Tetrahedron Letters No. 41, pp 3743 - 3746, 1976. Pergamon Press. Printed in Great Britain.

THIONYL CHLORIDE/TRIETHYLAMINE : A POWERFUL REAGENT FOR REGIOSPECIFIC AND STEREOSPECIFIC FORMATION OF OLEFINS FROM β-HYDROXYSELENIDES

- stereospecific deoxygenation of di- and trisubstituted epoxides
- a [C.C] connective route to di-, tri- and tetrasubstituted olefins.

J. Rémion and A. Krief *
Department of Chemistry, Facultés Universitaires
Notre-Dame de la Paix, 61, rue de Bruxelles,
B-5000 Namur (Belgium).

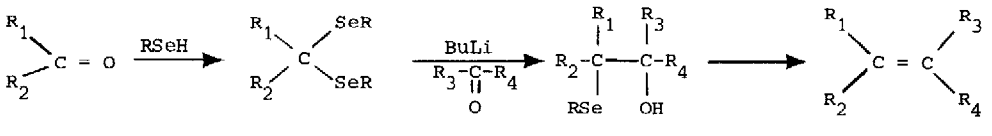
(Received in UK 20 August 1976; accepted for publication 27 August 1976)

In a recent report [1a] we have proposed new synthetic routes to disubstituted olefins 6 from β-hydroxy selenides 5 using acidic [2] [p-toluenesulfonic acid (method A), or perchloric acid (method B)] or basic media [trifluoroacetic anhydride/triethylamine (method C)] [2]. We also demonstrated that all these transformations are highly stereospecific.

This paper deals with the introduction of a powerful reagent for such transformation as well as the extension of the former report [1a] to the synthesis of tri- or tetra substituted olefins. Finally we give some experimental support to the mechanism of this transformation [1].

In the course of this work, we found that thionyl chloride/ triethylamine in methylene chloride (method D) is the most appropriate reagent for such transformation 5 → 6 (Scheme I or Scheme II, table I). It is a cheap, readily available reagent, which reacts rapidly at room temperature with all differently substituted β-hydroxy selenides 5, producing olefins, even the tetrasubstituted ones, in excellent yield without any rearranged products (table I, method D) [3]. The overall process described in Scheme I discloses a powerful synthetic route to olefins from carbonyl compounds 4; it is superior to the Wittig reaction, e.g., 1,2-diphenyl-3-methyl-2-butene is obtained in 72% overall yield from deoxybenzoin. This olefin is not accessible by other methods including isopropylidene triphenyl phosphorane(which quantitatively enolises deoxybenzoin)

SCHEME I



1 2 4 5 6

TABLE I

R	R_1	R_2	R_3	R_4	Yield in purified $\underline{5}$	Method used (*)	Yield in purified $\underline{6}$	Entry
C_6H_5	H	H	H	$C_{10}H_{21}$	69	D (22) A (41)	70 71	a
CH_3	H	C_6H_{13}	H	C_6H_{13}	82	D (3) E (12)	88 86	b
C_6H_5	CH_3	CH_3	H	$C_{10}H_{21}$	50	D (2) A (26) B (13)	90 30 * 31	c
CH_3	CH_3	CH_3	H	$C_{10}H_{21}$	80	D (2) A (9) B (9)	80 59 * 22	d
CH_3	H	C_6H_{13}	C_3H_7	C_3H_7	65	D (2) A (17)	80 61	e
CH_3	CH_3	CH_3	C_9H_{19}	CH_3	63	D (1)	83	f
CH_3	CH_3	CH_3	$CH_2C_6H_5$	C_6H_5	80	D (2) C (1) A (8)	85 93 48 *	g

Method : A : p-toluenesulfonic acid/pentane/reflux - B : $HClO_4$/ether/25°C - C : $(CF_3CO)_2O/CH_2Cl_2$/ triethylamine/25°C - D : $SOCl_2/CH_2Cl_2$/triethylamine/25°C - E : NaH/THF/25°C, phosphochloridite/25°C.

