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Silylation of *gem*-Dichlorobicyclo[*n*.1.0]alkanes and Alkenes with Me₃SiCl/Li/THF Reagent: The Dramatic Influence of Lithium Quality†

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The silylation of *gem*-dichlorobicyclo[*n*.1.0]alkanes and alkenes with Me₃SiCl/Li/THF reagent was studied under various experimental conditions. The disilylated derivatives were systematically isolated as the major product when using Li containing 1% of Na, while the chlorosilylated derivatives were isolated when using Li containing only 0.01% of Na. These results show the dramatic influence of lithium quality upon the reaction outcome.

Introduction

Cyclopropylsilanes are of interest due to their original reactivity.¹ In this context, silylcyclopropane moieties included in a polycyclic structure constitute useful tools to access to functional polycyclic derivatives, so it is important to have an efficient preparation of these synthons. We have previously proposed a synthesis of *gem*-bis(trimethylsilyl)bicyclo[*n*.1.0]alkanes and alkenes (*n* = 4 or 6) by silylation of the dichloro derivatives using Me₃SiCl/Li/THF reagent.² The disilylation product was obtained in 60%–65% yield with the saturated series, and in 40%–45% yield along with the chlorosilylated derivatives (10%–15% yield) with the unsaturated series. For this work, we used lithium ingot from Prolabo, which was granulated in mineral oil prior to use. More recently, when these compounds were needed for synthetic applications, we reproduced these experiments using metal from Aldrich. This change surprisingly resulted in the chlorosilylated derivatives as the major products. This prompted us to reinvestigate this reaction in relation to the experimental conditions and especially the lithium used.

Results and Discussion

Silylation of 7,7-dichlorobicyclo[4.1.0]hept-2-ene, **1**, and 9,9-dichlorobicyclo[6.1.0]non-2-ene, **2**, with lithium and trimethylchlorosilane (TMSCl) in THF medium was studied under various conditions. The experiments were conducted using three kinds of lithium, which contained 0.01%,^{3a} 0.1%,^{3b} and 1% of Na, respectively.^{3c} The influence of the reagent ratio, which was expected to have an influence on the course of the reaction, was also systematically studied, especially in the case of compound **2**, which was chosen as a model for defining the optimum conditions for the respective production of the chlorosilylated or disilylated compounds. The

reaction mixtures were analyzed by gas chromatography, and the results are reported in Table 1. They show the dramatic influence of the percentage of sodium contained in lithium upon the reaction outcome. Indeed, using optimum conditions to perform disilylation, we isolated as the major product the disilylated derivatives **B** with Li ("1% Na"), while the chlorosilylated derivatives **A** were isolated with Li ("0.01% Na") (Scheme 1, Table 1, entries 1, 5, 6, and 14). Lithium at 0.1% Na content led to intermediate behavior (Table 1, entries 3, 4, 12, and 13). In each case, **A** or **B** was the major product, along with small amounts of unreacted starting material and monochloro (**C**) or monosilyl compounds (**D**). Each of them was isolated by fractional distillation as previously reported.² The possible reaction pathways for all these products are depicted in Scheme 2. They involve electron transfer from the metal onto the substrate, leading to radical anions and then to radicals⁴ (**a** or **b**) by losing Cl[−]. Capture of an electron by **a** or **b** followed by the silylation of the corresponding anion give, respectively, **A** or **B**. Hydrogen trapping from the solvent leads to the byproducts **C** and **D**. Theoretically, obtaining **A** requires only 1 equiv of TMSCl for 2 equiv of Li, while **B** requires 2 equiv of TMSCl for 4 equiv of Li. As expected, examination of Table 1 shows that the ratio of reactants was also very significant:

(i) An increase in the quantity of metal and/or TMSCl leads to an increase in the amount of disilylated compounds **B** obtained, but it is worth noting that 3 equiv of TMSCl (instead of the 2 equiv theoretically required) are necessary to obtain **B** in good yields (see Table 1, entries 5, 14, and 15).

(ii) An excess of TMSCl is always necessary to limit side-reactions with the solvent and to make all of the substrate react.

(iii) An excess of lithium is necessary to obtain the chlorosilylated derivatives **A** (see Table 1, entries 8 and 10). Using 2 or 3 equiv led to the same ratio of **B**, but the ratio of **A** is weaker with 2 equiv, due to an important part of the substrate which was recovered unreacted.

