

First Examples of Seleno-Claisen Rearrangements of Allyl Vinyl Selenides

Yannick Vallée* and Mark Worrell

Laboratoire de Chimie des Composés Thio-organiques, URA CNRS 480, ISMRA, 14050 Caen, France

Allyl vinyl selenides easily undergo a [3.3] sigmatropic rearrangement under mild conditions to give γ -unsaturated reactive selenocarbonyl compounds, which can be trapped by cyclopentadiene or water.

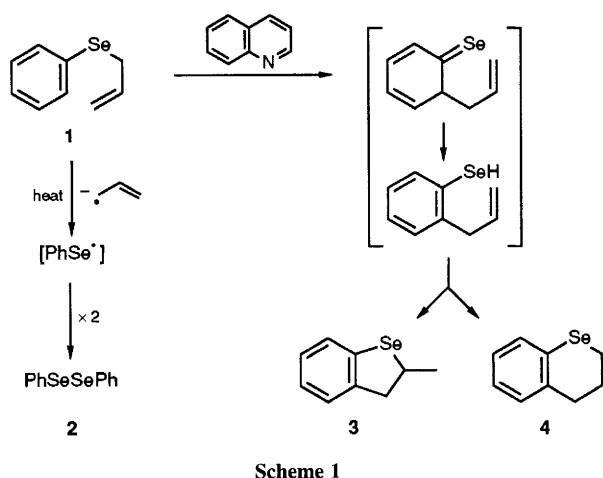
Since the pioneering work of Kwart and coworkers,¹ which described the thermal behaviour of allyl phenyl sulfide, the thio-Claisen rearrangement has received considerable interest.² More particularly, the rearrangement of allyl vinyl sulfides has been recognized as a powerful tool in the stereoselective formation of carbon-carbon bonds.³ In sharp contrast, in spite of the known usefulness in synthesis of organic selenium compounds, the [3.3] sigmatropic process involving allyl vinyl selenides was unknown before this work.⁴

Such a lack of interest for this potentially useful reaction is probably owing to the known propensity of organic selenides to give selenyl radicals when heated.⁵ In fact, it has been reported that heating allyl phenyl selenide **1** at 600 °C under flash vacuum thermolysis conditions does not lead to Claisen products, but to diphenyl diselenide **2** via a radical pathway⁶ (Scheme 1). However, in 1967, Kataev *et al.* reported that the thermolysis of **1** in boiling quinoline (237 °C) gave **3** (and

perhaps **4**) in 15 to 30% yield.⁷ The formation of **3** should result from the cyclisation of an intermediate selenol, the 'eneselenol' tautomer of the selone formed by the Claisen rearrangement. We have repeated this experiment and found that the major product was the diselenide **2**, with **3** being only a minor product (molar ratio **2**:**3** = 80:20, determined by ¹H NMR of the crude product).

We found the seleno-Claisen rearrangement of allyl vinyl selenides **5a**, **b** to occur in considerably milder conditions (Scheme 2). These compounds were synthesized by successive treatment of the corresponding vinylic Grignard reagent⁸ by selenium and allyl bromide.† However, in the first example (R

† This method can be used to synthesize stable vinyl selenides. For instance treatment of CH₂CHSeMgBr by benzyl bromide gave CH₂CHSeCH₂Ph in 80% yield.



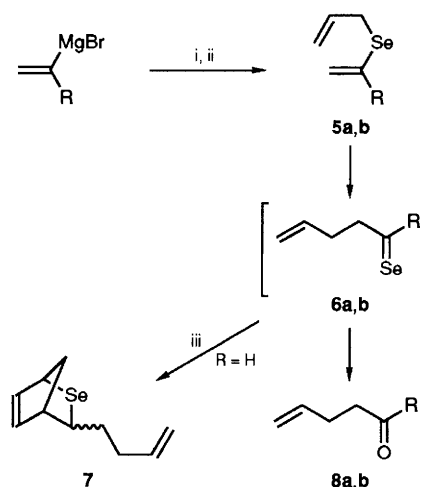
(R = H), the ^1H NMR of the crude product, recorded immediately after its extraction, was not in good agreement with the proposed structure **5a**. The observation of a multiplet between δ 2.0 and 2.5 suggested the formation of by-products resulting from the oligomerisation of the intermediate selenoaldehyde **6a**.[‡]

