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REACTION OF SELENIUM DIOXIDE WITH 3-HYDROXY-1,6-DIOLEFINS. Formation of 8-oxa-3-selenabicyclo[3,2,1^{1,5}]octanes and other selenoorgano compounds

Manuel Medarde*, Jose Luis López*, Mª Angeles Morillo, Fernando Tomé, Marta Adeva and Arturo San Feliciano

Departamento de Química Orgánica y Farmacéutica. Facultad de Farmacia. Av. Campo Charro s/n. E-37007 SALAMANCA. Spain. (FAX-34-23-294515).

Abstract.- The formation of selenium containing products during the reaction of selenium dioxide with hydroxydiolefins has been confirmed through the synthesis and reactivity studies with selected model compounds. The isolation of 8-oxa-3-selenabicyclo[3,2,1^{1,5}]octanes and dimeric selenium compounds has been observed with cyclohexanic and cyclopentanic derivatives.

In a previous study on the synthesis of a linally derivative obtained from natural sources,¹ we observed the formation of selenium containing compounds during the selenium dioxide oxidation of linally acetate.² Afterwards, we have observed that this secondary reaction is the responsible for the main reaction products in the treatment of linalool under the same conditions.³ We have now initiated a more detailed study of the reaction of other hydroxydiolefins with selenium dioxide, in order to know the general character of this transformation and to gain a deeper insight into its mechanism.

With this purpose we synthesized 3-hydroxy-1,6-diolefins according to scheme 1, by allylation of ketones followed by treatment with vinylmagnesium bromide. The model compounds obtained were subjected to treatment with SeO₂ in methanol at reflux until the complete disappearance of the starting material was observed by TLC.



Scheme1 i : 1) Pyrrolidine/benzene reflux, 2) CH2=CHCH2Br, 3) H2O reflux; ii : CH2=CHMgBr/THF/reflux

From the reaction mixture, selenium containing products 2-4 together with a lower amount of allylic oxidation products 5 were isolated.⁴ The latter are the usual products from the treatment of olefins with selenium dioxide, resulting from the ene-reaction/2,3-sigmatropic rearrangement/hydrolysis.⁵ Their stereochemistry was unequivocally established by the formation of their acetonides 10.6

The selenium compounds have two different structures: type 2, derived from the addition of a methanol molecule, and dimeric types 3 and 3' (symmetric) and 4 (no symmetric), derived from the addition to two molecules of the substrate. The reaction of 2 with hydrogen peroxide⁷ to produce aldehydes 6^8 and the nBu₃SnH/AIBN reduction⁹ of dimeric compounds 3+3'+4, to hydrocarbons 7-9, support the structures of these selenium products (Scheme 2). These results confirm the general character of this kind of reaction with the 3-hydroxy-1.6-diolefin substructure, that was suspected following the results obtained from linalool. Thus, the presence of one hydroxyl group in an adequate spatial disposition favours the addition reaction of selenium species to the double bonds of the molecule, in major extension and with different results than those observed for linalyl acetate. The difference between dimers 3. 3' and 4, lies in the relative stereochemistry at C-2 in both sides of the dimer that can account for the spectral differences (moleties of 3.3' and 4 with relative structure *trans*).



i: $H_2O_2(30\%)/CH_2Cl_2 0^{\circ}C$; ii nBu₃SnH/AIBN/C₆H₆ 2h.reflux; iii: (CH₃)₂C(OCH₃)₂/Acetone/TMSCl 5h. r.t. Scheme 2; Reaction of 3-hydroxy-1,6-diolefins with SeO₂ and further transformations of the reaction products

The reaction can be explained as a double electrophilic attack of a selenium species to both double bonds of the molecule, completed by the intramolecular addition of the hydroxyl group and the attack of one methanol to produce compounds type 2. Dimeric compounds can be explained as result of the initial attack to the allylic double bond completed by the intramolecular addition of the hydroxyl group, followed by a second attack of the selenium to the other molecule of the starting material (Scheme 3). The actual Se species (SeX₂) responsible for the selenium products must be a reduced selenium produced in the allylic oxidation and other reactions with non isolated organic material. More detailed studies with other hydroxydiolefins carrying other substituents and having different separations between both double bonds, as well as the study of the effect of modifications in the conditions of reaction and the reactive species of selenium, are now under progress.



Scheme 3: Mechanism proposal for the formation of 2-4.

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- 4.- Isolated yields. From 1a: 2a(33%), 3a+3'a+4a(10%) pure 3'a(5%); from 1b: 2b(22%), 3b+3'b+4b(21%), 5b(17%); from 1c: 2c(5%), 3c+3'c+4c(40%), 5c(41%). 3+3'+4 obtained as mixtures (GC/MS), only 3'a was isolated in one experiment.
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- 8.- Aldehydes 6 are spontaneously formed from the selenoxide (detected by NMR) by: 1) selenoxide elimination to selenenic acidolefin 2 intramolecular addition of the acid to the olefin to form a hemiacetal 3) conversion of the hemiacetal into the aldehyde.
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