From these results, it appears that the optimum experimental conditions are as follows:

† Dedicated to Professor Raymond Calas on the occasion of his 80th birthday.

* Abstract published in *Advance ACS Abstracts*, August 1, 1995.

(1) For a review see: Paquette, L. A. *Chem. Rev.* **1986**, *86*, 733.

(2) Laguerre, M.; Grignon-Dubois, M.; Dunoguès, J. *Tetrahedron* **1981**, *37*, 1161. Grignon-Dubois, M.; Dunoguès, J.; Ahra, M. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 216.

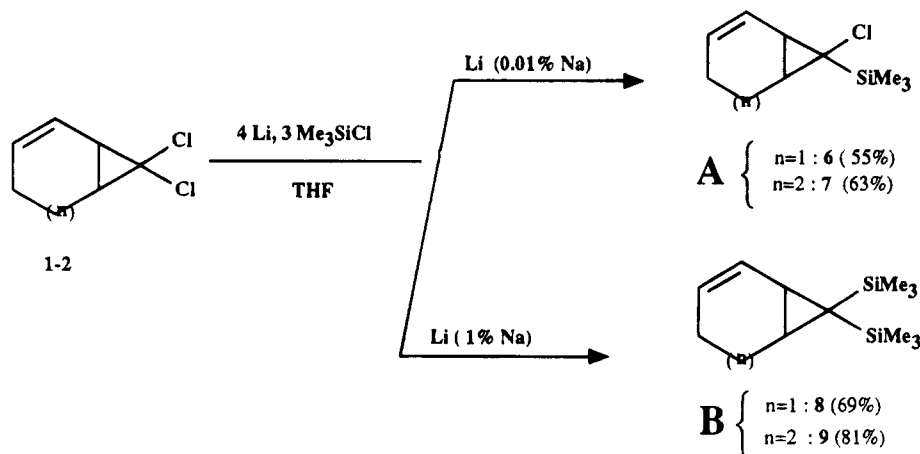
(3) (a) Lithium wire, 0.01% sodium content, Aldrich (ref. 22,091-4). (b) Granulated lithium, 0.1% sodium content, from Prolabo (ref. Z 4996.150). (c) Lithium wire, 1% sodium content, from Aldrich (ref. 27,832-7).

(4) See, for example: Calas, R. J. *Organomet. Chem.* **1980**, *200*, 11.

Table 1. Reductive Silylation of 1–5

entry no.	substrate	% Na	reactant ratio (equiv)		product ratio (%), ^a R,R' ^b				
			Li	TMSCl	H,Cl	Cl,Cl	H,Si	Cl,Si (<i>anti</i> / <i>syn</i>) ^c	Si,Si
1	1	0.01	4	3	3	11		64 (85/15)	22
2			3	1.5		9		77 (80/20)	14
3		0.1	4	3	2	3	7	20 (90/10)	68
4			3	1.5	5	2	9	44 (85/15)	40
5		1	4	3			5	13 (90/10)	82
6	2	0.01	4	3	2	2		73 (80/20)	23
7			4	2	5	3	4	69 (85/15)	19
8			3	1.5	1	7		86 (85/15)	6
9			3	1	5	24		65 (85/15)	6
10			2	1.5	5	28		59 (80/20)	8
11			2	1	7	31		59 (85/15)	3
12		0.1	4	3	2	2	8	19 (90/10)	69
13			3	1.5	2	5	4	31 (90/10)	57
14		1	4	3					100
15			4	2			8	7 (90/10)	85
16	3 ^d	0.01	3	1.5	2	7	8	59 (60/40)	12
17		1	4	3			5	10 (53/47)	95
18	4	0.01	3	1.5	3	4	7	71 (55/45)	15
19		1	4	3			3	11 (51/49)	96
20	5	0.01	3	1.5		5	10	77 (55/45)	8
21		1	4	3					100

^a Product ratios were determined by GC and NMR. ^b R and R' are cyclopropyl substituents. ^c *Anti*/*syn* stereochemistry is related to the trimethylsilyl group position with respect to the polymethylene bridge. ^d 7-(2'-Tetrahydrofuranyl)norcarane was also characterized in the reaction mixture.

Scheme 1

(i) 3 equiv of Li ("0.01% Na") and 1.5 equiv of TMSCl are required to obtain the chlorosilylated compounds **A** (Table 2).

(ii) 4 equiv of Li ("1% Na") and 3 equiv of TMSCl are required to obtain the disilylated compounds **B** (Table 3).

