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Chemo- and Regioselectivity in the Lewis Acid-Induced Reaction of Sterically Unhindered Isocyclic Allylsilanes with 3-Butyn-2-one.

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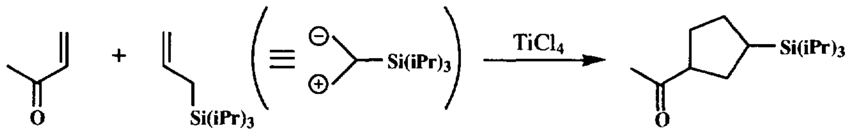
Abstract : The primordial influence of the ring size in the Lewis acid-promoted reaction of sterically unhindered isocyclic allylsilanes with 3-butyn-2-one is reported. In all the cases, the classical Sakurai-Hosomi reaction is, for the most part or fully, suppressed. With cyclohexanic frameworks, allyltrimethylsilanes like **1a-c** afford mainly or solely H-ene components. This chemoselectivity is quite different from the one of cyclopentanic core compounds **1d-f** which act primarily as [2 +2] cycloaddition agents at the expense of the H-ene products procedure. Furthermore, the regioselectivity of the H-ene products formation is opposite for the two skeletons. Using Me_2AlCl, the [2 +2] cyloaddition of five carbon atoms isocyclic allylsilanes proceeds with complete chemoselectivity and provides an efficient synthesis of functionalized bicyclo [3. 2. 0] heptenes. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The catalysed conjugate addition of allylsilanes to α, β-enones, called Sakurai-Hosomi reaction, is of wide scope for carbon-carbon bond construction in organic synthesis[1]. However, the Lewis acid-mediated [3+2] cycloaddition of allylsilanes to α, β-insaturated carbonyl compounds is presently considered as an efficient method for the synthesis of silyl- substituted cyclopentanes[2a-f]. The aim is the suppression of the classical Sakurai-Hosomi reaction by using sterically hindered allylsilanes, *e.g.* allyltriisopropyl or allyltriphenylsilanes.

The allylsilane serves as the synthetic equivalent of a 2-silyl-substituted 1,3-dipole and the process is believed to involve an intermediate silicon stabilized delocalized cation[2d] (Scheme 1).



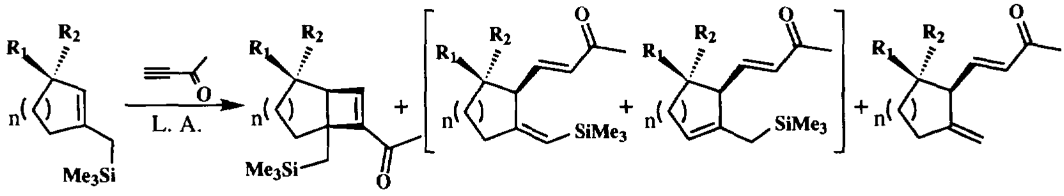
Scheme 1

In 1993, during the course of our studies on the H-ene reaction[3] of cyclohexanic core allylsilanes with 3-butyn-2-one[4], we reported, *a contrario* of these well established facts, the formation of minor amounts of a cyclobutene by-product by a competitive ZnI_2 catalysed [2+2] cycloaddition[5,6]. Recently, two papers concerning the [2+2] cycloaddition of allyltriisopropylsilane to electrophilic olefins[7] and unsaturated esters[8] have been published. For all of these approaches, when sterically unhindered allylsilanes were employed, *e.g.* allyltrimethylsilane, very poor yields of the expected products were obtained[9].

Herein, we report in full on our studies of the Lewis acid-promoted reactions of six and five carbon atoms isocyclic allylsilanes sterically unhindered at the silicon atom with 3-butyn-2-one and show the primordial influence of the ring size on the progress of the reaction.

RESULTS AND DISCUSSION

Our results are presented in the general Scheme 2.



1 a-f **2 a-f** *[2+2]* **3 a-f** + **4 a-f** *H-ene* **5 a-f** *Sakurai*

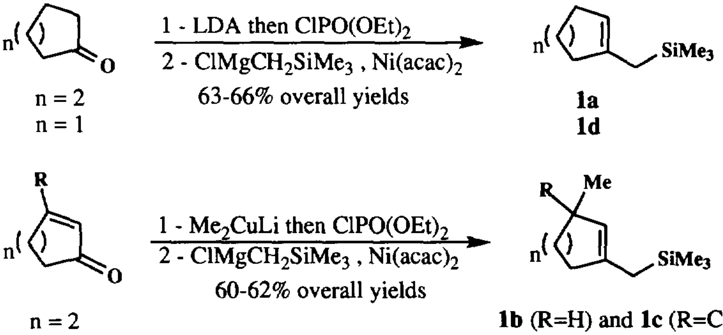
n = 2
a : $R_1 = R_2 = H$
b : $R_1 = H$, $R_2 = CH_3$
c : $R_1 = CH_3$, $R_2 = CH_3$

n = 1
d : $R_1 = R_2 = H$
e : $R_1 = H$, $R_2 = CH_3$
f : $R_1 = CH_3$, $R_2 = CH_3$

Scheme 2

- *Synthesis of allylsilanes* ***1a-c*** *(n = 2) and* ***1d-f*** *(n = 1).*

Their preparation was efficiently achieved in two steps based on the procedure of Kumada[10].



n = 2
n = 1

1a
1d

n = 2
n = 1

1b (R=H) and **1c** ($R=CH_3$)
1e (R=H) and **1f** ($R=CH_3$)

Scheme 3

The treatment of commercially available cycloalkanones (cycloalkenones) by LDA (Me_2CuLi) then $ClPO(OEt)_2$ led to the corresponding enol phosphates. A modified[11] Kumada experimental sequence ($ClMgCH_2SiMe_3$ added in small portions during 10 hours rather than in one portion alone) applied to the enol phosphates gave the allylsilanes in good overall yield (Scheme 3).

- *Reactivity of cyclohexanic core allylsilanes **1a-c** (n = 2) and cyclopentanic core allylsilanes **1d-f** (n = 1).*

Our initial attempts using different kinds of strong Lewis acids, which are generaly used in the Sakurai-Hosomi reaction at low temperature ($TiCl_4$, $SnCl_4$, $BF_3.OEt_2$), were unsuccessful because complex mixtures were obtained. Therefore, we focused our attention on the use of milder Lewis acids.

