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Efficient regeneration of aldehydes from their corresponding 1,3-oxathiolanes in the absence of solvent

Farhad Shirini *, Seyyedeh Kobra Mirhashemi, Aysa Pourvali, Masoumeh Abedini

Department of Chemistry, College of Science, University of Guilan, Rasht 41335, Islamic Republic of Iran

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Abstract

A mild and efficient method for the oxidative deprotection of 1,3-oxathiolanes with $Fe(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ in the absence of solvent is reported.

Keywords: Oxidative deprotection; 1,3-Oxathiolanes; $Cu(NO_3)_2{\cdot}3H_2O$; $Fe(NO_3)_3{\cdot}9H_2O$; Solvent-free conditions

Protection and deprotection of organic functions are important processes during multi-step organic synthesis [1]. The choice of a method which is used for the functional group transformations depends on its simplicity, highest yields of the desired products, short reaction times, low cost of the process and ease of the work-up procedure.

Oxathioacetalization of is important reaction widely used for the protection of carbonyl group during a multi-step organic synthesis [1]. Direct oxidative deprotection of 1,3-oxathiolanes to their corresponding carbonyl compounds is of value to synthetic organic chemists and have attracted much attentions. There are several reagents available for deprotection of 1,3-oxathiolanes, which of them isoamyl nitrate [2], chloramine-T [3], TMSOTf [4], TMSOTf/*p*-nitorbenzaldehyde [5], polymer-supported *p*-nitrobenzaldehyde [6], NCS-$AgNO_3$ [7], I_2-$AgNO_2$ [8], NBS [9], glyoxylic acid/Amberlyst-15/MW [10] and $V(HSO_4)_3$ [11] are examples. Although these methods are suitable for many synthetic conditions, the disadvantages, such as long reaction times, tedious work-up, low yields of the products, unavailability of the reagents, use of expensive reagents, use of large amounts of the reagents and, in some cases, inapplicability in deprotection of non-benzylic oxathiolanes, clearly identified a need to introduce new methods for such functional group transformations.

1. Experimental

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. Yields refer to isolated products. Products were characterized by their physical constants, comparison with authentic samples [12] and IR and NMR

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* Corresponding author.
E-mail address: shirini@guilan.ac.ir (F. Shirini).

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Table 1
Regeneration of aldehydes in the absence of solvent[a,b].

Entry	Product	$Fe(NO_3)_3{\cdot}9H_2O$		$Cu(NO_3)_2{\cdot}3H_2O$	
		Time (min)	Yield (%)	Time (min)	Yield (%)
1	PhCHO	15	92	9	90
2	2-ClC$_6$H$_4$CHO	10	95	5	95
3	3-ClC$_6$H$_4$CHO	5	90	5	92
4	4-ClC$_6$H$_4$CHO	6	92	6	90
5	2-BrC$_6$H$_4$CHO	3	90	5	85
6	2-NO$_2$C6H4CHO	25	95	13	95
7	3-NO$_2$C$_6$H$_4$CHO	6	90	9	92
8	4-NO$_2$C$_6$H$_4$CHO	15	87	7	85
9	2-MeC$_6$H$_4$CHO	5	90	6	92
10	3-MeC$_6$H$_4$CHO	2	85	5	90
11	4-MeC$_6$H$_4$CHO	5	90	4	90
12	4-Me$_2$CHC$_6$H$_4$CHO	3	90	5	87
13	2-MeOC$_6$H$_4$CHO	5	90	7	90
14	3-MeOC$_6$H$_4$CHO	8	92	5	90
15	Furfural	45	80	20	85
16	PhCH(Me)CHO	35	85	15	90
17	PhCH$_2$CH$_2$CHO	14	90	16	92
18	PhCOMe	10	–[c]	10	–[c]

[a] Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy.
[b] Yields are based on isolated products.
[c] Mixture of unidentified products.

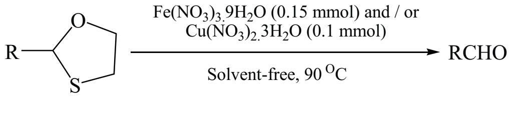
spectroscopy. The purity determination of the substrates and reaction monitoring were accompanied by TLC on silica gel polygram SILG/UV 254 plates.

