

Lewis acid catalysed M-ene, H-ene, and cycloaddition reactions of allylic stannanes and silanes with methyl propiolate

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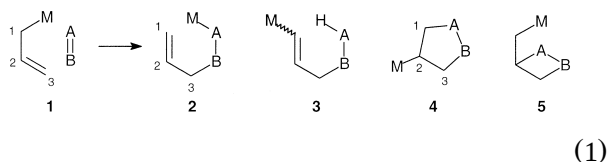
Abstract

The products of the reaction of methyl propiolate with cyclohexene and some allyl and cyclohex-2-enyl silanes and stannanes (H-ene and M-ene adducts, and [2 + 2] and [3 + 2] cycloadducts) have been determined, and rationalised in terms of the probable reaction mechanism. The allylstannanes show only the M-ene reactions to give a mixture of the *E*- and *Z*-adducts, and it has been confirmed that the reaction of allylsilanes can give both the [2 + 2] (cyclobutene) and [3 + 2] (cyclopentene) cycloadducts, which has been a matter of some dispute. © 1998 Elsevier Science S.A.

Keywords: Ene reaction; Metalloene reaction; Sakurai reaction; Allylsilanes; Allylstannanes

1. Introduction

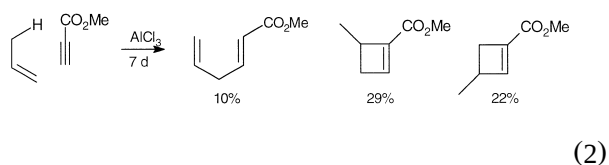
The metalloene (M-ene) reaction, **1** → **2** where M is an organometallic group, is a variant of the hydrogen ene (H-ene) reaction, **1** → **2** where M is hydrogen [1]; the enophile A=B can be ¹O₂, RN=NR, RCH=O, RCH=CHR, RC≡CR, SO₂, etc. The Sakurai reaction [2], in which an allylsilane adds to an enone in the presence of (usually) TiCl₄ may be regarded as a variant of the metalloene reaction.



Under some conditions, the M-ene product **2** may be accompanied by the H-ene product **3**, and/or the [3 + 2] cycloadduct **4** (involving a 1,2-shift of an organometallic group). This last type of reaction is known, for example, where M is R₃Si, R₃Ge, R₃Sn, or R₃Pb and A=B is a triazolinedione [3–5], where M is R₃Sn and

A=B is an aldehyde [6] or singlet oxygen [4], and (in the presence of Lewis acids) when M is R₃Sn or R₃Si and A=B is an enone [7–9], and these reactions have been exploited in organic synthesis for constructing metallocyclopentane and metallocyclopentene rings [7,8,10,11].

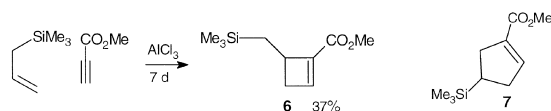
[2 + 2] Cycloadducts **5** are sometimes observed in the reaction of hydrocarbon enes with singlet oxygen (A=B = O=O) to give a 1,2-dioxetan [12,13], with *N*-methyltriazolinedione (A=B = N=N) to give a diazetidene [14], or of propene with methyl propiolate (A=B = C≡C) to give a cyclobutene (Eq. (2)) [15].



The first [2 + 2] cycloaddition with allylmetallic compounds was reported in 1975 by Abel and Rowley who showed that allyltrimethylsilane reacted with perfluoroacetone at –20°C to give the oxetan [16]. In 1979 Snider reported that allyltrimethylsilane and methyl propiolate reacted in the presence of AlCl₃ to give the [2 + 2] cycloadduct **6** (Eq. (3)) [15], and several reports

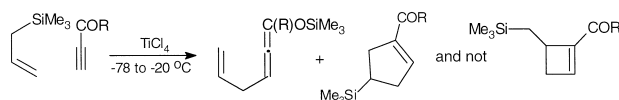
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followed of the formation of cyclobutenes from allylsilanes and yneones [17], or cyclobutenes from allylsilanes and eneones [18–22], under Sakurai conditions.



