SHORT PAPER

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A convenient method for the reductive desulfonylation of some sulfones by the Sm/HOAc system[†]

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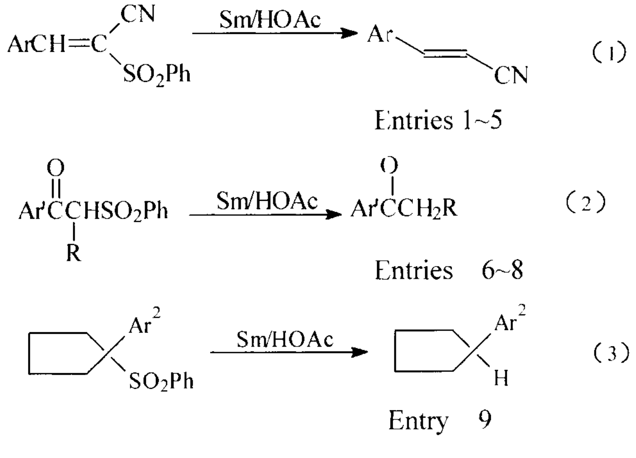
Metallic samarium can be used in desulfonylation in the presence of glacial acetic acid. The reaction is illustrated here for nine substrates, which include α-phenylsulfonyl cinnamonitriles, β-ketosulfones and phenylsulfonyl cycloheptane.

Keywords: metallic samarium, reductive desulfonylation

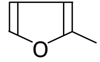
The use of sulfones[1,2] in organic synthesis depends upon the ease of removal of these activating groups. The most important transformation is the replacement of the C–S bond with a C–H bond. Many methods can be used for the reductive desulfonylation of sulfones. The most important reagents include Raney nickel, lithium in amines, sodium amalgam and samarium diiodide. Künzer[3] has been reported reductive desulfonylation of phenyl sulfones by SmI_2–HMPA. Though SmI_2 is a useful reagent for reductive desulfonylation, storage is difficult because it is very sensitive to air oxidation and in general, it has been used invariably in stoichiometric amounts. On the other hand, metallic samarium is stable in air and its strong reducing power ($Sm^{3+}/Sm = -2.41V$) is similar to that of magnesium ($Mg^{2+}/Mg = -2.37V$). These properties prompted us to use the more convenient and cheaper samarium directly as a reductant instead of SmI_2. Recently, there are some reports on the direct use of Sm in organic synthesis.[4] In this paper we wish to report that the reductive desulfonylation can be carried out by Sm/HOAc System. The results are shown in Table 1.

Various substrates ,including α-phenylsulfonyl cinnamonitriles (Table 1,entries 1~5), β-ketosulfones (Table 1, entries 6~8) and phenylsulfonyl cycloheptane (Table 1, entry 9), were used in the Sm/HOAc reduction system and the results are summarized in Table 1. We have found that, reductive desulfonylation does not occur, in the absence of HOAc.



Scheme 1

Table 1 Reductive desulfonylation by Sm/HOAc system

Entry	Ar	Ar[1]	R	Ar[2]	Yield/%[a]
1	C_6H_5				91
2	*p*-$CH_3C_6H_4$				91
3	*p*-ClC_6H_4				87
4	*p*-BrC_6H_4				90
5					72
6		C_6H_5	H		82
7		*p*-BrC_6H_4	H		75
8		C_6H_5	$C_6H_5CH_2$		70
9				C_6H_5	67

[a]Isolated yield. [b]Reaction condition: RT 2h (for entries 1–5); RT 3h (for entries 6–8); RT 5h (entry 9).

When samarium powder was replaced with zinc powder, the desulfonylation of α-phenylsulfonyl cinnamonitriles could be also carried out, but the yield are moderate (in 60-70%).

When samarium reacts with glacial acetic acid in C_2H_5OH at room temperature, the samarium partly dissolves and the surface of the samarium become dark green. When substrates containing the sulfone group are added to the solution, we found that the solution colour changed to yellow (the colour of Sm^{3+}).

