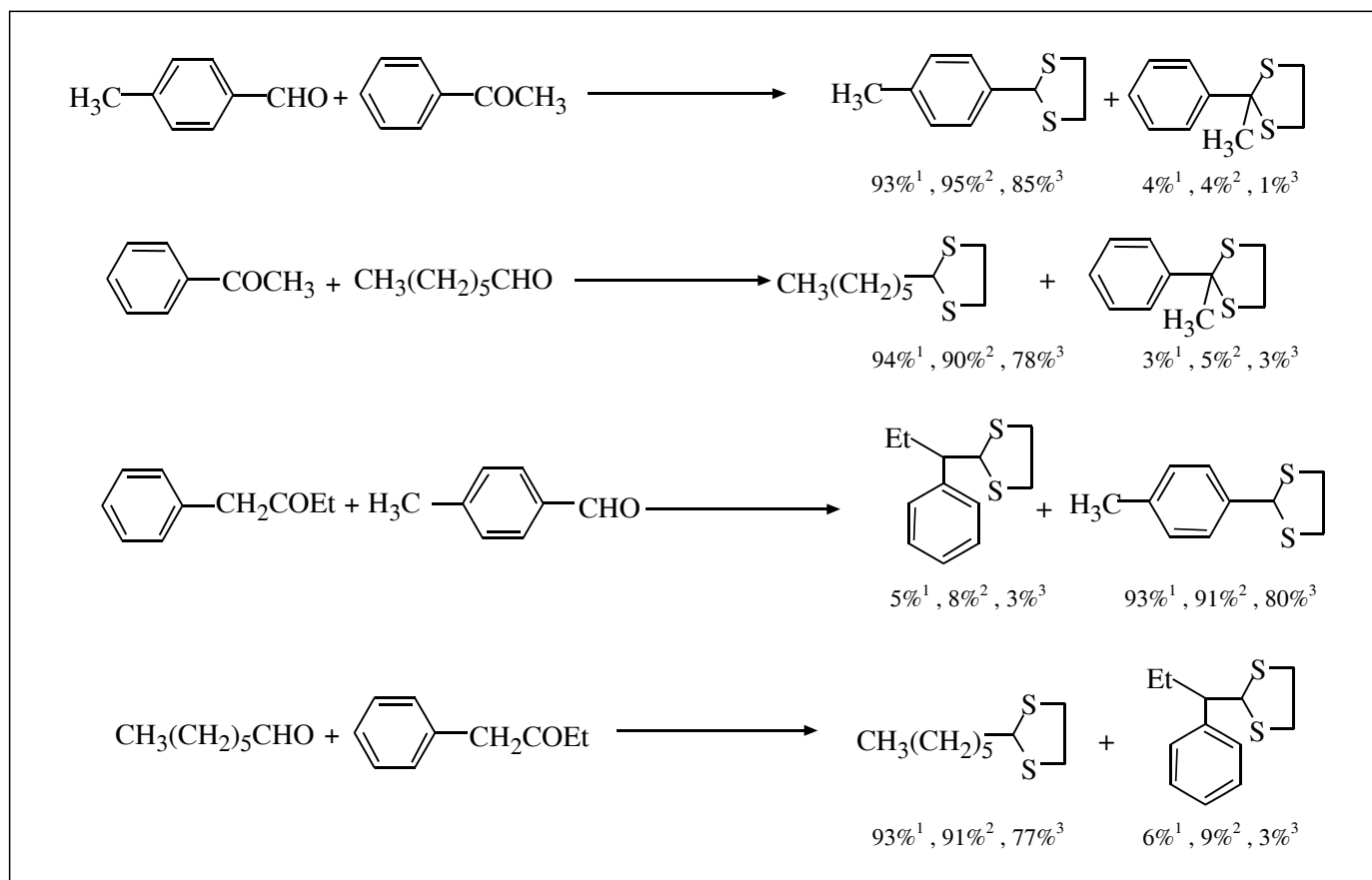
silica gel with aluminium chloride in refluxing carbon tetrachloride. The capacities of these polymeric catalysts were determined as mmol of metal chloride per gram of the polymeric catalyst. Dithioacetalization of carbonyl compounds with these catalysts was carried out in 1,2-dichloroethane, dichloromethane, chloroform and benzene. 1,2-Dichloroethane proved to be the best. The optimum molar ratio of carbonyl compound to Ps-AlCl₃ and Ps-FeCl₃ was 1:0.4 and for SiO₂-AlCl₃ was 1:0.25. In all these dithioacetalization reactions these catalysts were stable under the reaction condition, and during reactions no leaching of acid moieties was observed. These polymeric catalysts are very stable at room temperature and could be stored as