Under these conditions, the saturated substrates **3–5** (Scheme 3, Tables 1–3) respectively led to **10–12** using Li at "0.01% Na" (3 equiv) and **13–15** using Li at "1% Na" (4 equiv). Compared to our previous results,¹ all the product yields have been increased of about 20%. These results confirm the dramatic influence of lithium quality on the silylation outcome. It is well-known that lithium, due to its manufacturing process,⁵ always contains small amounts of sodium, which was said to play a role in its efficiency in the silylation processes. However, to the best of our knowledge, this is the first time a systematic study of this factor and such an important effect related to a relatively small variation

in sodium amount are reported. Moreover, it is worth noting that lithium contains other metallic impurities, which can be as abundant as sodium (see Experimental Section).

The chlorosilylated compounds were isolated as an *anti*/*syn*⁶ isomeric mixture, which was separated by distillation. Their stereochemistry has been unambiguously attributed using ²⁹Si NMR on the basis of the ³J-(²⁹Si,¹H) coupling constant values.⁷ It is worth noting that the *anti*/*syn* ratio is always close to 85/15 from **1–2**, but 55/45–60/40 from **3–5**. The larger predominance of the *anti* isomer with unsaturated substrate shows the effect of the double bond on the stereochemistry and will be discussed below.

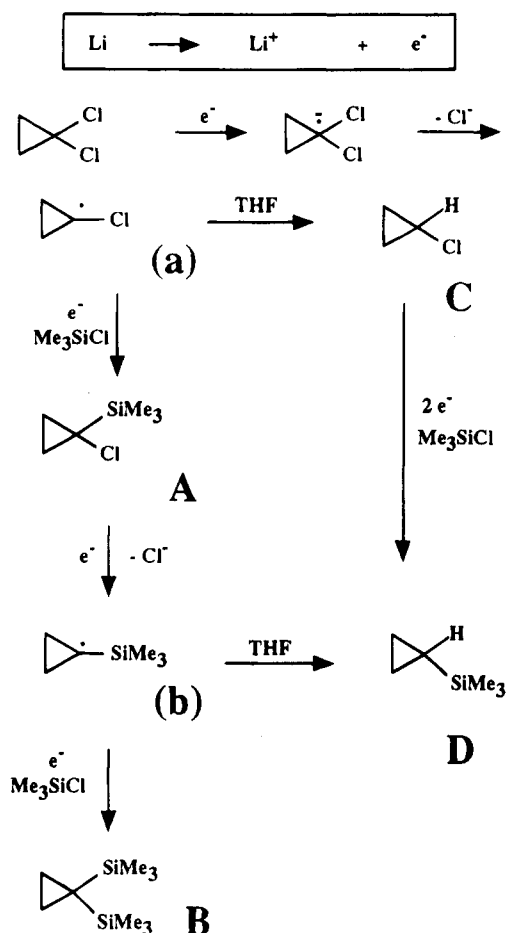
Replacement of a halogen of *gem*-dihalocyclopropanes by a trimethylsilyl group had been previously accomplished. Compound **10** was obtained as an *anti*/

(5) Guntz, M. C. *R. Acad. Sci.* **1983**, 117C, 732. Ruff, O.; Johannsen, O. *Z. Electrochem.* **1906**, 12, 186.

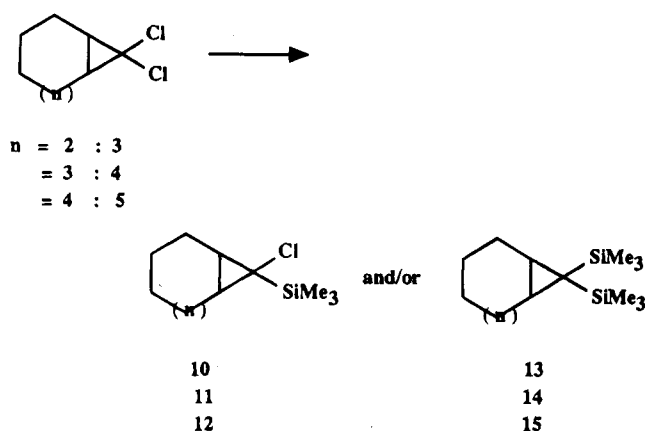
(6) The *anti*/*syn* stereochemistry is related to the trimethylsilyl group or the negative charge position with respect to the polymethylene bridge.

