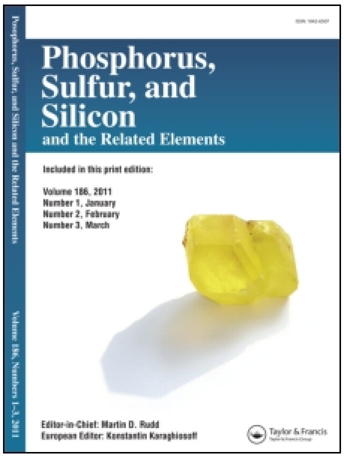

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Ammonium Eneselenolates: Stereochemical and Spectroscopic Properties

Toshiaki Murai[a]; Shuuya Hayakawa[a]; Youhei Miyazaki[a]; Shinzi Kato[a]
[a] Department of Chemistry, Faculty of Engineering, Gifu University, Gifu, Japan

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Ammonium Eneselenolates: Stereochemical and Spectroscopic Properties

TOSHIAKI MURAI, SHUUYA HAYAKAWA, YOUHEI MIYAZAKI and SHINZI KATO

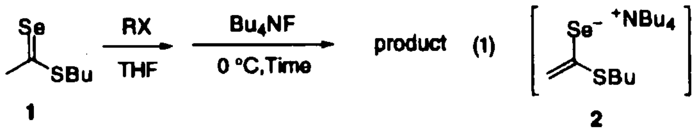
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193 Japan

The efficient generation and alkylation of ammonium ene selenolates have been described. The synthesis of ketene seleno thioacetals having a variety of functional groups was attained. The stereoselectivity of the generation of ammonium eneselenolates was compared between selenoic acid *O*-esters and selenothioic acid *S*-esters.

Keywords: ammonium eneselenolates; ketene selenothioacetals; selenoic acid *O*-esters; selenothioic acid *S*-esters

In contrast to the rich chemistry of enolates[1] and their sulfur isologues[2], much less attention has been paid to enolates involving a selenium atom, i.e., eneselenolates[3,4]. However, recent dramatic progress on the chemistry of selenocarbonyl compounds[5] stimulated us to explore their use as precursors to eneselenolates. As a matter of fact, limited examples of the deprotonation of selenoamides and selenoesters have been reported[4]. Very recently, we have disclosed that the reaction of selenothioic acid *S*-esters (RC(Se)SR') with tetrabutylammonium fluoride (TBAF) efficiently gives ammonium eneselenolates[6].We report the detail of the generation of ammonium eneselenolates and their reactions with a wide range of alkyl halides.

The purple selenothioacetic acid *S*-butyl ester (**1**)[7] turned light brown almost instantly by adding a THF solution of TBAF, that was indicative of the formation of ammonium eneselenolate **2** (eq 1).

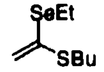
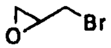
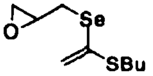
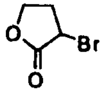
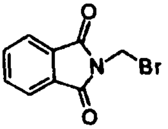
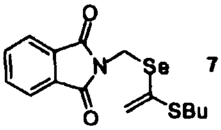
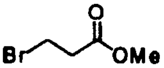
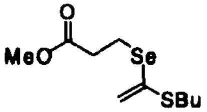
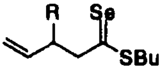


To efficiently trap **2**, alkyl halides were added to the reaction mixture prior to the addition of a THF solution of TBAF. As a result, functionalized ketene selenothioacetals[8], that are of synthetically interest but have been studied to a much lesser extent compared to the chemistry of ketene dithioacetals[9], were obtained in good to high yields. The results are listed in Table 1. The use of ethyl iodide gave ketene selenothioacetal **4** in 81% yield (entry 1). Alkyl halides bearing oxygen-containing functional groups were also used. In the reaction of epibromohydrin, α-bromo-γ-butyrolactone, *N*-(bromomethyl) phthal imide, and methyl 3-bromopropionate, the substitution reaction selectively took place at the bromine-substituted carbon atom to give the products **5** – **8** (entries 2 – 5), and oxygen-containing functional groups were inert toward ammonium eneselenolate **2**. On the contrary, the reaction with epichlorohydrin gave the product **12**, that was derived from the ring opening of the epoxy ring (eq 2). A similar cyclized product **13** was obtained from 3-bromo-1-propanol (eq 3). In these reactions the initial product may be *Se*-β- or γ-hydroxyalkyl ketene selenothioacetals **14** and **15**. Then, the intramolecular cyclization of **14** and **15** took place to form **12** and **13** as observed for the reaction of the lithium eneselenolate derived from ester **1** with oxiranes[10].

