

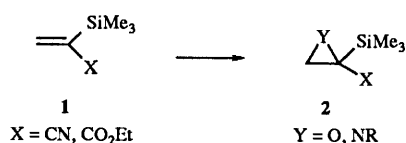
Reactions of α -trimethylsilylvinyl carbanions with carboxylic acid derivatives: the relationship between product distribution and substrate reactivity

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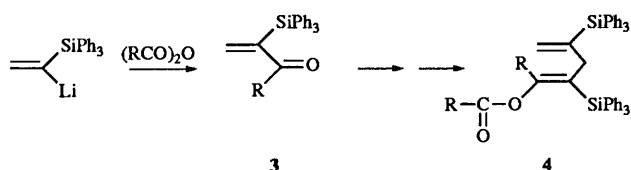
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The reaction between α -trimethylsilylvinyl carbanions and carboxylic acid derivatives gives α,β -unsaturated carbonyl compounds which, under the reaction conditions, undergo further conjugate addition. Further reactions can also occur, depending upon the reactivities of the enolates and of the carboxylic acid derivatives.

2-Silylpropenenitriles and 2-silylpropenoic acid esters, **1** are useful precursors to the corresponding epoxides and aziridines, **2**.^{1,2,3}



One route to the 2-silylpropenoic acid derivatives is *via* reaction of an α -trialkylsilylvinyl carbanion with an alkyl chloroformate. Brook and Duff have reported reactions of α -lithiovinyltriarylsilanes with such activated carbonyl compounds.⁴ The reaction of α -lithiovinyltriphenylsilane with acetic anhydride at -78°C gave the α,β -unsaturated ketone **3**



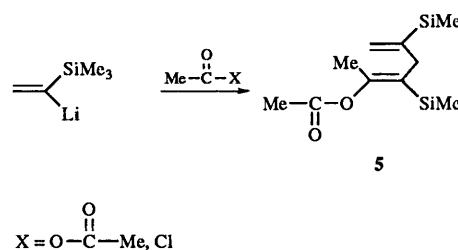
whereas at room temperature this underwent further conjugate addition to give **4**. With *trans*-1-lithio-2-phenyl-1-triphenylsilene only the vinyl ketone was observed, presumably because of steric and electronic factors. The corresponding Grignard reagents gave similar results.

Stork has used α -silyl substituted vinyl ketones extensively in conjugate addition reactions involving enolates.⁵ The presence of the trimethylsilyl group stabilises the enolate and thus avoids the problems of reversibility and polymerisation. Thus, it is not unexpected that the α,β -unsaturated ketones formed from α -trialkylsilylvinyl carbanions undergo further conjugate addition.

As part of our studies of the preparation of small-ring silyl substituted heterocycles of the type **2**, we needed to obtain compounds such as **1** and thus undertook a study of the susceptibility of α,β -unsaturated ketones to undergo further reaction when formed from α -methylsilylvinyl carbanions.

Results and discussion

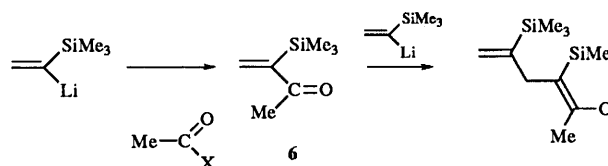
We examined the products of the reaction of α -trimethylsilylvinyl carbanions with carboxylic acid derivatives with varying reactivity.



Reaction of α -trimethylsilylvinyl carbanions with anhydrides and acid chlorides

We repeated the work of Brook and Duff using α -trimethylsilylvinyl carbanions obtained from the corresponding vinyl bromide⁶ and *tert*-butyllithium in tetrahydrofuran (THF) at -110°C . We isolated only the product of conjugate addition and subsequent acylation, **5**, in almost quantitative yield. Reaction with ethanoyl chloride gave a similar product also in high yield.

In these experiments the α -trimethylsilylvinyl carbanion is formed *in situ* and the carboxylic acid derivative added dropwise. Thus, if the carbanion reacts with the carboxylic acid derivative almost as soon as it is added to give the α,β -unsaturated ketone, there will be an excess of the carbanion remaining that will further react through conjugate addition, before more of the carboxylic acid derivative is supplied.

