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SYNTHESES OF SELENOTHIOIC AND DISELENOIC ACID ESTERS

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This review covers synthetic methods of three types of selenium counterparts of dithioic acid esters, *e.g.* selenothioic acid *Se*-esters, selenothioic acid *S*-esters, and diselenoic acid esters. These generally utilize a combination of electrophilic thio- or seleno-acylating agents and nucleophilic organoselenium or -sulfur compounds. Observed trends in the stability of the esters are also discussed.

Keywords: Diselenoic acid esters; seleno-Claisen rearrangement; selenoketenes; selenothioic acid *S*-esters; selenothioic acid *Se*-esters; thioacylating agents

CONTENTS

1. INTRODUCTION

The chemistry of dithioic acid esters has been extensively studied for over thirty years, and the results have proved their importance and usefulness both from the synthetic and the industrial point of view.[1] In contrast, only

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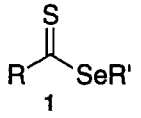
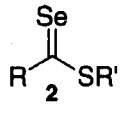
scattered examples of the selenium counterparts of dithioic acid esters had been known until very recently mainly because of lack of appropriate synthetic procedures. The present review outlines synthetic methods for the three types of acyclic esters **1–3**.[2] One of the most powerful synthetic routes to dithioic acid esters involves reactions of carbon disulfide. As a matter of fact, selenium isologues of carbon disulfide such as carbon diselenide are known, but cannot be handled readily because of their instability.[3] Accordingly, the key step in the synthesis of **1–3** is to use less accessible thio- and selenoacylating agents efficiently.



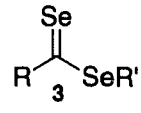
1

selenothioic acid Se-esters



2

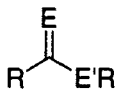
selenothioic acid S-esters



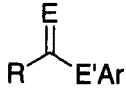
3

diselenoic acid esters

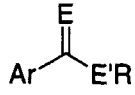
The trends in the stabilities of the esters have also been examined. On the basis of the substituents next to the thio- or selenocarbonyl group and those attached to the selenium or sulfur atom the esters can be classified into the following four types **I–IV**, i.e. aliphatic acid alkyl esters, **I**, aliphatic acid aryl esters **II**, aromatic acid alkyl esters **III**, and aromatic acid aryl esters **IV**. Dithioic acid esters of all these types are known as stable compounds. In contrast, the substitution of the sulfur atom of the thiocarbonyl group with a selenium atom dramatically changes the stability of the esters as discussed later.



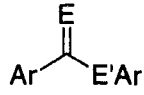
I



II



III



IV

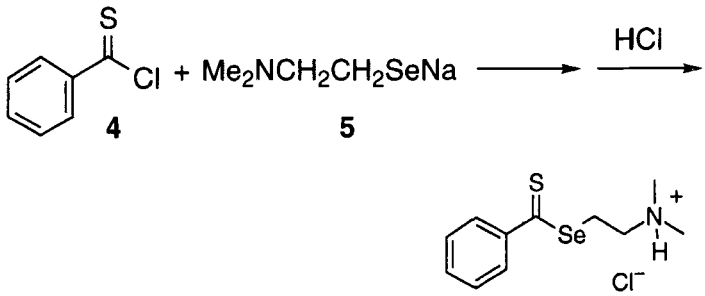
E, E' = S or Se

2. SELENOTHIOIC ACID *Se*-ESTERS

Eight methods for the synthesis of selenothioic acid *Se*-esters **1** have so far become known (methods A–H, eqs. 1–8).[4–9] The first synthesis of selenothiobenzoic acid *Se*-ester utilizing thiobenzoyl chloride **4** as a thio-

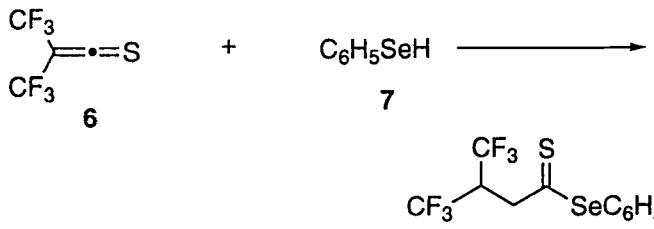
acylating agent was reported in 1964 (method A).[4] Since then, thioacyl chlorides **10** (methods A, D, and E),[4,6] the thioketene **6** (method B),[5] dithioic acid thioanhydrides **8** (method C),[6] 1-methyl-2-thioacylthiopyridinium salts **12** (method F)[7] and thioic acid *O*-esters **14** (method G)[8] have been employed as thioacylating agents. To introduce arylselenenyl and alkylselenenyl groups benzeneselenol **7** (method B)[5] and a variety of metal selenolates such as sodium **5, 9, 13** (method C, D, and F),[6,7] silyl **11** (method E),[6] and aluminum selenolates **15** (method G)[8] have been used. Among these methods, method C allowed the synthesis of a series of derivatives whose spectroscopic properties have been disclosed.[6] In the selenenylation of thioacyl chlorides **10** the use of sodium areneselenolates **9** gives the esters in better yields than the use of silyl selenides **11** probably because **9** is more nucleophilic than **11**.[6] In method G the high affinity of the aluminum atom of **15** toward the oxygen atom of **14** makes the reaction highly efficient to give the esters **1** in generally good to high yields.[8] The thiocarbonyl group can tolerate the reaction conditions. As a unique method the treatment of alkynyl phenyl selenide **16** with sulfur to give the α-thioxo selenothioic acid *Se*-phenyl ester **17** in 12% yield (method H).[9]