Table 1. Dithioacetalization of carbonyl compounds using 1,2-ethanedithiol catalyzed SiO₂-AlCl₃, Ps-AlCl₃ and Ps-FeCl₃^{a-b}.

Entry	R ₁	R ₂	Time (h)	Yield (%) ^c	Entry	R ₁	R ₂	Time (h)	Yield (%) ^c
1	Ph	H	1.2 ¹	95	9	PhCH=CH	H	1.4 ¹	93
			3.5 ²	98				3.9 ²	95
			4.1 ³	91				4.4 ³	82
2	<i>p</i> -MeC ₆ H ₄	H	1.4 ¹	94	10		H	1.2 ¹	92
			3.3 ²	98				2.15 ²	98
			4.2 ³	89				3.9 ³	88
3	<i>p</i> -ClC ₆ H ₄	H	1.3 ¹	94	11	PhCH ₂	CH ₃	1.35 ¹	96
			3.2 ²	96				5 ²	30
			4.4 ³	90				7 ³	2
4	<i>p</i> -NO ₂ C ₆ H ₄	H	1.1 ¹	95	12	-(CH ₂)-	-(CH ₂)-	1.7 ¹	95
			3.8 ²	97				5 ²	30
			4.5 ³	90				6 ³	5
5	PhCH ₂ CH ₂	H	1.8 ¹	94	13	PhCH ₂	C ₂ H ₅	2.5 ¹	94
			5.1 ²	91				5 ²	20
			5.9 ³	89				7 ³	4
6	PhCH ₂	H	1.5 ¹	93	14	n-Butyl	CH ₃	2.1 ¹	93
			5.3 ²	95				4 ²	30
			6 ³	87				4.2 ³	2
7	n-Hexyl	H	1.6 ¹	93	15	Ph	CH ₃	3 ¹	29
			3 ²	95				5 ²	12
			4.7 ³	88				7 ³	2
8	n-Heptyl	H	1.8 ¹	93	16	Ph	Ph	3 ¹	9
			4.7 ²	92				5 ²	5
			5.5 ³	85				8 ³	2

^(a) The molar ratio of substrate/dithiol is: 1:1.1-1.2; ^(b) Reactions carried out in 1,2-dichloroethane in the presence of SiO₂-AlCl₃¹, Ps-AlCl₃², and Ps-FeCl₃³; ^(c) Isolated and GC yield. Products were GC pure and were identified by comparison of their IR, ¹H NMR and ¹³C NMR spectra with those of the authentic samples.

Table 2. Dithioacetalization of a mixture of aldehyde and ketone using of $\text{SiO}_2\text{-AlCl}_3$, Ps-AlCl_3 , and Ps-FeCl_3 .^a



^(a) Molar ratio of sub.1/sub.2 (1:1 mmol), 1,2-ethanedithiol (1.1-1.2 mmol) and $\text{SiO}_2\text{-AlCl}_3$ (0.25 mmol)¹, Ps-AlCl_3 (0.4 mmol),² Ps-FeCl_3 (0.4 mmol).³

Reactions carried out in 1,2-dichloroethane for 5 h. Yields are based on GC and NMR.

a bench top catalyst for months without appreciable change in their reactivities.

