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Chemocontrolled Reduction of α-Keto Esters by Hydrides : a Possible Solution for Selective Reduction of the Ester Function

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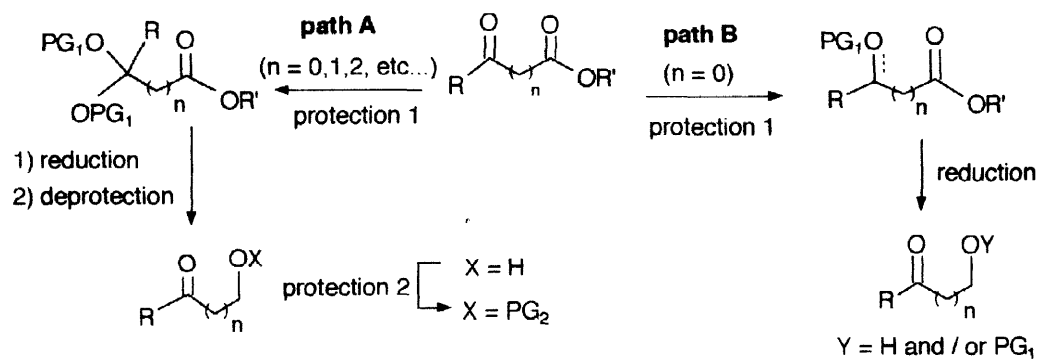
Abstract : α- keto primary alcohols or α-silyloxy ketones have been obtained with a high level of selectivity from enolic α-keto esters in two steps, with the reduction of the α-silyloxy α,β-unsaturated ester by $LiAlH_4$ as the key step. The methodology developed in this work represents a "reversed" chemoselective reduction of the ester group instead of the keto of an enolic α-keto ester due to a one-pot sequential ester reduction-desilylation or silyl migration process.

In their continuing quest to synthesize increasingly sophisticated, often therapeutically active molecules, chemists are often confronted with the difficulties of chemoselectivity between functional groups possessing comparable reactivity. In this context, one of the main problems is that of discriminating one π C-O bond from other carbonylated functional groups in a molecule with a high degree of selectivity. Due to the broad range of existing reducing agents [1], it is relatively easy to perform selective reductions by following the "normal order of reactivity", that is for example the reduction of a ketone or an aldehyde in preference to an ester or an amide. By contrast, the development of short chemical processes that would allow a reversal of this expected selectivity, favouring reduction of the less reactive π C-O bond remains an elusive goal, and methods allowing such a reversal of selectivity are rare. The selective formation of the enolate of the ketone function from a keto ester or a keto nitrile combined with the in-situ reduction of the ester or nitrile function[2], is the only known straightforward method allowing such a reversed order of reduction. However, this unique strategy suffers from restrictions due to the sensitivity of the enolate chemistry, and the use of multi-step protection-deprotection manipulations often remains mandatory to achieve such a reversed selective reduction (Scheme 1, path A).



Scheme 1

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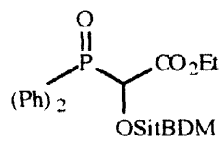
In connection with our recent work concerning the reactivity of α-keto esters towards $NaBH_4$[3], we report herein a complementary approach to the enolization-hydride reduction[2] which employed trialkylsilyls as a protecting group for the ketone (Scheme 1, path B). This method represents a straightforward two-step procedure for the "reversed" chemoselective reduction of α-keto esters, which takes advantage of the ease of removal of a trialkylsilyl group from an oxygen by aluminohydrides[4] together with the fact that trialkylsilyls are excellent migrating groups[5].

Thus, highly selective transformation of α-silyloxy-α,β-unsaturated esters into α-keto primary alcohol were achieved upon simple treatment by $LiAlH_4$. Depending on the conditions used, the related silyloxy ethers could also be obtained after internal migration of trialkylsilyl group[5], thus improving the scope of this reaction.

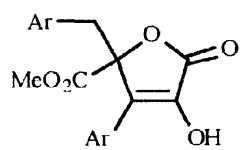
RESULTS AND DISCUSSION

The requisite (Z)-1-silyloxy propenoates **2a$_c$-d$_c$**[6] (see Table 1) as well as the unsubstituted silyloxy ethyl propenoates **6a** and **6b** (see Table 2) were prepared from the parent enolizable α-keto esters[7] by using the classic[8] triethylamine/DMAP/chlorosilane or silyl triflate procedure in dichloromethane. Propenoates **2f** and **2g** (see Table 3) were obtained as mixtures of *cis* and *trans* isomers (which could be easily separated by flash chromatography on a column of silicagel) by Wittig-Horner condensations[9] between 2-diphenylphosphine oxide-2-*tert*butyldimethylsilyloxy ethyl acetate *i* and the suitable aldehydes. We chose our usual 2-hydroxy-3-(3,4-dimethoxyphenyl) methyl propenoate **1a** as a model[3] for the beginning of this study. Two distinct trialkylsilyl groups were first considered. The *tert*butyldimethylsilyl (tBDMS) group was used as a moderately robust protecting group and the *tert*butyldiphenylsilyl (tBDPS) as a more resistant one[8]. We observed that depending on the silyl chloride concentration the formation of a cyclic aldol dimer *ii* (Figure 1) competes with that of the expected silyl enol ether **2a$_c$**. Thus, the initial reaction carried out with tBDMSCl as the electrophile at a concentration of 0.33M, gave 30% of the dimer. Concentrations lower than 0.2 M were found to be a prerequisite for the silylation to occur cleanly. This observation complements a statement recently advanced by Hoffman and co-workers, according to which the aforementioned competition was base dependent[10].

Figure 1



i



ii

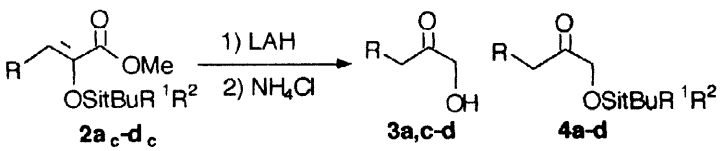
Ar = 3,4-diMeOC$_6$H$_3$

As expected, the introduction of the more hindered tBDPS group was problematic and only 7% of the desired silylated product **2b$_c$** was isolated in the same conditions as above with the dimer being obtained as the major product. No further attempts by using the *tert*butyldiphenylsilyl triflate-lutidine conditions or changing the catalyst were made to optimize the yield of **2b$_c$**[11]. However, a 13% yield of **2b$_c$** was obtained by using 3 equivalents of chlorosilane, whereas the use of imidazole in THF or DMF gave no trace of the desired silyl enol ether.

