Selenoxide Fragmentation Leading to Allylic Amides

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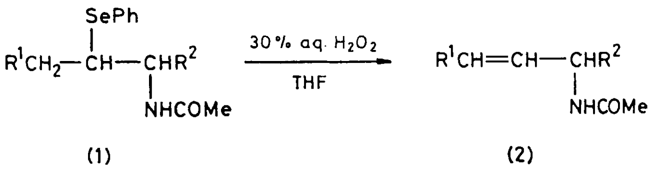
Summary Oxidation–fragmentation of β-amidoalkyl phenyl selenides produces allylic amides selectively.

In double-bond formation by oxidation–fragmentation of β-hetero-substituted-alkyl phenyl selenides, the regiochemistry has been well established in the cases where the heteroatom is oxygen,[1] sulphur,[2] or chlorine.[1b,3] However, little is known about the reactions of selenides bearing a nitrogen functional group on the β-position of the alkyl group, the only reports showing that in the oxidation of β-dimethylaminoalkyl phenyl selenides[4] an elimination away from the dimethylamino-group leading to allylic amines is moderately favoured, and that a mixture of allyl azide and vinyl azide (isomer ratio 3 : 2) is formed by oxidation of β-azidocyclohexyl phenyl selenide.[5] We report here that oxidation–fragmentation of the easily accessible β-amidoalkyl phenyl selenides (**1**)[6] produces the allylic amides (**2**) selectively (Scheme 1).



$$R^1CH_2\text{—}\overset{\text{SePh}}{CH}\text{—}\underset{\text{NHCOMe}}{CHR^2} \xrightarrow[\text{THF}]{30\%\ \text{aq. } H_2O_2} R^1CH{=}CH\text{—}\underset{\text{NHCOMe}}{CHR^2}$$

(1) (2)

Scheme 1

In a typical reaction, 30% aqueous H_2O_2 (20 mmol) was added dropwise to a solution of 2-acetamidocyclopentyl phenyl selenide (2·0 mmol) in tetrahydrofuran (THF) (30 ml) at 0 °C and the resulting solution was stirred at

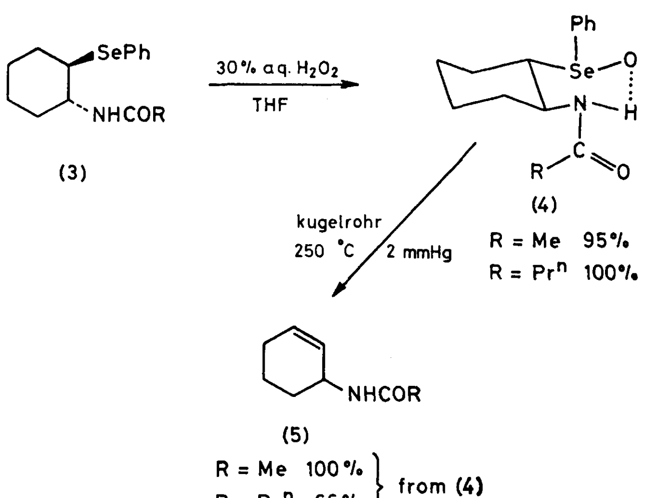
20 °C for 2 h. After the usual work-up, basic products were separated from diphenyl diselenide by extraction with 0·5 M aqueous HCl. The aqueous layer was rendered alkaline by addition of NaOH pellets and extracted with chloroform. Evaporation of solvent from this extract gave pure 3-acetamidocyclopentene (83%) as the sole product.

As shown in the Table, seven- and eight-membered ring β-amido-selenides as well as linear compounds also gave allylic amides selectively in excellent yields under the same conditions. As β-amido-selenides can be prepared by one-pot aminoselenation of olefins,[6] these reactions constitute a good method for conversion of olefins into allylic amides.[7]

Table. Yields of allylic amides.[a]

β-Amido-selenide (**1**) R^1	 R^2	% Yield[b] of allylic amide (**2**)
$-[CH_2]_2-$		83
$-[CH_2]_4-$		82
$-[CH_2]_5-$		84[c]
H	Me (*threo*)	68
H	Me (*erythro*)	68

[a] Carried out using the β-amido-selenide (**1**) (2 mmol) and 30% aq. H_2O_2 (20 mmol) in THF (20 ml) at 0—20 °C for 2 h. [b] Isolated yield (see text). [c] Isolated by column chromatography (silica gel; n-hexane–ethyl acetate, 1 : 1—1 : 2).



Scheme 2

When six-membered ring β-amido-selenides (**3**) were treated under the same conditions the allylic amides were not formed, and instead white solids were obtained which were characterized as the selenoxides (**4**) [ν_{max}(SeO) 816 (R=Me) and 805 (R=Prⁿ†) cm^{-1}].‡ The stability§ of these selenoxides (**4**) seems to be due to the formation of an intramolecular hydrogen bond between the hydrogen atom of the amido-group and the oxygen atom of the selenoxide as depicted in Scheme 2.[8] The dihedral angle of the C–Se and C–N bonds (both substituents being equatorial on the cyclohexane framework‡) seems to be critical for the formation of an intramolecular hydrogen bond since selenoxides were not isolated from non-six-membered ring compounds or linear β-amido-selenides. Selenoxide fragmentation of (**4**; R=Me) in boiling tetrahydrofuran (for 1 h) or *p*-xylene (for 3 h) produced the allylic amide (**5**; R=Me) selectively, but only in moderate yields (43 and 63% respectively). The yields of (**5**) were improved without loss of selectivity by pyrolysis of (**4**) using kugelrohr distillation (250 °C; 2 mmHg) (Scheme 2).

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† Prepared by a method analogous to that in ref. 6 using butyronitrile as solvent.

‡ Satisfactory i.r. and ^1H n.m.r. data as well as combustion analytical data were obtained. The stereochemistry of (**4**) and (**5**) was determined by the ^1H n.m.r. coupling constants for the hydrogen atom attached to the carbon atom bearing the selenium functional group (d of t; *J* 4—5 and 11—12 Hz, respectively).

§ The selenoxides (**4**) can be stored almost indefinitely at room temperature.

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