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Note

$CeCl_3$/Sm System Induced Reductive Cleavage of the Se-Se Bond in Diaryl Diselenides: A Novel Method for the Synthesis of β-Selenoesters and β-Selenonitriles

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The Se-Se bond in diselenides was reduced by $CeCl_3$/Sm system to produce selenolate anions, which react with α,β-unsaturated esters or α,β-unsaturated nitriles to afford β-selenoesters and β-selenonitriles, respectively.

INTRODUCTION

Organoselenium compounds have received considerable attention as useful synthetic reagents and intermediates in organic synthesis.[1-3] β-selenoesters are useful intermediates in the synthesis of natural compounds.[4] Some methods for the preparation of β-selenoesters and β-selenonitriles have been published. A useful approach is the Michael reaction of seleno anion with α,β-unsaturated esters or nitriles. For example, selenols react with α,β-unsaturated esters or nitriles.[5] Diaryl diselenides react with α,β-unsaturated esters or nitriles using $NaBH_4$ [6] or SmI_2 [7] as reductant, or with carbon monoxide and water using selenium under high pressure and high temperature.[8]

Cerium chloride is a very cheap, nontoxic and water-tolerant reagent.[9] This trivalent lanthanide salt has been found very useful in organic synthesis.[10] For example, Cerium trichloride reacted with organic lithium such as CH_3Li,[11] n-BuLi[12] to form an organic cerium reagent which can be used as a selective magnesium reagent. Due to its excellent stereoselectivity, the reductive system of $NaBH_4$-$CeCl_3$[13] has been widely used in organic total synthesis.

Because of the great potentials of samarium reagents in organic synthesis, much attention has been focused on the reductive reactions induced by them.[14] $TiCl_4$/Sm,[15] $ZrCl_4$/Sm,[16] $HgCl_2$/Sm[17] and $CoCl_2$/Sm[18] have been found useful reductants in organic synthesis. But to the best of our knowledge, there has been no report on the $CeCl_3$/Sm applied in organic synthesis. In view of the importance of organoselenium compounds, especially β-selenoesters and β-selenonitriles in organic synthesis mentioned above, we chose the cleavage of the Se-Se bond to evaluate the reductive ability of $CeCl_3$/Sm and find a new preparation procedure of β-selenoesters and β-selenonitriles.

Herein we wish to report a new reagent $CeCl_3$/Sm to reductive cleavage of Se-Se bond to produce selenolate anions, which react with α,β-unsaturated esters or nitriles in situ to afford β-selenoesters and β-selenonitriles, respectively.

EXPERIMENTAL SECTION

Melting points were uncorrected. IR spectra were obtained on a PE-683 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a PMX-60MHz instrument. All ^{1}H NMR samples were measured in CCl_4 using TMS as internal standard. The solvent THF was freshly distilled from sodium/benzophenone ketyl prior to use. The reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere.

GENERAL PROCEDURE

Under nitrogen atmosphere, metallic samarium powder (3 mmol), cerium(III) chloride (1 mmol) and diselenide (0.5 mmol) were placed in a three-necked reaction flask and THF (10 mL) was added in one portion. The resulting mixture was magnetically stirred at 40 °C for 4 h. Samarium powder almost completely disappeared, and the cleavage of the Se-Se bond was indicated by the dissipation of the yellow mixture due to diselenide. To the mixture was added successively α,β-unsaturated esters (1.5 mmol) or α,β-unsaturated nitriles (1.5 mmol) in THF (2 mL) and t-butyl alcohol (0.1 mL in order to prevent polymerization) and stirred for given times (see Table 1, TLC as monitored). When the reaction was finished, dilute HCl (0.1 M, 10 mL) was added to quench the reaction and the mixture was extracted with ether (15 mL × 2); after the extracts were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure, the residue was then purified by preparative TLC on Silica gel with light petroleum and ethyl ether (5:1) as eluent.

Scheme I

$$\text{ArSeSeAr} \xrightarrow[\text{40 °C 4 h}]{\text{CeCl}_3\text{/Sm}} [\,\text{ArSe}^-\,] \xrightarrow[\text{R. T. 4 h}]{\text{CH}_2\text{=C(R)X}} \text{ArSeCH}_2\text{CH(R)X}$$

In summary, a novel method for the preparation of β-selenoesters has been provided, the advantages of which are easily available and cheap materials, single product, simple manipulation, and mild and neutral conditions.

DATA OF THE PRODUCTS

1[7] $PhSeCH_2CH_2CO_2Me$, Oil; IR ν_{max} (cm^{-1}) 3090, 3080, 3020, 2960, 2940, 2860, 1750, 1590, 1480, 1445, 1350, 1290, 1220, 1170, 1070, 1020, 1000, 957, 740, 685, 660; ^{1}H NMR 7.10-7.60 (5H, m), 3.53 (3H, s), 2.90 (2H, t), 2.66 (2H, t).

2[7] $PhSeCH_2CH_2CO_2Et$, Oil; IR ν_{max} (cm^{-1}) 3095, 3080, 2990, 2940, 2920, 2890, 2880, 1750, 1590, 1485, 1440, 1380, 1350, 1220, 1170, 1020, 740, 685, 660; ^{1}H NMR 7.07-7.70 (5H, m), 4.00 (2H, q), 2.97 (2H, t), 2.63 (2H, t), 1.67 (3H, t).

