Tetrahedron 65 (2009) 8447–8459

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tetrahedron report number 886

Biotransformations on organic selenides and tellurides: synthetic applications

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ARTICLE INFO

Article history:
Received 17 June 2009
Available online 3 July 2009

Contents

1. Introduction

The chemistry of organoselenium compounds experienced remarkable progress in the 1970s,[1] and the same occurred with the organic tellurium chemistry in the 1980s.[2] However, at that time the chirality of the organochalcogen compounds was not addressed as a fundamental aspect for their application in organic synthesis. In contrast, due to the importance of the chirality in biological processes, nowadays racemic compounds are hardly considered for synthetic purposes. Besides the use of compounds from the natural chiral pool, two main approaches are considered in the preparation of enantiomericaly pure compounds, chiral homogeneous catalysis and biocatalysis.[3] Despite the resistance of synthetic organic chemists to employ biological materials as reagents,[4] some biocatalytic strategies, such as the enzymatic kinetic resolution of alcohols, are now routinely used in synthetic chemistry laboratories.[5] Notwithstanding this fact, until recently, the use of biocatalytic methods to prepare enantiomericaly enriched organoselenium and organotellurium compounds were very scarce.

At this point it is important to mention that the use of organoselenium and, to a larger extent, organotellurium compounds, is avoided by synthetic organic chemists, who very often believe that they are very bad smelling compounds, and claim that tellurium-based compounds are unstable to the light and air. These observations are indeed true for low molecular weight alkyl selenides and tellurides, especially for the non-functionalized ones. Introduction of additional functional groups to the structure of a bad smelling selenide or telluride very often produces a neutral smelling derivative as illustrated in Figure 1.

All the compounds commented in this article present an odor not more unpleasant than the organic compounds usually employed in an organic synthesis laboratory. Additionally, they are air- and light-stable compounds that can be purified by column

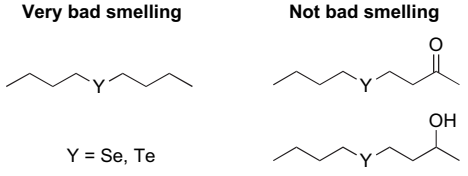

Figure 1.

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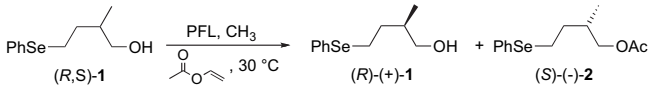
0040-4020/$ – see front matter
doi:10.1016/j.tet.2009.06.121

chromatography. When stored under refrigeration, the selenides do not degrade to an observable extent; however, the tellurides are less stable, and after a few days some decomposition can be detected by the darkening of the samples. When in solution in the presence of the air, the tellurides are slowly transformed into amorphous white solids, presumably oxidation products. However, by taking the proper care, evaporating the solvent immediately after the work-up, the tellurides can be safely manipulated in the presence of light and air.

The article is organized in four sections: (a) Kinetic enzymatic resolution of alcohols and amines containing selenium and tellurium in their structure; (b) Enzymatic oxidation of selenium and tellurium containing substrates; (c) enzymatic reduction of selenium and tellurium containing substrates; (d) miscellanea.

2. Kinetic enzymatic resolution of hydroxyselenides and hydroxytellurides

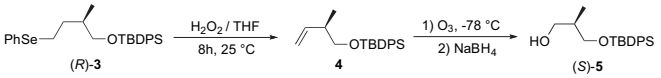
The kinetic enzymatic resolution of secondary alcohols is one of the most investigated enzymatic transformations used in organic synthesis laboratories.[5] Although less studied, the enzymatic resolution of chiral alcohols that have the hydroxy group bonded in a remote location from the chiral center also gives good enantiomeric excesses.[5] The first report of an enzymatic resolution involving a hydroxyselenide describes the resolution of a primary alcohol with the chiral center α to the carbinol carbon.[6] Compound **1** was selectively esterified by reaction with vinyl acetate in chloroform at 30 °C in the presence of *Pseudomonas fluorescens lipase* (PFL). At 60% conversion, the alcohol (*R*)-(+)-**1** was obtained in 38% yield and 98% ee (Scheme 1). At 40% conversion, the acetate (*S*)-(−)-**2**, was obtained in 36% yield and **3** was treated with hydrogen peroxide giving **4**, which on ozonolysis furnished (*R*)-**5**, a chiral building block used in asymmetric synthesis (Scheme 2).



