

ACYLATION OF 1,3-BIS(TRIMETHYLSILYL)-PROPENE AND 1,8-BIS(TRIMETHYLSILYL)-1,7-OCTADIENE.

OBTENTION OF (\pm)-1-ALKYL-2,5-DIVINYLCYCLOPENTANOLS.

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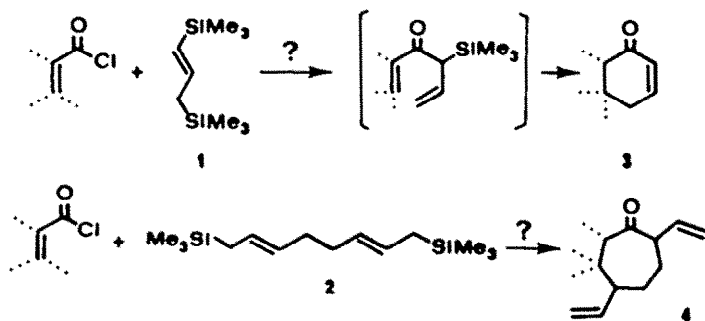
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Summary: The addition of α,β -ethylenic acyl chlorides to 1,3-bis(trimethylsilyl)-propene **1** leads to propenyl-alkenyl-ketones **7**, while addition of acyl chlorides with 1,8-bis(trimethylsilyl)-1,7-octadiene **2** gives 1-alkyl-2,5-divinylcyclopentanol **10** and 1-acyl-2-trimethylsilylmethyl-3-vinylcyclopentane **12** and **13**.

Acylation of olefins is a well-known reaction in the preparation of α,β -enones. However, the scope of this reaction is generally limited by the presence of numerous by-products (β -halo-ketones, β,γ -enones or β -acyloxyketones).¹ Mechanistic studies mainly concern the use of anhydrides and zinc chloride. They emphasize a carbonium ion intermediate² although a concerted "ene" process has also been proposed.³ The accepted mechanism for the addition of acyl chlorides supposes an acyl cation addition giving a β -acyl-carbocation, which either adds a chloride ion or loses a proton.^{4,5,6}

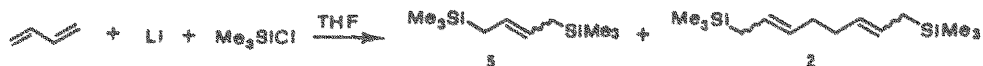
The introduction of a trimethylsilyl group directly on the olefin gives rise to a cleaner reaction, producing α,β -enones,^{7,8} and the Calas-Dunogues' report on the reaction of allylsilanes, which exclusively give β,γ -enones resulting from allylic transposition, proved to be an important advance in silicon chemistry.^{9,10}

The possibility of a cyclization by condensation of α,β -ethylenic acyl chlorides with either 1,3-bis(trimethylsilyl)propene¹¹ **1** or 1,8-bis(trimethylsilyl)-1,7-octadiene **2** in the presence of a Lewis acid, came to our attention. In this way, the intermediate α,β -enones could lead to cyclohexenones **3** or cycloheptanones **4** by intramolecular Sakurai additions.^{12,13}

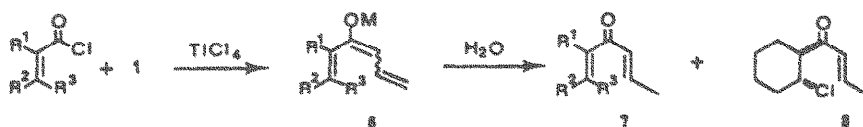


The disilane **2** has been prepared before as a by-product (0.06 %) by reductive dimerisation of 1,3-butadiene using lithium (sand) and chlorotrimethylsilane.¹⁴ We have observed that if the condensation is carried out with pieces of lithium in place of the sand, the yield of **2** increases to 60-65 %. Electron transfer to butadiene produces the butadiene radical-anion;

this dimerizes to give the dimer dianion,¹⁵ which is trapped by chlorotrimethylsilane. The use of lithium with a large surface prevents dimerization by a second electron transfer giving the butadiene dianion precursor of 5. This very cheap synthesis represents an alternative to the previous method¹⁶ although 2 is a mixture of E,E, Z,Z and Z,E isomers.



Condensation of ethylenic acyl chlorides with disilylpropene 1 in the presence of TiCl_4 gives only the divinylketones 7 (or chloro-enones 8). These ketones must be formed during work up, since, in the reaction conditions, the divinylketones 7 themselves are cyclized to cyclopentenones (for example, 7c undergoes a Nazarov cyclization^{17,18}). Plausible intermediates are the titanium or silyl dienolate 6.

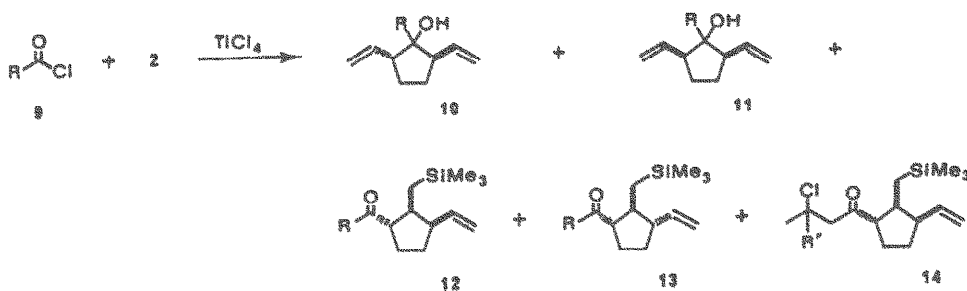


a ; $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{CH}_3$; 7a¹⁹ : 65 % yield.

b ; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{CH}_3$; 7b¹⁷ : 65 % yield.

c ; $\text{R}^1-\text{R}^2 = -(\text{CH}_2)_4-$, $\text{R}^3 = \text{H}$; 7c¹⁷ : 45 % yield; 8¹⁷ : 45 % yield.

