Selenium Stablized Anions. Conversion of β-Hydroxy Selenides into Olefins

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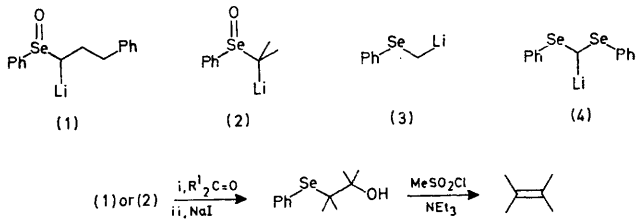
Summary Sulphonylation of β-hydroxy selenides, prepared by addition of organometallic compounds to carbonyl compounds, results in reductive elimination to give olefins under unusually mild conditions.

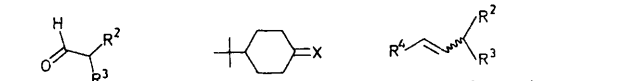
THE addition of functionalized organolithium reagents to carbonyl compounds followed by reductive elimination comprises a large class of olefin-forming reactions whose most important characteristic is assurance of double bond positional specificity. The Wittig reaction and its modifications is the most important of these,[1] but reactions involving silane,[2] sulphide, [3] sulphoxide,[4] sulphone,[5] and sulphoximide[6] eliminations have also been developed. We report the transformation of β-hydroxy selenides into olefins.

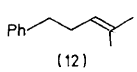
TABLE. Conversion of carbonyl compounds into olefins by reductive elimination of β-hydroxy selenides

Organolithium reagent	Carbonyl compound	Olefin	Yield/% Selenide	Yield/% Olefin
(1)	(5)	(10)	87	70
(1)	Me_2CO	(12)	88	73
(2)	(7)	(8)	82	91
(3)	(7)	(9)	75	98
(4)	(6)	(11)	77	81

β-Hydroxy selenides can be prepared by addition of selenenyl acetates to olefins,[7] by opening of epoxides with PhSeNa,[8] or by reaction of α-lithio selenides [9,10] and selenoxides[10] with carbonyl compounds. We have used aliphatic selenides as starting materials since these are readily







available by displacement of tosylates, mesylates, and halides with the nucleophile PhSeNa. The procedure

developed involves *in situ* oxidation of selenides to selenoxides (THF, 0 °C, $ClC_6H_4CO_3H$-*m*), deprotonation (−78 °C, 2 equiv. of $LiNPr^i_2$), reaction with a carbonyl compound (−78 °C), and reduction back to hydroxy selenide (NaI, $NaHSO_3$, HOAc, 0 °C).† The reduction occurs under sufficiently mild conditions that selenoxide *syn* elimination[11,12] is not a problem.

The β-hydroxy selenides, prepared in this way from α-lithio selenoxides such as (**1**) or (**2**) or directly by reaction with α-lithio selenides such as (**3**) or (**4**), are cleanly converted into olefins when $MeSO_2Cl$ (3 equiv.) is added at room temperature to a solution of the hydroxy selenide in CH_2Cl_2 containing Et_3N (5 equiv.),‡ The reaction probably involves the reverse of the usual mechanism (*anti* stereochemistry) for electrophilic addition of selenenyl and sulphenyl halides, acetates, and sulphonates. The excess of $MeSO_2Cl$ is required for good yields. It is probably involved in removal of the selenenyl methanesulphonate which, formally, is a product of the reaction, but which was not isolated.

The elimination is applicable to the preparation of variously substituted olefins in fair to good yields, including the tetrasubstituted systems for which the Wittig reaction usually fails.[1] Double bond stereochemistry is determined by the ratio of diastereomeric hydroxy selenides. The principal advantages of this method are the wide range of readily available lithium reagents and the mildness of the conditions.

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† Other reducing agents (*e.g.*, $SnCl_2$–$POCl_3$–py) can be used. This reagent also causes reductive elimination under slightly more vigorous conditions (J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 1959, 112).

‡ Hydroxy sulphides are converted into stable mesylates under these conditions (B. M. Trost, K. Hiroi, and S. Kurosumi, *J. Amer. Chem. Soc.*, 1975, **97**, 438).

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