Regio- and Stereoselective Synthesis of Silyl Enol Ethers Using a New Base Electrogenerated from Hexamethyldisilazane

Dominique Bonafoux, Michel Bordeau,* Claude Biran,* Philippe Cazeau, and Jacques Dunogues

Laboratoire de Chimie organique et organométallique (URA 35 CNRS), Université Bordeaux I, F-33405 Talence, France

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The hexamethyldisilazane magnesium salt, a new base readily electrogenerated in an undivided cell fitted with a sacrificial magnesium anode, using a normally equilibrating medium (DME/15% vol HMPA mixture), exhibited a surprising regioselectivity leading to the less highly substituted silyl enol ethers from unsymmetrical ketones. This regioselectivity was not temperature dependent, but was strongly dependent on the nature and proportions of the solvent/cosolvent mixture. Moreover, the reaction was different in pure NMP, and exclusively afforded, from 2-pentanone, the new silylated aldol (56% yield) which resulted from the condensation of the less highly substituted enolate with the ketone.

Introduction

Since Iversen and Lund[1] first showed, about 20 years ago, the synthetic utility of electrogenerated bases (EGBs) in organic chemistry, those new reagents have instigated an increasing interest.[2] Knowing that silyl enol ethers are very useful compounds in organic synthesis,[3] it seemed quite attractive to investigate the enolization of some ketones using EGBs and to test the regio- and stereoselectivities in this reaction.

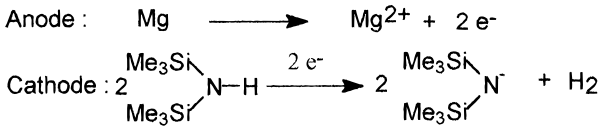
A few months ago, we reported a stereoselective synthesis of silyl enol ethers using, as the electrogenerated base, the magnesium salt of 2-pyrrolidone ($(2\text{-pyrr})_2Mg$).[4] Unfortunately, this electrogenerated base was not basic enough to react with ketones less acidic than 2-methylcyclopentanone.

In this paper, we report the preparation of a new electrogenerated base which is the magnesium salt of hexamethyldisilazane, $[(Me_3Si)_2N]_2Mg$ **(1)**, and its ability in leading regioselectively to the less highly substituted silyl enol ether of some unsymmetrical ketones. To our knowledge, only lithium, sodium, and potassium salts of hexamethyldisilazane (HMDS) have already been involved as bases to prepare silyl enol ethers.[5] Moreover, in this work, although $[(Me_3Si)_2N]_2Mg$ was used in a solvent mixture containing 15% (vol) of hexamethylphosphoramide (HMPA) in 1,2-dimethoxyethane (DME) at −75 °C, the regioselectivity in forming the less highly substituted silyl enol ether was comparable to the well-known kinetic method involving lithium diisopropylamide (LDA) at −78 °C in an aprotic and nonequilibrating medium.[6]

Results and Discussion

In order to choose between a one- and a two-step procedure,[4] the peak potential of the probase (HMDS) was measured by cyclic voltammetry (−2.31 V/SCE) in DME with tetrabutylammonium tetrafluoroborate (0.1 M) at a 1-mm-diameter Pt disk (sweep rate 200 mV s^{-1}). As ketones are reduced at potentials in between −2 and −2.6 V/SCE,[4] of the same order as this of HMDS, it was easier and also safer to first reduce the probase to form the EGB before allowing it to react with ketones in order to avoid any undesired reduction of the carbonyl group. The probase (HMDS) (40 mmol) was dissolved in DME containing 14.6% (vol) of HMPA (69 mmol) initially present in the solution as a complexing cosolvent able to dissociate the supporting electrolyte (3 mmol of Et_4NBF_4), and to ensure a good conductivity, so that the electroreduction can occur.

Scheme 1



The electrochemical reduction of HMDS was performed at room temperature and constant current (0.10 A dm^{-2}) in an undivided cell, using a magnesium bar as the anode and a cylindrical stainless steel grid as the cathode, until 1.5 F mol^{-1} was passed. The reactions occurring at the electrodes, during this process, are given in Scheme 1.

