REGIO-AND STEREOCHEMISTRY OF THE ZnC1, MEDIATED CONVERSION

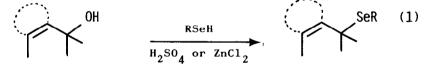
OF 3-HYDROXYLVINYL SELENIDES INTO 1, 3-BIS(SELENO)-PROPENES

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The title process extends the scope of a recently reported reaction, gives general access to the largely unknown 1,3-bis(seleno)-propenes and reveals interesting aspects of allylic nucleophilic substitution.

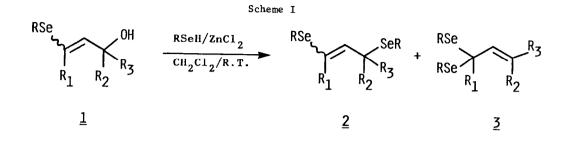
The ability of certain alcohols to form thioethers with thiols in strongly acidic medium has led to the recognition that allylic and benzylic alcohols can be transformed efficiently into the corresponding sulfides  $^{2,3}$  or selenides  $^{4}$  when reacted with thiols or selenols in the presence of Brönsted  $^{2}$  or Lewis  $^{3,4}$  acids (Eq. 1).



For our work on selenium stabilized allyl cationic systems we needed 3-hydroxyvinyl selenides <u>1</u> and 1,3-bis(seleno)-propenes <u>2</u>. The latters may also be considered as useful formyl vinyl anion equivalents <sup>5</sup> or selenoallyl anion precursors  $^{6,7}$ .



We therefore examined transformation of 1 into 2 via the above mentioned reaction and herein we report the most salient features of the results we obtained (SchemeI). Substitution of the hydroxyl group proceeds in good yield in all cases which shows that the reported reactions <sup>4</sup> are not limited to unfunctionalized allyl alcohols. In many cases however two main products are formed, the desired 1,3-bis(seleno)-propenes 2 and 1,1-bis(seleno)-2-propenes 3.



Entry	Starting <u>l</u>				R	<u>2</u> (E:Z)	:	3	Yield (%) in <u>2+3</u>
	R <sub>1</sub>	<sup>R</sup> 2	R <sub>3</sub>						
1	Me	н	н	z	Me	100(34:66)	:	0	54
2	H	н	н	z	"	100(40:60)	:	0	73
3	н	н	н	Е	"	100(100:0)	:	0	82
4	н	Me	н	z	п	68(66:34)	:	32	60
5	н	Me	н	E	- 11	70(7 <b>0:</b> 30)	:	30	63
6	н	Me	Me	Z	11	0	:	100	79
7	н	Me	Me	E		0	:	100	80
8	н	н	н	Z	Ph	100(50:50)	:	0	75
9	н	н	н	E	17	100(100:0)	:	0	79
10	н	Me	н	Z	- 11	67(70:30)	:	33	68
11	н	Me	н	Е	"	66(100:0)	:	34	64
12	н	Me	Me	Z	"	0	:	100	63
13	н	Me	Me	E	"	o	:	100	61
14	Me	H	н	Z	"	100(37:63)	:	0	81

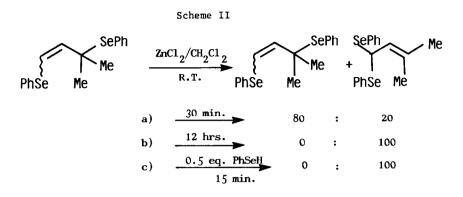
The structure of these products and the geometrical configuration of 2 are closely connected to and depend on the intimate mechanisms of the allylic nucleophilic substitution reactions involved. In spite of the tremendous amount of work devoted to the latter subject <sup>8</sup> it is hardly possible to make predictions about the precise nature of the products to be expected from such novel substrates as <u>1</u> and under heterogeneous conditions. Indeed, the sensitivity of allyl selenides towards 1,3-sigmatropic rearrangement catalyzed by acid and/or light <sup>9</sup> is another complicating factor to be considered in addition to those related to the  $S_{N1}$ ,  $S_{N2}$ ,  $S_{N2}$ ,  $S_{N1}$ , and ion pair mechanisms.

Thus entries 1,2,8 and 14 show that even primary Z-alcohols change their configuration to a large extent (34-50 %; entries 1,2,8,14) while primary E alcohols undergo substitution with complete retention (entries 3 and 9). This pattern is quite different from that observed in solvolysis 10 or in substitution with organometallics 8.

We have also found that reaction temperature was an important factor for the geometrical isomerisation and, quite surprisingly, changing the solvent did not modify the E/Z ratio. When the title transformation was carried out on 3-methyl-3-phenylseleno-2-buten-1-ol (Z) in dichloromethane at 21,0,-40 and  $-78^{\circ}$ C E/Z ratios in the corresponding <u>2</u> of 37/63; 37/63; 16/84 and 12/88 respectively were observed. On the other hand the same reaction effected on 3-phenylseleno-2-propen-1-ol (Z) in benzene, carbon tetrachloride, dichloromethane, 1,2-di-chloroethane and nitromethane <sup>11</sup> almost invariably produced a 1:1 mixture of E and Z 1,3-bis-(phenylseleno)-propenes.

Since it is known that  $\gamma$ -substitution of primary substrates occurs especially with soft organometallics <sup>12,13</sup>, a plausible explanation of our results could be that a large fraction of primary alcohols <u>1</u> suffer  $\gamma$ -attack to give <u>3</u> as the first product. Under the influence of the acidic medium the latter would then rearrange rapidly <sup>9</sup> and completely to <u>2</u>. This view is in agreement with our further results. As one proceeds to secondary alcohols <u>1</u> a ratio of 2:1 is observed for products <u>2</u> and <u>3</u> together with a higher degree of isomerisation (entries 4,5 and 10,11). Finally, tertiary alcohols give exclusively the acetals <u>3</u> (entries 6,7,12,13).

On the basis of additional experiments shown in Scheme II it cannot be excluded that tertiary alcohols react by both  $S_{N1}$  (or ion pair) and  $S_{N2}$ , mechanisms producing eventually a mixture of the corresponding 2 and 3. In these cases however and under the experimental conditions (i.e. in the presence of selenol, Scheme IIc) 2 is rapidly rearranged into 3, the sole isolated product.



We are currently investigating the generality of the last two observations as well as the role played by the above mentioned 1,3-sigmatropic rearrangement in the regio-and stereochemical outcome of these allylic substitution reactions.

All the compounds (1, 2 and 3) discussed in this paper have been properly characterized by spectroscopic (<sup>1</sup>HNMR, IR, Mass) and combustion analytical means <sup>14</sup>.

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## References and Notes

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- 14) Details on the preparation of these compounds will be given in a forthcoming full paper.

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