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SYNTHETIC ROUTE TO VINYL SELENIDES AND VINYL SELENOXIDES

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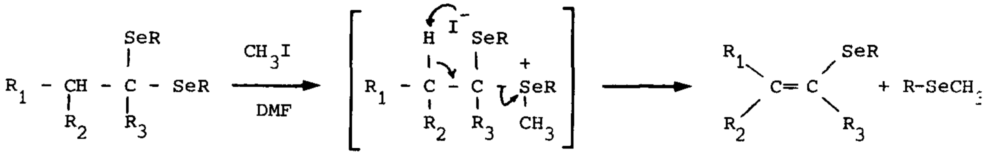
Vinyl selenides should be powerful building blocks in organic synthesis; they are nucleophiles and should be activated as electrophiles for example by oxidation to the hiterto unknown vinyl selenoxides. Vinyl selenides have already been prepared by isomerisation of allyl phenyl-selenides [1], addition of phenyl selenol to an acetylenic compound [2] or by a C-C connective route from an aldehyde [3] as described by Reich.

We report on a new method of vinyl selenide synthesis [4] as well as the behaviour of vinyl selenides toward oxidants.

We found that selenoacetals, easily prepared from carbonyl compounds [5], are transformed to vinyl selenides [6] 2 when reacted with methyl iodide in DMF (Scheme I, Table I). Generally the more substituted olefin is formed.

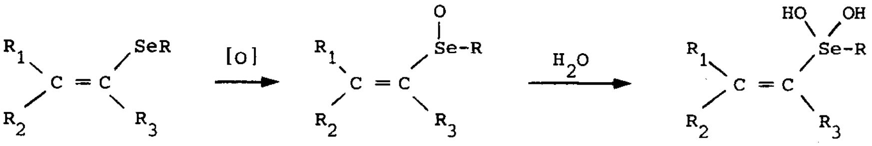


1

2

R	R_1	R_2	R_3	Yield
CH_3	H	C_5H_{11}	H	50
CH_3	H	C_9H_{19}	H	65
CH_3	H	C_8H_{17}	CH_3	65
CH_3	H	C_5H_{11}	CH_3	60
CH_3	H	$CH_2-CH_2-CH_2-CH_2$		65
CH_3	CH_3	$CH_2-CH_2-CH_2-CH_2$		53
C_6H_5	H	H	H	65
C_6H_5	H	C_5H_{11}	H	65
C_6H_5	H	H	CH_3	60

Vinyl selenides react with 1.1 equivalent of sodium periodate in methanol (method A)[7] or 1 equivalent of m-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 (method B)[8] at room temperature : vinyl selenoxides 3 are obtained in high yield [7,8].

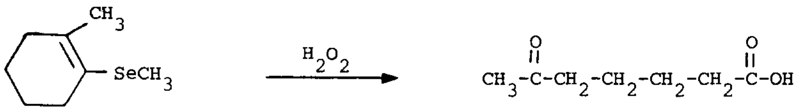


2 3 4

R	R_1	R_3	Yield %
C_6H_5	H	H	95(A)
C_6H_5	C_5H_{11}	H	90(A) - 95(B)
C_6H_5	C_8H_{17}	CH_3	96(A) - 83(B)
CH_3	C_9H_{19}	H	97(A)
CH_3	C_5H_{11}	CH_3	90(A)
C_6H_5	C_5H_{11}	CH_3	87(B)
CH_3	C_9H_{19}	H	77(B)

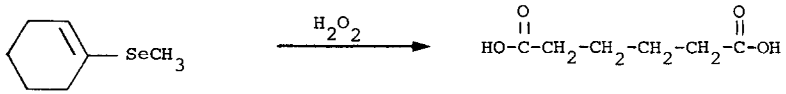
These compounds 3 release oxygen and decompose back to vinyl selenide slowly at 25°C and more rapidly at higher temperature or when treated with sodium thiosulfate solution (5 hrs, 25°C). The selenoxides 3 are moderately hygroscopic (3 → 4) and do not release easily oxygen under these conditions [9].

A somewhat surprising result arises from the reaction of H_2O_2 (excess) on vinyl selenides[10,11] which leads to the cleavage of the C=C double bond. For instance, vinyl selenides 2, in which the substituents R_1, R_2 and R_3 are alkyl groups, are transformed to ketone and carboxylic acid functionalities, as exemplified below (60% yield).



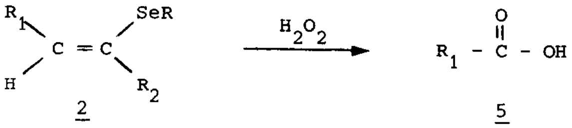
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

When R_2 is a hydrogen in selenoxide 2, we do not succeed in trapping the corresponding aldehyde and acid : two carboxylic acid functions are isolated in these cases. For instance, 1-selenomethyl-2-methyl-1-cyclohexene produces adipic acid in 75% yield.



