Samarium Diiodide Mediated Coupling of Aroyl Chlorides

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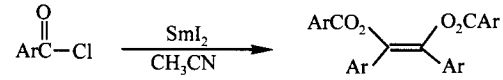
α,α′-Stilbenediol dibenzoate compounds were synthesized in moderate to good yields through the coupling of aroyl chloride promoted by samarium diiodide under mild conditions.

Keywords Samarium diiodide, aroyl chloride, α,α′-stilbenediol dibenzoate compounds

Since pioneering studies by Kagan and co-workers, samarium diiodide has been demonstrated to be a strong one-electron transfer reducing agent with particular efficiency.[1] The utilization of SmI_2 in organic chemistry was dramatically documented.[2] Herein we wish to report a novel one-pot procedure for the coupling of aroyl chlorides to synthesize α,α′-stilbenediol dibenzoate compounds promoted by samarium diiodide. The reaction proceeds efficiently in moderate to good yields at ambient temperature. Literature procedures for the synthesis of α,α′-stilbenediol dibenzoate compounds include reductive coupling of benzoyl chloride with reagents such as sodium amalgam,[3-6] lithium amalgam,[7] tetracarbonyl nickel,[8] zero-valent samarium,[9] pentacarbonyliron,[10] hexaalkylditin,[11] 1,2:5,6-dibenzocyclooctatetraene dianion,[12] mercury cathete[13,14] and highly reactive copper and nickel.[15] However, most of these methods have some disadvantages in relation to their general applicability, selectivity, availability, operational simplicity, or yields. As a result, there is always a considerable interest in finding more convenient methods. Our investigation shows that the reductive coupling of aroyl chlorides with SmI_2 provides a facile procedure for preparing α,α′-stilbenediol dibenzoate compounds.

Scheme 1



1 2

When aroyl chlorides **1** were treated with samarium diiodide in anhydrous acetonitrile for about ten minutes at room temperature, α,α′-stilbenediol dibenzoate compounds **2** were obtained in good yields, with a minor byproducts 1,2-diketones produced (Scheme 1). The results were summarized in Table 1.

Table 1 Reaction of aroyl chlorides with samarium diiodide

Entry	Ar	Time (min)	Yield[a] (%)	*cis*/*trans*[b,c]
a	C_6H_5	10	85	94:6
b	*p*-$CH_3C_6H_4$	10	80	95:5
c	*p*-$CH_3OC_6H_4$	10	79	93:7
d	*p*-Br-C_6H_4	8	70	90:10
e	*p*-Cl-C_6H_4	8	80	95:5
f	2,4,6-$(CH_3)_3C_6H_2$	10	80	95:5

[a] Isolated yields. [b] Pure *cis* isomer was obtained by recrystallization. [c] Ratio of *cis* to *trans* isomers was determined by NMR spectroscopy.

Aliphatic acid chlorides have also been treated with samarium diiodide in acetonitrile for 0.5 h. Unexpectedly, only α-diketones were obtained in moderate yields (Scheme 2). An exception is the case of β-diphenyl acetyl chloride **3**. When **3** was treated with samarium di-

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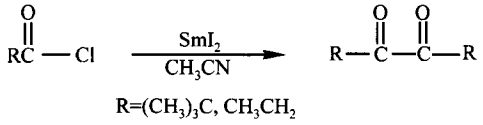
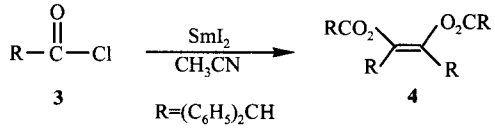
iodide in acetonitrile for 15 min, α-diketone product was not obtained while product **4** was obtained in good yield (yield:84; ratio of *cis*/*trans* = 94/6; Scheme 3).

Scheme 2

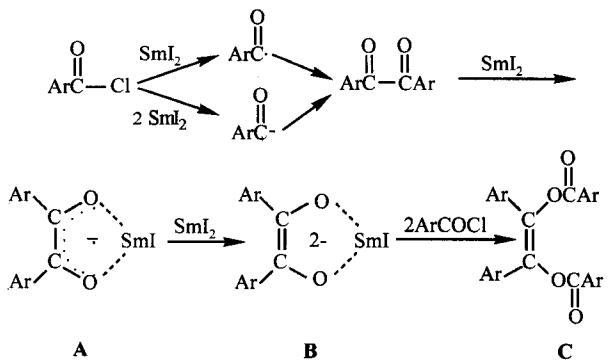


Scheme 3



Although the detailed mechanism of this reaction is not clear at this stage, it is likely that the reaction starts by an electron transfer from samarium diiodide to aryol chloride, the radical anion is thus formed. Then it cleaved into $(ArCO)^{\cdot}$ and Cl^{-}. The radical $ArCO^{\cdot}$ may dimerize into 1,2-diketones or reduce to an acyl anion species, which on acylation gives the corresponding diketones.[16] On treatment with highly reactive SmI_2 in THF, 1,2-diketones are presumably transformed to the stilbenediol radical anion **A**, then **A** is reduced into the dianion **B**. Addition of excess aroyl chloride to the dianion suspension gives the corresponding α,α′-stilbenediol dibenzoate compounds **C**[15] (Scheme 4).