Compound **2a$_c$** was first investigated in a systematic study (Table 1, entries 1-3). Treatment of a THF solution of **2a$_c$** with one equivalent of a commercially available 1M solution of $LiAlH_4$ (LAH) in THF at room

temperature provided very rapidly (less than 5 minutes) a single polar product (Rf = 0.18 in petroleum ether/ethyl acetate 5-5) which was assigned as the keto primary alcohol **3a** (entry 1). When the hydride addition was performed at -100°C (external temperature), the starting material appeared to be unreactive under nearly -50°C. Above this temperature, the reaction proceeded smoothly and two slightly more polar products, the α-silyloxy ketone **4a** and the 1-hydroxymethyl enoxy silane **5a** (for structure, see Scheme 2) first appeared in a roughly 1/1 ratio before **3a** was formed as the major product at the end of the reaction, between -25°C and 0°C. After hydrolysis with aqueous NH_4Cl at 0°C, only **3a** was detected (entry 2) meaning that both **4a** and **5a** undergo desilylation during hydrolysis. Replacing THF by Et_2O as the solvent enabled us to essentially produce the α-silyloxy ketone **4a** along with a small amount of the alcohol **3a**, whose formation was probably favoured by the solvation of the reagent by THF (entry 3). As previously observed for reaction carried out in THF, an approximatively 1/1 ratio of **4a** and **5a** was detected by TLC before hydrolysis which in this case promoted predominantly a migration of the silyl group instead of its removal. Surprisingly, similar results were obtained with the tBDPS derivative **2b** (entries 4-5).

Table 1. Addition of LAH to various 3-aryl-2-silyloxy methyl propenoates **2**



2a c-d c **3a,c-d** **4a-d**

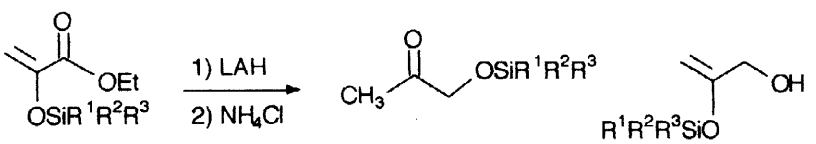
entry	R^1, R^2	R	substrate	solvent	conditions	ratio **3**				combined yield
1	Me	3,4-diMeOC$_6H_3$	**2a c**	THF	r.t.	**3a**	(100)	**4a**	(0)	90%
2	"	"	"	"	-100°C to 0°C	"	(100)	"	(0)	85%
3	"	"	"	Et_2O	-100°C to -20°C	"	(20)	"	(80)	96%[b]
4	Ph	"	**2b c**	THF	-100°C to -15°C	**3b**	(100)	**4b**	(0)	93%
5	"	"	"	Et_2O	-100°C to -15°C	"	(10)	"	(90)	88%[b]
6	Me	p-ClC$_6H_4$	**2c c**	THF	-100°C to +5°C	**3c**	(100)	**4c**	(0)	80%
7	"	"	"	Et_2O	-100°C to -10°C	"	(60)	"	(40)	79%
8	"	"	"	"	-100°C to -50°C	"	(trace)	"	(>97)	96%
9	"	m-$NO_2C_6H_4$	**2d c**	THF	-100°C to +5°C	**3d**	(100)	**4d**	(0)	71%
10	"	"	"	Et_2O	-100°C to -10°C	"	(40)	"	(60)	71%
11	"	"	"	"	-100°C to -50°C	"	(trace)	"	(>97)	68%

a : Yields of isolated products after purification by flash chromatography. b : Yields evaluated from ^1H NMR spectra on yhe basis of the relative integrations.

Electron-deficient α-silyloxy-α,β-unsaturated esters of cis stereochemistry, such as (Z)-2-(*p*-chloro- and *m*-nitrophenyl)-1-*tert*butyldimethylsilyloxy methyl propenoates **2c$_c$** and **2d$_c$** respectively, were also investigated (Table 1, entries 6-11). Similar levels of selectivity as those previously observed with the model compound **2a$_c$** could be reached (entries 6, 8, 9 and 11). Indeed, reactions carried out in THF yielded the α-keto primary alcohols **3c-d** specifically (entries 6 and 9) whereas the silyloxy analogues **4c-d** could be almost exclusively formed in ether (entries 8 and 11). However, it is worth mentioning that reactions performed in ether had to be carefully monitored and quenched at a lower temperature than previously in order to avoid desilylation (entries 8, 11 *vs* 7, 10) which, in these cases, appeared to be a favorable process above -50°C.

The use of the non-substituted, commercially available ethyl pyruvate was next envisioned in order to expand the scope of the reaction. With this reagent, both the very hindered triisopropyl silyl (TIPS) group and its tBDMS analogue were easily introduced by treatment with the appropriate trifluorosulfonates, yielding the expected enol ethers **6a** and **6b** in 77% and 73% respectively. Curiously, desilylation did not take place at all regardless of the conditions (solvent, temperature) or the substrates used (Table 2). In sharp contrast to the case of the aromatic analogues **2a-d$_c$**, 1-hydroxymethyl enoxy silanes **8a-b** were almost exclusively formed in the medium as revealed by TLC monitoring. Even when the temperature was allowed to rise to -10°C, only a trace of the α-silyloxy ketones **7a-b** was detected. This trend was considerably reversed during hydrolysis upon which the silyl migration proceeded intensively. Thus, the silyloxy ketone **7b** was isolated in every case as the sole product from the TBS derivative **6b**, resulting from a complete silyl migration (entries 1,2). A lower degree of selectivity was observed with the TIPS derivative **6a**, and mixtures of 1-hydroxymethyl enoxy silane **8a** and α-silyloxy ketone **7a** were generally obtained. In these cases, the more robust TIPS group was less prone to shift, and only a partial migration occured upon hydrolysis. The improved level of migration observed when hydrolysis was performed at -60°C rather than at -10°C (entries 5 *vs* 4) is a somewhat surprising and as yet unclear result.

Table 2. Addition of LAH to enol ethers derived from ethyl pyruvic ester **6**



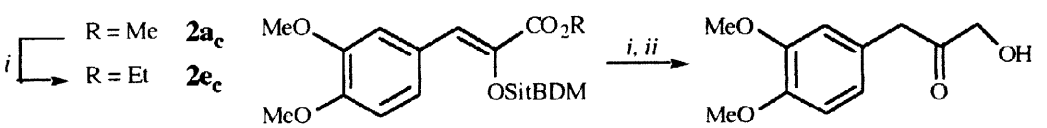
6a R^1, R^2, R^3 = iPr **7a** **8a**

6b R^1 = tBu R^2, R^3 = Me **7b** **8b**

entries	substr.	solvent	conditions	ratio **7** / **8**	combined yield[a]
1	**6b**	THF	-100°C to -20°C	100 0	93%
2	"	Et_2O	-100°C to -10°C	100 0	93%
3	**6a**	THF	-100°C to -10°C	57 43	100%
4	"	Et_2O	-100°C to -10°C	15 85	100%
5[b]	"	"	-100°C to -10°C	40 60	88%

a : Ratios and yields determinated from the ^{1}H NMR spectra on the basis of the relative integrations.
b : Hydrolysis was performed at -60°C.

In order to determine whether the aryl moiety or the nature of the ester group (methyl *vs* ethyl and *a fortiori* other alkyls) was responsible for the desilylation process, the ethyl ester **2e$_c$** was also investigated. **2e$_c$** was obtained from **2a$_c$** by transesterification with 1.3 equivalents of NaOEt in ethanol[12], the reaction of **2e$_c$** itself with LAH in THF from -100°C to -5°C yielded the keto primary alcohol **3a** in 83% (Scheme 2).



