Stereoselective Synthesis of (*E*)-Cinnamates with Sm/HOAc

FAN, Xue-Sen[a,b](范学森) **ZHANG, Yong-Min**[*,a,c](张永敏)

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

[b] *Department of Chemistry, Henan Normal University, Xinxiang, Henan 453002, China*

[c] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

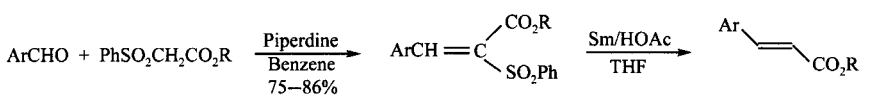
The reductive desulfonylation of α-phenylsulfonylcinnamates promoted by Sm/HOAc led to the corresponding (*E*)-cinnamates stereoselectively in good yields under mild conditions.

Keywords Samarium, reduction, desulfonylation, (*E*)-cinnamates

The development of methods for the stereoselective formation of carbon-carbon double bonds could be considered as one of the most important challenges in organic synthesis. Being useful reagents and intermediates in organic synthesis, α,β-unsaturated esters have received considerable attention.[1] Up to now, many methods have been reported for the preparation of (*E*)-cinnamates, for example, rhodium-catalyzed dehydrogenation cross-coupling of arenes with olefin,[2] palladium-catalyzed vinylation of organic halides (Heck-type reaction),[3] palladium-catalyzed alkoxycarbonylation of vinyl halides,[4] Wittig-Horner reaction of $(EtO)_2POCH_2COOR$ with aldehydes,[5] or esterification of corresponding (*E*)-cinnamic acids with alcohols using *p*-toluenesulfonic acid as catalyst.[6] However, in most of these cases, total control of the stereoselectivity of the carbon-carbon double bond formation remained unresolved. In addition, these methods always suffered from using expensive catalysts, or rather harsh conditions.

As a powerful, versatile and ether-soluble one-electron transfer reductant, samarium diiodide has been widely applied in organic synthesis.[7] Though SmI_2 is a useful reagent, its storage is difficult due to its sensitivity to air. In contrast, metallic samarium is stable in air and its strong reducing power (Sm^{3+}/Sm −2.41 V) is similar to that of magnesium (Mg^{2+}/Mg −2.37 V) and superior to that of zinc (Zn^{2+}/Zn −0.71 V). These properties prompted us to use the more convenient and cheaper metallic samarium directly as a reductant instead of samarium(II) iodide. Recently, there have been reports on the direct use of metal samarium in organic synthesis.[8] Herein (Scheme 1) we wish to report the stereoselective synthesis of (*E*)-cinnamates (**4**) via reductive desulfonylation of α-phenylsulfonylcinnamates (**3**), which can be conveniently prepared through base-catalyzed condensation of aromatic aldehydes (**1**) and phenylsulfonylacetates (**2**), promoted by Sm/HOAc under mild conditions. The results are summarized in Table 1.

Scheme 1



1 2 3 4

* E-mail: yminzhang@mail.hz.zj.cn

Received February 22, 2001; revised April 29, 2001; accepted May 11, 2001.

Project supported by the National Natural Science Foundation of China (No. 20072003) and the Natural Science Foundation of Zhejiang Province, China.

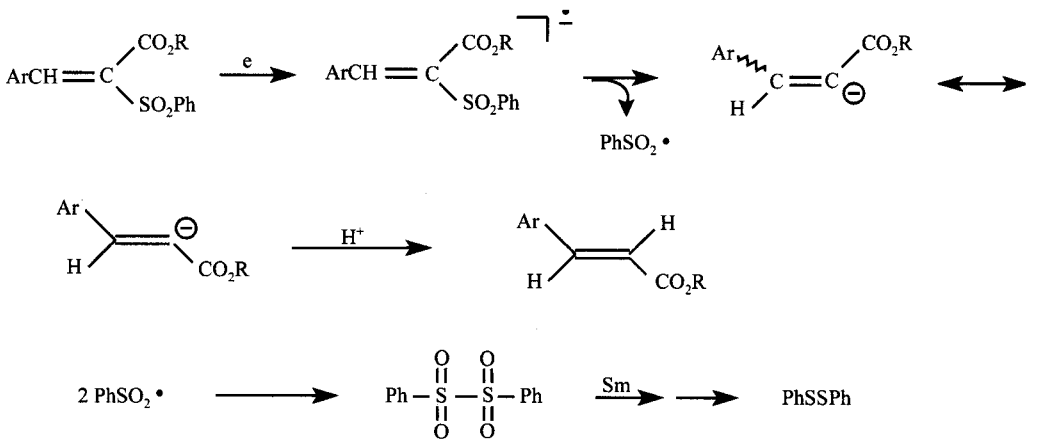
Table 1 Synthesis of (*E*)-cinnamates with Sm/HOAc

