**Tetrahedron Letters No. 17, pp 1385 - 1388, 1976. Pergamon Press. Printed in Great Britain.**

# NEW REGIOSPECIFIC ROUTES TO OLEFINS FROM β-HYDROXY SELENIDES [1]

- a stereospecific deoxygenation of epoxides
- a [C,C] connective route to olefins

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**(Received in UK 2 February 1976; accepted for publication 15 March 1976)**

β-Hydroxy selenides are potentially useful intermediates in organic synthesis [2]. They can be both easily and specifically activated, leading to many valuable organic compounds such as allyl alcohols [2], epoxides [3], halohydrins [4], alcohols [4] or in one case to an olefin [3b,c].

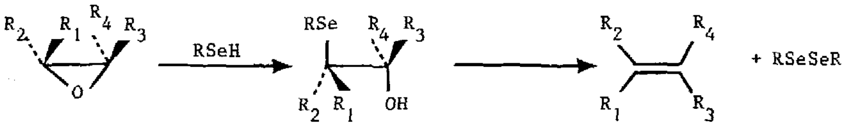
*The present report discloses their potentiality as olefinic precursors under various reaction conditions.*

We found, for instance, that β-hydroxy selenides can be transformed (in good to excellent yield) to olefins by acidic treatment [5,6] [p-toluenesulfonic acid/pentane/reflux (method A), perchloric acid/ether/25°C (method B) ] or, in the case of sensitive compounds, by treatment with 2 equivalents of trifluoroacetic anhydride in methylene chloride in the presence of triethylamine (method C) [5,6].

Under the described conditions the conversion is highly stereospecific [7] (>95 %) and occurs formally by trans-elimination of the "hydroxyl" and "selenyl" moieties [8].

Since β-hydroxy selenides can be easily and stereospecifically obtained by trans opening of the corresponding epoxide by phenyl or methyl selenol [9], the whole process can be proposed as an efficient method for the stereospecific conversion of epoxides to olefins (scheme I).

SCHEME I

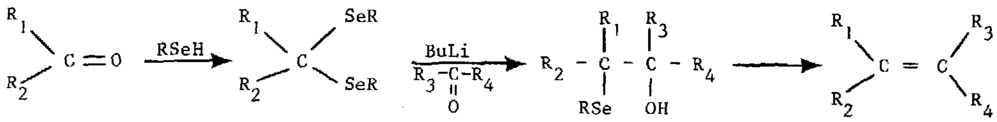


| | | | |
|---|---|---|---|
| $R_1,R_4 = C_3H_7$ | $R_2,R_3 = H$ | $R = C_6H_5$ | Methods A,B,C |
| $R_1,R_4 = C_3H_7$ | $R_2,R_3 = H$ | $R = CH_3$ | Methods A,B,C |
| $R_1,R_3 = CH_3,C_5H_{11}$ | $R_2,R_4 = H$ | $R = C_6H_5$ | Methods A, B |

β-Hydroxy selenides can also be conveniently obtained by the reaction of an α-seleno carbanion with a carbonyl compound and in our recent publications [10] we have widely exemplified the generality of such reactions which allow the formation of the carbon-carbon bond even from highly substituted or enolisable carbonyl compounds and highly substituted α-seleno acetals, the later compounds being very accessible from carbonyl compounds [11].

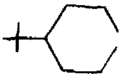
Scheme II summarizes this new and efficient route for the [C,C] connective synthesis of olefins.

SCHEME II



1 2 4 5 6

Our process is competitive with the Wittig reaction and in certain cases superior [12]. Various examples are given in Table I.

| R | $R_1$ | $R_2$ | $R_3$ | $R_4$ | Yield in purified 5 | Method used (::) | Yield in purified 6 |
|---|---|---|---|---|---|---|---|
| $C_6H_5$ | H | H | H | $nC_{10}H_{21}$ | 71 | A(40) | 71 |
| $CH_3$ | H | H | H | $nC_{10}H_{21}$ | 71 | A(18) | 35 |
| | | | | | | C(15) | 25 |
| $C_6H_5$ | H | H |  | | 68 | A(18) | 65 |
| $C_6H_5$ | H | $nC_6H_{13}$ | H | $nC_6H_{13}$ | 75 | A(8) | 70 |
| | | | | | | B(7) | 94 |
| | | | | | | C(15) | 65 |
| $CH_3$ | H | $nC_6H_{13}$ | H | $nC_6H_{13}$ | 82 | A(7) | 62 |
| | | | | | | B(72) | 85 |
| | | | | | | C(15) | 75 |
| $C_6H_5$ | H | $CH_3$ | H | $nC_{10}H_{21}$ | 80. | A(10) | 65 |

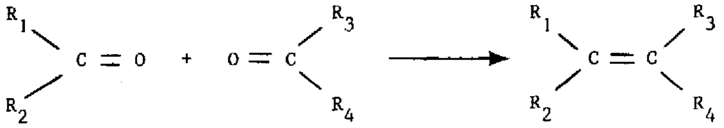
(::) Refer to reaction time (in hours)

Method A : p-toluenesulfonic acid/pentane/reflux - method B : $HClO_4$/ether/25°C

Method C : $(CF_3CO)_2O/CH_2Cl_2$/triethylamine

Finally, the versatility of our last method (the selenoacetal route) is enhanced by the fact that the olefin is formally obtained from two carbonyl compounds, each can conveniently be activated by selenium as a selenoacetal (Scheme III).