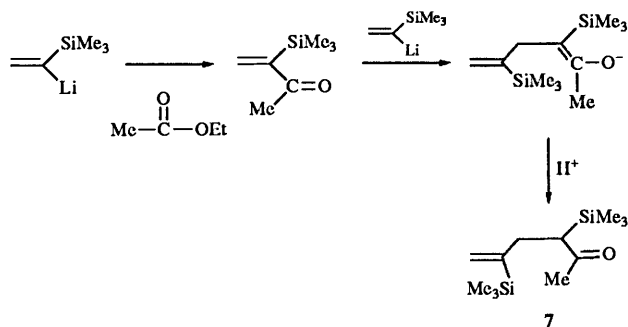


The reaction of alkyllithium reagents with α,β -unsaturated ketones often leads to 1,2- as well as 1,4-addition.⁷ However, in our studies only 1,4-addition to **6** was observed and no product of 1,2-addition was ever obtained. Further acylation of the enolate leads to attack at the oxygen rather than the corresponding Claisen reaction, as is common with such reactive acylating agents.⁸

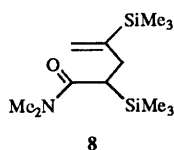
Reaction of α -trimethylsilylvinyl carbanions with esters and carbamate derivatives

We examined a number of less reactive acylating agents to discover if the same pattern of behaviour was observed.

Reaction of the α -trimethylsilylvinyl carbanion with ethyl ethanoate gives the simple product of conjugate addition **7** with no further acylation, reflecting the lower reactivity of the ester relative to the anhydride.

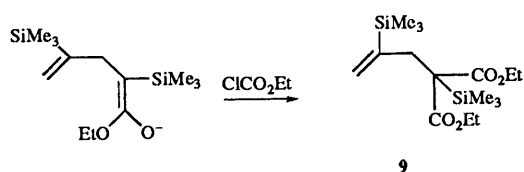


A similar outcome was observed using *N,N*-dimethylcarbamoyl chloride which gave the amide **8**, although in this case the yield was low.

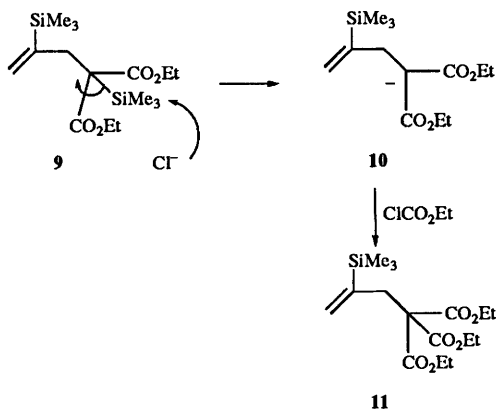


Reaction of α -trimethylsilylvinyl carbanions with alkyl chloroformates

The use of more reactive acylating agents led to further reaction of the conjugate addition product. In this case, instead of attack at oxygen, carbon acylation gave the diester **9**. This preference for carbon rather than oxygen acylation is common with alkyl chloroformates.⁹



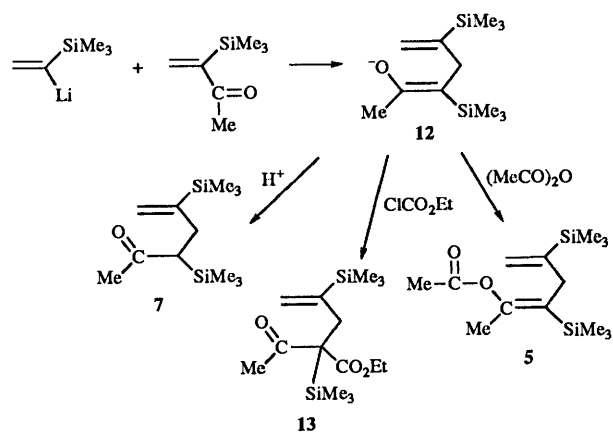
Interestingly this diester reacts further *via* nucleophilic attack of the chlorine at the silicon to give a malonate-type enolate **10**, which is then converted into the triester **11** (65% overall).



