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Novel acylation of a vinyl group by the reaction of an aldehyde and a vinylselenonium ylide

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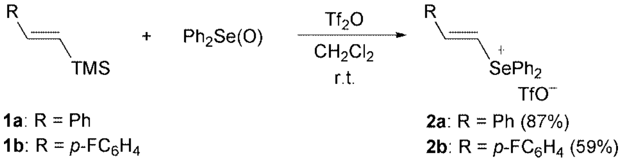
Vinylselenonium ylide, which was generated from (*Z*)-vinylselenonium salt with a base such as sodium or potassium hydride, reacted with aromatic aldehydes to produce the α,β-unsaturated ketones, which were obtained in better yields from the aldehydes with an electron-withdrawing group than from those with an electron-donating group.

Generally, vinylonium salts, for example vinylphosphonium,[1] sulfonium,[2] and selenonium[3] salts, are utilized as Michael acceptors against nucleophiles to produce saturated alkyl ylides, which are among the most important synthons of the C–C bond forming reaction. If the α-hydrogen of a vinylonium salt is abstracted by a base, a vinyl onium ylide is formed. There have been few reports about the reactivity of vinylphosphonium ylide, which reacts with carbonyl compounds to afford allene derivatives through the Wittig olefination.[4] However, reports on the reaction of other vinylonium ylides with carbonyl compounds have been lacking.

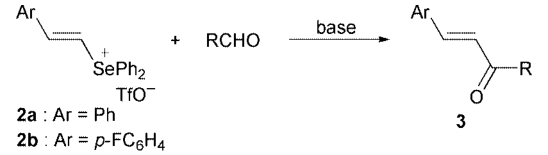
In the course of our studies on alkenylselenonium salts,[5] we have focused on the reactivity of vinylselenonium ylides with great interest. To our astonishment, the reactions of vinylselenonium ylides with aromatic aldehydes did not bring about the Wittig type reaction but caused an acylation reaction of a vinyl group. Although there have been a few reports on the efficient acylation of the vinyl group using aldehyde *via* alkoxyvanadium[6] or alkoxyzirconocene intermediates,[7] our reaction is quite different from these reactions which use an organometallic reagent. This transformation is a novel and original reaction, and would attract the interest of many chemists in the unprecedented behavior of vinyl ylides. We report herein the first example of acylation reactions of vinylselenonium ylides with aldehydes affording *trans*-chalcone derivatives efficiently *via* umpolung of a carbonyl group like the Lapworth condensation.[8]

Firstly, vinylselenonium salts bearing an α-hydrogen were prepared from the reactions of vinylsilanes with diphenyl selenoxide and Lewis acid in CH_2Cl_2 at rt by reference to the procedure for alkynylselenonium salts (Scheme 1).[9]† (*E*)-Trimethylstyrylsilanes **1a** and **1b** reacted cleanly in the presence of trifluoromethanesulfonic anhydride for 4 and 2 h to afford the vinylselenonium triflates **2a** and **2b** in 87% and 59% yield, respectively, with retention of configuration. The (*Z*) stereochemistry of **2b** was established by observation of the NOE enhancement (10%) between the α-vinylic proton and *ortho*-protons of the *Z*-aryl group.

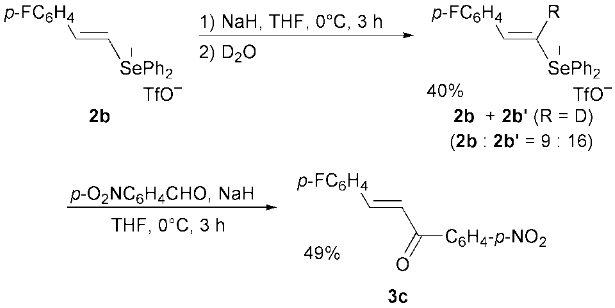


Scheme 1

Next, we investigated the reactions of vinylselenonium ylides with aldehydes (Scheme 2). The ylides were generated by the reaction of vinylselenonium salts **2** with sodium hydride. The reaction of vinylselenonium salt **2a** (1 equiv.) with *p*-nitrobenzaldehyde (1 equiv.) in the presence of 1.3 equiv. of sodium hydride at 0 °C for 3 h in THF gave *p*-nitrophenyl styryl ketone **3a** in 65% yield but did not proceed at −78 °C. Since *p*-chlorobenzaldehyde gave *p*-chlorophenyl styryl ketone **3b** (11%) with recovery of the aldehyde (30%), 2 equiv. of sodium hydride were used and the yield of **3b** was improved up to 58%. However, the reactions with benzaldehyde or *p*-tolualdehyde gave complex mixtures including unreacted aldehyde, and α,β-unsaturated ketones were not isolated. To confirm the formation of the vinylselenonium ylide, vinylselenonium salt **2b** was stirred with 1 equiv. of sodium hydride in THF at 0 °C for 3 h without the aldehyde, followed by treatment with D_2O to afford a mixture of **2b** and **2b′** (**2b**:**2b′** = 9:16) in 40% yield. The mixture of **2b** and **2b′** was treated with sodium hydride in the presence of *p*-nitrobenzaldehyde under the same conditions as for the reaction of **2a** with *p*-nitrobenzaldehyde to give the compound **3c**, which contained no deuterium, in 49% yield (Scheme 3). This finding indicated that the above reactions proceeded *via* a vinylselenonium ylide. On the other hand, the reaction of vinylselenonium salt **2b** and benz(aldehyde-*d*) with sodium hydride in DMF at 0 °C for 4 h was conducted to trace the hydrogen atom of an aldehyde. 3-(4-Fluorophenyl)-1-phenylpropenone **3d** obtained in 14% yield did not contain any deuterium.