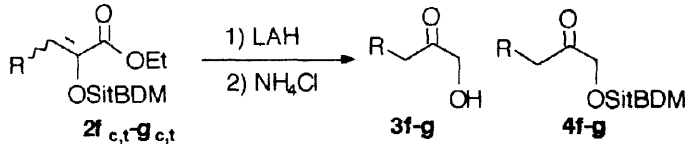
i : 1.3 eq. NaOEt, EtOH, r.t., 2h30, 50%. *ii* : 1 eq. LAH, THF, -100°C to -5°C, then aq. NH_4Cl, 83%.

Scheme 2

It is clear from this last result that substitution on the double bond of type **2** substrates is a prerequisite for desilylation to occur upon reduction with LAH.

Only Z-propenoates (**2a$_c$-e$_c$**) have been so far studied. Since the substitution pattern of the double bond of the starting species **2** seems to influence considerably the outcome of the reaction, particularly with respect to the desilylation process for reactions conducted in THF (see Table 1, entries 1, 2, 4, 6, 9 *vs* Table 2, entries 1, 3), we became next interested in studying the behaviour of E-2-silyloxy propenoates **2$_t$** in our reaction. Both Z and E isomers of two other aromatic substrates, **2f$_c$**, **2f$_t$** and **2g$_c$**, **2g$_t$**, bearing the phenyl and the furyl groups, respectively, were then considered for this purpose. Additionally, the two latter (**2g$_c$** and **2g$_t$**) gave us the opportunity to evaluate the compatibility of our method with molecules bearing a sensitive functionality. Results are collected in Table 3.

Table 3. Addition of LAH to both Z and E isomers of 3-phenyl- and 3-furyl-2-*tert*Butyldimethylsilyloxy ethyl propenoates **2f$_{c,t}$** and **2g$_{c,t}$**



2f$_{c,t}$-g$_{c,t}$ **3f-g** **4f-g**

entry	R	stereoch.	substrate	solvent	conditions	ratio **3**/**4**	combined yield[a]
1	C_6H_5	Z	**2f$_c$**	THF	-100°C to 20°C	**3f** (100) **4f** (0)	77%
2	"	"	"	Et_2O	-100°C to -15°C	" (20) " (80)	83%
3	"	E	**2f$_t$**	THF	-100°C to 0°C	" (100) " (0)	93%
4	"	"	"	Et_2O	-100°C to -20°C	" (52) " (27)	79%
5	furyl	Z	**2g$_c$**	THF	-100°C to20°C	**3g** (100) **4g** (0)	77%
6	"	"	"	Et_2O	-100°C to -15°C	" (10) " (90)	73%
7	"	E	**2g$_t$**	THF	-100°C to +5°C	" (100) " (0)	73%
8	"	"	"	Et_2O	-100°C to -20°C	" (53) " (47)	86%

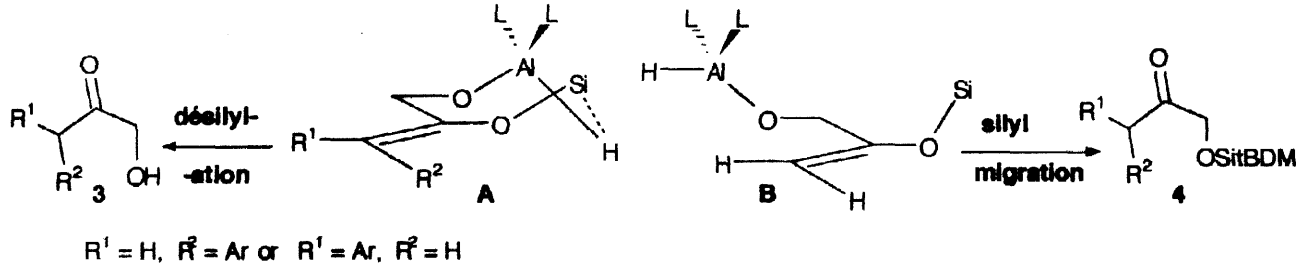
a : Yields of isolated products after purification by flash chromatography.

All four compounds reacted smoothly with LAH, providing evidence that our procedure tolerates both Z and E stereochemistry as well as sensitive units, here examplified by the furyl moiety. Both compounds of Z stereochemistry **2f$_c$** and **2g$_c$** showed the same behaviour than their analogues **2a$_c$-e$_c$**, providing silyloxy ketones **4f** and **4g** selectively when reactions were conducted in Et_2O (entries 2 and 6) and keto primary alcohols **3f** and **3g** solely in THF (entries 1 and 5). The same specificity in favour of **3f** and **3g** was obtained with the E isomers **2f$_t$** and **2g$_t$** through reductions in THF (entries 3 and 7). However, a decrease of the usual selectivity was observed for reactions driven in Et_2O, which, in turn, gave equal proportions of **3f** and **4f** or even were **3g** selective (entries 4 and 8 *vs* Table 1, entries 3, 5, 8 and 11).

Desilylation of tBDMS ethers by DIBAH has recently been reported by Corey et *al.*[4], and the authors mentioned that 2 hours of reaction at room temperature were required for the desilylation to proceed to completion. According to that, and in close connection with our results, it is reasonnable to assume that systems, in which a silyloxy group and a proximal tethered alkoxyhydridoaluminate can interact

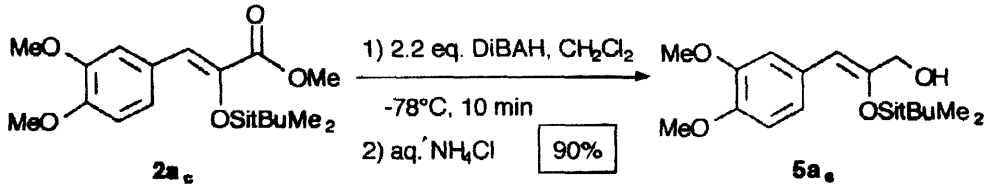
intramolecularly, might undergo desilylation easier than do simple silyloxy ethers through intermolecular reactions[4]. The facile desilylation we observed in THF for the substituted propenoates $2a_c$-$2g_c$ and $2f_t$-$2g_t$ may be rationalized by such an entropic activation through a cyclic seven-membered ring transition state as depicted in Figure 2. Accordingly, the alkoxyhydridoaluminates resulting from the initial reaction between LAH and the substrates probably adopt the less sterically demanding conformation in which the allylic strain is minimized (transition state **A**). Such a conformation, in which the silyl moiety and the newly created hydridoaluminate are forced in close proximity, may allowed an intramolecular desilylation to occur to finally yield the α-keto primary alcohols **3**. This hypothesis is supported by the rapidity at which the complete desilylation proceeded for our reactions performed at low temperature as compared with the Corey' s team results[4].

Figure 2. possible transition state for the desilylation of type **2** esters in THF solution.



In absence of substituent at the terminus of the double bond, the aluminium and the silicon atoms probably hold in a more distal arrangement due to a greater steric flexibility. This would lead to the more stable, sterically permitted transition states **B**, in which intramolecular desilylation is prevented, regardless of the solvent used. It then results only a silyl migration process which probably occurs via an intermolecular pathway, and which is completed upon hydrolysis.

This mechanistic speculation should be corroborated by a reaction wherein DiBAH is used as the reducer. Since this reagent bears one hydrogen atom, reduction should occur without desilylation. Indeed, we were delighted to find that reduction of the ester function of $2a_c$ readily occured without any desilylation or silyl migration by treatment with 2.2 equivalents of DiBAH at -78°C following by a usual aqueous NH_4Cl hydrolysis, yielding the expected allyl alcohol $5a_c$ (scheme 3).



