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Evidence of an equilibrium between selenides and osmium(VIII) reagents and selenoxides and osmium(VI) reagents

Alain Krief,*[a] Alexandra Destree,[b] Virginie Durisotti,[b] Nicolas Moreau,[b] Caroline Smal[b] and Catherine Colaux-Castillo[a]

[a] *Laboratoire de Chimie Organique de Synthèse, Département de Chimie, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium. E-mail: alain.krief@fundp.ac.be; Fax: +32 8172 4536; Tel: +32 8172 4539*

[b] *Laboratoire de Travaux Pratiques de Chimie Organique 1^{iere} Licence, Département de Chimie, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium*

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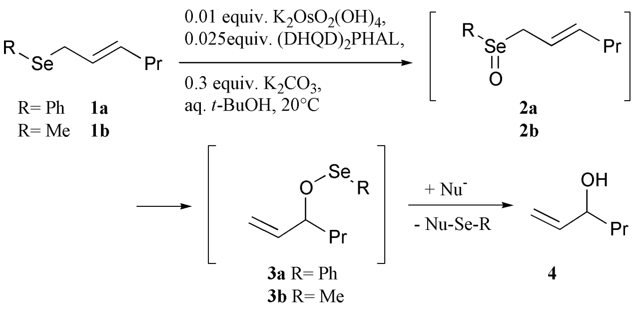
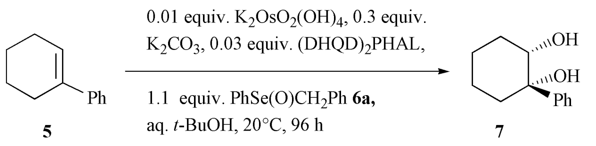
Driving the equilibrium between selenides and osmium(VIII) reagents with selenoxides and osmium(VI) by a subsequent reaction (rearrangement of allyl selenoxides to allyl alcohols or addition of osmium(VIII) species on C=C double bonds) to one side, allows the transformation of methyl geranyl selenides to linalool and of methyl citronellyl selenoxide to 6,7-dihydroxy citronellyl selenide.

We recently described[1] that AD-mix-β, a commercially available mixture containing potassium osmate dihydrate ($K_2OsO_2(OH)_4$, the pre-oxidant), $(DHQD)_2PHAL$ (the chiral ligand), potassium carbonate (the base) and potassium ferricyanide (the co-oxidant) invented by Sharpless,[2] reacts with 2-hexenyl phenyl- and methyl-selenides **1** to produce, the corresponding allyl alcohols **4** in good yields (Scheme 1). These result from (i) the selective oxidation, by osmium(VIII) species, of the selenium atom of allyl selenides leading to the corresponding selenoxides **2** and (ii) rearrangement of the later to allyl alcohols **4** by the well known cascade [2,3] sigmatropic rearrangement (**2** → **3**) followed by seleninate-selenophilic substitution (Scheme 1).



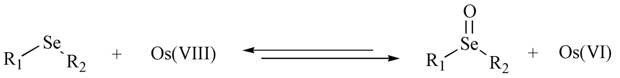
Scheme 1

We also recently described that selenoxides could advantageously replace potassium ferricyanide, in AD-mix monitored dihydroxylation of olefins (Scheme 2).[1]



Scheme 2

These results, which seem at first contradictory, can be explained by an equilibrium involving four different species (Scheme 3).



Scheme 3

This equilibrium, if it exists, could be displaced in one or the other direction by coupling a subsequent reaction such as the transformation of (i) allyl seleninates to allyl alcohols (Scheme 1) or (ii) olefins to diols (Scheme 2).

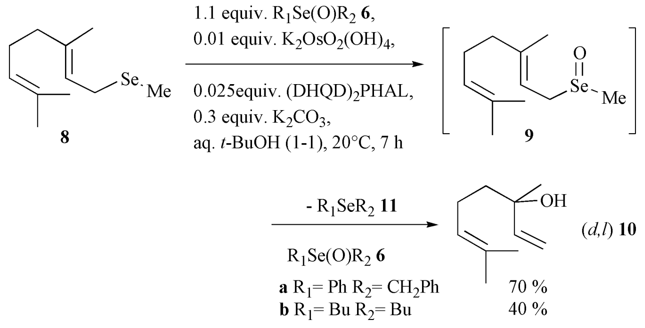
We have now found that potassium osmate dihydrate is able to catalyze the oxygen transfer from some selenoxides to other selenides favoring thus the equilibrium between two selenides and the corresponding selenoxides.