Acylation of disilyloctadiene 2 leads only to cyclopentyl derivatives 10-13, even when the α , β -ethylenic acyl chlorides 9g, 9h and 9i are used. In the case of the divinylcyclopentanols, only one isomer, 10, is obtained (with a trans relation between the vinyl groups (as noted from the ¹³C NMR data). Although the 1-acyl-2-trimethylsilyl methyl-3-vinylcyclopentanes have three chiral centres, the major product obtained was 12, with only a small amount of isomer tentatively assigned as 13. The stereochemistry ascribed to 12b or 13b is supported by the use of the shift reagent $\text{Pr}(\text{fod})_3$ in the ¹³C NMR spectrum.²⁰



a ; $\text{R} = \text{CH}_3$; 10a : 53.3 % ; 12a : 31.8 % ; 13a : 5.2 %.

b ; $\text{R} = \text{iso-C}_3\text{H}_7$; 10b : 33.6 % ; 12b : 38.5 % ; 13b : 8 %.

c ; $\text{R} = \text{n-C}_5\text{H}_{11}$; 10c : 50 % ; 12c : 27.5 % ; 13c : 2.5 %.

d ; $\text{R} = \text{n-C}_{11}\text{H}_{23}$; 10d : 55 % ; 12d : 20.5 % ; 13d : 4.5 %.

e ; $\text{R} = \text{C}_6\text{H}_5-\text{CH}_2$; 10e : 51 % ; 12e : 34 % ; 13e : 6 %.

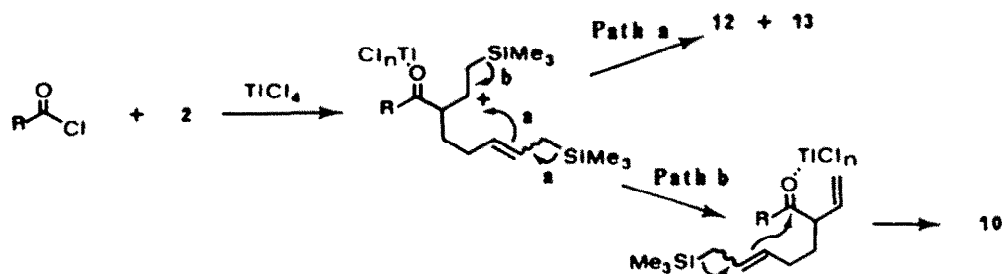
f ; $\text{R} = \text{C}_6\text{H}_5$; 11f : 15.3 % ; 12f : 52.3 % ; 13f : 22.4 %.

g ; $\text{R} = \text{CH}_3-\text{CH}=\text{CH}-$; 12g : 40 % ; 13g : 10 % ; 14 ($\text{R}' = \text{H}$) : 39 %.

h ; $\text{R} = (\text{CH}_3)_2\text{C}=\text{CH}-$; 14 ($\text{R}' = \text{CH}_3$) : 69 %.

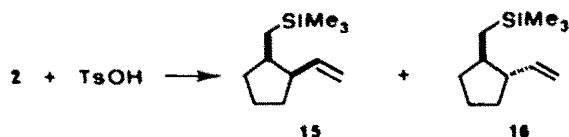
i ; $\text{R} = \text{C}_6\text{H}_5-\text{CH}=\text{CH}-$; 12i : 81 % ; 13i : 9 %.

The pathways by which these products are formed is illustrated in outline in Scheme 1.

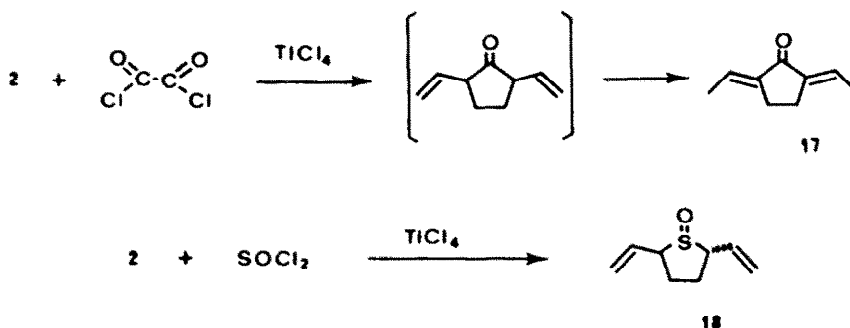


Scheme 1

The protolysis of disilyloctadiene 2 also involves a cyclisation, but, the reaction is less stereoselective (95 % yield; 15 : 65 %, 16 : 35 %, stereochemistry tentative).²¹



In contrast to the reactivity of the monoacyl chlorides 9, the condensation of oxalyl chloride or thionyl chloride with 2 leads to a single product, either 17 (yield : 75 %) or 18 (yield : 55 %), respectively. Although the 2,5-divinyltetrahydrothiophene-1-oxides have three chiral centres, only the trans isomer 18 is obtained.²²



Conclusion.

