

New Rearrangement of Phenylseleno- and Trimethylsilylmethyl Groups in 2-Hydroxy-3-trimethylsilylpropyl Selenides

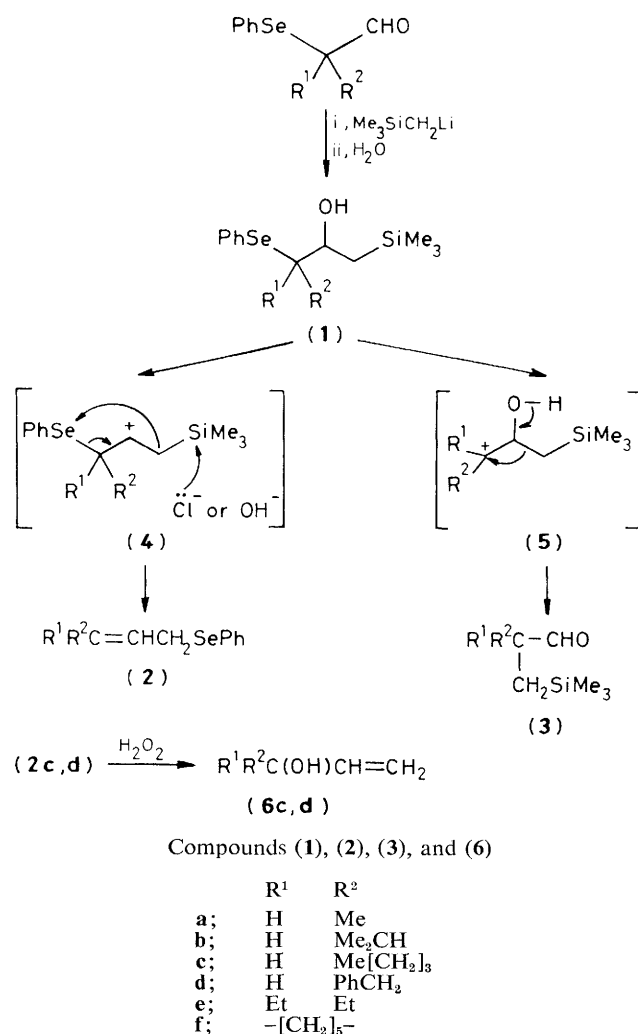
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2-Hydroxy-3-trimethylsilylpropyl selenides, readily prepared by the reaction of α -phenylselenoaldehydes and trimethylsilylmethyl-lithium, are transformed into primary allylic selenides and β -trimethylsilylpropanals by acid-catalysed dehydroxysilylation accompanied by a phenylseleno-shift, and by silver-induced rearrangement of the trimethylsilylmethyl group, respectively.

Brownbridge and Warren described an efficient formation of allylic sulphides from 2-hydroxyalkyl phenyl sulphides by phenylthio-migration.¹ In contrast, we now show that treat-

ment of 2-hydroxy-3-trimethylsilylpropyl selenides (**1**) with tin(II) chloride gives mainly the allylic selenides (**2**) by dehydroxysilylation and facile migration of the phenylseleno-group,



Scheme 1

and that a novel rearrangement of the trimethylsilylmethyl group was found by treatment of (1) with silver nitrate–Celite to give β -trimethylsilylpropanals (3) (Scheme 1).

Compound (1) was prepared by treatment of the corresponding α -phenylselenoaldehyde² with $\text{Me}_3\text{SiCH}_2\text{Li}$ (ca. 0.5M in hexane) at -78°C in Et_2O . It was treated with a catalytic amount of tin(II) chloride (ca. 10–20 mol%) in CH_2Cl_2 at room temp. for 2–3 h to give the allylic selenide (2), whose phenylseleno-group is attached to the primary carbon atom of the allylic system (Table 1).

The phenylseleno [1,3]-shift can be thought to occur in the following manner: (i), a fast rearrangement of the initially formed secondary or tertiary allylic selenide, derived from the usual Peterson olefination in the reaction medium; (ii), a spontaneous shift promoted by desilylation of the intermediary species (4).

In contrast with the secondary selenides (1a–d), the tertiary selenides (1e, f) gave the allylic selenides in low yield, but surprisingly gave the corresponding β -trimethylsilylpropanals (3) on treatment with SnCl_2 (entries 5 and 7). This new rearrangement was considered to arise from faster elimination of the phenylseleno-group than the hydroxy-group forming the stable tertiary carbocation (5). The predominant migration

Table 1. Transformation of 2-hydroxy-3-trimethylsilylpropyl selenides (1) into the allylic selenides (2) and the β -trimethylsilylpropanals (3).

Entry	(1) (% yield) ^a	Method ^b	Products (% yield) ^c
1	a (85)	A	(2a) (63) [55] ^d
2	b (75)	A	(2b) (86) [65] ^d
3	c (84)	A	(2c) (63) [64] ^d
4	d (68)	A	(2d) (57) [56] ^d
5	e (92)	A	(2e) (20); (3e) (46)
6	e	B	(3e) (83)
7	f (73)	A	(2f) (16); (3f) (26)
8	f	B	(3f) (85)

^a The yields of (1) were obtained by treatment of the corresponding α -phenylselenoaldehydes with $\text{Me}_3\text{SiCH}_2\text{Li}$ in Et_2O at -78°C . Compound (1) was purified by Florisil column chromatography.

^b Method A: catalyst SnCl_2 (ca. 10–20 mol%), CH_2Cl_2 [5 ml per mmol of (1)], room temp., 2–3 h; method B: AgNO_3 (2 equiv.)–Celite, CH_2Cl_2 [5 ml per mmol of (1)], room temp., 30 min. AgNO_3 –Celite was prepared by addition of a solution of AgNO_3 (2 mmol) in MeCN (2 ml) to an ether (6 ml) suspension of Celite-545 (1 g) and evaporation of the solvents. Compounds (2) and (3) were isolated by Florisil column chromatography (hexane–ether as eluant). ^c All compounds were characterized on the basis of ^1H n.m.r. (60 MHz), i.r., and mass spectral analysis. Isolated yield based on the purified selenides (1). ^d Total yield from the corresponding aldehydes without purification of (1).

of the trimethylsilylmethyl group over hydrogen is noteworthy. We attempted, therefore, the selective formation of (3) by treatment with silver ions. Treatment of the tertiary selenides (1e) and (1f) with AgNO_3 –Celite in CH_2Cl_2 at room temp. for 30 min gave the aldehydes (3e) and (3f) exclusively (entries 6 and 8). The silver ion should have sufficient affinity for the selenium atom to eliminate the phenylseleno-group from (3e) and (3f).

Krief and co-workers recently reported that treatment of 2-hydroxyalkyl selenides with AgBF_4 caused the same rearrangement, but this method was limited to hindered derivatives; both carbon atoms bearing the seleno-group and the hydroxy-group were tertiary.³ Our findings of a novel migration of the trimethylsilylmethyl group are therefore quite important; Me_3SiCH_2 can migrate from a secondary to a tertiary carbon atom.

Further oxidation of the allylic selenides (2c) and (2d) with H_2O_2 ⁴ gave the secondary allylic alcohols (6c) (73%) and (6d) (91%) via 2,3-sigmatropic rearrangement of the intermediary selenoxides. The total transformation of (1) into (6) is also interesting as an α -hydroxyolefination of aldehydes. These reactions considerably increase the usefulness of α -phenylselenoaldehydes in chemical synthesis.

Received, 16th July 1982; Com. 829

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