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Arene-Catalysed Lithiation of 1,4-Dichlorobut-2-enes and 3,4-Dichlorobut-1-ene and Reaction with Electrophiles: A Common Reaction Pathway

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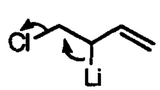
Abstract: The reaction of (*Z*) or (*E*)-1,4-dichlorobut-2-ene (**1**,**2**), or 3,4-dichlorobut-1-ene (**3**) with an excess of lithium powder and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (5 mol %) in the presence of an electrophile [$(CH_2)_4CO$, Bu^tCHO, Me_3SiCl] in THF at 0°C yields, after hydrolysis, the corresponding 1,4- and 1,2-disubstituted compounds (*Z*/*E*)-**4** and **5**, the ratio of them being independent on the starting material. In the case of compounds **4** the Z-diastereomer is largely the major one. When dichlorodiethylsilane was used as electrophile the corresponding substituted silacyclopentene **6** was the only reaction product isolated. A possible mechanism involving dilithiated species is proposed.

INTRODUCTION

Very recently[1] we discovered that the use of an excess of lithium powder and a catalytic amount of an arene is even more reactive as lithiating mixture than the corresponding lithium-arene (stoichiometric ratio) solutions[2]. This methodology has been applied to the preparation of reactive organolithium intermediates[3] such as dilithiated molecules[4] or functionalised organolithium compounds[5] under very mild reaction conditions. Precursors for these processes are not only chlorinated materials[6], but also sulfonates[7a] and sulfates[7b,c], nitriles[8], sulfones[9], carbonyl derivatives[10] and saturated heterocycles such as aziridines[11], azetidines[12], tetrahydrofurans[13] and dioxolanes[14]. In this paper we report the 4,4'-di-*tert*-butylbiphenyl (DTBB)-catalysed lithiation of 1,4-dichlorobut-2-enes (**1**,**2**) and 3,4-dichlorobut-1-ene (**3**)[15] under Barbier-type reaction conditions. By this way it is possible to obtain the expected 1,4- and 1,2-disubstitution products, which are not accessible by conventional tandem lithiation-electrophilic substitution from **1-3** because the first obtained monolithiated intermediates **I** and **II**, respectively, undergo very fast lithium chloride δ- or β-elimination to yield butadiene, even at very low temperatures[16].

