CHEMISTRY LETTERS, pp. 661-664, 1991

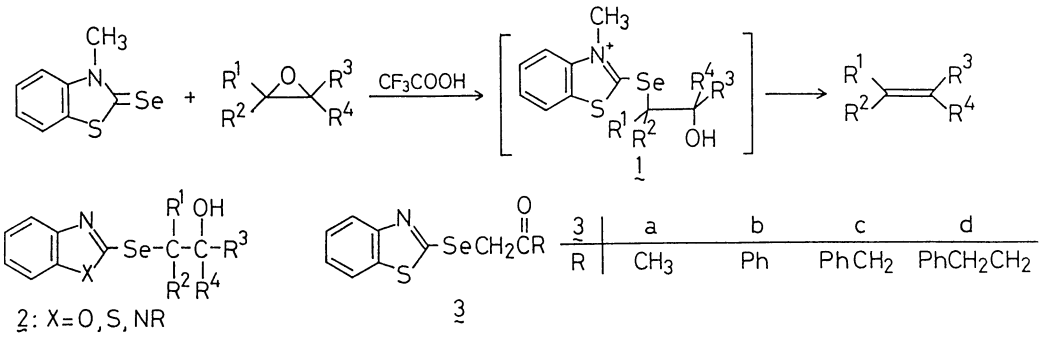
Preparation of 1,4-Dienes from 2-(2-Hydroxyalkylseleno)benzothiazoles by the Reaction involving Se→O Aza-aromatic Ring Rearrangement

Koichi SHIBATA, Hirofumi SHIONO, and Oyo MITSUNOBU*
Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, 6-16-1 Chitosedai, Setagaya-ku, Tokyo 157

The reaction of 2-(acylmethylseleno)benzothiazoles with allylic Grignard reagents in the presence of $BF_3 \cdot OEt_2$ gave the corresponding 2-(2-hydroxyalkylseleno)benzothiazoles which, on treatment with NaH and Ph_3P, 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]

Calo and coworkers have reported the deoxygenation of epoxides to the corresponding olefins by the reaction with 3-methyl-(3H)benzothiazole-2-selone in the presence of trifluoroacetic acid, where the intermediacy of a thiazolium salt 1 is proposed (Scheme 1).[3] It would therefore be reasonable to assume that 2-(2-hydroxyalkylseleno) aza-aromatic compounds of general formula 2 can be converted into the olefins under the conditions where Se→O rearrangement of the aza-aromatic residue takes place. We report herein a convenient procedure for the preparation of 1,4-dienes using the reaction involving Se→O aza-aromatic ring rearrangement.

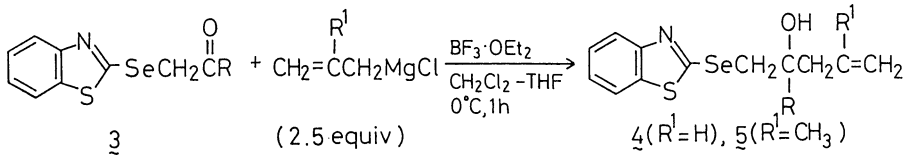


Scheme 1.

The starting materials for this study, 2-(acylmethylseleno)benzothiazoles 3, were prepared by the reaction of 2-(sodioseleno)benzothiazole with α-halo ketones in good to excellent yields.[4)]

At the outset, the reaction of 2-(acetonylseleno)benzothiazole (3a) with Grignard reagents was examined. Although allylmagnesium chloride gave a mixture of products, the reaction in the presence of $BF_3 \cdot OEt_2$ (1.2 equiv. with respect to 3a) afforded the desired carbonyl addition product 4a in 36% yield (Table 1, Entry 1). The yield of 4a depended upon the amount of $BF_3 \cdot OEt_2$; when 4 equiv. of $BF_3 \cdot OEt_2$ was used, 4a was isolated in a 95% yield (Scheme 2; Table 1, Entries 1-4).[5)]

Under the same conditions, 2-(benzoylmethylseleno)-, 2-(phenylacetylmethylseleno)-, and 2-(3-phenylpropionylmethylseleno)benzothiazoles (3b, 3c, and 3d) reacted with allylmagnesium chloride or 2-methyl-2-propenylmag-



3 4(R1=H), 5(R1=CH3)

	3, 4, 5			
	a	b	c	d
R	CH_3	Ph	$PhCH_2$	$PhCH_2CH_2$

Scheme 2.