Scheme 3

This compound was stable upon NH_4Cl hydrolysis but on the other hand was prone to silyl migration upon purification by flash chromatography on silica gel or storage in a dichloromethane solution at room temperature. The same trend could be observed with the other unsaturated esters $2b_c$-d_c and **6a-b** which readily

yielded the corresponding allyl alcohols **5b$_c$-d$_c$** and **8a-b** upon the action of 2.2 equivalents of DiBAH (see experimental section).

The remarkable solvent effect enabling us to isolate keto α-primary alcohols **3a,c-d,f-g** when reactions were run in THF or α-silyloxy ketones **4a-g** when Et_2O was used as the solvent, especially in the cis series (Table 1, entries 2 *vs* 3, 7 *vs* 8, 11 vs 9 and Table 3, entries 1 *vs* 2, 5 *vs* 6), could be reliable to a critical change of the aggregates of the alkoxyhydridoaluminates generating in the medium[13], depending on Et_2O or THF was used as the solvent. In fact, our results could be supported by a recent article focusing on the structural assignment of sodium and lithium alkoxyhydridoaluminates of defined stoechiometry[14]. It was found, especially when hindered alkoxy groups were involved, that poorly alkoxylated species (monoalkoxytrihydridoaluminates and dialkoxydihydridoaluminates) strongly differ structurally at the solid state, depending on they originate from a THF or an Et_2O solution. Species having crystallised from a THF solution were shown to have one or two free hydride(s), the metal being preferentially coordinated to the oxygen atoms of the alkoxy groups (ref.14, Figures 3, 4, 6). In contrast, structures originating from an Et_2O solution have their hydrides "blocked" by coordination to the metal (ref. 14, Figures 1 and 5). Regarding our hypothesis, the fundamental requirement for the desilylation of type **2** compounds to occur (regardless of the mode by which it proceeds, *i.e.* intra- or intermolecularly) is that the alkoxyhydridoaluminated species, in their existing form in solution, must have at least one free hydride. Due to the stoechiometric relationship between LAH and substrates **2**, it is likely that monoalkoxytrihydridoaluminates (and eventually dialkoxydihydridoaluminates due to disproportionation[14]), be the preponderant existing species. By close analogy with the above observations[14], it is likely that these active species bear one or two hydrides free which can then accomplished the desilylation, for reactions carried out in THF. On the other hand, the hydrides would be preferentially coordinated to lithium in Et_2O, thus precluding any further desilylation. However, this rationale seems to be concerned only with Z-substrates **2$_c$**, the E isomers lacking of selectivity in Et_2O. This highlights the complexity of the reaction, and suggests that the structural organization of alkoxyhydridoaluminates of allylic alcohols in solution may be stereochemically dependent.

The fact that similar results were obtained whatever the tBDMS derivatives **2a$_c$, c$_c$-g$_c$** or a tBDPS analogue **2b$_c$** was used suggests that the migratory aptitude of both the TBDMS and the tBDPS groups in strongly reductive or basic conditions is similar. On the other hand, the lesser level of silyl migration observed with the TIPS group (Table 2, entries 3-5 *vs* 1-2) confirms one more time the better robustness of this last as compared with its TBDMS and tBDPS analogues[8].

In summary, we have adapted a known methodology[2] in order to chemoselectively reduce the ester function of enolizable α-keto esters in two steps. Upon treatment of the readily accessible silyloxy propenoates **2** with LAH, the corresponding keto α-primary alcohols **3** were exclusively obtained for reactions carried out in THF. Improvement of the scope of this reduction was achieved by performing the reductions in Et_2O, in which the competing formation of the α-silyloxy ketones **4** was observed with good (with the Z-substrates) or no (with the E-substrates) selectivity. The facile hydroxy ketones **3** formation probably resulted from the ester reduction with a concomittant partial intramolecular desilylation which was completed during hydrolysis. The use of Et_2O as a solvent supressed this desilylation and a silyl migration from the enolic oxygen to the newly created

alcohol function was the major pathway, yielding the silyloxy ketones. Unsubstituted α-keto esters only exhibit this last kind of reactivity and exclusively yielded α-silyloxy ketones. Due to the recent emergence of numerous and diversified modes of preparation of α-keto esters[15], this work will undoubtly offer new applications in synthesis.

EXPERIMENTAL

General procedures and instrumentation

Mp determinations were carried out on a Reichert-Thermopan apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a Bruker AM 300 spectrometer, as solutions in deuteriochloroform. Chemical shifts are referenced to tetramethylsilane and *J*-values are given in Hz and rounded to the nearest 0.1 Hz. Mass spectral analyses were performed on a Ribermag 10-10 mass spectrometer. For flash chromatography, Merck silical gel 60 (230-400 mesh ASTM) was used. THF was freshly distilled over $LiAlH_4$, Et_2O over sodium and benzophenone and dichloromethane over CaH_2. Dry glassware for moisture-sensitive reactions was obtained by open-drying and assembly under argon. An inert atmosphere was obtained with a stream of dry argon and glassware equipped with rubber septa ; the transfer of reagents was performed by syringes or cannula techniques.

General procedure for the silylation of type 1 enolic α-keto esters

In a 50 ml three-necked flask equipped with a funnel and a rubber septum, fitted and flushed three times with argon, the ester **1** (1 equivalent) and 1,4-dimethylaminopyridine (0.2 equivalent) were dissolved in anhydrous dichloromethane (5ml/mmol). Triethylamine (1 equivalent) and a 1M solution of *tert*butyldimethylsilylchloride in dichloromethane or *tert*butyldiphenylchlorosilane (1.1 equivalents) were added dropwise. The resulting solution was stirred vigorously until total disappearance of the starting material, and the solvent was carefully evaporated. The residue was dissolved in diethyl ether (Et_2O, 5ml/mmol) and the residual ammonium salt was extracted three times by water. After drying over Na_2SO_4 and evaporation of the solvent, the oily crude mixture was purified by flash chromatography (petroleum ether (PE) : Et_2O 6-4).

Z-2-[3,4-Dimethoxyphenyl]-1-*tert*butyldimethylsilyloxy methyl propenoate $2a_c$

Yield 85%, white solid, m.p. 30°C. ^1H NMR δ 0.1 (s, 6H), 0.91 (s, 9H), 3.75 (s, 3H), 3.84 (s, 2 x 3H), 6.77 (m, 2H), 7.2 (m, 2H). ^{13}C NMR δ -3.2, 19.1, 26.4, 52.5, 56.3, 56.5, 111.2, 113.3, 120, 124, 127.6, 139.5, 149, 149.7, 166.6. m/z (%) 354 (M^++2, <1), 353 (M^++1, 4), 352 (M^+, 30), 337 (10), 295 (93), 280 (22). Anal. Found: C, 63.77; H, 8.51. Calc. for $C_{18}H_{28}O_5Si$: C, 64.06; H, 8.36.