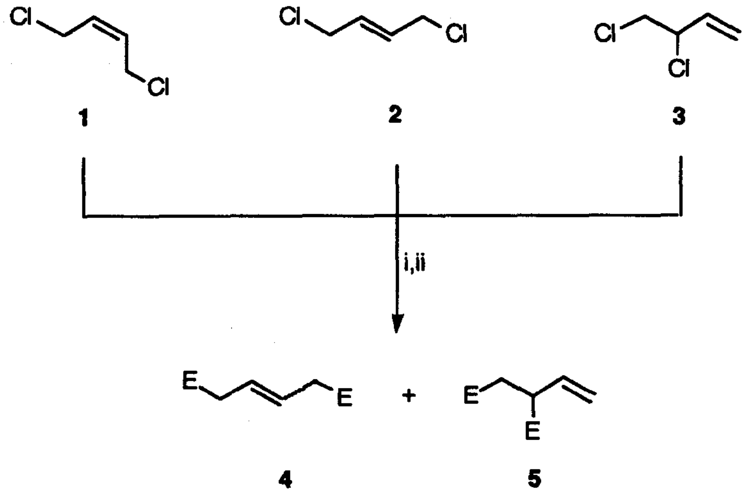
I



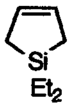
II

RESULTS AND DISCUSSION

The reaction of (*Z*)-1,4-dichlorobutene (**1**) with an excess of lithium powder [1/7 molar ratio (theoretic 1/4 molar ratio)] and a catalytic amount of DTBB (1/0.05 molar ratio; 5 mol %[17]) in the presence of cyclopentanone (1/2 molar ratio) as electrophile in THF at 0°C led, after hydrolysis with water, to a 1.3/1 mixture of the coresponding products **4a** and **5a**, resulting from a 1,4- or a 1,2-disubstitution, respectively. For compounds **4a**, the *Z*-diastereomer was the major one (*Z*/*E* ratio: 8/1) (Scheme 1 and Table 1, entry 1). The reaction has to be carried out under Barbier-type reaction conditions described above in order to avoid undesirable by-processes: the sequential procedure (a) DTBB-catalysed lithiation of compound **1** at -100°C for 1 h (disappearance of the starting material by GLC) and (b) addition of cyclopentanone at -100 to 20°C gave no reaction products of the type **4** or **5**[18]. Curiously, the same products ratio was exactly obtained starting either from (*E*)-1,4-dichlorobut-2-ene (**2**) or 3,4-dichlorobut-1-ene (**3**) under the same reaction conditions (Barbier-type), although the yields are slightly different (Scheme 1 and Table 1, entries 2 and 3).



a : $E=\overline{(CH_2)_4C}OH$
b : $E=Bu^tCHOH$
c : $E=Me_3Si$



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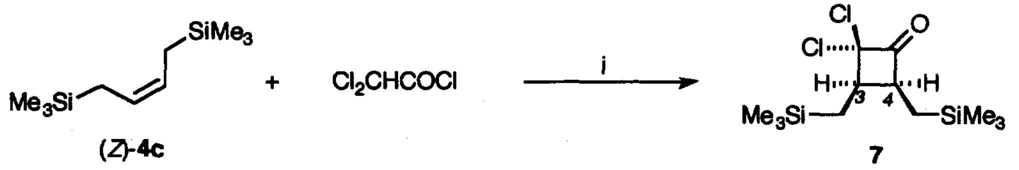
Scheme 1. *Reagents and conditions*: i, Li, DTBB cat. (5 mol %), $E^+=\overline{(CH_2)_4C}O$, Bu^{t}CHO, Me_3SiCl, THF, 0°C; ii, H_2O.

As expected, the same reaction of dichlorinated derivatives **1-3** but with pivalaldehyde as electrophilic reagent gave a complicated mixture of diastereomers; however, interesting features of these processes are (a) the same **4b**/**5b** molar ratio was obtained (*ca.* 1/1.5) in all cases, (b) the Z-diastereomers [(Z)-**4b**] was also the major ones, the *Z/E* ratio being the same in the three cases (11/1), and (c) the same proportion of diastereomers was obtained for (Z)-**4b** (3/2) and **5b** (8/4/4/1), independently on the starting material (Scheme 1 and Table 1, entries 4-6). Finally, we studied the above decribed reaction with chlorotrimethylsilane as electrophile: the same results were also obtained with each dichlorinated precursor **1-3**, the **4c**/**5c** ratio being much higher than in the former cases (*ca.* 40/1) and again diastereomer (Z)-**4c** was the major component in the *Z/E*-mixture (7/1) (Scheme 1 and Table 1, entries 7-9).

In order to take advantage of the tendency of the reaction shown in Scheme 1 to give a Z-stereochemistry for 1,4-adducts we studied the reaction of the three dichlorinated materials with dichlorodiethylsilane: in all cases the expected 1,1-diethylsilacyclopent-3-ene (**6**) was the only reaction product isolated (72, 70 and 83% from starting materials **1**, **2** and **3**, respectively, after distillation) (Scheme 1).

The stereochemistry of compounds **4** was assigned in all cases after isolation of the pure major Z-diastereomers; all isolated products (Z)-**4** did not show any IR absortion at 960-980 cm^{-1}, characteristic of the *E*-configuration and present bands at 665-730 cm^{-1} typical for Z-geometry[19]. The corroboration of this result by NMR presented difficulties due to the high symmetry of the molecules in both Z- and *E*-diastereomers. For this reason we transformed the major diastereoisomer (Z)-**4c** into the cyclobutanone **7** by reaction with *in situ* generated dichloroketene[20] (68% isolated yield; Scheme 2). In this adduct **7** we found a *ca.* 20% n.O.e. between the protons attached to the C_3 and C_4 atoms confirming the proposed *cis*-configuration.



