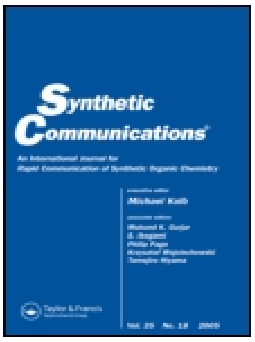

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THE NOVEL PREPARATION OF HYDROCINNAMONITRILES VIA THE REDUCTION OF α-PHENYLSULFONYL CINNAMONITRILES WITH $SmI_2/CH_3OH/THF$ SYSTEM

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Abstract: Hydrocinnamonitriles were readily obtained via the reduction of α-phenylsulfonyl cinnamonitriles by $SmI_2/CH_3OH/THF$ system.

Hydrocinnamonitriles are important organic compounds. Hydrolysis of hydrocinnamonitrile gives the corresponding acid, and cyclization can take place by the reaction of hydrocinnamic acid with hydrogen fluoride.[1,2] Many methods have been reported for the preparation of hydrocinnamonitrile. For example, by the substitutions of alkyl halides or sulfonate esters by cyanide ion;[3] by the conversion of aldoximes into nitriles using trichloroacetyl chloride;[4] by the nitroxyl-mediated electrooxidation of amines to nitriles and carbonyl compounds;[5] by the treatment of acid chlorides with sulfonamide in sulfolane;[6] by demethoxy carbonylation of activated methyl ester, employing

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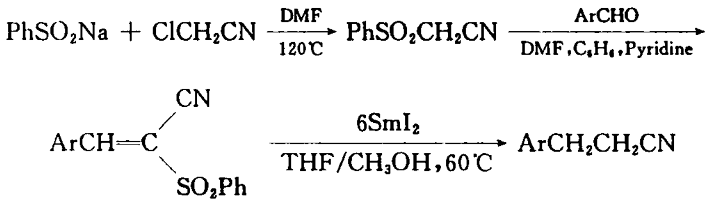
stoichiometric amounts of 4-aminothiophenol and catalytic quantites of caesium carbonate[7]; by cyanomethylation of the corresponding halide[8]. The application of samarium diiodide (SmI_2) in organic synthesis has received more and more attention in the last decade.[9-12] In this paper, we wish to report that SmI_2 reduces α-phenylsulfonyl cinnamonitriles to hydrocinnamonitriles at 60℃ in the presence of methanol in moderate to good yields (Table 1).



$$PhSO_2Na + ClCH_2CN \xrightarrow[120℃]{DMF} PhSO_2CH_2CN \xrightarrow[DMF, C_6H_6, Pyridine]{ArCHO}$$

$$ArCH{=}C(CN)(SO_2Ph) \xrightarrow[THF/CH_3OH, 60℃]{6SmI_2} ArCH_2CH_2CN$$

1 **2**

Table 1 The preparation of hydrocinnamonitriles

Entry	Ar	Reaction time(h)	Yield(%)[a]
2a	C_6H_5	6	67
2b	p-ClC_6H_4	4	70
2c	o-ClC_6H_4	6	60
2d	p-$CH_3C_6H_4$	4	83
2e	m-$CH_3C_6H_4$	4. 5	67
2f	p-BrC_6H_4	4	68
2g	p-$CH_3OC_6H_4$	4. 5	62
2h	p-$(CH_3)_2NC_6H_4$	5	82
2i	2,6-$Cl_2C_6H_3$	8	70

a. Isolated yields based on the substrate **1**.

In our experimental work, we found that when α-phenylsulfonyl cinnamonitrile was added to a deep blue solution of 6 equiv. SmI_2 in THF/CH_3OH

at 60°C, the mixture became yellow within 4—8h. The by-product of the reaction is diphenyldisulfide. The crude product was purified by preparative TLC on silica gel. It is well known that nitriles are important in synthetic organic chemistry, since they are versatile intermediates commonly used for many functional group transformations and carbon-carbon bond forming reactions. Hydrocinnamonitriles are usually prepared according to known methods.[3-8] Alternatively, they can be obtained from the condensation of aldehydes with acctonitrile followed by the selective reduction. Cinnamonitriles can be obtained from aldehydes by different methods such as dehydration of cyanohydrins;[13] Wittig-Horner reaction of diethyl cyanomethane phosphonate;[14] condesation of acetonitrile with KOH[15] or with butyllithium followed by dehydration.[16] Many methods[17] have been reported about the selective reduction of α,β-unsaturated nitriles. The two methods chiefly used are catalytic hydrogenation and electrochemical reduction. Some of the methods mentioned above suffer from disadvantages (strong base, organometallic reagents, etc) and the obtained α,β-unsaturated cinnamonitriles would still need to be reduced into hydrocinnamonitriles. In our experiments, α-phenyl sulfonyl cinnamonitriles can be readily obtained by the condensation of aldehyde with phenylsulfonyl cyanomethane in the presence of pyridine. Therefore, desulfonylation and selective reduction can be carried out in one pot. The new method offers the some distinct advantages, such as easily available starting materials, moderate to high yields, mild and neutral conditions, as well as easy operation. We think that the present method provide a useful method for the preparation of hydrocinnamonitriles.

