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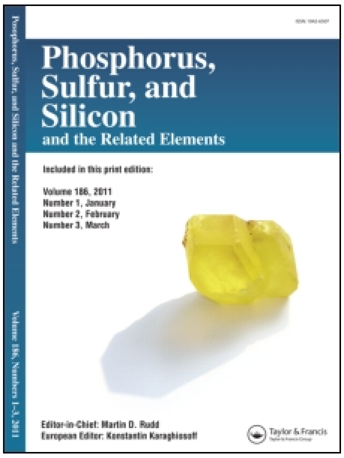

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Carbonylation of Lithium Enolates of Esters and Amides with Carbon Monoxide and Selenium

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Lithium enolates of esters, amides, and an acylsilane undergo carbonylation with carbon monoxide with the aid of selenium under mild conditions to yield the corresponding selenol esters after trapping with alkyl iodides.

Keywords Amide; carbon monoxide; carbonylation; ester; lithium enolate; selenium

INTRODUCTION

We recently disclosed novel carbonylation of lithium enolates of ketones and aldehydes with CO mediated by selenium giving rise to 1,3-dioxoalkanes.[1–3] We also proposed that this reaction proceeds via a unique carbonylation mechanism comprised of *O*-carbonylation and subsequent migration of the SeCO moiety to the α-carbon. This successful result lead us to examine carbonylation of other carbonyl compounds. Here we describe carbonylation of lithium enolates of esters, amides, and an acylsilane with CO and selenium Scheme 1.

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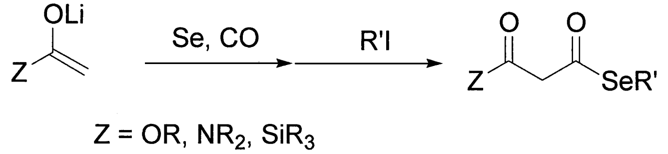

SCHEME 1

RESULTS AND DISCUSSION

At first, carbonylation of lithium enolates of esters was examined by using similar reaction conditions as in the cases of carbonylation of lithium enolates of ketones. Ethyl isobutylate (**1a**, 2.0 mmol) was added at −78°C under Ar to a deep red solution obtained by mixing Se (2.4 mmol) and LDA (2.4 mmol) in THF. Then Ar was replaced with CO (1 atm) and the solution was warmed up to 20°C. After stirring for 14 h, MeI (4 mmol) was added. The usual workup gave the expected selenol ester **2a** in 82% yield (Table I, run 1). When the reaction time was shortened to 3 h, **2a′** was obtained in 27% yield after trapping with BuI together with 37% of the corresponding α-selenoester **3a′** (run 2) (Scheme 2).

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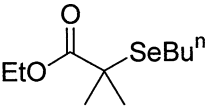
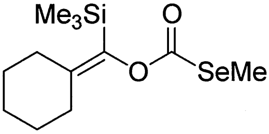


3a'

SCHEME 2

The results obtained using several other lithium enolates of esters are given in Table I. Methyl cyclohexanecarboxylate (**1b**) and ethyl 2-methyl-4-pentenoate (**1c**) also can be carbonylated to give the expected product **2b** and **2c** in high yields (runs 3 and 4). 2-Carboethoxy-1,3-dithian (**1d**) did not afford the desired product **2d** at 20°C; however, **2d** was obtained in 38% when carbonylation was performed at −23°C (run 5). Thiolester **1e** underwent carbonylation efficiently within 2 h giving **2e** in 83% (run 6). In contrast, selenolester **1f** gave **2f** only in 23% yield due probably to fragmentation of lithium enolate of **1f** (run 7).

We then investigated carbonylation of amides and an acylsilane and the results are added in Table I. *N*-Methyl-*N*-phenylisobutylamide (**1g**) and *N*,*N*-diphenylisobutylamide (**1h**) afforded the desired products under the same conditions. The yields are moderate; however, product selectivities are high (runs 8 and 9). Acylsilane **1i** also can be carbonylated to give 31% of **2i** along with 8% of *O*-carbonylation product **4i** (run 10) (Scheme 3).



4i

SCHEME 3

The fact that *O*-carbonylation product **4i** was obtained would suggest that the present reaction seems to proceed via a similar mechanism as in the case of carbonylation of ketones and aldehydes as shown in Scheme 4. Thus, enolates **5** react with Se to afford selenolates **6**, which then react with CO to give lithium selenocarbonates **8** as an initial carbonylation intermediate via **7**. Then **8** undergoes [1,3]-rearrangement rapidly to lithium selenocarboxylates **9** giving the corresponding selenol esters **2**. In the case of an enolate of an acylsilane, **8** (Scheme 4) was trapped with MeI yielding *O*-carbonylation product.