method A



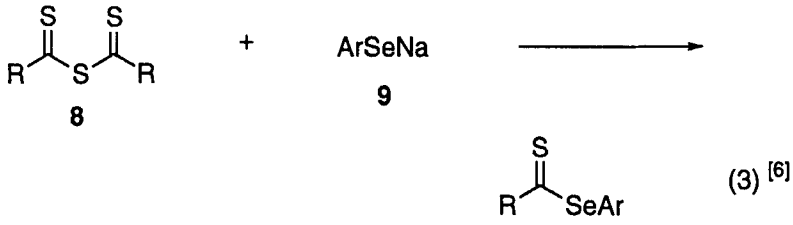
(1) [4]

method B



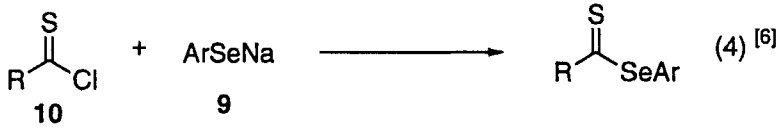
(2) [5]

method C



(3) [6]

method D

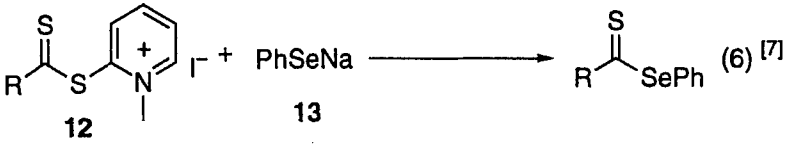


(4) [6]

method E

(5) [6]

method F

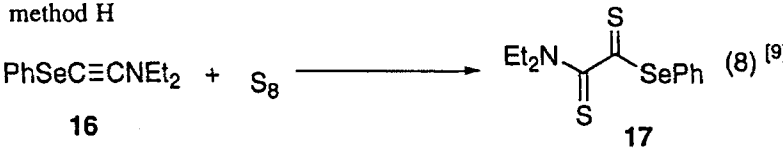


(6) [7]

method G

(7) [8]

method H



(8) [9]

The syntheses of a series of selenothioic acid *Se*-esters **1** are listed in Table I. These results have shown that all four types of selenothioic acid *Se*-esters mentioned above, i.e. **I–IV** (E = S, E′ = Se) are thermally stable and can be handled in air. The esters of types **I** and **II** are yellow to orange, whereas those of types **III** and **IV** are red to reddish pink. In their visible spectra absorptions due to n-π^* transitions are observed at about 490 nm for **I** and **II**. The corresponding absorptions of **III** and **IV** are shifted to longer wavelength by about 50 nm.[6]

TABLE I Selenothioic acid *Se*-esters

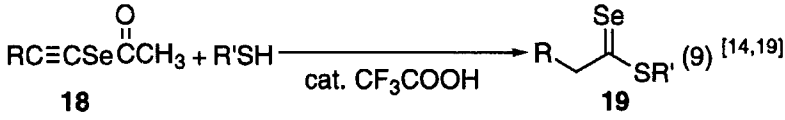
C_n	*method*	R – C(=S) – Se – R′ *R*	*R′*	*yield (%)*	*ref.*
C_4	G	CH_3CH_2	CH_3	61	[8]
C_6	G	2-thienyl	CH_3	75	[8]
C_7	G	CH_3CH_2	i-C_4H_9	96	[8]
C_8	C	CH_3	C_6H_5	89	[6]
	G	n-C_5H_{11}	C_2H_5	26	[8]
	G	C_6H_5	CH_3	91	[8]
C_9	C	C_2H_5	C_6H_5	51	[6]
	G	n-C_7H_{15}	CH_3	98	[8]
	G	cyclo-$C_6H_{11}CH_2$	CH_3	85	[8]
	G	$C_6H_5CH_2$	CH_3	94	[8]
C_{10}	C	n-C_3H_7	C_6H_5	68	[6]
	C	i-C_3H_7	C_6H_5	77	[6]
	B	$(CF_3)_2CH$	C_6H_5	96	[5]
C_{11}	G	$C_6H_5CH_2$	C_2H_5 + Cl^-	94	[8]
	A	C_6H_5	$CH_2CH_2N(CH_3)_2$	54	[4]
	C	n-C_4H_9	C_6H_5 H	60	[6]
C_{12}	C	n-C_5H_{11}	C_6H_5	69	[6]
	G	$C_6H_5CH_2$	i-C_4H_9	63	[8]
C_{13}	C	cyclo-C_6H_{11}	C_6H_5	83	[6]
	C	C_6H_5	C_6H_5	44	[6]
	D			60	[6]
	E			12	[6]
	F			51	[7]
	C	4-ClC_6H_4	C_6H_5	78	[6]
	D			80	[6]
	E			37	[6]
C_{14}	C	4-$CH_3C_6H_4$	C_6H_5	73	[6]
	D			77	[6]
	E			12	[6]
	C	4-$CH_3C_6H_4$	4-ClC_6H_4	70	[6]
	C	4-$CH_3OC_6H_4$	C_6H_5	68	[6]
	D			31	[6]
C_{15}	C	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	81	[6]
C_{17}	G	n-$C_{15}H_{31}$	CH_3	90	[8]
	C	ferrocenyl	C_6H_5	46	[6]

