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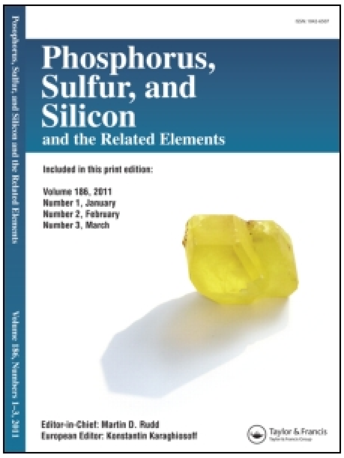

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Generation of Selenoaldehydes via Retro Diels-Alder Reaction and Their Behavior in the Reaction with Some Enophiles

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Generation of Selenoaldehydes via Retro Diels–Alder Reaction and Their Behavior in the Reaction with Some Enophiles

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The [4 + 2] cycloadducts of selenoaldehydes and anthracene regenerate selenoaldehydes in situ *quantitatively under neutral conditions via thermal retro Diels–Alder reaction. The reactions of selenoaldehydes generated by this method with 2-silyloxy-1,3-butadiene, 2-methoxyfuran, and 5-ethoxyoxazoles are described.*

Keywords 3-Selenazoline; penta-2,4-dienoate; retro Diels–Alder reaction; selenoaldehyde; selenacyclohexanone

INTRODUCTION

In recent decades, there has been a growing interest in organoselenium chemistry.[1–3] Some of the compounds bearing a carbon-selenium double bond, a so-called selenocarbonyl group, have been paid attention as building blocks in organic synthesis and as important intermediates in the synthesis of selenium-containing heterocycles.[4–6] Among them selenoaldehydes generally have been considered to be a highly reactive dienophile for cycloaddition reactions. Several synthetic methods of these reactive selenoaldehydes have already been reported.[7–9] We have also described an efficient method for the straightforward synthesis of selenoaldehydes and their *in situ* trapping by a conjugated diene.[10–12] The synthetic procedure involves the reaction of aldehydes with bis(dimethylaluminum) selenide, $(Me_2Al)_2Se$, in which aluminum plays a key role to replace the carbonyl oxygen with a selenium atom.

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However, the cycloaddition by this method was inapplicable to 1,3-dienes substituted by oxygen and/or nitrogen atoms because of the coordination of the aluminum to a lone pair of electrons on those atoms. So, another protocol for selenoaldehyde synthesis was required in order to attain the cycloaddition reaction with a heteroaom-functionalized 1,3-diene. We selected retro Diels–Alder reaction for generation of selenoaldehydes. In this paper we describe the formation of selenoaldehydes under neutral conditions via thermal retro Diels–Alder reaction and their reaction behavior with some heteroatom-substituted enophiles.

RESULTS AND DISCUSSION

The reaction of aromatic and aliphatic aldehydes with $(Me_2Al)_2Se$ in the presence of anthracene gave the [4+2] cycloadducts (**1**) of the corresponding selenoaldehydes and anthracene in good yields as a stable solid in the most cases. These cycloadducts were very stable at room temperature after purification by column chromatography on silica gel. The results are summarized in Table I. Heating of a toluene solution of **1** (R = aromatic) and 2,3-dimethyl-1,3-butadiene at 100°C for 30 min gave the cycloadducts of the corresponding selenoaldehydes and 2,3-dimethyl-1,3-butadiene in excellent yields. This indicates the thermal retro Diels–Alder reaction of **1** proceeds efficiently under the above conditions to regenerate selenoaldehydes quantitatively. Cycloadducts **1** with an aliphatic substituent were very stable at 100°C in toluene,

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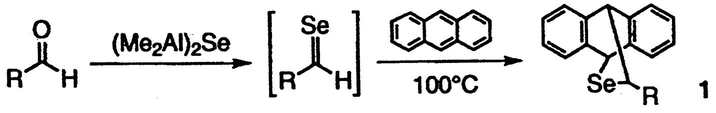
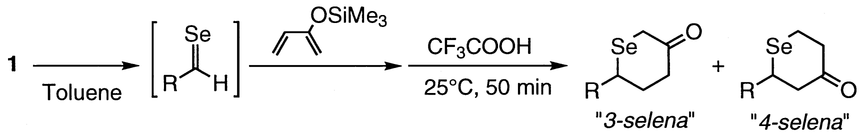
TABLE I [4 + 2] Cycloaddition of Selenoaldehydes with Anthracene



R	Time (h)	Yield (%)[a]	M.p. (°C)
Ph	4.0	85	134–135
p-$MeOC_6H_4$	4.0	66	120–121
p-$CF_3C_6H_4$	4.0	96	142–143
p-$MeSC_6H_4$	4.0	73	144-145
p-NCC_6H_4	4.0	90	157–158
p-FC_6H_4	4.0	91	116–117
n-Pr	6.0	60	106–108
$PhCH_2CH_2$	6.0	40	140–142

[a] Isolated yield.

