Preparation of 1,4-Dienes from 2-(2-Hydroxyalkylseleno)benzothiazoles by the Reaction Involving Se→O Azaaromatic Ring Rearrangement

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The reactions of 2-(2-oxoalkylseleno)benzothiazoles with allylic Grignard reagents in the presence of $BF_3 \cdot OEt_2$ gave the corresponding 2-[(2-alkyl-2-hydroxy-4-pententyl or 2-alkyl-2-hydroxy-4-methyl-4-pentenyl)seleno]benzothiazoles which, on treatment with Ph_3P and NaH, afforded 1,4-dienes in good to excellent yields.

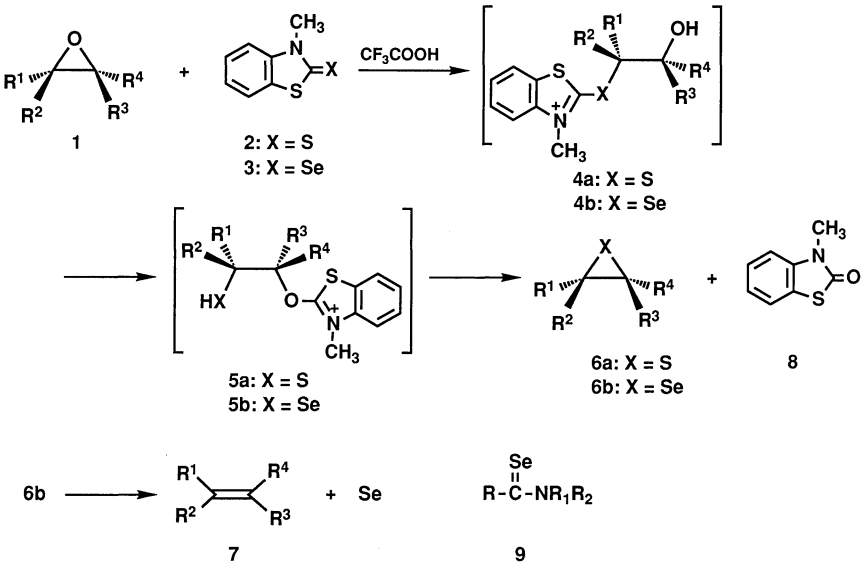
The use of selenium compounds as reagents in organic synthesis has aroused considerable interest.[1] Although selenium anionic species generally exhibit high nucleophilicity, the selenium function once introduced into a substrate could be utilized as leaving group in the subsequent functional group manipulation steps.[2] These properties resemble closely to those of homologous sulfur compounds. Compared with sulfur compounds, however, selenium compounds have longer covalent radius and lower bond energy and therefore their reactivities often present marked differences. As a typical example, epoxide **1** reacts with 3-methyl-2(3*H*)-benzothiazolethione (**2**) to give the corresponding episulfide **6a**,[3] while the reaction of 3-methyl-2(3*H*)-benzothiazoleselone (**3**) with **1** affords olefin **7** (Scheme 1).[4]

These processes are presumed to proceed through the rearrangement of 3-methyl-2-benzothiazolio group from the chalcogen atom to oxygen atom as shown in Scheme 1. Thus, the reaction of **1** with **2** or **3** affords alcohol **4** which successively converted into thiol **5a** or selenol **5b** through S→O or Se→O 3-methyl-2-benzothiazolio group rearrangement. Intramolecular displacement gives rise to thiirane **6a** or selenirane **6b**. In the reaction of **1** with **3**, because of instability of seleniranes, selenium extrusion from **6b** successively takes place to give olefin **7** with retention of configuration of the original epoxide.[5] Sonoda and co-workers have reported that selenoamides **9** can also be utilized in the place of **3**.[6]

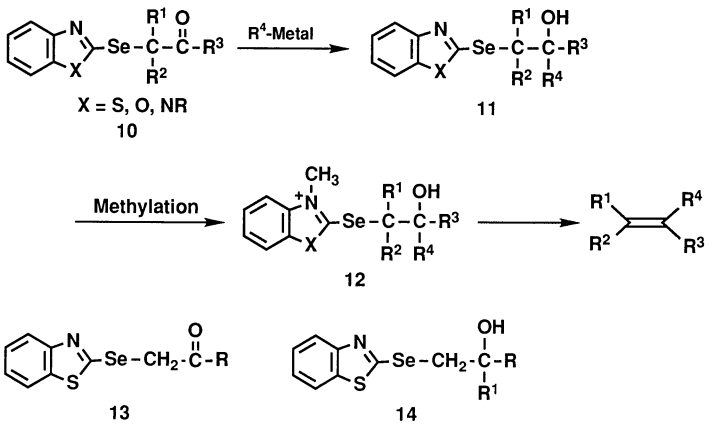
These results suggest that a variety of olefins could be prepared from 1-[(azaaryl)seleno]-2-alkanols with general structure **12** which would be formed by the reaction of the corresponding carbonyl compounds **10** with organometallic reagents or reducing reagents and subsequent *N*-methylation (Scheme 2). In this paper, we wish to describe the reaction of 2-(2-oxoalkylseleno)benzothiazoles **13** with Grignard reagents and conversion of the resulting 2-(2-hydroxyalkylseleno)benzothiazoles (**14**) into olefins.[7]

Results and Discussion

Preparation of 2-(2-Oxoalkylseleno)benzothiazoles. In order to prepare 2-(2-oxoalkylseleno)benzothiazoles **13**, the reaction of α-halo ketons with 2-benzothiazoleselenolate ion (**16**) was examined. According to the literature procedure,[8] NaSeH generated by reduction of selenium with $NaBH_4$ in water[9] reacted with 2-

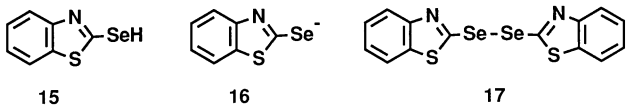


Scheme 1.

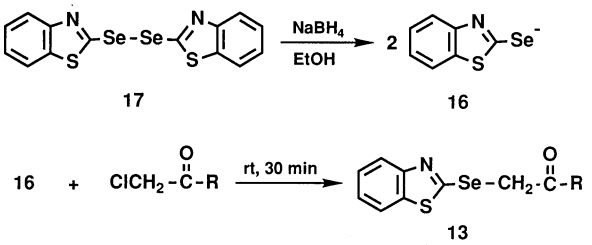


Scheme 2.

chlorobenzothiazole under reflux for 1 h where the product obtained, in fact, was bis(2-benzothiazolyl) diselenide (**17**; yield 22%) rather than the expected 2-benzothiazoleselenol (**15**). This result indicated that **15** is apt to be oxidized under the reaction conditions.[10] The failure of the reported procedure to afford consistent and efficient results promoted us to examine an alternative procedure which involves reductive cleavage of **17**. After several experiments under a variety of conditions (see Experimental), the following procedure was found to give **17** in acceptable yield. Thus, 2-chlorobenzothiazole reacted with NaSeH in ethanol, followed by treatment with H_2O_2 to give **17** in 61% isolated yield (Scheme 3).



Scheme 3.



Scheme 4.

The diselenide **17** thus prepared was treated with $NaBH_4$ in ethanol to generate **16**,[11] which in turn reacted smoothly with α-chloro ketones giving the expected **13** in good to excellent yields (Scheme 4).

Reactions of 2-(2-Oxoalkylseleno)benzothiazoles with Grignard Reagents. Of the four reaction sites in seleno ketone **13** (the C-2 of thiazolyl ring, selenium atom, methylene carbon atom, and carbonyl carbon atom), the carbonyl group would be most reactive toward an organometallic reagent. Therefore the reaction of **13** with Grignard reagents would result in the formation of 2-(2-hydroxyalkylseleno)benzothiazoles **14**, the key intermediates in the present study. Contrary to our expectation, however, the reaction of 2-(acetonylseleno) benzothiazole (**13a**) with 1 equiv of 2-phenylethylmagnesium bromide in tetrahydrofuran (THF) afforded 2-(2-phenylethylseleno)benzothiazole (**19**) and 2-(2-hydroxy-2-methyl-4-oxopentylseleno)benzothiazole (**21**) in 32 and 48% yields, respectively, rather than the expected carbonyl addition product **18a** (Scheme 5; Table 1, Entry 1).

