

Aldol-type Condensation vs. Vinyl Selenide Formation from Selenoacetals

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Rapid addition of a tertiary amine to tin(IV) chloride–selenoacetal mixtures leads to the corresponding vinyl selenides in good yield, whereas slow addition of the amine base gives aldol condensation products.

Selenium-stabilised carbocationic species have proved valuable electrophiles in carbon–carbon bond-forming reactions.¹ However, carbenium ions bearing heteroatomic substituents on the positively charged carbon may follow other reaction paths, depending on their structure and on the reaction

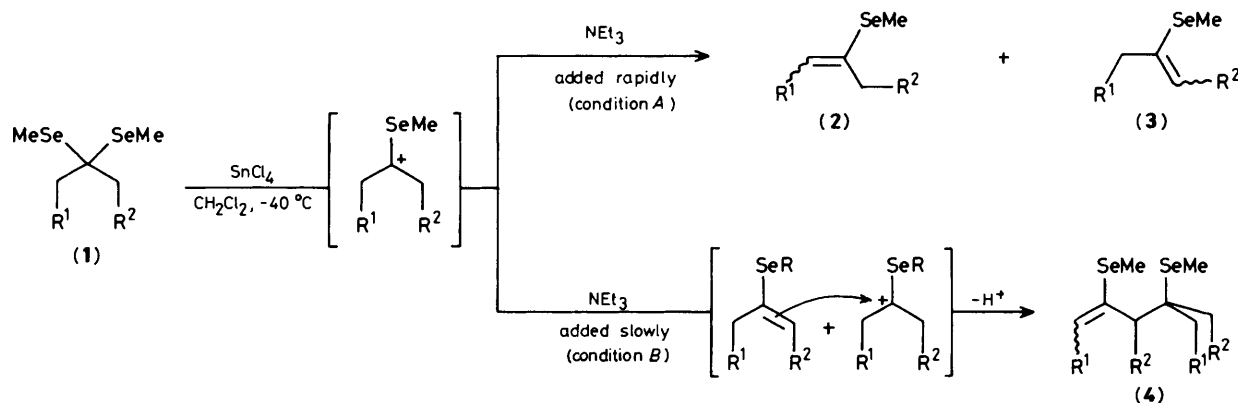
conditions used.² We report here our preliminary results on two such alternative pathways occurring in the absence of an external nucleophile (Scheme 1).

Thus, when a mixture of tin(IV) chloride and a methyl selenoacetal is treated rapidly with an excess of triethyl-

Table 1. Lewis acid and base promoted reactions of selenoacetals.

Entry	Selenoacetal (1)		Conditions ^a	Products (% yield) ^b			
	R ¹	R ²		(2)	(3)	(4)	(5)
1	H	H	A	43			
2	H	H	B			37	0
3	Me	H	B		40	40(90:10)	0
4	Et	H	A	0	40		
5	Et	H	B			68	0
6	C ₅ H ₁₁	H	A	0	78		
7	C ₅ H ₁₁	H	B			71(90:10)	0
8	C ₈ H ₁₇	H	A		79		
9	Pr	Me	A	0	78(67:33)		
10	Pr	Me	B	0	60(75:25)	0	0
11	Ph	H	A	22	44		
12		-[CH ₂] ₂ -	A	84			
13		-[CH ₂] ₃ -	A	91			

^a A: NEt₃ added rapidly; B: NEt₃ added slowly. ^b E:Z ratios in parentheses; elemental analyses and spectral (i.r., ¹H and ¹³C n.m.r., and mass) data are in agreement with structures (2)–(4).

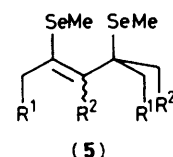


amine, a fast reaction occurs to give the vinyl selenide arising from elimination of the elements of methaneselenol[†] from the starting acetal[‡] (Table 1, condition A).