(7) Grignon-Dubois, M.; Ahra, M.; Laguerre, M.; Barbe, B.; Pétraud, M. *Spectrochim. Acta* **1989**, 45A, 911.

Scheme 2



Scheme 3



syn mixture (60/40; 70% yield) by reacting 7-chloro-7-bromonorcarane with BuLi and TMSCL^{8a} and as the single *anti* isomer (24% yield) by reacting cyclohexene with bis(trimethylsilyldichloromethyl)mercury at 120 °C for 6 days.^{8b} Using TMSCL/Mg/THF reagent with dibromonorcarane only led to the disilylated compound,^{8c} whereas TMSCL/Mg/HMPA led to the bromosilylated derivative (68% yield, *anti/syn* 28:72).^{8d} In order to determine which of the metal or the solvent was responsible for the stereoselectivity in this last case, we

(8) (a) Seyferth, D.; Lambert, R. L., Jr.; Massol, M. *J. Organomet. Chem.* **1975**, *88*, 255. (b) Seyferth, D.; Hanson, E. M. *J. Organomet. Chem.* **1971**, *27*, 19. (c) Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1975**, *88*, 287. (d) Shimizu, N.; Tsuno, Y. *Mem. Fac. Sci. Kyushu Univ., Ser. C* **1979**, *12*, 95; *Chem. Abstr.* **1980**, *92*, 110576z.

Table 2. Reductive Silylation of 1–5 Using 3 Equiv of Li (0.01% Na) and 1.5 Equiv of TMSCL

substrate	product ratio (%), ^a R,R' ^b					Cl,Si yield (%)
	H,Cl	Cl,Cl	H,Si	Cl,Si (<i>anti/syn</i>) ^c	Si,Si	
1		9		77 (80/20)	14	55
2	1	7		86 (85/15)	6	63
3	2	7	8	59 (60/40)	12	45
4	3	4	7	71 (55/45)	15	51
5		5	10	77 (55/45)	8	56

^a Product ratios were determined by GC and NMR. ^b R and R' are cyclopropyl substituents. ^c *Anti/syn* stereochemistry is related to the trimethylsilyl group position with respect to the polymethylene bridge.

Table 3. Reductive Silylation of 1–5 Using 4 Equiv of Li (1% Na) and 3 Equiv of TMSCL

substrate	product ratio (%), ^a R,R' ^b					Si,Si yield (%)
	H,Cl	Cl,Cl	H,Si	Cl,Si (<i>anti/syn</i>) ^c	Si,Si	
1			5	13 (90/10)	82	69
2					100	81
3			5	10 (53/47)	95	78
4			3	11 (51/49)	96	80
5					100	83

^a Product ratios were determined by GC and NMR. ^b R and R' are cyclopropyl substituents. ^c *Anti/syn* stereochemistry is related to the trimethylsilyl group position with respect to the polymethylene bridge.

investigated the silylation of 3–5 using Mg in THF medium under reflux.⁹ Our results (Table 4) show that a significant amount of starting material was almost systematically recovered, and the selectivity was not as good as with Li. Moreover, the reactivity decreased when the size of the bicycloalkanes increased. Without an activating agent (Table 4, entries 1 and 2), no silylation occurred. Adding 2 equiv of HMPA¹⁰ only led to a small amount of chlorosilylated products in a 1:1 ratio. In the case of quinoline and isoquinoline derivatives, silylation yields were improved and the reaction times shortened by adding small amounts of Zn to the TMSCL/Mg/THF reagent.¹¹ Indeed, examination of entries 5 and 6 (Table 4) shows that the addition of 0.3 equiv of Zn increases the silylation power, but 51% of 4 was still recovered unreacted, confirming the weaker reactivity of the larger ring. Using 0.3 equiv of Zn associated to 0.06 equiv of CuCl (Table 4, entries 8–11) led to better results. During these reactions, the mixture turned a brick color after some hours of heating, which could indicate the formation of metallic copper. The same phenomenon was observed during the methylation of olefins by the Simmons–Smith procedure,^{12a} especially when using the Zn/CuCl reagent.^{12b} More precise investigation into the CuCl effect is necessary to conclude, but it could play the same role as the impurities contained in lithium. Concerning the stereochemistry of the monosilylation process, examination

(9) We also studied silylation of 1–5 with TMSCL/Mg/HMPA, but only small amounts of silylated products were detected, even after 72 h at 80 °C.