When the reaction of **13a** with 2-phenylethylmagnesium bromide (2.5 equiv) was carried out in the presence of CuI, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) or BF_3·OEt_2, a complex mixture of products was again produced without any detectable formation of the

Table 1. Reaction of **13a** with $PhCH_2CH_2MgBr$ (0°C, 1 h)

Entry	$PhCH_2CH_2MgBr$/molar equiv	Additive (equiv)	Products and Yields/%						Recov./%[a]
			17	**19**	**20**	**21**	**22**	**23**	**13a**
1	1.0	—	9	32[a]	—	48	4	—	—
2	0.5	—	3	23	—	32	+	—	54
3	2.5	CuI (0.13)	2	33	7	5	9	—	—
4	2.5	TMEDA (2.5)	—	18	7	6	30	10	10
5[b]	2.5	BF_3·OEt_2 (4.0)	—	19	—	3	19[a]	11[a]	10

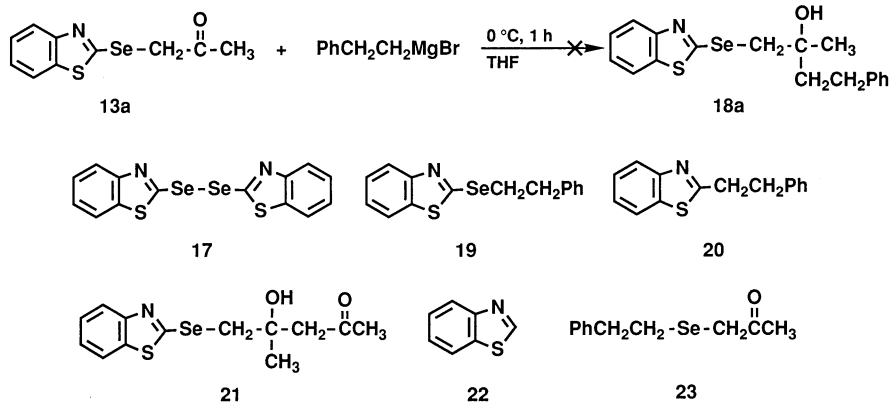
a) Yield of crude product. b) THF–CH_2Cl_2 was used as a solvent.

expected carbonyl addition product **18a** (Table 1, Entries 3, 4, and 5).

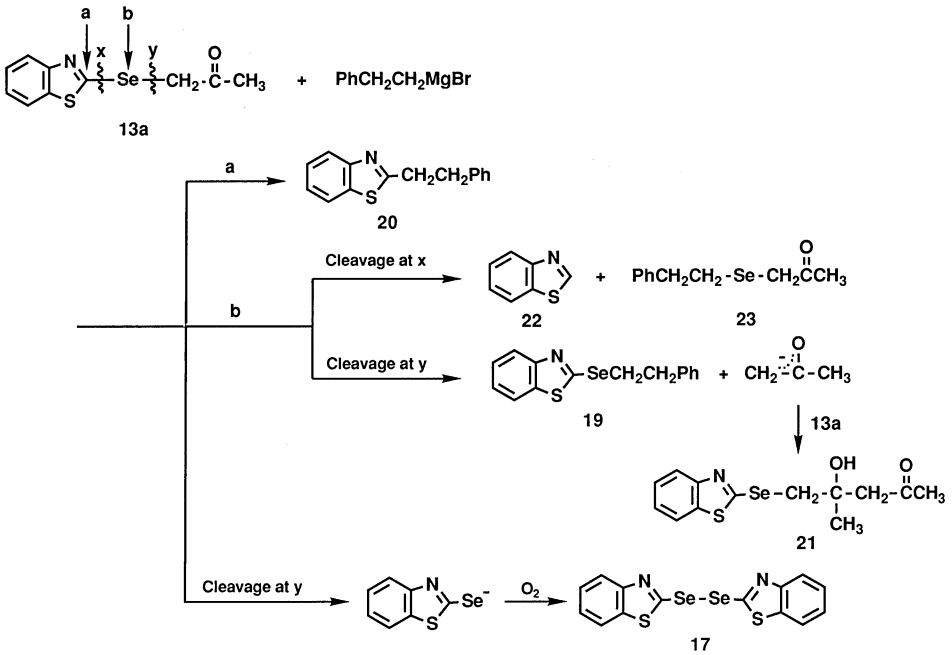
All the products isolated and identified in these experiments could be rationalized by the assumption that the Grignard reagent attacked soft reaction sites rather than the carbonyl group.[12] Thus, the formation of **20** suggested that the Grignard reagent reacted at the C-2 of thiazolyl ring (Scheme 6; path a). Compounds **19** and **21** would arise from the reaction at the selenium atom, followed by bond cleavage between selenium and the methylene carbon atom (Scheme 6; path b–y). On the other hand, when bond cleavage between the selenium and the thiazolyl ring took place after the Grignard reagent had attacked the selenium atom, **22** and **23** were formed (Scheme 6; path b–x). The formation of diselenide **17** suggested the bond cleavage between selenium and the methylene carbon atom.

It would therefore be reasonable to assume that harder organometallic reagent than 2-phenylethylmagnesium bromide is expected to react at the hard carbonyl group. As expected, the reaction of allylmagnesium chloride with **13a** afforded the carbonyl addition product **24a** in 10% yield (Table 2, Entry 1). Although the yield was low, the result encouraged us to optimize the reaction conditions.

Since Lewis acids are known to activate the reaction of organometallic reagents with carbonyl compounds,[13] the reaction of **13a** with allylic Grignard reagents was carried out in the presence of $BF_3{\cdot}OEt_2$ (Scheme 7). When **13a** was allowed to react with allylmagnesium chloride (2.5 equiv) in the presence of 1.2 equiv of $BF_3{\cdot}OEt_2$, **24a** was obtained in 36% yield (Table 2, Entry 2). It was found that the yield of **24a** dramatically increased to 69, 80, and 95% as the amount of $BF_3{\cdot}OEt_2$ increased to 2.2, 3.2, and



Scheme 5.

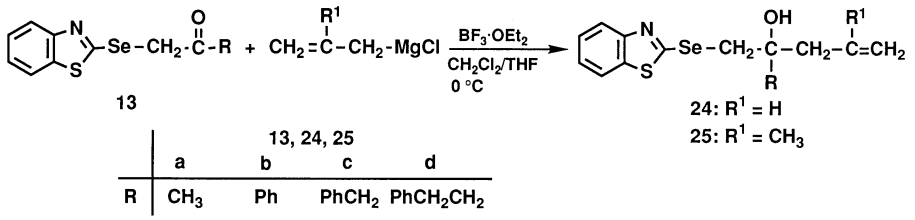


Scheme 6.

Table 2. Reaction of **13** with Allylic Grignard Reagents (2.5 equiv)

Entry	Substrate		Reagent	$BF_3 \cdot OEt_2$	Time	Product	Method[a]; Yield/%	
	No.	R	R	equiv	h	**24** or **25**	A	B
1[b]	**13a**	CH_3	H	—	3.3	**24a**	10	
2			H	1.2	0.25	**24a**	36	
3			H	2.2	1.0	**24a**	69	
4			H	3.2	1.0	**24a**	80	
5			H	4.0	1.0	**24a**	95	
6			CH_3	4.0	1.0	**25a**	74	
7	**13b**	Ph	H	2.5	1.0	**24b**		>99
8			H	4.0	1.0	**24b**	83	>99
9			CH_3	2.5	1.0	**25b**		>99
10			CH_3	4.0	1.0	**25b**	71	>99
11	**13c**	$PhCH_2$	H	2.5	10.5[c]	**24c**		>99
12			H	4.0	1.0	**24c**	74	>99
13			CH_3	2.5	1.5	**25c**		>99
14			CH_3	4.0	1.0	**25c**	96	>99
15	**13d**	$PhCH_2CH_2$	H	2.5	6.0	**24d**		>99
16			H	4.0	1.0	**24d**	73	>99
17			CH_3	2.5	24.0[d]	**25d**		90
18			CH_3	4.0	1.0	**25d**	74	>99

a) See text. b) 1.2 equiv of the Grignard reagent were used. c) Reaction was carried out at 0 °C for 1 h and then at room temperature for 9.5 h. d) Reaction was carried out at 0 °C for 6 h and then at room temperature for 18 h. Ten percent of **13d** was recovered.