This study establishes a straightforward two-step synthesis of (\pm)-1-alkyl-2,5-divinylcyclopentanols from butadiene and acyl chlorides, and offers a new strategy for the preparation of cyclopentanoids.

The unexpected results concerning the unformed ketones 3 and 4 may provoke new studies aimed at a better understanding of the factors involved in the acylation reaction of alkenes.

EXPERIMENTAL

General Methods. ^1H NMR spectra were determined with a Varian EM 360 (60 MHz) or a Varian XL 200 (200 MHz) spectrometers. ^{13}C spectra of CDCl_3 solutions were recorded on a Varian XL 200 (50,309 MHz) with Me_4Si as the internal standard. The multiplicities were determined by the J-modulated spin echo techniques. Mass spectra were obtained on a Varian MAT 311 spectrometer.

1,3-Bis(trimethylsilyl)propene 1.¹¹ To a soln of allyltrimethylsilane (24.8 g, 0.2 mol) in 160 mL HMPA and powder magnesium (14.4 g, 0.6 at. gr.) at 90 °C was added TiCl_4 (0.6 mL) and chlorotrimethylsilane (130 g, 1.2 mol). The mixture was stirred for 30 hr and then cooled and poured into ice water. The organic phase was separated and washed with water (4 times) and brine, dried on MgSO_4 , filtered and distilled to yield 94 g (51 %) of 1 (b.p. 82 °C/20 torr) with spectral characteristics identical to those previously reported.

1,7-Bis(trimethylsilyl)octa-2,6-diene 2. 1,3-Butadiene (40.5 g, 0.75 mole) was added during 4 h to pieces (Ca , 10x10x1.5 mm) of lithium or lithium in wire (diameter 3 mm)(3.5 g, 0.5 at-gr) and trimethylchlorosilane (59 g, 0.5 mol) in 125 ml of THF with stirring at 0 °C. After stirring 10 h at 0°C and 18 h at r. t., the suspension is filtered with glass wool for removed lithium, and hydrolysed. After usual work-up, the diene 2 was isolated by distillation (bp 90-105 °C (1 mmHg)). Yield : 39 g (62 %).

General procedure for acylation. Titanium tetrachloride (2.3 mL, 20 mmol) and anhydrous CH_2Cl_2 (30 mL) were cooled to -90 °C and acyl chloride (20 mmol) in anhydrous CH_2Cl_2 (10 mL) was added. Then allylsilane 1 (4.10 g, 22 mmol) or 2 (5.60 g, 22 mmol) in anhydrous CH_2Cl_2 was slowly added. The solution was allowed to stir at -90 °C for 2 hr and at -70 °C for 2h. The reaction mixture was then poured into ice water, the aqueous phase was separated and extracted with CH_2Cl_2 and finally the combined organic layers were washed with water and brine, dried over MgSO_4 , filtered and concentrated to afford a yellow oil. Column chromatography (or flash chromatography) on silica gel (elution with pentane- Et_2O) furnished products.

Condensation of 1 with crotonyl chloride. 2,5-Heptadien-4-one (7a). The reaction of 1 and crotonyl chloride (2.09 g, 20 mmol) gave 7a. ^{19}F NMR (CCl_4) δ 6.55 (2, q, $J = 16.0$ Hz, $d_{\perp} = 6.0$ Hz), 6.10 (2, d, $J = 16.0$ Hz), 1.79 (6, d, $J = 6.0$ Hz); IR (neat) 1620 cm^{-1} .

Condensation of 1 with seneciroyl chloride. 2-Methyl-2,5-heptadien-4-one (7b). The reaction of 1 and seneciroyl chloride (2.37 g, 20 mmol) gave 7b. ^1H NMR (CCl_4) δ 6.7 (1, d, $J = 15.8$ Hz, q, $J = 6.8$ Hz), 5.93 (1, d, $J = 15.8$ Hz), 6.1 (1, s (br)), 2.13 (3, s (br)), 1.50 (3, s (br)), 1.87 (3, d, $J = 6.8$ Hz); ^{13}C NMR δ 190.40 (s), 155.39 (s), 141.63 (d), 133.60 (d), 122.86 (d), 27.78 (q), 20.89 (q), 18.20 (q); IR (neat) 1620, 1240, 970, 865 cm^{-1} .

Condensation of 1 with 1-cyclohexenylcarbonyl chloride. Obtention of 7c and 8. The reaction of 1 and 1-cyclohexenylcarbonyl chloride (2.88 g, 20 mmol) gave a mixture of 7c (45 % yield) and 8 (45 % yield).¹⁷ 7c : ^1H NMR (CDCl_3) δ 6.80 (1, d, $J = 15.0$ Hz, q, $J = 5.8$ Hz), 6.74 (1, m), 6.54 (1, d, $J = 15.0$ Hz), 1.90 (3, d, $J = 5.8$ Hz), 2.20 (4, m), 1.64 (4, m); ^{13}C NMR δ 191.44 (s), 142.12 (d), 139.99 (d), 139.79 (s), 26.48 (d), 26.17 (t), 23.44 (t), 22.02 (t), 21.65 (t), 18.37 (q); IR (neat) 1705, 1635, 1210, 990 cm^{-1} ; UV (methanol) $\lambda_{\text{max}} = 245$ nm, ($\epsilon = 9000$). 8 : ^1H NMR (CDCl_3) δ 6.94 (1, d, $J = 15.8$ Hz, q, $J = 6.8$ Hz), 6.19 (1, d, $J = 15.8$ Hz), 4.16 (1, t, $J = 10.8$ Hz, $d_{\perp} = 4.5$ Hz), 2.96 (1, t, $J = 10.8$ Hz, $d_{\perp} = 4.0$ Hz), 1.94 (3, d, $J = 6.8$ Hz); ^{13}C NMR δ 200.15 (s), 143.73 (d), 131.35 (d), 59.22 (d), 55.89 (d), 36.41 (t), 30.38 (t), 25.85 (t), 24.71 (t), 18.38 (q); IR (neat) 1677, 1640, 1625, 1270, 1180, 965, 730 cm^{-1} .