(10) (a) Biran, C. Ph.D. Thesis, Université Bordeaux I, France, 1972. (b) Calas, R.; Duffaut, N.; Biran, C.; Bourgeois, P.; Piscioti, F. *C. R. Acad. Sci.* **1968**, *267C*, 322.

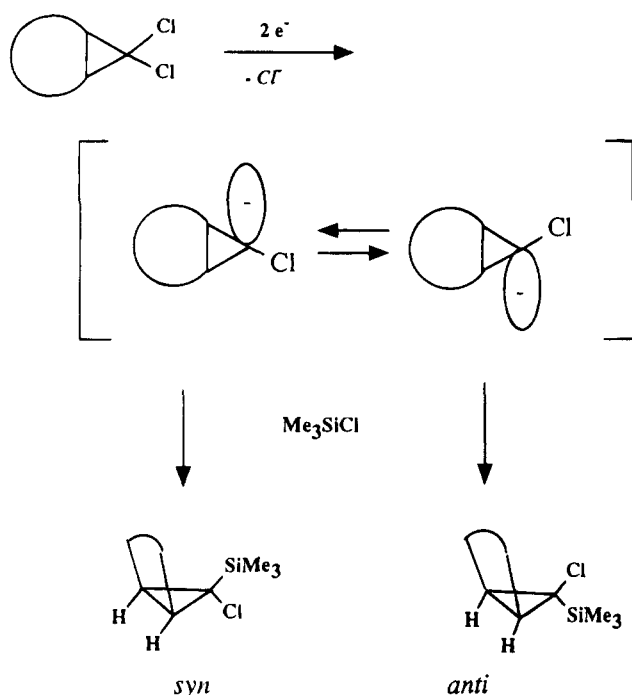
(11) Grignon-Dubois, M.; Fialeix, M.; Léger, J. M. *Can. J. Chem.* **1993**, *71*, 754. Grignon-Dubois, M.; Gauffre, J. C. Results to be published.

(12) (a) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 5323. *Ibid.* **1959**, *81*, 4256. (b) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057.

Table 4. Reductive Silylation of 3–5 Using TMSiCl/Mg/THF Reagent Activated by HMPA, Zn, and CuCl

entry no	substrate	reagent ratio (equiv) product		production ratio (%), ^a R,R'			
		Mg	activating agent	Cl,Cl	H,Si	Cl,Si (<i>anti/syn</i>) ^c	Si,Si
1	3	2		88	traces	traces	
2	4	2		90			
3	3	2	2 HMPA	80		20 (50/50)	traces
4	4	2	2 HMPA	86	traces	14 (60/40)	traces
5	3	3	0.3 Zn		25	15 (<i>anti</i>)	30
6	4	3	0.3 Zn	51		49 (50/50)	
7	3	3	0.3 Zn + 0.03 CuCl	20	22	8 (<i>anti</i>)	47
8	4	3	0.3 Zn + 0.03 CuCl	31		69 (55/45)	
9	5	3	0.3 Zn + 0.03 CuCl	28	8	60 (65/35)	3

^a Product ratios were determined by GC and NMR. ^b R and R' are cyclopropyl substituents. ^c *Anti/syn* stereochemistry is related to the trimethylsilyl group position with respect to the polymethylene bridge.

Scheme 4

of Table 4 shows that the *anti/syn* ratio remains almost the same as with Li, despite the difference in the reaction temperature.

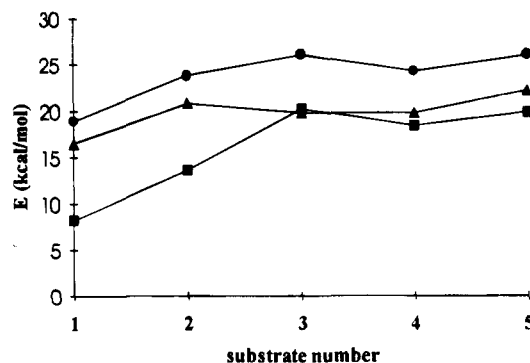
The stereoselectivity of the monosilylation step can have several origins. First, the intermediate anion may be configurationally unstable and isomerize to the thermodynamically favorable isomer (Scheme 4).¹³ We have previously shown that silylation of the monochlorinated derivatives with TMSiCl/Li/THF was not stereoselective but led to a 50:50 *anti/syn* mixture from a single isomer.¹⁴ The systematic predominance of the *anti* isomer could also mean that the replacement of a chlorine atom occurs preferentially at the outer side of 1–5, which is the less sterically hindered, or is a result of thermodynamical control.