The anodic current efficiency (percentage of consumed metal relative to the theoretical mass corresponding to charge passed) was about 116%, showing that no significant undesired chemical reductive process took place during the electrolysis. The $[(Me_3Si)_2N]_2Mg$ is therefore a real electrogenerated base. Moreover, this salt is quite stable and can be kept, in this medium, for 24 h at room temperature under a nitrogen atmosphere without any decomposition. This new electrochemical preparation of **1** is much easier than those involving Grignard reagents,[5] diorganomagnesium compounds,[7] or transmetalation of mercury or zinc amides.[8]

The ketone (20 mmol, 0.5 molar equiv/HMDS) was added to the solution containing $[(Me_3Si)_2N]_2Mg$ at −75

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(5) Lockman, L.; Sorm, M. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3449.

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Scheme 2

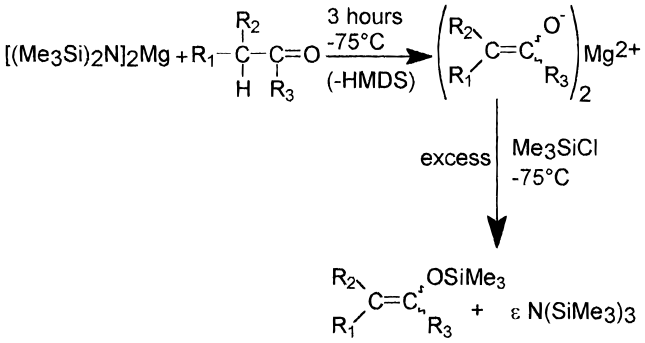
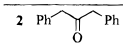
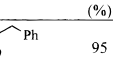
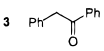
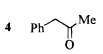
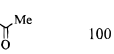
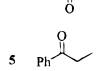
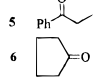
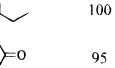
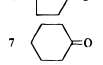
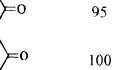
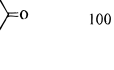
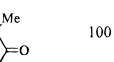
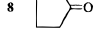
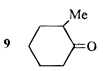
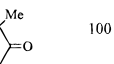
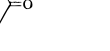
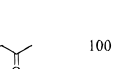


Table 1. Silyl Enol Ethers Obtained from the $[(Me_3Si)_2N]_2Mg$ Electrogenerated Base

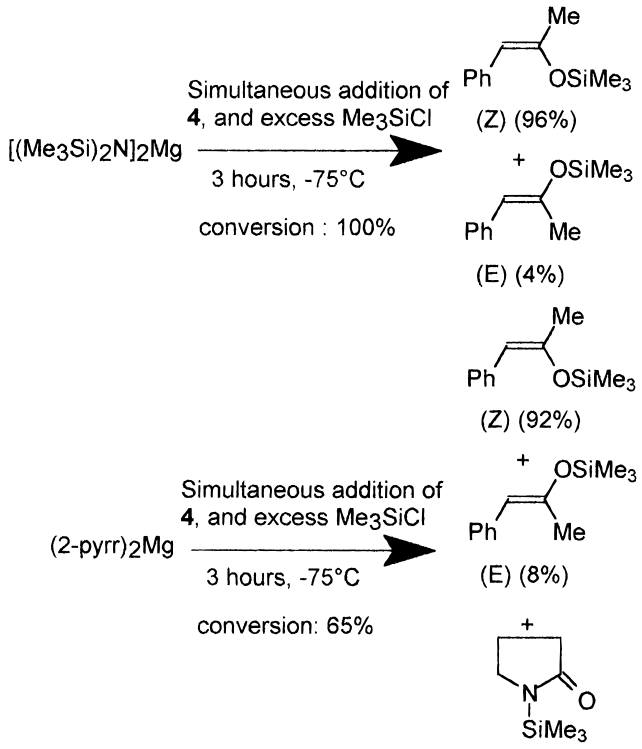
N°	Ketone	Conversion (%)	Enoxysilane	Isomer (%)	Yield (%) [a]	Yield (%) [b]
2		95	12 	100 sole isomer[c]	95	40
3		95	13 	100 (Z)	72	40
4		100	14 	96 (Z) 4 (E)	90	58
5		100	15 	100 (Z)	71	49
6		95	16 		90	50
7		100	17 		86	40
8		100	18  19 	91 9	90	70
9		100	20  21	95 5	90	45
10		100	22  23 	97 3	75	40
11		100	24  25	84 16	71	30