3[7] $PhSeCH_2CH_2CO_2Bu$-n, Oil; IR ν_{max} (cm^{-1}) 3100, 3080, 2990, 2940, 2920, 2880, 1750, 1600, 1485, 1440, 1380, 1350, 1220, 1170, 1020, 740, 680, 660; ^{1}H NMR 7.03-7.60 (5H, m), 3.97 (2H, t), 2.97 (2H, t), 2.60 (2H, t), 1.20-1.60 (4H, m), 0.90 (3H, t).

4[7] $PhSeCH_2CH_2CN$, Oil; IR ν_{max} (cm^{-1}) 3100, 3080, 2990-2940, 2875, 2260, 1590, 1485, 1445, 1420, 1310, 1270, 1200, 1070, 1020, 1000, 935, 890, 740, 690, 660; ^{1}H NMR 7.06-7.60 (5H, m), 2.93 (2H, t), 2.53 (2H, t).

5[7] $PhSeCH_2CH(CH_3)CO_2Me$, Oil; IR ν_{max} (cm^{-1}) 3090, 3080, 2990, 2960, 2940, 1740, 1590, 1485, 1460, 1440, 1380, 1350, 1200, 1160, 1020, 1000, 900, 820, 740, 690, 670; ^{1}H NMR 7.03-7.60 (5H, m), 3.50 (3H, s), 3.00 (2H, d), 2.50-2.80 (1H, m), 1.15 (3H, d).

6[19] o-$MeC_6H_4SeCH_2CH_2CO_2Me$, Oil; IR ν_{max} (cm^{-1}) 3100, 3080, 3020, 2980, 2960, 2940, 2885, 2800, 1739, 1600, 1580, 1480, 1440, 1380, 1350, 1280, 1225, 1200, 1170, 1130, 1040, 1010, 980, 890, 840, 740, 650; ^{1}H NMR 7.10-7.60 (4H, m), 3.53 (3H, s), 2.93 (2H, t), 2.57 (2H, t), 2.33 (3H, s).

7[19] o-$MeC_6H_4SeCH_2CH_2CO_2Et$, Oil; IR ν_{max} (cm^{-1}) 3100, 3080, 3020, 2990, 2980, 2950, 2885, 1736, 1600, 1580, 1475, 1460, 1380, 1350, 1220, 1200, 1035, 860, 830, 740, 650, 610; ^{1}H NMR 6.93-7.43 (4H, m), 4.00 (2H, q), 2.93 (2H, t), 2.56 (2H, t), 2.33 (3H, s), 1.16 (3H, t).

8[19] o-$MeC_6H_4SeCH_2CH_2CO_2Bu$-n, Oil; IR ν_{max} (cm^{-1}) 3100, 3080, 3020, 2980, 2960, 2940, 2880, 1734, 1600, 1475, 1460, 1420, 1380, 1350, 1275, 1220, 1200, 1170, 1060, 1035, 980, 960, 940, 740, 650; ^{1}H NMR 6.96-7.50 (4H, m), 3.93 (2H, t), 2.93 (2H, t), 2.56 (2H, t), 2.33 (3H, s), 1.30-1.60 (4H, m), 1.00 (3H, t).

9[19] o-$MeC_6H_4SeCH_2CH_2CN$, Oil; IR ν_{max} (cm^{-1}) 3100, 3080, 3020, 2990, 2960-2940, 2890, 2880, 2249, 1600, 1580, 1470, 1460, 1420, 1380, 1350, 1275, 1220, 1200, 1170, 1060, 1035, 980, 960, 940, 740; ^{1}H NMR 6.93-7.40 (4H, m), 2.87 (2H, t), 2.47 (2H, t), 2.33 (3H, s).

10[19] o-$MeC_6H_4SeCH_2CH(CH_3)CO_2Me$, Oil; IR ν_{max} (cm^{-1}) 3090, 3080, 3020, 2990, 2960, 2890, 1734, 1590, 1580, 1485, 1440, 1380, 1350, 1270, 1200, 1020, 1000, 900, 820, 740, 690, 660; ^{1}H NMR 6.93-7.40 (4H, m), 3.50 (3H, s), 2.97 (2H, d), 2.50-2.80 (1H, m), 2.33 (3H, s), 1.15 (3H, d).

Table 1. Synthesis of the β-Selenoesters and β-Selenonitriles

Entry	Ar	R	X	Reaction Time/h	Yield[a] (%)
1	Ph	H	CO_2Me	4	73
2	Ph	H	CO_2Et	4	78
3	Ph	H	CO_2Bu-n	4	84
4	Ph	H	CN	4	72
5	Ph	CH_3	CO_2Me	4	51
6	o-$CH_3C_6H_4$	H	CO_2Me	4	78
7	o-$CH_3C_6H_4$	H	CO_2Et	4	81
8	o-$CH_3C_6H_4$	H	CO_2Bu-n	4	76
9	o-$CH_3C_6H_4$	H	CN	4	70
10	o-$CH_3C_6H_4$	CH_3	CO_2Me	4	53

[a] Isolated yields based on diselenides.

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Key Words

Arylseleno esters; Arylseleno nitriles; Samarium; Cerium(III) chloride.

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