- In a first typical procedure, a mixture of allylsilanes **1** (1 equiv), anhydrous ZnI_2 (1.5 equiv), butynone (2 equiv) and molecular sieves 4Å (in the case of **1b, c**) in CH_2Cl_2 was stirred at room temperature for 12 hours. The reaction was monitored by TLC showing the formation of three compounds for **1a,** mainly one for **1b**, solely one for **1c**, but always three compounds for **1d-f** (Table 1, ZnI_2).

In the absence of MS 4Å, the ZnI_2-induced reaction proceeded smoothly but provided significant isomerisation of the double bond of the starting materials **1b** or **1c**, leading to unwanted rearranged products.

- In a second procedure, the reaction was catalysed by Me_2AlCl which is also a mild Lewis acid and a proton scavenger[12]. In this case, the reaction went to completion more quickly (20 min), with less equivalent of reagents (1.1 equiv of butynone; 1.2 equiv of Me_2AlCl) and at a lower temperature (-30°C). The highest reactivity of this Lewis acid allowed the reaction to be more selective and so provided a sole product for **1a-c** and for **1d-f** (Table 1, Me_2AlCl).

The different products were separated by column chromatography on silica gel. Each structure was established by relevant spectroscopic data (IR, ^1H and ^{13}C NMR, DEPT experiment) and microanalysis always included.

Compounds	L. A.	2+2	H-ene	Sakurai	Overall Yield
		% **2**	% (**3** : **4**)	% **5**	
n = 2 :					
1a	ZnI_2	19	70 (1 : 3)	11	70
1b	"	4	93 (1 : 3)	3	72
1c	"	-	100 (1 : 3)	-	77
n = 1 :					
1d	ZnI_2	63	21 (3 : 1)	16	85
1e	"	66	22 (4 : 1)	12	84
1f	"	74	16 (4 : 1)	10	88
n = 2 :					
1a	Me_2AlCl	-	100 (0 : 1)	-	92
1b	"	-	100 (0 : 1)	-	93
1c	"	-	100 (0 : 1)	-	90
n = 1 :					
1d	Me_2AlCl	100	-	-	93
1e	"	100	-	-	91
1f	"	100	-	-	91

Table 1 : Lewis Acid-induced Reaction of Allysilanes **1a-c** (n=2) and **1d-f** (n = 1) with 3-butyn-2-one . Ratios of products were determined by capillary GLC analysis.

- Structure Determination :

The structure of **2a** as a bicyclo [4.2.0] octene derivative has been previously determined[5] ; the structures of the products **2d-f** (n = 1) as bicyclo [3.2.0] heptenes are proved in the same manner. Both ^1H and ^{13}C chemical shifts of the $-C\underline{H}_2SiMe_3$ are consistent with a direct bonding to the Si atom (Table 2). A two-dimensional C, H correlation experiment[13] (COLOC) ran for **2d** ($R_1 = R_2 = H$) showed three bond cross-peaks from the H ($-Si(C\underline{H}_3)_3$) to C ($-\underline{C}H_2SiMe_3$) and conversely from the H ($-C\underline{H}_2SiMe_3$) to C ($-Si(\underline{C}H_3)_3$). In the case of **2e**, the allylic proton on the ring juncture resonated as a broad singlet at $\delta_H = 2.39$. The absence of significant coupling constants showed clearly the *trans* relationship with the tertiary one in α position.

Products	2d	2e	2f
^1H $-C\underline{H}_2SiMe_3$	1.17 s	1.34 and 0.93 (AB, J=-14.7 Hz)	1.31 and 0.89 (AB, J=-14.8 Hz)
^{13}C $-\underline{C}H_2SiMe_3$	24.1	25.5	25.5

Table 2 : Selected ^1H (200 MHz) and ^{13}C (50 MHz) NMR data ($CDCl_3$) of the bicyclo [3.2.0] heptenes **2d-f**.

The structural assignments and ratios of the unseparable mixture of H-ene products **3a-c** /**4a-c** and **3d-f** / **4d-f** were also established by means of careful ^1H and ^{13}C studies[14]. The major **4a-c** and minor **4d-f** allylsilanes were characterized by an upfield $-C\underline{H}_2SiMe_3$ signal as an AB system (Table 3).

Products	^1H $-C\underline{H}_2SiMe_3$	^{13}C $-\underline{C}H_2SiMe_3$
n = 2 :		
4a	1.23 and 1.40 (AB, J=-13.2 Hz)	18.3
4b	1.21 and 1.37 (AB, J=-13.0 Hz)	25.7
4c	1.20 and 1.35 (AB, J=-13.8 Hz)	23.0
n = 1 :		
4d	1.30 and 1.45 (AB, J=-14.2 Hz)	19.3
4e	1.28 and 1.42 (AB, J=-14.0 Hz)	20.4
4f	impossible data shift	20.0

Table 3 : Selected ^1H (200 MHz) and ^{13}C (50 MHz) NMR data ($CDCl_3$ δ values) of the major allylsilanes **4a-c** (n=2) and minor allysilanes **4d-f** (n = 1).

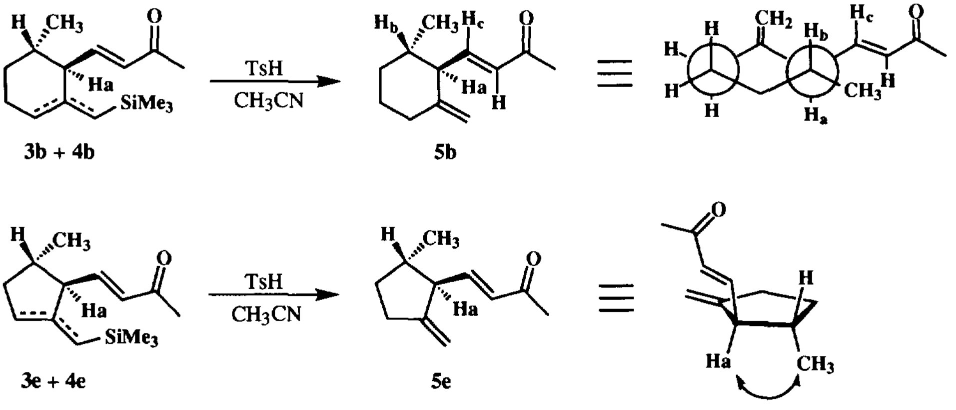
In the ^{13}C NMR spectra, regioisomers **3a-c** / **4a-c** (n = 2) and **3d-f** / **4d-f** (n = 1) were identified by the chemical shifts of the quaternary sp^2-hybridized carbons which are quite different. Those of the vinylic isomers **3a-c** and **3d-f** gave more downfield signals than those of the allylic isomers **4a-c** and **4d-f** (Table 4).

