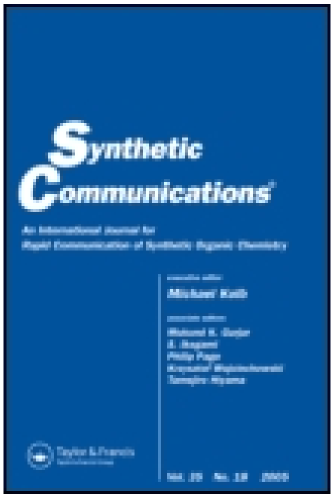
This article was downloaded by: [Stony Brook University]
On: 03 November 2014, At: 09:24
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A Facile Deprotection of Dithioacetals by $FeCl_3$/KI

Subhash P. Chavan [a] , Priti B. Soni [a] , Ramesh R. Kale [a] & K. Pasupathy [a]
[a] Division of Organic Chemistry: Technology , National Chemical Laboratory , Pune, India

Published online: 17 Aug 2006.

To cite this article: Subhash P. Chavan , Priti B. Soni , Ramesh R. Kale & K. Pasupathy (2003) A Facile Deprotection of Dithioacetals by $FeCl_3$/KI, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:6, 879-883, DOI: 10.1081/SCC-120016345

To link to this article: http://dx.doi.org/10.1081/SCC-120016345

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 6, pp. 879–883, 2003

A Facile Deprotection of Dithioacetals by $FeCl_3$/KI

Subhash P. Chavan,* Priti B. Soni, Ramesh R. Kale, and K. Pasupathy

Division of Organic Chemistry: Technology,
National Chemical Laboratory, Pune, India

ABSTRACT

Carbonyl compounds were regenerated from corresponding dithioacetals *via* refluxing with $FeCl_3$/KI and methanol as a solvent.

Key Words: $FeCl_3$; KI; Dithioacetals.

Dithioacetals are frequently used to protect carbonyl compounds in the course of total syntheses and hence several systems[1] have been reported for their deprotection. Some of them include use of transition metals (Hg^{2+}, Ce^{4+}, Tl^{3+}).[2–4] However most of these methods

---

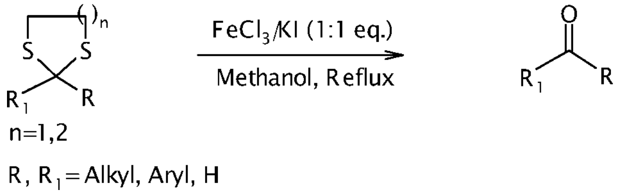
*Correspondence: Subhash P. Chavan, Division of Organic Chemistry: Technology, National Chemical Laboratory, Pune 411008, India; Fax: +91-20-5893614; E-mail: spchavan@dalton.ncl.res.in.

DOI: 10.1081/SCC-120016345
0039-7911 (Print); 1532-2432 (Online)
www.dekker.com

involve use of toxic, corrosive oxidants in stoichiometric amounts at elevated temperatures. In connection with our interest in exploring the utility of $FeCl_3$ we have recently demonstrated the unique efficiency of $FeCl_3$ to function both as a Lewis acid[5] in catalyzing ionic Diels–Alder reactions as well as an oxidising agent[6] in effecting iodoetherification and iodolactonisation. Our interest in developing methods for deprotection of oxathioacetals[7,8] and dithioacetals[9] encouraged us to investigate the reaction with one equivalent of $FeCl_3$/KI. It was surmised that $FeCl_3$/KI combination could serve as an excellent reagent as the source of iodonium ion/iodine. These in turn would react with dithioacetal thereby making it a better leaving group, thus helping in regeneration of carbonyl compounds. Recent report on utility of $FeCl_3$ by Kamal *et al.*[10] for deprotection of dithioacetals prompts us to disclose our findings. Although the reaction reported by Kamal *et al.* is efficient, $FeCl_3$ has to be used in a very large excess. This becomes really unattractive especially when it has to be used on a large scale. Herein we report that dithioacetals are efficiently deprotected in the presence of $FeCl_3$ and KI in very short time (Sch. 1).

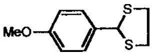
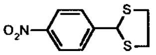
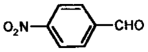
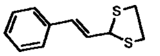
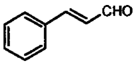
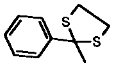
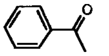
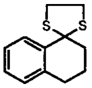
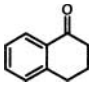
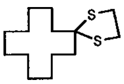
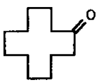
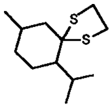
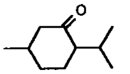
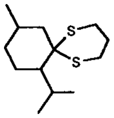
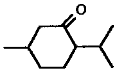
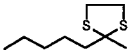
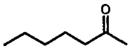
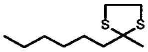
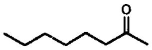
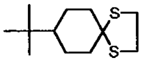
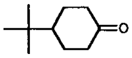
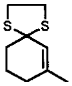
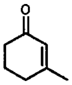
It is interesting to note that the reaction does not proceed with either $FeCl_3$ (1 eq) or KI (1 eq) alone. After considerable trials it was concluded that combination of $FeCl_3$ and KI in the ratio 1:1 is required for clean transformation. The reaction is fast and the product is isolated by a simple aqueous workup.