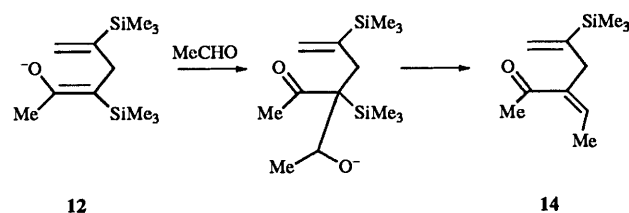
Such formation of tricarboxylic esters has been reported,^{9,10} however, this is the first instance where the carbanion is generated through a desilylation.⁷ The same type of product is obtained if methyl chloroformate is substituted for ethyl chloroformate. This provides a simple high yielding route to these highly functionalised tricarboxylic acids.¹¹

Reactions of α -trimethylsilylvinyl carbanions with α,β -unsaturated carbonyl compounds

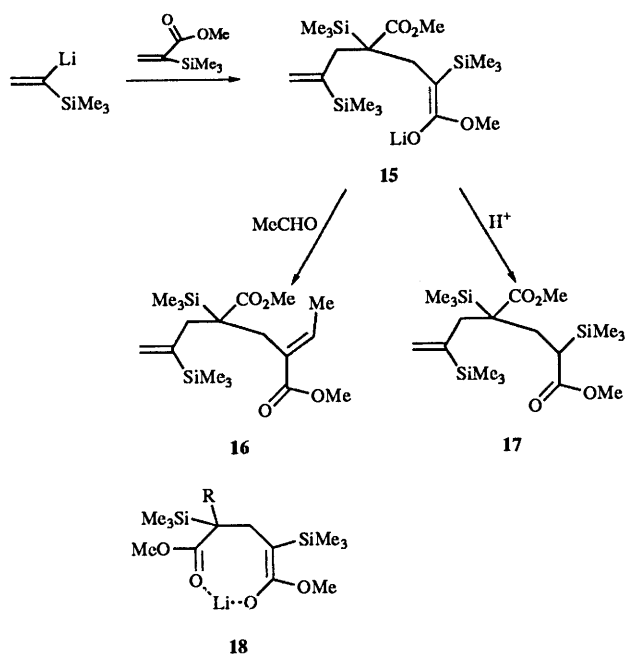
To confirm our mechanistic proposals we prepared the intermediate α,β -unsaturated ketones and esters by an alternative route. Oxidation of the allyl alcohol formed from reaction of the trimethylsilylvinyl carbanion with acetaldehyde led to the α,β -unsaturated ketones and esterification of the acrylic acid formed from reaction of the trimethylsilylvinyl carbanion with carbon dioxide led to the α,β -unsaturated ester.



Reaction of the α -trimethylsilylvinyl carbanion with one equivalent of the α,β -unsaturated ketone at -110°C led to the conjugate addition product **12**. The enolate could then be quenched with water to give the α -trimethylsilylketone **7**, treated with an alkyl chloroformate to give the ketoester **13**, or treated with ethanoic anhydride to give the oxygen acylated product **5**. Interestingly, under the conditions of this reaction no desilylation to give the more stable enolate ion was observed. Treatment of the product of conjugate addition with an aldehyde gives the dienone **14** *via* a Peterson reaction. Similar products of a sequential Michael addition and Peterson condensation of a silyl vinyl ketone have been reported by Tsuge.¹²



The reaction of the α -trimethylsilylvinyl carbanion with the α,β -unsaturated ester gave a completely different set of products. In this case the product of conjugate addition underwent further reaction with the α,β -unsaturated ester to give **15**. Irrespective of the ratio of the carbanion to the α,β -unsaturated ester we always obtained the product from two conjugate additions. This type of behaviour has been observed before in the reaction of methyl 2-(trimethylsilyl)propenoates with organo-magnesiums and -lithiums.¹³ This may be because as soon as the acrylate is added dropwise to the carbanion, a reaction takes place to form the product of one conjugate addition. This depletes the concentration of the α -trimethylsilylvinyl lithium in the vicinity of the added α,β -unsaturated ester hence further conjugate addition can compete successfully for the remaining carbonyl. The product of the second conjugate addition seems to be particularly stable so does not undergo further reaction. This stability may arise from complexation to give the cyclic chelate **18**. This type of intermediate chelate has been proposed for similar Michael reactions.^{14,15} Reaction of **15** with acetaldehyde¹⁶ and water gave **16** and **17** respectively,



as single diastereoisomers. This again points to the formation of a chelated species **18**, at least in the transition state, where one configuration is favoured.^{14,16,17}

