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Communications

Melamine Trisulfonic Acid as a New, Efficient and Reusable Catalyst for the Chemoselective Oxathioacetalyzation of Aldehydes

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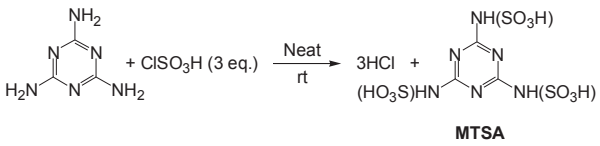
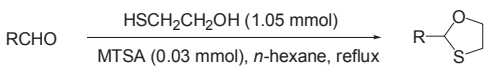
1,3-Oxathiolanes are synthetically important protecting groups for aldehydes due to their considerable stability under a variety of reaction conditions, ease of formation and removal, equality to acyl carbanions in C-C bond forming reactions,[1] and use in enantioselective synthesis of tertiary α-hydroxy acids and glycols.[2]

Usually the preparations of 1,3-oxathiolanes were carried out by the reaction of aldehydes with 2-mercaptoethanol under catalysis of reagents such as HCl,[3] *p*-TsOH,[4] $ZrCl_4$,[5] $HClO_4$,[6] TMSOTf,[7] OTAB,[8] NBS,[9] TBAB,[10] MeS_2/Br_2,[11] PAS,[12] PPS/SiO_2,[13] $TaCl_5/SiO_2$,[14] $MoO_2(acac)_2$,[15] Alumina sulfuric acid,[16] $Bi(NO_3)_3$,[17] $Sn(HPO_4)_2{\cdot}H_2O$,[18] Amberlyst®-15,[19] $Y(OTf)_3$,[20] I_2,[21] HBF_4-SiO_2[22] and $H_3PW_{12}O_{40}/SiO_2$.[23] However, many of these procedures suffer from one or more of the following dissadvantages: harsh reaction conditions, long reaction times, low yields, use of corrosive, expensive or moisture-sensitive reagents, destruction of the catalyst in work-up procedure, special efforts require to prepare the catalysts and tedious work-up procedure. Therefore, there is a scope to develop an alternative method for the protection of aldehydes as 1,3-oxathiolanes.

In recent years, the introduction of new reagents for the functional group transformations, became an important part of our research program.[24-27] In continuation of these studies, herein, we wish to report the preparation of melamine trisulfonic acid, as a new catalyst (Scheme 1), and its application in the promotion of the oxathioacetalyzation of aldehydes with 2-mercaptoethanol. All reactions were performed in *n*-hexane at reflux temperature and under completely heterogeneous reaction conditions in excellent yields (Scheme 2, Table 1).



Scheme 1



Scheme 2

Optimization of the reaction conditions showed that the best results were obtained in refluxing *n*-hexane when the relative ratio of the substrate, 2-mercaptoethanol and MTSA was 1:1.05: 0.03, respectively. After that, the different types of alehydes, including aliphatic and aromatic ones were subjected to oxathioacetalyzation under the determined conditions.

As shown in Table 1, all types of the above mentioned substrates were efficiently converted to their corresponding 1,3-oxathiolanes in good to high yields during relatively short reaction times. It is very important to note that the progress of the reaction is so depends to the presence of MTSA in the reaction mixture, that the reaction did not proceed in the absence of this reagent even after prolonged heating (Table 1, entry 11). Because of the stability of ketones under the above mentioned conditions (Table 1, entries 14, 15), the reported method can be used for the chemoselective oxathioacetalyzation of aldehydes in

Table 1. MTSA catalyzed formation of 1,3-oxathiolanes[a,b]

Entry	Substrate	Time (min)	Yield (%)	Reference
1	PhCHO	7	92	15
2	$2\text{-}NO_2C_6H_4CHO$	3	90	12
3	$4\text{-}NO_2C_6H_4CHO$	4	87	21
4	$4\text{-}CNC_6H_4CHO$	15	75	21
5	$2\text{-}ClC_6H_4CHO$	5 (7, 10)[c]	90 (87, 85)[c]	29
6	$4\text{-}ClC_6H_4CHO$	6	90	11
7	$4\text{-}BrC_6H_4CHO$	5	95	13
8	$4\text{-}MeC_6H_4CHO$	18 (20, 24)[c]	92 (90, 90)[c]	14
9	$4\text{-}MeOC_6H_4CHO$	28	90	21
10	$2\text{-}MeOC_6H_4CHO$	35	85	29
11	PhCHO	30	0[d]	-
12	$PhCH_2CH_2CHO$	19	90	14
13	$CH_3(CH_2)_3CHO$	21	85	21
14		45	0[e]	-
15	Ph_2CO	60	0[e]	-
16	$PhCHO + Ph_2CO$	10	100[f] + 0[f]	-