Scheme 7.

4 equiv (Table 2, Entries 3, 4, and 5). The reaction of **13a** with 2-methyl-2-propenylmagnesium chloride in the presence of 4 equiv of $BF_3 \cdot OEt_2$ afforded **25a** in 74% yield.

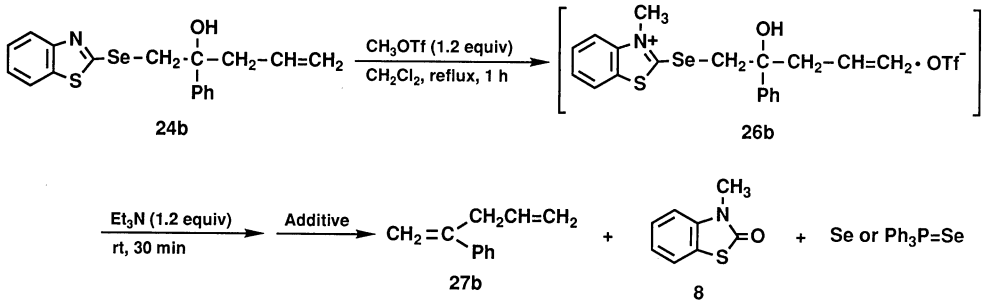
Under the same conditions, 2-(benzoylmethylseleno) benzothiazole (**13b**), 2-(2-oxo-3-phenylpropylseleno) benzothiazole (**13c**), and 2-(2-oxo-4-phenylbutylseleno) benzothiazole (**13d**) also reacted smoothly with allylic Grignard reagents to give the corresponding carbonyl addition products in 71—96% yields (Table 2, Entries 8, 10, 12, 14, 16, and 18).

In these experiments, allylic Grignard reagents were added to a mixture of substrates and $BF_3 \cdot OEt_2$ (Table 2; Method A). When the substrates were added to a mixture of Grignard reagents and $BF_3 \cdot OEt_2$ (Table 2; Method B), the corresponding addition products were obtained in quantitative yields except for one case (Table 2, Entry 17).

With respect to Method B, 2.5 equiv of $BF_3 \cdot OEt_2$ were sufficient to complete conversion of the substrates into the desired products, while longer time was required for the completion of the reaction (Table 2). These results suggest that an activated anionoid reagent would be formed by the addition of $BF_3 \cdot OEt_2$ to allylic Grignard reagents.[13]

Preparation of 1,4-Dienes. As described above, the carbonyl addition products **24** and **25** became readily available, the conversion of **24** and **25** into olefins was next studied.

In the reaction course depicted in Scheme 1, a 3-methylthiazolium type intermediate **4** seems important for addition–elimination reaction (**4**→**5**) and intramolecular displacement by selenium anion (**5**→**6**). Thus, methylation of **24b** was examined. Since no reaction took place when **24b** was treated with methyl triflate (1.2 equiv) in CH_2Cl_2 at room temperature as indicated by silica gel thin layer chromatography (TLC; solvent: hexane–ethyl acetate=20 : 1), the solution was heated under reflux for 1 h where the substrate was converted into a zero-mobility component without any detectable formation of 3-methyl-2(3*H*)-benzothiazolone (**8**) and selenium. Although no attempt was made to isolate and characterize the product, the formation of a polar component suggested the formation of thiazolium salt **26b** rather than expected 2-phenyl-1,4-pentadiene (**27b**). In order to generate oxido anion from **26b**, 1.2 equiv of triethylamine was added to the mixture, liberating selenium as a red precipitate. The mixture was refluxed



Scheme 8.

Table 3. Conversion of **24b** into Olefin **27b** via Thiazolium Triflate **26b**

Entry	Additives/equiv	Conditions[a]		Products and Yield/%		
		Temp	Time/h	**27b**	**8**	Se
1[b]	—	—	—	57	75	36
2	TFA (1.0)	RT	0.5	62	92	47
3	Ph_3P (1.2)	Reflux	3.5	65	79	91[c]

a) Reaction conditions after the additives had been added. b) After addition of Et_3N, the mixture was refluxed for 3 h. c) Yield of Ph_3P=Se.

Table 4. Conversion of **24** and **25** into 1,4-Dienes **27** and **28**

Entry	R	R^1	Substrate	Products and Yield/%		
			24 or **25**	**27** or **28**	**30**	**31**
1	Ph	H	**24b**	**27b**; 94	96	97
2	Ph	CH_3	**25b**	**28b**; 98	93	96
3	$PhCH_2$	H	**24c**	**27c**; 82	93	92
4	$PhCH_2$	CH_3	**25c**	**28c**; 89	92	92
5[a]	$PhCH_2CH_2$	H	**24d**	**27d**; 64	85	57[b]
6	$PhCH_2CH_2$	H	**24d**	**27d**; 83	83	95
7	$PhCH_2CH_2$	CH_3	**25d**	**28d**; 82	86	90

a) Reaction was carried out in the absence of Ph_3P at room temperature. b) Yield of selenium. An unidentified product, presumably polymer, was also obtained in 10-weight % yield based on **24d** used.

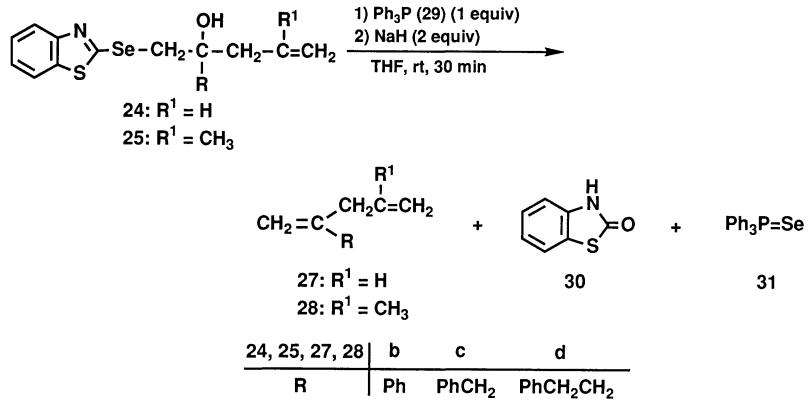
for 3 h to give **27b, 8,** and selenium in 57, 75, and 36% yields, respectively (Scheme 8; Table 3, Entry 1).

Calo et al. have demonstrated that the presence of an acid is indispensable in the deoxygenation of epoxide by 3-methyl-2(3*H*)-benzothiazoleselone. Trifluoroacetic acid is reported to be an acid of choice and other acids including acetic acid, *p*-toluenesulfonic acid, and perchloric acid are less satisfactory.[4] Thus the methylated solution was at first treated with triethylamine as above, followed by treatment with trifluoroacetic acid (1 equiv) at room temperature for 30 min, where **27b, 8,** and selenium were isolated in 62, 92, and 47% yields, respectively (Table 3, Entry 2). Although the yield of **8** increased to 92%, those of **27b** and selenium were still low. In order to facilitate selenium extrusion, the reaction was carried out in the presence of triphenylphosphine (1.2 equiv) to afford **27b, 8,** and triphenylphosphine selenide in 65, 79, and 91% yields, respectively (Table 3, Entry 3).

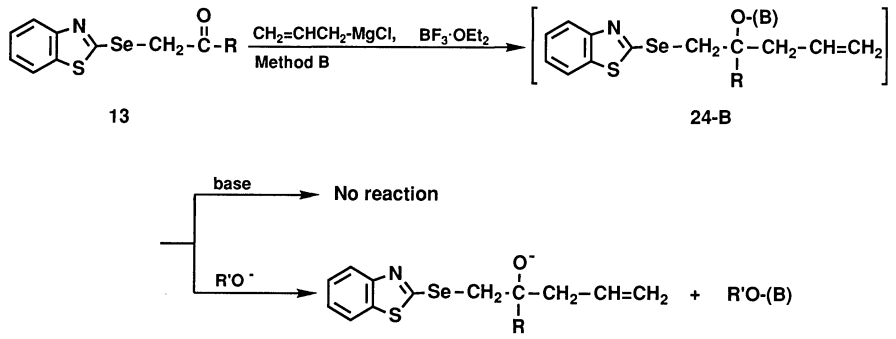
It was found that the methylation of the benzothiazolyl ring is not essential for the Se→O azaaromatic ring rearrangement. Thus, when **24d** was treated with NaH (2 equiv) at room temperature for 30 min, the expected diene **27d**, 2(3*H*)-benzothiazolone (**30**), and selenium were obtained in 64, 85, and 57% yields, respectively (Table 4, Entry 5).