Entry	Ar	R	Yield (%)[a]
1	C_6H_5	CH_3	78
2	p-$CH_3C_6H_4$	CH_3	71
3	p-$CH_3C_6H_4$	CH_3	0[b]
4	p-BrC_6H_4	CH_3	81
5	p-ClC_6H_4	CH_3	82
6	o-ClC_6H_4	CH_3	78
7	C_6H_5	C_2H_5	79
8	p-$CH_3C_6H_4$	C_2H_5	75
9	p-ClC_6H_4	C_2H_5	80
10	3,4-$CH_2O_2C_6H_3$	C_2H_5	85

[a] Isolated yields. [b] In the absence of HOAc. Reaction conditions: THF, rt, 3—4 h.

It was found that in the presence of Sm/HOAc, the reductive desulfonylation of α-phenylsulfonylcinnamates underwent smoothly at room temperature, affording (*E*)-cinnamates stereoselectively in moderate to good yields. IR spectra showed that there was not the characteristic bond of sulfonyl group (SO_2) in the products. ^1H NMR spectra indicated that only (*E*)-cinnamates (J = 14—18 Hz) were formed and (*Z*)-cinnamates (J = 6—12 Hz) was not detected at all. It was also found that the above reaction could not take place in the absence of HOAc. A possible mechanism is depicted in Scheme 2. In fact, PhSSPh, the by-product of the reaction, has been separated from the reaction mixture, which is in accordance with this proposed mechanism.

Scheme 2



In conclusion, with high yields, mild conditions, as well as available starting materials, the present work may provide a useful method for the preparation of (*E*)-cinnamates. Further studies on the new application of Sm/HOAc are now in progress in our laboratory.

Experimental

Melting points were uncorrected. Infrared spectra were recorded on a Shimadzu IR-408 spectrometer in KBr or film with absorption in cm^{-1}. ^1H NMR spectra were recorded on a Bruker AC—80 spectrometer as $CDCl_3$ solutions. J values are in Hz. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. α-Phenylsulfonylcinnamates were prepared according to the literature (shown in Scheme 1).[9]

General procedure for the synthesis of (E)-cinnamates

Samarium powder (0.30 g, 2 mmol), glacial acetic acid (0.5 mL), THF (5 mL) and α-phenylsulfonyl methyl cinnamate (0.37 g, 1 mmol) were mixed in a three-necked round bottom flask. The mixture was magnetically stirred at room temperature until the substrate was almost consumed (monitored by TLC). When the reaction was completed, water (10 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (2 × 20 mL). The extracts were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The

residue was then purified by preparative TLC on silica gel to give pure products.

Methyl cinnamate mp 32—33℃ (Lit.[10] 34—35.5℃). IR ν: 3080, 2945, 1715, 1630, 1510, 1445, 1310, 765, 680 cm^{-1}. ^1H NMR δ: 3.74 (s, 3H), 6.38 (d, J = 16.0 Hz, 1H), 6.95—7.36 (m, 5H), 7.65 (d, J = 15.9 Hz, 1H).

Methyl p-methyl-cinnamate mp 53—55℃ (Lit.[11] 55—56℃). IR ν: 3080, 2940 - 1710, 1635, 1443, 1460, 1305, 1182, 965 cm^{-1}. ^1H NMR δ: 2.36 (s, 3H), 3.79 (s, 3H), 6.38 (d, J = 16.1 Hz, 1H), 7.21—7.51 (m, 4H), 7.70 (d, J = 16.0 Hz, 1H).

Methyl p-bromo-cinnamate mp 74—76℃ (Lit.[11] 75—77℃). IR ν: 3080, 2940, 1715, 1635, 1510, 1315, 960 cm^{-1}. ^1H NMR δ: 3.80 (s, 3H), 6.35 (d, J = 16.0 Hz, 1H), 7.18—7.43 (m, 4H), 7.74 (d, J = 16.0 Hz, 1H).

