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Oxidation of Allylselenides with the Sharpless AD-reagents

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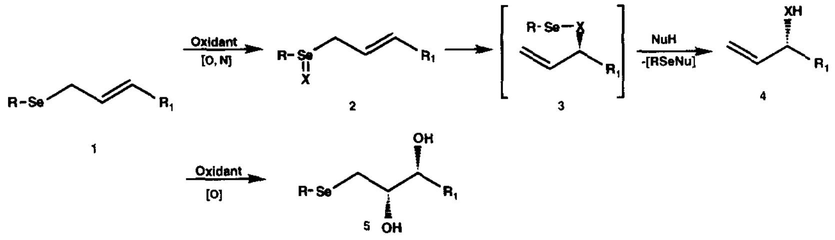
Abstract : Allylselenides are efficiently oxidized by AD-mix reagents. Oxidation takes chemoselectively place on the selenium atom of allylselenides bearing a methylseleno or a phenylseleno moiety, but chemoselectively occurs on the C,C double bond of the corresponding *o*-nitrophenyl derivatives.

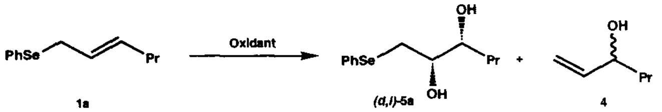
Oxidation of allylselenides has been the subject of intensive work over the last ten years.[1-3] The reaction constantly occurs on the selenium atom and produces after [2,3]-sigmatropic rearrangement of the intermediate allylic-selenoxide or -selenimide, allyl alcohols or allyl amine in high yields and with modest enantiomeric excess when chiral oxidants are used (Scheme 1).[3]

Scheme 1



We now report the first successful oxidation of the C,C double bond of an allyl selenide. The reaction takes place with 1-phenylseleno-2-hexene **1a** and stoichiometric amounts of osmium tetroxide in pyridine[4] ((i) OsO_4, benzene-pyridine, 20°C, 2h (ii) $Na_2S_2O_5$, **5a** : 70%, Scheme 2, entry a).

Scheme 2



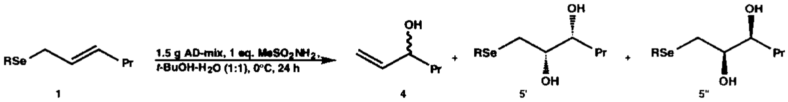
Entry	Conditions	5a %	4 %
a	(i) 1.1 eq. OsO_4, benzene-pyridine (1-1), 0°C, 2h (ii) aq. $Na_2S_2O_5$	70	-
b	cat. OsO_4, 1.1 eq. NMO, acetone-H_2O (2.5-1), 20°C, 24h	7	32
c	cat. OsO_4, 1.1 eq. $K_3Fe(CN)_6$,*t*-BuOH-H_2O (1-1), 20°C, 24h	-	61

Surprisingly however, 3-hydroxy-1-hexene **4**, resulting from initial oxidation on the selenium atom, is mainly or exclusively formed under conditions which uses instead catalytic amounts of osmium tetroxide and stoichiometric amounts of N-methyl morpholine (NMO, 1.1 eq., Scheme 2, entry b) or of potassium ferricyanide ($K_3Fe(CN)_6$, 1.1 eq., Scheme 2, entry c) as co-oxidants. Allyl selenides possess two different nucleophilic sites of different softness. Apparently the presence of pyridine (Scheme 2, entry a) modifies the softness of the oxidant and changes the site of attack (Scheme 2, compare entry a to entries b,c).

We also decided to check the reactivity of allyl selenides towards AD-mix reagents which contain trace amounts of osmium tetroxide as reagent, chiral diamines as catalyst and potassium ferricyanide as the co-oxidant. These reagents discovered by Sharpless, have been described to effect the enantioselective dihydroxylation of various olefins,[5] including allyl ethers[5a] and allyl sulfides.[5b,c]

We found that 1-phenylseleno-2-hexene **1a** reacts with AD-mix-α or -β (1.5 g, 1 eq. $MeSO_2NH_2$, *t*-BuOH-H_2O, 0°C, 24h) and delivers 3-hydroxy-1-hexene **4** exclusively in the first case and mixed with a small amount of the diol **5a** in the second one (7%; Scheme 3, compare entry b to entry a). These results clearly show that AD-mix reagents behave differently towards allylic phenyl sulfides and -selenides, reacting selectively on the C,C double bond of the former[5b,c] and on the selenium atom of the later.