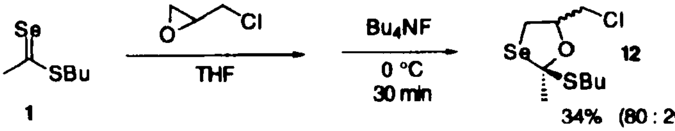
When allylic bromides were employed as alkylating agents, the γ,δ-unsaturated selenothioic acid *S*-esters **9** – **11** were formed as products (entries 6 – 8). The ester **1** may be selectively allylated at the selenium atom in the initial step of the reaction to form allylic vinyl selenides, which then undergo seleno-Claisen rearrangement. A similar allylation was observed for the reaction of ester **1**, allylic bromides, and Et_3N, but two molecules of allylic groups were generally incorporated into the products[11]. Diallylation of **1** took place with allylic bromide **16** to give the product **17** (eq 4). The highly stereoselective allylation was attained in the reaction of ester **11** with allyl bromide, although the stereochemisty of the product has not yet been determined (eq 5).

Secondly, focus has been laid on the stereochemistry of the formation of ketene selenoacetals. The treatment of selenothioic acid *S*-ester **19** with TBAF and methyl iodide gave ketene selenothioacetal **20** with *Z*-selectivity of 88:12 in 82% yield (eq 6). The high stereoselectivity of the formation of ketene selenoacetal **22** was also observed for the deprotonation of selenoic acid *O*-ester **21** with TBAF followed by the methylation (eq 7), but the stereochemistry of the major products of these two reactions was reverse.

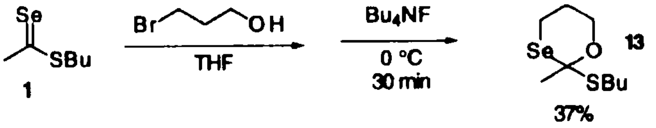
Table 1. Reaction of selenothioacetic acid *S*-butyl ester (1) with TBAF and alkyl halides.[a]

Entry	RX	Temp. Time	Product		Yield (%)[b]
1	EtBr	0 °C 3 min		4	81
2		0 °C 30 min		5	47
3		0 °C 30 min		6	73
4		0 °C 30 min		7	94
5		0 °C 30 min		8	59
					
6	R = Me	0 °C 1 h		9	73
7	R = Ph	0 °C, 30 min r.t., 1 h		10	66
8	R = CO_2Et	0 °C 30 min		11	61

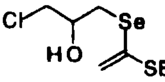
[a] Selenothioacetic acid *S*-butyl ester (1) (0.195 g, 1.0 mmol) was treated with a THF solution of tetrabutylammonium fluoride (1.5 mL, 1.5 mmol) and alkyl halides (1.0 mmol). [b] Isolated yield.


Se
SBu
1
Cl
O
THF
Bu_4NF
0 °C
30 min
Se
O
Cl
SBu
12
34% (80 : 20)

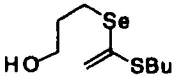
(2)


Se
SBu
1
Br
OH
THF
Bu_4NF
0 °C
30 min
Se
O
SBu
13
37%

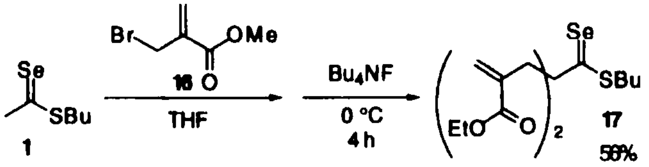
(3)