As shown in the Table, this reaction is limited to selenoacetals derived from ketones. Selenoacetals derived from aldehydes do not react; they are recovered unchanged after several hours treatment at -40°C . Under more forcing conditions (0 or 25°C for several hours) however, they decompose in an uncontrollable fashion leading to dimethyl diselenide and a small amount of aldehyde as the sole identified products. This behaviour of selenoacetals derived from aldehydes, coupled with the earlier observation that they do not react, in the presence of Lewis acids, with *O*-silyl

[†] The reaction is reminiscent of ketene thio- and seleno-acetal formation from the corresponding ortho esters under similar conditions;³ use of other tertiary amines such as Pr₂ EtN (Hünig's base) gives identical results.

[‡] In a typical experiment, to a cooled (-40°C) solution of 2,2-bis(methylseleno)octane (300 mg, 1 mmol) and SnCl₄ (286 mg, 1.1 mmol) in dichloromethane (3 ml) a solution of NEt₃ (111 mg, 1.1 mmol) in dichloromethane (1 ml) was added in one portion. After 5 min at -40°C the mixture was heated to room temperature, diluted with Et₂O (20 ml) and filtered through Celite. The ethereal solution was treated with a few drops of NaBH₄/aq. MeOH to eliminate the dimethyl diselenide formed, and concentrated. Preparative layer chromatography (SiO₂/pentane; R_F 0.70–0.75) gave 2-methylseleno oct-1-ene (160 mg, 78%) as a pale yellow oil.



enols,^{1a} indicates that the monoalkyl-substituted selenocarbenium ions are too unstable to be formed under these conditions.

Selenoacetals of aliphatic methyl ketones invariably give the terminal vinyl selenide (3) rather than the internal one (2) (Table, entries 4, 6, and 8), suggesting that the elimination reaction is under strong kinetic control.[§] This seems to hold also in the case of 3,3-bis(methylseleno)heptane, which gives 3-methylselenohept-2-ene free from the other regioisomer (entry 9). In the case of 1-phenyl-2,2-bis(methylseleno)propane (entry 11) both isomers (2) and (3) are formed, in the ratio 1:2, which is somewhat surprising since one would expect benzylic hydrogen to be more acidic and the corresponding vinyl selenide (2) more stable. It is also possible that steric hindrance to the approach of the base triethylamine plays an important role in determining these regioselectivities. Finally, cyclic selenoacetals (entries 12 and 13) give the vinyl selenides in high yields.

[§] The same regiochemistry is observed when the reactions are carried out at 0 or 25°C and when the reaction mixtures are worked up after 1–4 h.

On the other hand, slow introduction of triethylamine into the reaction mixture (conditions *B*) totally changes the course of the reaction, at least for selenoacetals derived from methyl ketones. In most cases no vinyl selenide is found in the products [except for 2,2-bis(methylseleno) butane, entry 3]; an aldol type auto-condensation takes place instead.¶ This change can be interpreted as a result of the slow formation of the terminal vinyl selenide (**3**), followed by its immediate capture by another selenocarbenium ion and loss of a second proton giving rise to (**4**). Selenoacetals having both R¹ and R² different from hydrogen do not undergo autocondensation (they only give vinyl selenides, but in lower yield than under conditions *A*: entry 10) presumably because then the vinyl selenide is too encumbered to react further. The autocondensation product (**5**) is never formed in detectable quantity, most likely for steric reasons again.

The reactions described here represent (i) a new and easy access to various types of vinyl selenide, complementing

existing methods of synthesis,⁴ and (ii) a simple preparation of the homoallylic bis-selenides (**4**). The synthetic usefulness of the latter is being further investigated.

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¶ In a representative experiment, to a cooled (-40 °C) solution of 2,2-bis(methylseleno)octane (300 mg, 1 mmol) and SnCl₄ (286 mg, 1.1 mmol) in dry dichloromethane (2 ml) a solution (2 ml) of NEt₃ (120 mg, 1.2 mmol) in CH₂Cl₂ was added dropwise through a glass capillary tube. The addition took 1.5 h; the mixture was then allowed to warm to room temperature. Et₂O (20 ml) was added, and the mixture was filtered (Celite) and concentrated. P.l.c. of the residue (SiO₂/pentane; R_F 0.30—0.35) gave the corresponding autocondensation product (**4**) (145 mg, 71%) (Table, entry 7).