[a] Yield of silyl enol ether after distillation of HMDS. [b] Yield of doubly distilled colorless and odorless silyl enol ether. [c] Unknown stereochemistry.

°C under nitrogen atmosphere, and was allowed to react at this temperature for 3 h to give the corresponding magnesium enolate; the latter was further trapped with an excess of Me_3SiCl (Scheme 2). The results are summarized in Table 1.

Under these conditions, the conversion of ketones to the corresponding silyl enol ethers occurred in high yields. Even though the probase HMDS was used in excess (2 molar equiv/ketone), almost no trace of tris(trimethylsilyl)amine was observed, which is an advantage for the purification of the silyl enol ethers. This low nucleophilicity of $[(Me_3Si)_2N]_2Mg$ was confirmed and compared with that of $(2\text{-pyrr})_2Mg$ by the following experiments: the enolization of benzyl methyl ketone **(4)** was

Scheme 3



realized by adding simultaneously the ketone (20 mmol) and Me_3SiCl (150 mmol) to the EGB. This enolization was complete with $[(Me_3Si)_2N]_2Mg$ but not with $(2\text{-pyrr})_2Mg$ (65% conversion), which behaved, under the same conditions, as a weak but better nucleophile than $[(Me_3Si)_2N]_2Mg$, leading to *N*-(trimethylsilyl)-2-pyrrolidone (Scheme 3).

Moreover, ketones **3**, **4, 5**, and **8** lead stereoselectively to the sole *Z* isomer. This stereoselectivity has already been observed when the magnesium salt of 2-pyrrolidone is used as the EGB under the same conditions.[4] The silyl enol ether **12** corresponding to ketone **2** had been supposed first to be the *Z* isomer, although no spectroscopic data supported this assumption. The presence of HMPA in the solvent mixture, during enolization, was assumed to be responsible for this stereoselectivity. Indeed, HMPA which was initially used to ensure a good conductivity during the electrolysis is also responsible for the equilibration of enolates leading essentially to the *Z* isomer, even at low temperatures.[9] This equilibration readily occurs when a two-step procedure is used, *i.e.*, when the enolization is performed in the absence of Me_3SiCl.[9b]

On the other hand, in the case of unsymmetrical ketones **8**, **9**, **10**, **11**, two regioisomers could be formed, but in spite of the equilibrating conditions, only the less highly substituted silyl enol ether was formed, except for benzyl methyl ketone (**4**), which is known to lead more easily to the thermodynamic isomer, as already reported by House.[6a] This regioselectivity is surprising as a two-step procedure was used under conditions which were

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(9) (a) Davis, F. A.; Sheppard, A. C.; Chen, B. C.; Haque, M. *J. Am. Chem. Soc.* **1990**, *112*, 6679. (b) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495. (c) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (d) Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959.

(10) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunoguès, J. *Tetrahedron* **1987**, *43*, 2075.

(11) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736.