Products	^{13}C δ $C_{quat}(sp^2)$ (Vinylsilanes)	Products	^{13}C δ $C_{quat}(sp^2)$ (Allylsilanes)
n = 2 :		n = 2 :	
3a	157.6	**4a**	134.2
3b	157.1	**4b**	133.2
3c	156.5	**4c**	133.4
n = 1 :		n = 1 :	
3d	161.8	**4d**	142.0
3e	162.3	**4e**	141.2
3f	162.5	**4f**	141.6

Table 4 : ^{13}C (50 MHz) NMR data ($CDCl_3$ δ values) for $C_{quat}(sp^2)$ in the mixture **3a-c** / **4a-c** (n=2) and **3d-f** / **4d-f** (n = 1).

- NOESY analysis of **3a** / **4a** indicated for the minor vinylic isomer **3a** a NOE effect between the exocyclic vinylic hydrogen (δ_H = 5.29 ppm) and the equatorial allylic proton of the cycle (δ_H = 2.20-2.10 ppm). In the same way, in the mixture **3d** / **4d**, the major vinylic isomer **3d** displayed a significant NOE between the signal of the exocyclic vinylic hydrogen (δ_H = 5.52 ppm) and the signal of the cyclic allylic hydrogens (δ_H = 2.09-2.31 ppm). This showed the Z configuration of the exocyclic double bond for **3a** and **3d**.

- We also established the stereochemistry of compounds **3b** / **4b** and **3e** / **4e**. For this purpose, exposure of each mixture of regioisomers to catalytic amounts of *p*-toluenesulfinic acid using wet refluxing acetonitrile as the solvent[14] gave a single product, **5b** and **5e**, respectively (Scheme 4). The ^1H NMR spectra indicated that **5b** (and so **3b** / **4b**) is consistent with the *trans* relative configuration of the methyl group and the enone chain borne by the cycle. The bisallylic proton H_a resonated as a broad triplet (δ = 2.45 ppm) with coupling constants $J_{ab} = J_{ac}$ = 10.2 Hz. Among the possible conformations and configurations, only the *trans* diequatorial geometry of the methyl and enone groups is consistent with this fact[15] : the dihedral angle between the two hydrogens H_a and H_b is ~180°.

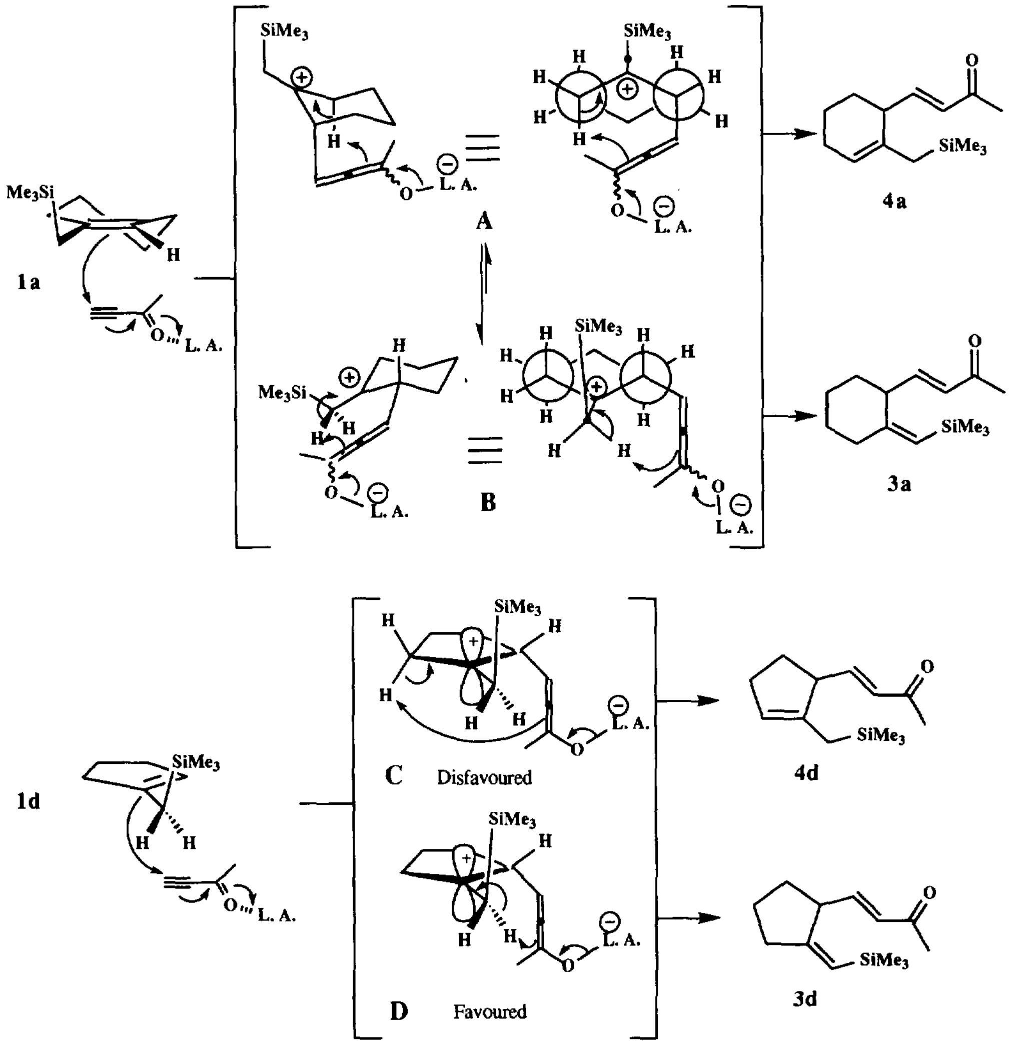


Scheme 4

This analysis is not possible for **5e**. In this case the relative stereochemistry of the substituents of the cycle was determined by a NOESY experiment. A NOE plot for the bisallylic hydrogen H_a (δ = 2.35 ppm) and the methyl hydrogens (δ = 0.77 ppm) established the close proximity of these protons and therefore the *trans* relationship of the methyl group and the enone chain (Schema 4).