(3)

However, in 1990, Knölker showed that the cyclic products from the Sakurai reaction of some allylsilanes and eneones or yneones in the presence of TiCl_4 are not the [2 + 2] cycloadducts as was believed, but rather the [3 + 2] cycloadducts (Eq. (4)) [8,23]; the evidence included unambiguous X-ray crystallography. (In Eq. (4), the Sakurai reaction is represented as involving conjugate 1,4-addition across the eneone or yneone system; 1,2-addition can not be excluded, but the silyl group is hydrolysed off during the hydrolytic work-up, and the mode of addition does not appear to have been established.)



(4)

At this time, the nature of all the cyclobutenes reported as byproducts of the Sakurai reactions was under question, but in 1994 Monti et al. [24] showed that the reaction of 1-trimethylsilylmethylcyclohexene with 3-butyne-2-one in the presence of ZnI_2 did give the [2 + 2] adduct (19%) rather than the [3 + 2] adduct (together with 11% of the Sakurai product and 70% of the H-ene product). In particular, they reinvestigated Snider's reaction [15] of allyltrimethylsilane with methyl propiolate in the presence of AlCl_3 (Eq. (3)) and showed that it did indeed give the [2 + 2] cycloadduct **6** (96%), but that a small amount of the [3 + 2] adduct **7** (4%) was also formed. There continues to be a great deal of interest in the way various factors such as the temperature [25], the size of the alkyl groups in the silane [26], the nature of the catalyst [27], and the substituents on the allylic double bond [27] can be used to control the size of the ring which is formed.

We have studied the ene reactions of allylstannanes and related compounds of Group 14 metals where the enophile $\text{A}=\text{B}$ is either singlet oxygen or an azo compound [4,5,28–30]. There appears to have been no report of the metalloene reaction of allylstannanes with alkynes, and we now describe the results of an investigation of the ene reactions of cyclohexene and of

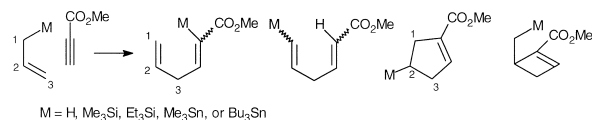
allylsilanes and allylstannanes with methyl propiolate as the enophile. The aim was to determine the relative course of the reactions when $\text{M} = \text{R}_3\text{Sn}$, R_3Si , or H , and to investigate further the question of the [2 + 2] or [3 + 2] structures of the cycloadducts.

2. Results

Methyl propiolate was chosen as the eneophile to allow a direct comparison with the results obtained by Snider et al. on its H-ene reaction with allylic hydrocarbons and allyltrimethylsilane [15]. Ethylaluminum dichloride was used as the catalyst because it acts both as a Lewis acid and also as a Brønsted base which will scavenge adventitiously formed protic acids which might cause decomposition or rearrangement of the reactants or products [31]. One molar equivalent of EtAlCl_2 was used as it complexes more strongly with the acrylate products than the propiolate reactant [31].

The reactivity followed the sequence $\text{M} = \text{H} < \text{SiR}_3 < \text{SnR}_3$; in the presence of the catalyst, the stannanes reacted exothermically with methyl propiolate at room temperature with the development of a brown colour, and these reactions were therefore carried out at 0°C .

The potential initial products corresponding to compounds **2**–**5** are shown in Eq. (5), but vinylmetallic groups are susceptible to protodemetalation [32,33] during chromatography on silica gel, and from these products, only the demetallated hexadienoic acids, $\text{M} = \text{H}$, (**10**, **11**, **13**, and **19**) were isolated. The products were identified mainly by ^1H and ^{13}C NMR spectroscopy.