Since the yields of diene and selenium were again lower than that of **30**, the reaction was carried out in the presence of triphenylphosphine (**29**) to facilitate deselenation. Thus, **29** (1 equiv) and sodium hydride (2 equiv) were successively added to a solution of **24d** in THF at room temperature to give **27d, 30**, and triphenylphosphine selenide (**31**) in 83, 83, and 95% yields, respectively (Table 4, Entry 6). Under the same conditions, various 1,4-dienes **27b—d, 28b—d** were prepared in 82—98% isolated yield (Scheme 9, Table 4).

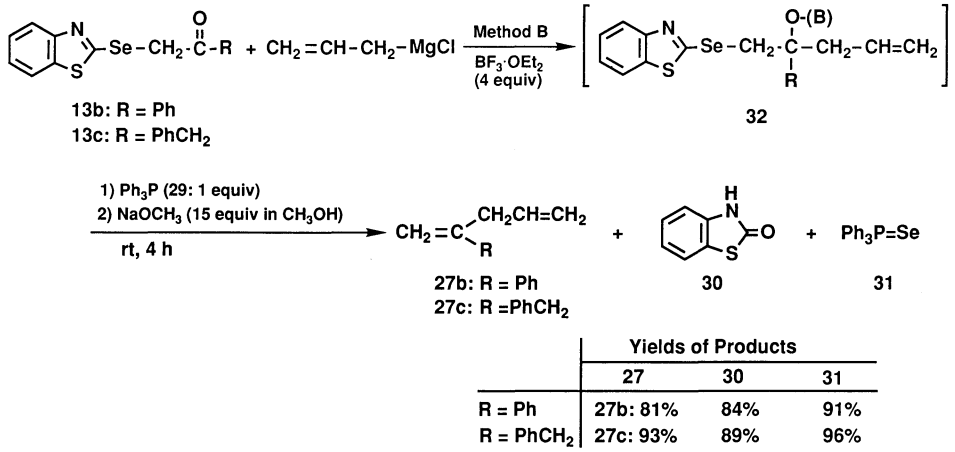
Since the reaction of **13** with allylic Grignard reagents gave the corresponding carbonyl addition products in quantitative yields, we next focused our attention on the procedure by which olefins can be obtained without



Scheme 9.



Scheme 10.

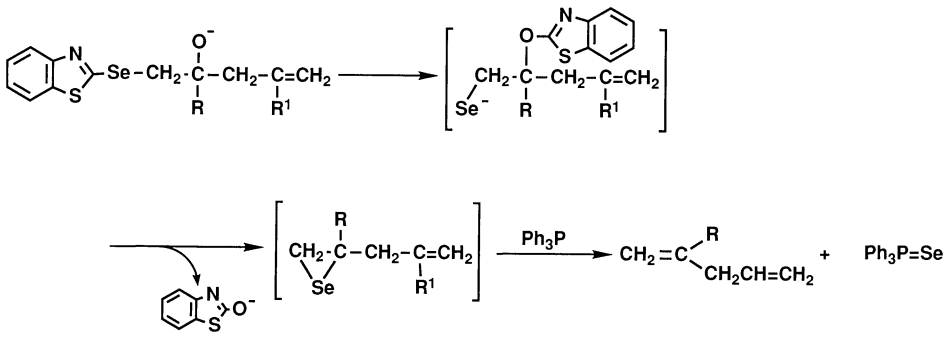


Scheme 11.

isolation of the addition products **24** and **25** (one-pot procedure).

When 2-(benzoylmethylseleno)benzothiazole (**13b**) was allowed to react with allylmagnesium chloride by method B, followed by reflux for 3 h, the diene **27b** was not formed as indicated by thin layer chromatography of the crude reaction mixture. Similarly, **24b** prepared as above (method B) was successively treated with triphenylphosphine (**29**; 1 equiv) and triethylamine (5 equiv), no reaction practically took place. Even when more strong base such as sodium hydride was used in the place of triethylamine, **24b** was again isolated in 97% yield without any detectable formation of **27b**.

These results suggest that the carbonyl addition product (**24, 25**) prepared by method B forms a tight complex with BF_3 which does not generate oxido anion by the treatment with bases. Although no attempt was made to elucidate the structure of the complex, that involving a boron-oxygen bond such as **24-B** (Scheme 10) is most probable. It would therefore be reasonable to



Scheme 12.

assume that an alkoxide is the reagent of choice to promote the formation of oxido anions of **24** and **25** by ligand exchange reaction (Scheme 10).

As expected, when the solution resulted from the reaction of **13b** with allylmagnesium chloride by method B was treated with NaOMe (15 equiv) in MeOH at room temperature for 4 h, olefin **27b** and **30** were obtained in 66 and 89% yields, respectively. Since the yield of **27b** was again lower than that of **30**, the reaction with NaOMe was carried out in the presence of **29** (1 equiv) affording **27b, 30**, and **31** in 81, 84, and 91% yields, respectively. By the same procedure, **13c** was also successfully converted into diene **27c** in 93% yield (Scheme 11).

In summary, through the reactions described herein, a convenient procedure for the preparation of 1,4-dienes has been developed. Although the reaction mechanism of the formation of olefins has not yet been elucidated, that involving the rearrangement of benzothiazolyl residue from selenium atom to oxygen atom would be most likely (Scheme 12). Since a variety of methods for the preparation of 2-(2-hydroxyalkylseleno)azoles of general structure **11** would be conceivable, the work described suggests a number of interesting possibilities for further work.

Experimental

General. All the melting points were obtained on Yanagimoto melting point apparatus and uncorrected. IR spectra were recorded on a JASCO Model A-302 spectrometer. ^{1}H NMR spectra were obtained on a JEOL JNM GX-270 (270 MHz) spectrometer in deuteriochloroform solution using tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-SX-102 mass spectrometer operating under El or FAB conditions. The reactions using selenium compounds were carried out in a well-ventilated hood with caution. All reactions were monitored by thin layer chromatography (TLC; silica gel). Preparative thin layer chromatography was performed on 20 cm×30 cm silica gel plates (Merck silica gel 60 PF_{254} Art. 7749) using UV light for detection and acetonitrile (distilled from P_2O_5) was used for extraction. Column chromatography was carried out on silica gel (Merck silica gel 60 PF_{254} Art. 7734). All solvents used for the reactions were purified by ordinary methods. Elemental analyses were performed by RIKEN Institute, Wako, Saitama.

α-Chloro Ketones. Chloroacetone and phenacyl chloride were purchased from Tokyo Kasei Inc.

1-Chloro-3-phenyl-2-propanone. To a solution of chloroacetyl chloride (10.2 ml, 128 mmol) in THF (100 ml) was added 100 ml of benzylmagnesium chloride (107 mmol, 1.1 M in THF; 1 M=1 mol dm^{-3}) over a period of 5 min at −78 °C and stirred for 1 h at the temperature under argon.[14] To the resulting solution, aqueous saturated NH_4Cl and ether were added and filtered through Hyflo Super-Cel. The ethereal layer was dried with magnesium sulfate. The solvent was evaporated and the residue was separated by column chromatography (hexane–ethyl acetate=20 : 1) to give 1.99 g (11%) of 1-chloro-3-phenyl-2-propanone as slightly yellow syrup. ^{1}H NMR δ=3.84 (2H, s), 4.10 (2H, s), and 7.18—7.36 (5H, m).

1-Chloro-4-phenyl-2-butanone. To a mixture of CuI (0.896 g, 4.7 mmol) and chloroacetyl chloride (6.5 ml, 81 mmol) in THF (94 ml) was added 66 ml of 2-phenylethylmagnesium bromide (86 mmol, 1.3 M in THF) over a period of 15 min at −78 °C and stirred for 45 min at the temperature under argon. To the resulting solution, 80 ml of hydrochloric acid (2 M) and ether were added and filtered through Hyflo Super-Cel. The ethereal layer was separated, the aqueous layer was extracted with ether, and the combined organic layer was dried with magnesium sulfate. The solvent was evaporated and the residue was distilled under nitrogen (128—131 °C/5 mmHg; 1 mmHg≈133.322 Pa) to give 7.02 g (48%) of 1-chloro-4-phenyl-2-butanone. ^{1}H NMR δ=2.86 (2H, t, J=4.62 Hz), 2.87 (2H, t, J=4.62 Hz), 3.99 (2H, s), and 7.14—7.29 (5H, m).