Regioselectivity of the ene-reaction

We suggested that the H-ene reaction reverse regioselectivity can be explained by the geometry of the intermediate zwitterion. The Lewis acid-promoted *anti* S_E' approach[16] of allylsilane and butynone, followed by the nucleophilic addition of the allylsilane at the β-ynone position (regardless of unsaturated bonds orientation) produced the β-silyl cation which can act in different ways (Scheme 5).



Scheme 5

In the case of a six membered cycle like **1a**, a molecular model examination showed that the completion of the H-ene reaction is favoured with a well positioned endocyclic axial hydrogen *via* a chair-like transition-state (A). The stereoelectronic effects and the steric accessibility of this hydrogen are important determining factors[17]: when a butynone-Me_2AlCl complex was used, the reaction was rapid and this conformation provided **4a** as the sole product because the endocyclic axial C-H bond and the σ C-Si bond were each coplanar with the empty carbon p-orbital. With the milder complexant ZnI_2, the reaction time was far longer and the reaction could progress partly through a more stable intermediate with the enolate chain in equatorial position (B). In this intermediate the α-silyl hydrogen alone had the correct geometry for the reaction and provided minor **3a**.

Reversely, with cyclopentanic core allylsilane like **1d**, the endocyclic hydrogen was in a disfavourable position with respect to the enolate chain (C). There is a favourable proximity only with a methylene hydrogen in the exocyclic α-silylated position (D) : the vinylic compound **3d** was obtained in higher amount than the allylic one **4d**. However, in the transition state this C-H bond must turn coplanar with the empty carbon p-orbital and consequently must perturb the σ C-Si bond hyperconjugaison[18]: the stereoelectronic effects are disfavourable and the same intermediate collapsed to give the [2+2] cycloadducts which were the major (ZnI_2) or sole (Me_2AlCl) products. This result runs in agreement with the easier formation of a [3.2.0] heptane *versus* a [4.2.0] octane by [2+2] cycloaddition; in the case of $TiCl_4$-promoted [2+2] cycloaddition of ethyl propiolate and *ter*-$BuMe_2Si$ enol ethers, the yield is good when cyclopentanone enol ether is used but a correspondingly lower yield is obtained with cyclohexanone enol ether[19].

CONCLUSION

In summary the present work pointed out two major facts.

* The chemoselectivity is completely different when cyclohexanic (**1a-c**) or cyclopentanic (**1d-f**) framework allylsilanes are used. With the former, the [2+2] cycloaddition is only a marginal pathway and the practically (ZnI_2-induced) or entirely (Me_2AlCl-induced) sole products are the H-ene reaction components. On the opposite, with the latter, the [2+2] cycloaddition is always the main (ZnI_2-induced) or exclusive (Me_2AlCl-induced) process. In the two cases, a crowded Si functionality is not a necessary condition for the almost or fully complete suppression of the Sakurai-Hosomi reaction. So, with **1d-f**, even sterically small trimethylsilyl compounds can act as [2+2] cycloaddition agents[7, 8] and furnish cyclobutene derivatives.

* The regioselectivity of the H-ene reaction products formation depends dramatically upon the cyclic core. With the cyclohexanic structure, the H-ene regioselectivity is preferentially (ZnI_2-induced) or entirely (Me_2AlCl-induced) for the methylene hydrogen-shift from the endocyclic non-silylated position (**4 a-c** >**3 a-c**). On the other hand, with the cyclopentanic one, the major H-ene type compound is obtained *via* the hydrogen-shift preferentially from the α-silyl position (**3 d-f** > **4 d-f**).

In the continuation of this work, complementary mechanistic and experimental studies are going to be investigated and the results will be reported in a further publication.

EXPERIMENTAL SECTION

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or C_6D_6 solution on either Brucker AMX-400 or Brucker AM-200 spectrometers using TMS as internal reference. Infrared spectra were obtained as film using a Perkin-Elmer 257 Infrared Spectrophotometer. Routine monitoring of reactions was performed using Merck 60F 254 silicagel, aluminium supported TLC plates. Column chromatogaphy was performed using Silica-gel 60 (230-400 mesh). GLC analyses were carried out on a Chrompack 9001 using WCOT Fused Silica column (25 m x 0.32 mm i.d.; CP-Wax-52 CB stationary phase). Microanalyses were performed on a Technicon CHN Analyser at our University. CH_2Cl_2 was distilled from powdered CaH_2.

Typical procedures :

- Using ZnI_2 :

A mixture of isocyclic allylsilane **1a-f** (4 mmol, 1 equiv), anhydrous ZnI_2 (6 mmol, 1.5 equiv) and butynone (8 mmol, 2 equiv) 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 components ratio was determined by GLC analysis of the crude product (column temperature was initiated at 70°C and raised to 200°C at a rate of 10°C/ min). The residue was then chromatographed on silica gel (gradient pentane / ether). In the case of allylsilanes **1b** and **1c**, molecular sieves 4A (0,6 g) were added to prevent a significant isomerisation of the double bond of the starting materials leading to rearranged products. **1a-c** : yields 70-77% ; **1d-f** : yields 84-88%.

- Using Me_2AlCl :

To a solution of allylsilane **1a-f** (4 mmol, 1 equiv) and butynone (4.4 mmol, 1.1 equiv) in CH_2Cl_2 (20 mL) at - 30°C was added dropwise Me_2AlCl (1M in CH_2Cl_2, 4.8 mL, 1.2 equiv). After 20 minutes, the reaction was quenched by addition of saturated $NaHCO_3/H_2O$ solution. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 10mL). The organic extracts were dried over magnesium sulfate, filtered and concentred *in vacuo*. The residue was chromatographed on silica gel (pentane / ether 50 : 1). **1a-f :** yields 90-93%.