Table 2. Comparison of Our Method with Other Common Chemical Routes to Silyl Enol Ethers. Influence of Temperature on the Respective Amounts of Regioisomers

N°	Ketone	Enoxysilane	Et_3N, NaI, Me_3SiCl (%)[10]	LDA, Me_3SiCl -78° (%)[6a, 11]	$[(Me_3Si)_2N]_2Mg$, HMPA, Me_3SiCl[b], -75°C (%)	T_{amb}(%)
8		18 	5	99	91	83
		19 	95	1	9	17
9		20 	10	99	95	89
		21 	90	1	5	11
10		22 	95	98[a]	97	96
		23 	5	2[a]	3	4
11		24 	60	88[a]	84	82
		25 	40	12[a]	16	18

[a] Experiments performed in this work according to ref 11 procedure. [b] This work.

expected to be equilibrating, so this equilibration should have occurred during the 3 h of enolization. The regioselectivity using our new EGB is compared to those of other bases commonly used for the synthesis of silyl enol ethers in Table 2.

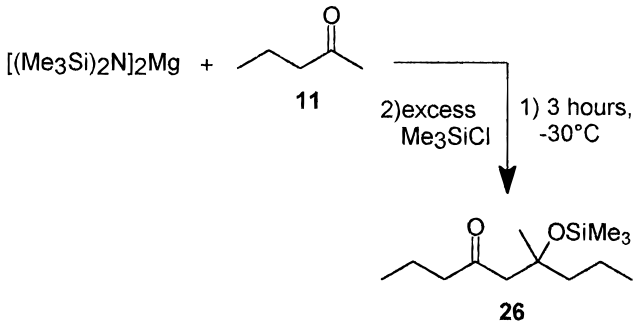
It must be pointed out that our method is the only one mentioned in Table 2, which involves an expected equilibrating medium (HMPA) and a two-step procedure. In spite of these conditions, which usually lead to the more substituted enolates, the use of $[(Me_3Si)_2N]_2Mg$ shows a surprising regioselectivity in forming the less highly substituted silyl enol ethers. The use of this EGB is even almost as effective as the well-known kinetic method involving LDA at −78 °C in the presence of Me_3SiCl (complementary experiments were also performed with this last reagent in the case of ketones **10** and **11** for comparison, cf. Table 2). These results led us to verify if this selectivity was a consequence of the low temperature used in this synthesis (−75 °C) or simply a particular property of this new EGB. But, the enolization of ketones **8**, **9**, **10**, and **11**, using the same method at room temperature, led to almost the same regioselectivity. Thus, the reaction temperature does not seem to have a direct influence on the observed regioselectivity (Table 2). Indeed, even at room temperature in the presence of HMPA, the equilibration of magnesium enolates does not take place when $[(Me_3Si)_2N]_2Mg$ is used as the EGB.

Thus, this regioselectivity leading to the less highly substituted silyl enol ether seems to be a consequence of the nature of the base.

In order to approach the real composition of the magnesium enolate mixture immediately formed after deprotonation, we tried to carry out the enolizations of ketone **8** and **11** under the same conditions but in the presence of Me_3SiCl (20 mL, 150 mmol). The percentages of the formed isomers **18** and **19** from **8** were then 93% and 7%, respectively, and **24** and **25** from **11** were then 90% and 10%, respectively, showing only a slight improvement in the regioselectivity of the reaction when the trapping agent is present during the enolization step.

As $[(Me_3Si)_2N]_2Mg$ had previously never been used as a base for silyl enol ether synthesis, we had to compare its reactivity with that of its lithium analog. We chose 2-pentanone (**11**) as a model because its enolization had been studied with a two-step procedure with and without an equilibrating medium.[12] The results are compared in Table 3.

Scheme 4



Thus, the use of the magnesium salt of HMDS provides more regioselectivity than does use of its lithium salt. Moreover, unexpectedly, the formation of **24** is even more regioselective with **1** in an expected equilibrating medium than with $[(Me_3Si)_2N]Li$ in a nonequilibrating medium. Although Li and Mg enolates are usually known to have a similar reactivity toward Me_3SiCl,[13] the nature of the cation associated with $(Me_3Si)_2N^-$ influences the reactivity of the base in this case.

In order to understand the role of HMPA in this synthesis, we tried to replace it by *N*-methyl-2-pyrrolidone (NMP), which is a good solvent in electrochemical synthesis. The reaction conditions were the same as above; 3 h of enolization followed by the addition of Me_3SiCl. The results concerning 2-pentanone (**11**) are summarized in Table 4 for different DME/cosolvent mixtures.