Table 1. Reaction of 3 with allylic Grignard reagents

Entry	Substrate	$CH_2=C(R^1)CH_2MgCl$	$BF_3 \cdot OEt_2$	Product	Method[a)] and yield/%	
	R	R^1	equiv.	4 or 5	A	B
1	3a	CH_3	H	1.2	4a	36[b)]
2	3a	CH_3	H	2.2	4a	69
3	3a	CH_3	H	3.2	4a	80
4	3a	CH_3	H	4.0	4a	95
5	3a	CH_3	CH_3	4.0	5a	74
6	3b	Ph	H	4.0	4b	83 100
7	3b	Ph	CH_3	4.0	5b	71 100
8	3c	$PhCH_2$	H	4.0	4c	74 100
9	3c	$PhCH_2$	CH_3	4.0	5c	96 100
10	3d	$PhCH_2CH_2$	H	4.0	4d	73 100
11	3d	$PhCH_2CH_2$	CH_3	4.0	5d	74 100

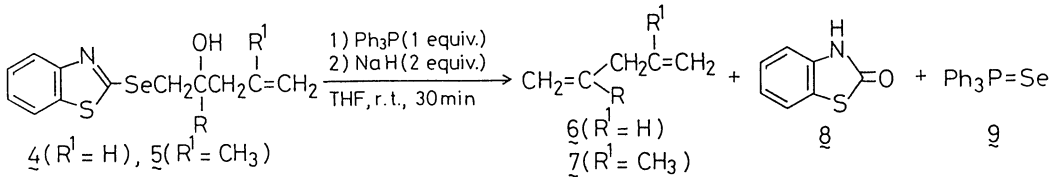
a) Method A: Grignard reagents (2.5 mmol) were added to a mixture of 3 (1 mmol) and $BF_3 \cdot OEt_2$. Method B: Compound 3 (1 mmol) was added to a mixture of Grignard reagents (2.5 mmol) and $BF_3 \cdot OEt_2$.

b) Reaction time: 0.25 h.

nesium chloride to afford the corresponding adducts in 71-96% yields as summarized in Table 1.

In these experiments, allylic Grignard reagents were added to a mixture of substrates and $BF_3 \cdot OEt_2$ (Table 1; Method A). When the substrates were added to a mixture of Grignard reagents and $BF_3 \cdot OEt_2$,[5] the corresponding adducts were obtained in quantitative yields (Table 1; Method B).

Conversion of 4 and 5 to olefins was next investigated (Scheme 3). When 4d was treated with NaH (2 equiv.) at room temperature for 30 min, the expected 1,4-diene 6d, benzothiazol-2-one (8), and selenium were obtained in 64%, 85%, and 57% yields, respectively (Table 2, Entry 5). Since the yields of diene and selenium were lower than that of 8, the reaction was carried out in the presence of triphenylphosphine to facilitate deselenation. Thus, triphenylphosphine (1 equiv.) and NaH (2 equiv.) were successively added to a solution of 4d in THF, and the resulting mixture was



	4, 5, 6, 7		
	b	c	d
R	Ph	$PhCH_2$	$PhCH_2CH_2$

Scheme 3.