Products data :

(Cyclohex-1-enylmethyl)-trimethyl-silane **1a**[10].

(3-methyl-cyclohex-1-enylmethyl)-trimethyl-silane **1b.**

Anal % : calcd C 72.44 H 12.16 found C 72.57 H 12.12. IR υ (neat) : 3040, 1660, 1250, 860 cm^{-1}.
^1H-NMR ($CDCl_3$) : δ 0.00 (s, 9H), 0.93 (d, 3H, J = 7.0), 1.02-1.16 (m, 1H), 1.39 (s, 2H), 1.44-1.82 (m, 3H), 1.77-1.93 (m, 2H), 2.15 (m, 1H), 5.06 (br s, 1H). ^{13}C-NMR ($CDCl_3$) : δ -1.2 (3 CH_3), 22.1 (CH_2), 22.4 (CH_3), 27.8 (CH_2), 30.5 (CH), 31.2 (CH_2), 31.4 (CH_2), 125.8 (CH), 134.6 (C).

(3,3-dimethyl-cyclohex-1-enylmethyl)-trimethyl-silane **1c**.

Anal % : calcd C 73.38 H 12.32 found C 73.20 H 12.27. IR υ (neat) : 3020, 1660, 1260, 860 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ 0.01 (s, 9H), 0.95 (s, 6H), 1.38 (s, 2H), 1.32-1.45 (m, 2H), 1.53-1.70 (m, 2H), 1.77-1.90 (m, 2H), 4.95 (br s, 1H). ^{13}C-NMR ($CDCl_3$) : δ -1.0 (3 CH_3), 20.5 (CH_2), 27.9 (CH_2), 30.7 (2 CH_3), 31.4 (CH_2), 32.0 (C), 37.5 (CH_2), 130.3 (CH), 132.9 (C).

(Cyclopent-1-enylmethyl)-trimethyl-silane **1d**[10].

(3-methyl-cyclopent-1-enylmethyl)-trimethyl-silane **1e**.

Anal % : calcd C 71.34 H 11.97 found C 71.40 H 11.92. IR υ (neat) : 3045, 1660, 1250, 870 cm^{-1}. ^{1}H-NMR (C_6D_6) : δ 0.03 (s, 9H), 0.97 (d, 3H, J = 7.4), 1.24-1.43 (m, 1H), 1.49 (s, 2H), 1.95-2.12 (m, 1H), 2.12-2.27 (m, 2H), 2.73 (m, 1H), 5.09 (d, 1H, J = 1.6). ^{13}C-NMR (C_6D_6) : δ -1.2 (3 CH_3), 21.9 (CH_3), 21.5 (CH_2), 33.4 (CH_2), 37.7 (CH_2), 40.5 (CH), 128.8 (CH), 140.8 (C).

(3,3-dimethyl-cyclopent-1-enylmethyl)-trimethyl-silane **1f**.

Anal % : calcd C 72.44 H 12.16 found C 72.28 H 12.20. IR υ (neat) : 3040, 1660, 1250, 870 cm^{-1}. ^{1}H-NMR (C_6D_6) : δ 0.00 (s, 9H), 1.08 (s, 6H), 1.46 (d, 2H, J = 0.9), 1.66 (t, 2H, J = 7.2), 2.23 (br t, 2H, J = 7.0), 4.99 (d, 1H, J = 0.9). ^{13}C-NMR (C_6D_6) : δ -1.2 (3 CH_3), 21.4 (CH_2), 29.1 (2 CH_3), 37.3 (CH_2), 40.3 (CH_2), 45.3 (C), 133.7 (CH), 138.8 (C).

1-(5-trimethylsilanymethyl-bicyclo[3.2.0]hept-6-en-6-yl)-ethanone **2d**.

Anal % : calcd C 70.21 H 9.97 found C 70.36 H 9.94. IR υ (neat) : 3020, 1680, 1630, 1250, 850 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ - 0.01 (s, 9H), 1.17 (s, 2H), 1.41-1.86 (m, 6H), 2.16 (s, 3H), 2.73 (d, 1H, J = 6.1), 6.56 (d, 1H, J = 0.9). ^{13}C-NMR ($CDCl_3$) : δ 0.3 (3 CH_3), 24.1 (CH_2), 24.3 (CH_2), 25.9 (CH_3), 26.0 (CH_2), 34.1 (CH_2), 50.9 (CH), 56.7 (C), 144.1 (CH), 150.9 (C), 194.2 (CO).

1-(2-methyl-5-trimethylsilanymethyl-bicyclo[3.2.0]hept-6-en-6-yl)-ethanone **2e**.

Anal % : calcd C 71.12 H 10.23 found C 71.00 H 10.25. IR υ (neat) : 3020, 1680, 1630, 1250, 850 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ - 0.10 (s, 9H), 0.83 (d, 3H, J = 7.2), 0.93 and 1.34 (AB, 2H, J = - 14.7), 1.18-1.91 (m, 5H), 2.10 (s, 3H), 2.39 (br s, 1H), 6.55 (d, 1H, J = 1.0). ^{13}C-NMR ($CDCl_3$) : δ 0.0 (3 CH_3), 19.7 (CH_3), 25.5 (CH_2), 25.6 (CH_3), 30.9 (CH_2), 32.1 (CH_2), 32.3 (CH), 56.9 (C), 57.9 (CH), 144.8 (CH), 150.0 (C), 194.2 (CO).

1-(2,2-dimethyl-5-trimethylsilanymethyl-bicyclo[3.2.0]hept-6-en-6-yl)-ethanone **2f**.

Anal % : calcd C 71.93 H 10.46 found C 71.83 H 10.51. IR υ (neat) : 3020, 1680, 1630, 1250, 850 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ - 0.01 (s, 9H), 0.90 (s, 3H), 0.95 (s, 3H), 0.89 and 1.31 (AB, 2H, J = - 14.8), 1.17-1.45 (m, 3H), 1.72-1.90 (m, 1H), 2.11 (s, 3H), 2.25 (br s, 1H), 6.62 (d, 1H, J = 1.0). ^{13}C-NMR ($CDCl_3$) : δ 0.0 (3 CH_3), 25.5 (CH_2), 25.7 (CH_3), 27.3 (2 CH_3), 33.3 (CH_2), 37.4 (C), 37.8 (CH_2), 57.2 (C), 61.5 (CH), 143.8 (CH), 150.8 (C), 194.0 (CO).