3. SELENOTHIOIC ACID *S*-ESTERS

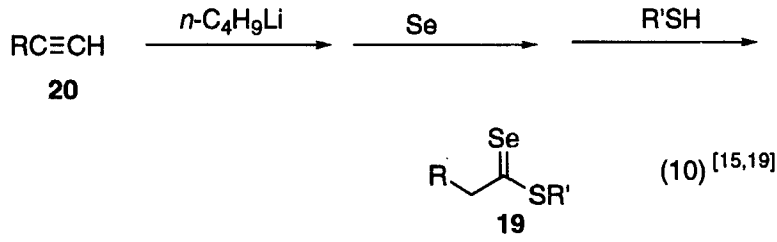
Selenothioic acid *S*-esters had remained elusive until very recently in spite of the fact that the generation and stabilization of selenocarbonyl compounds such as selenoaldehydes and selenoketones have been studied in great depth for the last 15 years.[10] This is partly due to the unfounded expectation of instability of the selenothioic acid *S*-esters **2**. However, according to recent results the stability of the esters **2** is highly variable depending on the substituents as well as on the reaction conditions. In particular, the esters of types **II** and **IV** (E = Se, E′ = S), which might be considered to be stable on the basis of the stability of other reactive molecules, exhibit much lower stability than the esters with simple alkyl groups. In earlier work the synthesis of esters having rather unstabilizing carbon skeletons was attempted.

As early as 1962 the synthesis of selenothioic acid *S*-esters was reported,[11] and the esters noted to be unstable. Later, the synthesis of such esters from 1-butyne, selenium, and ethanethiol,[12] and from selenoimonium salts and hydrogen selenide were studied,[13] but no details were made available. Since then, no further examples of such esters have appeared except for two cyclic compounds containing a selenothiocarboxyl group.[3]

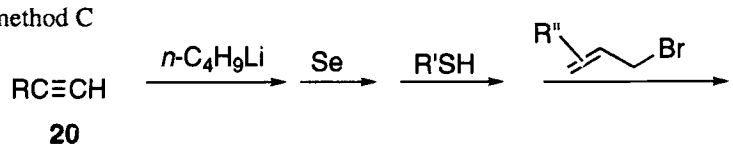
method A



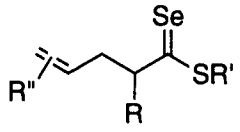
method B



method C

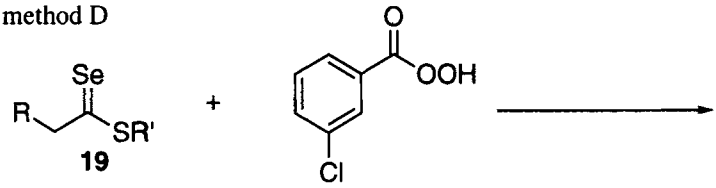


20

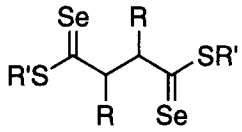


21 (11) [17,18]

method D

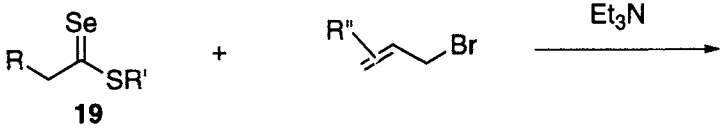


19

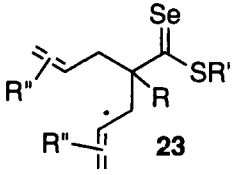


22 (12) [14]

method E

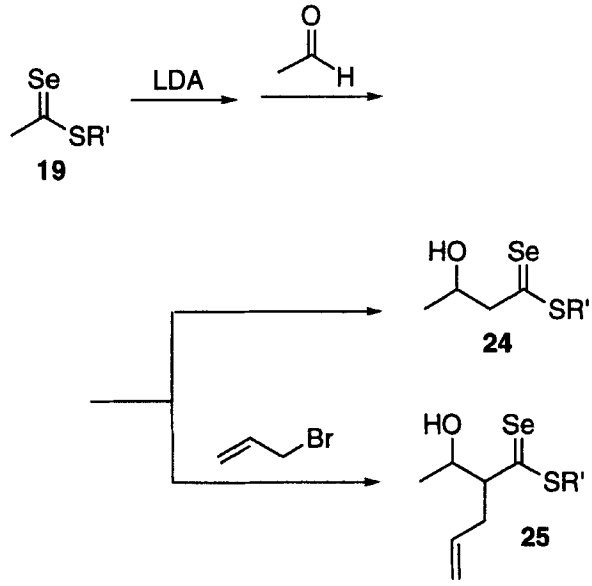


19



23 (13) [16,18]

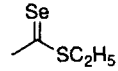
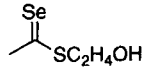
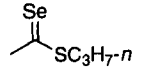
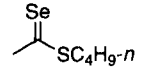
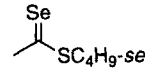
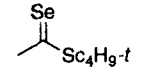
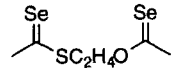
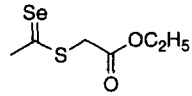
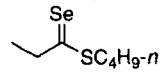
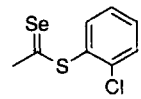
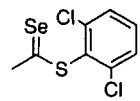
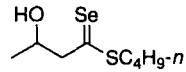
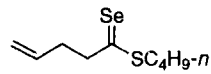
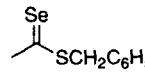
method F