It must be pointed out that the use of NMP instead of HMPA as the cosolvent needs a higher amount (35% vol of NMP minimum) to ensure a good conductivity during the electrolysis of HMDS. Moreover, the replacement of HMPA by NMP led to very surprising results. Indeed when pure NMP was used at −30 °C, the sole product of the reaction was the new silylated aldol **26** (isolated in 56% yield), which resulted from the condensation of the less highly substituted enolate anion with **11** (Scheme 4).

On the other hand, when NMP was used as the cosolvent, the equilibration of enolates took place, leading to a mixture of silyl enol ethers. Moreover, the more NMP used, the more the aldol **26** was formed. These results may be a consequence of the dissociative power of the medium which was stronger for the DME/NMP mixtures used (minimum 310 mmol of NMP, 3.8 mol L^{-1}, $\epsilon_{25} = 32$) than for our basic DME/HMPA mixture (69 mmol of HMPA, 0.84 mol L^{-1}, $\epsilon_{25} = 30$). Indeed, the higher the polarity of the solvent mixture, the more magnesium enolates are present, in the solution, as very loose solvent-separated ion pairs wearing an appreciable fraction of the negative charge at the α-C atom.[14] Those solvated enolate ions are certainly responsible for the formation of the silylated aldol **26**, when a DME/NMP mixture containing more than 35% NMP by volume (310 mmol) is used. Nevertheless, when only 35% (vol) NMP

(12) Xie, L.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3123.
(13) Mekelburger, H. B. *Comprehensive Organic Synthesis*; Trost B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 1.
(14) House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514.

Table 3. Comparison between Li and Mg Used as the Cations, in the Reactivity of HMDS Metallic Salts, toward Ketone 11

HMDS salt	basic molar equiv/ketone	solvent	cosolvent	molar equiv/ketone	*T* (°C)	enoxysilanes (%) **24**	enoxysilanes (%) **25**	ref
$(Me_3Si)_2NLi$	3	THF			−60	72	28	12
	3	THF	HMPA	9	−60	60	40	12
$[(Me_3Si)_2N]_2Mg$	2	DME	HMPA	3.5	−75	84	16	*a*, *b*
	2	DME	HMPA	9	−75	76	24	*a*

[a] This work. [b] Our usual conditions.

Table 4. Influence of the DME/Cosolvent Mixture on the Regioselectivity of Formation of Silyl Enol Ethers from 2-Pentanone (11)

cosolvent % vol	cosolvent mmol	*T* (°C)	convsn (%)	enoxysilanes (%) **24**	enoxysilanes (%) **25**	silylated aldol **26** (%)
35 NMP[a]	310	−75	60	33	67	trace
		−30	70	31	69	trace
50 NMP[a]	410	−75	95	38	62	50
pure NMP[b,c]		−30	100	0	0	100
54 HMPA	310	−30	0			

[a] Aldol condensation took place as a side reaction leading to 6-methyl-6-(trimethylsiloxy)nonan-4-one (**26**). [b] The sole silylated aldol **26** was obtained. [c] A lower temperature was not allowed because of the NMP's mp, −24 °C.

was used, **26** appeared as a negligible side product and the equilibration of enolates took place leading, as expected with a two-step procedure, to a mixture of silyl enol ethers in which the major regioisomer is the more highly substituted one (**25**). Thus, in this DME/NMP mixture, the enolates leading to **24** and **25** must be more tightly bound ion pairs with a relatively low negative charge on the α-C atom. Beyond 35% (vol) NMP, the solvent mixture becomes polar enough to solvate the magnesium cations.