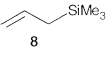
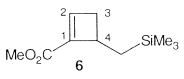
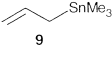
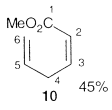
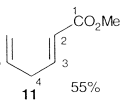
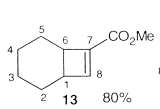
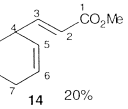
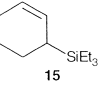
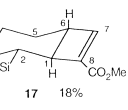
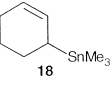
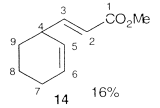
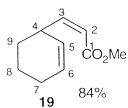
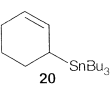
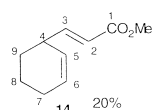
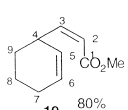
$\text{M} = \text{H}, \text{Me}_3\text{Si}, \text{Et}_3\text{Si}, \text{Me}_3\text{Sn}, \text{or } \text{Bu}_3\text{Sn}$

(5)

The reaction conditions and products are given in Table 1.

As protodestannylation of the metallohexadienoate products occurred on work-up, compounds such as **10** and **11** could in principle be formed by either an M-ene or an H-ene process. To check this, the reaction of allyltributyltin (**9**) and methyl propiolate was carried out in a sealed NMR tube. After 16 h at 0°C , the mixture showed two ^1H NMR triplets, one at δ 6.17 (J 6.87, J ^{119}Sn 55.19, J ^{117}Sn 52.79 Hz) and the other at δ 7.78 (J 7.58, J ^{119}Sn 88.69, J ^{117}Sn 84.79 Hz), and these signals were lost when trifluoroacetic acid was added. This confirms that in the product, tin, which is acid-labile, is coupled to a deshielded vinylic proton which is adjacent to a methylene group, and would be compatible with a mixture of the *E* and *Z* M-ene adducts [32,33].

Table 1
EtAlCl₂-catalysed reaction of allylic compounds with methyl propiolate

Ene	Time /h	Temp. /°C	Yield %	Products
	120	25	65	
	16	0	72	 45%  55%
	168	25	90	 80%  20%
	120	25	83	 82%  18%
	16	0	85	 16%  84%
	16	0	75	 20%  80%

In the H-ene reaction of allylic hydrocarbons with methyl propiolate, Snider reported the formation of only the *E*-dienoates [15], whereas in the M-ene reactions of the allylstannanes, we obtain a mixture of the *E*- and *Z*-products.

Our ¹H and ¹³C NMR spectra of methyl 4-(trimethylsilylmethyl)cyclobut-1-ene-1-carboxylate (**6**) were identical to those reported by Monti et al. [24]. As they point out, the presence of two signals at high field (δ 0.53 and 1.24, ²*J* = 14.6 Hz), coupled to one further proton, identifies the Me₃SiCH₂CH= group; the signal at higher field suggests that the corresponding proton is located in the shielding region of the carbonyl group. The small amount (4%) of the [3 + 2] cycloadduct which they report may have escaped detection. In this system, the products are similar whether AlCl₃ or EtAlCl₂ is used as the catalyst.

No cyclic product could be detected from the reaction of allyltrimethylstannane **9**, cyclohexenyltrimethylstannane **18**, or cyclohexenyltributylstannane **20**; all three, particularly the cyclohexenylstannanes, gave only the methyl hexa-2,5-dienoate, with a preponderance of the *E*-isomer, though this does not necessarily reflect the stereochemistry of the ene reactions (see below).

