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Regioselective Catalysed H-Ene Reaction of Allylsilanes with 3-Butyn-2-one Application to a New Synthesis of (±)-γ-Ionone

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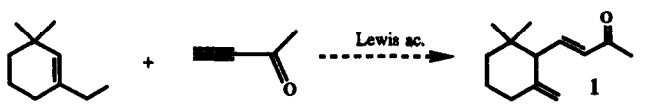
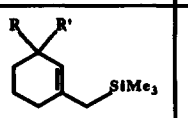
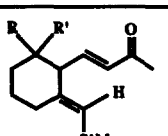
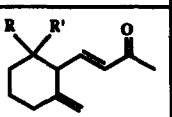
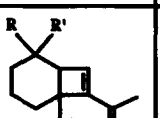
Abstract: An unexpected ZnI_2 catalysed regioselective H-ene reaction between allylsilanes and butynone in the presence of molecular sieves 4A is reported. The silyl group dramatically enhanced the rate of the reaction which is used as a key for a new synthesis of (±)-γ-ionone.

The Lewis acid catalysed conjugate addition of allylsilanes to α,β-enones described by Sakurai[1] is highly efficient and the reaction is of wide scope for the synthesis of natural products[2].

In the context of our interest for violet fragrance compounds, in particular γ-ionone **1** which is difficult to synthesize differently[3], the potentiality of a similar approach starting from 3-butyn-2-one may be imagined. This approach would allow to construct in one pot the conjugate enone chain and the exocyclic methylene.



We have investigated the target reaction using three diversely substituted six-membered ring models **2a-c**. Results are shown in the Table.

Substrates [a]	Products [b, c, d] (relative yield) [e]			Yields [f]
	H-ene reaction	Sakurai reaction	[2+2] cycloadd.	
				
2a R=R'=H	**3a** (70%)	**4a** (11%)	**5a** (19%)	70%
2b R=H R'=CH_3	**3b** (93%)	**4b** (3%)	**5b** (4%)	72%
2c R=R'=CH_3	**3c** (100%)	—	—	77%

[a] Synthesized from ref. 8. [b] All compounds showed analytical and spectroscopic data consistent with the assigned structure. [c] Typical procedure: a mixture of allylsilane **2** (4 mmol, 1 equiv.), anhydrous ZnI_2 (1,5 equiv.), butynone (2 equiv.) and molecular sieves 4A (0,6 g) in CH_2Cl_2 (15 ml) was stirred at room temperature for 12 hours. After filtration and removal of the solvent under reduced pressure, the residue was subjected to chromatography (silica). [d] In the absence of MS 4A, the ZnI_2 catalysed ene reaction proceeds smoothly but provides significant isomerisation (≃ 40%) of the double bond of the starting materials **2b** or **2c**, leading to rearranged products. [e] Product distribution in mol % of each compound after column chromatography separation. [f] Yields refer to isolated pure materials.

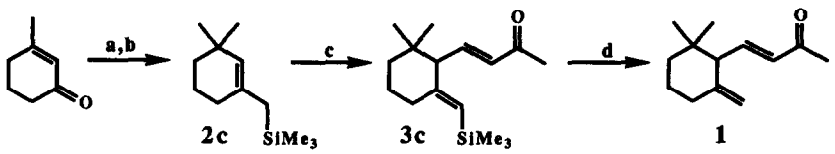
The expected product **4** is formed in appreciable yield (11%) only when the ring is not bearing methyl substituents. Overall, the major (from **2a**), practically exclusive (from **2b**), or exclusive (from **2c**) product is the one arising from a H-ene reaction.

The ene reaction of allylic derivatives of group 14 metals has constituted a powerful methodology for selective bond formation[4]. However, carbon-carbon bond formation of allylsilanes with alkynes activated enophiles seems hitherto to have not been observed.

Our results show that the dramatically higher rate (12 hours) and completely regiocontrolled ene reaction with allylsilanes **2a-c** are in sharp contrast with the ene reaction of alkenes without the silyl group, which require longer times[5] (several days) and give mixtures of regioisomers[5b] under the same reaction conditions and with the same enophile.

This result may been explained by the fact that the carbon-metal bond hyperconjugation will tend to stabilise the incipient carbenium[4b] and the silyl group substantially speeds up the abstraction of the hydrogen atom adjacent to it[6].

Vinylsilanes can be converted to olefins in the presence of catalytic amounts of p-toluenesulfinic acid[7] using wet refluxing acetonitrile as the solvent. This procedure applied to vinylsilane **3c** yields (±)-γ-ionone **1** without isomerisation of the double bond. The overall synthesis is described in the following scheme.



a) Me_2CuLi, THF then $ClPO(OEt)_2$, HMPA (83%); b) $Ni(acac)_2$, Me_3SiCH_2MgCl (72%);
c) butynone, ZnI_2, MS 4A, CH_2Cl_2 (77%); d) cat. p-toluenesulfinic acid, wet CH_3CN (86%).

We are currently investigating the application of this highly regioselective H-ene reaction to other violet fragrance compounds.

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