Effect of reaction conditions on the product distribution

The problems associated with the further conjugate addition of the α,β -unsaturated carbonyl compounds partly arise as they are formed in the presence of an excess of carbanion. This can be alleviated by carrying out an inverse addition. In this case, for most of the addition, the carbonyl compound is in an excess and can therefore compete successfully with the α,β -unsaturated carbonyl. This can be experimentally difficult because the carbanion needs to be kept at low temperature otherwise it will decompose.

These inverse additions were examined by syringing the cold carbanion into a precooled solution of the ethyl chloroformate. Unfortunately the yields of this reaction were low, nevertheless the major product was the simple α,β -unsaturated ester, as predicted. Changing the solvent from tetrahydrofuran to hexane, but nevertheless employing the usual addition procedure, led to the α,β -unsaturated ester in good yield. In the less polar solvent the α -trimethylsilylvinyl lithium would be more covalent and therefore less reactive, allowing the rate of carbonyl addition to the reaction mixture to compete with that of conjugate addition.

Experimental

NMR spectra were recorded as solutions in deuteriochloroform on a JEOL EX400 NMR spectrometer using Me₄Si as internal standard; *J* values are given in Hz. IR spectra were obtained as Nujol mulls or thin films using sodium chloride plates on a Nicolet 205 FT-IR spectrometer. Mass spectra were run on a VG20-250 quadrupole instrument equipped with an Ion Tech fast atom bombardment (FAB) gun. 'Ether' refers to diethyl ether.

Reaction of carbonyl compounds with (1-lithiovinyl)trimethylsilane

Acetic anhydride, acetyl chloride, ethyl acetate and *N,N*-dimethylcarbamoyl chloride were reacted with (1-lithiovinyl)trimethylsilane. Identical reaction conditions were used in each case. The general procedure is described for the reaction with acetic anhydride.

3,5-Bis(trimethylsilyl)hexa-2,5-dien-2-yl acetate **5**

A stirred solution of (1-bromovinyl)trimethylsilane (3.04 g, 0.017 mol) in dry THF (50 cm³) was cooled to -110 °C under nitrogen. *tert*-Butyllithium (0.019 mol) in pentane (11.2 cm³) was added dropwise over 10 min, while the temperature was maintained below -100 °C throughout. The bright yellow solution was stirred for a further 30 min at -100 °C. Acetic anhydride (0.025 mol) was added dropwise over 10 min and the temperature maintained at -100 °C for a further 20 min, after which the mixture was allowed to warm slowly to room temperature and stirred for an additional 17 h. Saturated aq. ammonium chloride was added to the mixture at 0 °C, which was then extracted with ether. The organic layer was dried (MgSO₄) and evaporated under reduced pressure to give an oil, which was purified by column chromatography on silica gel with hexane as the eluent to afford pure 3,5-bis(trimethylsilyl)hexa-2,5-dien-2-yl acetate **5** (85%). Quenching the anion with acetyl chloride gave the same product (80%); δ_{H} (400 MHz) 0.07 (9 H, s, SiMe₃), 0.12 (9 H, s, SiMe₃), 2.03 (3 H, s, CH₃), 2.05 (3 H, s, CH₃CO), 2.78 (2 H, s, C=C-CH₂-C=) and 5.42-5.47 (2 H, m, CH₂=); δ_{C} (400 MHz) -1.23, 0.26 (2 × SiMe₃), 20.58 (CH₃), 21.40 (CH₃CO), 34.33 (CH₂), 121.07 (CCH₃), 123.75 (CH₂=), 149.95 (CSi), 152.15 (CSi) and 169.54 (CO); δ_{Si} (400 MHz) -3.65 and -3.30 (Found: C, 58.9; H, 9.7. C₁₄H₂₈O₂Si₂ requires C, 59.1; H, 9.9%).