Scheme 2. *Reagents and conditions*: i, NEt_3, hexane, 20°C.

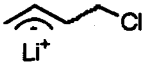
Considering the possible reaction mechanism, it is necessary to explain the obtention of the Z-products **4** as the major components in relation to their *E*-diastereomers. Moreover, since the final reaction products ratio is the same independently of the starting dichlorinated materials, it is obvious that the possible reaction intermediates should be common in the three cases. Thus, once the first lithiation takes place, the short-live intermediates of the type **I** or **II** (see *supra*) equilibrate to the more stable delocalised allylic system **III**; this monoanion has then two possible alternatives (besides the destructive elimination reaction to give 1,3-butadiene; see Introduction): (a) rapid reaction with the electrophile E^+ present in the reaction media to yield, after a new lithiation, the new anion **IV**, which by reaction with another molecule of electrophile would yield the mixture of products **4** and **5**, and (b) rapid lithiation to yield dianions **V** or **VI**[21], which condense successively with two molecules of electrophile to yield the obtained products **4** and **5**. The only way to understand the observed major Z-stereochemistry in products **4** is, in our opinion, to accept that an important part of the reaction goes

Table 1. Preparation of Compounds **4** and **5**

Entry	Starting material	Electrophile E+	Global yield [%][a]	Products[b] no.: **4** [%] (*Z/E*)[c]	no.: **5** [%]	**4/5** ratio
1	**1**	$(CH_2)_4CO$	55	**4a**: 31 (8/1)	**5a**: 24	1.3/1
2	**2**	$(CH_2)_4CO$	30	**4a**: 17 (8/1)	**5a**: 13	1.3/1
3	**3**	$(CH_2)_4CO$	52	**4a**: 30 (8/1)	**5a**: 22	1.3/1
4	**1**	Bu^{t}CHO	81	**4b**: 32 (11/1)[d]	**5b**: 49[e]	1/1.5
5	**2**	Bu^{t}CHO	69	**4b**: 26 (11/1)[d]	**5b**: 43[e]	1/1.6
6	**3**	Bu^{t}CHO	70	**4b**: 27 (11/1)[d]	**5b**: 43[e]	1/1.6
7	**1**	Me_3SiCl	86	**4c**: 84 (7/1)	**5c**: 2	42/1
8	**2**	Me_3SiCl	80	**4c**: 78 (7/1)	**5c**: 2	39/1
9	**3**	Me_3SiCl	90	**4c**: 88 (7/1)	**5c**: 2	44/1

[a] Isolated yield after flash-chromatographic separation of compounds **4** and **5** based on starting material **1-3**. [b] All isolated products were >95% pure from GLC and/or 300 MHz ^1H NMR. [c] From GLC. [d] (*Z*)-**4b** was separated (flash chromatography) in two diastereomers (3/2 ratio). [e] Mixture of 4 diastereomers by ^{13}C NMR and/or GLC (8/4/4/1 ratio).

through intermediate **VI**[21-25] instead of **V** (or **IV**), which would give the mixture of 1,2- and 1,4-adducts, the thermodynamically most stable (*E*)-**4** being the major one. On the other hand, an argument against the step-by-step transformation **III**→**VII**→→**4**+**5** is the following result: when the starting material **1**, **2** or **3** was allowed to react with a deficiency of lithium naphthalenide[26] (1/0.5 molar ratio; slow addition of the lithiation reagent) in the presence of a deficiency of chlorotrimethylsilane (1/0.5 molar ratio) at 0°C, no monosilylated products of the type **VII** (E=Me_3Si) were isolated, although all starting material was consumed; only traces of compound (*Z*)-**4c** could be detected by GLC. A last comment on the neccessary Barbier-type reaction conditions should be done: in absence of the electrophile, highly reactive intermediates of type **V** or **VI** decompose[27] or deactivate[28] (under the tried reaction conditions).