(14) [20]

To generate a selenocarbonyl group the substitution of the oxygen atom of thioic acid *S*-esters with a selenium atom may be possible. However, a selenium version of Lawesson's reagent to convert a C=O group to a C=Se group has not yet been developed. Alternatively, the combination of selenoacylating agents with sulfenylating agents may be possible. The first successful isolation of selenothioic acid *S*-alkyl esters **19** was reported in 1993 by Kato *et al.* (method A, eqn. 9).[14] The selenoketene intermediates **26**,[21,22] generated from selenoacetic acid *Se*-alkynyl esters **18**, are employed as selenoacylating agents. In a series of selenothioic acid *S*-esters, the esters of type **I** were isolated as blue-violet liquid by this method A. These results first implied that esters of the types **II–IV** could also be easily isolated. Since then, several synthetic procedures have been developed for aliphatic esters of types **I** and **II** (E = Se, E′ = S) (methods **B-F**, eqn. 10–14).[15–20] The synthetic results concerning esters of type **I** and **II** are listed in Table II. Methods B and C also involve selenoketene intermediates **26** which are obtained by protonation of lithium alkyneselenolates

TABLE II Aliphathic selenothioic acid *S*-esters

C_n	method	starting material	ester	yield (%)	ref.
C_4	B	**20** R = Me_3Si		51	[15,19]
	B	**20** R = Me_3Si		44	[19]
C_5	A	**18** R = Me_3Si		30	[14]
C_6	B	**20** R = Me_3Si		98	[15,19]
	B	**20** R = Me_3Si		54	[15,19]
	B	**20** R = Me_3Si		42	[15,19]
	B	**20** R = Me_3Si		44	[19]
	B	**20** R = Me_3Si		20	[15]
C_7	B	**20** R = CH_3		34	[19]
C_8	B	**20** R = Me_3Si		40	[19]
	B	**20** R = Me_3Si		18	[19]
	F	**19** R = H, R' = C_4H_9-*n*		41	[20]
C_9	C	**20** R = Me_3Si		74	[18]
	B	**20** R = Me_3Si		83	[15,19]

(*continued*)

TABLE II (*Continued*)

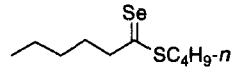
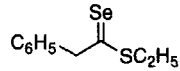
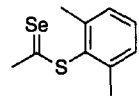
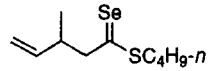
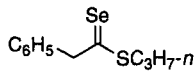
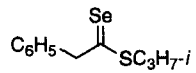
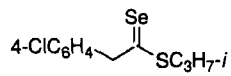
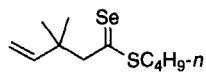
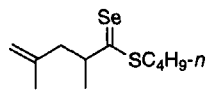
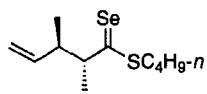
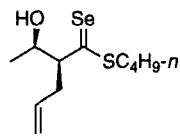
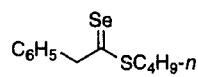
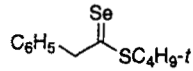
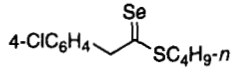
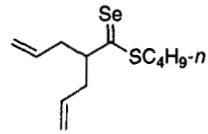
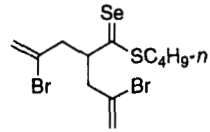
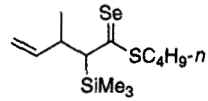
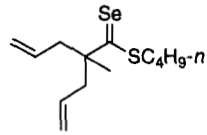
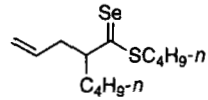
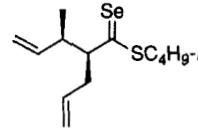
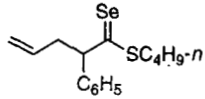
C_n	method	starting material	ester	yield (%)	ref.
C_{10}	B	**20** R = C_4H_9-*n*		58	[15,19]
	A	**18** R = C_6H_5		48	[14,19]
	B	**20** R = C_6H_5		10	[19]
	B	**20** R = Me_3Si		17	[19]
	C	**20** R = Me_3Si		37	[18]
C_{11}	A	**18** R = C_6H_5		70	[14]
	A	**18** R = C_6H_5		54	[14]
	A	**18** R = C_6H_5		46	[19]
	C	**20** R = Me_3Si		37	[18]
	E	**19** R = CH_3, R' = C_4H_9-*n*		79	[18]
	E	**19** R = CH_3, R' = C_4H_9-*n*		48	[17,18]
	F	**19** R = H, R' = C_4H_9-*n*		89	[20]
C_{12}	A	**18** R = C_6H_5		55	[14]
	B	**20** R = C_6H_5		29	[18]

TABLE II (*Continued*)