3,5-Bis(trimethylsilyl)hex-5-en-2-one **7**. When the reaction was carried out using ethyl acetate as the quenching agent, 3,5-bis(trimethylsilyl)hex-5-en-2-one (75%) was obtained; δ_{H} (400 MHz) 0.10 (9 H, s, SiMe₃), 0.11 (9 H, s, SiMe₃), 2.04 (3 H, s, CH₃), 2.19 (1 H, m, CHSi), 2.67-2.75 (2 H, m, CH₂CH) and 5.27-5.46 (2 H, m, CH₂=C); δ_{C} (400 MHz) -1.51, -2.46 (2 × SiMe₃), 31.57 (CH₃), 32.63 (CH₂), 47.63 (CHSi), 123.67 (CH₂=C), 151.40 (C=CSi) and 209.33 (CO).

N,N*-Dimethyl-2,4-bis(trimethylsilyl)pent-4-enamide **8*. When *N,N*-dimethylcarbamoyl chloride was used as the quenching agent a dark green reaction mixture was obtained which gave a brown oil on work-up. The oil was cooled in a solid CO₂-acetone bath and a dark solid precipitated, the NMR of which showed mainly *N*-methyl groups. This procedure was repeated several times and the mother liquor concentrated to give the product which was contaminated with hydrocarbon material. The product was obtained pure (6.6%) by column chromatography on silica, using hexane as the eluent; ν_{max} (film)/cm⁻¹ 3115-2810, 1635, 1395, 1250, 1135, 1040, 915, 848, 740 and 665; δ_{C} (400 MHz) -1.76, -0.83 (2 × SiMe₃), 32.30 (CH₃), 32.79 (CH₂), 48.31 (CHSi), 124.17 (CH₂=C), 152.08 (CH₂=CSi) and 209.94 (CO); *m/z* 271, 256, 198, 172 and 73 (Found: C, 57.0; H, 10.6. C₁₃H₂₉NOSi₂ requires C, 57.5; H, 10.6%).

Triethyl 3-trimethylsilylbut-3-ene-1,1,1-tricarboxylate **11**

A stirred solution of (1-bromovinyl)trimethylsilane (3.04 g, 0.017 mol) in THF (50 cm³) was cooled to -110 °C under nitrogen. *tert*-Butyllithium (0.019 mol) in pentane (11.2 cm³) was added dropwise over 10 min, while the temperature was maintained below -100 °C throughout. The bright yellow solution was stirred for a further 30 min at -100 °C then cooled to -110 °C. Ethyl chloroformate was added dropwise over 10 min and the temperature maintained at -110 °C for a further 20 min after which the mixture was allowed to warm slowly to room temperature and stirred for an additional 17 h. Saturated aq. ammonium chloride was added to the mixture at 0 °C, which was then extracted with ether. The organic extract was dried and purified by flash column chromatography to give triester **11** (70%); ν_{max} (film)/cm⁻¹ 2983-2961, 1745, 1298, 1256, 1218, 1064 and 844; δ_{H} (400 MHz) 0.15 (9 H, s, Me₃Si), 1.29 (9 H, q, 3 × CH₂CH₃), 3.02 (2 H, s, CH₂C(CO₂Et)), 4.25 (6 H, t, 3 × CH₂CH₃), 5.48 (1 H, s, H_aH_bC=) and 5.69 (1 H, s, H_aH_bC=) (the geminal coupling constant between H_a and H_b was apparently zero);

δ_c (400 MHz) -0.8 (Me₃Si), 14.8 (CH₃), 37.6 (CH₂-CSi), 62.8 (CH₂O), 66.5 [C(CO₂Et)₃], 127.3 (H₂C=), 147.0 (CSiMe₃) and 167.5 (C=O); δ_{si} -2.1 ; m/z 345 ([M + H]⁺, 20.6%), 329 [M - Me], 66.1), 257 (CH₂C(CCO₂Et)₃, 44.4), 227 (43.2), 211 (70.0), 197 (29.6), 183 (41.7), 181 (36.8), 153 (39.8), 75 (47.4) and 73 (100) (Found: [M - Me]⁺, 329.1421). C₁₅H₂₅O₆Si requires $M - CH_3$, 329.1420) (Found: C, 55.8 ; H, 8.6 . C₁₆H₂₈O₆Si requires C, 55.8 ; H, 8.2%).