2-Chlorobenzothiazole. This compound was prepared by modifying a literature procedure.[15] To 40 g (0.24 mol) of 2-mercaptobenzothiazole was added 150 ml (1.85 mol) of sulfuryl chloride at 0 °C. The ice bath was removed and the mixture was stirred for 3 h at room temperature. The resulting yellow thick solution was slowly poured onto ice. When a foaming subsided, about 300 ml of benzene was added. The benzene layer was separated, the aqueous layer was extracted with benzene, and the combined organic layer was dried with magnesium sulfate. The solvent was evaporated and the residue was distilled (bp 70—73 °C/2 mmHg; lit,[15] bp 132—134 °C/21 mmHg) to give 35.5 g (87%) of 2-chlorobenzothiazole. IR (neat) 720, 750, 1000, 1015, 1075, 1235, 1305, 1420, and 1480 cm^{-1}.

An Attempt to Prepare 2-Benzothiazoleselenol (15).[16] According to the literature procedure,[8] the reaction of 2-chlorobenzothiazole with NaHSe was attempted. Thus, to 0.192 g (2.43 mmol) of selenium suspended in 1.5 ml of water

was added $NaBH_4$ (0.193 g, 5.08 mmol) in 1.3 ml of water with stirring at room temperature under nitrogen. After 5 min, 2-chlorobenzothiazole (0.26 ml, 2.0 mmol) was added, refluxed for 45 min, and cooled to room temperature. To the solution was added 1 M-sulfuric acid (2—3 ml) to give yellow precipitate. The solid was separated by filtration and washed with water to give 0.324 g (76%) of crude **17** (mp 174—177°C) which was recrystallized from ethanol (yellow crystals, 0.038 g, 22%, mp 173—174°C). The expected **15** could not be obtained. ^1H NMR of **17** δ=7.33 (2H, dt, J=7.58 and 0.99 Hz), 7.44 (2H, dt, J=7.58 and 0.66 Hz), 7.81 (2H, dd, J=7.58 and 0.66 Hz), 7.98 (2H, dd, J=7.58 and 0.99 Hz). MS m/z 428 (M^+), 294, 214, 134.

Bis(2-benzothiazolyl) Diselenide (17).[16] **Method A.** Reaction of 2-chlorobenzothiazole with Na_2Se_2.[9] To a mixture of selenium powder (3.00 g, 38 mmol) and $NaBH_4$ (1.14 g, 30 mmol) was poured 150 ml of cold ethanol (saturated with nitrogen) at 0°C. After vigorous foaming had subsided, the solution was refluxed for 3 h, followed by the addition of 2-chlorobenzothiazole (3.90 ml, 30 mmol) in ethanol (4 ml) and refluxed for 2.2 h. Air was passed through the refluxing mixture for 5—10 min to remove any H_2Se. The boiling solution was filtered through Hyflo Super-Cel. The filtrate was evaporated and a small amount of ether was added to the residue with stirring. The solid was filtered and washed with water to give crude **17** (3.74 g, 59%) which was recrystallized from THF affording **17** as yellow crystals (2.90 g, 45%, mp 179—180°C).

Method B. Air oxidation (in situ) of 2-benzothiazoleselenol (**15**). To a mixture of selenium powder (6.32 g, 80 mmol) and $NaBH_4$ (3.34 g, 88 mmol) was poured 150 ml of cold ethanol (saturated with nitrogen) at 0°C. After vigorous foaming had subsided, the ice bath was removed and stirred at room temperature. When the solution was not colorless after the foaming subsided, a small amount of $NaBH_4$ was added until it turned colorless. 2-Chlorobenzothiazole (10.4 ml, 80 mmol) in ethanol (10 ml) was added to the solution, refluxed for 3 h, and acidified by the addition of 1 M-hydrochloric acid under reflux. In order to oxidize **15** and remove H_2Se, air was passed through the solution for 10 min under reflux. The mixture was filtered through Hyflo Super-Cel still hot. The filtrate was evaporated under reduced pressure to 20—30 ml and 30 ml of water was added with stirring. The crude product was filtered and washed with ether and water. Air was passed through the filtrate for 20–30 min and precipitates were collected by filtration. This procedure (air-bubbling and filtration) was repeated several times until no **17** formed. The combined solids were recrystallized from THF to give 7.16 g (42%) of **17**.

Method C. Oxidation (in situ) of 2-benzothiazoleselenol (**15**) with hydrogen peroxide. Sodium borohydride (4.03 g, 106 mmol) was added portionwise to a suspension of selenium powder (7.58 g, 96 mmol) in ethanol (180 ml, saturated with nitrogen). When the solution was yet purple, a small amount of $NaBH_4$ was added until it turned colorless. After foaming had subsided, 2-chlorobenzothiazole (10.4 ml, 80 mmol) in ethanol (10 ml) was added, refluxed for 4 h, and then air was passed through the mixture for 10 min under reflux. The boiling mixture was filtered through Hyflo Super-Cel. The filtrate was cooled to room temperature and 18 ml of aqueous 1 M-sodium hydroxide solution containing 10% hydrogen peroxide was added with stirring. The solid thus formed was filtered, washed with water, and recrystallized from THF giving **17** (10.4 g, 61%).

Preparation of Grignard Reagents. 2-Phenylethylmagnesium bromide. To a mixture of magnesium turnings (0.85 g, 35 mmol) and THF (10 ml) was added dropwise a solution of 2-phenylethyl bromide (5.4 ml, 40 mmol) in THF (5 ml) over a period of 2.5 h at 0°C and stirred an additional hour under nitrogen.

Allylic Grignard reagents. To a mixture of magnesium turnings (0.70 g, 28.7 mmol) and THF (7 ml) was added dropwise a solution of allyl chloride or 2-methyl-2-propenyl chloride (23 mmol) in THF (4 ml) over a period of 2 h at 0°C and stirred an additional hour under nitrogen. The Grignard reagents prepared were titrated before use.[17]

2-(2-Oxoalkylseleno)benzothiazole (13). A typical procedure. Sodium borohydride (0.84 g, 22 mmol) was added portionwise to a suspension of **17** (4.26 g, 10 mmol) in ethanol (43 ml), refluxed for 15 min, and allowed to cool to room temperature. Phenacyl chloride (3.1 g, 20 mmol) in ethanol (20 ml) was added and stirred for 30 min at room temperature. After the solvent had been evaporated under reduced pressure, dichloromethane and water were added to the residue and filtered through Hyflo Super-Cel. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to give crude **13b** (6.48 g, 98%, mp 93—96°C). Recrystallization from ethanol yielded **13b** as light yellow crystals (5.76 g, 87%, mp 95—98°C). ^1H NMR δ=4.95 (2H, s), 7.30—7.63 (5H, m), 7.80 (1H, d, J=7.26 Hz), 7.93 (1H, d, J=7.59 Hz), 8.07 (2H, dd, J=8.25 and 1.32 Hz). MS m/z 333 (M^+), 228, 214, 135, 105, 77. Found: C, 53.78; H, 3.28; N, 4.23%. Calcd for $C_{15}H_{11}NOSSe$: C, 54.11; H, 3.33; N, 4.21%.

2-(Acetonylseleno)benzothiazole (13a). This compound was isolated by column chromatography (hexane–ethyl acetate=5 : 1) in 96% yield as yellow crystals (mp 45—47°C). ^1H NMR δ=2.39 (3H, s), 4.32 (2H, s), 7.31 (1H, dt, J=7.26 and 0.99 Hz), 7.41 (1H, ddd, J=7.93, 7.25, and 0.99 Hz), 7.78 (1H, dd, J=7.25 and 0.99 Hz), 7.91 (1H, dd, J=7.93 and 0.99 Hz). MS m/z 271 (M^+), 256, 229, 214, 135, 43. Found: C, 44.58; H, 3.36; N, 5.18%. Calcd for $C_{10}H_9NOSSe$: C, 44.33; H, 3.35; N, 5.17%.

