On the Radical Brook Rearrangement. Reactivity of α-Silyl Alcohols, α-Silyl Alcohol Nitrite Esters, and *β*-Haloacylsilanes under Radical-Forming Conditions

M. D. Paredes and R. Alonso*

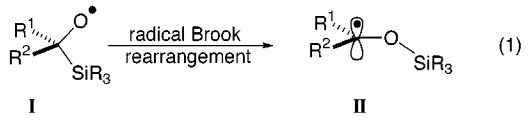
Departamento de Química Orgánica y Unidad Asociada al CSIC, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Received August 11, 1999

Two alkoxyl radical generation methods, lead tetraacetate treatment of alcohols and photolysis of nitrites, were applied to α-silyl alcohols **21** and to the corresponding nitrites **25** with a view to forming α-silyl alkoxyl radicals **23** and studying their possible radical Brook rearrangement to α-silyloxy carbon radicals **24**. LTA treatment of **21** led to their quick and efficient conversion into mixed acetyl-silyl acetals **33** under very mild conditions. Photolysis of α-alkylmonosubstituted α-silyl nitrites **25** to the corresponding aldehydes is considered to proceed through α-silyl alkoxyl radical intermediates **23**. A concerted process is, however, proposed for the case of the benzyl nitrites analogues. On the basis of these results, it is postulated that resonance stabilization can have a major influence on the evolution of α-silyl alkoxyl radicals: should this stabilization be possible, they quickly evolve by α-silyl fragmentation; otherwise, they tend to undergo radical Brook rearrangement. It was also found that the radical Brook rearrangement of α-silyl cyclopropyloxyl radicals generated from *β*-bromoacylsilanes under standard tin-radical conditions is too slow to compete with *β*-fragmentation.

Introduction

Starting materials and intermediates featuring silicon-bearing groups are now common place in organic syntheses, regardless of whether the end-product does or does not contain silicon. Besides being able to protect sensitive functional groups (where silicon mainly behaves as an spectator preserving the integrity of the protected functionality), there are other instances where the presence of silicon in an organic species greatly affects its reactivity.[1] A notable example in the field of radical chemistry is the case of α-silyl alkoxyl radicals **I**, which because of the geminal silyl group can evolve to carbon radicals **II** (eq 1). This type of conversion, known as the



I II (1)

radical Brook rearrangement,[2] was initially proposed in 1981 to explain the formation of cyclopropanes **5** by photoreaction of acylsilanes **1** with electron-poor olefins **2** (Table 1, entry 1).[3] ESR spectroscopy subsequently showed the migration of the silyl group to be extraordinarily fast, proceeding even at −83 °C for the simple trimethylsilylmethyloxyl radical **7** (Table 1, entry 2).[4] At the same time it was successfully used as the basis of a new synthesis of cyclopentanols and cyclohexanols **13** from, respectively, *δ*- and *ϵ*-halogenated acylsilanes **10** (Table 1, entry 3).[5a]

As a result of the above reports, the radical Brook rearrangement came to be regarded as the process most likely to be undergone by α-silyl alkoxyl radicals, preferred over other processes usually followed by nonsilyl-substituted alkoxyl radicals. In fact further syntheses were based on the rearrangement of variously functionalized analogues of **11** (Table 1, entry 3), obtained from acylsilanes by 1,5- or 1,6-*exo* cyclization of carbon radicals.[5b] Moreover, an ab initio study of the rearrangement **14** → **16** (Table 1, entry 4) predicted energy barriers in total agreement with the experimentally observed ease of silyl migration.[6]

However, not all the results obtained to date have conformed to the above pattern. In particular it has been reported that α-silyl alkoxyl radicals **18**, formed from α,*β*-unsaturated epoxysilanes **17** (Table 1, entry 5), do not undergo the expected Brook rearrangement; instead they eject the trimethylsilyl radical, which subsequently re-

* To whom correspondence should be addressed. Fax 34-981-547085. e-mail: qoraa@correo.usc.es.

(1) For a recent review on the use of silyl groups to control stereochemistry, see: Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063−2192. For their use as tethers, see: Stork, G.; Suhi, M. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054−7056. Bols, M.; Skrydstrup, T. *Chem. Rev.* **1995**, *95*, 1253−1277. Fensterbank, L.; Malacria, M.; Sieburth, S. McN. *Synthesis* **1997**, 813−854. Hutchinson, J. H.; Daynard, T. S.; Gillard, J. W. *Tetrahedron Lett.* **1991**, *32*, 573−576.

