Pergamon

Tetrahedron Letters 44 (2003) 9349–9351

TETRAHEDRON
LETTERS

SmI_2-mediated elimination reaction of trichloromethyl carbinols: a facile method to synthesize vinyl dichlorides

Jian Li,[a] Xiaoliang Xu[a] and Yongmin Zhang[a,b,*]

[a]*Department of Chemistry, Zhejiang University (Campus Xixi), Hangzhou 310028, PR China*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China*

Received 10 June 2003; revised 18 September 2003; accepted 8 October 2003

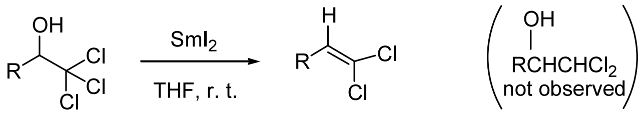
Abstract—Samarium diiodide-mediated elimination reaction provides a simple and general method to synthesize vinyl dichlorides from trichloromethyl carbinols directly in good to excellent yields.
© 2003 Elsevier Ltd. All rights reserved.

As synthetically important intermediates,[1] vinyl dihalides has drawn much attention from synthetic chemists especially when they were found to be key intermediates in the syntheses of anti-HIV chemicals.[2] In the literature, these compounds are generally prepared through Wittig-type reactions.[3] However, the requirements of phosphorous for Wittig reactions somehow limit their attractiveness due to problems of toxicity and volume of waste streams generated.

Up to now, by using trichloromethyl carbinols or their esters as starting materials, several methodologies have been reported to lead to vinyl dihalides. Nevertheless, most of these methods experience derivatization of trichloromethyl carbinols such as acetylation and mesylation.[2,4] On the other hand, some other methods also suffer from low yields, long reaction time or high reaction temperature, which lower their synthetic usefulness to some extent.[5] Thus, to develop a new procedure still remains desirable especially when trichloromethyl carbinols are used as starting materials in reactions without any derivatization.

As a powerful, versatile, and ether-soluble one-electron transfer reducing agent, SmI_2 has played an ever-increasing role in organic synthesis.[6] Among many other methods, SmI_2-mediated reductive elimination is a powerful method to realize alkenes and has been extensively developed.[7] To the best of our knowledge, SmI_2-mediated procedure to prepare vinyl dichlorides has not been reported up to date. Here, we report a facile synthesis of vinyl dichlorides from trichloromethyl carbinols promoted by SmI_2 in THF at room temperature.

Our first attempt was carried out with two trichloromethyl carbinols as model substrates. Fortunately, when these alcohols were added to a solution of SmI_2 in THF, expected results were observed with the corresponding vinyl dichlorides being afforded in high yields (Scheme 1). According to a usual α-elimination reaction, dichloromethyl carbinols **B** may be the major product. In fact, no carbinols **B** were observed and only the desired vinyl dichlorides **A** were obtained. The above results therefore provoke our interests since SmI_2 induced direct elimination of a hydroxy group has been scarcely reported.[7c]



A **B**

	Yield (%)
R = Ph,	85
R = 4-Cl-Ph	91

Scheme 1.

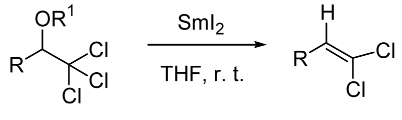
Keywords: samarium diiodide; vinyl dichloride; elimination; trichloromethyl carbinol.

* Corresponding author. Tel.: +86-571-8517-8611; fax: +86-571-8880-7077; e-mail: yminzhang@mail.hz.zj.cn

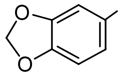
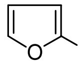
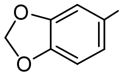
0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2003.10.085

A wide range of structurally varied trichloromethyl carbinols **1** underwent elimination reactions by this procedure to give the corresponding vinyl dichlorides in high yields, as shown in Table 1. It was noteworthy that this reaction also proceeded well with an aliphatic trichloromethyl carbinol **1** (entry 12). When unsaturated carbinol was used (entry 11), the corresponding elimination reaction took place as well and its original double bond remained intact. Acetates of some trichloromethyl carbinols were also suitable substrates for reductive elimination under the same reaction conditions. According to literature,[7] chelation of Sm(III) with the carbonyl oxygen of the acetoxy group produces a six-membered ring (Scheme 2). Elimination from intermediate **I** affords vinyl dichlorides.

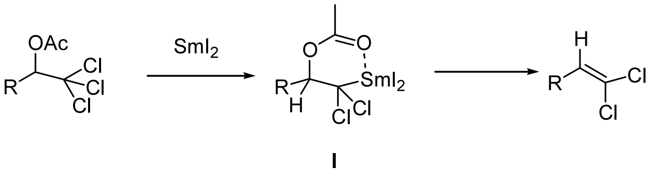
Table 1. SmI_2-mediated reductive elimination reaction of trichloromethyl carbinols



1 **2**

Entry	R	R^1	Product	Time (min)	Yield [a](%)
1	Ph	H	**2a**	5	85
2	4-Cl-C_6H_4	H	**2b**	5	91
3	2-Cl-C_6H_4	H	**2c**	5	94
4		H	**2d**	3	83
5	4-CH_3O-C_6H_4	H	**2e**	3	85
6	2-CH_3O-C_6H_4	H	**2f**	5	93
7		H	**2g**	5	78
8	4-CH_3-C_6H_4	H	**2h**	5	85
9	3-Br-C_6H_4	H	**2i**	3	84
10	4-OH-C_6H_4	H	**2j**	5	87
11	Ph-CH=CH(t)	H	**2k**	5	70
12	*t*-Bu	H	**2l**	8	75
13	Ph	Ac	**2a**	3	81
14	4-Cl-C_6H_4	Ac	**2b**	5	90
15	2-Cl-C_6H_4	Ac	**2c**	3	96
16		Ac	**2d**	5	85
17	2-CH_3O-C_6H_4	Ac	**2f**	3	87
18	4-CH_3-C_6H_4	Ac	**2h**	3	92
19	3-Br-C_6H_4	Ac	**2i**	5	85

[a] Isolated yields



Scheme 2.