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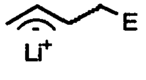
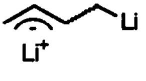


IV



V

VI

VII

From the results described here we conclude that the arene-catalysed lithiation of dichlorobutenes **1-3**, under the described Barbier-type reaction conditions, allows the preparation of disubstituted compounds **4** and **5** (the *Z*-diastereoisomer being the major one in the case of compound **4**), the products ratio being independent of the starting material and the same in each case. Apart from mechanistic considerations (the probable participation of an intermediate of the type **VI**) the practical interest of this process is that it is possible to work with the industrial mixture of **1+2+3** for carrying out the reactions shown in this study.

EXPERIMENTAL PART

General.- M.p.s are uncorrected and were measured on a Reichert thermovar apparatus. IR spectra were determined with a Pye Unicam SP3-200 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in a Bruker AC-300 using $CDCl_3$ as solvent and $SiMe_4$ as internal standard; chemical shifts are given in δ (ppm) and the coupling constants (J) are measured in Hz. ^{13}C NMR assignments were made on the basis of DEPT experiments. MS (EI) were recorded with a Hewlett Packard EM/CG HP-5988A spectrometer. The purity of volatile distilled products and the chromatographic analyses (GLC) were determined with Hewlett Packard HP-5890 instrument equipped with a flame ionisation detector and a 12 m HP-1 capillary column (0.2 mm diam, 0.33 µm film thickness), using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=270°C, T_{column}=60°C (3 min) and 60-270°C (15°C/min); retention times (J_r) are given under these conditions. Thin layer chromatography (TLC) was carried out on Scheleicher & Schnell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using a mixture of hexane/ethyl acetate as eluant; R_f values are given under these conditions. Microanalyses were performed by the Microanalyses Service of the University of Alicante. Solvents were dried by standard procedures[29]. Lithium powder (Strem), starting chlorinated materials **1-3** as well as DTBB and the electrophiles used were commercially available (Aldrich, Fluka) and were used as received.

Lithiation of Dichlorinated Materials **1-3** *under Barbier-Type Reaction Conditions. Isolation of Compounds* **4-6**. *General Procedure.*-To a blue suspension of lithium powder (100 mg, 14 mmol) and DTBB (26 mg, 0.1 mmol) in THF (5 ml) was slowly added a solution of the starting compound **1**, **2** or **3** (2 mmol) and the corresponding electrophile (4 mmol)[30] in THF (5 ml) during 45 min at 0°C under argon. Then, the resulting blue mixture was hydrolysed with water (5 ml), neutralised with 2 M HCl and extracted with diethyl ether (3x10 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated (*ca.* 60 Torr) yielding a residue, which was purified by flash chromatography (silica gel, hexane/ethyl acetate) for compounds **4** and **5** or by distillation for compound **6**[31]. Products ratios and yields are included in Table 1. Analytical, physical and spectroscopic data follow. In the case of minor diastereomers, when isolation in pure form was not possible, their structure was assigned from their data in the corresponding crude reaction mixture and/or by tandem GLC-MS.

(Z)-*1,4-Bis-(1-hydroxycyclopentyl)but-2-ene* [(*Z*)-**4a**]: t_r=13.64 min, R_f=0.23 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3350 (OH), 3000, 1630, 720 (HC=C) and 1005 cm^{-1} (C-O); δ_H 1.45-1.90 (16 H, m, 8xring CH_2), 2.05 (2 H, br s, OH), 2.39 (4 H, d, *J*=5.5, 2xCH_2C=C) and 5.72 (2 H, t, *J*=5.5, HC=CH); δ_C 23.7 (4 C), 39.55 (4 C) (8xring CH_2), 38.7 (2 C, 2xCH_2C=C), 81.95 (2 C, 2xC-O) and 128.5 (2 C, C=C); *m/z* 206 (M^+-H_2O, 1%), 122 (87), 107 (16), 94 (10), 93 (60), 85 (100), 83 (10), 81 (19), 80 (22), 79 (23), 68 (15), 67 (70), 57 (20), 55 (44), 54 (10), 43 (20) and 41 (43) (Found: C, 72.4; H, 10.9. $C_{14}H_{24}O_2 \cdot 1/2H_2O$ requires C, 72.06; H, 10.80).