TABLE II Reaction of Selenoaldehydes with 2-Trimethylsilyloxy-1,3-butadiene



R	Temp. (°C)	Time (h)	Total yield (%)[a]	"*3-selena*" : "*4-selena*"[b]
p-NCC_6H_4	110	5.0	89	59:41
p-$CF_3C_6H_4$	110	5.0	83	51:49
p-$CF_3C_6H_4$	160	3.0	93	50:50
p-FC_6H_4	110	5.0	88	42:58
p-$MeSC_6H_4$	110	5.0	89	42:58
Ph	110	5.0	87	40:60
p-$MeOC_6H_4$	110	4.0	80	36:64
n-Pr	160	5.0	85	23:77

[a] Isolated yield.
[b] Determined by ^{1}H NMR.

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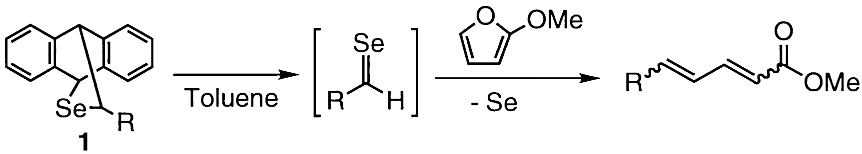
but the heating at 160°C resulted in the regeneration of aliphatic selenoaldehydes in situ effectively. Thus, **1** can serve as convenient and clean precursors of selenoaldehydes.[13,14]

Cycloadducts **1** were heated with 2-trimethylsilyloxy-1,3-butadiene at 110°C or 160°C, followed by addition of trifluoroacetic acid to afford a mixture of 3- and 4-selenacyclohexanones in good yields.[13] The results are shown in Table II. The regiochemistry in this cycloaddition reaction was influenced by the electronic character of a substituent R on selenoaldehydes. *p*-Cyanophenyl substituted selenoaldehyde gave 3-selena adduct as the slightly preferential product, while that with a *p*-methoxyphenyl substituent formed 4-selena adduct preferentially. Selenoaldehyde with *n*-propyl group as a donor substituent exhibited the regiochemical result with preference of 4-selena adduct, though selectivity was not high.

The reaction of aromatic and aliphatic selenoaldehydes, generated via thermal retro Diels–Alder reaction from **1**, with 2-methoxyfuran gave methyl penta-2,4-dienoates in high yields along with the deposition of elemental selenium as shown in Scheme 1. We have already reported the above reaction with detail results containing mechanistic considerations.[15]

5-Alkoxyoxazoles correspond to the compounds replaced by the C4 atom of the above 2-methoxyfuran with a nitrogen atom, and also are cyclic 2-azadienes. Thermally generated selenoaldehydes from



SCHEME 1 Reaction of selenoaldehydes with 2-methoxyfuran.

1 reacted with 5-ethoxyoxazoles to afford 1:1 adducts having 3-selenazoline structure as a mixture of diastereomers in good yields. The Diels–Alder-type adducts were not detected. The results are summarized in Table III. The yields in the reaction at 160°C generally were higher than those at 90°C. A major isomers in the reaction of selenoaldehydes with 5-ethoxy-4-methyl-2-phenyloxazole was assigned to *trans*, which refers to the relationship between the phenyl and the ester groups, on the basis of NOE measurement.

The reaction mechanism for the formation of 3-selenazoline products has not been established, but the most likely pathway, at the present stage, may be as follows. The Diels–Alder reaction of selenoaldehyde with 5-ethoxyoxazole affords two regioisomeric [4 + 2] cycloadducts that would be at equilibrium with each other under thermal conditions. The isomer having an orthoester structure would be expected readily to undergo C—Se bond cleavage selectively to give the betaine intermediate,

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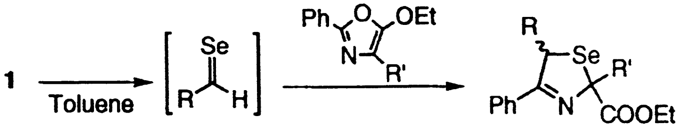
TABLE III Reaction of Selenoaldehydes with 5-Ethoxyoxazoles



R	R′	Temp. (°C)	Time (h)	Yield (%)[a]	*trans* : *cis*[b]
Ph	Me	90	4.0	65	85:15
Ph	Me	160	2.0	95	69:31
p-MeOC$_6$H$_4$	Me	160	2.0	91	70:30
p-NCC$_6$H$_4$	Me	160	2.0	88	78:22
PhCH$_2$CH$_2$	Me	160	3.0	96	69:31
n-Pr	Me	160	3.0	67	67:33
p-NCC$_6$H$_4$	H	160	2.0	95	71:29
p-MeOC$_6$H$_4$	H	160	2.0	88	69:31
PhCH$_2$CH$_2$	H	160	3.0	91	80:20

[a] Isolated yield.

[b] Determined by ^{1}H NMR.

followed by the ring opening and the recyclization to yield an isomeric mixture of 3-selenazoline compound. The similar reaction of thioaldehydes with 5-alkoxyoxazole already has been reported through both experimental[16] and theoretical[17] studies, in which the reaction mechanism involves the Diels–Alder reaction as the first step.

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