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UNUSUAL REACTIVITY OF SELENOBORANES TOWARDS EPOXIDES : NEW SELECTIVE ROUTES TO β-HYDROXYSELENIDES AND ALLYLALCOHOLS

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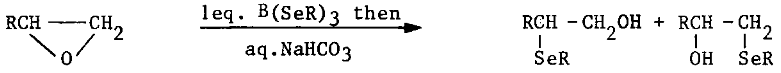
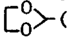
Selenoboranes react with terminal,α,β- di-and trisubstituted epoxides to produce β-hydroxyselenides (or olefins) in the two first cases and allyl alcohols in the last one. A very high stereodescrimination has been observed for α,β-disubstituted epoxides : the cis epoxide being much more reactive.

Trisphenylseleno- [1] and trismethylseleno- [2]boranes have recently been successfully used for the selenoacetalization of carbonyl compounds [1,2]. The last reaction does not require an acid catalyst [2]. During the screening of the reactivity of selenoboranes with other functional groups, we were faced with their unusual reactivity with epoxides. Thus we found that selenoboranes (1mol.eq.) react with epoxides (1mol.eq.) in $CHCl_3$ (1ℓ/mol.) at room temperature or below (25° or 0°). The nature of the product obtained after hydrolysis of the reaction mixture, is strictly dependent upon the nature and the number of substituents attached to the oxirane ring, and in some cases (e.i. α,β-disubstituted epoxides) also depends upon the stereochemistry of the starting epoxide.

The reaction which can be exothermic, is particularly rapid (⩽ 20°,⩽ 1hr) for terminal epoxides. It produces β-hydroxyselenides in which the selenium atom is mainly attached to the less substituted carbon atom if an alkyl group is present on the epoxide ring and to the more substituted one if the substituent is a phenyl group. The last results markedly contrast with the behaviour of selenolate ions [3a,3c], which lead to a mixture of regioisomers (Scheme I, entry e). Interestingly, a high function selectivity is observed since the acetal group, which is usually affected by the reagent (if >5h)[4] remains unchanged under the conditions used (Scheme I, entry c).

SCHEME I



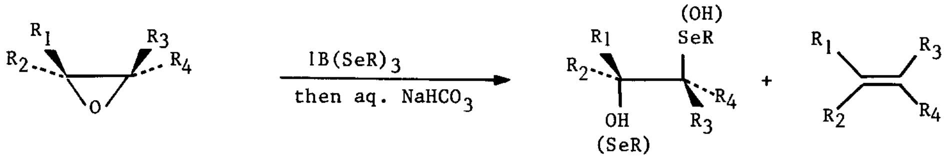
	R	Conditions	Yield (%)	Yield (%)
a	C_6H_{13}	$B(SeCH_3)_3$/0°/0.7h	-	81
b	C_6H_{13}	$B(SeC_6H_5)_3$/0°/0.7h	13	85
c	 $-(CH_2)_8$	$B(SeCH_3)_3$/20°/1h	0	70
d	C_6H_5	$B(SeCH_3)_3$/0°/0.5h	63	0
e	C_6H_5	$(CH_3Se)_2/NaBH_4/CH_3OH$	26	34
f	C_6H_5	$B(SeC_6H_5)_3$/-25°/0.5h	70	0

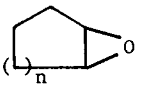
α,β-disubstituted epoxides also react with selenoboranes but there is a tremendous difference of reactivity between the cis and the trans isomers [5]. The reaction is exothermic with the former and goes to completion after 1 hr at 20° whereas the trans epoxides require much longer time (∿54h at 20°)to reach the same level of conversion.

The cisepoxides produce a regioisomeric mixture of the two β-hydroxyselenides resulting from the ring opening by an <u>anti</u> fashion, when the reaction mixture is quenched after 1h with aqueous $NaHCO_3$ (see Scheme II). Stirring for prolonged period of time(∿1 day at 20°)leads to increasing yield of cis olefins probably resulting from the slow decomposition of the intermediary β-seleno borate [6].

