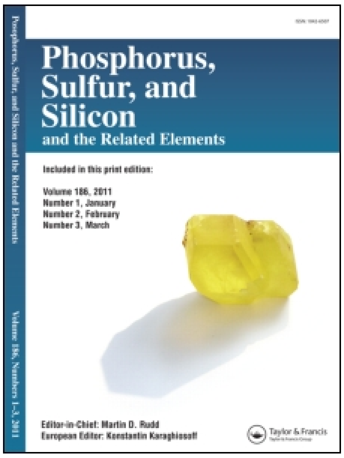

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Silicon-Mediated Synthesis of Selenoaldehydes and Selenoacylsilanes and Their Hetero Diels-Alder Reactions

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Silicon-Mediated Synthesis of Selenoaldehydes and Selenoacylsilanes and Their Hetero Diels–Alder Reactions

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Bis(trimethylsilyl)selenide (HMDSS) reacts efficiently with aldehydes in the presence of $CoCl_2 6H_2O$ *to afford selenoaldehydes, which are trapped as Diels–Alder adducts by different dienes. The reaction can be applied to acylsilanes, to afford selenoacylsilanes, isolated as their cycloadducts.*

Keywords Diels–Alder cycloadditions; selenoacylsilanes; selenoaldehydes; selenoheterocycles; silyl-selenide

INTRODUCTION

Selenium-containing heterocycles represent a very interesting class of compounds due to their useful reactivity in organic synthesis and their potential biological applications.[1] A convenient route to access heteroatom-containing molecules can be envisioned in hetero Diels–Alder reactions,[2] and selenocarbonyl compounds are in fact recognized as very reactive intermediates for the introduction of selenium into organic molecules, being able to act as powerful 2π dienophiles in cycloaddition reactions, and so providing a useful and convenient approach to different functionalized heterocycles.[3] Despite this interest, a limited number of synthetic methodologies for their preparation have been reported, mainly due to the instability of the desired selenocarbonyl derivatives under the preparative conditions.[4]

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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Several synthetic methods describe the generation of selenoaldehydes through base-catalyzed elimination reactions from α-silyl selenocyanates[5] or selenenyl derivatives[6] by heating alkylidene phosphoranes with elemental selenium[7] or through the reaction of ArLi with selenoformates.[8] Direct conversion of carbonyl compounds to selenocarbonyls is probably the more convenient way to approach these derivatives, and several methods have been reported based on the use of bis(diboryl)selenide,[9] bis(trimethylsilyl)selenide under BuLi[10] or Lewis acid catalysis,[11] and bis(dimethylaluminum)selenide.[12] Selenoaldehydes can also be generated through retro Diels–Alder reactions under different conditions.[13]

RESULTS AND DISCUSSION

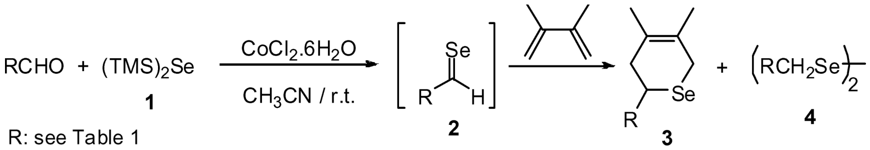
Our longtime interest in the development of organosilicon-based procedures for the synthesis of sulphur-containing compounds led us recently to uncover a simple and general access to thiocarbonyl derivatives, such as thioaldehydes, thioketones, and thioacylsilanes through our hexamethyldisilathiane (HMDST)-based thionation procedure of carbonyl compounds, which proved mild enough for the synthesis of such derivatives.[14]

Thus, due to the relevance that selenium containing molecules have gained in recent years, both from the synthetic and biological side, we were attracted by the possibility of developing a smooth, mild access to another class of compounds such as selenocarbonyl derivatives, that due to their high reactivity often show difficulties in preparation. Thus, taking advantage of the high degree of versatility shown by HMDST in the delivery of sulfur functionalities, we reasoned that a possible approach to selenoaldehydes could be found through the direct treatment of aldehydes with another silyl chalchogenide, namely bis(trimethylsilyl)selenide (hexamethyldisilaselenane, HMDSS), under suitable catalytic conditions.