In an attempt to better understand the stereochemistry of the silylation, molecular mechanics calculations have been performed for all the chlorosilylated and disilylated products. For this purpose, we used the PC-

Table 5. MMX Steric Energies (kcal/mol) for Chlorosilylated and Disilylated Derivatives

substrate	Cl,Si ^a		substrate	Si,Si
	<i>anti</i>	<i>syn</i>		
6	16.5	18.9	8	8.2
7	20.8	23.8	9	13.6
10	19.8	26.0	13	20.2
11	19.8	24.2	14	18.4
12	22.2	26.0	15	19.9

^a *Anti/syn* stereochemistry is related to the trimethylsilyl group position with respect to the polymethylene bridge.

**Figure 1.** MMX steric energies for compounds 6–15: (■), Si,Si; (▲), Cl,Si *anti*; (●), Cl,Si *syn*.

MODEL program¹⁵ on a PC-compatible computer.) Energy minimization was performed in the program using the MMX force field, which is a modification of Allinger's MM2 and MMP1 programs.¹⁶ The minimum MMX energies are reported in Table 5 and Figure 1. They show that the steric energies of the disilylated products are always lower than those of their chlorosilylated homologues (compound 13 expected, for which we found a 0.4 kcal/mol difference in energies between 13 and the *anti* isomer of 10). The lowest energies are observed for the disilyl unsaturated compounds 8 and 9. Examination of the energy summary (see Table 6 and Experimental Section) shows that the greater torsion and bending contributions in all the disilyl products compared to the *syn/anti* chlorosilyl isomers are counterbalanced by stabilizing van der Waals and electrostatic contributions. It is interesting to note that the most important effects are observed with the unsaturated compounds 8 (−3.5 kcal/mol for each contribution) and 9 (−2.1 to −3.7 kcal/mol). With the saturated disilyl compounds 13–15, we observed a

(13) α -Bromocyclopropyl anions have been reported to exist in equilibrium. See, for example, ref 8a.

(14) Ahra, M.; Grignon-Dubois, M.; Dunoguès, J. *Organomet. Chem.* **1984**, 271, 15. The calculated strain energies (see ref 15) of the two 9-trimethylsilylbicyclo[6.1.0]nonane isomers (18.7 kcal/mol for the *anti* and 24.1 kcal/mol for the *syn*) show the greatest stability of the *anti* form.

(15) Program: PCMODEL, Version 4.1; Serena Software: P.O. Box 3076, Bloomington, IN 47402-3076.

(16) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, 99, 8127. (b) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, 95, 3893.

Table 6. Summary of the Contributions to the MMX Energy

product	total <i>E</i> (kcal/mol)	energy contributions ^a (kcal/mol)					
		STR	BND	S-B	TOR	vdW	QQ
6 <i>anti</i>	16.5	0.6	6.3	-0.2	6.5	-0.2	3.5
<i>syn</i>	18.9	0.7	6.9	-0.2	8.3	-0.4	3.6
7 <i>anti</i>	20.8	0.9	6.3	-0.1	9.3	0.8	3.6
<i>syn</i>	23.8	0.9	8.9	-0.1	9.6	1.0	3.5
10 <i>anti</i>	19.8	0.8	6.0	-0.2	10.3	0.5	2.4
<i>syn</i>	26.0	1.1	9.9	-0.3	10.5	2.2	2.6
11 <i>anti</i>	19.8	0.9	6.8	-0.1	8.7	1.1	2.4
<i>syn</i>	24.2	1.0	10.5	-0.1	8.7	1.5	2.6
12 <i>anti</i>	22.2	1.0	7.8	0	9.5	1.5	2.4
<i>syn</i>	26.0	1.2	11.0	0	9.4	1.8	2.6
8	8.2	1.1	8.1	-0.2	8.4	-3.5	-5.7
9	13.6	1.4	10.3	-0.1	9.7	-2.0	-5.7
13	20.2	1.6	11.7	-0.2	10.5	-0.8	-2.6
14	18.4	1.6	12.2	-0.1	8.8	-1.5	-2.6
15	19.9	1.7	12.5	0.1	9.5	-1.3	-2.6

^a For the definition of the different contributions, see Experimental Section.