(E)-*1,4-Bis-(1-hydroxycyclopentyl)but-2-ene* [(*E*)-**4a**]: t_r=13.48 min; δ_C 23.85 (4 C), 39.45 (4 C) (8xring CH_2), 44.65 (2 C, 2xCH_2C=C), 81.5 (2 C, 2xC-O) and 130.1 (2 C, HC=CH); *m/z* 206 (M^+-H_2O, 0.3%), 123 (10), 122 (100), 107 (25), 94 (16), 93 (66), 85 (91), 83 (10), 81 (21), 80 (26), 79 (22), 68 (21), 67 (88), 57 (20), 55 (51), 43 (18) and 41 (35).

3,4-Bis-(1-hydroxycyclopentyl)but-1-ene (**5a**): t_r=13.08 min, R_f=0.29 (hexane/ethyl acetate 3/2); ν_{max} (film) 3360 (OH), 3060, 1630, 990, 910 (HC=C) and 1005 cm^{-1} (C-O); δ_H 1.50-1.90 (18 H, m, 9xCH_2), 2.40 (3 H, m, CHC=C, 2xOH), 5.12 (1 H, dd, *J*=9.9, 2.0, 1 H of CH_2=C), 5.15 (1 H, dd, *J*=17.2, 2.0, 1 H of CH_2=C) and 5.88 (1 H, dt, *J*=17.2, 9.9, CH=C); δ_C 23.35, 23.65, 23.85, 23.9, 37.05, 38.35, 39.95, 40.5, 41.55 (9xCH_2), 50.65 (*C*HC=C), 82.5, 83.95 (2xC-O), 116.95 (*C*H_2=C) and 141.9 (*C*H=C); *m/z* 206 (M^+-H_2O, 1%), 140 (10), 122 (66), 107 (26), 93 (54), 91 (10), 85 (100), 83 (12), 81 (20), 80 (22), 79 (32), 77 (11), 68 (17), 67 (75), 57 (26), 55 (62), 54 (10), 53 (13), 43 (26), 42 (11) and 41 (51) (Found: C, 73.9; H, 11.1. $C_{14}H_{24}O_2 \cdot 1/4H_2O$ requires C, 73.48; H, 10.79).

(Z)-*2,2,9,9,-Tetramethyldec-5-ene-3,8-diol* [(*Z*)-**4b**], major diastereomer: t_r=11.72 min, R_f=0.44 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3440 (OH), 3000, 715 (HC=C), 1065 and 1005 cm^{-1} (C-O); δ_H 0.88 (18 H, s, 6xCH_3), 1.92 (2 H, br s, 2xOH), 2.11, 2.21 (4 H, 2 m, 2xCH_2), 3.22 (2 H, dd, *J*=9.9, 2.7, 2xCHO) and 5.62 (2 H, m, HC=CH); δ_C 25.75 (6 C, 6xCH_3), 29.75 (2 C, 2xCH_2), 34.8 [2 C, 2 *C*$(CH_3)_3$], 78.95 (2 C, 2xC-O) and 130.0 (2 C, HC=CH); *m/z* 210 (M^+-H_2O, 0.1%), 124 (19), 109 (29), 87 (78), 83 (20), 71 (17), 70 (100), 69 (39), 67 (10), 57 (75), 55 (26), 45 (19), 43 (29) and 41 (66) (Found: C, 73.7; H, 12.7. $C_{14}H_{28}O_2$ requires C, 73.63; H, 12.36). Minor diastereomer: t_r=11.72 min; δ_C 25.6 (6 C, 6xCH_3), 29.3 (2 C, 2xCH_2), 34.85 [2 C, 2 *C*$(CH_3)_3$], 78.85 (2 C, 2xC-O) and 129.95 (2 C, HC=CH).