Methyl p-chloro-cinnamate mp 70—71℃ (Lit.[11] 72—73℃). IR ν: 3085, 2945, 1715, 1635, 1515, 1310, 968 cm^{-1}. ^1H NMR δ: 3.81 (s, 3H), 6.34 (d, J = 15.9 Hz, 1H), 7.25—7.61 (m, 4H), 7.76 (d, J = 16.0 Hz, 1H).

Methyl o-chloro-cinnamate Oil.[12(a)] IR ν: 3090, 2950, 1710, 1630, 1310, 967, 772 cm^{-1}. ^1H NMR δ: 3.74 (s, 3H), 6.38 (d, J = 16.0 Hz, 1H), 6.98—7.26 (m, 4H), 7.78 (d, J = 16.0 Hz, 1H).

Ethyl cinnamate Oil.[5(a)] IR ν: 3080, 2935, 1705, 1635, 1300, 770, 680 cm^{-1}. ^1H NMR δ: 1.32 (t, J = 7.1 Hz, 3H), 4.20 (q, J = 7.1 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 6.98—7.35 (m, 5H), 7.75 (d, J = 16.0 Hz, 1H).

Ethyl p-methyl-cinnamate Oil.[12(b)] IR ν: 3080, 2930, 1710, 1632, 1302, 968 cm^{-1}. ^1H NMR δ: 1.23 (t, J = 7.1 Hz, 3H), 2.19 (s, 3H), 4.13 (q, J = 7.1 Hz, 2H), 6.36 (d, J = 16.0 Hz, 1H), 6.99—7.32 (m, 4H), 7.76 (d, J = 16.0 Hz, 1H).

Ethyl p-chloro-cinnamate Oil.[5(a)] IR ν: 3070, 2940, 1715, 1635, 1314, 1190, 965 cm^{-1}. ^1H NMR δ: 1.23 (t, J = 7.1 Hz, 3H), 4.07 (q, J = 7.1 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 7.30—7.64 (m, 4H), 7.58 (d, J = 16.0 Hz, 1H).

Ethyl 3,4-methylenedioxy-cinnamate mp 63—65℃ (Lit.[5(b)] 66.6—67.3℃). IR ν: 3085, 2915, 1705, 1630, 1310, 880 cm^{-1}. ^1H NMR δ: 1.24 (t, J = 7.1 Hz, 3H), 4.15 (q, J = 7.1 Hz, 2H), 6.05 (s, 2H), 6.39 (d, J = 16.0 Hz, 1H), 6.98—7.29 (m, 3H), 7.52 (d, J = 16.0 Hz, 1H).

References

1 (a) Franklin, A. S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2451.
(b) Shen, Y. *Acc. Chem. Res.* **1998**, *31*, 584.
2 Koushi, S.; Toshiyasu, S.; Yuko, T.; Keisuke, W.; Masato, T. *Chem. Lett.* **1988**, *4*, 685.
3 Tuyet, J. *Tetrahedron Lett.* **1994**, *35*, 4705.
4 Andre, M.; Francis, P.; Jean-Francois, C.; Yves, C.; Jacques, B. *Tetrahedron Lett.* **1991**, *32*, 4705.
5 (a) Piechucki, C. *Synthesis* **1974**, 869.
(b) Francoise, T.; Andre, F. *Synthesis* **1979**, 884.
6 Jordan, J. B.; Richard, F. *J. Org. Chem.* **1961**, *26*, 2991.
7 (a) Molander, G. A. *Org. React.* **1994**, *46*, 211.
(b) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.
8 Yanada, R.; Negoro, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1997**, *38*, 3271 and references cited therein.
9 Beck, G.; Gunther, D. *Chem. Ber.* **1973**, *106*, 2758.
10 Heinz, A. S.; Albrecht, M. *Chem. Ber.* **1962**, *95*, 1284.
11 Gunter, P. S.; Josef, T. *Chem. Ber.* **1966**, *99*, 2663.
12 Buckingham, J. *Dictionary of Organic Compounds* Chapman and Hall, New York, 5th ed., **1982**, (a) p. 1195; (b) p. 4009.

(E0102221 JIANG, X.H.; LING, J.)