C_n	method	starting material	ester	yield (%)	ref.
C_{12}	A	**18** R = C_6H_5		33	[14]
	B	**18** R = Cl-C_6H_4		13	[15]
	E	**19** R = H, R' = C_4H_9-*n*		80	[16,18]
	E	**19** R = H, R' = C_4H_9-*n*		59	[16,18]
C_{13}	C	**20** R = Me_3Si		51	[18]
	E	**19** R = CH_3, R' = C_4H_9-*n*		71	[18]
	E	**19** R = C_4H_9-*n*, R' = C_4H_9-*n*		99	[16,18]
	E	**19** R = CH_2=CHCHCH_3 R' = C_4H_9-*n*		48	[16]
	E	**19** R = C_6H_5 R' = C_4H_9-*n*		80	[14]

(*continued*)

TABLE II (*Continued*)

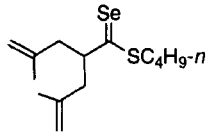
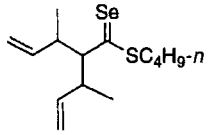
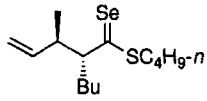
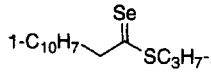
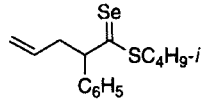
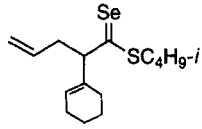
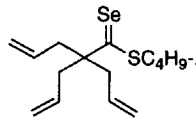
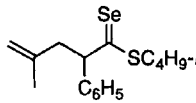
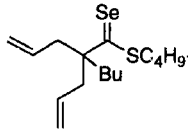
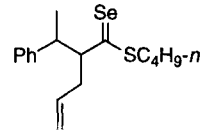
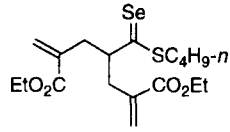
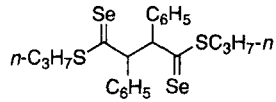
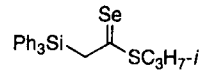
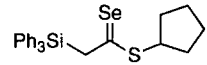
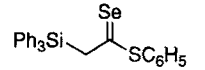
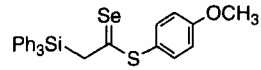
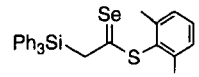
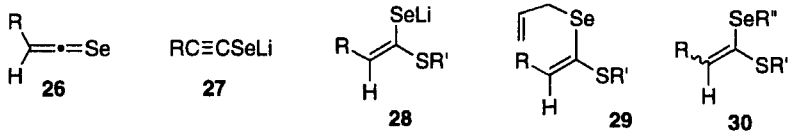
C_n	method	starting material	ester	yield (%)	ref.
C_{14}	E	**19** R = H, R' = C_4H_9-*n*		72	[16,18]
	E	**19** R = H, R' = C_4H_9-*n*		57	[16,18]
	E	**19** R = C_4H_9-*n*, R' = C_4H_9-*n*		47	[16,18]
	A	**18** R = 1-$C_{10}H_7$		40	[19]
C_{15}	C	**20** R = C_6H_5		55	[17]
	C	**20** R = 		58	[17]
C_{16}	E	**19** R = H, R' = C_4H_9-*n*		90	[16,18]
	C	**20** R = C_6H_5		57	[17]
	E	**19** R = C_4H_9-*n*, R' = C_4H_9-*n*		48	[16,18]

TABLE II (*Continued*)

C_n	method	starting material	ester	yield (%)	ref.
C_{17}	C	**20** R = $C_6H_5CH(CH_3)$		49	[17]
C_{18}	E	**19** R = H, R' = C_4H_9-*n*		68	[16,18]
C_{22}	B	**20** R = C_6H_5, R' = C_3H_7-*n*		11	[14]
C_{23}	B	**20** R = Ph_3Si		24	[19]
C_{25}	B	**20** R = Ph_3Si		59	[19]
C_{26}	B	**20** R = Ph_3Si		23	[19]
C_{27}	B	**20** R = Ph_3Si		46	[19]
C_{28}	B	**20** R = Ph_3Si		29	[19]

27. Method B is a straightforward route to the esters from commercially available materials. The reaction of (trimethylsilyl)acetylene with alkanethiols proceeds most effectively to give selenothioacetic acid *S*-alkyl esters as deep pink liquids in moderate to high yields. The desilylation of the starting (trimethylsilyl)acetylene takes place mainly during the purification by column chromatography on silica gel. As for the reaction of (triphenylsilyl)acetylene, the silyl group remains in the final esters. In contrast, the

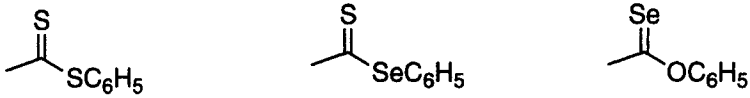
corresponding reaction of aliphatic and aromatic acetylenes gives the esters in only moderate yields. In this reaction the addition of the lithium thiolate generated *in situ* to the selenoketene intermediate **26** may take place to form the lithium eneselenolate intermediate **28**. In the case of the reaction of phenylacetylene the quantitative formation of **28** (R = C_6H_5) was confirmed by ^1H and ^{13}C NMR.[17] Thus, the lower yields of **19** in method B are mainly due to the less effective process to construct a selenothiocarboxyl group from **28** by aqueous work-up. α-Aryl esters **19** (R = Ar) can be obtained in better yields by method A although it requires a longer reaction time.[14,19]



