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Intramolecular Cyclization of 2-(Alkoxycarbonyl)allylsilanes with Ynones. Nucleophilic and Electrophilic Aspects of the 2-(Alkoxycarbonyl)allylsilane Moiety

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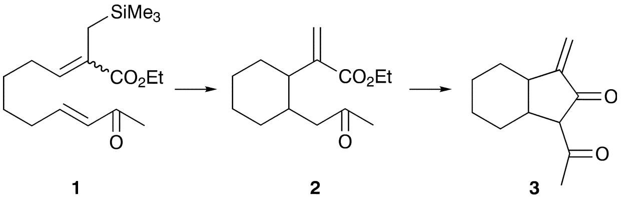
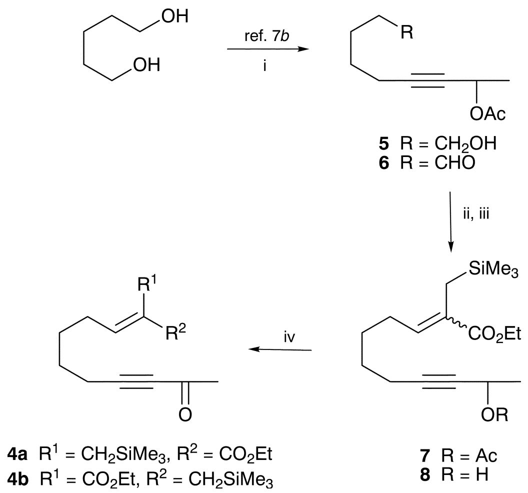
The 2-(alkoxycarbonyl)allylsilane moiety acts simultaneously as both nucleophile and electrophile when ethyl 10-oxo-2-(trimethylsilylmethyl)undec-2-en-8-ynoate is treated with tetrabutylammonium fluoride.

Organic silicon compounds are versatile carbanion equivalents in organic synthesis and have been applied to the synthesis of various carbocycles.[1] 2-(Ethoxycarbonyl)allylsilane constitutes a simple organic bifunctional unit having both nucleophilic and electrophilic character. Thus this moiety formally can react both with electrophiles (acting as an allylsilane) and with nucleophiles (acting as an α,β-unsaturated ester). We have developed an intramolecular reaction of this unit with carbonyls as a new synthetic method towards α-methylene-γ-lactones,[3] based on the former reaction mode (intramolecular Hosomi–Sakurai reaction). Recently we reported a synthesis of the bicyclo[4.3.0]nonane ring by intramolecular cyclization of **1**[7] (Scheme 1). In this reaction, the 2-(ethoxycarbonyl)allylsilane moiety also reacts as an allylsilane at the γ-position giving only a six-membered ring (**2** and/or **3**). In order to find out whether 2-(ethoxycarbonyl)allylsilane always acts as an allylsilane in the reaction with a conjugated carbonyl group, we planned to study the cyclization reaction with ynones, and here report that tetrabutylammonium fluoride (TBAF) treatment of compound **4** proceeds by two reaction modes, both of which are different from that of the corresponding enone **1**.



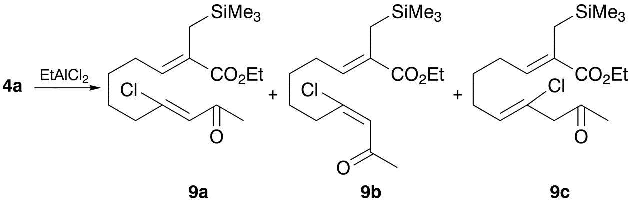
Scheme 1



Scheme 2 *Reagents and conditions*: i, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, −60 °C; ii, $(EtO)_2POCH(CO_2Et)CH_2SiMe_3$, NaH, DME, r.t.; iii, K_2CO_3, EtOH, r.t.; iv, MnO_2, CH_2Cl_2, r.t.