1,3-Dithiolanes were obtained in excellent yields in the presence of Ps-AlCl_3 , Ps-FeCl_3 and $\text{SiO}_2\text{-AlCl}_3$ from various aliphatic and aromatic aldehydes containing electron donating and withdrawing groups using 1,2-ethanedithiol (Table 1, entries 1-10).

Dithioacetalization of aliphatic ketones using Ps-AlCl_3 and Ps-FeCl_3 was very slow (entries 11-14). Notably, under the same condition aliphatic ketones were thioacetalized in the presence of $\text{SiO}_2\text{-AlCl}_3$ in excellent yields (entries 11-14). As shown in Table 1 aromatic ketones were dithioacetalized very slowly in the presence of these catalysts (entries 15-16). The results show that the order of catalytic activity of these catalysts is $\text{SiO}_2\text{-AlCl}_3 > \text{Ps-AlCl}_3 > \text{Ps-FeCl}_3$ (Table 1).

While it is reported [24] that AlCl_3 alone catalyzes dithioacetalization of aldehydes and ketones with monothiols efficiently, we noticed that dithioacetaliza-

tion of aldehydes with monothiols such as n-BuSH, EtSH, or PhSH in the presence of $\text{SiO}_2\text{-AlCl}_3$, Ps-AlCl_3 and Ps-FeCl_3 resulted in the recovery of most of the starting materials with formation of a small amount of dithioacetals. For example, dithioacetalization of 4-methyl benzaldehyde and phenylacetaldehyde with n-BuSH in the presence of $\text{SiO}_2\text{-AlCl}_3$ under reflux condition resulted in recovery of 70 and 80% of starting materials after 6 h, respectively.

The efficiency of AlCl_3 [24] is attributed to the strong affinity of AlCl_3 for oxygen, thereby facilitating the breakdown of the complexed hemithioacetal to the more accessible trivalent carbonium ion intermediate, while in the presence of $\text{SiO}_2\text{-AlCl}_3$, Ps-AlCl_3 and Ps-FeCl_3 presumably, the complex hemithioacetal does not completely break down into the carbonium ion because of moderate Lewis acidity of AlCl_3 and FeCl_3 being supported on polymer compared to AlCl_3 and FeCl_3 alone.

In order to examine the chemoselectivity of

dithioacetalization using, Ps-AlCl_3 , Ps-FeCl_3 and $\text{SiO}_2\text{-AlCl}_3$, equimolar mixtures of different aldehydes and ketones were allowed to react with limited amount of 1,2-ethanedithiol. As shown in Table 2 very high chemoselectivity was observed in each case. The observed chemoselectivity of these catalysts towards aldehydes and ketones is presumably due to their mild catalytic activities and also to difference in steric bulkiness of the carbonyl compounds. It is important to mention that AlCl_3 alone is not a chemoselective catalyst in dithioacetalization of aldehydes and ketones [24].

CONCLUSION

In conclusion, the advantages of the present method may be summarized as useful chemoselectivities accompanied by high yields of the desired products, easy work-up procedures, and mild reaction conditions. In addition, the use of these solid acid catalysts has resulted in a reduction in the unwanted and hazardous waste that is produced during conventional homogeneous processes. These catalysts are re-usable and after each reaction, can be regenerated and re-used with negligible loss in their activities. The chemoselectivity of these catalysts is suitable for selective protection of aldehydes in the presence of keto carbonyl functions and can be used in synthesis of complex molecules by multi-step processes. We believe that the efficiency of these catalysts are probably attributed to their strong affinity for carbonyl oxygen facilitating the formation of the intermediate hemithioacetal. Also, the hydrophobic nature of the polystyrene and water trapping nature of silica gel can be important in catalytic activities of these catalysts.

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