The trans epoxideslead mainly to the trans olefins in good yield when the reaction is quenched as usual after long reaction time (> 24h). Quenching after 2/3 hrs leadshowever to a low yield of β-hydroxyselenides (mixture of regioisomers, <u>anti</u> ring opening) beside unreacted epoxides.

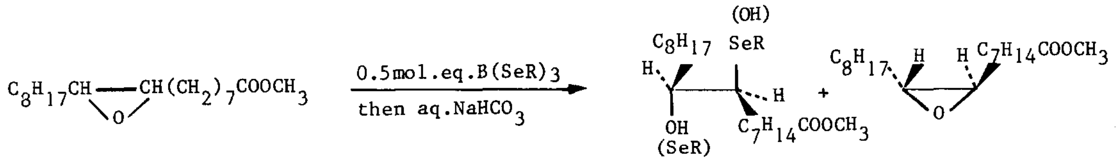
SCHEME II



R_1	R_2	R_3	R_4			
C_5H_{11}	H	CH_3	H	$B(SeCH_3)_3$/20°/1.5h	72	0
				$B(SeC_6H_5)_3$/20°/0.8h	77	0
C_8H_{17}	H	$-C_7H_{14}COOCH_3$	H	$B(SeCH_3)_3$/20°/1h	67	0
				$B(SeCH_3)_3$/20°/49h	17	52
				$B(SeC_6H_5)_3$/20°/0.6h	77	0
C_5H_{11}	H	H	CH_3	$B(SeCH_3)_3$/20°/24h	52	15
C_8H_{17}	H	H	$-C_7H_{14}COOCH_3$	$B(SeCH_3)_3$/20°/54h	-	71
				$B(SeC_6H_5)_3$/20°/3h	22	63
		n = 1		$B(SeCH_3)_3$/20°/0.5h	72	-
		n = 2			76	-
		n = 3			77	-

We have run competitive reaction of selenoboranes (0.5 mol.eq.) on a stereoisomeric mixture(1eq.) of α,β-distubstituted epoxides. The difference of reactivity between the cis and the trans isomer is so important that only the cis leads to the corresponding β-hydroxyselenide [7] after one hour ; the trans epoxide being recovered unchanged in high yield [8] (Scheme III). Since β-hydroxyselenides can be stereoselectively (100%) transformed to epoxides [9], this method allows the straight forward separation of stereoisomeric mixture of epoxides. Interestingly, the selectivity we have observed here was not found if selenolates $[(CH_3Se)_2/NaBH_4/CH_3OH, 20°]$ are substituted to selenoboranes (ring opening at random on both stereoisomers).

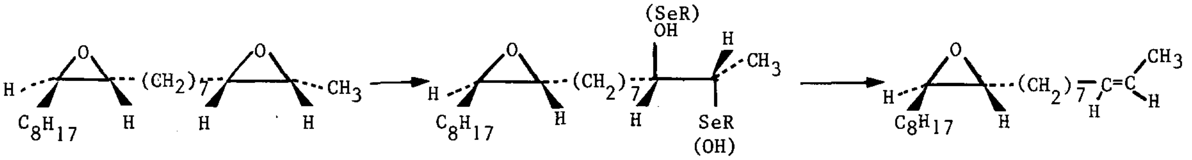
SCHEME III



0.5mol.eq cis/0.5mol.eq trans	$B(SeCH_3)_3$/20°/1h	62%	92%
0.5mol.eq cis/0.5mol.eq trans	$B(SeC_6H_5)_3$/-25°/1.2h	73%	84%

The high stereodescrimination observed has also been used for the chemioselective deoxygenation of the cis oxirane moiety present in a trans-cis diepoxide (Scheme IV) and interestingly the corresponding trans-trans diepoxide is inert under the same experimental conditions.