The transient formation of the unsaturated selenoaldehyde **6a** was unambiguously proved by trapping it with a diene. An excess of cyclopentadiene was added to a solution of **5a** in tetrahydrofuran (THF) and the reaction mixture was stirred for four days at room temperature. The expected adduct **7** was isolated in 49% yield (*endo*:*exo* = 4:1).⁹

Compound **5b** is more stable than **5a** and does not undergo significant rearrangement at room temperature. However, when it was heated at 84 °C in a water–dimethoxyethane (DME) mixture for 20 h,¹⁰ the ketone **8b**¹¹ resulting from the hydrolysis of the intermediate selenone **6b** was isolated in 61% yield. The selenoaldehyde **6a** also reacts with water but the yields of the expected aldehyde **8a** remained poor (less than

[‡] It is often thought that the evolution products of selenoaldehydes are their trimers. However, this idea has been developed in early studies¹² (for instance treatment of aldehydes by H_2Se) in which the intermediacy of selenoaldehydes is not clearly established. In our case, a complex mixture was obtained from which we were not able to isolate any pure trimer. In addition to the unresolved multiplets that we attributed to oligomeric **6a** (δ 2.0–2.5, CH_2CH_2 ; 3.1–3.5, CHSe ; 4.8–7.0, CH_2CH) a doublet at δ 3.05 was assigned to **5a** (SeCH_2).

§ Experimental procedure: to a solution of vinylmagnesium bromide in THF⁸ (0.45 mol dm^{-3} , 10 ml) was added powdered selenium (0.36 g, 4.5 mmol) at 0 °C. The mixture was stirred for 15 min before addition of allyl bromide (0.39 ml, 4.5 mmol). After a further 20 min stirring, 2 ml of freshly distilled cyclopentadiene was added. The reaction was then stirred for four days in the dark at room temperature, a further 2 ml of cyclopentadiene being added after the second day. The reaction was quenched with a saturated solution of ammonium chloride in water and extracted with pentane. The organic layer was dried over Na_2SO_4 , filtered and evaporated. The residue obtained was chromatographed on silica gel using pentane (to elute dicyclopentadiene) and then a 1:1 mixture of pentane and CH_2Cl_2 . Compound **7** (0.47 g, 2.19 mmol) was isolated as a slightly green oil. ^1H NMR (270 MHz, CDCl_3 , major isomer probably *endo*): δ 1.2–2.4 (m, 6H), 3.0–3.3 (m, 1H, 4-H), 4.0–4.3 (m, 2H, 1- and 3-H), 4.8–5.2 (m, 2H, terminal CH_2), 5.65 (dd, $^3J_{\text{H,H}}$ 3 and 5 Hz, 1H, 1 ethylenic norbornenic H), 5.7–5.9 (m, 1H, CH of the vinyl group), 6.45 (dd, $^3J_{\text{H,H}}$ 3 and 5 Hz, 1H, ethylenic norbornenic H). The minor *exo* isomer was detected particularly by a signal at δ 6.33 (dd). ^{13}C NMR (*endo*): δ 34.1 (CH_2), 34.2 (CH_2), 46.7 (CH), 49.5 (CH), 52.8 (CH_2), 54.4 (CH), 115.1 (CH_2), 128.5 (CH), 138.2 (CH), 138.3 (CH). MS (*m/z*, %) 214 (M^+), 8, with the expected pattern due to Se isotopes, 133 (70), 91 (100), 66 (C_5H_6^+ , 19). High resolution MS: calc. for $\text{C}_{10}\text{H}_{14}^{80}\text{Se}$ 214.0257, found 214.0237.



Scheme 2 a; R = H b; R = Ph **Reagents and conditions:** i, Se., THF; ii, allyl bromide; iii, cyclopentadiene, room temp., 4 days; iv, H_2O , DME, 84 °C, 20 h

15%) even when the reaction was carried out in hot water–DME, owing to competitive oligomerisation.

Thus, the seleno-Claisen rearrangement is a new efficient way to selenocarbonyl compounds, allowing access to reactive γ -unsaturated seleno-aldehydes and ketones.¹²

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