weaker van der Waals contribution (-0.8 to 1.5 kcal/mol) and a comparable electrostatic one (2.6 kcal/mol). The smaller energy values of disilylated products compared to the chlorosilylated ones are in good agreement with the lower selectivity of the silylation process (mono/di) with Mg at reflux than with Li at 0 °C. For the chlorosilylated compounds, the *anti* isomer is always more stable than the *syn* isomer. This difference in energy is essentially due to the greater torsion and bending contributions in all the *syn* isomers, which can be attributed to the steric hindrance of the silyl group. It is interesting to note that the larger the *syn* - *anti* difference in energy, the smaller the *syn*/*anti* ratio. This shows that silylation with lithium is not thermodynamically controlled or, if so, only in part, the regiochemistry being rather governed by the equilibrium rate of the anion stereoisomers. In the case of the unsaturated compounds, a repulsive interaction between the π electrons of the double bond and the cyclopropyl charge could destabilize the *syn* anion. Unfortunately, the MMX force field does not allow calculations for cyclopropyl anions.

Experimental Section

Materials. THF (SDS purex) was distilled from sodium benzophenone ketyl and degassed before use by an ultrasonic cleaning bath. Trimethylchlorosilane was distilled from magnesium powder prior to use. All *gem*-dichlorobicycloalkanes and alkenes were prepared using phase transfer reactions.¹ Lithium wire from Aldrich was cut into small pieces and then

washed with THF just prior to use. On request, Aldrich Chemical Co. provided us with the following product information, which shows that lithium contains many more metallic impurities than sodium. In fact, the product that contains 0.01% of Na actually contains a greater amount of silicon impurity:

(i) Lithium wire, 0.01% sodium content from Aldrich (ref. 22,091-4) (ppm): Si, 280; Na, 230; Ca, 210; Cs, 190; K, 55; Al, 30; Fe, 20; Sn, 20; Mg, 10; Ba, 4; Cu, 3.

(ii) Lithium wire, 1% sodium content from Aldrich (ref. 27,832-7) (ppm): Na, 5100; Ca, 340; Si, 190; K, 90; Fe, 85; Mg, 20; Ag, 15; Ba, 15.

Granulated lithium (0.1% Na) from Prolabo was used as received. Despite our repeated requests, it was impossible to obtain detailed product information from this company.

Silylation: Typical Procedures. All the reactions were carried out under an argon atmosphere by employing vacuum line techniques. The ratios of reactants are given in Tables 1 and 4.

TMSCl/Li/THF. To a vigorously stirred suspension of lithium in THF (200 mL) and *gem*-dichlorobicycloalkane (0.1 mol) was added TMSCl dissolved in THF (10 mL) dropwise over a period of 0.5 h. During the addition, the temperature was maintained at 0 °C. The mixture was then stirred for 5 h at this temperature. Most of the THF and unreacted TMSCl were evaporated, and then cyclohexane (50 mL) was added, leading to precipitation of LiCl, which was filtered off. After evaporation of the solvent, this procedure was repeated twice. The solvent was distilled off *in vacuo*, and the crude product was analyzed by GC, using a Perkin-Elmer IGC 15 apparatus (Silicon OV-101 (5%) on Chromosorb P). The resulting ratios of products thus determined have been corrected for detector response, using weighed samples of pure authentic sample. The constituents of the mixture were isolated by distillation under reduced pressure using a spinning band apparatus. All the products isolated were identical to the sample previously described.^{1,5,6,17}

TMSCl/Mg/THF. The reactions were conducted as described above, but replacing Li by Mg, alone or associated with Zn, Zn, and CuCl or HMPA (Table 4). During the addition of TMSCl, the temperature was kept at reflux of THF. The mixture was stirred for 72 h at this temperature, and then the workup was carried out as described above.

Molecular Modeling. Calculations were performed on a 486 PC-compatible running the program PC-Model, Version 4.1.¹⁵ The dielectric constant used throughout the calculations was 1.5. Each calculated total energy reported in Table 5 consisted of stretching (STR), bending (BND), stretching-bending (S-B), torsional (TOR), van der Waals (vdW), and electrostatic (QQ) contributions (Table 6).

OM950313G

(17) Marchand, A.; Gervais, P.; Ahira, M.; Grignon-Dubois, M. *Spectrochim. Acta* **1987**, *43A*, 539. *Ibid.* **1988**, *44A*, 263.