

Entry	Starting <u>1</u>				R	<u>2</u> (E:Z)	:	<u>3</u>	Yield (%) in <u>2+3</u>
	R ₁	R ₂	R ₃	Z					
1	Me	H	H	Z	Me	100(34:66)	:	0	54
2	H	H	H	Z	"	100(40:60)	:	0	73
3	H	H	H	E	"	100(100:0)	:	0	82
4	H	Me	H	Z	"	68(66:34)	:	32	60
5	H	Me	H	E	"	70(70:30)	:	30	63
6	H	Me	Me	Z	"	0	:	100	79
7	H	Me	Me	E	"	0	:	100	80
8	H	H	H	Z	Ph	100(50:50)	:	0	75
9	H	H	H	E	"	100(100:0)	:	0	79
10	H	Me	H	Z	"	67(70:30)	:	33	68
11	H	Me	H	E	"	66(100:0)	:	34	64
12	H	Me	Me	Z	"	0	:	100	63
13	H	Me	Me	E	"	0	:	100	61
14	Me	H	H	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 subject⁸ it is hardly possible to make predictions about the precise nature of the products to be expected from such novel substrates as 1 and under heterogeneous conditions. Indeed, the sensitivity

of allyl selenides towards 1,3-sigmatropic rearrangement catalyzed by acid and/or light ⁹ 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.

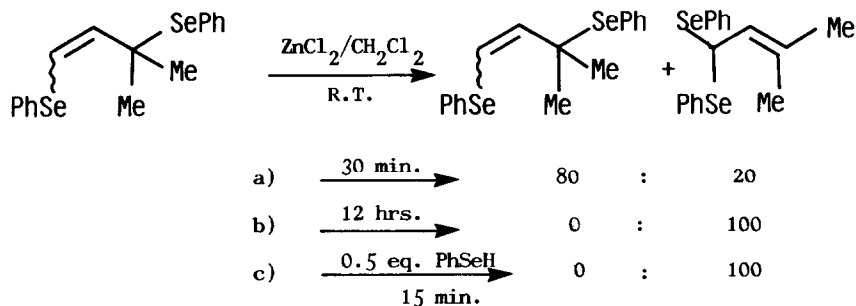
Thus entries 1,2,8 and 14 show that even primary Z-alcohols change their configuration to a large extent (34-50 %; entries 1,2,8,14) while primary E alcohols undergo substitution with complete retention (entries 3 and 9). This pattern is quite different from that observed in solvolysis ¹⁰ or in substitution 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°C E/Z ratios in the corresponding 2 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-dichloroethane and nitromethane ¹¹ almost invariably produced a 1:1 mixture of E and Z 1,3-bis-(phenylseleno)-propenes.

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

Scheme II



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 ($^1\text{H NMR}$, IR, Mass) and combustion analytical means ¹⁴.

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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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