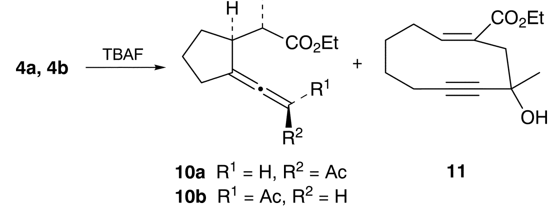
The cyclization precursors **4a** and **4b** were prepared according to the route shown in Scheme 2. The two isomers, **4a** and **4b**, were separated by silica gel column chromatography.

Lewis acid promoted cyclization of **4** was carried out using $BF_3{\cdot}OEt_2$, $TiCl_4$ and $SnCl_4$; however only complex mixtures or unreacted material were obtained. Three HCl-adducts **9a–c** were obtained in 77% total yield when **4a** was treated with $EtAlCl_2$ (Scheme 3).



Scheme 3

In contrast, when **4a** was treated with TBAF, two cyclization products, **10** (**10a**:**10b** = 1:1) and **11**, were obtained in 36 and 24% yields, respectively (Scheme 4). The isomer **4b** also gave **10** and **11**; however the yields were only 13 and 9%, respectively. The structures of **10** and **11**, including the stereochemistry, were determined from spectral data, details of which are reported in the full text.



Scheme 4

The formation of **10a**,**b** from **4a**,**b** can be explained by 1,4-addition of the ynone enolate to the conjugated ester in which TBAF was used as an organic base.[9] According to this mechanism, the trimethylsilyl group does not play any

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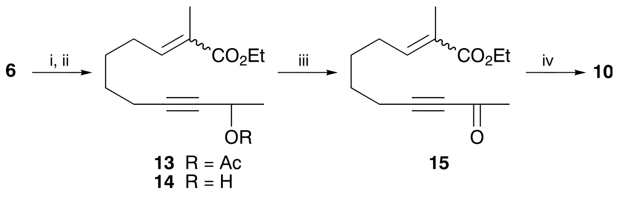
*To receive any correspondence.



Scheme 6 *Reagents and conditions:*
i, $(EtO)_2POCH(CO_2Et)CH_2SiMe_3$, NaH, DME, r.t.; ii, K_2CO_3, EtOH, r.t.; iii, MnO_2, CH_2Cl_2, r.t.; iv, TBAF, THF, r.t.

role in the cyclization reaction, and is simply eliminated in the presence of the fluoride anion. To confirm this, the desilylated compound **15** (*E*:*Z* = 5:1), prepared from **6**, was treated with TBAF under the same reaction conditions giving **10** in 31% yield but without being accompanied by **11** (Scheme 6).

As for the formation of **11**, although the reaction mechanism is not yet clear, relative yields from each of **4a** and **4b** suggest that the cyclization is not a direct 1,2-addition of the α-position of the allylsilane to the carbonyl, *i.e.*, the yield was lower from **4b** which has the same geometry as the product **11**.

In conclusion, it has been revealed that the cyclization of 2-(ethoxycarbonyl)allylsilane with ynones proceeds by a different mode from that with enones. Although two reaction modes (as an allylsilane and as an α,β-unsaturated ester) are possible, this moiety normally acts as an allylsilane at the γ-position on treatment with fluoride anion,[10] while 1,2-addition of a carbonucleophile to an ester carbonyl is also a common reaction.[11] In contrast, **4** reacted both as an allylsilane and as an α,β-unsaturated ester *at the same time*, *i.e.* **11** and **10** are the products of the former and the latter reaction modes, respectively. Moreover, in the formation of **11**, the reaction site (the α-position of the allylsilane) was different from that of the analogous enone **1** (γ-position; Scheme 1). This work also provides a new entry to exocyclic allenone systems.[12]

Techniques used: ^{1}H NMR, ^{13}C NMR, IR, UV, MS, elemental analysis, column chromatography

References: 13

Schemes: 6

Figures: 2

Table 1: ^{1}H NMR data for the α,β-unsaturated ketone moiety of **9a–c**

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