SCHEME III



McMurry recently proposed examples of such methodology; however his work in this field is restricted to the use of the same two carbonyl compounds ($R_1 = R_3$, $R_2 = R_4$) [14].

This report is voluntarily restricted to the case of disubstituted β-hydroxy selenides, but in the case of tri- or tetra-substituted compounds [12] our proposed methods were successful in 60-70 % yields (we have several examples of such conversions); nevertheless further research is necessary [1,9,12] to optimise the reaction conditions.

## References and Notes

1) a) A preliminary report of this work : A. Krief : Premières Journées Belges de chimie organique - 10-11 Novembre 1975, Knokke-le-Zout (Belgium)

   b) The preliminary report on the conversion of β-hydroxy selenides to olefins using mesyl bromide in triethyl amine which recently appeared :
   H.J. Reich and F. Chow, J. Chem. Soc. Chem. Comm., 790 (1975)
   prompt us to disclose part of our work on the subject.

2) a) K.B. Sharpless and R.F. Lauer, J. Amer. Chem. Soc., 95, 2697 (1973)

   b) W. Dumont, P. Bayet and A. Krief, Angew. Chem., Int. Ed., 13, 804 (1974)

   c) D. Seebach and A.K. Beck, ibid, 13, 805 (1974)

3) a) W. Dumont and A. Krief, Angew. Chem., Int. Ed., 14, 350 (1975)

   b) D. Van Ende, W. Dumont and A. Krief, Angew. Chem., Int. Ed., 14, 700 (1975)

   c) we also observed that olefins can be formed in 40 % yield by heating β-hydroxy selenides with methyl iodide for 2 days.

   d) D. Van Ende and A. Krief, Tet. Lett. (in press)

4) unpublished results from our laboratory

5) Other conditions have been used such as : p-toluenesulfonic acid in benzene, $H_2SO_4$ in THF for acidic media ; tosyl chloride-triethyl amine in methylene chloride, trifluoromethanesulfonyl chloride-triethyl amine in methylene chloride for basic media. All these results will be disclosed in the full paper.

6) Typical experiments :

Method A : *The β-hydroxy selenide ($5\ 10^{-4}$ m) and p-toluenesulfonic acid ($5\ 10^{-4}$ m) are refluxed in pentane (4 ml); the reaction is monitored by TLC (Thin Layer Chromatography, $SiO_2$ Merck). After completion the reaction mixture is poured into sodium bicarbonate solution (10 ml), extracted with ether, dried, then purified by PLC (Preparative Layer Chromatography, $SiO_2$ Merck, eluted with pentane : olefin rf. 0.67, diselenide rf. 0.14).*
*The diselenide can be easily removed from the organic layer by oxidation ($H_2O_2$).*
Method B : *The β-hydroxy selenide ($3.4\ 10^{-4}$ m) in ether (2 ml) is stirred at 25°C with an etheral extract of aqueous 70 % perchloric acid ($1.4\ 10^{-3}$ m, 0.4 ml). After completion the work up is similar to that used in Method A.*
Method C : *To a solution of the β-hydroxy selenide ($5\ 10^{-4}$ m) and triethylamine ($2\ 10^{-3}$ m) in $CH_2Cl_2$ or $CCl_4$ (2 ml) is added trifluoroacetic anhydride ($1\ 10^{-3}$ m) at 20°C; after completion the work up is similar to that used in Method A.*

7) The crude mixture was analyzed by V.P.C. (gas chromatography) on a silver nitrate impregnated column and olefinic compounds were identified with authentic samples.

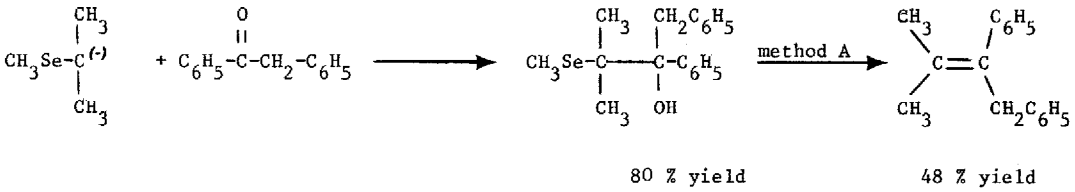
8) Work is in progress for the elucidation of the mechanism of this reaction which may occur via a seleniranium ion : G.H. Schmid and D.G. Garratt, Tet. Lett., 46, 3991 (1975)

9) For the selenophenyl case see ref. 2a. Work is in progress to determine the stereochemistry of ring opening of the tri- and tetra-substituted epoxides by selenols.

10) See ref. 2b, 2c, 3a, 3b, 3d. β-Hydroxy selenides are obtained as a mixture of stereoisomers; work is in progress in our laboratory to develop new stereospecific [C,C] connective synthesis of these compounds.

11) see ref. 2b, 2c, 3a, 3b. New routes to selenoacetals will be proposed promptly.

12) We achieved the synthesis of the 1,2-diphenyl-3-methyl-2-butene from deoxybenzoin. This compound is not accessible by other methods including phosphorus ylids or α-silyl carbanions. Ref. 13



13) W. Dumont and A. Krief, Angew. Chem. (in press) and references cited herein.

14) J.E. McMurry and M.P. Fleming, J. Amer. Chem. Soc., 96, 4708 (1974)