Thus aldehydes were reacted with HMDSS **1** under inert atmosphere at room temperature, in the presence of $CoCl_2 6H_2O$ and 2,3-dimethyl-1,3-butadiene as trapping agent.

The reaction proved efficient in generating the selenoaldehyde **2**, as shown by the isolation of the corresponding Diels–Alder cycloadduct **3** (Scheme 1), albeit in not satisfactory yield, due to the formation of appreciable amounts of the reduction product, the diselenide **4**, together with minor amounts of the trimer.

As already reported, this result outlines that HMDSS shows a remarkable reducing activity towards selenocarbonyl compounds also under the present conditions.[9,11]



SCHEME 1

With the aim to minimize polymerization and/or further reduction of the in situ generated selenoaldehyde, $(TMS)_2Se$ was added portionwise to the reaction mixture, thus leading to a remarkable increase of the yield. Portionwise addition of HMDSS favours the slow generation of selenoaldehydes, so preventing their accumulation with consequent efficient in situ trapping by the diene, and minimizing trimerization or reduction processes.[15]

Thus, on performing the reaction in the presence of 2,3-dimethyl-1,3-butadiene, a variety of 2-substituted 4,5-dimethyl-3,6-dihydro-*2H*-selenopyrans **3** were obtained starting from a representative range of selenoaldehydes. Aromatic, heteroaromatic, and aliphatic aldehydes can be efficiently converted into their corresponding seleno derivatives (Table I), making bis(trimethylsilyl)selenide a useful reagent under $CoCl_26H_2O$ catalysis. However, the cycloadducts **3** were labile toward exposure to air, and caused partial decomposition during purification on silica gel.

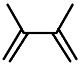
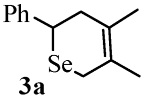
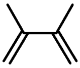
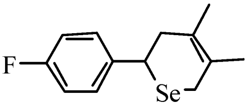
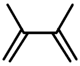
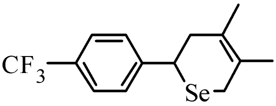
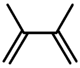
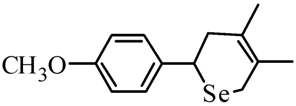
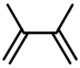
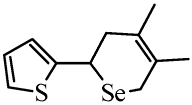
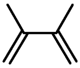
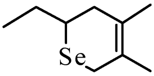
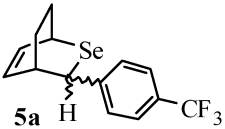
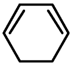
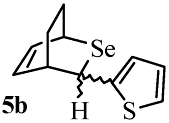
Differently from what was observed by Segi and et al.,[12] in the present conditions, the α, β-unsaturated thiophene-2-selenoaldehyde did not undergo [4+2] dimerization, no trace of the corresponding head-to-head (or head-to-tail) dimer ever being evidenced.

An interesting aspect is the stereochemical control of the Diels–Alder cycloaddition when 1,3-cyclohexadiene was used as a trapping agent. The reaction of selenoaldehydes occurs with preference for the formation of the *endo* adduct (*endo:exo* 95:5), according to what was previously reported by other authors.[5,10]

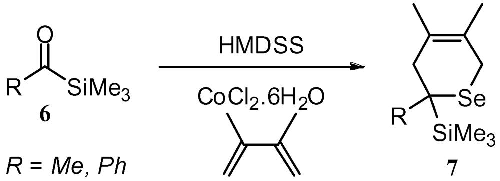
The versatility of the present methodology is further testified by its application to more reactive species, such as silylketones. Thus, when acylsilanes **6** were treated with HMDSS and $CoCl_26H_2O$, this time the formation of the desired selenoacylsilane was evidenced by the isolation of the 2-silyl-dihydroselenopyran **7** (Scheme 2), formed through cycloaddition with the diene, thus disclosing a novel access to this unreported class of silylated seleno heterocycles, whose reactivity is currently being investigated in our laboratory.