In summary, the SmI$_2$-mediated reduction elimination of trichloromethyl carbinols offers a facile, convenient and efficient method for the synthesis of useful vinyl dichlorides.[9] The advantages of this method are the readily available starting materials,[8] the mild reaction conditions, the short reaction time and high yields. Thus, the present method will broaden the scope of SmI$_2$-mediated elimination reaction and will be useful in organic synthesis.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Project No. 20072033) and Specialized Research Fund for the Doctoral Program of Higher Education of China.

References

1. (a) Ramirej, F.; Desai, N. B.; McKelvie, N. J. *J. Am. Chem. Soc.* **1962**, *84*, 1745–1747; (b) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769–3772.
2. (a) Wang, Z.; Campagna, S.; Yang, K.; Xu, G.; Pierce, M. E.; Fourtunak, J. M.; Confalone, P. N. *J. Org. Chem.* **2000**, *65*, 1889–1891; (b) Tanaka, H.; Yamashita, S.; Yamamoue, M.; Torii, S. *J. Org. Chem.* **1989**, *54*, 444–450.
3. (a) Speziale, A. J.; Ratts, K. W. *J. Am. Chem. Soc.* **1962**, *84*, 854–859; (b) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769–3772; (c) Bandzouzi, A.; Lakhrissi, M.; Chapleur, Y. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1471–1473; (d) Chaplerur, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 449–450.
4. (a) Wang, Z.; Campagna, S.; Xu, G.; Pierce, M. E.; Fortunak, J. M.; Confalone, P. N. *Tetrahedron Lett.* **2000**, *41*, 4007–4009; (b) Calvet, F.; Mejuto, M. N. *J. Chem. Soc.* **1936**, 554–556; (c) Kiehlmann, E.; Bianchi, R. J.; Reeve, W. *Can. J. Chem.* **1969**, *47*, 1521–1527; (d) Gajewski, R. P.; Jackson, J. L.; Jones, N. D.; Swartzendruber, J. K.; Deeter, J. B. *J. Org. Chem.* **1989**, *54*, 3311–3317.
5. (a) Wolf, R.; Steckhan, E. *J. Chem. Soc.* **1986**, 733–740; (b) Bitter, I.; Toke, L.; Bende, Z.; Ádám, É. K.; Soós, R. *Tetrahedron* **1984**, *40*, 4501–4506; (c) Ranu, B. C.; Samanta, S.; Das, A. *Tetrahedron Lett.* **2002**, *43*, 5993–5995; (d) Lavielle, G.; Combret, J.-C.; Villieras, J. *Bull. Soc. Chim. Fr.* **1971**, 2047–2053.
6. (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698; (b) Krief, A.; Laval, A. M. *Chem. Rev.* **1999**, *99*, 745–777; (c) Molander, G. A. *Acc. Chem. Res.* **1998**, *31*, 603–609; (d) Molander, G. A.; Harris, C. R. *Tetrahedron* **1998**, *54*, 3321–3354; (e) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307–338; (f) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29–68; (g) Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. *Synlett* **1992**, 943–961.
7. For examples: (a) Concellon, J. M.; Bernad, P. J.; Pére-Andrés, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2384–2386; (b) Concellon, J. M.; Bernad, P. J.; Pére-Andrés, J. A.; Rodríguez-Solla, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2773–2775; (c) Concellon, J. M.; Huerta, M. *Tetrahedron Lett.* **2003**, *44*, 1931–1934; (d) Concellon, J. M.; Bardales, E. *Org. Lett.* **2002**, *4*, 189–191; (e) Concellon, J. M.; Bernad, P. J.; Bardales, E. *Org. Lett.* **2001**, *3*, 937–939
8. (a) Corey, E. J.; Link, J. O.; Shao, Y. *Tetrahedron Lett.* **1992**, *33*, 3435–3438; (b) Aggarwal, V. A.; Mereu, A. *J. Org. Chem.* **2000**, *65*, 7211–7212.
9. A typical procedure is as follows: A solution of trichloromethyl carbinol (1 mmol) in dry THF (3 mL) was added to the solution of SmI$_2$ (2.2 mmol) in THF (20 mL) at room temperature under nitrogen atmosphere. The deep blue color of the solution changed to yellow slowly. After being stirred for 5 min (Table 1), the reaction mixture was quenched with 0.1 M hydrochloric acid (5 mL) and extracted with ether (3×20 mL). The organic phase was successively washed with brine (15 mL), water (20 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure to give the crude products, which were purified by preparative TLC using cyclohexane as eluant. All products were characterized by IR, ^{1}H NMR, Mass spectroscopy and elemental analysis. For example: 1,1-dichloro-2-(4-chlorophenyl)-ethene (**2b**): oil. ν_{max}(film)/cm^{-1}: 2925, 1610, 1592; 1530. δ_H (CDCl$_3$): 7.50–7.48 (2H, m), 7.37–7.35 (2H, m), 6.83 (1H, s). m/z (%): 206 (M$^+$, 100), 208 (M$^+$+2, 96), 171 (44); 136 (74). Anal. calcd C$_8$H$_5$Cl$_3$ C, 46.31; H, 2.43. Found C, 46.23; H, 2.46%