$HO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

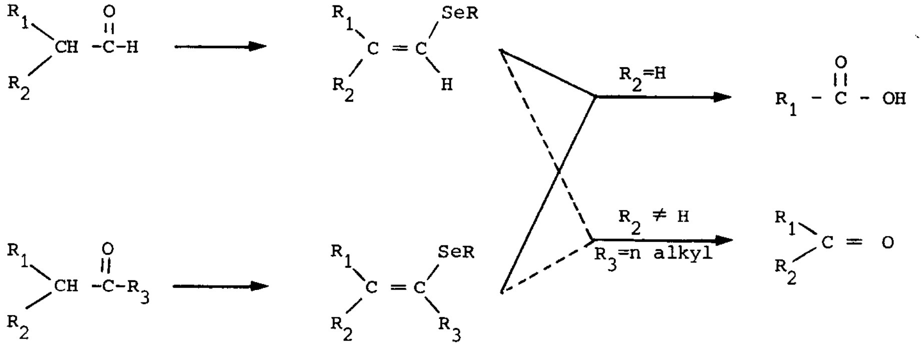
This reaction seems to be general as shown in the following table :



R	R_1	R_2	Yield of 5 %
CH_3	C_9H_{19}	H	70
C_6H_5	C_5H_{11}	H	83
C_6H_5	C_5H_{11}	CH_3	73

Vinyl selenoxide 3 should be an intermediate in this reaction and this could be supported by the oxidation of the independently synthesized 1-(phenylseleninyl)-2-octene to hexanoic acid (62%). Work is in progress to understand the mechanism of this reaction.

The transformation outlined below, which takes advantage of the two reactions presented in this paper, describes a new degradation pathway of aldehydes and ketones to carbonyl compounds. The interest in this reaction lies in the high selectivity in synthesizing specifically the more substituted vinyl selenide from a carbonyl compound and the simplicity of the reagent for the C=C bond cleavage.



References

1. a) Allyl phenyl selenide was transformed[1b,c] to 1-propenyl phenyl selenide by refluxing with sodium ethylate in ethanol for 18 hrs. The yield in propenyl phenyl selenide was 75%.

   b) A. Anciaux, A. Eman, W. Dumont, D. Van Ende and A. Krief, Tet. Lett., 1613 (1975)

   c) D.S. Tarbell and M.A. McCall, J. Amer. Chem. Soc., 74, 48 (1952)

2. a) L.M. Kataeva, I.V. Anonimova, L.K. Yuldasheva and E.G. Kataev, Zh. Obshch. Khim, 32, 3965 (1962)

   b) J. Gosselck and E. Wolters, Z. Naturforsh. B, 17, 131 (1962)

3. M.J. Reich and F. Chow, J. Chem. Soc. Chem. Comm., 790 (1975)

4. For other synthesis, W. Dumont, M. Sevrin and A. Krief, submitted for publication

5. W. Dumont and A. Krief, Angew. Chem., 1977, in press and references cited herein

6. To a mixture of 1-1-diphenylseleno-ethane in DMF (20 ml) is added iodomethane (10^{-1} mole). The solution is stirred at 80°C for 2 hrs*. Then ether (100 ml) is added and the solution is washed with thiosulfate, then with water. The ether solution is dried. The 1-phenylselenoethylene is purified by distillation (bp_{25} : 104°C).
   * prolonged period of reaction even at room temperature substantially lowers the yield of the vinyl selenide.

7. 1-phenylselenoethylene (10^{-3} mole) in methanol (50 ml) and H_2O (15 ml) is reacted with $NaIO_4$ (1.1×10^{-3} mole) during 15 min at 10°C and 4 hrs at 20°C. Then chloroform (60 ml) is added, the solution is washed with $NaHCO_3$, water, then dried. Removal of the solvent leads to the corresponding selenoxide.

8. 1-methylseleno-1-heptene (10^{-3} mole) in CH_2Cl_2 (5 ml) is reacted with MCPBA (10^{-3} mole) during 2 hrs at 20°C. Ether (60 ml) is then added. The solution is washed with a solution of $NaHCO_3$ in water, then with water and finally dried. Evaporation of the solvent affords the selenoxide analytically pure.

9. Structure 4 is tentitatively assigned to these compounds. NMR spectra (CCl_4) discloses a peak* at 4.5ppm which disappearswhen the solution is dried over magnesium sulfate.
   * displaced by dilution.

10. 1-methylseleno-1-heptene (10^{-3} mole) in THF (5 ml) is reacted with H_2O_2 (1 ml, ca 8.10^{-3} mole) during 30 min at 0°C and 2 hrs at 20°C.
    Usual work up and purification affords hexanoic acid (83% yield).

11. Prof. Paul Grieco informed us of a similar observation.