Condensation of 2 with acetyl chloride (9a). The reaction of 2 and 9a (1.57 g, 20 mmol) gave a mixture of 10a (55 %), 12a (32 %) and tentatively 13a (4 %). **1-Methyl-2,5-divinylcyclopentanol (10a)** : bp 61°C (18 mmHg); ^1H NMR (CDCl_3) δ 5.7 (2, m), 5.03 (4, m), 1.06 (3, s); ^{13}C NMR δ 139.64 (d), 137.55 (d), 116.70 (t), 114.46 (t), 81.54 (s), 54.85 (d), 52.86 (d), 28.02 (t), 27.82 (t), 23.82 (q); IR (neat) 3450, 3080, 1640, 1095, 1000, 915, 865, 840 cm^{-1} ; found : C, 78.88; H, 10.58; $\text{C}_{10}\text{H}_{16}\text{O}$ requires C, 78.95; H, 10.53. 12a : bp 85 °C (7 mmHg); ^1H NMR (CDCl_3) δ 5.6 (1, m), 4.93 (2, m), 2.25 (3, s), 0.56 (2, m), 0.1 (9, s); ^{13}C NMR δ 210.17 (s), 138.83 (d), 114.86 (t), 58.75 (d), 47.62 (d), 41.32 (d), 29.88 (t), 28.92 (q), 26.73 (t), 16.93 (t), -1.10 (q)(3C); IR (neat) 3080, 1710, 1640, 1250, 1160, 915 cm^{-1} ; found : C, 69.65; H, 10.74; $\text{C}_{13}\text{H}_{24}\text{OSi}$ requires C, 69.64; H, 10.72.

Condensation of 2 with isobutyryl chloride (9b). The reaction of 2 and 9b (2.07 g, 20 mmol) gave a mixture of 10b (33.6 %), 12b (38.5 %) and 13b (8 %). **1-Isopropyl-2,5-divinylcyclopentanol (10b).** ^1H NMR (CDCl_3) δ 5.88 (2, m), 4.97 (4, m), 2.53 (1, sept, $J = 7.2$ Hz), 0.88 (6, d, $J = 7.2$ Hz); ^{13}C NMR δ 139.50 (d), 139.24 (d), 115.67 (t), 114.42 (t), 85.82 (s), 55.34 (d), 49.08 (d), 34.63 (d), 29.63 (t), 29.02 (t), 17.75 (q), 17.69 (q); IR (neat) 3500,

3080, 1640, 1000, 915 cm^{-1} ; mass spectrum m/e 180 (0.2), 165 (0.3) (HRMS calcd for $\text{C}_{11}\text{H}_{17}\text{O}$ 165.1279, found 165.1281), 162 (2) (HRMS calcd for $\text{C}_{12}\text{H}_{18}$ 162.1408, found 162.1400), 152 (12), 109 (19), 71 (60), 55 (26), 43 (100). **12b**: ^1H NMR (200 MHz, CDCl_3) δ 5.77 (1, d, $J = 16.78$ Hz, $d \downarrow = 10.7$ Hz, $d \downarrow = 8.1$ Hz), 4.99 (2, m), 2.67 (1, sept, $J = 6.8$ Hz), 1.09 (3, d, $J = 6.8$ Hz), 1.085 (3, d, $J = 6.8$ Hz), 0.62 (1, $\frac{1}{2}$ AB, $J = 14.6$ Hz, $d \downarrow = 9.2$ Hz), 0.35 (1, $\frac{1}{2}$ AB, $J = 14.6$ Hz, $d \downarrow = 5.8$ Hz), -0.01 (9, s); ^{13}C NMR δ 217.11 (s), 139.29 (d), 115.00 (t), 56.40 (d), 47.43 (d), 42.07 (d), 40.52 (d), 30.32 (t), 27.44 (t), 18.31 (q), 18.27 (q), 16.95 (t), -0.81 (q) (3C); IR (neat) 3080, 1710, 1640, 1250, 910 cm^{-1} ; mass spectrum m/e 252 (2) (HRMS calcd for $\text{C}_{15}\text{H}_{28}\text{OSi}$ 252.1909, found 252.1913), 237 (9), 209 (12), 196 (4), 171 (18), 165 (10), 155 (5), 137 (6), 119 (7), 107 (6), 75 (18), 73 (100), 59 (10), 43 (41). **13b**: ^1H NMR (200 MHz, CDCl_3) δ 5.70 (1, d, $J = 16.8$ Hz, $d \downarrow = 10.2$ Hz, $d \downarrow = 8.1$ Hz), 5.02 (2, m), 2.67 (1, sept, $J = 6.8$ Hz), 1.09 (3, d, $J = 6.8$ Hz), 1.08 (3, d, $J = 6.8$ Hz), 0.92 (2, t, $J = 7.2$ Hz), -0.04 (9, s); ^{13}C NMR δ 217.11 (s), 142.77 (d), 113.62 (t), 53.44 (d), 50.43 (d), 44.87 (d), 41.03 (d), 16.66 (t), -0.54 (q) (3C); IR (CCl_4) 3080, 1710, 1640, 1250, 910 cm^{-1} ; mass spectrum was similar to that for **12b**.