(E)-*2,2,9,9,-Tetramethyldec-5-ene-3,8-diol* [(*E*)-**4b**]: t_r=12.08 min; *m/z* 210 (M^+-H_2O, 0.1%), 124 (11), 109 (23), 87 (60), 71 (20), 70 (100), 69 (31), 57 (58), 55 (15), 45 (11), 43 (15) and 41 (28).

2,2,7,7-Tetramethyl-4-vinyloctane-3,6-diol (**5b**), first (major) diastereomer: t_r=11.11 min, R_f=0.59 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3390 (OH), 3060, 1630, 990, 910 (HC=C) and 1005 cm^{-1} (C-O); δ_H 0.85, 0.89 (18 H, 2 s, 6xCH_3), 1.37 (1 H, ddd, *J*=14.2, 10.3, 4.6, 1 H of CH_2), 1.80 (1 H, ddd, *J*=14.2, 7.9, 1.6, 1 H of CH_2), 2.41 (2 H, br s, 2xOH), 2.63 (1 H, m, CHC=C), 3.26 (1 H, s, CHO), 3.30 (1 H, dd, *J*=10.3, 1.6, CHO), 4.95-5.10 (2 H, 2 m, CH_2=C) and 6.02-6.15 (1 H, m, CH=C); δ_C 25.65 (3 C), 26.8 (3 C) (6xCH_3), 34.85, 35.75 (2x*C*CH_3), 37.75 (*C*H_2CO), 42.65 (*C*HC=C), 77.15, 80.95 (2xCHO), 116.0 (*C*H_2=C) and 139.75 (*C*H=C); *m/z* 227 (M^+-1, 0.2%), 153 (11), 135 (17), 124 (12), 109 (32), 87 (72), 83 (35), 71 (21), 70 (100), 69 (53), 67 (11), 57 (85), 55 (28), 45 (15), 43 (24) and 41 (70) (Found: C, 73.7; H, 12.9. $C_{14}H_{28}O_2$ requires C, 73.63; H, 12.36). Second diastereomer: t_r=11.21 min; δ_C 25.55 (3 C), 26.8 (3 C) (6xCH_3), 33.35 (*C*H_2CO), 35.0, 36.1 (2x*C*CH_3), 44.35 (*C*HC=C), 77.1, 80.55 (2xCHO), 114.4 (*C*H_2=C) and 143.45 (*C*H=C); *m/z* 227 (M^+-1, 0.1%), 153 (10), 135 (15), 124 (10), 109 (33), 87 (63), 83 (28), 71 (17), 70 (100), 69 (33), 57 (59), 55 (21), 43 (17) and 41 (35). Third diastereomer: t_r=11.11 min; δ_C 25.6 (3 C), 26.8 (3 C) (6xCH_3), 34.75, 36.0 (2x *C*CH_3), 36.05 (*C*H_2CO), 42.75 (*C*HC=C), 76.8, 82.5 (2xCHO), 116.55 (*C*H_2=C) and 138.6 (*C*H=C). Fourth (minor) diastereomer: t_r=11.04 min; *m/z* 227 (M^+-1, 0.3%), 153 (11), 135 (20), 124 (15), 109 (35), 87 (75), 83 (39), 71 (25), 70 (100), 69 (52), 67 (10), 57 (65), 55 (24), 45 (10), 43 (20) and 41 (40).

(Z)-*1,4-Bis(trimethylsilyl)but-2-ene* [(*Z*)-**4c**][23]: t_r=6.90 min, R_f=0.71 (hexane); ν_{max} (film) 3000, 1635, 695 (HC=C), 1250, 860 and 790 cm^{-1} ($SiCH_3$); δ_H 0.01 (18 H, s, 6xCH_3), 1.41 (4 H, m, 2xCH_2) and 5.30 (2 H, m, HC=CH); δ_C -1.7 (6 C, 6xCH_3), 17.85 (2 C, 2xCH_2) and 123.15 (2 C, HC=CH); *m/z* 200 (M^+, 2%), 97 (16), 73 (100), 45 (25) and 43 (12).