4-(2-trimethylsilanylmethylene-cyclohexyl)-but-3-en-2-one **3a**.

Anal % : calcd C 71.12 H 10.23 found C 71.33 H 10.19. IR υ (neat) : 3040, 1675, 1620, 1250, 845 cm^{-1}. ^1H-NMR ($CDCl_3$) : δ 0.04 (s, 9H), 2.10-2.20 (m, 2H), 2.19 (s, 3H), 3.39 (m, 1H), 5.29 (d, 1H, J = 0.9), 6.04 (dd, 1H, J = 16.1, 1.9), 6.85 (dd, 1H, J = 16.1, 4.8). ^{13}C-NMR ($CDCl_3$) : δ 0.1 (3 CH_3), 21.7 (CH_2), 27.1 (CH_3), 28.4 (CH_2), 32.7 (CH_2), 36.5 (CH_2), 44.4 (CH), 124.9 (CH), 131.6 (CH), 150.6 (CH), 157.6 (C), 197.8 (CO).

4-(6-methyl-2-trimethylsilanylmethylene-cyclohexyl)-but-3-en-2-one **3b**.

Anal % : calcd C 71.93 H 10.46 found C 71.72 H 10.50. IR υ (neat) : 3040, 1680, 1620, 1250, 840 cm^{-1}. ^1H-NMR ($CDCl_3$) : δ 0.00 (s, 9H), 0.82 (d, 3H, J = 7.0), 2.19 (s, 3H), 3.10 (m, 1H), 5.35 (d, 1H, J = 1.0), 5.99 (dd, 1H, J = 15.9, 1.6), 6.56 (dd, 1H, J = 15.9, 8.9). ^{13}C-NMR ($CDCl_3$) : δ 0.4 (3 CH_3), 22.1 (CH_2), 25.5 (CH_3), 27.4 (CH_3), 35.3 (CH_2), 36.0 (CH_2), 42.5 (CH), 49.2 (CH), 127.5 (CH), 147.3 (CH), 150.4 (CH), 157.1 (C), 197.5 (CO).

4-(2,2-dimethyl-6-trimethylsilanylmethylene-cyclohexyl)-but-3-en-2-one **3c**.

Anal % : calcd C 72.66 H 10.67 found C 72.69 H 10.70. IR υ (neat) : 3040, 1670, 1620, 1250, 840 cm^{-1}. ^1H-NMR ($CDCl_3$) : δ 0.06 (s, 9H), 0.86 (s, 3H), 0.92 (s, 3H), 2.00-2.20 (m, 2H), 2.86 (d, 1H, J = 8.7), 5.28 (s, 1H), 6.04 (d, 1H, J = 15.9), 6.99 (dd, 1H, J = 15.9, 8.9). ^{13}C-NMR ($CDCl_3$) : δ 0.6 (3 CH_3), 23.3 (CH_2), 27.1 (CH_3), 29.8 (2 CH_3), 32.9 (C), 34.7 (CH_2), 35.8 (CH_2), 56.5 (CH), 126.1 (CH), 131.9 (CH), 147.5 (CH), 156.5 (C), 198.4 (CO).

4-(2-trimethylsilanylmethylene-cyclopentyl)-but-3-en-2-one **3d**.

Anal % : calcd C 70.21 H 9.97 found C 70.05 H 10.01. IR υ (neat) : 3040, 1675, 1620, 1250, 850 cm^{-1}. ^1H-NMR (C_6D_6) : δ 0.08 (s, 9H), 1.32-1.41 (m, 3H), 1.58-1.66 (m, 1H), 1.89 (s, 3H), 2.09-2.31 (m, 2H), 3.13 (br t, 1H, J = 6.6), 5.52 (q, 1H, J = 1.8), 6.02 (br d, 1H, J = 16.0), 6.53 (dd, 1H, J = 16.0, 6.6). ^{13}C-NMR (C_6D_6) : δ 0.1 (3 CH_3), 23.5 (CH_2), 26.9 (CH_3), 33.8 (CH_2), 37.1 (CH_2), 45.9 (CH), 122.9 (CH), 130.7 (CH), 149.4 (CH), 161.8 (C), 196.3 (CO).

4-(5-methyl-2-trimethylsilanylmethylene-cyclopentyl)-but-3-en-2-one **3e**.

Anal % : calcd C 71.12 H 10.23 found C 71.31 H 10.19. IR υ (neat) : 3035, 1680, 1620, 1250, 850 cm^{-1}. ^1H-NMR (C_6D_6) : δ 0.07 (s, 9H), 0.80 (d, 3H, J = 6.6), 0.96-1.13 (m, 1H), 1.43-1.72 (m, 2H), 1.91 (s, 3H), 2.12-2.36 (m, 2H), 2.65 (m, 1H), 5.54 (br q, 1H, J = 1.9), 6.02 (dd, 1H, J = 15.9, 1.2), 6.53 (dd, 1H, J = 15.9, 7.4). ^{13}C-NMR (C_6D_6) : δ 0.3 (3 CH_3), 19.3 (CH_3), 27.0 (CH_3), 32.2 (CH_2), 36.7 (CH_2), 41.8 (CH), 54.6 (CH), 123.7 (CH), 131.0 (CH), 148.8 (CH), 162.3 (C), 195.8 (CO).

4-(2,2-dimethyl-5-trimethylsilanylmethylene-cyclopentyl)-but-3-en-2-one **3f**.