2-(3-Phenylacetylmethylseleno)benzothiazole (13c). This compound was obtained in 97% yield as yellow crystals (mp 75—77°C). The product washed thoroughly with hexane was practically pure as indicated by NMR and TLC, the compound being used in the next step without further purification. ^1H NMR δ=3.99 (2H, s), 4.25 (2H, s), 7.21—7.37 (6H, m), 7.44 (1H, dt, J=7.59 and 0.99 Hz), 7.82 (1H, dd, J=7.59 and 0.99 Hz), 7.92 (1H, dd, J=7.59 and 0.99 Hz). MS m/z 347 (M^+), 256, 228, 214, 133, 91, 77. Found: C, 55.31; H, 3.77; N, 3.94%. Calcd for $C_{16}H_{13}NOSSe$: C, 55.38; H, 3.78; N, 4.04%.

2-(2-Oxo-4-phenylbutylseleno)benzothiazole (13d). This compound was obtained as brownish yellow crystalls and recrystallized from ethanol (yield 73%, mp 84—85°C). ^1H NMR δ=2.96 (2H, t, J=6.59 Hz), 3.05 (2H, t, J=6.59 Hz), 4.20 (2H, s), 7.15—7.29 (5H, m), 7.31 (1H, dt, J=7.59 and 0.98 Hz), 7.43 (1H, dt, J=7.59 and 0.66 Hz), 7.79 (1H, dd, J=7.59 and 0.66 Hz), 7.90 (1H, dd, J=7.59 and 0.98 Hz). MS m/z 361 (M^+), 256, 229, 215, 135, 105, 91, 77. HRMS Found: m/z 361.0037. Calcd for $C_{17}H_{15}NOSSe$: M, 361.0040.

Reaction of 13a with 2-Phenylethylmagnesium Bromide. A.

Reaction in the absence of an additive (Table 1, Entry 1). To a solution of **13a** (0.540 g, 2 mmol) in THF (3 ml) was added 2.4 ml of 2-phenylethylmagnesium bromide (2 mmol, 0.82 M in THF) at 0 °C and the mixture was stirred for 1 h at the temperature under argon. The reaction was quenched by the addition of aqueous saturated ammonium chloride and dichloromethane. The resulting mixture was filtered through Hyflo Super-Cel. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried with magnesium sulfate, filtered and evaporated under reduced pressure. The products were separated by column chromatography (benzene–ethyl acetate=10 : 1) to give **17, 19, 21**, and **22**. Yields were summarized in Table 1 (Entry 1).

2-(2-Phenylethylseleno)benzothiazole (19). A syrup. ^{1}H NMR δ=3.19 (2H, t, J=7.75 Hz), 3.57 (2H, t, J=7.75 Hz), 7.16—7.36 (6H, m), 7.41 (1H, ddt, J=7.91, 6.92, and 0.99 Hz), 7.78 (1H, dd, J=7.91 and 0.99 Hz), 7.94 (1H, dd, J=7.91 and 0.66 Hz). MS m/z 319 (M^+), 228, 214, 135, 105, 91, 77.

Benzothiazole (22). A pale yellow liquid. ^{1}H NMR δ=7.40 (1H, dt, J=7.68 and 1.36 Hz), 7.49 (1H, dt, J=7.68 and 1.36 Hz), 7.92 (1H, dd, J=7.68 and 1.36 Hz), 8.14 (1H, dd, J=7.68 and 1.36 Hz), 8.96 (1H, s).

2-(2-Hydroxy-2-methyl-4-oxopentylseleno)benzothiazole (21). A syrup. ^{1}H NMR δ=1.43 (3H, s), 2.16 (3H, s), 2.80 (1H, d, J=16.98 Hz), 2.98 (1H, d, J=16.98 Hz), 3.63 (1H, d, J=13.03 Hz), 3.69 (1H, d, J=13.03 Hz), 5.16 (1H, s), 7.30 (1H, dt, J=7.91 and 0.66 Hz), 7.40 (1H, dt, J=7.91 and 0.66 Hz), 7.77 (1H, dd, J=7.91 and 0.66 Hz), 7.88 (1H, dd, J=7.91 and 0.66 Hz). MS m/z 329 (M^+), 272, 229, 215, 149, 135.

B. Reaction in the presence of CuI (Table 1, Entry 3). To a mixture of **13a** (0.270 g, 1.0 mmol) and CuI (0.025 g, 0.13 mmol) in THF (3 ml) was added 2.1 ml of 2-phenylethylmagnesium bromide (2.5 mmol, 1.2 M in THF) over a period of 30 min at 0 °C and the mixture was stirred for additional 30 min at the temperature under argon. Aqueous saturated ammonium chloride solution and dichloromethane were added and filtered through Hyflo Super-Cel. The resulting mixture was worked up as above and products were separated by TLC (hexane–ethyl acetate=10 : 1) to give **17, 19, 20, 21**, and **22** as summarized in Table 1 (Entry 3).

2-(2-Phenylethyl)benzothiazole (20). Brownish yellow crystals (mp 38—40 °C). ^{1}H NMR δ=3.21 (2H, t, J=8.08 Hz), 3.43 (2H, t, J=8.08 Hz), 7.19—7.38 (6H, m), 7.46 (1H, t, J=7.92 Hz), 7.84 (1H, d, J=7.92 Hz), 7.99 (1H, d, J=7.92 Hz). MS m/z 239 (M^+), 162, 148, 136, 91, 77.

C. Reaction in the presence of TMEDA (Table 1, Entry 4). To a solution of **13a** (0.270 g, 1.0 mmol) and TMEDA (0.38 ml, 2.5 mmol) in THF (3 ml) was added 2.1 ml of 2-phenylethylmagnesium bromide (2.5 mmol, 1.2 M in THF) at 0 °C and the mixture was stirred for 1 h at the temperature under argon. After work-up as above the products were separated by TLC to give **19, 20, 21, 22**, and **23** as summarized in Table 1 (Entry 4).

(2-Phenylethylseleno)acetone (23). A syrup. ^{1}H NMR δ=2.32 (3H, s), 2.81—2.88 (2H, m), 2.93—3.00 (2H, m), 3.21 (2H, s), 7.19—7.33 (5H, m). MS m/z 242 (M^+), 184, 105, 91, 77.

D. Reaction in the presence of BF_3·OEt_2 (Table 1, Entry 5). To a solution of **13a** (0.270 g, 1.0 mmol) in dichloromethane (3 ml) was added BF_3·OEt_2 (0.49 ml, 4 mmol) at 0 °C and stirred for 40 min at the temperature, followed by the addition of 1.9 ml of 2-phenylethylmagnesium bromide (2.5 mmol, 1.3 M in THF) under argon. The reaction was continued for 1 h at 0 °C and the reaction mixture was worked up as above. The products were separated by TLC (hexane–ethyl acetate=5 : 1) to give **19, 21, 22,** and **23** as summarized in Table 1 (Entry 5).

Reaction of 13 with Allylic Grignard Reagents. Method A (Table 2). A typical procedure. To a solution of **13a** (0.270 g, 1.0 mmol) in dichloromethane (3 ml) was added BF_3·OEt_2 (0.49 ml, 4 mmol) at 0 °C and stirred for 40 min at the temperature. Allylmagnesium chloride (1.5 ml, 2.5 mmol, 1.7 M in THF) was then added to the resulting mixture and the mixture was stirred for 1 h at 0 °C. Usual work-up and separation of crude reaction mixture by TLC (hexane–ethyl acetate=10 : 1) gave **24a** in 95% yield (Table 2, Entry 5).

2-(2-Hydroxy-2-methyl-4-pentenylseleno)benzothiazole (24a). A syrup. ^{1}H NMR δ=1.37 (3H, s), 2.46 (2H, d, J=7.26 Hz), 3.46 (1H, d, J=13.19 Hz), 3.56 (1H, d, J=13.19 Hz), 4.42 (1H, bs), 5.14 (1H, dd, J=16.16 and 0.99 Hz), 5.16 (1H, dd, J=10.06 and 0.99 Hz), 5.92 (1H, ddt, J=16.16, 10.06, and 7.26 Hz), 7.29 (1H, dt, J=8.58 and 1.32 Hz), 7.39 (1H, ddd, J=8.58, 7.26, and 1.32 Hz), 7.75 (1H, ddd, J=8.58, 1.32, and 0.66 Hz), 7.88 (1H, ddd, J=7.26, 1.32, and 0.66 Hz). MS m/z 313 (M^+), 272, 215, 149, 135. HRMS Found: m/z 313.0016. Calcd for $C_{13}H_{15}NOSSe$: M, 313.0040.