26 **27** **28** **29** **30**

To construct a selenothiocarboxyl group the allylation of the intermediates **28** effectively proceeds to lead to α-allylated esters **21** as in method C (eqn. 11).[17,18] In this case, the allylation may initially take place at the selenium atom of **28** to form an allylic vinyl selenide **29**, followed by seleno-Claisen rearrangement to give **21**. This may be proved by the addition of alkyl iodides and prenyl bromides to the solution of **28** to give the ketene selenothioacetals **30**, although in moderate yields.[17]

The reaction with aromatic thiols has also been carried out by method B (eqn. 10). For example, in the reaction with benzenethiol, the reaction mixture gradually turns blue, which is indicative of the formation of the selenothioic acid *S*-phenyl ester, but the color instantly changed to yellow when the mixture was treated with water at room temperature. This is in marked contrast to the fact that dithioacetic acid *S*-phenyl ester **31**,[23] selenothioacetic acid *Se*-phenyl ester **32**,[6] and selenoic acid *O*-phenyl ester **33**[24] could be purified by distillation.



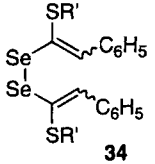
31 **32** **33**

To enhance the stability of the *S*-aryl esters bulky substituents were introduced to the carbon atom α to the selenocarbonyl group of the esters.

Nevertheless, these *S*-aryl esters are more labile than *S*-alkyl esters even at low temperatures. The major decomposition process of the *S*-aryl esters has been confirmed to be self-condensation to give dimers and oligomers.[19]

Skeletal transformations of the esters **19** can lead to a variety of derivatives with reemergence of the selenothiocarboxyl group under certain reaction conditions. Oxidation of **19** (R = C_6H_5) with *m*-CPBA, followed by stirring in xylene, gives the selenothiosuccinic acid *S*-ester **22** in 11% yield (method D).[14] The initial product of the oxidation is the diselenide **34**, which undergoes seleno-Cope rearrangement to form **22**.

Allylations of the esters **19** with allylic bromides in the presence of Et_3N proceed smoothly to give the α-allylic esters **23** (method E, eqn. 13). Since no reaction takes place between **19** and Et_3N, and since the esters **19** gradually decompose when mixed with allylic bromides, intermediate selenoxonium ions **35** may initially be formed in method E. Then, deprotonation of **35** may give rise to the allylic vinyl selenides **29**, which undergo seleno-Claisen rearrangement to form the esters **23**. Noteworthy is that two allylic groups have been introduced to the carbon atom α to the selenocarbonyl group of a selenothioacetic acid *S*-ester **19** (R = H) in one operation at 0 °C in as little as two hours. Even three allylic groups can be introduced when the reaction continues for 2 days at 66 °C with three equiv. of allyl bromide. These esters possessing quaternary carbon centers have been obtained in high yields. This is in sharp contrast to the reaction of dithioic acid esters where it generally takes more than one day to introduce one allylic group.[25] The γ-carbon atom of allylic bromides is introduced in the position α to the selenocarbonyl group of **19**. The stereoselectivity of the allylations is also high, and the relative stereochemistry of even three successive carbon atoms can be controlled to some extent to give the *meso* form **23'** predominantly.



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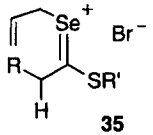

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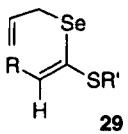

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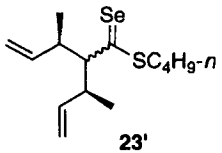


23'

An aldol type reaction of an ester **19** (R = H) is also successful (method F, eqn. 14).[20] Treatment of the ester with LDA generates the lithium eneselenolate **28** (R = H). It reacts with acetaldehyde at –78 °C in 10 min to give the β-hydroxy selenothioic acid *S*-ester **24** in moderate yield. This is

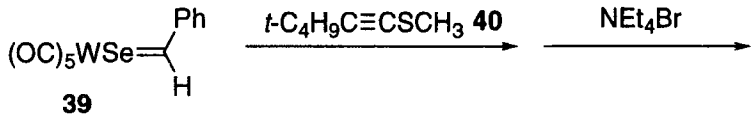
the first example of selenocarbonyl compounds with a hydroxy group. The hydroxy group does not affect the stability of the ester. When the reaction mixture of **28** (R = H) and acetaldehyde is treated with allyl bromide prior to the aqueous work-up, the allyl group is selectively introduced to the position α to the selenocarbonyl group of **19**. The product where the allylation has taken place at the hydroxy group of **25** is not observed.

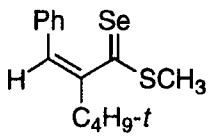
The synthesis of a variety of aromatic selenothioic acid *S*-esters, *i.e.* esters of type **III**, has been achieved by method G (eqn. 15)[26,27] similarly to the reaction of thioic acid *O*-esters with aluminum selenolate described in Eq. 7. The results are summarized in Table III. The selenocarbonyl group of the aromatic selenoic acid *S*-esters **36** does not affect the reaction course which gives the esters **38** as deep blue liquids in moderate to high yields. The aluminum thiolates **37** have been generally prepared by reaction of trimethylaluminum with thiols in toluene. The results of the synthesis of **38** are listed in Table III. The esters **38** are sufficiently stable to be handled in air. However, they gradually decompose to thioic acid *S*-esters with liberation of red selenium more easily than the aliphatic esters **19** when exposed to air.