Scheme 2



Scheme 3

On the basis of these results, we propose a plausible mechanism for the reactions of vinylselenonium salts with aldehydes (Scheme 4). Vinylselenonium ylide **4** is formed from the reaction of vinylselenonium salt **2** with sodium hydride followed by reaction with an aldehyde to produce betaine **5**. Deprotonation from the betaine **5** by a base gives rise to the β-elimination to generate allenoate ion **6**, which isomerizes to the α,β-unsaturated carbonyl compound **3**.

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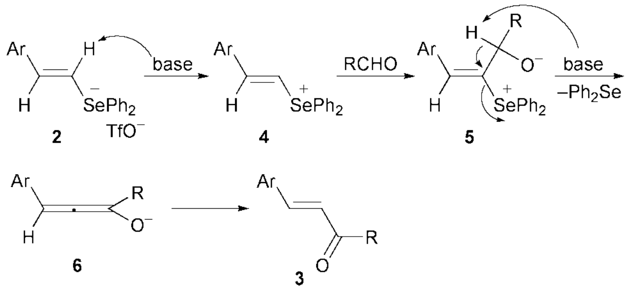

Scheme 4

Next, potassium hydride, as a stronger base than sodium hydride, was adopted in this reaction to improve the yield of compound **3** (Table 1).‡ The reaction of p-nitrobenzaldehyde with 2 equiv. of vinylselenonium salt **2a** in the presence of 3 equiv. of potassium hydride in THF at 0 °C for 0.5 h afforded the chalcone derivative **3a** in excellent yield (entry 1). The reactions of p-halobenzaldehydes also gave the corresponding α,β-unsaturated carbonyl compounds **3b** and **3e** in high yields compared with the reactions using sodium hydride (entries 2 and 3). Although no chalcone derivative had been obtained from the reaction of benzaldehyde or p-tolualdehyde using sodium hydride, *trans*-chalcone **3f** was given using potassium hydride in THF–DMSO (13 : 1) at −30 °C in up to 60% yield (entry 5); moreover, the reaction with p-tolualdehyde bearing the electron-donating group afforded chalcone derivative **3g** in moderate yield (entry 6).

Table 1 Reactions of vinylselenonium salt **2a** with aldehydes in the presence of KH[a]

Entry	RCHO	Conditions	Product (% yield)
1	p-O$_2$NC$_6$H$_4$CHO	KH, THF, O °C, 0.5 h	**3a** (94)
2	p-ClC$_6$H$_4$CHO	KH, THF, O °C, 0.5 h	**3b** (77)
3	p-BrC$_6$H$_4$CHO	KH, THF, O °C, 0.5 h	**3e** (76)
4	PhCHO	KH, THF, −10 °C, overnight	**3f** (43)
5		KH, THF–DMSO,[b] −30 °C, 2 h	**3f** (60)
6	p-MeC$_6$H$_4$CHO	KH, THF–DMSO,[b] −30 °C, 3.5 h	**3g** (49)

[a] **2a**: RCHO : KH = 2 : 1 : 3. [b] THF : DMSO = 13 : 1.

In conclusion, we have shown the first example of the reactions of vinylselenonium ylides with aldehydes, which proceed *via* the β-elimination of the adducts of the vinylselenonium ylides and the aldehydes because the selenonio group is a good leaving group to produce *trans*-chalcone derivatives. The results described in this paper implies that the vinylselenonium ylides would react with other carbonyl compounds differently from vinylphosphonium ylides, and we continue our study on the vinylselenonium ylides to exploit their new reactions.

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Notes and references

† *A typical example*: Trifluoromethanesulfonic anhydride (0.8 cm^3, 4.7 mmol) was added dropwise to a stirred solution of diphenyl selenoxide (1.1 g, 4.3 mmol) and (*E*)-trimethylstyrylsilane (0.84 g, 4.7 mmol) in dichloromethane (30 cm^3) at 0 °C. The mixture was stirred at rt for 4 h. After the solvent was evaporated under reduced pressure, the precipitate was washed several times with ether and recrystallised from CH$_2$Cl$_2$–Et$_2$O to afford 1.82 g (87%) of **2a** as colorless prisms: mp 113–114 °C; δ_H 7.41 (d, 1H, J 16.0), 7.50 (t, 2H, J 8.0), 7.63–7.71 (m, 9H), 7.73–7.90 (m, 6H); FABMS m/z 337 [M − TfO]$^+$; Found: C, 51.8; H, 3.5. C$_{21}$H$_{17}$F$_3$O$_3$SSe requires C, 52.0; H, 3.5%.

‡ *A typical example*: Potassium hydride (12 mg, 0.3 mmol) was added to a stirred solution of vinylselenonium salt **2a** (97 mg, 0.2 mmol) and p-bromobenzaldehyde (19 mg, 0.1 mmol) in THF (3 cm^3) at 0 °C. The mixture was stirred at the same temperature for 0.5 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over MgSO$_4$. After the solvent was evaporated under reduced pressure, the residue was separated by preparative TLC (hexane–AcOEt = 5 : 1) to give **3e** (22 mg, 76%) as colorless powder: δ_H 7.42–7.43 (m, 3 H), 7.48 (d, 1H, J 16.0), 7.64 (d, 4H, J 8.0), 7.82 (d, 1H, J 16.0), 7.89 (d, 2H, J 8.0); EIMS m/z 287 (M)$^+$; Found: C, 62.9; H, 4.0. C$_{15}$H$_{11}$BrO requires C, 62.7; H, 3.9%.

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