Z-2-[3,4-Dimethoxyphenyl]-1-*tert*butyldiphenylsilyloxy methyl propenoate $2b_c$

Yield 13%, colorless oil. ^1H NMR δ 1 (s, 9H), 3.12 (s, 3H), 3.88 (s, 3H), 3.95 (s, 3H), 6.78 (s, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 7.33-7.43 (m, 6H), 7.52 (dd, *J* = 8.3 Hz, *J* = 1.9 Hz, 1H), 7.7-7.75 (m, 4H). ^{13}C NMR δ 19.9, 26.7, 51.2, 55.9, 56.1, 110.8, 113.2, 118, 123.6, 127.5, 127.8, 129.4, 133.7, 134.7, 139.4, 148.6, 149.3, 165.2. m/z (%) 478 (M^++2, <1), 477 (M^++1, 7), 476 (M^+, 21), 461 (17), 419 (71), 417 (6). Anal. Found: C, 70.73; H, 6.67. Calc. for $C_{28}H_{32}O_5Si$: C, 70.56; H, 6.76.

Z-2-[4-Chlorophenyl]-1-*tert*butyldimethylsilyloxy methyl propenoate $2c_c$

Yield 70%, orange solid, m.p. 47°C. ^1H NMR δ 0.13 (s, 6H), 0.93 (s, 9H), 3.81 (s, 3H), 6.78 (s, 1H), 7.29 (d, *J* = 8.6 Hz, 2 x 1H), 7.62 (d, *J* = 8.6 Hz, 2 x 1H). ^{13}C NMR δ -3.9, 18.6, 25.8, 52.2, 117.6, 128.4, 131, 132.6,

133.6, 140.7, 165.7. m/z (%) 330 (M^++2, <1), 329 (M^++1, 4), 328 (M^++2 + M^+, <1), 327 (M^++1, 4), 326 (M^+, 8), 291 (93), 269 (22), 254 (). Anal. Found: C, 58.85; H, 7.11. Calc. for $C_{16}H_{23}O_3ClSi$: C, 58.79; H, 7.09.

Z-2-[3-Nitrophenyl]-1-*tert*butyldimethylsilyloxy methyl propenoate 2d$_c$

Yield 81%, white solid, m.p. 59°C. ^{1}H NMR δ 0.16 (s, 6H), 0.93 (s, 9H), 3.81 (s, 3H), 6.84 (s, 1H), 7.49 (t, J = 8 Hz, 1H), 7.87 (ddd, J = 8 Hz, J = 2.1 Hz, J = 1.1 Hz, 1H), 8.1 (ddd, J = 8 Hz, J = 1.8 Hz, J = 1.1 Hz, 1H), 8.63 (dd, J = 2.1 Hz, J = 1.8 Hz, 1H). ^{13}C NMR δ -3.8, 18.6, 25.6, 52.4, 115.9, 122.5, 124, 129, 135.4, 135.8, 142.5, 148.2, 165.2. m/z (%) 339 (M^++2, <1), 338 (M^++1, 6), 337 (M^+, 34), 293 (93), 280 (22), 265 (). Anal. Found: C, 57.12; H, 6.62. Calc. for $C_{16}H_{23}O_5NSi$: C, 56.96; H, 6.87.

Z-2-[3,4-Dimethoxyphenyl]-1-*tert*butyldimethylsilyloxy ethyl propenoate 2e$_c$

In a 50 ml two-necked flask fitted and flushed three times with argon, the ester **2a** (0.63 g, 1.79 mmol) was dissolved in anhydrous ethanol (9 ml). Sodium (53 mg, 1.3 equivalents) was introduced in small portions over 15 minutes. The solution was then stirred for a further 2h30 and hydrolyzed by 10 ml of an aqueous solution of NH_4Cl. A volume of dichloromethane (9 ml) was added, and after decantation, the aqueous phase was saturated by NaCl and extracted three times by dichloromethane. The organic layer was dried over Na_2SO_4, filtered and carefully evaporated, yielding a yellow oily crude mixture which was purified by flash chromatography on silica gel (PE : Et_2O 7-3).

Yield 50%, colorless oil. ^{1}H NMR δ 0.12 (s, 6H), 0.96 (s, 9H), 1.35 (t, J = 7.1 Hz, 3H), 3.89 (s, 2x 3H), 4.26 (q, J = 7.1 Hz, 2H), 6.81 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 1.9 Hz, 1H), 7.27 (dd, J = 8.1 Hz, J = 1.9 Hz, 1H). ^{13}C NMR δ -3.2, 14.3, 18.6, 25.9, 55.8, 56, 61.2, 110.6, 112.7, 119.2, 123.4, 127.1, 139.3, 148.4, 149, 165.7.

General procedure for the formation of ***2f and 2g*** *via the Wittig-Horner reaction*

In a 50 ml three-necked flask equipped with a funnel, a low temperature thermometer and a rubber septum, fitted and flushed three times with argon, the 2-diphenylphosphine oxide-2-*tert*butyldimethylsilyloxy ethyl acetate (1 equivalent) was dissolved in anhydrous THF (5ml/mmol) and HMPA (3 equivalents). This solution was cooled to -78°C and commercially available 1M solution of lithium *bis*trimethylsilyl amide in THF (1.1 equivalents) was added dropwise. The resulting pale yellow cold solution was stirred vigorously for ten minutes at -78°C and a THF solution of the appropriate aldehyde (benzaldehyde or furfural (1,1 equivalents, 5 ml of solvent/mmol)) was added dropwise. The cryogenic bath was then removed and the resulting pale yellow solution was stirred vigorously to room temperature, stirred for an additional 1 hour and quenched with an aqueous solution of NH_4Cl. THF was carefully evaporated, and the aqueous layer was extracted three times with petroleum ether. After drying over Na_2SO_4 and evaporation of the solvent, the oily crude mixtures were purified by flash chromatography (PE : Et_2O 98-2).

Z-3-[Phenyl]-1-*tert*butyldimethylsilyloxy ethyl propenoate 2f$_c$

Yield 50%, colorless oil. ^{1}H NMR δ 0.13 (s, 6H), 0.95 (s, 9H), 1.37 (t, J = 7.15 Hz, 3H), 4.28 (q, J = 7.15 Hz, 2H), 6.87 (s, 1H), 7.28 (t, J = 8 Hz, 2H), 7.37 (dd, J = 8 Hz, J = 1.1 Hz, 1H), 7.68 (dd, J = 8 Hz, J = 1.1 Hz, 1H). ^{13}C NMR δ -3.9, 14.3, 18.6, 25.8, 61.3, 118.9, 128, 128.1, 129.8, 134.2, 140.7, 165.5. m/z (%) 308 (M^++2, <1), 307 (M^++1, <1), 306 (M^+, 3), 291 (5), 249 (90). Anal. Found: C, 67.00; H, 8.32. Calc. for $C_{16}H_{23}O_5NSi$: C, 66.62; H, 8.55.

E-3-[Phenyl]-1-*tert*butyldimethylsilyloxy ethyl propenoate 2f$_t$

Yield 7%, colorless oil. ^{1}H NMR δ 0.24 (s, 6H), 1 (s, 9H), 1.13 (t, J = 7.15 Hz, 3H), 4.12 (q, J = 7.15 Hz, 2H), 6.43 (s, 1H), 7.1-7.3 (m, 5H). ^{13}C NMR δ -4.7, 13.7, 18.3, 25.6, 60.9, 120.1, 127.1, 127.8, 128.7, 129.8, 134.7, 165.