method G

(15) [26, 27]

method H





(16) [28]

Noteworthy is the reaction of the aluminum thiolate derived from benzenethiol **37** (R = C_6H_5). Similarly to the reaction of **37** (R = alkyl) the reaction mixture gradually turns green, which is indicative of the formation of the ester **38** (R = C_6H_5). However, in the aqueous work-up of the mixture it only

TABLE III Aromatic selenothioic acid *S*-esters

ester 38			*ester 38*		
Ar	*R*	*yield, %*	*Ar*	*R*	*yield, %*
C_6H_5	CH_3	90	4-$CH_3C_6H_4$	C_4H_9-*n*	30
C_6H_5	C_2H_5	56	4-$CH_3OC_6H_4$	C_4H_9-*n*	13
C_6H_5	C_4H_9-*n*	76	2-$CH_3C_6H_4$	C_4H_9-*n*	80
C_6H_5	C_4H_9-*t*	56	4-$CH_3OC_6H_4$	C_6H_5	0
			2-naphthyl	CH_3	72

gives a yellow solution which does not contain the desired ester. These results suggest that the esters of type **IV** (E = Se, E′ = S) are thermally the most labile.

General synthetic methods for selenothioic acid *S*-esters with alkenyl and alkynyl groups have not yet been developed. However, method H leading to α,β-unsaturated selenothioic acid *S*-ester **41**[28] has proved the stability of such kinds of derivatives. In method H, the tungsten complex of selenobenzaldehyde **39** has been treated with the alkynyl sulfide **40**, followed by decomplexation with ammonium bromide to give the ester **41**.

The selenothioic acid *S*-esters exhibit colors from purple to deep blue-green depending on the substituents. In their visible spectra absorptions due to π-π* transitions and n-π* transitions have been observed at about 340 and 575 nm, respectively.

On the basis of the present results a general trend for the stability of selenothioic acid *S*-esters **2** can be schematically proposed in Chart 1. The aliphatic acid *S*-alkyl esters **I** are the most stable among the four types of esters **I–IV**. Substitution of an alkyl group attached either to the selenocarbonyl group or to the sulfur atom with an aryl group reduces the stability of the esters **II** and **III**. Attempts to isolate aromatic acid *S*-aryl esters **IV** have not yet been successful. These trends are in sharp contrast to those of a series of better known selenoesters[29] and dithioic acid esters,[1] where all types of derivatives possessing alkyl and aryl groups have been reported to be stable. It should also be noted that the isolation of enolizable selenoaldehydes and selenoketones has not yet been reported, whereas aromatic derivatives can be isolated.[10]

The stability of the esters **I** can also be compared qualitatively on the basis of the substituents of the carbon atom α to the selenocarbonyl group (Chart 2). The α-tri- or disubstituted esters **I-1** and **I-2** are the most stable. Then, the stability of the unsubstituted esters **I-4** is higher rather than that of the monosubstituted esters **I-3**. Of special interest is that selenium, sulfur isologues of acetic acid esters **19** (R = H) can be synthesized most effectively and easily handled in air.[19]