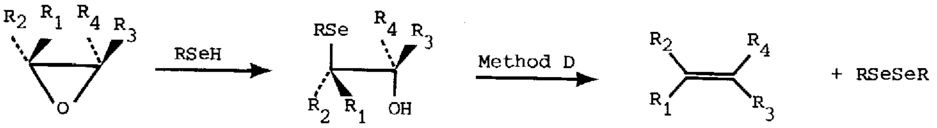
(*) Refer to reaction time in hours - The yields are quoted for analytically pure compounds.

** Ketones are also formed : see following text.*

Interestingly we found that, using method D, di- and trisubstituted olefins are stereospecifically formed from the corresponding β-hydroxyselenides by trans elimination of the hydroxyl and selenyl moieties (Scheme II).

In the case of trisubstituted β-hydroxyselenides, this is the first report of their regio- and stereospecific formation (70% yield) as well as their stereospecific transformation to olefins (80% yield).

SCHEME II

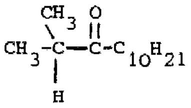


R_1, R_3 : H R_2, R_4 : C_8H_{17} R : CH_3 94 % yield

R_1 : C_2H_5 ; R_2 : C_5H_{11} ; R_3 : C_7H_{15} ; R_4 : H : R : C_6H_5 80 % yield

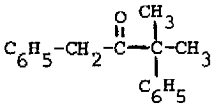
Others reagents have been used for the transformation of β-hydroxyselenides to olefins.

An acidic reaction medium (method A or B)[1a,2] has been successfully used in the synthesis of tri- or tetra substituted olefins, see table I. The yields,however, are lower than those obtained by method D, or when disubstituted analogs are reacted in the same acid media (method A,B). Moreover, rearranged carbonyl compounds are formed in such acidic media. e.g.2-methyl-3-tridecanone 7 and 1,3-diphenyl-3-methyl-2-butanone 8 are formed respectively in 26% and 47% yield[6] (see Table I, Entry c or d, method A, and Entry g method A).



$CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-C_{10}H_{21}$

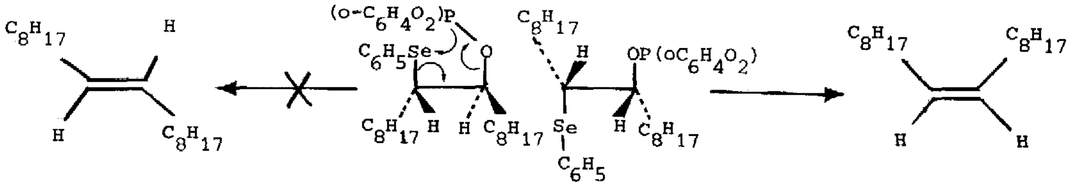
7



$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-\underset{C_6H_5}{\overset{CH_3}{C}}-CH_3$

8

We also once performed the reaction of : NaH/Phosphochloridite (method E) [a reagent already used[7] for the transformation of β-hydroxysulfides to olefins] with a β-hydroxyselenide. The reaction works very well and the olefin is much faster produced than described in the case of sulfur analogs, but from the stereochemistry of the formed olefin, we must conclude that the mechanism proposed by the authors[7] is inoperant at least in our case.(For a tentative explanation of the mechanism of this reaction: see below.)



Method E.

Finally, we are interested in the mechanism of transformation of β-hydroxyselenide → olefin. All the results described in the former paper and this paper agree with the intermediate formation of a seleniranium salt[8]. Further support of this hypothesis is deduced from the following experiments :

Z and E octadecene are readily transformed[8] to their corresponding seleniranium hexafluoroantimonates [CD_2Cl_2, $C_6H_5SeSbF_6$, - 78°C]. From the N.M.R. spectra of an aliquot,it can be observed that the transformation is complete [N.M.R. CD_2Cl_2 : 11a , Ha : 5,1 ppm (80%) + 4,9 ppm (20%) 11b Ha : 4.8 ppm]