Trimethyl 3-trimethylsilylbut-3-ene-1,1,1-tricarboxylate.

When the reaction was carried out using methyl chloroformate as the quenching agent, trimethyl 3-trimethylsilylbut-3-ene-1,1,1-tricarboxylate was isolated (74%); ν_{max} (film)/cm⁻¹ 3040 , 2960 , 1750 (C=O), 1680 (C=C), 1270 , 1150 and 860 ; δ_H (400 MHz) 0.06 (9 H, s, SiMe₃), 2.99 (2 H, s, CH₂), 3.74 (9 H, s, 3 × OMe), 5.41 and 5.54 (1 H each, J 1.6 , CH₂=C); δ_c (400 MHz) -1.03 (SiMe₃), 37.39 (CH₂), 53.76 (OCH₃), 127.11 (CH₂=), 147 (CSi), 167.67 (CO) and 175.88 (C); δ_{si} (400 MHz) -1.96 ; (Found: C, 58.9 ; H, 9.7 . C₁₃H₂₂NO₆Si requires C, 59.1 ; H, 9.9%).

Ethyl 2-oxo-3,5-bis(trimethylsilyl)hex-5-ene-3-carboxylate 13

(1-Lithiovinyl)trimethylsilane was generated as described in the above procedure using 3.04 g (0.017 mol) of (1-bromovinyl)trimethylsilane. To this cold yellow solution, was added dropwise 1-trimethylsilylvinyl methyl ketone¹⁸ (2.45 g, 0.017 mol) in a little dry THF whilst the temperature was maintained at -100 °C. The mixture was stirred for a further 20 min at -100 °C after which it was allowed to warm up gradually to -20 °C. Ethyl chloroformate (0.025 mol) was then added dropwise, the reaction mixture was allowed to warm up slowly to room temperature and it was stirred for a further 17 h. Saturated aq. ammonium chloride was added to the mixture at 0 °C, which was then extracted with ether. The organic extract was dried (MgSO₄), evaporated and purified by column chromatography on silica using hexane-ether as eluent to give pure ester **13** (74%); ν_{max} (film)/cm⁻¹ 3060 , 2900 , 1750 , 1445 , 1360 , 1250 , 1150 , 1100 and 840 ; δ_H (400 MHz) 0.07 (9 H, s, SiMe₃), 0.08 (9 H, s, SiMe₃), 1.27 (3 H, t, J 7.8 , CH₃), 2.09 (3 H, s, CH₃CO), 2.84 (2 H, s, CH₂), 4.16 (2 H, q, J 7.8 , OCH₂) and 5.27 and 5.43 (1 H, d, J 2 and 1 H, d, J 2.4 , CH₂=C); δ_c (400 MHz) -1.43 (SiMe₃), 0.00 (SiMe₃), 14.70 (CH₃), 19.97 (CH₃CO), 33.88 (CH₂), 64.43 (OCH₂), 121.46 (CSi), 123.59 (CH₂=C), 149.66 (CSi), 151.27 (CO₂R) and 153.32 (CO); δ_{si} (400 MHz) -3.34 , -3.29 ; m/z 314 (1%), 299 (2), 241 (2), 235 (4), 224 (4), 209 (3), 181 (4), 169 (10), 163 (13), 146 (33), 137 (34), 127 (20), 115 (18), 103 (10), 97 (15), 73 (100), 43 (20) and 29 (25) (Found: C, 57.3 ; H, 9.9 . C₁₅H₃₀O₃Si requires C, 57.3 ; H, 9.6%).

Methyl 2-oxo-3,5-bis(trimethylsilyl)hex-5-ene-3-carboxylate.