Condensation of 2 with hexanoyl chloride (9c). The reaction of 2 and 9c (2.7 g, 20 mmol) gave a mixture of **10c** (50 %), **12c** (27.5 %), **13c** (2.5 %). **1-Pentyl-2,5-divinylcyclopentanol (10c)**: ^1H NMR (CDCl_3 , 200 MHz) δ 5.82 (2, m), 5.08 (4, m), 2.6 (1, t, $J = 8.0$ Hz, $d \downarrow = 3.5$ Hz), 2.41 (1, q, $J = 8.5$ Hz), 2.11 (1, m), 1.81 (2, m), 1.42 (5, s (br)), 1.28 (5, s (br)), 0.88 (3, t, $J = 6.7$ Hz); ^{13}C NMR δ 139.64 (d), 137.96 (d), 117.07 (t), 114.61 (t), 84.07 (s), 53.67 (d), 51.39 (d), 36.32 (t), 32.52 (t), 28.19 (t), 27.82 (t), 22.68 (t) (2C), 14.07 (q); mass spectrum m/e 208 (0.8) (HRMS calcd for $\text{C}_{14}\text{H}_{24}\text{O}$ 208.1827, found 208.1830), 180 (39), 153 (8.5), 140 (9), 137 (13), 124 (12), 109 (19), 99 (100), 83 (24), 79 (14), 71 (78), 55 (33), 43 (89); IR (CCl_4) 3480, 1640, 1120, 1000, 915 cm^{-1} . **12c**: ^1H NMR (200 MHz, CDCl_3) δ 5.72 (1, m), 5.00 (2, m), 2.40 (1, m), 2.28 (1, t, $J = 6.0$ Hz), 1.30 (5, m), 0.88 (3, t, $J = 6.5$ Hz), 0.40 (2, m), -0.07 (9, s); ^{13}C NMR δ 213.21 (s), 139.20 (d), 114.97 (t), 58.16 (d), 47.74 (d), 42.36 (t), 41.69 (d), 31.46 (t), 30.14 (t), 27.09 (t), 23.34 (t), 22.46 (t), 17.10 (t), 13.88 (q), -0.89 (q) (3C); IR (neat) 3080, 1710, 1640, 1250, 910 cm^{-1} ; mass spectrum m/e 280 (0.8) (HRMS calcd for $\text{C}_{17}\text{H}_{32}\text{OSi}$ 280.2222, found 280.2230), 265 (8), 199 (13), 99 (10), 73 (100), 43 (25). **13c**: ^1H (200 MHz, CDCl_3) δ 5.60 (1, m), 5.00 (2, m), 2.25 (2, t, $J = 6.0$ Hz), 1.30 (5, m), 0.83 (3, t, $J = 6.5$ Hz), 0.01 (9, s); IR (neat) 3080, 1710, 1640, 1250, 910 cm^{-1} ; ^{13}C NMR δ 213.05 (s), 142.68 (d), 113.62 (t), 63.38 (d), 54.95 (d), 50.45 (d), 39.10 (t), 36.63 (t), 32.40 (t), 31.33 (t), 26.92 (t), 16.11 (t), 14.03 (q), -0.08 (q) (3C); mass spectrum was similar to that for **12c**.

Condensation of 2 with dodecanoyl chloride (9d). The reaction of 2 and 9d (4.37 g, 20 mmol) gave a mixture of **10d** (55 %), **12d** (20.5 %) and tentatively **13d** (4.5 %). **1-Undecanyl-2,5-divinylcyclopentanol (10d)**: ^1H NMR (CDCl_3) δ 5.77 (2, m), 4.98 (4, m), 1.27 (16, s (br)), 0.87 (3, t, $J = 7.0$ Hz); ^{13}C NMR δ 139.62 (d), 137.95 (d), 117.06 (t), 114.59 (t), 84.06 (s), 53.62 (d), 51.37 (d), 36.35 (t), 31.96 (t), 30.29 (t), 29.68 (t) (2C), 29.65 (t) (2C), 29.40 (t), 28.15 (t), 27.80 (t), 23.00 (t), 22.72 (t), 14.14 (q); mass spectrum m/e 292 (3) (HRMS calcd for $\text{C}_{20}\text{H}_{36}\text{O}$ 292.2766, found 292.2779), 277 (2), 274 (0.3) (HRMS calcd for $\text{C}_{20}\text{H}_{34}$ 274.2660, found 274.2657), 264 (100), 237 (8), 224 (5), 183 (41), 152 (9), 137 (26), 124 (24), 119 (12), 109 (58), 95 (50), 85 (44), 83 (38), 81 (32), 71 (46), 67 (41), 57 (94), 55 (55), 43 (80); IR (neat) 3500, 3080, 1640, 1000, 915 cm^{-1} . **12d**: ^1H NMR (CCl_4) δ 5.93 (1, m), 4.89 (2, m), 1.35 (5, m), 1.25 (18, s (br)), 0.83 (3, t, $J = 5.5$ Hz), 0.38 (2, m), -0.05 (9, s); ^{13}C NMR δ 213.10 (s), 139.28 (d), 115.01 (t), 58.24 (d), 47.76 (d), 42.46 (t), 41.77 (d), 31.90 (t), 29.60 (t) (3C), 29.46 (t) (2C), 29.33 (t) (2C), 29.26 (t), 22.67 (t), 17.13 (t), 14.09 (q); mass spectrum m/e 364 (0.1), 349 (1.3) (HRMS calcd for $\text{C}_{22}\text{H}_{41}\text{OSi}$ 349.2926, found 349.2923), 336 (1.2), 283 (1.4), 228 (5.3), 185 (6.4), 183 (13), 157 (10), 143 (5), 115 (4), 101 (42), 88 (100), 73 (28), 70 (16), 57 (13), 55 (13), 43 (21); IR (neat) 3080, 1710, 1250, 910 cm^{-1} .