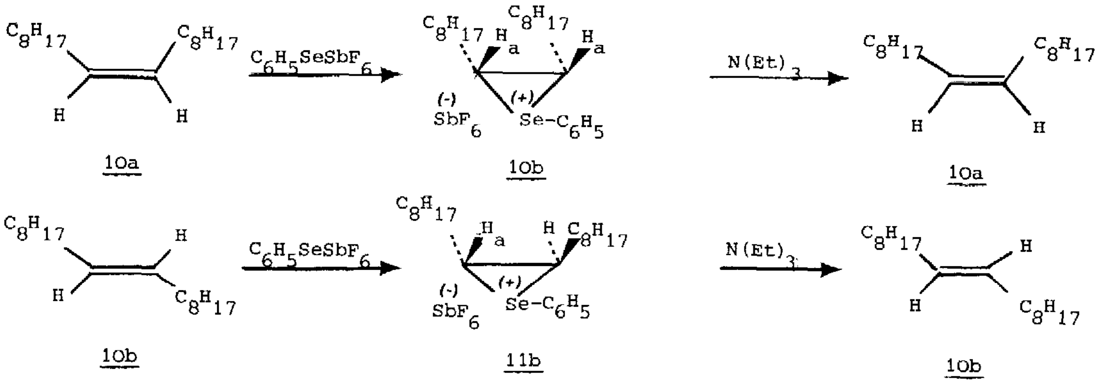
These compounds 11 give rise to polymeric materials when standing at 25°C for 12 hrs. However they are instantaneously * and quantatively stereoselectively transformed back to olefins [10a (containing 15% of 10b) and 10b] by addition of triethylamine ** (Scheme III).

---

* a control experiment was also realized in the N.M.R. probe at room temperature.

** the stereochemistry of the formed olefins 11a → 10a, 11b → 10b are deduced from the N.M.R. spectrum of their thionocarbonates[9].

SCHEME III.



REFERENCES.

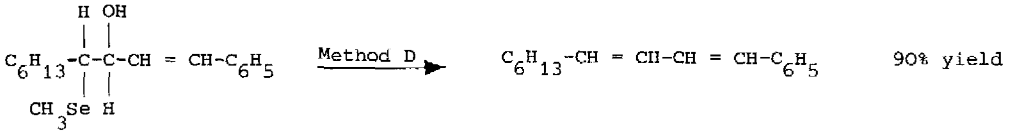
1a) J. Rémion, W. Dumont and A. Krief. Tet. Letters 1385 (1976).

b) H.J. Reich and F. Chow. J. Chem. Soc. Chem. Comm. 790 (1975).

c) A.M. Leonard-Coppens and A. Krief : submitted to publication. This paper deals with a new stereospecific [C.C] connective synthesis of β-hydroxyselenide. Some more examples of their transformation using method D were described.

2) Typical experiments for method A,B,C are included in the former report ref. 1a).

3) Method D was also successfully used for the transformation of a α-β unsaturated β-hydroxyselenides [4] to a diene. Unpublished results from our Laboratory.



$$C_6H_{13}-\underset{CH_3Se}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-CH=CH-C_6H_5 \xrightarrow{\text{Method D}} C_6H_{13}-CH=CH-CH=CH-C_6H_5 \quad 90\%\ \text{yield}$$

4) D. Van Ende and A. Krief. Tet. Letters 457 (1976).

5) Typical experiment.

To a solution of the β-hydroxyselenide (5.10^{-4}m) and triethylamine ($3.5.10^{-3}$m) in CH_2Cl_2(4ml) is added thionylchloride (1.10^{-3}m) in CH_2Cl_2 (2ml) at 20°C; the reaction is monitored by T.L.C. (thin layer chromatography SiO_2 Merck). After completion, the reaction mixture is poured into water, extracted with ether, washed with HCl 1% (10ml) and water (10ml). The organic layer is dried and purified by P.L.C. (preparative layer chromatography SiO_2 Merck, eluted with pentane : olefin rf. 0.8, diselenide rf. 0.23).

6) The structure of these compounds has been deducted from their I.R. and N.M.R. spectra.

7) I. Kuwajima, S. Sato and Y. Kurata. Tet. Letters 737 (1972).

8) G.H. Schmid and D.G. Garratt. Tet. Letters 3991 (1975).

9) A. Krief, L. Hevesi, J.B. Nagy, E.G. Derouane. Submitted for publication.