The ratio of the [2 + 2] cycloaddition **13** and H-ene

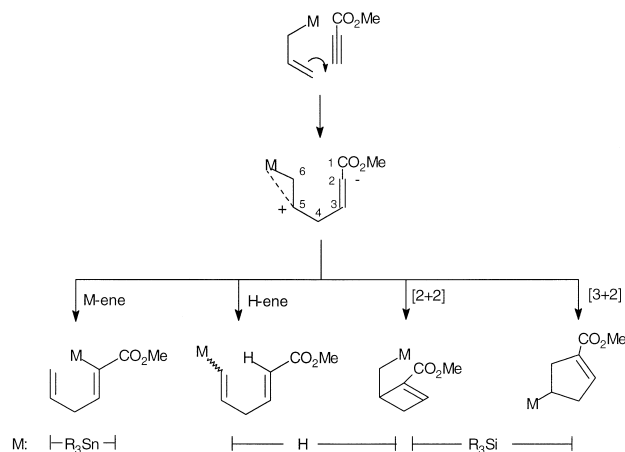
products **14** (80 : 20) which was obtained from cyclohexene **12** is similar to that which was reported (83 : 17) where ethyl propiolate was the enophile and AlCl₃ was the catalyst [15]. Again the behaviour of AlCl₃ and EtAlCl₂ is similar.

The reaction between triethylsilyl cyclohexene **15** and methylpropiolate gave the [2 + 2] cycloadduct **17** and the [2 + 3] cycloadduct with silyl shift **16** in the ratio 18 : 82. In the ¹H NMR spectrum, **16** and **17** are clearly differentiated by the signals of the protons on the bridgehead carbon atoms. As shown by decoupling irradiation, in **17** H-1 couples with H-6 and H-2 with the coupling constants 4.78 and 4.65 Hz respectively, to give a distinctive triplet for H-1 at δ 3.10. Coupling of H-6 with H-1 and H-7, and with the axial and equatorial protons at H-5 results in a more complex multiplet at δ 2.85. In **16**, the bridgehead protons H-1 and H-5 show less well resolved multiplets at δ 2.76 and 2.93 respectively.

Compounds **16** and **17** were further characterised by a detailed study of the ¹³C NMR spectra. The values of ¹*J*(CH) for the olefinic CH groups are within the range which is normally observed for cyclo- and bicyclo-alkenes [34,35]. The chemical shifts for the carbon atoms carrying the triethylsilyl groups were determined by the INEPT and APT techniques, and found to be 41.86 for **16** and 18.45 for **17**, in line with the rule that they should be downfield for a bicyclic five-membered ring, and up-field for a six-membered ring [35,36].

3. Discussion

The mechanism which is normally accepted for the reaction of an allylmetallic compounds and an enophile is illustrated for the case of methyl propiolate in Scheme 1.



Scheme 1.

When the enophile is the carbonyl group of an aldehyde or ketone, or the double or triple bond of an unsaturated carbonyl compound, Lewis acids can catalyse the reaction by associating at the oxygen and increasing the electrophilicity of the enophile, or sometimes by transmetalation of the allylmetallic reagent.

The best evidence for the formation of an initial complex between the ene and the enophile is the intramolecular isotope effects which are observed when *gem*-, *trans*-, and *cis*-2,3-dimethylbut-2-ene- d_6 reacts with methyl propiolate in the presence of EtAlCl_2 [37]. The precise structure of this intermediate, which is represented in Scheme 1 for the sake of simplicity as a zwitterion, is open to question, but all the possibilities involve the development of positive charge on the ene, which can be stabilised by the interaction with the metal M.

The nature of the products is then governed by the nature of the reaction between the nucleophilic and electrophilic moieties of the intermediate. Nucleophilic substitution by C-2 at M gives the M-ene product, and at hydrogen gives the H-ene product; nucleophilic substitution at C-6 with displacement of M onto C-5 gives the [3 + 2] cycloadduct, and nucleophilic addition at C-5 gives the [2 + 2] cycloadduct.

The reactivity and chemoselectivity which we observe can be rationalised as follows.

The strength of the interaction of M with a positive charge in the β -position is well established to increase in the sequence $\text{H} < \text{R}_3\text{Si} < \text{R}_3\text{Sn}$ [38], and if the formation of the intermediate is rate-determining, this will account for the increase of reactivity $\text{HC}=\text{C}=\text{C} < \text{R}_3\text{SiC}=\text{C}=\text{C} < \text{R}_3\text{SnC}=\text{C}=\text{C}$ which we observe, whatever the fate of the intermediate.