Experimental

The solvent tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl before use. ^1H-NMR spectra were recorded on a JEOL PMX 60si instrument using TMS as internal standard. IR spectra were recorded with a PE-683 spectrometer. α-Phenylsulfonyl cinnamonitriles **1** were prepared according to known literature[18].

General procedure for the synthesis of hydrocinnamonitriles by samarium diiodide. The solution of α-phenylsulfonyl cinnamonitriles (1 mmol) and 0.5ml methyl alcohol was added to deep blue solution of SmI_2(6 mmol) in 30ml THF under nitrogen. The mixture was stirred at 60℃. When deep blue solution turned yellow (about 4 — 8h) and was cooled into room temperature. A dilute solution of hydrochloric acid (5% 5ml) and ethyl ether (20ml) was added. The organic layer was separated and the aqueous layer was extracted with ethyl ether (2×20ml). The combined organic layer was washed with saturated sodium thiosulfate (20ml) and brine (20ml) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel (cyclohexane/acetate as eluent). The products were identified by IR and ^1H-NMR spectra and elemental analyses.

$C_6H_5CH_2CH_2CN$:[19] Oil, IR(film), 2244cm^{-1}(CN), ^1H-NMR (δ CCl_4): 7.10 (s,5H), 2.85(t,2H,J=7.5Hz), 2.50(t,2H,J=7.5Hz)

p-$ClC_6H_4CH_2CH_2CN$:[20] Oil, IR(film), 2240cm^{-1}(CN), ^1H-NMR (δ CCl_4): 7.45(d,2H,J=8Hz), 7.03(d,2H,J=8Hz), 2.79(t,2H,J=7Hz), 2.49(t, 2H,J=7Hz)

o-$ClC_6H_4CH_2CH_2CN$:[21] Oil, IR(film), 2246cm^{-1}(CN), ^1H-NMR (δ CCl_4): 7.14—7.28(m,4H), 2.85(t,2H,J=7Hz), 2.54(t,2H,J=7Hz)

p-$CH_3C_6H_4CH_2CH_2CN$:[22] Oil, IR (film), 2242cm^{-1} (CN), ^1H-NMR (δ CCl_4): 7.03(s,4H), 2.80(t,2H,J=7Hz), 2.42(t,2H,J=7Hz), 2.24(s, 3H) m-$CH_3C_6H_4CH_2CH_2CN$:[23] Oil, IR (film), 2240cm^{-1} (CN), ^{1}H-NMR (δ CCl_4): 7.09(s,4H), 2.75(t,2H,J=7Hz), 2.40(t,2H,J=7Hz), 2.30(s, 3H)

p-$BrC_6H_4CH_2CH_2CN$:[24] Oil, IR(film), 2245cm^{-1}(CN), ^{1}H-NMR (δ CCl_4): 7.42(d,2H,J=8Hz), 7.06(d,2H,J=8Hz), 2.90(t,2H,J=7Hz), 2.55(t, 2H,J=8Hz)

p-$CH_3OC_6H_4CH_2CH_2CN$:[25] Oil, IR (film), 2246cm^{-1} (CN), ^{1}H-NMR (δ CCl_4): 7.10(d,2H,J=8Hz), 6.77(d,2H, J=8Hz), 3.70(s,3H), 2.85 (t,2H,J=7Hz), 2.42(t,2H,J=7Hz)

p-$(CH_3)_2NC_6H_4CH_2CH_2CN$:[26] Oil, IR (film), 2244cm^{-1} (CN), ^{1}H-NMR (δ CCl_4): 7.07(d,2H,J=8Hz), 6.63(d,2H,J=8Hz), 2.87(s,6H), 2.80 (t,2H,J=7Hz), 2.53(t,2H,J=7Hz)

2, 6-$Cl_2C_6H_3CH_2CH_2CN$: Oil, IR (film), 2245cm^{-1} (CN), ^{1}H-NMR (δ CCl_4): 7.23−6.92(m,3H), 2.92(t,2H,J=7Hz), 2.60(t,2H,J=7Hz)

Anal. Calad. for $C_9H_7Cl_2N$: C 54.00 H 3.58 N 7.33 Found: C 53.72 H 3.42 N 7.29

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