**SHORT PAPER**

*J. Chem. Research (S),*
2003, 340–341

# Synthesis of *trans*-stilbenes utilising decarbonylation of α-chloro chloroformates mediated by samarium diiodide[†]

**Zhifang Li[a] and Yongmin Zhang[a, b]***

[a]*Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou, Zhejiang, 310028, P.R. China*

[b]*Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, P. R. China*

---

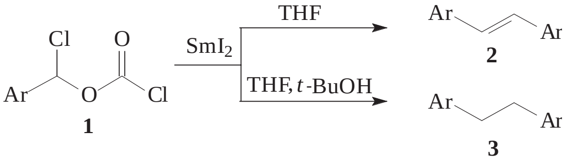
A new synthesis of *trans*-stilbenes has been achieved by decarbonylation of α-chloro chloroformates mediated by samarium diiodide in THF; this one pot reaction is completed within a few minutes at room temperature.

---

**Keywords:** *trans*-stilkenes, α-chloro chloroformates, samarium diiodide

---

Recently, samarium metal, its salts and organosamarium compounds have been widely employed as useful reagents in organic synthesis.[1] Subsequent to the pioneering work by Kagan and his coworkers, samarium diiodide has been extensively investigated as a mild, neutral and versatile one-electron transfer reductant.[2] The utilisation of samarium diiodide in synthetic organic chemistry has been well documented, for example in radical cyclisations,[3] ketyl–olefin coupling reactions,[4] Barbier-type reactions,[5] Reformatsky reactions[6] and reductive coupling cyclizations.[7] Although many examples exist of the reductive coupling of acid halides,[8] there are only a limited number of examples of the decarbonylation of acid halides.[9] Kagan[9b] reported the decarbonylation of α-alkoxyacid chlorides and α-aminoacid chlorides by the action of samarium diiodide. It was therefore of interest to study the action of α-chloro chloroformates mediated by samarium diiodide. Our investigation shows that the reductive coupling of α-chloro chloroformates with $SmI_2$ provides a facile procedure for the preparing of *trans*-stilbenes.



**Scheme 1**

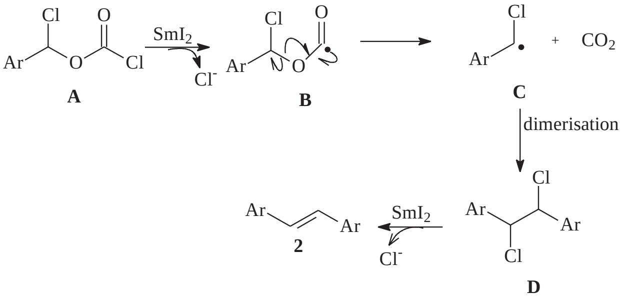
When α-chloro chloroformates (**1**) were treated with samarium diiodide in THF for about 5 minutes at room temperature, *trans*-stilbenes (**2**) were obtained in good yields (Scheme 1). The results are listed in Table 1. It is interesting to note that in the presence of *t*-BuOH, the dechlorination reduction product 1,2-diphenylethane (**3**) was isolated.

Although the detailed mechanism of this reaction is not clear at this stage, it is likely that the reaction is started by an electron transfer from samarium diiodide to α-chloro chloroformates (**A**); thus the radical anion is formed. It cleaves into $(ArCHClCO_2)^{\cdot}$ (**B**) and $Cl^-$. Carbon dioxide is evolved from the radical[9a] (**B**), then the radical $(ArCHCl)^{\cdot}$ (**C**) is formed. The radical (**C**) may dimerise into (**D**). (**D**) may then undergo dechlorination in the presence of samarium diiodide, and the corresponding stilbene (**2**) is formed.

**Table 1** The synthesis of *trans*-stilbenes

| Entry | Ar | Time/min | M.p./°C (lit m.p./ °C) | Yields of **2** or **3**/%[a] (product) |
|---|---|---|---|---|
| 1 | $C_6H_5$ | 5 | 123 (122–124[11]) | 90 (**2a**) |
| 2 | $C_6H_5$ | 10 | 50–53 (52[14]) | 75[b] (**3a**) |
| 3 | 2-$CH_3$ $C_6H_4$ | 5 | 83–85 (82.5–84[11]) | 86 (**2b**) |
| 4 | 4-$CH_3$ $C_6H_4$ | 5 | 178–179 (180[11]) | 90 (**2c**) |
| 5 | 4-$CH_3O$ $C_6H_4$ | 5 | 209–210 (210–211[11]) | 87 (**2d**) |
| 6 | 4-Cl $C_6H_4$ | 4 | 177–179 (178[12]) | 85 (**2e**) |
| 7 | 3-Cl $C_6H_4$ | 4 | 95 (94–95[12]) | 95 (**2f**) |
| 8 | 3-Br $C_6H_4$ | 4 | 109–111 (108–110[12]) | 80 (**2g**) |
| 9 | 4-F $C_6H_4$ | 4 | 107–108 (103–106[13]) | 85 (**2h**) |

[a]Isolated yields.
[b]In the presence of *t*-BuOH, 1,2-diphenylethane was obtained.



**Scheme 2**

In conclusion, under mild conditions, α-chloro chloroformates can undergo decarbonylation to afford *trans*-stilbenes conveniently. The mild reaction conditions, readily available starting materials, simple operations and high yields make this method superior to previous strategies.