When $\text{M} = \text{R}_3\text{Sn}$, the principal route which is followed is the M-ene reaction, with perhaps a small H-ene component. This is in accord with the usual high reactivity of a tin centre to a nucleophile. The vinyl–tin bond in trimethylvinylstannane is 9 times more reactive towards protic acids than is the corresponding bond in 2-trimethylstannylacrylate [33], and both are broken during chromatography on silica. On hydrolysis, the α -stannylacrylates give mixtures of the *E* and *Z* protic acrylates [33], hence the ratio of *E*- and *Z*-hexa-dienoates which we observe reflects the stereochemistry of the hydrolysis and not that of the M-ene reaction.

When $\text{M} = \text{H}$, there is now no possibility of a metalloene route. The interaction of the proton with the β -positive charge (hyperconjugation) is weak [38], inhibiting migration in the [3 + 2] cyclisation, but permitting attack of the carbon nucleophile at C-5, leaving the [2 + 2] cycloaddition and the H-ene reaction in competition to a degree depending on the structure of the alkene [15]. [2 + 2] Cycloadditions can be observed in isolation when the relevant hydrogen atoms are absent or are

sterically unavailable, as in the reaction of adamantylideneadamantane with singlet oxygen [12,13] or with a triazolinone [14].

When $\text{M} = \text{R}_3\text{Si}$, the interaction with the β -positive charge is more significant, but this [38], and its reactivity towards the carbon nucleophile, is much weaker than when $\text{M} = \text{R}_3\text{Sn}$. The major reactions which are observed are the [2 + 2] and the [3 + 2] cycloadditions, though with other enophiles, the H-ene reaction may predominate.

4. Conclusions

The chemoselectivity of the reaction of allylic compounds with enophiles is very dependent on the identity of the metallic group M, of the nature of the ene and enophile and of any catalyst, and on the reaction conditions.

Our results confirm Monti's demonstration that, under appropriate conditions, the reactions of allylsilanes with acetylenes can lead to both [2 + 2] (cyclobutene) and [3 + 2] (cyclopentene) cycloadducts [24].

The allylstannanes which we have investigated, unlike the allylsilanes, react chemoselectively with methyl propiolate by the M-ene route, to give, after hydrolysis, the methyl hexa-2,5-dienoates. This reaction may be useful in synthesis, though one limitation would be its lack of stereoselectivity. Previous work has shown that in general the M-ene reaction can be enhanced by the use of a more electropositive metal (e.g. Sn rather than Si), by introduction of electronegative ligands at the metal (e.g. ClBu_2Sn rather than Bu_3Sn), and by the use of a polar solvent [30].

Sterically hindering ligands on the metal (e.g. $\text{R}_3\text{Si} = \text{Pr}_3\text{Si}$ rather than Me_3Si) on the other hand slow the M-ene reaction so that the cyclisation reactions may become dominant [25,39], and lower temperatures favour the [2 + 2] cycloaddition over the [3 + 2] cycloaddition [25,26].

By a judicious choice of these various parameters, the reactions can be directed towards the required product.

5. Experimental

^1H And ^{13}C NMR spectra were recorded on solutions in CDCl_3 on a Varian VXR-400 spectrometer, shifts being referenced to the solvent (δH 7.24, δC 77.00). Coupling constants are in Hz. Mass spectra were recorded on a VG 7070H spectrometer, and IR spectra on a Perkin Elmer PE983 instrument. Column chromatography was carried out on Merck silica gel 60.

The reactants **9**, **15**, **18**, and **20** were prepared as described previously [4].

5.1. Reaction of allylmetallic compounds with methyl propiolate

These reactions were carried out by Snider's procedure [31]. The general method was as follows.