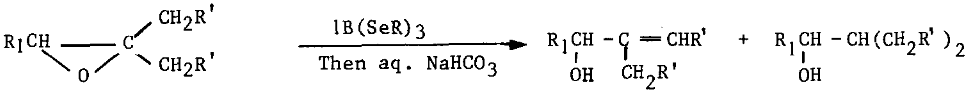
SCHEME IV



1mol.eq.	$B(SeCH_3)_3$/0°/1h	77%	$SOCl_2/NEt_3$	[3b]	60% (not optimized)
	$B(SeC_6H_5)_3$/0°/0.7h	91%			

Finally trisubstituted epoxides do not produce β-hydroxyselenides but instead allyl alcohols[10,11] in which the hydroxy group is regioselectively linked to the less substituted carbon atom (Scheme V). Surprinsingly, saturated alcohol is also isolated in some cases (Scheme V).

SCHEME V



	R_1	R'			
a	C_8H_{17}	H	$B(SeCH_3)_3$/20°/8h	76%	8%
b	C_6H_{13}	CH_3	$B(SeCH_3)_3$/20°/23h	65%	25%
c	C_6H_{13}	CH_3	$B(SeC_6H_5)_3$/20°/1.5h	76%	-

The differences of reactivity are surprising and we are currently studying their reasons.

References and notes

1. D.L.J. Clive and S. Menchen, J. Org. Chem., 44, 1883 (1979) and references cited.

2. a) A. Cravador and A. Krief, C.R. Acad. Sci. Paris, série C, 289, 267 (1979).
   b) For the preparation of B(SeCH$_3$)$_3$, W. Siebert, W. Ruf and R. Full, Z. Naturforsh, 30b 642 (1975).

3. a) K.B. Sharpless and R.F. Lauer, J. Amer. Chem. Soc., 95, 2697 (1973).
   b) J. Rémion and A. Krief, Tet. Letters, 3743 (1976) and references cited.
   c) Results close to ours have been observed when oxidostyrene is reacted with Me$_3$SiSeC$_6$H$_5$ in the presence of ZnI$_2$.
   N. Miyoshi, K. Kondo, S. Murai and N. Sonoda, Chem. Letters, 909 (1979).

4. A. Cravador and A. Krief, unpublished results.

5. Higher reactivity of cis epoxides realtive to trans isomer has been in some cases noticed.
   a) J.M. Towsend and K.B. Sharpless, Tet. Letters, 3313 (1972).
   b) Cis oxidocyclododecene reacts much faster with aqueous HBr than the trans isomer.
   P. Marcotte and K.B. Sharpless, unpublished.
   The author thanks Prof. K.B. Sharpless for this information.
   c) D.L.J. Clive and S.M. Menchen, J. Org. Chem., 45, 2347 (1980).

6. β-hydroxyselenides in which the hydroxyl function is transformed to a better leaving group produce olefins in high yield (see ref. 3b).

7. The crude β-hydroxyselenide has been transformed to olefin using PI$_3$ which is known to stereospecifically remove the hydroxyl and selenyl moieties in an anti fashion [3b,7a]. Only the cis olefin is observed in our case GC [2].

   7a) S. Halazy and A. Krief, J.C.S. Chem. Comm., 1137 (1979) and unpublished results.

8. Only pattern of the trans epoxide is observed in the NMR spectra.

9. a) K.B. Sharpless, K.M. Gordon, R.F. Lauer, D.W. Patrick, S.P. Singer and M.W. Young, Chemica Scripta, 8A, 9 (1975).
   b) A.M. Léonard-Coppens and A. Krief, Tet. Letters, 3227 (1976).

10. For other syntheses of allylalcohols from epoxides, see ref. 3a, 9a and 10a.
    a) H. Yamamoto and H. Nozaki, Angew. Chem. Int. Ed., 169 (1978).

11. The allyl alcohol (Scheme IV, entry c) is identical to an authentic sample prepared unambiguously from heptanal and 3-lithio 3 methylseleno pentane followed by reaction of the resulting β-hydroxyselenides with tBuO$_2$H Alumina [11a].
    a) D. Labar, W. Dumont, L. Hevesi and A. Krief, Tet. Letters, 1145 (1978).

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