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Stereoselective Synthesis of (*E*)-Cinnamonitriles with the SmI$_2$/THF/MeOH System†

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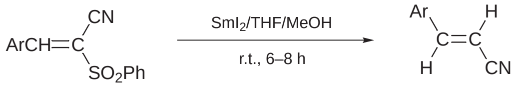
α-Phenylsulfonylcinnamonitriles are readily reduced by SmI$_2$/THF/MeOH to give the corresponding (*E*)-cinnamonitriles in good yields under mild conditions.

Cinnamonitriles are important intermediates of organic synthesis. Cinnamoacids and α,β-unsaturated acylamides were obtained by hydrolysis of cinnamonitriles. The saturated nitriles can be prepared by the selective reduction of cinnamonitriles. Many methods can be used for the synthesis of cinnamonitriles, such as the reaction of cinnamaldehyde and dimethylsulfur diimide,[1] by the reaction of the thallium reagent ArTl(O$_2$CCCl$_3$)$_2$,[2] by Wittig–Horner reaction of (EtO)$_2$POCH$_2$CN and aldehyde,[3] the treatment of acid chloride with sulfonamide[4] and the condensation of aldehyde and nitroethane.[5]

Samarium diiodide (SmI$_2$) is a powerful one-electron transfer reductant[6] but which cannot reduce the cyano group.[7] Recently, Huang *et al.*[8] reported that (*Z*)-cinnamonitriles were prepared in 78–98% yield by the desulfonylaton of α-phenylsulfonylcinnamonitriles in the presence of NaHTe. This prompted us to use SmI$_2$ for the desulfonylation of α-phenylsulfonylcinnamonitriles. We found that (*E*)-cinnamonitriles were obtained in 68–85% yield under mild conditions (Scheme 1). Some results are summarized in Table 1.



Scheme 1

Table 1 shows that α-phenylsulfonylcinnamonitriles undergo reductive desulfonation in the presence of samarium diiodide in THF-MeOH solution to give the corresponding (*E*)-cinnamonitriles in moderate to good yields at room temperature. The chloro and bromo group of the aromatic ring have no effect on the desulfonylation. IR spectra show that the sulfonyl group (SO$_2$) is lost. ^{1}H NMR spectra show that (*Z*)-cinnamonitriles ($J = 6$–12 Hz) have not been formed in the crude products of the reaction. All products gave satisfactory mp, IR and ^{1}H NMR spectra.

Table 1 Synthesis of (*E*)-cinnamonitriles with SmI$_2$/THF/MeOH

Entry	Ar	Yield*(%)	Mp/°C (lit.)	IR (neat or KBr) (cm^{-1})	^{1}H NMR (CCl$_4$ or CDCl$_3$), δ (J/Hz)
a	C$_6$H$_5$	68	18–20 (22.5)[9]	2212, 1630, 1330, 965	5.60 (d, 1 H, $J = 16.5$) 7.26 (d, 1 H, $J = 16.5$) 7.30 (s, 5 H)
b	p-MeC$_6$H$_4$	85	68–70 (70–71)[10]	2215, 1633, 1380, 1300, 965	2.26 (s, 3H) 5.43 (d, 1 H, $J = 16.7$) 7.15 (d, 1 H, $J = 16.7$) 6.10–7.30 (m, 4 H)
c	m-MeC$_6$H$_4$	79	Oil[10]	2210, 1617, 1380, 1317, 967	2.23 (s, 3 H) 5.63 (d, 1 H, $J = 16.6$) 7.13 (d, 1 H, $J = 16.6$) 7.06 (s, 4 H)
d	p-ClC$_6$H$_4$	74	81–83 (84–85)[10]	2217, 1635, 1315, 965, 800	5.43 (d, 1 H, $J = 16.7$) 7.27 (d, 1 H, $J = 16.7$) 7.30 (s, 4 H)
e	o-ClC$_6$H$_4$	71	38–40 (41–42)[12]	2215, 1627, 1314, 967, 772	5.56 (d, 1 H, $J = 16.5$) 7.12 (d, 1 H, $J = 16.5$) 7.24 (s, 4 H)
f	p-MeOC$_3$H$_4$	73	62–64 (64)[10]	2210, 1618, 1380, 1310, 965	3.76 (s, 3 H) 5.50 (d, 1 H, $J = 16.5$) 7.20 (d, 1 H, $J = 16.5$) 6.56–7.33 (m, 4 H)
g	p-BrC$_6$H$_4$	70	102–104 (105–106)[10]	2215, 1637, 1312, 968, 778	5.56 (d, 1 H, $J = 16.4$) 7.26 (d, 1 H, $J = 16.4$) 7.30 (s, 4 H)
h	p-Me$_2$NC$_6$H$_4$	76	165–168 (168–169)[11]	2210, 1615, 1380, 1318, 970	2.97 (s, 6 H) 5.43 (d, 1 H, $J = 16.6$) 6.70 (d, 1 H, $J = 16.6$) 6.40–7.15 (m, 4 H)

* Isolated yields.

In conclusion, with its chemoselectivity, stereoselectivity, mild and neutral condition, as well as simple operation, we think that the present procedure may be useful for the synthesis of (*E*)-cinnamonitriles.

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Experimental

Tetrahydrofuran (THF) was freshly distilled from sodium–benzophenone prior to its use. MeOH was purified by distillation. IR spectra were recorded on a PE-683 spectrometer, ^{1}H NMR spectra with a JEOL PMX-60SI (60 MHz) spectrometer using TMS as internal standard. α-Phenylsulfonyl cinnamonitriles were prepared according to the literature.[13]

General Procedure for the Synthesis of (E)-*Cinnamonitriles.*—To a stirred deep blue solution of SmI_2 (3 mmol) in 20 ml THF was added a solution of α-phenylsulfonylcinnamonitrile (1 mmol) in 2 ml THF and MeOH (2 mmol) by syringe. The mixture was then stirred at room temperature, whereupon it changed from deep blue to yellow. The reaction was terminated with dilute hydrochloric acid (5%, 10 ml). The solution was extracted with diethyl ether (30 ml × 3). The combined organic layers were washed with a saturated solution of sodium thiosulfate (20 ml), followed by brine (20 ml) and then dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by preparative TLC on silica gel (cyclohexane–ethyl acetate, 3:1, eluent).

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