(E)-*1,4-Bis(trimethylsilyl)but-2-ene* [(*E*)-**4c**][23]: t_r=6.84 min, R_f=0.71 (hexane); δ_H -0.01 (18 H, s, 6xCH_3), 1.40 (4 H, m, 2xCH_2) and 5.22 (2 H, m, HC=CH); δ_C -1.9 (6 C, 6xCH_3), 22.8 (2 C, 2xCH_2) and 124.35 (2 C, HC=CH); *m/z* 200 (M^+, 3%), 112 (11), 97 (16), 73 (100), 45 (22) and 43 (10).

3,4-Bis(trimethylsilyl)but-1-ene (**5c**)[23]: t_r=6.15 min; *m/z* 112 [M^+-$Si(CH_3)_4$, 6%], 97 (13), 74 (10), 73 (100), 45 (24) and 43 (16).

1,1-Diethylsilacyclopent-3-ene (**6**)[32]: t_r=4.97 min, R_f=0.68 (hexane); ν_{max} (film) 3000, 1605, 695 (HC=C), 1230 and 1010 ($SiCH_2CH_3$); δ_H 0.64 (4 H, q, *J*=7.9, 2x$C\mathit{H}_2CH_3$), 0.96 (6 H, t, *J*=7.9, 2x$CH_2C\mathit{H}_3$), 1.26 (4 H, s, 2xCH_2C=C) and 5.85 (2 H, s, HC=CH); δ_C 4.65 (2 C, 2x *C*H_2CH_3), 7.5 (2 C, 2x *C*H_3CH_2), 14.05 (2 C, 2x *C*H_2C=C) and 131.20 (2 C, HC=CH); *m/z* 142 (M^++2, 3%), 141 (M^++1, 9), 140 (M^+, 64), 112 (12), 111 (81), 84 (11), 83 (100), 81 (12), 58 (13), 55 (20) and 53 (11).

Preparation of Compound **7**.-To a solution of (*Z*)-**4c** (400 mg, 2 mmol) and dichloroacetyl chloride (0.20 ml, 2.1 mmol) in hexane (10 ml) was added triethylamine (0.35 ml, 2.5 mmol) at room temperature over a period of 10 min. The resulting mixture was treated with water (10 ml) and extracted with diethyl ether (2x5 ml). The organic layer was then dried over anhydrous Na_2SO_4, evaporated (15 Torr) and the resulting residue was purified by flash chromatography (silica gel, hexane) to yield the title compound (68% yield): t_r=12.28 min, R_f=0.22 (hexane); ν_{max} (film) 1795 (C=O), 1250 and 860 ($SiCH_3$); δ_H 0.07, 0.13 (18 H, 2 s, 9xCH_3), 0.72 (1 H, dd, *J*=15.0, 10.0, 1 H of CH_2Si), 0.74 (1 H, dd, *J*=14.5, 11.0, 1 H of CH_2Si), 0.93 (1 H, dd, *J*=14.5, 11.0, 1 H of CH_2Si), 0.95 (1 H, dd, *J*=15.0, 10.0, 1 H of CH_2Si), 3.07 (1 H, dt, *J*=10.0, 5.4, CH) and 3.64 (1 H, dt, *J*=11.0, 5.4, CH); δ_C -1.3 (3 C), -0.9 (3 C) (6xCH_3), 13.2, 13.3 (2xCH_2Si), 47.55, 55.65 (2xCH), 89.15 (CCl_2) and 198.1 (C=O); *m/z* 297 (M^++2-CH_3, <0.1%), 295 (M^+-CH_3, <0.1%), 128 (21), 113 (34), 95 (10), 93 (25), 73 (100), 45 (25) and 43 (11).

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