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A PUMMERER-TYPE REARRANGEMENT OF SELENIDES

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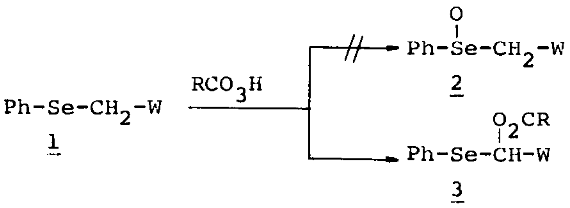
Abstract: A Pummerer-type rearrangement has been observed in the course of the oxidation of selenides of type 1. The main isolated product was the hemiselenoacetal 3.

In the last decade the versatility of selenium containing compounds has been recognized in synthetic organic chemistry[1]. They are applied as efficient synthetic tools for the construction of a number of functionalities. One of the most frequently used transformations of these compounds is the oxidation - elimination sequence, which leads to the formation of a carbon-carbon double bond under very mild conditions. The oxidation of selenides to selenoxides usually can be performed in excellent yields with a variety of oxidizing agents /e.g. peracids/.

In the course of our investigation aimed at the preparation of selenium containing active methylene compounds, a new type of reaction was observed. We wish to publish our observation in this communication.

The starting materials of the experiments are represented with the general formula 1 /Scheme/. In general, these compounds do not possess hydrogen β to the phenylselenenyl group, that is formation of a carbon-carbon double bond is impossible, and in all cases W is an electron-withdrawing group /Table/. These materials were oxidized with peracids /40-80 mg/ml of chloroform, 2.0-2.3 eq. peracid added portionwise or in solution, 30 min. at $0^{o}C$, 2-3 hr at room temperature, purification with chromatography/. Surprisingly enough, no selenoxide formation /2/ could be detected, the sole selenium containing aliphatic product was the hemiselenoacetal /3/. In all reactions diphenyl diselenide could be isolated in relatively high yield, as selenium containing byproduct /25-35%/. The results are summarized in the Table.

Scheme



Table[a]

Product[b]	W	R	Yield[c] /%/
4	CO_2Me	m-Cl-C_6H_4	37
5	$\underset{\underset{O}{\|}}{C}-/CH_2/_2CO_2Me$	m-Cl-C_6H_4	43
6	$\underset{\underset{O}{\|}}{C}-/CH_2/_2CO_2Me$	Me	40
7	C≡N	m-Cl-C_6H_4	45
8	C≡N	Me	58

a/ starting materials were prepared from the corresponding halides and sodium phenyl selenide and were identified by spectroscopy; b/ for spectral data see ref. 2/; c/ not optimized isolated yields.

The reaction published here can be regarded as a version of the well-known Pummerer rearrangement[4] of sulfur compounds. This procedure ensures an access to specially protected oxo funtionalities, which can serve as useful synthetic intermediates in certain cases[5].

References

1/ For example: D.L.J. Clive, Tetrahedron, 1978, 34, 1049., H.J.Reich, Accts. Chem.Res., 1979, 12, 22.; A.Krief, Tetrahedron, 1980, 36, 253.

2/ Abbreviations in spectral data are the following: IR /film, cm^{-1}, ν_{CO}/, ^1H NMR /$CDCl_3$, δ, ppm, CH, the coupling constants are given for the ^{77}Se satellite-peaks, see ref.3/; MS / m/e /: 4: R_f/10 hexane - 1 ethyl acetate/: 0.19; IR: 1750 /broad/; ^1H NMR: 6.63 /J_{sat}= 22 Hz/; MS: 139 /parent peak/, 384 /3%/ $M^{+\cdot}$; 5: R_f/2 hexane - 1 ethyl acetate/: 0.44; IR: 1740 /broad/; ^1H NMR: 6.67 /J_{sat}= 23 Hz/; MS: 139 /parent peak/, 440 /1%/ $M^{+\cdot}$; 6: R_f/3 hexane- - 1 ethyl acetate/: 0.21; IR: 1730 /broad/; ^1H NMR: 6.42 /J_{sat}= 22 Hz/; MS: 145 /parent peak/, 344 /19%/ $M^{+\cdot}$; 7: R_f/10 hexane - 1 ethyl acetate/: 0.28; IR: 1740; ^1H NMR: 6.85 /J_{sat}= 25 Hz/; MS: 139 /parent peak/, 361 /3%/ $M^{+\cdot}$; 8: R_f/10 hexane - 1 ethyl acetate/: 0.19; IR: 1760; ^1H NMR: 6.52 /J_{sat}= 24 Hz/; MS: 77 /parent peak/, 255 /40%/ $M^{+\cdot}$. All compounds have satisfactory elemental analysis.

3/ T.N. Huckerby in Ann. Rep. on NMR Spectroscopy, Edited by E.F.Mooney, Academic Press, New York, 1972, Vol. 5A, p.62. and references cited therein.

4/ G.A. Russel, G.J. Mikol, in Mechanisms of Molecular Migrations, Edited by B.S. Thyagarayan, Interscience Publishers, 1968, Vol. 1, p. 157.

5/ We are grateful to Drs. L. Pusztay, K. Horváth, and J. Hollós for recording the IR NMR and MS spectra, respectively, and for the help in the interpretation. Mrs. M. Szebeni's valuable technical assistance is acknowledged here.

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