2-(2-Hydroxy-2-phenyl-4-pentenylseleno)benzothiazole (24b). Yellow crystals (mp 105—107 °C; from ethanol). ^{1}H NMR δ=2.18 (2H, dt, J=6.92 and 2.64 Hz), 3.77 (1H, d, J=13.36 Hz), 3.92 (1H, d, J=13.36 Hz), 5.09 (1H, dq, J=5.61 and 2.64 Hz), 5.14 (1H, dq, J=12.86 and 2.64 Hz), 5.20 (1H, bs), 5.74 (1H, ddt, J=17.75, 10.23, and 6.92 Hz), 7.23—7.51 (7H, m), 7.76 (1H, dt, J=7.92 and 0.66 Hz), 7.92 (1H, dt, J=8.58 and 0.66 Hz). MS m/z 375 (M^+), 334, 253, 229, 215, 149, 135. HRMS Found: m/z 375.0171. Calcd for $C_{18}H_{17}NOSSe$: M, 375.0196.

2-(2-Benzyl-2-hydroxy-4-pentenylseleno)benzothiazole (24c). A syrup. ^{1}H NMR δ=2.46 (2H, ddd, J=7.25, 1.98, and 1.32 Hz), 2.99 (2H, s), 3.48 (2H, s), 4.30 (1H, bs), 5.17 (1H, dt, J=17.47 and 1.32 Hz), 5.21 (1H, ddt, J=10.22, 1.98, and 1.32 Hz), 6.00 (1H, ddt, J=17.47, 10.22, and 7.25 Hz), 7.23—7.36 (6H, m), 7.39 (1H, dt, J=8.25 and 1.32 Hz), 7.73 (1H, dd, J=7.91 and 1.32 Hz), 7.79 (1H, dd, J=8.25 and 1.32 Hz). MS m/z 389 (M^+), 348, 298, 215, 149, 135. HRMS Found: m/z 389.0332. Calcd for $C_{19}H_{19}NOSSe$: M, 389.0353.

2-[2-Hydroxy-2-(2-phenylethyl)-4-pentenylseleno]benzothiazole (24d). White crystals (mp 54—55 °C). ^{1}H NMR δ=1.95 (1H, dd, J=9.57 and 6.26 Hz), 1.96 (1H, dd, J=9.57 and 6.26 Hz), 2.53 (2H, d, J=7.25 Hz), 2.75 (1H, dd, J=9.57 and 6.26 Hz), 2.79 (1H, dd, J=9.57 and 6.26 Hz), 3.40 (1H, ddt, J=16.82, 9.56, and 7.26 Hz), 3.51 (1H, d, J=6.93 Hz), 3.55 (1H, d, J=6.93 Hz), 4.68 (1H, s), 5.169 (1H, d, J=9.56 Hz), 5.174 (1H, d, J=16.82 Hz), 7.21—7.26 (6H, m), 7.36 (1H, dt, J=7.92 and 0.99 Hz), 7.70 (1H, d, J=7.92 Hz), 7.88 (1H, d, J=7.92 Hz). MS m/z 403 (M^+), 362, 215, 149, 135. HRMS Found: m/z 403.0533. Calcd for $C_{20}H_{21}NOSSe$: M, 403.0510.

2-(2-Hydroxy-2-methyl-4-methyl-4-pentenylseleno)benzothiazole (25a). A syrup. ^{1}H NMR δ=1.38 (3H, s), 1.90 (3H, s), 2.42 (2H, s), 3.47 (1H, d, J=13.19 Hz), 3.64 (1H, d, J=13.19 Hz), 4.18 (1H, s), 4.78—4.79 (1H, m), 4.94 (1H, sextet, J=1.32 Hz), 7.28 (1H, dt, J=7.76 and 0.99 Hz), 7.39 (1H, dt, J=7.76 and 0.99 Hz), 7.74 (1H, dd, J=7.76 and 0.99 Hz), 7.88 (1H, dd, J=7.76 and 0.99 Hz). MS m/z 327 (M^+), 272, 215, 149, 135. HRMS Found: m/z 327.0193. Calcd for $C_{14}H_{17}NOSSe$: M, 327.0196.

2-(2-Hydroxy-2-phenyl-4-methyl-4-pentenylseleno)benzothiazole (25b). Yellow crystals (mp 79—81°C). ^{1}H NMR δ=1.57 (3H, s), 2.76 (1H, d, J=13.19 Hz), 2.83 (1H, d, J=13.19 Hz), 3.80 (1H, d, J=13.19 Hz), 3.98 (1H, d, J=13.19 Hz), 4.76 (1H, s), 4.88 (1H, s), 4.88 (1H, bs), 7.22—7.37 (7H, m), 7.76 (1H, dd, J=7.58 and 1.32 Hz), 7.92 (1H, dd, J=7.58 and 1.32 Hz). MS m/z 389 (M^+), 334, 253, 215, 149, 135. Found: C, 58.71; H, 4.84; N, 3.64%. Calcd for $C_{19}H_{19}NOSSe$: C, 58.66; H, 4.92; N, 3.60%.

2-(2-Hydroxy-2-benzyl-4-methyl-4-pentenylseleno)benzothiazole (25c). A syrup. ^{1}H NMR δ=1.95 (3H, s), 2.44 (2H, s), 2.96 (1H, d, J=13.52 Hz), 3.06 (1H, d, J=13.52 Hz), 3.46 (1H, d, J=13.52 Hz), 3.56 (1H, d, J=13.52 Hz), 4.25 (1H, s), 4.82 (1H, s), 4.98 (1H, s), 7.24—7.41 (7H, m), 7.71—7.77 (2H, m). MS m/z 403 (M^+), 348, 312, 272, 215, 135. HRMS Found: m/z 403.0538. Calcd for $C_{20}H_{21}NOSSe$: M, 403.0510.

2-[2-Hydroxy-2-(2-phenylethyl)-4-methyl-4-pentenylseleno]benzothiazole (25d). A syrup. ^{1}H NMR δ=1.95 (3H, s), 1.97—2.06 (2H, m), 2.48 (1H, d, J=13.69 Hz), 2.55 (1H, d, J=13.69 Hz), 2.68—2.84 (2H, m), 3.56 (1H, d, J=13.36 Hz), 3.67 (1H, d, J=13.36 Hz), 4.45 (1H, s), 4.85 (1H, s), 4.98 (1H, s), 7.14—7.33 (6H, m), 7.41 (1H, dt, J=7.76 and 0.99 Hz), 7.77 (1H, d, J=7.91 Hz), 7.89 (1H, d, J=7.76 Hz). MS m/z 417 (M^+), 362, 215, 149, 135. HRMS (FAB Polyethylene glycol 400 matrix) Found: m/z 418.0744. Calcd for $C_{21}H_{24}NOSSe$: M+H, 418.0744.

Reactions of 13 with Allylic Grignard Reagents. Method B (Table 2). A typical procedure. To 1.6 ml of allylmagnesium chloride (2.5 mmol, 1.58 M in THF) was added BF_3·OEt_2 (0.49 ml, 4 mmol) at 0°C and stirred for 5 min at the temperature under argon. A solution of **13b** (0.332 g, 1.0 mmol) in THF (3.5 ml) was then added and stirred for 1 h at 0°C. The resulting mixture was worked up as above and products were separated by column chromatography (hexane–ethyl acetate=5 : 1) to afford **24b** in quantitative yield (Table 2, Entry 7).

Preparation of 1,4-diene 27b from 24b via 26b. Procedure A (Table 3, Entry 1). To a solution of **24b** (0.75 g, 2 mmol) in dichloromethane (6 ml) was added methyl trifluoromethanesulfonate[18] (0.27 ml, 2.4 mmol) at room temperature under argon and the mixture was refluxed for 1 h. Inspection of the reaction mixture by TLC (hexane–ethyl acetate=20 : 1) indicated that the starting material was converted into zero-mobility component. Triethylamine (0.31 ml, 2.4 mmol) was added and the solution was refluxed for 3 h. After the reaction mixture had been cooled to room temperature, water and dichloromethane were added. Insoluble selenium was collected by filtration (yield; 36%) and washed successively with water and dichloromethane. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was separated by column chromatography to give **27b** and **8** in 57 and 75% yields, respectively.