Since the nature and proportions of the cosolvent influence this reaction, we have studied the influence of the solvent. The same reaction was thus tried under our standard conditions (69 mmol of HMPA), but using THF as the solvent instead of DME. The conductivity in THF is not as good as it is in DME. The amounts of isomers **24** and **25**, obtained in THF, were respectively 76% and 24% instead of 84% and 16% in DME. DME is therefore the better solvent for achieving a good regioselectivity of formation of the less highly substituted silylated enol ethers. This result is not surprising as DME is known not to equilibrate silyl enol ethers in the presence of enolate anions.[6a]

$[(Me_3Si)_2N]_2Mg$ is a bulky base, so the selectivity could also be the result of steric interactions with the ketone. In order to check this hypothesis, we have examined the enolization of 2-methylcyclopentanone (**8**) in the presence of other EGBs.

First, we compare, in Table 5, the reactivity of the magnesium salts of 2-pyrrolidone, diisopropylamine, and HMDS. These three EGBs were obtained as described above in the case of HMDS. The enolization conditions were still the same, but the solvent mixture was DME/NMP (35 % vol).

The equilibration of the enolates, using this two-step procedure in this DME/NMP mixture, took place with those three EGBs. Moreover, this equilibration is particularly important with $[(Me_3Si)_2N]_2Mg$ and is even higher with ketone **8** than with ketone **11**, under the same conditions (Table 5). The equilibration is even also higher with NMP at −75 °C than with HMPA at −30 °C.

Table 5. Regioselectivity of Formation of Silyl Enol Ethers from 2-Methylcyclopentanone (8) for Different Solvent Mixtures DME/NMP or DME/HMPA

EGB	NMP (mmol)	HMPA (mmol)	*T* (°C)	convrsn (%)	enoxysilanes (%) **18**	enoxysilanes (%) **19**
$(2\text{-pyrr})_2Mg$	310		−75	45	1	99
$(iPr_2N)_2Mg$	310		−75	95	29	71
$[(Me_3Si)_2N]_2Mg$	310		−75	80	21	79
	310		−30	80	20	80
		310	−30[a]	100	35	65

[a] A lower temperature cannot be allowed with this solvent mixture.

Thus, the nature and proportions of the cosolvent in the solvent mixture are both important parameters in determining the regioselectivity of formation of silyl enol ethers by this method. Indeed, when only 15% (vol) of HMPA is used, the less highly substituted isomers are obtained with a good regioselectivity (Table 1), but when 35% (vol) of HMPA is used, the equilibration of the enolates takes place as expected, leading to isomer **19**.

Conclusion

$[(Me_3Si)_2N]_2Mg$, a new EGB easily prepared under electrolytic conditions, appears to be convenient for the preparation of the less highly substituted silyl enol ethers derived from ketones when used in a DME/HMPA (15% vol) mixture as the solvent. Moreover the regioselectivity remains excellent at room temperature.

These results can be explained in terms of the formation of a stable complex, not characterized at this time, in which the structure of the enolate is blocked, preventing the possible equilibration process.

Experimental Section

General. All the materials used for silyl enol ether syntheses were of reagent grade and used without preliminary purification, except for DME, THF, and Me_3SiCl, which were distilled over sodium benzophenone ketyl for the formers and magnesium powder for the latter. All air-moisture sensitive reactions were performed under a positive pressure of dry nitrogen. The cyclic voltammetry, NMR, gas chromatography, and mass spectroscopy instrumentation has already been described elsewhere.[4,15] Proton and carbon NMR spectra were recorded in $CDCl_3$, and chemical shifts are reported downfield from tetramethylsilane.

General Procedure for the Preparation of Silyl Enol Ethers. Electrolyses were carried out at room temperature in an undivided cell fitted with a sacrificial magnesium anode and a stainless steel grid cathode described previously.[4,15] The electrodes were separated by a polypropylene mesh.