Condensation of 2 with phenylacetyl chloride (9e). The reaction of 2 and 9e (3.1 g, 20 mmol) gave a mixture of **10e** (51 %), **12e** (34 %) and tentatively **13e** (6 %). **1-Benzyl-2,5-divinylcyclopentanol (10e)**: ^1H NMR (CDCl_3) δ 7.22 (5, s (br)), 5.77 (2, m), 4.97 (4, m), 2.72 (2, AB, $J = 15$ Hz), 2.05 (2, m), 1.55 (4, m); ^{13}C NMR δ 139.27 (d), 138.22 (d), 137.60 (s), 130.63 (d) (2C), 128.14 (d) (2C), 126.40 (d), 116.87 (t), 115.72 (t), 83.13 (s), 54.44 (d), 50.44 (d), 41.81 (t), 28.12 (t), 28.00 (t); mass spectrum m/e 228 (0.5) (HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}$ 228.1514, found 228.1520), 200 (4), 164 (3), 160 (4), 136 (8), 118 (10), 109 (15), 91 (100), 67 (16), 55 (12), 43 (8); IR (neat) 3580, 1640, 1120, 920 cm^{-1} . **12e**: ^1H NMR (CCl_4) δ 7.29 (5 s (br)), 5.75 (1, m), 4.99 (2, m), 3.72 (2, s (br)), 2.68 (2, m), 1.70 (5, m), 0.44 (2, m), 0.00 (9, s); ^{13}C NMR δ 211.46 (s), 141.74 (d), 134.11 (s), 129.61 (d), 129.56 (d), 128.61 (d), 126.89 (d), 115.12 (t), 57.64 (d), 49.73 (t), 47.72 (d), 41.80 (d), 30.22 (t), 27.55 (t), 16.99 (t), -0.82 (q) (3C); mass spectrum m/e 300 (7) (HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{OSi}$ 300.1909, found 300.1914), 285 (5), 210 (4), 209 (17), 181 (3), 165 (4), 155 (4), 137 (3), 129 (8), 119 (7), 91 (16), 73 (100), 59 (5), 45 (5); IR (neat) 1710, 1250, 910, 860 cm^{-1} .

Condensation of 2 with benzoyl chloride (9f). The reaction of 2 and 9f (2.85 g, 20 mmol) gave 11f (15.3 %), 12f (52.3 %) and 13f (22.4 %). **1-Phenyl-2,5-divinylcyclopentanol (11f):** $^1\text{H NMR}$ (CDCl_3) δ 7.22 (s, br), 5.85 (2, m), 4.83 (4, m), 1.85 (2, m), 1.48 (4, m); $^{13}\text{C NMR}$ δ 143.93 (s), 136.12 (d)(2C), 128.08 (d)(2C), 126.63 (d), 125.40 (d)(2C), 117.11 (t)(2C), 84.10 (s), 55.15 (d)(2C), 26.47 (t)(2C); mass spectrum m/e 214 (4)(HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}$ 214.1357, found 214.1355), 199 (1), 186 (8), 159 (8), 146 (26), 133 (5), 131 (7), 105 (100), 77 (26), 73 (4), 67 (5), 58 (20), 43 (50); IR (neat) 3500, 3070, 1640, 1115, 915 cm^{-1} . **12f:** $^1\text{H NMR}$ (CCl_4) δ 7.83 (2, m), 7.37 (3, m), 5.80 (1, m), 4.97 (2, m), 2.71 (1, m), 1.62 (6, m), 0.67 (2, m), 0.00 (9, s); $^{13}\text{C NMR}$ δ 202.82 (s), 139.39 (d), 137.38 (s), 132.75 (d), 128.52 (d)(2C), 128.40 (d)(2C), 115.05 (t), 53.21 (d), 47.98 (d), 41.62 (d), 30.64 (t), 29.36 (t), 17.55 (t), -0.80 (q)(3C); mass spectrum m/e 286 (10)(HRMS calcd for $\text{C}_{18}\text{H}_{26}\text{OSi}$ 286.1753, found 286.1757), 285 (12), 271 (20), 258 (21), 244 (4), 231 (17), 229 (6), 217 (14), 205 (25), 179 (7), 167 (6), 165 (15), 155 (4), 141 (6), 137 (9), 128 (4), 115 (4), 105 (44), 91 (5), 77 (17), 73 (100), 58 (11), 45 (12), 43 (33); IR (CCl_4) 3075, 1680, 1640, 1600, 1585, 1250, 1220, 1000, 915 cm^{-1} . **13f:** $^1\text{H NMR}$ (CCl_4) 7.85 (2, m), 7.40 (3, m), 5.92 (1, m), 4.98 (2, m), 2.71 (1, m), 1.62 (6, m), 0.92 (2, m), 0.02 (9, s); $^{13}\text{C NMR}$ δ 201.96 (s), 141.72 (d), 136.97 (s), 132.75 (d), 128.52 (d)(2C), 128.40 (d)(2C), 114.54 (t), 55.50 (d), 54.19 (d), 42.05 (d), 32.33 (t), 30.98 (t), 21.91 (t), -0.80 (q)(3C); IR (neat) 3090, 1680, 1600, 1590, 1250, 915 cm^{-1} ; mass spectrum was similar to that for 12f.