Ethylaluminium dichloride (4.0 cm³ of a 1 mol dm⁻³ solution in hexane) was syringed dropwise under argon into a solution of methyl propiolate (0.34 g, 4.0 mmol) in CH₂Cl₂ (5 cm³) at room temperature. The mixture was stirred for 30 min, then a solution of the corresponding allyl compound (4.0 mmol) in CH₂Cl₂ (5 cm³) at room temperature when M = Si, and at 0°C when M = Sn. The mixture was then stirred at the corresponding temperature for the period given in Table 1. The solvent was evaporated off, and the residue was chromatographed on silica gel using pentane/ether (5:1 v/v) as eluent. The mixture was examined by NMR to determine the ratio of the products, which were then separated by repeated chromatography.

5.2. Methyl 4-(trimethylsilylmethyl)cyclobut-1-ene-1-carboxylate (**6**) [15]

Clear oil. $\delta(\text{H})$ -0.01 (9H, s, SiMe₃), 0.55 (1H, dd, J 14.68 and 12.64, CHH'Si), 1.26 (1H, dd, J 14.68 and 3.06, CHH'Si), 1.98 (1H, dt, J 15.38 and 1.56, H-3), 2.62 (1H, ddd, J 15.38, 3.65, and 1.56, H'-3) 3.03 (1H, dddd, J 12.64, 3.65, 3.06, and 1.56, H-4), 3.70 (3H, s, OMe), 6.72 (1H, m, H-2). $\delta(\text{C})$ 144.05 ($J\text{H}$ 167.9, C-1), 144.10 (C-2), 39.11 (C-3), 36.19 (C-4), 20.28 (C-5), 50.95 (OMe), 162.59 (C=O) -1.02 (SiMe₃).

5.3. Methyl (Z)-hexa-2,5-dieneoate (**10**)

Clear oil. $\delta(\text{H})$ 3.42 (2H, ttd, J 7.48, 6.25, and 1.54, H-4), 3.80 (3H, s, OMe), 5.03 (2H, m, H-6), 5.78 (1H, dt, J 11.45 and 1.54, H-2), 5.82 (1H, ddt, J 16.63, 10.11, and 6.25, H-5), 6.24 (1H, dt, J 11.45 and 7.48, H-3). $\delta(\text{C})$ 37.59 (C-4), 51.69 (OMe), 116.50 (C-6), 119.75 (C-5), 135.44 (C-2), 147.22 (C-3), 165.81 (C=O). ν_{max} (neat) 2940, 2869, 1733, 1650, 1435, 1223 cm⁻¹. HRMS C₇H₁₀O₂, found 126.0680, calculated 126.0688.

5.4. Methyl (E)-hexa-2,5-dieneoate (**11**)

Clear oil. $\delta(\text{H})$ 2.96 (2H, ttd, J 7.99, 6.55, and 1.41, H-4), 3.85 (3H, s, OMe), 5.20 (2H, m, H-6), 5.82 (1H, dt, J 15.73 and 1.68, H-2), 5.85 (1H, dt, J 16.65, 10.15, and 7.99, H-5), 7.06 (1H, dt, J 15.73 and 6.55, H-3). $\delta(\text{C})$ 35.95 (C-4), 51.24 (OMe), 116.89 (C-6), 121.70 (C-5), 133.56 (C-2), 146.27 (C-3), 166.52 (C=O). These spectra are consistent with those reported previously [15,40].

5.5. Methyl bicyclo[4.2.0]-oct-7-ene-7-carboxylate (**13**)

Oil. $\delta(\text{H})$ 1.30 (1H, m), 1.40 (2H, m), 1.54 (2H, m), 1.75 (2H, m), 2.00 (1H, m), 2.77 (1H, ddd, J 10.30, 5.45, and 1.15, H-2), 3.04 (1H, dd, J 10.13 and 5.40, H-1), 3.70 (3H, s, OMe), 6.86 (1H, d, J 1.15, H-8). $\delta(\text{C})$ 150.52 ($J\text{H}$ 174.3, C-7), 141.63 (C-8), 40.06 (C-2), 38.38 (C-1), 23.80 (C-6), 23.59 (C-5), 18.92 (C-4), 18.33 (C-3), 51.10 (OMe), 162.85 (C=O).