To a solution of Et_4NBF_4 (0.6 g, 3 mmol) in DME (70 mL) were added HMPA (12 mL, 69 mmol) and HMDS (8.5 mL, 40 mmol). A constant current (0.1 A) was applied, at room temperature, until 1.5 F/mol of HMDS was passed. The

(15) Deffieux, D.; Bordeau, M.; Biran, C.; Dunoguès, J. *Organometallics* **1994**, *13*, 2415.

resulting mixture was transferred under argon to a two-necked round-bottomed flask and cooled to −75 °C. Then, the ketone (20 mmol) was added. After 3 h of stirring at this temperature, Me_3SiCl (20 mL, 150 mmol) was added to the resulting magnesium enolate mixture and the temperature was held constant for 30 min. DME and excess Me_3SiCl were evaporated. The residue was extracted with 80 mL of cold pentane and washed with ice-cold water. The aqueous layer was extracted several times with pentane (3 × 50 mL). The combined pentane extracts were washed with cold 5% aqueous HCl, then with water until neutrality, and dried over magnesium sulfate. After evaporation of pentane, the silyl enol ethers were separated from $Me_3SiOSiMe_3$ and HMDS by distillation. Analysis of the products was achieved by GC, ^1H, ^{13}C, IR, and mass spectroscopies. The ^1H and ^{13}C NMR and IR spectra of **12**−**15** and ^1H and ^{13}C NMR spectra of **16** and **17** are identical with these previously reported[4] for samples obtained from ketones **2**−**7** respectively using the 2-pyrrolidone magnesium salt as EGB.

2-(Trimethylsiloxy)-1,3-diphenylprop-1-ene (12). A sole isomer was formed. ^1H NMR: δ 0.24 (s, 9H), 3.62 (s, 2H), 5.53 (s,1H), 7.3−7.63 (m, 10H). ^{13}C NMR: δ 1.1, 44.3, 110.5, 125.9, 126.8, 127.3, 128.2, 128.4, 128.7, 129, 129.2, 129.5, 129.8, 137, 138.2, 152. IR (neat): 1650 cm^{-1}. MS *m*/*z*: 282 (M^+), 267 ($M^+ - CH_3$), 73 (100).

1-(Trimethylsiloxy)-1,2-diphenylethylene (*Z*) (13). ^1H NMR: δ 0.25 (s, 9H), 6.34 (s, 1H), 7.38−7.8 (m, 5H), 7.85−7.88 (m, 5H), in accordance with ref 9a for the *Z* isomer. ^{13}C NMR: δ 0.9, 110.7, 126.3, 126.4, 127, 128.2, 128.3, 128.4, 128.9, 129.7, 133.3, 136.8, 139.8, 151.1. IR (neat): 1630 cm^{-1}. MS *m*/*z*: 268 (M^+, 100), 253 ($M^+ - CH_3$), 73.

2-(Trimethylsiloxy)-1-phenylprop-1-ene (*Z*) (14). ^1H NMR: δ 0.24 (s, 9H), 1.97 (s, 3H), 5.41 (s, 1H), 7−7.5 (m, 5H), in accordance with refs 9a and 10 for the *Z* isomer. ^{13}C NMR: δ 1.0, 24.1, 108.5, 125.3, 127.1, 127.8, 128.1, 137.1, 149.4. IR (neat): 1650 cm^{-1}. MS *m*/*z*: 206 (M^+, 100), 191 ($M^+ - CH_3$), 73.

1-(Trimethylsiloxy)-1-phenylprop-1-ene (*Z*) (15). ^1H NMR: δ 0.13 (s, 9H), 1.76 (d, 2H, J^3 = 6.8 Hz), 5.34 (q, 1H, J^3 = 6.8 Hz), 7.24−7.5 (m, 5H). ^{13}C NMR: δ 0.5, 11.6, 105.1, 127.2, 127.8, 127.9, 128.4, 149.8, in accordance with ref 9a. IR (neat): 1655 cm^{-1}. MS *m*/*z*: 206 (M^+), 191 ($M^+ - CH_3$), 75 (100), 73.

1-(Trimethylsiloxy)cyclopent-1-ene (16). ^1H NMR: δ 0.13 (s, 9H), 2.0−2.14 (m, 2H), 2.16−2.25 (m, 4H), 4.53 (s, 1H). ^{13}C NMR: δ −0.1, 21.2, 28.6, 33.4, 101.8, 154.9. IR (neat): 1667 cm^{-1}. MS *m*/*z*: 156 (M^+), 155 (100), 141 ($M^+ - CH_3$), 75.