A wide variety of dithiolanes derived from ketones and aldehydes were shown to undergo facile deprotection under these conditions (Table 1). Both dithiolanes as well as dithiane (Entries 7 and 8 respectively) were deprotected with equal ease. The starting materials[11–15] and the products, all previously known compounds were identified by comparision of their physical and spectroscopic data with literature data.



Scheme 1.

Table 1. Deprotection of dithioacetals by $FeCl_3$/KI.

Entry	Dithioacetal	Product	Time (hr)	Yield (%)
1			3	90
2			4	91[a]
3			3	90
4			3	91
5			3	91
6			11	87[b]
7			7	89
8			6	89
9			5.5	90
10			7	91
11			6	92[c]
12			4	88

[a] M.p. = 106°C (lit.[16] M.p. = 106–106.5°C).
[b] based on recovery of the starting material.
[c] M.p. = 49°C (lit.[17] M.p. = 49–50°C).

In conclusion the present protocol[18] is efficient, nonhazardous, and therefore should find widespread utility in organic synthesis.

ACKNOWLEDGMENT

The authors PBS, RRK and KP thank CSIR, New Delhi for financial support. Funding from CSIR, New Delhi under YSA (SPC) scheme is gratefully acknowledged.

REFERENCES

1. Greene, T.W.; *Protecting Groups In Organic Synthesis*; Wiley Interscience: New York, 1981.
2. Fujita, E.; Nagao, Y.; Kaneko, K. Chem. Pharm. Bull. **1978**, *26,* 3743.
3. Ho, T.L.; Ho, H.C.; Wong, C.M. J. Chem. Soc. Chem. Commun. **1972**, 791.
4. Lipshutz, B.H.; Moretti, R.; Crow, R. Tetrahedron Lett. **1989**, *30*, 15.
5. Chavan, S.P.; Sharma, A.K. Synlett. **2001**, 667.
6. Chavan, S.P.; Sharma, A.K. Tetrahedron Lett. **2001**, *42*, 4923.
7. Ravindranathan, T.; Chavan, S.P.; Varghese, J.P. J. Chem. Soc. Chem. Commun. **1994**, 1937.
8. Chavan, S.P.; Soni, P.; Kamat, S.K. Synlett. **2001**, 1255.
9. Ravindranathan, T.; Chavan, S.P.; Tejwani, R.B.; Varghese, J.P. J. Chem. Soc. Chem. Commun. **1991**, 1750.
10. Kamal, A.; Laxman, E.; Reddy, P.S.M.M. Synlett, **2000**, 1476 and references cited therein.
11. Saraswathy, G.V.; Sankararaman, S. J. Org. Chem. **1994**, *59*, 4665.
12. Lindsey, J.S.; Prathapan, S.; Johnson, T.E.; Wagner, R.W. Tetrahedron **1994***, 50,* 8941.
13. Nickon, A.; Rodriguer, A.D.; Shirhatti, V.; Ganguly, R. J. Org. Chem. **1985**, *50*, 4218.
14. Hoppmann, A.; Weyerstahl, P.; Zummack, W. Liebigs Ann. Chem. **1977**, 1547**.**
15. Jnaneshwara, G.K.; Barhate, N.B.; Sudalai, A.; Deshpande, V.H.; Wakharkar, R.D.; Gajare, A.S.; Shingare, M.S.; Sukumar, R. J. Chem. Soc. *PT-I*, **1998,** 965.
16. Lieberman, S. V.; Connor, R. Org. Synth. Coll. **1943**, *2*, 441.
17. Schmerling, L.; J.A.C.S. **1947**, *69,* 1121.

18. General Procedure: A mixture of dithioacetal of p-methoxy benzaldehyde (212 mg, 1 mmol), $FeCl_3$ (162 mg, 1 mmol) and KI (166 mg, 1 mmol) was refluxed in methanol. Progress of the reaction was monitored by TLC. After the completion of the reaction, methanol was removed under reduced pressure and residue was extracted in ether. The ether extract was dried over anhydrous Na_2SO_4 and the organic layer was filtered. Evaporation of the solvent under reduced pressure furnished pure anisaldehyde (122 mg, 90%). IR (film, cm^{-1}) : $\nu = 3009$, 2739, 1684, 1578, 1511, 1461. ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 3.89$ (s, 3H), 7.01 (d, $J = 8.7$ Hz, 2H), 7.85 (d, $J = 8.7$ Hz, 2H), 9.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 190.6$, 164.4, 131.7, 129.7, 114.1, 55.3.

Received in the USA February 21, 2002