Using the same procedure as above with methyl chloroformate (0.025 mol) gave the title keto ester (65%) after isolation and purification; ν_{max} (film)/cm⁻¹ 3040 , 2960 , 1750 , 1680 , 1475 , 1375 , 1270 , 1250 , 1150 and 860 ; δ_H (400 MHz) 0.08 (9 H, s, SiMe₃), 0.13 (9 H, s, SiMe₃), 2.08 (3 H, s, CH₃), 2.28 (2 H, s, CH₂), 3.73 (3 H, s, OCH₃) and 5.41 – 5.77 (2 H, dd, J 2.4 ; CH₂=); δ_c (400 MHz) -1.23 (SiMe₃), 0.17 (SiMe₃), 20.09 (CH₃), 34.05 (OCH₃), 55.41 (CH₂), 121.73 (CSi), 123.76 (CH₂=), 149.86 (=CSi), 151.36 (CO₂R) and 154.10 (CO); δ_{si} (400 MHz) -3.25 ; m/z 300 (1%), 285 (1), 224 (3), 221 (2), 209 (4), 153 (4), 149 (7), 137 (38), 136 (30), 135 (5), 133 (3), 97 (12), 89 (24), 73 (100), 59 (19), 45 (13) and 29 (1) (Found: C, 55.6 ; H, 9.5 . C₁₄H₂₈O₃Si₂ requires C, 56.0 ; H, 9.4%).

3-Ethylidene-5-trimethylsilylhex-5-en-2-one 14. Using the same procedure as above with acetaldehyde gave diene **14** (63%) after purification; ν_{max} (film)/cm⁻¹ 3040 , 2960 , 1670 , 1640 , 1440 , 1250 and 860 ; δ_H (400 MHz) 0.12 (9 H, s, SiMe₃), 1.78 (3 H, d, J 7.2 , CH₃), 2.29 (3 H, s, OCH₃), 3.09 (2 H, s, $-CH_2-$), 5.21 – 5.25 (2 H, dd, J 1.96 and 1.92 , CH₂=) and 6.92 (1 H, q, J 6.8 , CH); δ_c (400 MHz) -1.23 (SiMe₃), 15.57 (CH₃), 26.25 (CH₃CO), 30.49 (CH₂), 122.92 (CH₂=), 140.50 (CH=), 149.17 (=CSi) and 199.55 (CO); δ_{si} (400 MHz) -2.86 ; m/z 196 (1%), 181 (15), 149

(24), 73 (100), 57 (15), 43 (19), 29 (4) (Found: C, 67.2 ; H, 10.2 . C₁₁H₂₀O₃Si requires C, 67.3 ; H, 10.3%).

Dimethyl 5,7-bis(trimethylsilyl)octa-2,7-diene-3,5-dicarboxylate 16

To a cold solution of (1-lithiovinyl)trimethylsilane in THF, generated from (1-bromovinyl)trimethylsilane (3.04 g) as described previously, was added methyl 2-trimethylsilylacrylate (0.017 mol) at -100 °C. The mixture was stirred at this temperature for a further 30 min, after which an excess of acetaldehyde was added dropwise and the mixture stirred for 17 h at room temperature. Hydrolytic work-up, extraction with ether and purification gave the diene **16** (65%); ν_{max} (film)/cm⁻¹ 2940 , 1720 , 1430 , 1250 , 1200 and 840 ; δ_H (400 MHz) 0.07 (9 H, s, SiMe₃), 0.08 (9 H, s, SiMe₃), 1.86 (3 H, d, J 7.3 , CH₃), 2.29 – 2.92 (4 H, m, CH₂CCH₂), 3.58 (3 H, s, OCH₃), 3.69 (3 H, s, OCH₃), 5.33 – 5.38 (2 H, dd, J 1.48 and 1.96 , CH₂=) and 6.04 (1 H, q, J 7.2); δ_c (400 MHz) -1.01 (SiMe₃), 0.88 (SiMe₃), 16.40 (CH₂), 35.74 (OCH₃), 35.85 (OCH₃), 51.54 (CH₂), 51.71 (CH₂), 123.96 (CH₂=C), 131.99 (C=CHCH₃), 139.99 (CSi), 148.84 (C), 169.52 (C) and 177.26 (CO); δ_{si} (400 MHz) -2.88 and 12.34 ; m/z 355 (M - CH₃, 0.7%), 323 (1), 271 (2), 257 (5), 197 (2), 183 (9), 167 (15), 153 (10), 147 (10), 117 (10), 105 (9), 89 (28), 73 (100), 59 (14) and 45 (10) (Found: C, 58.4 ; H, 9.4 . C₁₈H₃₄O₄Si₂ requires C, 58.3 ; H, 9.4%).