Table 2. Preparation of 1,4-dienes

Entry	Substrate			Products and yields/%[a]		
	4 or 5	R	R^1	6 or 7	8	9
1	4b	Ph	H	6b: 94%(81%)	96%(84%)	97%(91%)
2	5b	Ph	CH_3	7b: 98	93	96
3	4c	$PhCH_2$	H	6c: 82 (93)	93 (89)	92 (96)
4	5c	$PhCH_2$	CH_3	7c: 89	92	92
5	4d[b]	$PhCH_2CH_2$	H	6d: 64	85	57[c]
6	4d	$PhCH_2CH_2$	H	6d: 83	83	95
7	5d	$PhCH_2CH_2$	CH_3	7d: 82	86	90

a) The numbers in parentheses represent yields obtained in a one-pot procedure.

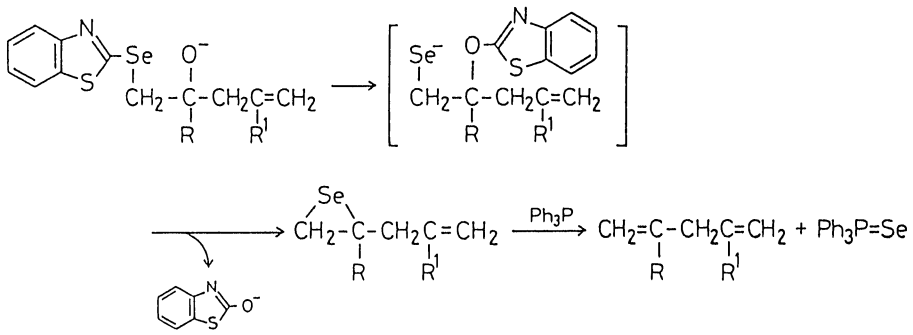
b) Reaction was carried out in the absence of Ph_3P at room temperature.

c) Yield of selenium. An unidentified product, presumably polymer, was also obtained in 10-weight% yield based on 4d used.

stirred for 30 min at room temperature to give 6d, 8 and triphenylphosphine selenide (9) in 83%, 83%, and 95% yields, respectively (Table 2, Entry 6). Under the same conditions, various 1,4-dienes (6b-6d, 7b-7d) were prepared in 82-98% isolated yields (Table 2).

The preparation of olefins by the present method can be performed in a one-pot procedure. Thus, after 3b or 3c was allowed to react with allylmagnesium chloride by method B, the resulting solution was in situ treated with triphenylphosphine (1 equiv.) and sodium methoxide (4 M, 3.8 ml, 15 equiv.) in methanol at room temperature for 4 h giving 6b or 6c in 81% or 93% yield, respectively (Table 2, Entries 1 and 3).

Although the reaction mechanism of the formation of olefins has not yet been elucidated, that involving Se→O rearrangement of benzothiazolyl residue would be most likely (Scheme 4).



Scheme 4.

References

1) See for example, C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis," Pergamon Press, Oxford (1986).

2) In substitution reaction, leaving groups have an inverse relation to nucleophiles. Thus, good nucleophiles are generally very hard to displace. See for example, J. M. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd ed, McGraw-Hill Book Company, New York, and Kogakusha Company, Ltd., Tokyo (1970).

3) V. Calo, L. Lopez, A. Mincuzzi, and G. Pesce, Synthesis, 1976, 200: See also, A. Ogawa, J. Miyake, S. Murai, and N. Sonoda, Tetrahedron Lett., 26, 669 (1985).

4) Reduction of 2,2'-dibenzothiazolyldiselenide by $NaBH_4$ in ethanol gave 2-(sodioseleno)benzothiazole, which in situ reacted with α-halo ketones to afford the corresponding 2-(acylmethylseleno)benzothiazoles in good yields (3a; 96%, 3b; 91%, 3c; 97%, 3d; 73%).

5) For a review of the reaction of organometallics in the presence of Lewis acids, see; Y. Yamamoto, Angew. Chem., Int. Ed. Engl., 25, 947 (1986).

(Received December 18, 1990)