## Experimental section

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points are uncorrected. $^1H$ NMR spectra were recorded on a Bruker AC-400 instrument as $CDCl_3$ solutions using TMS as an internal standard. Chemical shifts (δ) are reported in ppm and coupling constants *J* are given in Hz. IR spectra were taken as thin films with a Bruker Vector-22 infrared spectrometer. Elemental analyses were performed on a EA-1110 instrument. Metallic samarium and all solvents were purchased from commercial sources and were used without further purification. The starting material α-chloro chloroformates was prepared by the published method.[10]

*General procedure for the synthesis of trans-stilbene*: Under a dry nitrogen atmosphere, the α-chloro chloroformate (2 mmol, 1ml THF)

---

[*] To receive any correspondence. E-mail: yminzhang@mail.hz.zj.cn
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

were added to 30ml of 0.1M $SmI_2$ (3mmol) in THF. Then the mixture was stirred at room temperature. After given times (Table), the reaction mixture was quenched with hydrochloric acid (2 mol/l, 2 ml), and extracted with diethyl ether (3 × 15 ml). The combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel (1:10 ethyl acetate/cyclohexane). The products were identified by comparison with commercial samples (TLC, m.p., IR, $^1H$ NMR and MS).

*General procedure for the synthesis of 1, 2-diphenylethane*: Under a dry nitrogen atmosphere, the α-chloro chloroformate (2 mmol, 1ml THF) was added to 40ml of 0.1M $SmI_2$ (4mmol) in THF and t-BuOH (5 ml). Then the mixture was stirred at room temperature. After 10 min, the reaction mixture was quenched with hydrochloric acid (2 mol/l, 2 ml), and extracted with diethyl ether (2 × 10 ml). The combined organic layer was washed with saturated brine, dried over anhydrous $Na_2SO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel (1:10 ethyl acetate/cyclohexane). The products were identified by comparison with commercial samples (TLC, m.p., IR, $^1H$ NMR and MS).

We thank the National Natural Science Foundation of China (Project No.20072033) for financial support.

*Received 11 October 2002; accepted 5 February 2003*
*Paper 02/1597*

## References

1 Recent reviews: (a) H.B. Kagan and J.L. Namy, *Tetrahedron*, 1986, **42**, 6573; (b) G.A. Molander, *Chem., Rev.*, 1992, **92**, 29; (c) G.A. Molander, *Organic Reaction*, 1994, **46**, 211; (d) G.A. Molander and C.R. Harris, *Chem., Rev.*, 1996, **96**, 307; (e) A. Krief and M.A. Laval, *Chem. Rev.*, 1999, **99**, 745; (f) P.G. Steel, *J. Chem. Soc. Perkin Trans. I*, 2001, 2727.

2 P. Girard, J.L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.

3 (a) D.P. Curran, M.H. Chen and D. Kim, *J. Am. Chem. Soc.*, 1989, **111**, 6265; (b) S. Fukuzawa and T. Tsuchimoto, *Synlett*, 1993, 803.

4 (a) S. Fukuzawa, A. Nakanishi, T. Fujinami and S. Sakai, *J. Chem. Soc., Chem. Commun.*, 1986, 624; (b) K. Otsubo, J. Inanaga and M. Yamaguchi, *Tetrahedron Lett.*, 1986, **27**, 5763.

5 M. Sasaki, J. Collin and H.B. Kagan, *New J. Chem.*, 1992, **16**, 89; (b) J. Souppe; J.L. Namy and H.B. Kagan, *Tetrahedron Lett.*, 1982, **23**, 3497.

6 G.A. Molander, J.B. Etter, L.S. Harring and P.J. Thorel, *J. Am. Chem. Soc.*, 1991, **113**, 8036.

7 (a) J. Inanaga, Y. Handa, T. Tabuchi, K. Ostubo, M. Yamaguchi and T. Hanamoto, *Tetrahedron Lett.*, 1991, **32**, 6557; (b) S. Kamemasa, H. Yamamoto and S. Kobayashi, *Tetrahedron Lett.*, 1996, **37**, 8505; (c) L.–H. Zhou and Y.–M. Zhang, *Tetrahedron Lett.*, 1997, **38**, 8063.

8 (a) P. Girard, R. Couffignal and H.B. Kagan, *Tetrahedron Lett.*, 1981, **22**, 3959; (b) J. Souppe, J.L. Namy and H.B. Kagan, *Tetrahedron Lett.*, 1984, **25**, 2869; (c) J. Collin, F. Dallemer, J.L. Namy and H.B. Kagan, *Tetrahedron Lett.*, 1989, **30**, 7407; (d) J. Collin, J.L. Namy, F. Dallemer and H.B. Kagan, *J. Org. Chem.*, 1991, **56**, 3118; (e) S.M. Ruder, *Tetrahedron Lett.*, 1992, **33**, 2621; (f) J.L. Namy, M. Colomb and H.B. Kagan, *Tetrahedron Lett.*, 1994, **35**, 1723.

9 (a) M. Sasaki, J. Collin and H.B. Kagan, *Tetrahedron Lett.*, 1988, **29**, 4847; (b) J. Collin, J.L. Namy, G. Jones and H.B. Kagan, *Tetrahedron Lett.*, 1992, **33**, 2973.

10 M.J. Coghlan and B.A. Caley, *Tetrahedron Lett.*, 1989, **30**, 2033.

11 H.J. Bestmann and O. Kratzer, *Chem. Ber.*, 1963, **96**, 1899.

12 J.A. Stanfield and L.B. Reynolds, *J, Am. Chem. Soc.*, 1952, **74**, 2878.

13 R. Mayer, S. Scheithaure and D. Kunz, *Chem. Ber.*, 1966, **99**, 1393.

14 T. Kawaki and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3130.