Dimethyl 1,3,5-tris(trimethylsilyl)hex-5-ene-1,3-dicarboxylate 17

To a cold solution of (1-lithiovinyl)trimethylsilane, generated from (1-bromovinyl)trimethylsilane (3.04 g, 0.017 mol) as described above, was added dropwise methyl 2-trimethylsilylacrylate (0.017 mol) in a little dry THF. The mixture was stirred for a further 30 min at -100 °C after which it was allowed to warm up to room temperature and worked up as before. Purification on silica using hexane-ether as eluent gave diester **17** (65%); ν_{max} (film)/cm⁻¹ 3040 , 2906 , 1720 , 1608 , 1430 , 1250 , 1200 and 840 ; δ_H (400 MHz) 0.13 (9 H, s, SiMe₃), 0.16 (9 H, s, SiMe₃), 0.17 (9 H, s, SiMe₃), 2.11 – 2.77 (5 H, m, CH₂CCH₂CH), 3.65 (3 H, s, OCH₃), 3.69 (3 H, s, OCH₃) and 5.52 – 5.42 (2 H, m, CH₂=); δ_c (400 MHz) -2.07 , -1.78 , -1.03 (3 × SiMe₃), 29.93 (CH₂), 36.04 (CHSi), 51.40 (OCH₃), 51.54 (OCH₃), 124.68 (CH₂=), 148.6 (=CSi), 176 (CO) and 177 (CO); m/z 416 (0.3%), 401 (1), 343 (0.6), 218 (39), 203 (11), 183 (12), 167 (19), 147 (13), 109 (15), 89 (25), 73 (100), 59 (17), 45 (22) (Found: C, 54.8 ; H, 9.7 . C₁₉H₄₀O₄Si₃ requires C, 54.8 ; H, 9.7%).

References

- 1 E. Cölkün, *Silicon in Organic Chemistry*, Butterworths, London, 1981.
- 2 A. R. Bassindale, A. G. Brook, P. F. Jones and J. A. G. Stewart, *J. Organomet. Chem.*, 1978, **152**, C 25–28.
- 3 A. R. Bassindale, P. G. Taylor and Y. Xu, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1061.
- 4 A. G. Brook and J. M. Duff, *Can. J. Chem.*, 1973, **51**, 2024.
- 5 G. Stork and B. Ganem, *J. Am. Chem. Soc.*, 1973, **95**, 6152.
- 6 A. Ottolenghi, M. Fridkin and A. Zilkha, *Can. J. Chem.*, 1963, **41**, 2977.
- 7 E. I. Negishi, *Organometallics in Organic Synthesis*, Wiley, New York, 1980, vol. 1.
- 8 D. Caine, in *Carbon-Carbon Bond Formation*, ed. R. L. Augustine, Marcel Dekker, New York, 1979, vol. 1.
- 9 J. Skarzewski, *Tetrahedron*, 1989, **45**, 4593.
- 10 I. I. Lapkin, F. G. Saitkulova and V. V. Fotin, *Otkrytiya, Izobret., Prom. Obratzys, Tovarnye Znaki*, 1980, 105.
- 11 G. R. Newkome and G. R. Baker, *Org. Prep. Proced. Int.*, 1986, **18**, 117.
- 12 J. Tanaka, H. Kobayashi, S. Kanemasa and O. Tsuge, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1993.
- 13 J. Tanaka, S. Kanemasa, Y. Ninomiya and O. Tsuge, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 466.
- 14 J. Tanaka, S. Kanemasa, Y. Ninomiya and O. Tsuge, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 476.

- 15 T. Kumamoto, S. Aoki, M. Nakajima and K. Koga, *Tetrahedron: Asymmetry*, 1994, **5**, 1431.
- 16 O. Tsuge, S. Kanemasa and Y. Ninomiya, *Chem. Lett.*, 1984, 1193.
- 17 J. Tanaka, S. Kanemasa, H. Kobayashi and O. Tsuge, *Chem. Lett.*, 1989, 1453.
- 18 P. J. Garratt and A. Tsotinis, *Tetrahedron Lett.*, 1986, **27**, 2761.

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