Experimental

^1H NMR spectra were recorded on a Bruker AC-80 instrument. All NMR samples were measured using TMS as internal standard. IR psectra were obtained on a Perkin-Elmer 683 infrared spectrophotometer α-phenylsulfonyl cinnamonitriles and β-ketosulfones were prepared according to the literature.[5–7]

General procedure for the reductive desulfonylation: Samarium powder 0.45g (3 mmol), glacial acetic acid 5 ml, ethyl alcohol 1 ml and α-phenylsulfonyl cinnamonitrile 0.27g (1 mmol) were mixed in a three-necked round bottom flask. The mixture was stirred for 2 h at room temperature. The reaction was monitored by TLC. When the substrate had almost disappeared, the reaction mixture was treated with H_2O (20 ml) and diethyl ether (20 ml). The organic layer was separated and the aqueous layer was extracted with diethyl ether (20 ml). The combined organic layer were washed with brine (2 × 15 ml). After the solution was dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane / ethyl acetate as eluent 3 × 1). The products were identified by IR and ^1H NMR spectroscopy).

1. m.p. 19–21°C (Lit.[8] 22.5°C) ^1H NMR (δ_H) 5.58 (d, 1H, J=16.5Hz), 7.24 (d, 1H, J=16.5Hz), 7.31 (s, 5H); IR ν_{max}/cm^{-1} 3080, 2940, 2210, 1630, 1510, 1465, 1330, 965, 690.

2. m.p. 68.5–70°C (Lit.[9] 70–71°C) ^1H NMR (δ_H) 2.25 (s, 3H), 5.43 (d, 1H, J=16.6Hz), 7.15 (d, ^1H, J=16.6Hz), 6.10–7.30 (m, 4H); IR ν_{max}/cm^{-1} 3080, 2945, 2216, 1635, 1490, 1460, 1380, 1300, 695.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

3. m.p. 82–83.5°C (Lit.[9] 84–85°C) ^{1}H NMR (δ_H) 5.40 (d, 1H, J=16.7Hz), 7.25 (d, 1H, J=16.7Hz), 7.30 (s, 4H); IR ν_{max}/cm^{-1} 3080, 2940, 2215, 1635, 1510, 1460, 1315, 960, 800.

4. m.p. 102–104°C (Lit.[9] 105–106°C) ^{1}H NMR (δ_H) 2.97 (s, 6H), 5.54 (d, 1H, J=16.5Hz), 7.25 (d, 1H, J=16.5Hz), 7.30 (m, 4H); IR ν_{max}/cm^{-1} 3090, 2940, 2215, 1640, 1580, 1490, 1430, 1310, 1210, 1080, 970, 670.

5. Oil[10] ^{1}H NMR (δ_H) 5.10 (d, 1H, J=16.2Hz), 7.12 (d, 1H, J=16.2Hz), 6.50–7.75 (m, 3H); IR ν_{max}/cm^{-1} 3120, 2220, 1570, 1460, 1180, 1000, 870, 670.

6. Oil[11] ^{1}H NMR (δ_H) 2.42 (s, 3H), 7.20–8.09 (m, 5H); IR ν_{max}/cm^{-1} 3030, 2940, 2920, 1700, 1580, 1450, 1380, 1350, 1220, 950.

7. m.p. 48–50°C (Lit.[12] 51°C) ^{1}H NMR (δ_H) 5.50(s,3H), 7.15–7.70 (q, 4H), IR ν_{max}/cm^{-1} 3200, 3020, 1690, 1590, 1400, 1370, 1280, 1110, 1070, 1010, 860.

8. m.p. 66-68°C (Lit.[13] 68.5–69°C) ^{1}H NMR (δ_H) 2.95–3.36 (m, 4H), 7.13–7.90 (m, 10H); IR ν_{max}/cm^{-1} 3020, 2920, 1700, 1500, 1450, 1360, 1150, 750.

9. Oil[14] ^{1}H NMR (δ_H) 1.26–2.20 (m, 8H), 2.80–3.20 (m, 1H), 7.25 (s,5H); IR ν_{max}/cm^{-1} 3030, 2970, 2880, 1600, 1510, 1180, 1000, 730, 690.

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