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Interconversion of Oxathiolanes and Carbonyls under Essentially Identical Conditions+

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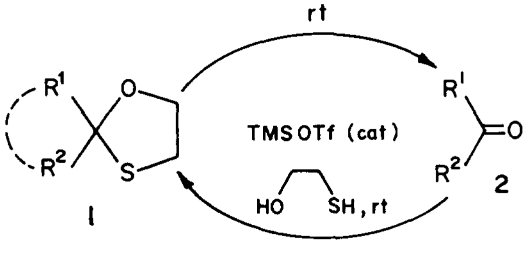
Abstract: *A catalytic, non-aqueous protocol for the interconversion of oxathiolanes and carbonyl compounds at room temperature is described.*

Oxathiolanes constitute important class of compounds as acyl anion equivalent[1a,b,c] in C-C bond formation and as protecting groups of carbonyl compounds[2]. Although a variety of methods for their formation are reported employing HCl[3], refluxing with p-TSA[4], TMSCl-NaI[5], $BF_3.Et_2O$[6],SO_2[7] these methods employ rather harsh conditions or are inconvenient to use. As compared to this, the conventional methods of deprotection employ even harsher conditions involving stoichiometric amounts of oxidants[1a,b] refluxing with Raney Ni[8] thus limiting their usage in a synthetic strategy and especially on a larger scale.

Development of mild protocol for deprotection of carbonyl compounds has been the focus of our and current interest.A recent publication[9] on deprotection of acetals prompts us to disclose our findings. In this connection we have recently introduced p-nitrobenzaldehyde/TMSOTf (cat.) as a useful reagent for deprotection of thioacetals[10] and oxathio-acetals[11]. Similarly polymer supported nitrobenzalehyde/TMSOTf (cat) was also shown to be efficient reagent for deprotection of oxathiolanes[12].

This communication describes TMSOTf as a mild, efficient and versatile catalyst in effecting facile conversion of carbonyls **2** to oxathiolanes **1** and vice-versa under essentially identical conditions (Scheme 1).



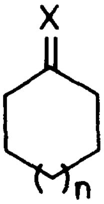
Scheme 1

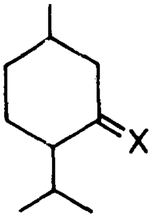
Oxathiolanes **1** were prepared by stirring the mixture of carbonyl compound **2** and mercaptoethanol in the presence of TMSOTf (cat), at room temperature (Table 1). It is evident from the table that a variety of oxathiolanes could be expeditiously prepared following the above protocol.

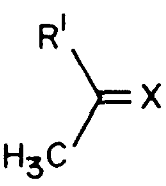
Interestingly, it was observed that 'activated'oxathiolanes when subjected to the treatment of same catalyst (TMSOTf), could be converted to carbonyl compounds in high yields (Table 2). It is obvious that the presence of an aryl ring seems to be an essential factor for successful transformation of **1** to **2** (exception entry 1). It is pertinent to mention that thiolanes **1** lacking an aryl group are resistant to TMSOTf and are recovered unchanged. This may be attributed to the ease of formation of stable benzyl carbocations on treatment with TMSOTf. Interestingly,when an equimolar mixture of benzophenone oxathiolane **19** and dithiolane **20** were treated with TMSOTf,selective and clean conversion of oxathiolane **19** to benzophenone **18** was observed,(benzophenone was isolated as its corrosponding alcohol after $NaBH_4$ reduction in 85% yield.), whereas benzophenone dithiolane was quantitatively recovered unchanged.

An interesting point which emerges from the above study is that oxathiolanes **1** and carbonyls **2** could be interconverted under essentially/identical conditions in a "merry-go-round" fashion. An illustrative example to highlight the above point is on treatment of **19** with TMSOTf (cat), complete and clean conversion to the ketone **18** was obtained (TLC). (If the reaction is quenched, ketone **18** can be isolated in 82% yield). However addition of mercaptoethanol to the same reaction mixture and TMSOTf (catalytic) and overnight stirring at room temperature furnishes oxathiolanes **19** in 80% isolated yield.

Although the exact mechanism of the above protocol seems to be uncertain at the moment, nevertheless, the conditions developed for interconversion of oxathiolane **1** and carbonyl **2** would find application in selective functional group transformations.



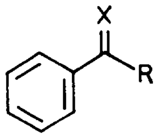


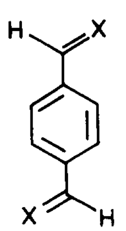


3. n = 1, X=O
3a X = SCH_2CH_2O
4. n = 2, X = O
4a X = SCH_2CH_2O
5. n = 7, X = O
5a X = SCH_2CH_2O

6. X = O
7. X = SCH_2CH_2O

8. $R^1 = C_5H_{11}$, X=O
9. $R^1 = C_5H_{11}$ SCH_2CH_2O
10. $R^1 = CH_2CH(CH_3)_2$, X = O
11. X = SCH_2CH_2O
$R^1 = CH_2CH(CH_3)_2$





12. R = H, X = O
13. R=H, X = SCH_2CH_2O
14. R = CH_3, X = O
15. R=CH_3, X = SCH_2CH_2O
16. R = CH_2CH_3, X = O
17. R=CH_2CH_3,X = SCH_2CH_2O
18. R = Ph, X = O
19. R=Ph, X = SCH_2CH_2O
20. X = SCH_2CH_2S, R=Ph.

21. X = O
22. X = SH_2CH_2O

TABLE - 1

Entry	Carbonyl	Oxathiolane	% Yield	Time
1	3	3a	76	10 min
2	4	4a	69	"
3	5	5a	76	"
4	6	7	68	"
5	8	9	65	"
6	10	11	63	"
7	12	13	50	"
8	14	15	68	"
9	16	17	61	3h.
10	18	19	72	10 min
11	21	22	78	"

TABLE - 2

Entry	Oxathiolane	Carbonyl	% Yield	Time
1	11	10	60	12 h
2	13	12	50	12 h
3	15	14	72	10 min.
4	17	16	69	15 min.
5	19	18	82	10 min
6	22	21	50	12 h

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