In summary, the present study coupled with the former study revealed that carbonylation of lithium enolates of a variety of carbonyl compounds with CO proceeded under mild conditions with the aid of selenium.

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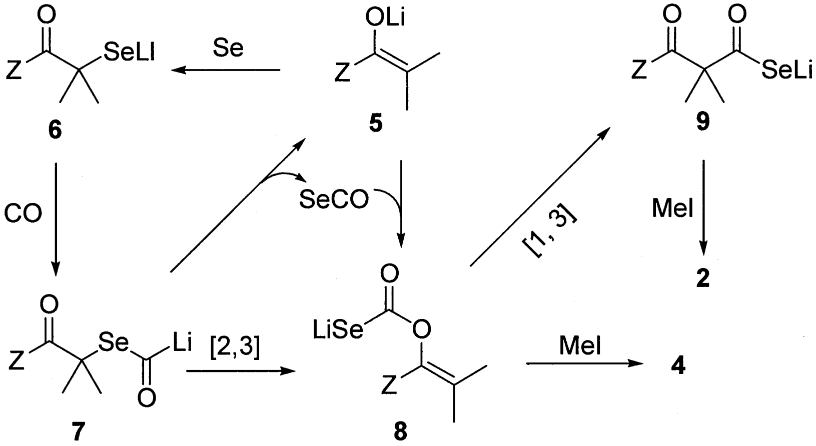

SCHEME 4 Possible reaction pathways.

EXPERIMENTAL

Typical Experimental Procedure

Selenium (2.4 mmol) was added to a THF (15 mL) solution of LDA, prepared from BuLi (1.60 M in hexane, 1.5 mL, 2.4 mmol) and diisopropylamine (2.6 mmol), at −78°C under argon. After stirring for 5 min, dry

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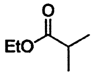
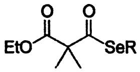
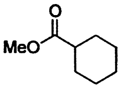
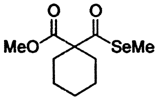
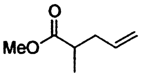
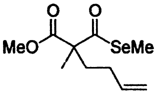
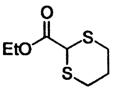
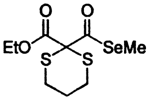
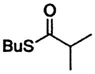
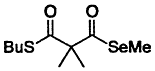
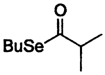
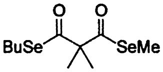
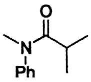
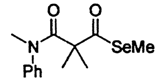
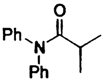
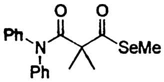
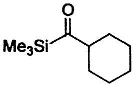
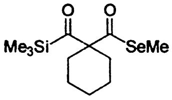
TABLE I Carbonylation of Lithium Enolates of Esters, Amides, and an Acylsilane[a]

Run	Substrate	Time (h)	Product	yield, %[b]
1	 **1a**	14		**2a**, 82 (R = Me)
2		3		**2a′**,27 (R = ^{n}Bu)
3	 **1b**	20		**2b**, 75
4	 **1c**	20		**2c**, 86
5	 **1d**	1		**2d**, 38
6	 **1e**	2		**2e**, 83
7	 **1f**	2		**2f**, 23
8	 **1g**	5		**2g**, 51 (75)[d]
9	 **1h**	6		**2h**, 62 (94)[d]
10	 **1i**	0.5		**2i**, 31[e]

[a] Conditions: substrate (2.0 mmol), LDA (2.4 mmol), Se (2.4 mmol), THF (25 mL), −78°C, 30 min, then 20°C, 30–60 min, CO (1 atm), 20°C, time shown in the table: Me$^{\mathrm{I}}$ (4.0 mmol), 20°C, 10 min.

[b] Isolated yield.

[c] Carbonylation was carried out at −23°C.

[d] Yield parentheses is based on reacted amide.

[e] *O*-Carbonylation product **4i** (8%) was also obtained.

ice-EtOH bath was removed. A red solution was obtained within 10 min and the solution was cooled again to −78°C. To the solution was added dropwise ethyl isobutylate (**1a**, 2.0 mmol) in THF (10 mL) over 10 min, and the stirring was continued for additional 20 min. Argon was evacuated and the reaction vessel was filled with CO. The reaction mixture was then warmed to 20°C. After 14 h, MeI (4.0 mmol) was added. Aqueous saturated NH_4Cl solution (100 mL) was added and the product was extracted with Et_2O (50 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to give a yellow residue. Purification by column chromathography using silica gel eluted with Et_2O yielded 389 mg (82%) of **2a** as a pale yellow oil.

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