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Oliver Schulze; Jürgen Voss

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Stereoselective Preparation of Bicyclic Selena and Telluraheterocycles Starting from the Chiral Pool

OLIVER SCHULZE and JÜRGEN VOSS

Institute of Organic Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

The preparation of seleno- and telluroesters by way of the Mitsunobu reaction[1] is not possible since seleno- and telluroacetic acid are unsuitable reagents. However, sodium hydrogen selenide and telluride can be conveniently prepared as *in situ* reagents. These powerful nucle-ophiles readily attack methyl 2,3-anhydro-5-O-mesyl- α -D-ribo-furanoside (1) to yield in a tandem reaction the selena- (3) – (5) and tellurabicyclics (11) as pure enantiomers.

The two 2,3-anhydro-5-O-mesylribofuranosides 1 and 2 are obtained from D-Xylose in a three-step synthesis.

Reaction of 1 and 2 with sodium hydrogen selenide, which is prepared by reduction of grey elemental selenium with sodium borohydride in sodium ethanolate solution, yields the selena-bicycloheptanes 3-5 in a tandem-reaction, i. e. first nucleophilic substitution of the mesylate groups by hydrogen selenide and subsequent intramolecular opening of the epoxide ring under formation of the selenetane (3, 5) or selenolane (4) moiety.

The product ratio 3:4 depends on the reaction temperature. No bicyclo[2.2.1]heptane derivative at all is formed from 2, which observation can be explained by steric hindrance of the intramolecular attack on C-2 caused by the β -position of the methoxy groups at C-1. Small amounts of the tricyclic 1,5-diselenocanes 6 and 7 are formed as by-products.

A third sclenetane, 10, is obtained from methyl 2,3-anhydro-α-D-ribo-furanoside 8 via the dimesylate 9.

Analogous reaction of 1 with sodium hydrogen telluride – once more prepared in situ from elemental tellurium and sodium borohydride – yields the elusive tellurabicyclo[2.2.1]heptane 11.

References

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