[a]Products were identified spectroscopically and also by the conversion of 1,3-oxathiolanes to the parent aldehydes. [b]Isolated yields. [c]Results obtained using recycled catalyst for the second and third times, respectively. [d]Reaction was performed in the absence of MTSA. [e]Starting material recovered intact. [f]Conversion.

Table 2. Comparison of the efficiency of MTSA in the oxathioacetalyzation of benzaldehyde, with other reported methods

Entry	Reagent	Catalyst load (mg)	Time (min)	Yield (%)	Reference
1	Al_2O_3-SO_3H	50	7 (**h**)	91	16
2	HBF_4·SiO_2	50	8	94	22
3	$Bi(NO_3)_3$	40	5 (**h**)	75	17
4	$MoO_2(acac)_2$	22	240	86	15
5	Amberlyst®-15	220	60	84	19
6	$Sn(HPO_4)_2$·H_2O	17	30	96	18
7	$Y(OTf)_3$	135	110	79	20
8	MTSA	11	7	92	Present method

the presence of ketones (Table 1, entry 16).

Our investigations clarified that MTSA is reusable for three times (Table 1, entries 5, 8). The same IR spectra of the reagent were obtained before and after its use in the reactions, which demonstrates the stability of its composition.

In order to show the efficiency of this method, Table 2 compares the results from the oxathioacetalyzation of benzaldehyde in the presence of MTSA and some of the other catalysts.

In conclusion, we developed an efficient and high yielding method for the chemoselective oxathioacetalyzation of aldehydes. Relatively short reaction times, high efficiency, heterogeneous reaction conditions, availability and recyclability of the reagent and easy work-up are among the other advantages of this method, which make this procedure a useful and attractive addition to the available methods. We are exploring further applications of MTSA for the other types of functional group transformations in our laboratory.

Experimental

Preparation of MTSA. A 250 mL suction flask charged with chlorosulfonic acid (5 mL, 75.2 mmol) was equipped with a gas inlet tube for conducting HCl gas overran adsorbing solution i. e. water. Melamine (3.16 g, 25.07 mmol) was added in small portions over a period of 30 min at room temperature. HCl gas evolved from reaction vessel immediately (Scheme 1). After completion of the addition of melamine, the mixture was shaken for 30 min, meanwhile, the residual HCl was exhausted by suction. The mixture was triturated with *n*-hexane (10 mL) and then filtered. The solid residue was washed with *n*-hexane (10 mL) and dried under vacuum. Melamine trisulfonic acid (7.9 g, 87%) was obtained as a white solid, which was stored in a capped bottle. mp 142 - 144 ^{o}C; IR ν 3133, 2621, 1654, 1509, 1175, 1069 cm^{-1}; Anal calcd for $C_3H_6N_6O_9S_3$ (366.3): C, 9.83%; N, 22.95%; H, 1.64%. Found: C, 9.81%; N, 22.95%; H, 1.64%. The presence of three atoms of sulfur per each molecule of MTSA is confirmed by the titration of MTSA in acetonitrile media with 1.0 M Bu_4NOH (MeOH), according to the previously reported method.[28]

General procedure. A mixture of the substrate (1 mmol), 2-mercapto ethanol (1.05 mmol) and MTSA (0.03 mmol, 0.011 g) in *n*-hexane was stirred at reflux temperature. The progress of the reaction was monitored by TLC. On completion the solvent was evaporated, CH_2Cl_2 (5 mL) was added and filtered. The solid residue was washed with CH_2Cl_2 (5 mL) and then dried; the recovered catalyst can be used for two reactions again. The organic layer was washed with saturated $NaHCO_3$, then with water and dried over $MgSO_4$. Evaporation of the solvent followed by column chromatography on neutral silica gel gave the requested 1,3-oxathiolan in excellent yields. Spectroscopic data are in agreement with previously reported.[11-15, 21, 29]

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