1-(Trimethylsiloxy)cyclohex-1-ene (17). ^1H NMR: δ 0.11 (s, 9H), 1.38−2.29 (m, 2H), 4.78 (s, 1H). ^{13}C NMR: δ 0.3, 22.3, 23.1, 24.5, 30, 104.1, 150.3. IR (neat): 1668 cm^{-1}. MS *m*/*z*: 170 (M^+), 155 ($M^+ - CH_3$), 75 (100).

5-Methyl-1-(trimethylsiloxy)pent-1-ene (18). ^1H NMR: δ 0.17 (s, 9H), 0.99 (d, 3H, J = 6.9 Hz), 1.2−1.5 (m, 2H), 2−2.5 (m, 3H), 4.53 (m, 1H). ^{13}C NMR: δ −0.1, 18.6, 26.7, 30.4, 39.2, 100.5, 158.5. IR (neat): 1646 cm^{-1}. MS *m*/*z*: 170 (M^+), 155 ($M^+ - CH_3$), 73 (100). All NMR, IR, and mass spectra are in accordance with ref 6a.

6-Methyl-1-(trimethylsiloxy)cyclohex-1-ene (20). ^1H NMR: δ 0.16 (s, 9H), 0.99 (d, 3H, J = 6.9 Hz), 1.25−1.8 (m, 4H), 1.93−2.09 (m, 2H), 2.1−2.21 (m, 1H), 4.81 (m, 1H,). ^{13}C NMR: δ 0.1, 18.4, 20.0, 24.0, 31.3, 33.3, 103.1, 153.8. IR (neat): 1660 cm^{-1}. MS *m*/*z*: 184 (M^+), 169 ($M^+ - CH_3$), 73 (100). All NMR, IR, and mass spectra are in accordance with ref 6a.

4-Methyl-2-(trimethylsiloxy)pent-1-ene (22). ^1H NMR: δ 0.25 (s, 9H), 0.75 (d, 6H, J = 6.5 Hz), 1.93 (m, 3H), 4.05 (s, 2H). ^{13}C NMR: δ 0.1, 22.0, 25.2, 45.8, 90.5, 158.2. IR (neat): 1660 cm^{-1}. ^1H NMR and IR spectra are in accordance with ref 10. MS *m*/*z*: 172 (M^+), 157 ($M^+ - CH_3$), 115 (100), 73.

2-(Trimethylsiloxy)pent-1-ene (24). ^1H NMR: δ 0.14 (s, 9H), 0.85 (t, 3H, J = 7.4 Hz), 1.51 (m, 2H), 1.93 (t, 2H, J = 7 Hz), 3.97 (s, 2H). ^{13}C NMR: δ 1.8, 13.5, 19.9, 38.5, 89.8, 160. IR (neat): 1662 cm^{-1}. ^1H NMR and IR spectra are in accordance with ref 10. MS *m*/*z*: 158 (M^+), 143 ($M^+ - CH_3$), 75, 45 (100).

6-Methyl-6-(trimethylsiloxy)nona-4-one (26). ^1H NMR: δ 0 (s, 9H), 0.79 (t, 6H), 1.18 (s, 3H,), 1.22−1.46 (m, 6H,), 2.3−2.49 (m, 4H, J_{AB} = 12.8 Hz). ^{13}C NMR: δ 2.4, 13.7, 14.4, 16.9, 17.5, 27.8, 45.5, 47.0, 53.9, 75.8, 210.8; DEPT experiments were performed to confirm this structure showing five CH_2 at 16.9, 17.5, 45.5, 47, and 53.9 ppm and no CH. IR (neat): 1721 cm^{-1}. MS *m*/*z*: 229 ($M^+ - CH_3$), 71 (100). Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.93; H, 11.47; O, 13.11; Si, 11.47. Found: C, 63.9; H, 11.52; O, 13.2.

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