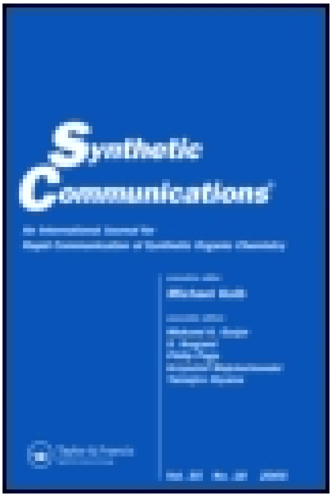

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Samarium Diiodide-Induced Reduction of Elemental Selenium Leading to a Selenolate Anion Species. A Selective Synthesis of Diacyl Diselenides

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SAMARIUM DIIODIDE-INDUCED REDUCTION OF ELEMENTAL SELENIUM LEADING TO A SELENOLATE ANION SPECIES. A SELECTIVE SYNTHESIS OF DIACYL DISELENIDES

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ABSTRACT: Elemental selenium was reduced by samarium diiodide in THF to produce selenolate anion species which reacted with acyl chlorides to give diacyl diselenides in good yields under mild and neutral conditions.

Samarium diiodide is a strong one-electron transfer reducing reagent and much attention has recently been paid to its utilization in organic synthesis[1]. We have previously reported some deoxygenation and reduction of organic substrates with SmI_2 and aldol-

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like reaction between a-haloketone and aldehydes mediated by SmI_2[2,3]. To our knowledge, most conventional methods for the preparation of diacyl diselenides made use of unstable and toxic reagents or alkali metal salts[4]. Here we wish to report that SmI_2 reduces elemental selenium to Se_2^{2-} species which reacts with acyl chlorides to give diacyl diselenides in good yields under mild and neutral conditions.

Samarium diiodide reduces amorphous selenium to Se_2^{2-} species with an excellent selectivity in THF[5]. We found that addition of amorphous selenium to a deep blue solution of SmI_2 in THF resulted in a rapid change of colour of the solution to brown, indicating that the amorphous selenium had been reduced by SmI_2. On the other hand, it was very difficult to reduce metallic selenium to Se_2^{2-} species with SmI_2; the THF solution was still deep blue after the mixture of metallic selenium and the solution of SmI_2 in THF was stirred for 12h, showing that the rate of reduction of metallic selenium by SmI_2 was very slow. The acylation of Se_2^{2-} species with acyl chlorides at room temperature in the presence of HMPA gave the exclusive diacyl diselenides in good yields. The advantages of the reaction are excellent selectivity, mild and neutral conditions, and simple operation. The reaction is shown in Scheme and the results are summarized in Table 1.

Scheme

$$\mathrm{Se} + \mathrm{SmI_2} \xrightarrow[\mathrm{THF}]{} \mathrm{Se_2}^{2-} \xrightarrow[\mathrm{HMPA}]{\mathrm{RCOCl}} \mathrm{RCOSe{-}SeCOR}$$

(a): $R=C_6H_5$
(b): $R=4\text{-}MeC_6H_4$
(c): $R=3\text{-}ClC_6H_4$
(d): $R=4\text{-}ClC_6H_4$
(e): $R=4\text{-}BrC_6H_4$
(f): $R=2\text{-}BrC_6H_4$
(g): $R=4\text{-}MeOC_6H_4$
(h): $R=CH_3(CH_2)_{10}$

Experimental

Mps were uncorrected. IR spectra were recorded with a PE-683 spectrometer. NMR spectra were recorded with a PMX-60 spectrometer, using TMS as internal standard.

General procedure:

The amorphous selenium(2mmol) was added to a stirred deep blue solution of SmI_2(2.2mmol) in THF(22ml) at room temperature under nitrogen. After 2-3minutes, the deep blue colour of the solution disappeared and the solution became brown. The resulting solution was stirred at room temperature under nitrogen for 0.5h. The HMPA(1ml) and acyl chloride(3mmol) in THF(2ml) were then added successively to the solution with syringe, and the mixture was stirred at room temperature under nitrogen for 5h. Then the reaction mixture was

Table 1. Physical properties of Diacyl Diselenides[a]

Entry	mp(lit.) °C[c]	Yield %[b]	IR(KBr) (cm^{-1})	^1H NMR($CDCl_3$), δ
(a)	130-131 (131-132)	87	1735 1680	7.40-8.02(10H,m)
(b)	109-110 (110-111.5)	86	1755 1710	2.40(6H, s) 7.18-7.94(8H, q, J=4.2Hz)
(c)	98-99	83	1722 1684	7.20-7.94(8H,m)
(d)	121-122 (122-124)	85	1730 1690	7.34-7.95(8H, q, J=4.5Hz)
(e)	152-153 (150-151)	82	1736 1702	7.56-7.97(8H, q, J=5.1Hz)
(f)	97-98 (94-95)	76	1737 1696	7.20-7.82(8H,m)
(g)	105-106 (106-107)	91	1721 1703	3.87(6H, s) 6.87-8.17(8H, q, J=4.8Hz)
(h)	60-61 (62-63)	94	1726	0.87(6H, t) 1.17-1.80(36H,m) 2.80(4H, t)

a. All products gave satisfactory elemental analyses;

b. Isolated yields; c. Ref. 4;

diluted with ether(40ml) and filtered. The ethereal solution was washed with water(40ml×3), dried over $MgSO_4$, and the solvent was removed by evaporation under reduced pressure. The crude product was purified by recrystallization from cyclohexane. The product was identified by elemental analysis, IR and NMR.

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