Cl
HO
Se
SBu

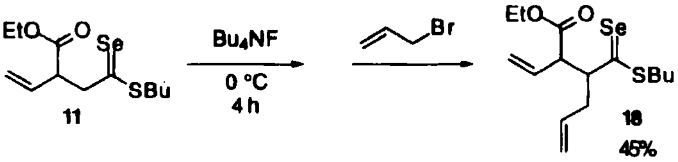
14


HO
Se
SBu

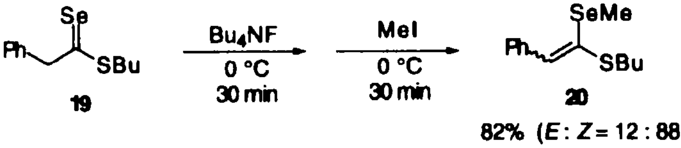
15


Se
SBu
1
Br
OMe
16 O
THF
Bu_4NF
0 °C
4 h
EtO
O
2
Se
SBu
17
58%

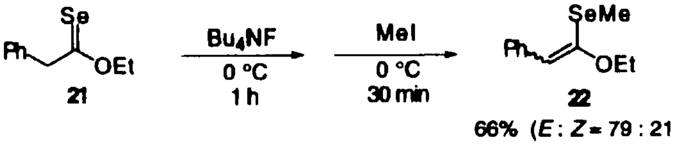
(4)


EtO
O
Se
SBu
11
Bu_4NF
0 °C
4 h
Br
EtO
O
Se
SBu
18
45%

(5)


Se
Ph
SBu
19
Bu_4NF
0 °C
30 min
MeI
0 °C
30 min
SeMe
Ph
SBu
20
82% (E : Z = 12 : 88)

(6)


Se
Ph
OEt
21
Bu_4NF
0 °C
1 h
MeI
0 °C
30 min
SeMe
Ph
OEt
22
66% (E : Z = 79 : 21)

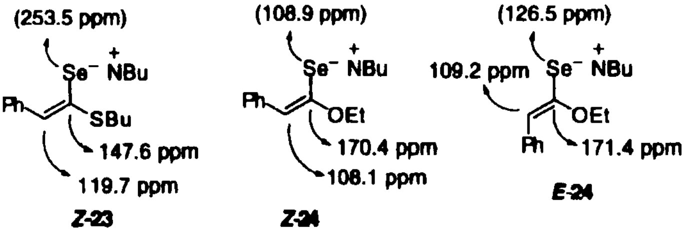
(7)

Finally, the generation of ammonium eneselenolates **23** and **24** was monitored by ^{1}H, ^{13}C, and ^{77}Se NMR spectra. The representative results of NMR spectra are shown in Table 2. The salt **24** appeared to be less stable than **23** since **24** gradually decomposed during the NMR measurement. The eneselenolate **23** was formed stereoselectively as a *Z*-isomer from ester **19**, and the signals due to *E*-isomer of **23** was not observed. Nevertheless, a small amount of *E*-**20** was formed in the methylation of **23**. This may be because of the partial isomerization of *Z*- **23** to *E*- **23** during the methylation. A similar partial isomerization was observed for the methylation of eneselenolate **24**. The *E* and *Z*-isomers of **24** were detected in a ratio of 66 : 34 by NMR spectra, but the ratio of *E*-isomer of **22** increased after the methylation of **24**.

In the ^{77}Se NMR spectra the signal of **23** and **24** were observed in the region lower than 100 ppm despite the fact that the selenium atom bearing the negative charge has generally been observed in the region higher than 0 ppm[12]. The signals due to the carbon atoms adjacent to the selenium atom were shifted to lower fields than those of the corresponding ketene selenoacetals **20** and **22**. Accordingly, the electrons on the selenium atom may be delocalized to the carbon-carbon double bonds in the ammonium eneselenolates to some extent.

In summary, ammonium eneselenolates were generated from selenothioic acid *S*-esters with TBAF with high efficiency. Alkylation of ammonium eneselenolates gave a variety of ketene selenothioacetals. The use of allylic bromides ended up as a formation of γ,δ-unsaturated esters. The stereoselectivity of the formation of ketene selenothio acetals was also disclosed. NMR studies have suggested that the electrons in the eneselenolate ions reside on the selenium atom, but are delocalized to the carbon-carbon double bond to some extent.

Table 2. ^{13}C and ^{77}Se NMR Chemical Shifts with Structures of **23** and **24** [a]



[a] The spectra were measured in THF-d_8. The chemical shifts of ^{77}Se NMR spectra are in parenthesis.

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