Z-3-[Furanyl]-1-*tert*butyldimethylsilyloxy ethyl propenoate 2g$_c$

Yield 42%, colorless oil. ^{1}H NMR δ 0.2 (s, 6H), 0.97 (s, 9H), 1.32 (t, J = 7.15 Hz, 3H), 4.23 (q, J = 7.15 Hz, 2H), 6.44 (ddd, J = 3.5 Hz, J = 1.9 Hz, J = 0.5 Hz, 1H), 6.76 (dd, J = 3.5 Hz, J = 0.5 Hz, 1H), 6.81 (d, J = 0.5 Hz, 1H), 7.41 (dt, J = 1.9 Hz, J = 0.5 Hz, 1H). ^{13}C NMR δ -3.6, 14.3, 18.7, 25.9, 61.2, 108.3, 111.8, 112.5, 138.6, 142.3, 150.1, 165. m/z (%) 281 (M-15, 7), 265 (4), 239 (87). Anal. Found: C, 61.05; H, 7.89. Calc. for $C_{16}H_{23}O_5NSi$: C, 60.94; H, 8.16.

E-3-[Furanyl]-1-*tert*butyldimethylsilyloxy ethyl propenoate 2g$_t$

Yield 7%, colorless oil. ^{1}H NMR δ 0.18 (s, 6H), 0.95 (s, 9H), 1.32 (t, J = 7.15 Hz, 3H), 4.26 (q, J = 7.15 Hz, 2H), 6.28 (d, J = 0.5 Hz, 1H), 6.40 (ddd, J = 3.5 Hz, J = 1.9 Hz, J = 0.5 Hz, 1H), 6.99 (dd, J = 3.5 Hz, J = 0.5 Hz, 1H), 7.36 (dt, J = 1.9 Hz, J = 0.5 Hz, 1H). ^{13}C NMR δ -4.8, 14.1, 18.2, 25.6, 60.9, 111.3, 111.9, 112.5, 139.6, 142.1, 149, 164.4.

General procedure for the silylation of ethyl pyruvic ester

In a 50 ml two-necked flask equipped with a funnel and a rubber septum, fitted and flushed three times with argon, the ethyl pyruvic ester (1 equivalent) and triethylamine (1 equivalent) were dissolved in anhydrous dichloromethane (5ml/mmol). This solution was cooled to 0°C and *tert*butyldimethylsilyltrifluoromethanesulfonate or triisopropylsilyltrifluoromethanesulfonate (1.05 equivalents) were added dropwise. The resulting solution was stirred vigorously for a further two hours under reflux. The solvent was next carefully evaporated, the residue was dissolved in Et_2O (5ml/mmol) and the residual ammonium salt was extracted three times by water. After drying over Na_2SO_4 and evaporation of the solvent, the oily crude mixture was purified by flash chromatography (PE : Et_2O 8-2).

1-Triisopropylsilyloxy ethyl propenoate 6a

Yield 77%, colorless oil. ^{1}H NMR δ 0.82 (q, J = 6.7 Hz, 3 x 1H), 1.05 (d, J = 6.7 Hz, 6 x 3H), 1.28 (t, J = 7.1 Hz, 3H), 4.2 (q, J = 7.1 Hz, 2H), 4.81 (d, J = 1.1 Hz, 1H), 5.46 (d, J = 1.1 Hz, 1H). ^{13}C NMR δ 12.4, 14.1, 17.8, 61, 102.3, 147.9, 164.4.

1-*Tert*butyldimethylsilyloxy ethyl propenoate 6b

Yield 73%, colorless oil. ^{1}H NMR δ 0.13 (s, 6H), 0.94 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H), 4.2 (q, J = 7.1 Hz, 2H), 4.84 (d, J = 1 Hz, 1H), 5.49 (d, J = 1 Hz, 1H). ^{13}C NMR δ -3.9, 14.1, 18.2, 25.5, 61.1, 103.8, 147.6, 164.5.

General procedure for the reduction of 1-trialkylsilyloxy unsaturated esters **2a-g and 6a-b with $LiAlH_4$.**

1 Mmol of substrate was placed in a 25 ml two-necked flask and purged twice with an argon atmosphere. Freshly distilled THF or Et_2O (5 ml) was added, and the solution was cooled to -100°C (external temperature). After 15 min, a commercially available solution of $LiAlH_4$ 1M in THF (1 ml, 1 equivalent) was added dropwise. The mixture was warmed gradually and the reaction monitored by tlc. When the starting material had completely disappeared, an aqueous NH_4Cl solution was carefully added, and then the reaction mixture allowed to warm to room temperature. The resulting gelatinous solution was filtered on Celite and

silica, and washed with Et_2O and water. After decantation, the aqueous phase was saturated with NaCl and extracted three times with Et_2O for reactions carried out in Et_2O or five times with ethyl acetate for reactions performed in THF. The organic layer was dried 24h over Na_2SO_4, filtered and evaporated (without heating in the case of the silyloxy compounds due to their volatility). The crude mixture was purified by flash chromatography on silica gel (PE : ethyl acetate 5-5 in the case of α-hydroxy ketones **3a,c-d**, PE : Et_2O 5 : 5 in the case of **3f-g**, and PE : Et_2O 8-2 in the case of α-silyloxy ketones **4a-d**, PE : Et_2O 9-1 in the case of **4f-g**, or directly studied by ^1H NMR as for the case of reductions of unbranched compounds **6a-b**.

3-[3,4-Dimethoxyphenyl]-2-oxo propanol 3a

Yield 85% from **2a**, 93% from **2b**, 83% from **2e**, colorless oil. ^1H NMR δ 3.02 (t, J = 4.1 Hz, 1H, OH), 3.65 (s, 2H), 3.85 (s, 2 x 3H), 4.27 (d, J = 4.1 Hz, 2H), 6.7 (d, J = 2 Hz, 1H), 6.74 (dd, J = 8.1 Hz, J = 2 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H). ^{13}C NMR δ 45.2, 55.8, 55.8, 67.4, 111.5, 112.3, 121.5, 125.1, 148.4, 149.2, 207.8. m/z (%) 212 (M^++2, <1), 211 (M^++1, 4), 210 (M^+, 41), 193 (10), 179 (17), 151 (100). Anal. Found: C, 62.35; H, 6.62. Calc. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71.

3-[4-Chlorophenyl]-2-oxo propanol 3c

Yield 80%, white solid, m.p. 57°C ^1H NMR δ 3.05 (t, J = 4.7 Hz, 1H, OH), 3.68 (s, 2H), 4.28 (d, J = 4.7 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2 x 1H), 7.30 (d, J = 8.5 Hz, 2 x 1H). ^{13}C NMR δ 44.8, 67.8, 129, 130.7, 131.1, 133.5, 206.8. m/z (%) 188 (M^++2, <1), 187 (M^++1, 4), 186 (M^++2, M^+, <1), 185 (M^++1, 4), 184 (M^+, 8), 169 (2), 167 (5), 155 (5), 153 (26), 148 (75), 127 (54), 125 (100). Anal. Found: C, 58.12; H, 5.02. Calc. for $C_9H_9O_2Cl$: C, 58.55; H, 4.91.