Scheme 4



In conclusion, the present work may provide a useful method for the synthesis of α,α′-stilbenediol dibenzoate compounds. The reaction has the advantages of easy availability of reagents, short reaction time, high stereoselectivity, mild conditions and good yields of products. Thus the method presented here may provide an alternative approach to the existing methods.

Experimental

Acetonitrile was distilled from phosphorus pentaoxide immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Infrared spectra were recorded on a Shimadzu IR-408 spectrometer in KBr with absorption in cm^{-1}. ^1H NMR spectra were determined on a Bruker AC-80 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were measured on an HP 5989B MS spectrometer.

General procedure for the synthesis of compounds **2**

Under nitrogen atmosphere, aroyl chlorides (4 mmol) dissolved in anhydrous acetonitrile (2 mL) was added to a solution of SmI_2 (4.1 mmol) in acetonitrile (25 mL). Then the mixture was stirred at room temperature. After ten minutes, the reaction mixture was quenched with hydrochloric acid (2 mol/L, 2 mL), and extracted with 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 acetate/cyclohexane).

2a m.p. 158—159℃ (Lit.[7] 159℃); IR ν: 3050, 1735, 1590, 1595, 1575, 1480, 1450, 1310, 1270, 1240, 1180, 1090, 1070, 1050, 1026, 770, 710 cm^{-1}; MS (70 eV) *m*/*z* (%): 420 (M^+, 27), 105 (100).

2b m.p. 150—153℃ (Lit.[7] 148—154℃); ^1H NMR δ: 2.28—2.44 (m, 12H), 7.05—8.10 (m, 16H); IR ν: 3030, 2925, 1736, 1590, 1485, 1440, 1420, 1375, 1265, 1240, 1210, 1170, 1125, 1100, 1080, 1050, 1020, 900, 830, 745, 690 cm^{-1}; MS (70 eV) *m*/*z* (%): 476 (M^+, 54), 119 (100), 91 (34).

2c m.p. 185—187℃ (Lit.[7] 187℃); ^1H NMR δ: 3.65—3.74 (m, 12H), 6.65—8.10 (m, 16H); IR ν: 3040, 2995, 1730, 1590, 1485, 1460, 1410, 1375, 1270, 1240, 1180, 1085, 1055, 1015,

830, 776, 700 cm^{-1}; MS (70 eV) *m/z* (%): 540 (M^+, 28), 135 (100), 107 (40), 92 (18).

2d m.p. 210—213℃ (Lit.[7] 214℃); ^1H NMR δ: 7.03—8.10 (m, 16H); IR ν: 3070, 1736, 1590, 1485, 1450, 1270, 1250, 1233, 1170, 1085, 1070, 1055, 1010, 830, 815, 750, 690 cm^{-1}; MS (70 eV) *m/z*(%): 736 (M^+, 10), 184 (100).

2e m.p. 167—169℃ (Lit.[15] 167—168℃); ^1H NMR δ: 7.10—7.97 (m, 16H); IR ν: 3080, 1740, 1590, 1485, 1400, 1270, 1245, 1170, 1080, 1045, 1005, 840, 825, 745 cm^{-1}; MS (70 eV) *m/z* (%): 736 (M^+, 10), 184 (100).

2f m.p. 235—237℃ (Lit.[7] 236—239℃); ^1H NMR δ: 1.85—2.53 (m, 36H), 6.95—7.43 (m, 8H); IR ν: 3040, 2940, 1736, 1605, 1445, 1370, 1235, 1150, 1045, 1040, 855 cm^{-1}; MS (70 eV) *m/z* (%): 588 (M^+, 60), 147 (100), 119 (20).

2,2,5,5-*Tetramethyl*-3,4-*hexanedione* b.p. 75—77℃/400 Pa (Lit.[17] 76—77℃/400 Pa); ^1H NMR δ: 0.89 (s, 18H); IR ν: 1710n cm^{-1}; MS (70 eV) *m/z*(%): 170 (M^+, 5.0), 85 (20.3), 57 (100.0).

3,4-*Hexanedione* b.p. 123℃ (Lit.[18] 123—125℃); ^1H NMR δ: 1.23 (t, J = 7.1 Hz, 6H), 2.53 (t, J = 7.2 Hz, 4H); IR ν: 1720 cm^{-1}.

4 m.p. 123—124℃ (Lit.[7] 125℃); ^1H NMR δ: 5.39 (d, J = 10 Hz, 4H), 7.4 (m, 40H); IR ν: 3060, 3030, 2920, 1710, 1600, 1480, 1450, 1440, 1090, 1070, 1050, 1020, 740, 730, 700 cm^{-1}; MS (70 eV) *m/z*(%): 780 (M^+, 9), 392 (17), 167 (100).

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