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NEW REAGENT FOR CONVERSION OF OLEFINS TO β-HYDROXYSELENIDES

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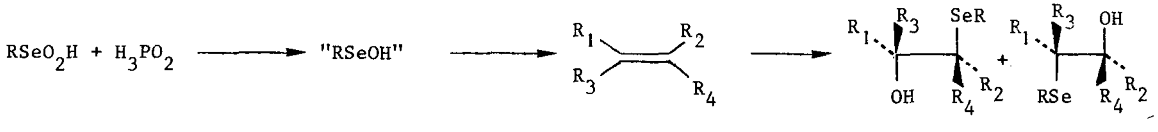
Thermal elimination of selenoxides has been documented recently as a highly potent mean of producing olefins [1-6a], allylalcohols [5,6b-10] and α,β-unsaturated carbonyl compounds [1,2,11,12] The by-product in these reactions is aryl (or alkyl) selenenic acid, a species which was described [1-3,11] to disproportonate rapidly to the corresponding diselenide and seleninic acid.

It occured to us that the reverse reaction, i.e. addition of selenenic acids[13] to olefins, would also be a very useful process, since it would allow the generation of a number of functionalities from olefins.

We present here our first efforts directed toward this goal. The key step of the reaction described on Scheme I, arises from the observation that unstable phenyl and methyl selenenic acid or alike can be formed [14] from readily available and easily handled phenyl [15a] and methyl [15b] seleninic acids and aqueous hypophosphorus acid (50%) at room temperature.

These intermediates are trapped in situ by a variety of olefinic products, when the reaction is carried out in THF solution, leading to the corresponding β-hydroxyselenides 5 in high to good yield ($RSeO_2H$, 1.5 eq.; H_3PO_2, 2.25 eq.; olefin, 1eq./THF)[16]. Interestingly, the whole process occurs in a relatively mild reducing and neutral medium.

Scheme I



1 2 3 4 5a 5b

Entry	R_1	R_2	R_3	R_4	R	Yield in <u>5</u> %	5a/5b	hr.
a	C_8H_{17}	H	H	H	CH_3	76	38/38*	2.5
b	C_8H_{17}	H	H	H	C_6H_5	91	62/29	1.5
c	C_5H_{11}	CH_3	H	H	CH_3	78	**	3.5
d	C_5H_{11}	H	H	CH_3	CH_3	76	**	3
e	C_8H_{17}	C_8H_{17}	H	H	CH_3	63	-	4.5
f	C_8H_{17}	H	H	C_8H_{17}	CH_3	38 (+)	-	4.5
g	C_8H_{17}	C_8H_{17}	H	H	C_6H_5	82	-	1
h	C_8H_{17}	H	H	C_8H_{17}	C_6H_5	74	-	3
i	CH_3	H	CH_3	$(CH_2)_2-\underset{CH_3}{\underset{\vert}{C}}HC_2H_5$	CH_3	80	80/00	1.5
j	CH_3	H	CH_3	$(CH_2)_2-\underset{CH_3}{\underset{\vert}{C}}HC_2H_5$	C_6H_5	86	86/00	1

* each regioisomer was separated by TLC SiO_2

** a mixture of regioisomers is obtained

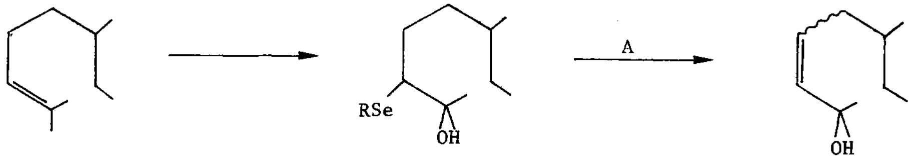
(+) starting olefin is also recovered (40%)

From our experimental results the following observations can be made :

1. Phenyl selenenic acid seems to react much faster than methyl selenenic acid.
2. Mono and trisubstituted olefins react quite rapidly whereas in the disubstituted cases the rate of the reaction is highly dependant on the length of the chain and the stereochemistry of the starting olefin - the Z isomer reacting faster than the E.
3. The reaction is highly regioselective in the case of trisubstituted olefins, the selenyl moiety being held by the less substituted carbon atom (no trace of the other isomer was detected by N.M.R.). However, a mixture of regioisomers is observed in the case of terminal olefins and their ratio is dependant on the nature of the selenenic acid and probably also on the experimental conditions used.
4. In the case of disubstituted olefins we have investigated the stereochemistry of the addition and found that the reaction is highly bistereoselective (>95%) and occured by trans addition of the hydroxyl and the selenyl moieties (by comparison with authentic samples of <u>5e</u> and <u>5f</u> obtained [17] stereoselectively (100%) respectively from Z and E 8-9 oxidooctadecene and potassium methyl selenolate).

β-hydroxyselenides are valuable intermediates in organic synthesis. They can be selectively transformed to epoxides [18,19], α-bromohydrins [20], allyl alcohols[5,6b-10], α,β-unsaturated carbonyl compounds [1,2,11,12], α-selenocarbonyl compounds [21,22], alcohols [21] and olefins [17].

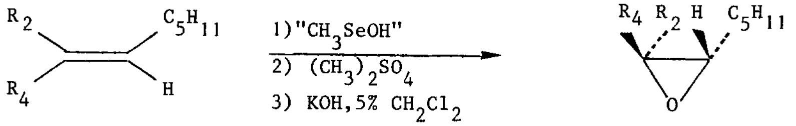
During this work, we had the opportunity to synthesize regioselectively (>95%) the allyl alcohol 6 , in very high yield, via the β-hydroxyselenides 5i and 5j.



R : C_6H_5 5j A^{7a}: H_2O_2,THF,20°C 6 70%

R : CH_3 5i A^{6b}: tbuOOH/Al_2O_3/THF,50°C 6 80%

We have also prepared the epoxides[19,23] 7c and 7d respectively via the β-hydroxyselenides 5c and 5d, respectively from Z and E octene. These epoxides were compared to authentic sample (from Z and E octene and perbenzoïc acid) and found to be of high stereochemical purity (>95%).



7c R_4 = H , R_2 = CH_3

7d R_4 = CH_3, R_2 = H

The behaviour of selenenic acid toward several functional groups is actively investigated in our laboratory as well as new synthetic methods for the generation of such reagents.

We already found that selenenic acid can be prepared from selenenic acid and diethyl phosphite and two reports from Sharpless [24] and Reich [25] just appeared which disclose the reactivity of selenenic acid prepared by other routes.

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16. To a mixture of seleninic acid ($1.5\ 10^{-3}$ mole) and olefin ($1.0\ 10^{-3}$ mole) in THF is added 50% aqueous hypophosphorous acid solution ($2.25\ 10^{-3}$ mole). After completion of the reaction (monitored by TLC SiO_2 Merck, 1:9 Ether/pentane) usual work up and PLC purification of crude products give the β-hydroxyselenide in the yields described in the text.
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