Scheme 3



Entry	**1**	RX	AD-mix	**4** % (e.e. %)	**5** (stereochemistry)	Yield in **5** % (**5'**/**5"**)
a	**1 a**	PhSe	β	81 (0)	**5a** (2*S*, 3*R*)$^+$	7 (97/3)
b	**1 a**	PhSe	α	83 (0)		0
c	**1 b**	MeSe	β	100 (0)		0
d	**1 c**	o-NO_2PhSe	β	0	**5c** (2*S*, 3*R*)$^+$	78 (97/3)
e	**1 c**	o-NO_2PhSe	α	0	**5c** (2*R*, 3*S*)$^+$	53 (7/93)

$^+$ Refers to the stereochemistry of the major enantiomer.[6]

We have carefully checked the enantiomeric excess of each compounds **4** and **5a** and found that whereas the allyl alcohol **4** was a racemate (Scheme 3, entries a,b) the diol **5a** was produced with high enantiomeric excess (Scheme 3, entry a).[6]

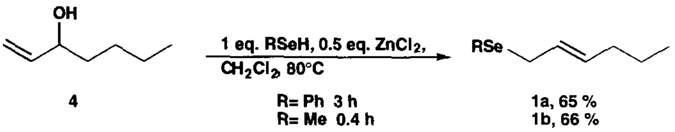
The formation of the racemic alcohol **4** implies the production of the racemic selenoxide **2a** prior to the sigmatropic rearrangement took place (Scheme 1). This could result from (i) a non-enantioselective oxidation of **1a** by AD-mix or (ii) the racemisation of the first formed optically active selenoxide.

We further found that the nature of the seleno group attached to the allylic moiety drastically influences the chemoselectivity of this reaction. Thus, whereas 1-methylseleno-2-hexene **1b**, which possesses the more nucleophilic seleno moiety, behaves similarly to its phenylseleno analog and delivers racemic **4** (Scheme 3, entry c), 1-*o*-nitrophenylseleno-2-hexene **1c**, with the least nucleophilic seleno moiety, selectively leads to the desired diol **5c** by oxidation of its C,C double bond (Scheme 3, entries d,e). Very high enantioselection is achieved from AD-mix-β (e.e.>94%, Scheme 3, entry d) and substantially lower selectivity is performed from AD-mix-α (e.e.> 86%, Scheme 3, compare entry e to entry d).[6]

The behavior of osmium tetroxide and of related reagents towards allyl selenides probably also depends upon the substitution of their C,C double bond. This topic is now under study.

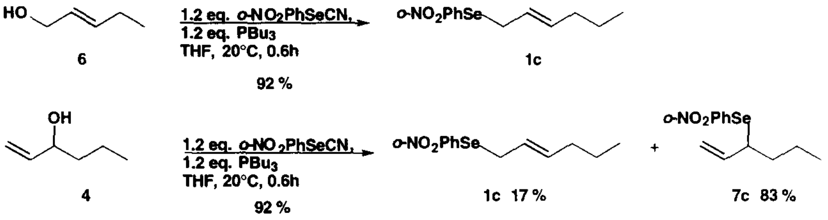
The *E*-allyl phenyl-**1a** and methyl-**1b** selenides bearing the seleno moiety at their terminus required for this study have been prepared with very high regio and stereocontrol from 3-hydroxy-1-hexene **4** and methyl- and phenylselenol in the presence of zinc chloride (Scheme 4).[7]

Scheme 4



The synthesis of the related 2-*E*-allyl *o*-nitrophenyl selenides **1c** is best achieved from 1-hydroxy-2-*E*-hexene **6**, *o*-nitrophenylselenocyanate and tributylphosphine according to Grieco (Scheme 5).[8,9] It is interesting to notice that the same product is formed besides large quantities of the isomeric 3(*o*-nitrophenylseleno)-1-hexene **7c**, when the same reaction is instead carried out on 3-hydroxy-1-hexene **4**. This is, to our knowledge, the first time that the Grieco reaction is not completely regioselective and that products resulting from an S_N' type reaction are observed (Scheme 5).[9,10]

Scheme 5



In conclusion we have achieved, by choosing the proper seleno moiety, the enantioselective oxidation of the C,C double bond of some allyl selenides.

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5. (a) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483, (b) Walsh, P. J.; Ho, P. T.; King, S. B.; Sharpless, K. B. *Tetrahedron Lett.* **1994**, *35*, 5129 (c) 2,3-dihydroxy-1-phenylthiohexane was obtained, as already reported, from AD-mix-β (71 % yield, 92 % e.e.) and in lower yield and e.e. from AD-mix-α (55 % yield, 77% e.e.).
6. The purity of the diols **5** was assessed by chiral HPLC on a 25 cm column : DAICEL CHIRACEL OD-H, cellulose carbamate phase supported on 5μm silica-gel, 1 ml/ min, UV detector 254 nm., Retention time (min., hexane : 2-propanol= 97:3)= **5'a** : 19.81, **5"a** : 25.12; (min., hexane : 2-propanol= 90:10) **5c"** : 26.17, **5c'** : 28.46. Their absolute stereochemistry was derived from the Sharpless rules.[5a,b]
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10. The allyl phenyl selenides bearing a terminal C,C double bond are prone to isomerise to the corresponding terminal selenides.[1j,2f] We however found in this study that the allyl *o*-nitrophenyl selenide **7c** does not rearrange under a large variety of conditions : UV (solar lamp, 2.5h; TsOH, benzene, 20°C, 6h or 80°C, 5h).

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