5.6. Methyl (E)-3-(cyclohex-2-enyl)propenoate (**14**)

Oil. $\delta(\text{H})$ 1.20–2.00 (6H, m), 2.92 (1H, m), 3.73 (3H, s, OMe), 5.51 (1H, dm, J 9.83 and 2.81, H-6), 5.78 (1H, dd, J 15.73 and 1.40, H-2), 5.79 (1H, dm, J 9.83 and 2.21, H-5), 6.91 (1H, dd, J 15.73 and 7.06, H-3).

The ¹H NMR spectra of the compounds (**13**) and (**14**) are consistent with those reported for the corresponding ethyl ester [15].

5.7. Methyl 8-triethylsilylbicyclo[3.2.1]oct-6-en-6-carboxylate (**16**)

Clear oil. $\delta(\text{H})$ 0.66 (6H, q, J 7.98, CH₂Si), 0.96 (9H, t, J 7.98, Me), 1.24 (1H, m), 1.38–1.60 (6H, complex, ring protons), 2.76 (1H, m), 2.93 (1H, m), 3.71 (3H, s, OMe), 6.99 (1H, d, J 3.00, H-7). $\delta(\text{C})$ 147.93 ($J\text{H}$ 168.2, C-7), 140.2 (C-6), 42.84 (C-5), 41.86 (C-8), 41.84 (C-1), 21.73 (C-2), 21.39 (C-3), 17.81 (C-8), 51.22 (OMe), 165.76 (C=O), 4.42 and 7.70 (SiEt₃). MS (70 eV) 280 (M⁺, 2), 251 (45), 133 (100), 117 (35), 105(44). HRMS (on mixture with isomer **17**), found 280.1785; C₁₆H₂₈O₂Si requires 280.1792.

5.8. Methyl 2-triethylsilylbicyclo[4.2.0]oct-7-ene-8-carboxylate (**17**)

Clear oil. $\delta(\text{H})$ 0.58 (6H, quartet, J 7.86, CH₂Si), 0.96 (9H, t, J 7.86, CH₃), 1.22 (1H, m), 1.40–1.55 (6H, complex), 2.85 (1H, m), 3.01 (1H, dd, J 4.78 and 4.65), 3.68 (1H, s, OMe), 6.72 (1H, d, J 1.28, H-7). $\delta(\text{C})$ 147.97 ($J\text{H}$ 173.1, C-7), 144.00 (C-8), 39.15 (C-1), 38.59 (C-6), 26.24 (C-5), 24.00 (C-4), 20.30 (C-3), 18.45 (C-2), 50.91 (OMe), 162.67 (C=O), 2.29 and 7.70 (SiEt₃). HRMS (on mixture with isomer **16**), found 280.1785; C₁₆H₂₈O₂Si requires 280.1792.

5.9. Methyl (Z)-3-(cyclohex-2-enyl)propenoate (**19**)

Oil. 1.36 (1H, m), 1.59 (1H, m), 1.72 (1H, m), 1.84 (1H, m), 1.98 (2H, m), 3.68 (3H, s, OMe), 4.06 (1H, m, H-4), 5.46 (1H, dm, J 9.96 and 2.24, H-6), 5.71 (1H, dd, J 11.42 and 1.06, H-2), 5.75 (1H, dm, J 9.96 and

3.45, H-5), 6.04 (1H, dd, J 11.42 and 10.04, H-3). $\delta(\text{C})$ 20.39, 24.72, 28.42, 34.85, 51.02 (OMe), 118.07 (C-6), 127.07 (C-2), 128.38 (C-5), 153.57 (C-3), 166.66 (C=O). ν_{max} (cm^{-1} , neat) 2929, 2846, 1720, 1633, 1432, 1195, 823. MS (70 eV) 166 (8, M^{+}), 150 (7), 134 (10), 105 (12), 91 (14), 79 (17), 53 (100). HRMS, found 166.0999, calculated for $\text{C}_{10}\text{H}_{14}\text{O}_2$, 166.0994.

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