Condensation of 2 with crotonyl chloride (9g). The reaction of 2 and 9g (2.09 g, 20 mmol) gave a mixture of 12g (40 %), 13g (10 %) and the chloro-ketone 14 ($\text{R}' = \text{H}$) (39 %). **12g:** $^1\text{H NMR}$ (CCl_4) δ 6.71 (1, d, $J = 15.2$ Hz, $q \perp = 6.4$ Hz), 6.01 (1, d, $J = 15.2$ Hz), 5.74 (1, m), 4.94 (2, m), 1.99 (3, d, $J = 6.4$ Hz), 0.64 (2, m), 0.11 (9, s); $^{13}\text{C NMR}$ δ 202.69 (s), 142.53 (d), 139.39 (d), 131.57 (d), 115.00 (t), 55.75 (d), 47.96 (d), 41.96 (d), 30.42 (t), 27.84 (t), 18.30 (q), 17.24 (t), -0.81 (q)(3C); mass spectrum m/e 250 (0.5)(HRMS calcd for $\text{C}_{15}\text{H}_{26}\text{OSi}$ 250.1752, found 250.1748), 235 (11), 225 (4), 209 (6), 199 (9), 165 (12), 137 (8), 91 (6), 75 (17), 73 (100), 69 (15), 43 (15); IR (neat) 3080, 1710, 1640, 1250, 915 cm^{-1} . **13g:** $^1\text{H NMR}$ (CCl_4) δ 6.71 (1, d, $J = 15.2$ Hz, $q \perp = 6.4$ Hz), 6.02 (1, d, $J = 15.2$ Hz), 5.75 (1, m), 4.94 (2, m), 1.99 (3, d, $J = 6.4$ Hz), 0.98 (2, m), 0.09 (9, s); $^{13}\text{C NMR}$ δ 202.01 (s), 142.40 (d), 141.80 (d), 131.71 (d), 114.42 (t), 56.79 (d), 55.39 (d), 42.15 (d), 32.21 (t), 29.92 (t), 21.75 (t), 15.28 (q), -0.70 (q)(3C); IR (neat) 3080, 1710, 1640, 1250, 915 cm^{-1} ; mass spectrum was similar to that for 12g. **Chloro-ketone 14 ($\text{R}' = \text{H}$):** $^1\text{H NMR}$ (CCl_4) δ 5.65 (1, m), 4.89 (2, m), 3.99 (1, m), 2.90 (2, s), 1.68 (3, d, $J = 10.5$ Hz), 0.6 (2, m), 0.00 (9, s); $^{13}\text{C NMR}$ δ 211.68 (s), 139.22 (d), 115.07 (t), 71.33 (d), 64.01 (t), 59.17 (d), 47.64 (d), 41.36 (d), 30.09 (t), 26.51 (t), 16.99 (t), 15.53 (q), -0.70 (q)(3C); IR (neat) 3090, 1720, 1640, 1250, 910 cm^{-1} ; mass spectrum m/e 271 (3)(HRMS calcd for $\text{C}_{14}\text{H}_{24}\text{OSi}^{35}\text{Cl}$ 271.1285, found 271.1296), 247 (5), 245 (10), 199 (6), 163 (4), 150 (13), 137 (15), 123 (15), 119 (15), 109 (67), 95 (43), 83 (35), 79 (37), 73 (62), 67 (100), 55 (60).

Condensation of 2 with saneciroyl chloride (9h). The reaction of 2 and 9h (2.37 g, 20 mmol) gave the chloroketone 14 ($\text{R}' = \text{CH}_3$) (69 %) and one isomer (15 %). **14 ($\text{R}' = \text{CH}_3$):** $^1\text{H NMR}$ (CCl_4) δ 5.63 (1, m), 4.87 (2, m), 2.90 (2, s), 1.68 (6, s), 0.53 (2, m), 0.00 (9, s); $^{13}\text{C NMR}$ δ 209.55 (s), 139.12 (d), 115.26 (t), 67.51 (s), 59.29 (d), 56.43 (t), 47.75 (d), 41.75 (d), 32.43 (q), 32.34 (q), 30.09 (t), 26.92 (t), 17.16 (t), -0.02 (q)(3C); mass spectrum (GC/MS): 287 (-Me)(2.3), 285 (Me)(7.2), 265 (-Cl)(55), 249 (-HCl, Me)(16), 209 (51), 181 (14), 119 (37), 108 (66), 93 (69), 91 (53), 79 (56), 73 (99), 55 (100); IR (neat) 3085, 1720, 1640, 1250, 920 cm^{-1} .