3-[3-Nitrophenyl]-2-oxo propanol 3d

Yield 71%, white solid, m.p. 89°C. ^1H NMR δ 3.05 (t, J = 3.6 Hz, 1H, OH), 3.85 (s, 2H), 4.37 (d, J = 3.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.55 (ddd, J = 7.6 Hz, J = 2.2 Hz, J = 1.6 Hz, 1H), 8.08 (dd, J = 2.2 Hz, J = 1.6 Hz, 1H), 8.15 (dt, J = 7.6 Hz, J = 2.2 Hz, 1H). ^{13}C NMR δ 44.5, 68.1, 122.6, 124.4, 129.7, 134.5, 135.1, 135.7, 205.8. m/z (%) 197 (M^++2, <1), 196 (M^++1, 4), 195 (M^+, 29), 178 (6), 164 (17), 149 (63), 136 (100). Anal. Found: C, 55.51; H, 4.92. Calc. for $C_9H_9O_4N$: C, 55.38; H, 4.64.

3-[Phenyl]-2-oxo propenol 3f

Yield 82% from **2f$_c$**, 93% from **2f$_t$**, white solid, m.p. 59°C. ^1H NMR δ 3 (t, J = 4.8 Hz, 1H, OH), 3.72 (s, 2H), 4.42 (d, J = 4.8 Hz, 2H), 7.15-7.4 (m, 5H) ^{13}C NMR δ -3.8, 18.6, 25.6, 52.4, 115.9, 122.5, 124, 129, 135.4, 135.8, 142.5, 148.2, 165.2. m/z (%) 152 (M^++2, 3), 151 (M^++1, <1), 150 (M^+, 8), 91 (100). Anal. Found: C, 72.06; H, 6.62. Calc. for $C_{16}H_{23}O_5NSi$: C, 71.98; H, 6.71.

3-[Furanyl]-2-oxo propenol 3g

Yield 78% from **2g$_c$**, 63% from **2g$_t$**, colorless oil. ^1H NMR δ 2.96 (t, J = 4.6 Hz, 1H, OH), 3.75 (s, 2H), 4.28 (d, J = 4.6 Hz, 2H), 6.22 (dd, J = 2.4 Hz, J = 0.8 Hz, 1H), 6.34 (dd, J = 3.2 Hz, J = 1.9 Hz, 1H), 7.37 (dd, J = 1.9 Hz, J = 0.8 Hz, 1H). ^{13}C NMR δ 38.5, 67.7, 108.9, 110.8, 142.6, 146.4, 205.3. m/z (%) 143 (M^++3, <1), 142 (M^++2, 3), 141 (M^++1, 1), 140 (M^+, 11), 81 (98). Anal. Found: C, 59.73; H, 5.72. Calc. for $C_{16}H_{23}O_5NSi$: C, 59.99; H, 5.75.

3-[3,4-Dimethoxyphenyl]-1-*tert*butyldimethylsilyloxy propane 4a

Yield 77%, colorless oil. ^1H NMR δ 0.07 (s, 6H), 0.92 (s, 9H), 3.61 (s, 2H), 3.74 (s, 2 x 3H), 4.24 (s, 2H), 6.73 (s, 1H), 6.74 (d, J = 8 Hz, 1H), 6.81 (d, J = 8 Hz, 1H). ^{13}C NMR δ -5.5, 18.3, 25.8, 44.9, 55.8, 55.9, 68.7, 111.3, 112.5, 121.6, 126.1, 148.1, 149, 208.3. m/z (%) 326 (M^++2, <1), 325 (M^++1, 2), 324 (M^+, 7), 293 (15), 201 (70), 151 (93). Anal. Found: C, 62.65; H, 8.93. Calc. for $C_{17}H_{28}O_4Si$: C, 62.92; H, 8.69.

3-[3,4-Dimethoxyphenyl]-1-*tert*butyldiphenylsilyloxy propane 4b

Yield 79%, colorless oil. ^{1}H NMR δ 1.11 (s, 9H), 3.75 (s, 2H), 3.8 (s, 3H), 3.86 (s, 3H), 4.27 (s, 2H), 6.68 (dd, J = 8 Hz, J = 1.8 Hz, 1H), 6.68 (d, J = 1.8 Hz, 1H), 6.78 (d, J = 8 Hz, 1H), 7.3-7.43 (m, 6H), 7.59-7.67 (m, 4H). ^{13}C NMR δ 19.6, 26.8, 45.1, 55.8, 55.9, 69.2, 110.5, 111.9, 121.6, 126.1, 127.8, 130, 132.4, 135.5, 149.1, 149.5, 208.3. m/z (%) 450 (M^++2, <1), 451 (M^++1, 3), 450 (13), 419 (18), 151 (97). Anal. Found: C, 72.15; H, 7.22. Calc. for $C_{27}H_{32}O_4Si$: C, 72.28; H, 7.19.

3-[4-Chlorophenyl]-2-oxo-1-*tert*butyldimethylsilyloxy propane 4c

Yield 96%, colorless oil. ^{1}H NMR δ 0.07 (s, 6H), 0.92 (s, 9H), 3.8 (s, 2H), 4.22 (s, 2H), 7.13 (d, J = 8.6 Hz, 2 x 1H), 7.28 (d, J = 8.6 Hz, 2 x 1H). ^{13}C NMR δ -5.5, 18.3, 25.8, 44.5, 68.9, 128.7, 130.9, 132.1, 132.9, 207.8. m/z (%) 302 (M^++2, <1), 301 (M^++1, 4), 300 (M^++2 + M^+, <1), 299 (M^++1, 4), 298 (M^+, 8), 269 (4), 267 (11), 263 (47), 241 (32), 125 (100). Anal. Found: C, 60.41; H, 7.50. Calc. for $C_{15}H_{23}O_2ClSi$: C, 60.28; H, 7.75.

3-[3-Nitrophenyl]-2-oxo-1-*tert*butyldimethylsilyloxy propane 4d

Yield 68%, colorless oil. ^{1}H NMR δ 0.1 (s, 6H), 0.92 (s, 9H), 3.87 (s, 2H), 4.25 (s, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.52 (ddd, J = 7.6 Hz, J = 2.1 Hz, J = 1.7 Hz, 1H), 8.07 (dd, J = 2.1 Hz, J = 1.7 Hz, 1H), 8.12 (dt, J = 7.6 Hz, J = 2.1 Hz, 1H). ^{13}C NMR δ -5.5, 18.2, 25.8, 44.6, 69.1, 122.1, 124.7, 129.3, 135.7, 136, 148.3, 207.3. m/z (%) 311 (M^++2, <1), 310 (M^++1, 5), 309 (M^+, 34), 263 (50), 251 (22), 136 (100). Anal. Found: C, 58.50; H, 7.37. Calc. for $C_{15}H_{23}O_4NSi$: C, 58.22; H, 7.49.

3-[Phenyl]-2-oxo 1-*tert*butyldimethylsilyloxy propane 4f

Yield 66% from **2f$_c$**, 26% from **2f$_t$**,, colorless oil. ^{1}H NMR δ 0.05 (s, 6H), 0.9 (s, 9H), 3.8 (s, 2H), 4.22 (s, 2H), 7.1-7.35 (m, 5H). ^{13}C NMR δ -5.6, 18.3, 25.7, 45.4, 68.8, 126.9, 128.6, 129.5, 130.2, 204.2. m/z (%) 264 (M^+, 8), 249 (17), 207 (100). Anal. Found: C, 67.97; H, 9.11. Calc. for $C_{16}H_{23}O_5NSi$: C, 68.13; H, 9.14.