2-Phenyl-1,4-pentadiene (27b). A pale yellow liquid. ^{1}H NMR δ=3.25 (2H, dt, J=6.59 and 0.99 Hz), 5.07 (1H, ddt, J=10.21, 1.98, and 0.99 Hz), 5.08 (1H, q, J=0.99 Hz), 5.03 (1H, dq, J=6.59 and 1.98 Hz), 5.39 (1H, q, J=0.99 Hz), 5.90 (1H, ddt, J=16.80, 10.21, and 6.59 Hz), 7.22—7.39 (3H, m), 7.41—7.45 (2H, m). MS m/z 144 (M^+), 129, 115, 103, 91, 77.

3-Methyl-2(3*H*)-benzothiazolone (8). Yellow crystals (mp 75—78°C; lit,[19] mp 76°C). ^{1}H NMR δ=3.42 (3H, s), 6.94—7.41 (4H, m).

Procedure B (Table 3, Entry 2). Methylation of **24b** (0.374 g, 1.0 mmol) was carried out in the same way as described in Procedure A. After triethylamine (0.15 ml, 1.2 mmol) had been added and the mixture was stirred for 30 min at room temperature, trifluoroacetic acid (0.07 ml, 1.0 mmol) was added and the solution was stirred for 30 min at the temperature. Aqueous saturated sodium hydrogencarbonate solution and dichloromethane were added. The resulting mixture was worked up as described in procedure A and the products were separated by column chromatography (hexane–ethyl acetate=10 : 1).

Procedure C (Table 3, Entry 3). Methylation of **24b** (0.374 g, 1.0 mmol) and subsequent treatment with triethylamine (0.15 ml, 1.2 mmol) were carried out in the same way as described in procedure B. To the resulting mixture was added a solution of triphenylphosphine (0.31 g, 1.2 mmol) in dichloromethane (1 ml). The mixture was refluxed for 3.5 h and then cooled to room temperature. The resulting mixture was worked up as described in procedure A and the products were separated by column chromatography (hexane–ethyl acetate=10 : 1).

Triphenylphosphine Selenide (31). White crystals (mp 184—185°C, lit,[20] mp 184—185°C). ^{1}H NMR δ=7.41—7.64 (9H, m), 7.66—7.77 (6H, m).

Direct Conversion of 24 or 25 into 1,4-Diene 27 or 28 (Table 4). A typical method. To a solution of **24b** (0.367 g, 0.98 mmol) and triphenylphosphine (0.257 g, 0.98 mmol) in THF (3 ml) was added sodium hydride (0.086 g, 1.96 mmol, 55% in mineral oil) at room temperature and stirred for 30 min at the temperature. Aqueous saturated ammonium chloride and dichloromethane were added and filtered through Hyflo Super-Cel. The organic layer was separated and aqueous layer was extracted with dichloromethane. The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to a small volume (solution A). Since the complete removal of the solvent caused ca. 5% loss of the dienes, aliquots of the solution A was then taken to determine molar ratio of products by NMR spectroscopy. After the last traces of solvents were removed under reduced pressure, the products were separated by TLC (hexane–ethyl acetate=20 : 1). The yields of dienes summarized in Table 4 were those calculated from the NMR spectra of the solution A based on isolated yield of **30**.

2-Benzyl-1,4-pentadiene (27c). A pale yellow liquid. ^{1}H NMR δ=2.71 (2H, ddd, J=6.92, 1.65, and 0.66 Hz), 3.34 (2H, s), 4.78 (1H, d, J=1.65 Hz), 4.86 (1H, d, J=1.65 Hz), 5.04 (1H, dq, J=17.14 and 1.65 Hz), 5.05 (1H, ddt, J=10.22, 1.65, and 0.66 Hz), 5.81 (1H, ddt, J=17.14, 10.22, and 6.92 Hz), 7.13—7.16 (5H, m). MS m/z 158 (M^+).

2-(2-Phenylethyl)-1,4-pentadiene (27d). A pale yellow liquid. ^{1}H NMR δ=2.32 (2H, t, J=7.59 Hz), 2.73 (2H, ddd, J=6.92, 1.96, and 0.98 Hz), 2.78 (2H, t, J=7.59 Hz), 4.80 (1H, s), 4.81 (1H, s), 5.05 (1H, ddt, J=10.22, 1.96, and 0.98 Hz), 5.07 (1H, dq, J=17.24 and 1.96 Hz), 5.82 (1H, ddt, J=17.24, 10.22, and 6.92 Hz), 7.08—7.30 (5H, m). MS m/z 172 (M^+), 157, 143, 131, 115, 104, 91. HRMS Found: m/z 172.1300. Calcd for $C_{13}H_{16}$: M, 172.1252.

2-Methyl-4-phenyl-1,4-pentadiene (28b). A pale yellow liquid. ^{1}H NMR δ=1.72 (3H, t, J=0.99 Hz), 3.21 (2H, q, J=0.99 Hz), 4.77 (1H, septet, J=0.99 Hz), 4.81 (1H, septet, J=0.99 Hz), 5.11 (1H, t, J=0.99 Hz), 5.43 (1H, d, J=0.99 Hz),

7.21—7.34 (3H, m), 7.40—7.51 (2H, m). MS m/z 158 (M^+).

2-Methyl-4-benzyl-1,4-pentadiene (28c). A pale yellow liquid. ^{1}H NMR δ=1.68 (3H, s), 2.67 (2H, s), 3.29 (2H, s), 4.73 (1H, m), 4.80 (1H, m), 4.84 (1H, m), 4.87 (1H, m), 7.14—7.31 (5H, m). MS m/z 172 (M^+), 157, 142, 130, 117, 104, 91, 81. HRMS Found: m/z 172.1289. Calcd for $C_{13}H_{16}$: M, 172.1252.

2-Methyl-4-(2-phenylethyl)-1,4-pentadiene (28d). A pale yellow liquid. ^{1}H NMR δ=1.67 (3H, dd, J=1.32 and 0.66 Hz), 2.31 (2H, t, J=7.59 Hz), 2.75 (2H, t, J=7.59 Hz), 2.78 (2H, dd, J=0.99 and 0.65 Hz), 4.76 (1H, dd, J=2.31 and 0.99 Hz), 4.81 (1H, dd, J=2.31 and 0.65 Hz), 4.82 (1H, dd, J=3.30 and 0.66 Hz), 4.86 (1H, dd, J=3.30 and 1.32 Hz), 7.15—7.30 (5H, m). MS m/z 186 (M^+), 171, 143, 129, 115, 104, 91. HRMS Found: m/z 186.1369. Calcd for $C_{14}H_{18}$: M, 186.1409.

2(3*H*)-Benaothiazolone (30). Yellow crystals (mp 133—135 °C, lit,[21] mp 136 °C). ^{1}H NMR δ=7.12—7.34 (3H, m), 7.41 (1H, d, J=7.23 Hz), 10.26 (1H, bs).

Preparation of 1,4-dienes 27b and 27c from 13b and 13c by a One-Pot Procedure (Scheme 10). A typical procedure. To a solution of allylmagnesium chloride (1.4 ml, 2.5 mmol, 1.75 M in THF) was added BF_3·OEt_2 (0.49 ml, 4 mmol) at 0 °C and the solution was stirred for 5 min at the temperature, followed by the addition of **13b** (0.332 g, 1.0 mmol) in THF (3.5 ml) under argon. The resulting solution was stirred for 1 h at 0 °C, allowed to warm to room temperature, and triphenylphosphine (0.332 g, 1.0 mmol) was added to it. When the triphenylphosphine was dissolved, 3.75 ml of sodium methoxide (15 mmol, 4 M in methanol) was added and the solution was stirred for 4 h at room temperature. 1 M-Hydrochloric acid and dichloromethane were added and the mixture was filtered through Hyflo Super-Cel. The filtrate was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by TLC (hexane–ethyl acetate=20 : 1) to give **27b, 30,** and **31** in 81, 84, and 91% yields, respectively.

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