Methyl geranyl selenide **8** and benzyl phenyl selenoxide **6a** were chosen as the two partners with the expectation that the equilibrium would take place and be drawn to completion by the cascade allyl selenoxide-[2,3] sigmatropic rearrangement and seleninate-selenophilic substitution to finally produce linalool **10** and benzyl phenyl selenide **11a**.

Typically, the reaction was carried out on **8** under conditions which mimic the AD-mix reaction shown in Schemes 1 and 2: [catalytic amounts of $K_2OsO_2(OH)_4$, $(DHQD)_2PHAL$ and potassium carbonate in aqueous *t*-BuOH] but in the absence of potassium ferricyanide.[1,2] After 7 h at 20 °C, *rac*-linalool (*d,l*) **10** was obtained in 70 % yield (Scheme 4).

We have also confirmed that methyl geranyl selenide **8** (i) is recovered unchanged if the same reaction is performed under the conditions reported just above, but in the absence of potassium osmate dihydrate, and (ii) is much more slowly oxidized when dibutyl selenoxide **6b** is used in place of benzyl phenyl selenoxide **6a** (Scheme 4). This suggests that each type of selenoxide has a different oxidative power and that dialkyl selenoxides are the least efficient of the series. We have, in fact, already described that dialkyl selenoxides are less efficient oxidants than alkyl benzyl, alkyl phenyl, benzyl phenyl or diphenyl-selenoxides in the AD reaction (SeOAD) using selenoxides as co-oxidants.[3]

We also found that potassium osmate dihydrate is able to catalyze, in the presence of water, the transformation of unsaturated selenoxides to the corresponding dihydroxyalkyl



Scheme 4

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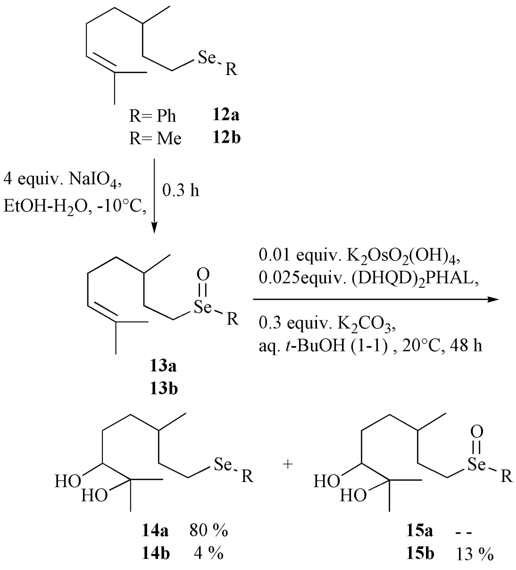
selenides. This results from the reduction of the selenoxide functionality to the selenide with consecutive dihydroxylation of the C=C double bond.

Thus, *rac*-citronellyl phenyl selenoxide **12a**, is efficiently (80% yield) transformed to phenyl 6,7-dihydroxy citronellyl selenide **14a** (Scheme 5) using catalytic amounts of $K_2OsO_2(OH)_4$ and $(DHQD)_2PHAL$ in aqueous *t*-BuOH (K_2CO_3, 20 °C, 48 h). We have confirmed that the reaction requires the presence of catalytic amounts of potassium osmate dihydrate to take place.



Scheme 5

The related methyl selenoxide **13b** reacts much more slowly and leads to an intractable mixture of the diol **14b** (4% after 48 h) and the corresponding selenoxide **15b** (13% after 48 h)† besides large amounts of unreacted starting material (Scheme 5). Apparently, the osmium tetroxide catalyzed dihydroxylation reaction is more sensitive to the nature of the selenoxide than is the osmium tetroxide catalyzed oxygen transfer from selenoxides to selenides.

In conclusion, we have shown that the Os(VI) to Os(VIII) and the selenoxide to selenide reaction couples are effectively highly interconnected and that they allow the transformation of selenides to selenoxides (Scheme 4) or the reverse reaction (Scheme 5). Work is in progress to use these observations in other practical syntheses.

Notes and references

† The mixture of 7,8-dihydroxy citronellyl selenide **14b** and of the corresponding selenoxide **15b** have been separated by TLC. The very polar **15b** has been reduced to **14b** on reaction with sodium bisulfite.

1 A. Krief, C. Colaux and W. Dumont, *Tetrahedron Lett.*, 1997, **38**, 3315.
2 H. C. Kolb, M. S. VanNieuwenhze and K. B. Sharpless, *Chem. Rev.*, 1994, **94**, 2483; and references cited.
3 A. Krief and C. Castillo-Colaux, *Tetrahedron Lett.*, 1999, **40**, 4189; A. Krief and C. Castillo-Colaux, *Synlett*, 2001, 501.