Anal % : calcd C 71.93 H 10.46 found C 71.99 H 10.47. IR υ (neat) : 3040, 1670, 1620, 1250, 850 cm^{-1}. ^1H-NMR (C_6D_6) : δ 0.09 (s, 9H), 0.77 (s, 3H), 0.83 (s, 3H), 1.31-1.50 (m, 2H), 1.89 (s, 3H), 2.18-2.43 (m, 2H), 2.72 (br d, 1H, J = 8.5), 5.52 (br q, 1H, J = 1.5), 6.04 (dd, 1H, J = 15.9, 0.9), 6.60 (dd, 1H, J = 15.9, 8.5). ^{13}C-NMR (C_6D_6) : δ 0.2 (3 CH_3), 24.7 (CH_3), 27.1 (CH_3), 28.5 (CH_3), 34.3 (CH_2), 37.1 (CH_2), 43.9 (C), 58.4 (CH), 124.4 (CH), 131.8 (CH), 146.7 (CH), 162.5 (C), 195.9 (CO).

4-(2-trimethylsilanylmethyl-cyclohex-2-enyl)-but-3-en-2-one **4a**.

Anal% : calcd C 71.12 H 10.23 found C 71.33 H 10.19. IR ν (neat): 3040, 1695, 1675, 1620, 1250, 845 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ - 0.02 (s, 9H), 1.23 and 1.40 (AB, 2H, J = - 13.2), 1.40-1.78 (m, 4H), 1.86-2.03 (m, 2H), 2.22 (s, 3H), 2.68 (m, 1H), 5.30 (t, 1H, J = 3.0), 5.98 (d, 1H, J = 15.9), 6.67 (dd, 1H, J = 15.9, 8.1). ^{13}C-NMR ($CDCl_3$) : δ -1.3 (3 CH_3), 18.3 (CH_2), 25.2 (CH_2), 25.6 (CH_2), 26.8 (CH_3), 28.3 (CH_2), 42.6 (CH), 121.9 (CH), 131.6 (CH), 134.2 (C), 151.2 (CH), 198.9 (CO).

4-(6-methyl-2-trimethylsilanylmethyl-cyclohex-2-enyl)-but-3-en-2-one **4b**.

Anal% : calcd C 71.93 H 10.46 found C 71.72 H 10.50. IR ν (neat): 3040, 1690, 1680, 1620, 1250, 840 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ - 0.08 (s, 9H), 0.90 (d, 3H, J = 6.7), 1.21 and 1.37 (AB, 2H, J = - 13.0), 1.48-1.70 (m, 3H), 1.85-2.05 (m, 2H), 2.18 (s, 3H), 2.32 (m, 1H), 5.30 (td, 1H, J = 3.7, 0.9), 5.96 (dd, 1H, J = 15.9, 0.7), 6.52 (dd, 1H, J = 15.9, 8.9). ^{13}C-NMR ($CDCl_3$) : δ -1.1 (3 CH_3), 19.4 (CH_3), 25.7 (CH_2), 26.5 (CH_2), 26.7 (CH_3), 32.1 (CH_2), 32.9 (CH), 50.7 (CH), 121.4 (CH), 132.3 (CH), 133.2 (C), 151.0 (CH), 198.0 (CO).

4-(6,6-dimethyl-2-trimethylsilanylmethylcyclohex-2-enyl)-but-3-en-2-one **4c**

Anal% : calcd C 72.66 H 10.67 found C 72.69 H 10.70. IR ν (neat): 3040, 1695, 1675, 1620, 1250, 840 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ - 0.03 (s, 9H), 0.81 (m, 3H), 0.92 (m, 3H), 1.20 and 1.35 (AB, 2H, J = - 13.8), 1.22-1.51 (m, 2H), 1.96-2.07 (m, 2H), 2.14 (d, 1H, J = 8.0), 2.23 (s, 3H), 5.30 (t, 1H, J = 3.8), 5.99 (d, 1H, J = 15.9), 6.58 (dd, 1H, J = 15.9, 8.9). ^{13}C-NMR ($CDCl_3$) : δ -1.0 (3 CH_3), 23.0 (CH_2), 25.8 (CH_2), 26.8 (CH_3), 28.7 (2 CH_3), 30.6 (CH_2), 32.6 (C), 54.3 (CH), 120.4 (CH), 132.4 (CH), 133.4 (C), 149.6 (CH), 198.8 (CO).

4-(2-trimethylsilanylmethyl-cyclopent-2-enyl)-but-3-en-2-one **4d**.

Anal% : calcd C 70.21 H 9.97 found C 70.05 H 10.01. IR ν (neat): 3040, 1700, 1675, 1620, 1250, 850 cm^{-1}. ^{1}H-NMR (C_6D_6) : δ - 0.05 (s, 9H), 1.30 and 1.45 (AB, 2H, J = - 14.2), 1.32-1.41 (m, 1H), 1.49-1.58 (m, 1H), 1.87 (s, 3H), 2.09-2.31 (m, 2H), 2.99 (br q, 1H, J = 7.8), 5.21 (br s, 1H), 6.01 (d, 1H, J = 15.9), 6.44 (dd, 1H, J = 15.9, 9.0). ^{13}C-NMR (C_6D_6) : δ -1.2 (3 CH_3), 19.3 (CH_2), 26.6 (CH_3), 31.1 (CH_2), 31.5 (CH_2), 52.5 (CH), 124.2 (CH), 131.2 (CH), 142.0 (C), 149.4 (CH), 196.5 (CO).

4-(5-methyl-2-trimethylsilanylmethyl-cyclopent-2-enyl)-but-3-en-2-one **4e**.

Anal % : calcd C 71.12 H 10.23 found C 71.31 H 10.19. IR ν (neat): 3035, 1695, 1680, 1620, 1250, 850 cm^{-1}. ^{1}H-NMR (C_6D_6) : δ - 0.04 (s, 9H), 0.93 (d, 3H, J = 6.9), 1.28 and 1.42 (AB, 2H, J = - 14.0), 1.89 (s, 3H), 2.40-2.48 (m, 2H), 2.61 (m, 1H), 5.16 (m, 1H), 6.04 (br d, 1H, J = 15.8), 6.43 (dd, 1H, J = 15.8, 9.4). ^{13}C-NMR (C_6D_6) : δ -1.1 (3 CH_3), 19.6 (CH_3), 20.4 (CH_2), 26.8 (CH_3), 39.9 (CH_2), 40.0 (CH), 60.9 (CH), 123.2 (CH), 131.7 (CH), 141.2 (C), 149.0 (CH), 196.3 (CO).