3-[Furanyl]-2-oxo 1-*tert*butyldimethylsilyloxy propane 4g

Yield 40% from **2g$_c$**, 67% from **2g$_t$**, colorless oil. ^{1}H NMR δ 0.06 (s, 6H), 0.9 (s, 9H), 3.84 (s, 2H), 4.23 (s, 2H), 6.18 (dd, J = 3.2 Hz, J = 0.8 Hz, 1H), 6.32 (dd, J = 3.2 Hz, J = 1.9 Hz, 1H), 7.34 (dd, J = 1.9 Hz, J = 0.8 Hz, 1H). ^{13}C NMR δ -5.6, 18.3, 25.7, 38.1, 68.8, 108.2, 110.6, 142, 147.6, 205.6. m/z (%) 254 (M^+, 19), 239 (10), 197 (100). Anal. Found: C, 61.02; H, 8.98. Calc. for $C_{16}H_{23}O_5NSi$: C, 61.37; H, 8.71.

2-Oxo 1-triisopropylsilyloxy propane 7a

Yield 57%, colorless oil. ^{1}H NMR δ 1.05 (d, J = 6.7 Hz, 6 x 3H), 1.17 (q, J = 6.7 Hz, 3 x 1H), 2.29 (s, 3H), 4.19 (s, 2H).

2-Oxo 1-*tert*butyldimethylsilyloxy propane 7b

Yield 93%, colorless oil. ^{1}H NMR δ 0.04 (s, 6H), 0.86 (s, 9H), 2.11 (s, 3H), 4.09 (s, 2H). ^{13}C NMR δ 0.9, 18.2, 25.7, 25.9, 69.5, 209.2.

General procedure for the reduction of 1-trialkylsilyloxy unsaturated esters **2a,c-d and 6a-b by DibAH**

In a 50 ml two-necked flask equipped with a funnel and a rubber septum, fitted and flushed three times with argon, the 1-silyloxy unsaturated ester (1 equivalent) was dissolved in anhydrous dichloromethane (5ml/mmol). This solution was cooled to -78°C and 2.2 equivalents of DiBAH were added dropwise. The resulting solution was stirred vigorously for a further ten minutes, and carefully quenched at -70°C by aqueous NH_4Cl. After the temperature was allowed to warm to approximately 0°C, the resulting gelatinous solution was filtered on Celite and silica, and washed with dichloromethane and water. The aqueous phase was extracted

three times with dichloromethane, the organic layer was subsequently dried over Na_2SO_4, filtered and evaporated (without heating in the case of the silyloxy compounds due to their volatility). The resulting allylic alcohols were pure enough to be directly studied by ^1H NMR without purification.

Z-3-[3,4-Dimethoxyphenyl]-2-*tert*butyldimethylsilyloxy prop-2-enol 5a$_c$

Yield 90%, white solid, m.p. 60°C ^1H NMR δ 0.11 (s, 6H), 0.91 (s, 9H), 1.92 (s large, 1H, OH), 3.85 (s, 2 x 3H), 4.1 (s, 2H), 5.65 (s, 1H), 6.77 (d, J = 8 Hz, 1H), 7.04 (dd, J = 8.3 Hz, J = 1.6 Hz, 1H), 7.08 (d, J = 1.6 Hz, 1H). ^{13}C NMR δ -3.5, 18.4, 25.9, 55.8, 55.8, 65.5, 108, 110.7, 111.9, 121.3, 128.8, 147.3, 148.3, 149.9. m/z (%) 326 (M^++2, <1), 325 (M^++1, 2), 324 (M^+, 10), 267 (32), 236 (20), 151 (100).

Z-3-[3,4-Dimethoxyphenyl]-2-*tert*butyldiphenylsilyloxy prop-2-enol 5b$_c$

Yield 89%, colorless oil. ^1H NMR δ 1.06 (s, 9H), 1.2 (t, J = 6.5 Hz, 1H, OH), 3.77 (d, J = 6.5 Hz, 2H), 3.82 (s, 3H), 3.88 (s, 3H), 5.68 (s, 1H), 6.83 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 1.9 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 7.35-7.45 (m, 6H), 7.75 (dd, J = 7.8 Hz, J = 1.6 Hz, 2 x 2H). ^{13}C NMR δ 19.2, 26.9, 55.9, 56, 65.2, 108.2, 110.7, 111.9, 121.6, 127.6, 127.8, 128, 128.5, 130, 130.2, 133.6, 135.2, 135.5, 148.3, 149.6, 149.9.

Z-3-[4-Chlorophenyl]-2-*tert*butyldimethylsilyloxy prop-2-enol 5c$_c$

Yield 86%, pale yellow oil, ^1H NMR δ 0.11 (s, 6H), 0.91 (s, 9H), 1.85 (t, J = 5.8 Hz, 1H, OH), 4.11 (d, J = 5.8 Hz, 2H), 5.69 (s, 1H), 7.22 (d, J = 8.6 Hz, 2 x 1H), 7.45 (d, J = 8.6 Hz, 2 x 1H). ^{13}C NMR δ -3.6, 18.4, 25.8, 65.2, 106.9, 128.1, 129.8, 131.3, 134.3, 151.8.

Z-3-[3-Nitrophenyl]-2-*tert*butyldimethylsilyloxy prop-2-enol 5d$_c$

Yield 81%, pale yellow oil ^1H NMR δ 0.17 (s, 6H), 0.93 (s, 9H), 1.95 (t, J = 6.2 Hz, 1H, OH), 4.16 (d J = 6.2 Hz, 2H), 5.8 (s, 1H), 7.4 (t, J = 8 Hz, 1H), 7.7 (ddd, J = 8 Hz, J = 2 Hz, J = 1.1 Hz, 1H), 7.97 (ddd, J = 8 Hz, J = 2 Hz, J = 1.1 Hz, 1H), 8.49 (t, J = 2 Hz, 1H). ^{13}C NMR δ -3.5, 18.4, 25.8, 64.8, 105.2, 120.6, 122.9, 128.7, 134.3, 137.6, 148.4, 154.

2-Triisopropylsilyloxy prop-2-enol 8a

Yield 88%, colorless oil ^1H NMR δ 1.05 (d, J = 6.7 Hz, 6 x 3H), 1.17 (q, J = 6.7 Hz, 3 x 1H), 1.2 (t, J = 5.6 Hz, 1H, OH), 3.95 (d, J = 5.6 Hz, 2H), 4.17 (d, J = 1.2 Hz, 1H), 4.28 (d, J = 1.2 Hz, 1H). ^{13}C NMR δ 12.5, 17.8, 64.2, 88.6, 157.8.

2-*Tert*butyldimethylsilyloxy prop-2-enol 8b

Yield 81%, colorless oil. ^1H NMR δ 0.17 (s, 6H), 0.92 (s, 9H), 1.88 (t, J = 6 Hz, 1H, OH), 3.94 (d, J = 6 Hz, 2H), 4.18 (d, J = 1.2 Hz, 1H), 4.32 (d, J = 1.2 Hz, 1H). ^{13}C NMR δ -4.7, 18.8, 25.6, 64.4, 89.7, 157.6.

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