General procedure: A mixture of the substrate (1 mmol), 0.06 g $Fe(NO_3)_3{\cdot}9H_2O$ (0.15 mmol) and/or 0.02 g $Cu(NO_3)_2{\cdot}H_2O$ (0.1 mmol) was heated in an oil bath (90 °C) for the specified time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with 10 mL CH_2Cl_2 and filtered. The solid residue was washed with 5 mL CH_2Cl_2. The organic layer was washed with 2 × 5 mL saturated $NaHCO_3$, and 10 mL water, and dried our $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compounds in good to high yields.

Typical procedure: A mixture of 2-phenyl-1,3-oxathiolane (1 mmol) (Table 1, entry 1), 0.06 g $Fe(NO_3)_3{\cdot}9H_2O$ (0.15 mmol) and/or 0.02 g $Cu(NO_3)_2{\cdot}H_2O$ (0.1 mmol) was heated in an oil bath (90 °C) for the specified time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with 10 mL CH_2Cl_2 and filtered. The solid residue was washed with 5 mL CH_2Cl_2. The organic layer was washed with 2 × 5 mL saturated $NaHCO_3$, and 10 mL water, and dried our $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel gave benzaldehyde in 92% and/or 90% yields, respectively.

2. Results and discussion

In continuation of our ongoing research program on the development of the applications of metal nitrates in organic reactions [13–16], we have found that $Fe(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ can be used as efficient reagents for the oxidative deprotection of 1,3-oxathiolanes to their corresponding carbonyl compounds. All reactions were performed in the absence of solvent at 90 °C in good to high yields (Scheme 1).



Scheme 1.

Yields and reaction times are tabulated in Table 1. Benzylic 1,3-oxathiolanes, including electron donating and withdrawing groups are oxidized to their corresponding aldehydes in high yields (Table 1). Substrates containing the ethereal linkages are efficiently converted to their corresponding aldehydes without cleavage of carbon–oxygen bond (Table 1, entries 13–15). This method is also very effective for the oxidation of aliphatic 1,3-oxathiolanes (Table 1, entries 16 and 17). Because of the formation of unidentified products, the method is not useful for regeneration of ketones from their 1,3-oxariolanes (Table 1, entry 18). Over-oxidation of the products to their carboxylic acids or esters was not observed by this method.

In conclusion, in this study we have developed a mild and efficient method for the regeneration of aldehydes from the related 1,3-oxathiolanes in the absence of solvent. Good to high yields of the products, short reaction times, solvent-free nature of the reaction conditions, use of inexpensive and stable reagents, use of relatively small amounts of the reagents and easy work-up procedure are worthy advantages of the present method.

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References

[1] T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, 2nd ed., Wiley, New York, 1991.
[2] K. Fuji, K. Ichikawa, E. Fujita, Tetrahedron Lett. 19 (1978) 3561.
[3] D.W. Emerson, H. Wynberg, Tetrahedron Lett. 12 (1971) 3445.
[4] T. Ravindranathan, S.P. Chavan, S.W. Dantale, Tetrahedron Lett. 36 (1995) 2285.
[5] T. Ravindranathan, S.P. Chavan, P.J. Vargese, et al. J. Chem. Soc., Chem. Commun. (1994) 1937.
[6] T. Ravindranathan, S.P. Chavan, M.M. Awachat, Tetrahedron Lett. 35 (1994) 8835.
[7] E.L. Eliel, K. Soai, Tetrahedron Lett. 21 (1981) 2859.
[8] K. Nishide, K. Yokota, D. Nakamura, et al. Heterocycles 44 (1997) 393.
[9] B. Karimi, H. Seradj, M.H. Taebi, Synlett (2000) 1798.
[10] S.P. Chavan, P. Soni, S.K. Kamat, Synlett (2001) 1251.
[11] F. Shirini, M. Abedini, M. Ghasemi, et al. Bull. Korean Chem. Soc. 10 (2009) 2479.
[12] Fluka Catalogue, Handbook of Fine Chemicals, 1997–1998.
[13] F. Shirini, M.A. Zolfigol, A.R. Abri, ARKIVOC II (2008) 14.
[14] F. Shirini, M.A. Zolfigol, M. Abedini, Scientia Iranica 15 (2008) 440.
[15] F. Shirini, M.A. Zolfigol, A.R. Abri, Chin. Chem. Lett. 19 (2008) 51.
[16] F. Shirini, H. Tajik, A. Aliakbar, et al. Synth. Commun. 31 (2001) 767.