4-(5,5-dimethyl-2-trimethylsilanylmethyl-cyclopent-2-enyl)-but-3-en-2-one **4f**.

Anal % : calcd C 71.93 H 10.46 found C 71.99 H 10.47. IR ν (neat): 3040, 1690, 1670, 1620, 1250, 850 cm^{-1}. ^{1}H-NMR (C_6D_6) : δ - 0.02 (s, 9H), 0.86 (s, 3H), 0.90 (s, 3H), 1.87 (s, 3H), 2.53 (br d, 1H, J = 9.9), 5.18

(s, 1H), 5.98 (d, 1H, J = 15.8), 6.48 (dd, 1H, J = 15.8, 9.9). ^{13}C-NMR (C$_6$D$_6$) : δ -1.1 (3 CH$_3$), 20.0 (CH$_2$), 25.1 (CH$_3$), 26.8 (CH$_3$), 29.6 (CH$_3$), 30.5 (CH$_2$), 46.8 (C), 63.6 (CH), 123.0 (CH), 132.5 (CH), 141.6 (C), 147.2 (CH), 196.4 (CO).

4-(2-methylene-cyclohexyl)-but-3-en-2-one **5a**.

Anal % : calcd C 80.44 H 9.82 found C 80.59 H 9.87. IR υ (neat) : 3050, 1680, 1650, 1620, 895 cm^{-1}. ^{1}H-NMR (CDCl$_3$) : δ 1.30-1.85 (m, 6H), 1.98-2.12 (m, 1H), 2.22-2.38 (m, 1H), 2.26 (s, 3H), 2.87 (m, 1H), 4.51 and 4.72 (2 br s, 2H), 6.06 (dd, 1H, J = 16.1, 1.2), 6.86 (dd, 1H, J = 16.1, 7.4). ^{13}C-NMR (CDCl$_3$) : δ 24.4 (CH$_2$), 26.9 (CH$_3$), 27.9 (CH$_2$), 33.2 (CH$_2$), 34.8 (CH$_2$), 46.2 (CH), 107.9 (CH$_2$), 131.1 (CH), 149.6 (CH), 149.7 (C), 198.3 (CO).

4-(6-methyl-2-methylene-cyclohexyl)-but-3-en-2-one **5b**.

Anal % : calcd C 80.85 H 10.18 found C 80.97 H 10.15. IR υ (neat) : 3050, 1680, 1650, 1620, 895 cm^{-1}. ^{1}H-NMR (CDCl$_3$) : δ 0.89 (d, 3H, J = 5.8), 1.05-1.35 (m, 4H), 1.30-1.50 (m, 1H), 1.70-2.25 (m, 2H), 2.28 (s, 3H), 2.45 (br t, 1H, J = 10.2), 4.49 and 4.75 (br s, 2H), 6.06 (dd, 1H, J = 16.3, 0.9), 6.75 (dd, 1H, J = 16.3, 9.2). ^{13}C-NMR (CDCl$_3$) : δ 20.5 (CH$_3$), 26.3 (CH$_2$), 26.6 (CH$_3$), 33.4 (CH$_2$), 35.1 (CH$_2$), 37.5 (CH), 53.6 (CH), 107.9 (CH$_2$), 132.5 (CH), 148.8 (CH), 149.4 (C), 197.6 (CO).

4-(2-methylene-cyclopentyl)-but-3-en-2-one **5d**.

Anal % : calcd C 79.96 H 9.39 found C 80.11 H 9.36. IR υ (neat) : 3050, 1680, 1650, 1620, 895 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$) : δ 1.12-1.71 (m, 4H), 1.87 (s, 3H), 2.00-2.23 (m, 2H), 2.76 (q, 1H, J = 8.4), 4.74 and 4.91 (d, 2H, J = 2.0), 5.96 (d, 1H, J = 15.8), 6.42 (dd, 1H, J = 15.8, 8.4). ^{13}C-NMR (C$_6$D$_6$) : δ 24.9 (CH$_2$), 26.7 (CH$_3$), 32.9 (CH$_2$), 33.6 (CH$_2$), 47.8 (CH), 107.8 (CH$_2$), 131.4 (CH), 148.4 (CH), 153.5 (C), 196.4 (CO).

4-(5-methyl-2-methylene-cyclopentyl)-but-3-en-2-one **5e**.

Anal % : calcd C 80.44 H 9.82 found C 80.31 H 9.79. IR υ (neat) : 3050, 1680, 1650, 1620, 895 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$) : δ 0.77 (d, 3H, J = 6.3), 1.33-1.68 (m, 3H), 1.88 (s, 3H), 2.00-2.30 (m, 2H), 2.35 (t, 1H, J = 8.9), 4.72 and 4.89 (br q, 2H, J = 2.3), 5.98 (d, 1H, J = 15.8), 6.38 (dd, 1H, J = 15.8, 8.9). ^{13}C-NMR (C$_6$D$_6$) : δ 18.2 (CH$_3$), 26.7 (CH$_3$), 32.2 (CH$_2$), 33.8 (CH$_2$), 41.6 (CH), 56.3 (CH), 107.8 (CH$_2$), 132.9 (CH), 147.6 (CH), 154.0 (C), 196.0 (CO).

4-(2,2-dimethyl-5-methylene-cyclopentyl)-but-3-en-2one **5f**.

Anal % : calcd C 80.85 H 10.18 found C 80.66 H 10.25. IR υ (neat) : 3050, 1680, 1650, 1620, 895 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$) : δ 0.63 (s, 3H), 0.79 (s, 3H), 1.14-1.40 (m, 2H), 1.87 (s, 3H), 2.13-2.30 (m, 2H), 2.43 (br d, 1H, J = 9.5), 4.75 and 4.90 (br q, 2H, J = 1.9), 6.00 (d, 1H, J = 15.8), 6.48 (dd, 1H, J = 15.8, 9.5). ^{13}C-NMR (C$_6$D$_6$) : δ 22.1 (CH$_3$), 26.9 (CH$_3$), 27.6 (CH$_3$), 30.0 (CH$_2$), 39.9 (CH$_2$), 43.8 (C), 59.3 (CH), 108.3 (CH$_2$), 133.6 (CH), 146.9 (CH), 153.7 (C), 198.2 (CO).

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