In conclusion, we have presented an alternative procedure to access selenoaldehydes that occurs under rather mild conditions, so that it can

TABLE I Synthesis of Selenoaldehydes and Their Trapping by a Diene

Entry	R	Diene	Adduct	Yield %[a,b,c]
1	Ph		 **3a**	45 (64)
2	p–F–C_6H_4		 **3b**	51 (70)
3	p–CF_3–C_6H_4		 **3c**	53 (71)
4	p–CH_3O–C_6H_4		 **3d**	41 (56)
5			 **3e**	54 (72)
6	CH_3CH_2		 **3f**	38 (51)
7	p–CF_3–C_6H_4		 **5a**	50 (70)[d]
8			 **5b**	57 (74)[d]

[a] Isolated products. In parenthesis is reported the yield before purification.
[b] All compounds showed spectroscopical data consistent with the assigned structure.
[c] Diselenides **4** were detected (10–20%).
[d] Endo:exo 95:5.



SCHEME 2

be efficiently applied even to the synthesis of more reactive molecules such as selenoacylsilanes.

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[15] *Typical procedure*: A CH_3CN solution (1 mL) of thiophene-2-carbaldehyde (50 mg, 0.45 mmol), 2,3-dimethyl-1,3-butadiene (184 mg, 2.25 mmol), and HMDSS (20 mg, 0.09 mmol) was treated under inert atmosphere at room temperature with $CoCl_2 \cdot 6H_2O$ (107 mg, 0.45 mmol) dissolved in 1.5 mL of CH_3CN. The mixture was added portionwise every 30 min with 20 mg of HMDSS, and the progress of the reaction was monitored by TLC (petroleum ether/diethyl ether 3:1). After the addition of 1 equiv. of HMDSS, the mixture was stirred overnight. After quenching with water, the product was extracted with diethyl ether and washed with water and brine. The resulting organic phase was then filtered to remove the dark precipitate and dried over Na_2SO_4. Evaporation of the solvent under vacuum gave 83 mg of crude 4,5-dimethyl-2-thienyl-3,6-dihydro-*2H*-selenopyran **3e**. Chromatographic purification (petroleum ether/diethyl ether 3:1) afforded 63 mg (54%) of **3e.** ^1H NMR (200 MHz, $CDCl_3$), δ (ppm): 1.75 (3H, s), 1.83 (3H, s), 2.68 (2H, bd, $J = 6$ Hz), 3.09 (1H, d, $J = 15$ Hz), 3.25 (1H, d, $J = 15$ Hz), 4.55 (1H, t, $J = 6$ Hz), 6.90–6.93 (3H, m). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ (ppm): 18.6, 19.0, 33.2, 34.1, 41.9, 119.8, 121.64, 122.2, 125.2, 126.1, 128.3. MS, *m/z* (I_{rel}, %): 258 (19) $[M]^+$, 176 (100), 143 (26), 97 (53), 77 (39), 65 (69). The reaction performed with cyclohexadiene afforded 2-(2-selena-bicyclo[2.2.2]oct-5-en-3-yl)thiophene **5b** (57%) (*endo:exo* 95:5). *Endo*-**5b**: ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.45–1.59 (1H, m), 1.71–1.92 (2H, m), 2.14–2.22 (1H, m), 3.02–3.06 (1H, m), 3.73–3.76 (1H, m), 5.02 (1H, d, J = 3.2 Hz), 6.28 (1H, ap t), 6.45 (1H, ap t), 6.81–6.86 (2H, m), 7.05 (1H, dd, J = 5.3, 1.5 Hz). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ (ppm): 25.4, 29.2, 38.1, 42.5, 46.1, 124.2, 124.5, 126.1, 126.6, 129.8, 136.8. MS, *m/z* (I_{rel}, %): 256 (10) $[M]^+$, 176 (50), 97 (100), 97 (53), 79 (57).