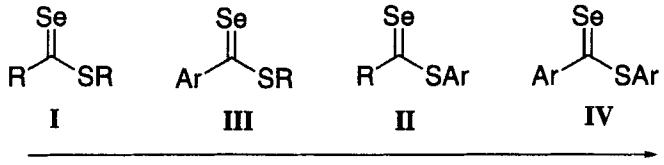


Chart 1

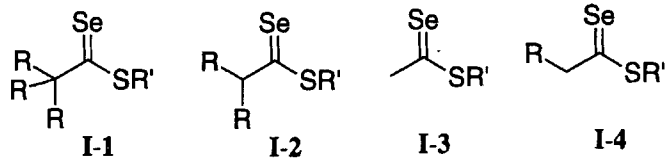


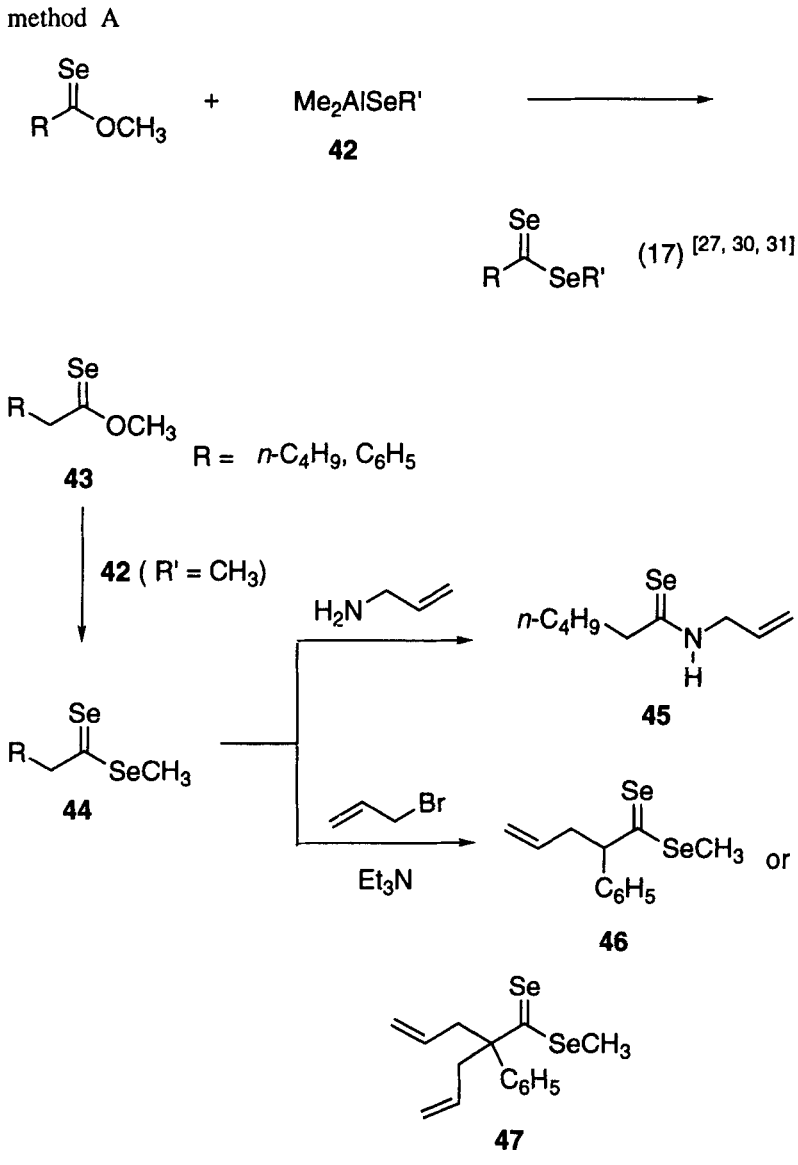
Chart 2

It is also noteworthy that the replacement of an *n*-butyl group attached to the sulfur atom of **I** with a *t*-butyl group reduces the stability of the esters. Thus, the introduction of a bulky group to the esters **I** does not necessarily enhance their stability.

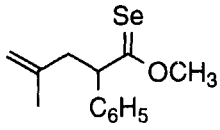
4. DISELENOIC ACID ESTERS

Much less attention has been paid to the chemistry of diselenoic acid esters **3**. The first synthesis of **3** was reported in 1993 by reaction of selenoic acid *O*-methyl esters with aluminum selenides (method A, eqn. 17).[27,30,31] A variety of aliphatic selenoic acid *O*-esters **43** have been employed to give blue green fractions after column chromatography. However, the products isolated contain the desired esters **44** as well as oligomers of **44**. The use of α-naphthyl selenoic acid *O*-ester **43** led to the corresponding ester **44** as a single product in 69% yield. The formation of unstable **44** in the reaction of **43** with **42** has been confirmed by further reaction of the mixture with allylamine leading to selenoamide **45** within 1 h (Scheme 1). The stabilization of the esters **44** is also successful when the reaction mixture of **42** and **43** is treated with allyl bromide and Et_3N. The esters **46** or **47** where one or two allyl groups are introduced to the carbon atom α to the selenocarbonyl group are obtained by simply changing reaction temperature and time. The

higher stability of α-disubstituted esters has been further illustrated by the synthesis of **49** from **48**.[27]



SCHEME 1



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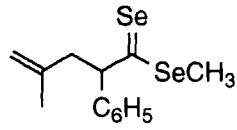

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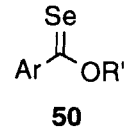

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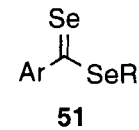

51

On the other hand, the reactions of aromatic selenoic acid *O*-methyl esters **50** with aluminum selenide cleanly proceed to give the corresponding esters **51** as green liquids, and they can be purified by column chromatography as a single product. The results are listed in Table IV. It should be noted that attempts to isolate aromatic acid aryl esters **IV** (E = Se, Se) have not yet been successful similar to the case of selenothioic acid *S*-esters **2**. These results suggest that the trend for the stability of diselenoic acid esters is partly different from that for the selenothioic acid *S*-esters **2** shown in Chart 1. Namely, the esters of type **I** (E, E′ = Se) are less stable than those of type **III**. In both cases the stability of esters of types **II** and **IV** is lower than that of other derivatives. Although further studies are necessary to disclose the factor responsible for the stability of the esters, it could be electronic and/or steric repulsion between the aromatic substituents on the sulfur or selenium atom and the selenium atom of the selenocarbonyl group.[32]

In summary, synthetic methods for three types of selenium counterparts of dithioic acid esters have been reviewed. Some of them still involve cumbersome procedures. However, the synthetic results have provided an important atlas of the stability of the esters. Most importantly, a number of esters are stable without any special bulky protecting groups, but still reactive. Modification of the structures around selenothio- and diselenocarboxyl groups is relatively easy. Further work with these esters should be directed to synthetic applications, materials related fields, and structural and theoretical chemistry.

TABLE IV Diselenoic acid esters

esters 51			*esters 51*		
Ar	*R′*	*yield, %*	*Ar*	*R′*	*yield, %*
C_6H_5	CH_3	91	4-$CH_3C_6H_4$	CH_3	64
C_6H_5	C_2H_5	46	2-$CH_3C_6H_4$	CH_3	37
C_6H_5	C_4H_9-*i*	5	4-$CH_3OC_6H_4$	CH_3	73
C_6H_5	C_6H_5	0	4-BrC_6H_4	CH_3	51
			2-CF_3I	CH_3	64

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