Condensation of 2 with cinnamoyl chloride (9i). The reaction of 2 and 9i (3.35 g, 20 mmol) gave a mixture of 12i (81 %) and tentatively 13i (9 %). **12i:** $^1\text{H NMR}$ (CCl_4) δ 7.54 (1, d, $J = 16.4$ Hz), 7.39 (s, br), 6.73 (1, d, $J = 16.4$ Hz), 5.91 (1, m), 5.04 (1, m), 0.67 (2, m), 0.11 (9, s); $^{13}\text{C NMR}$ δ 202.27 (s), 142.39 (d), 139.28 (d), 134.69 (s), 130.26 (d), 128.84 (d)(2C), 128.20 (d)(2C), 125.89 (d), 115.04 (t), 56.72 (d), 47.98 (d), 42.13 (d), 30.42 (t), 27.75 (t), 17.32 (t), -0.82 (q)(3C); mass spectrum m/e 312 (1.1)(HRMS calcd for $\text{C}_{20}\text{H}_{28}\text{OSi}$ 312.1909, found 312.1915), 297 (3), 221 (3), 211 (5), 181 (8), 167 (4), 155 (6), 147 (9), 142 (6), 137 (4), 131 (16), 127 (9), 103 (8), 91 (8), 77 (11), 73 (100), 59 (9), 45 (19), 44 (15); IR (neat) 3080, 1710-1605, 1250, 990, 915 cm^{-1} .

Protolysis of 2. Obtention of 1-Trimethylsilylmethyl-2-vinylcyclopentanes 15 and 16. To a stirred suspension of toluenesulfonic acid monohydrate (1.9 g, 10 mmol) in CH_2Cl_2 (25 mL) cooled at -80°C was added 2 (2.54 g, 10 mmol). The suspension was allowed to warm to r.t. in 16 h. The reaction mixture was then poured into ice water, after the usual work-up the isomers were separated by preparative GLC (order of elution on polar phase: 16-15). Overall yield: 95 %. **15 (65 %), 16 (35 %).** **15:** $^1\text{H NMR}$ (CCl_4) δ 5.74 (1, m), 4.94 (2, m), 0.56 (2, m), 0.00 (9, s); $^{13}\text{C NMR}$ δ 140.63 (d), 113.88 (t), 49.31 (d), 39.83 (d), 32.96 (t), 30.68 (t), 23.06 (t), 18.17 (t), -0.79 (q)(3C); IR (neat) 3080, 1640, 910, 790 cm^{-1} ; found: C, 72.58; H, 12.12; $\text{C}_{11}\text{H}_{22}\text{Si}$ requires: C, 72.53; H, 12.05. **16:** $^1\text{H NMR}$ (CCl_4) δ 5.78 (1, m), 5.02 (2, m), 0.95 (2, m), 0.05 (9, s); $^{13}\text{C NMR}$ δ 142.78 (d), 113.77

(t), 55.16 (d), 42.51 (d), 34.22 (t), 32.04 (t), 23.46 (t), 20.99 (t), -0.81 (q)(3C); IR (neat) 3080, 1640, 1250, 910 cm^{-1} .

2,5-Diethylidenecyclopentanone (17). Titanium chloride (7.59 g, 4.39 mL, 40 mmol) and anhydrous CH_2Cl_2 (100 mL) were cooled at -90°C and oxalyl chloride (5.08 g, 40 mmol) in anhydrous CH_2Cl_2 (25 mL) was added. Then **2** (10.16 g, 40 mmol) in anhydrous CH_2Cl_2 (50 mL) was slowly added. The solution was allowed to stir at -90°C for 2 hr and at -60°C during 24 h. After usual work-up, ketone **17** was isolated by chromatography on silica gel (pentane-diethylether 9:1). Yield: 4.08 g (75 %). **17**: m.p. 61°C (pentane); $^1\text{H NMR}$ (CDCl_3) δ 6.63 (2, q \downarrow = 6.8 Hz), 2.58 (4, s (br)), 1.82 (6, d \downarrow = 6.8 Hz); $^{13}\text{C NMR}$ δ 194.03 (s), 140.29 (s), 132.22 (d), 23.10 (t), 15.08 (q); mass spectrum m/e 136 (39)(12 eV; 136 100 %), 135 (8), 121 (10), 117 (3), 107 (5), 93 (24), 91 (14), 73 (21), 28 (100); IR (CDCl_3) 1705, 1640, 1245 cm^{-1} ; UV (ethanol) λ_{max} = 278 nm (ϵ = 14000); found: C, 79.44; H, 8.86; $\text{C}_9\text{H}_{12}\text{O}$, requires: C, 79.41; H, 8.82.

(*)-2,5-Divinylthiolane-1-oxide (18). Titanium chloride (3.8 g, 2.20 mL, 20 mmol) and anhydrous CH_2Cl_2 (60 mL) were cooled at -90°C and **2** (5.08 g, 20 mmol) in anhydrous CH_2Cl_2 (40 mL) was added. Then, thionyl chloride (2.4 g, 20 mmol) in anhydrous CH_2Cl_2 (25 mL) was slowly added. The solution was allowed to stir at -90°C for 5 h and at -60°C during 18 h. After usual work-up, sulfoxide **18** was isolated by distillation. Yield 1.72 g (55 %). **18**: oil, bp 65°C (1 mmHg); $^1\text{H NMR}$ (CCl_4) δ 5.6 (2H, m), 4.97 (4H, m), 3.88 (2H, t \downarrow = 6.5 Hz), 1.93 (4H, m); $^{13}\text{C NMR}$ δ 141.23 (d), 140.35 (d), 115.69 (t), 115.26 (t), 53.71 (d), 53.23 (d), 38.65 (t), 37.40 (t); IR (neat) 3085, 1640, 1250, 990, 915 cm^{-1} ; found: C, 61.57; H, 7.65; S, 20.45; $\text{C}_8\text{H}_{12}\text{OS}$ requires: C, 61.54; H, 7.69; S, 20.51.

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