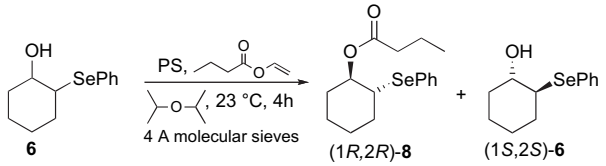
PFL = *Pseudomonas fluorescens lipase*

	(*R*)-(+)-1	(*S*)-(-)-2
e.e. (%)	98	>98
Yield (%)	38	36
Conversion (%)	60	40

Scheme 1.[6]

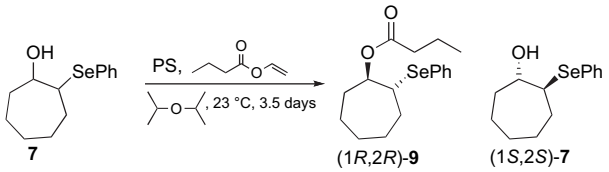


Scheme 2.[6]



	(1*R*,2*R*)-8	(1*S*,2*S*)-6
e.e. (%)	>99	96
Yield (%)	41	52

Scheme 3.[7]



	(1*R*,2*R*)-9	(1*S*,2*S*)-7
e.e. (%)	>99	88
Yield (%)	43	50

Scheme 4.[8]

trans-2-(Phenylseleno)-cyclohexan-2-ol **6**[7] and *trans*-2-(phenylseleno)-cycloheptan-1-ol **7**[8] were selectively acylated with vinyl acetate and vinyl butyrate in the presence of *Pseudomonas cepacia lipase* (PS), *Porcine pancreatic lipase* (PPL) and *Candida cylidracea lipase* (CCL). The best results were obtained with vinyl butyrate and PS, under the reaction conditions shown in Schemes 3 and 4. Under these conditions the alcohols (1*S*,2*S*)-**6** and (1*S*,2*S*)-**7** were obtained in 96% and 88% ee, respectively, and the acetates (1*R*,2*R*)-**8** and (1*R*,2*R*)-**9** were obtained in >99% ee. The selenide oxidation/elimination of the enantiomericaly enriched alcohols **6** and **7**, followed by the hydrolysis of the enantiomericaly pure esters **8** and **9**, make these compounds synthetic equivalents of the corresponding chiral allyl alcohols **10** and **11** (Fig. 2).

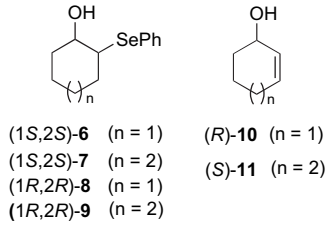


Figure 2.

Recently, a more detailed study on the influence of the selenide structure, temperature, solvent and enzyme in the kinetic enzymatic resolution of β-hydroxyselenides has been published.[9]

The influence of the temperature was studied using PPL, PSL and CALB in typical experiments at 5, 10, 20, 32 and 40 °C. Table 1 shows the effects of temperature and enzymes in the resolution of racemic **12a**. The enzymatic activity depends on the temperature employed. The temperature also had considerable effect on the enantioselectivity, but no influence in the stereochemical preference for the (*R*)-1-phenylselanyl-propan-2-ol (*R*)-**12a** enantiomer. The enantiopreference agrees with the Kazlauskas's rule, an extension of Prelog's rule for hydrolases.[10]

The highest stereoselectivities were obtained using PSL and CALB at 20–40 °C, and the best relation between enantiomeric excess and conversion was observed at 32 °C. In the reaction with PSL, both (*S*)-**12a** and (*R*)-**13a** were obtained in more than 92% ee at 32 °C (Table 1, entries 11 and 12). On the other hand, the best enantioselectivity was achieved in the reaction with CALB at 32 °C, when both (*S*)-**12a** and (*R*)-**13a** were obtained in more than 98% ee (Table 1, entries 18 and 19). Control of the reaction time and temperature, when PSL or CALB were used as biocatalysts, allowed the isolation of both (*S*)-**12a** and (*R*)-**13a** with >99% ee (Table 1, entries 9, 12, 17 and 19).

The influence of the solvent was also evaluated in the acylation of (*R*,*S*)-**12a** using PSL and CALB at 32 °C in some dry solvents