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ALLYLSELENIDES POSSESSING A TERMINAL DOUBLE BOND FIRST REGIOSELECTIVE SYNTHESIS AND REACTIONS

T. Di Giamberardino, S. Halazy, W. Dumont and A. Krief *

Facultés Universitaires Notre-Dame de la Paix
Department of Chemistry
61, rue de Bruxelles, B-5000 Namur (Belgium)

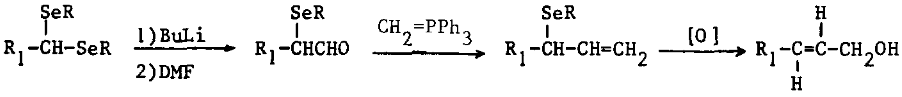
Allyl methyl selenides bearing a terminal double bond rearrange in the presence of even a trace of acid, whereas their phenyl analogues, contrary to what has been described, were found to be thermally stable but highly sensitive to light.

In the course of a study related to the synthesis of allyl alcohols 4($R=C_3H_7$ and C_5H_{11}) possessing the E stereochemistry, the acetates of which have been described as natural pheromones[1], we had occasion to test a new synthetic method which required the regioselective synthesis of allylselenides and the rearrangement of their oxides.

The interest of the research project was increased by the fact that no regioselective synthesis of this type of allylselenides has been described up to now[2], and because the stereochemistry of the allylalcohols resulting from the rearrangement of their oxides [2b-e,3] has not yet been determined.

The regioselective synthesis of allylmethyl- and allylphenyl-selenides 3 was readily achieved[2h] from methylenetriphenylphosphorane (from methyltriphenylphosphonium iodide and n-Buli in THF) and α-seleno-aldehydes, themselves prepared from α-selenoalkyllithiums and dimethyl formamide.

SCHEME



$$R_1-\overset{SeR}{\overset{|}{C}}H-SeR \xrightarrow[2)DMF]{1)BuLi} R_1-\overset{SeR}{\overset{|}{C}}HCHO \xrightarrow{CH_2=PPh_3} R_1-\overset{SeR}{\overset{|}{C}}H-CH=CH_2 \xrightarrow{[O]} R_1-\underset{H}{C}=\overset{H}{C}-CH_2OH$$

1 2 3 4

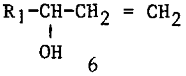
Entry	R_1	R	2 yield %	3 yield %	4 (method) yield (%)
a	C_3H_7	Me	70	84	(A):85 ; (B):75
b	C_5H_{11}	Me	75	85	(A):80
c	C_5H_{11}	Ph	74	60	(A):80 ; (B):80
d	C_6H_{13}	Ph	70	75	(A):70
e	C_6H_{13}	Me	75	91	

Method (A) : H_2O_2/CH_2Cl_2-pyridine   Method (B) : $NaIO_4$/methanol-water-buffer pH9

We found that these compounds 3 rearrange easily to their isomers 5 possessing an internal double bond under various conditions which will be discussed in the last part of this paper.

$R_1-CH = CH - CH_2SeR$

5



$$R_1-\underset{OH}{\underset{|}{C}}H-CH_2 = CH_2$$

6

Compound 3 can however be freed from the triphenylphoshine oxide formed concomitantly, by crystallization of the latter in pentane.

The transformation of the allyl selenides 3 to the allyl alcohols 4 has been rapidly achieved on oxidation of the former product with H_2O_2(20% aq. sol., CH_2Cl_2, pyridine, 20°, Method A) or with $NaIO_4$(methanol-water) in the presence of a pH9 buffer (Merck, 9461, Method B). In the absence of the buffer both the allyl alcohols 4 and 6 (4/6 = 70/30) are formed in the case of the methylseleno derivatives 3 (78% yield). The formation of 4 and 6 can be explained by the partial acid catalysed isomerisation of 3 to 5 prior to oxidative rearrangement. Some related examples will be described below.

In two cases [entry a(B), entry d(A)] we have checked the stereochemistry of the formed allyl alcohol 4 and found that only the E isomer is produced[4], (|GC|[2], ^1H and ^{13}C NMR, comparison with an authentic sample).

In the course of this work we made two interesting observations related to the ease with which allyl selenide 3 rearrange to their isomers. For example, the allyl methyl selenide 3 ($R_1=C_6H_{13}$) was found to be extremely acid sensitive[5], rearranging quantitatively to 5 on silica gel TLC plates or when reacted with p-toluenesulfonic acid (PTSA) in benzene (20° < 3 h). Its phenylseleno analogue ($R_1=C_6H_{13}$), although showing the same behaviour, is much less reactive. It can be purified by SiO_2 TLC without any precaution, but completely rearranges in the presence of PTSA in benzene[6,7] (20°, 5h).

On the other hand phenylseleno derivatives 3 are extremely photolabile. For example, 3 ($R_1=C_6H_{13}$) is quantitatively transformed into its regioisomer 5 on direct exposure, through pyrex, to sunlight ($CDCl_3$, 20°, 3h), to a U.V. lamp (Philips 4822 Al 134 30012, benzene 20°, 0.7h) or when illuminated with TL tubes present in the lab (benzene, 75°, 22h). Its methylseleno analogue is also photosensitive but to a much lower extent (U.V. lamp, 1h, 3/5 = 65/35 ; stable to sunlight, 3h).

Both methyl and phenyl derivatives 3($R=C_6H_{13}$) are stable when heated at 55° ($CDCl_3$, 6h) or at 75° (benzene, 20h) provided that light or acids are excluded. They however rearrange to 5 when heated at much higher temperature (decalin, 150°, 20h, 3/5 : $R = CH_3$ 40/60 ; $R=C_6H_5$: 0/100).

These results clearly demonstrate that allylselenides, especially the allyl phenyl selenides bearing a therminal double bond, are not particularly thermolabile contrary to recent reports[2a,8].

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4. H.J. Reich[2e] has described with one example that a mixture of regioisomeric allylphenyl selenides produces predominantly the primary allyl alcohols. This compound was pictured as the trans compound but he did not give evidence for such a description.
5. The corresponding allyl methyl sulfide is stable under the same conditions.
6. This finding can explain the scrambling of the selenyl moiety recently described by Itoh in the dehydroxysilylation of β-seleno β'-silyl alcohols[2i-k] catalysed by $SnCl_2$ or H^+.
7. For some related work in the sulfur series :
   a) P. Brownbridge, S. Warren, J. Chem. Soc. Commun. 820 (1975).
   b) P. Brownbridge, S. Warren, J. Chem. Soc. Perkin I 2125 (1976).
   c) P. Brownbridge, S. Warren, J. Chem. Soc. Perkin I 1131 and 2272 (1977).
8. We have heated (55°, 6h, $CDCl_3$), 2-methyl-3-phenylseleno-1-heptene, the compound originally described by Sharpless[2]. No rearrangement occurs if light is excluded. The isomerization is however complete on heating at 150° (light excluded, 20h), or on exposure to light (UV lamp, benzene, 20°, 0.3h), or to acid (PTSA, benzene, light excluded, 20°, 7h).

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