(2) For the radical Brook rearrangement, see refs 3−8. The ionic rearrangement was known previously: Brook, A. G. *J. Am. Chem. Soc.* **1958**, *80*, 1886−1889. A review can be found in Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77−84. For a recent use of the ionic Brook rearrangement as a key step in an efficient [3 + 4] annulation affording seven-membered carbocycles, see: Takeda, K.; Nakajima, A.; Takeda, M.; Hoshii, E. *Org. Synth.* S. F. Martin, Eds. **1998**, *76*, 199−213.

(3) Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 699−700.

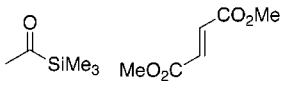
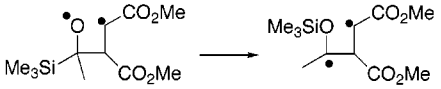
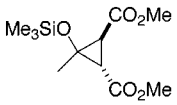
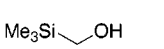
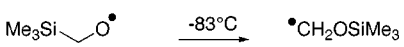
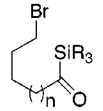
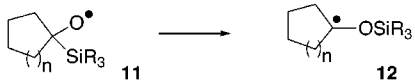
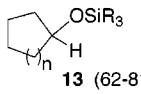
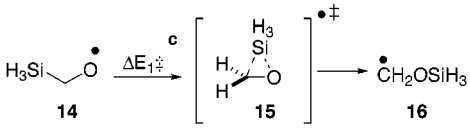
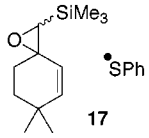
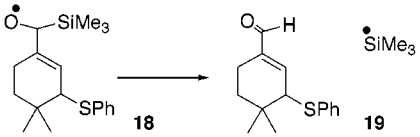
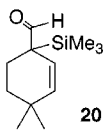
(4) Harris, J. M.; MacInnes, I.; Walton, J. C.; Maillard, B. *J. Organomet. Chem.* **1991**, *403*, C25−C28.

(5) (a) Tsai, Y.-M.; Cherng, C.-D. *Tetrahedron Lett.* **1991**, *32*, 3515−3518. (b) Chang, S.-Y.; Jiaang, W.-T.; Cherng, C.-D.; Tang, K.-H.; Huang, C.-H.; Tsai, Y.-M. *J. Org. Chem.* **1997**, *62*, 9089−9098 and references therein.

(6) Schiesser, C.; Styles, M. L. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2335−2340.

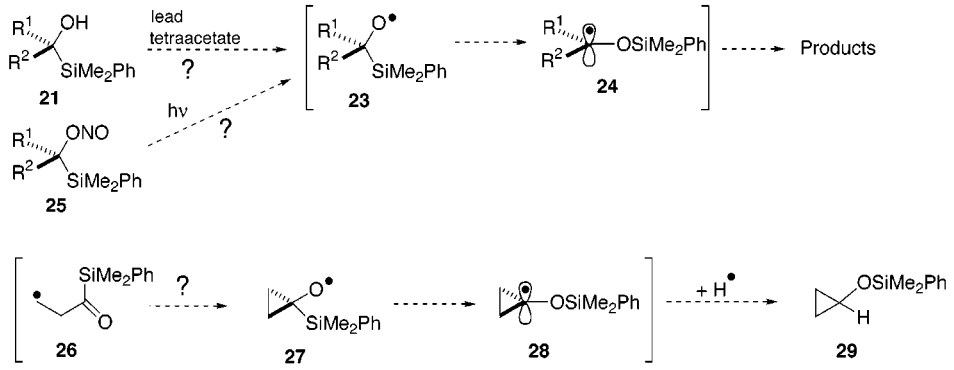
10.1021/jo9912855 CCC: $19.00
Published on Web 03/29/2000

Table 1. Selected Studies Involving α-silyl Alkoxyl Radicals

Entry main author[a]	Starting Materials / Reagents	Evolution of α-Silyl alkoxyl radical	Products
1 Dalton	 1 2	 3 4	 5 good yields
2 Walton	 6	 7[b] 8 (esr)	CH_3OSiMe_3 9
3 Tsai	 10 n = 1,2	 11 12	 13 (62-81%)
4 Schiesser		 14 15 16	
5 Robertson	 17	 18 19	 20 (> 60%)

[a] See refs 3, 4, 5, 6, and 7 for entries 1, 2, 3, 4, and 5, respectively. [b] α-Trimethylsilyl-hydroxymethyl radicals were also formed in addition to **7**. [c] A translocation barrier of 4.76 kcal mol^{-1} was predicted at the MP2/DZP + ZPVE level. See ref 6 for details.

Scheme 1



adds to the α,β-unsaturated system **19** to render the aldehyde **20**.[7] This *anomalous* result suggests that the fate of α-silyl alkoxyl radicals **I** may depend on the radical-generation method and/or the nature of the substrate. In the work reported herein we found additional evidence of this in experiments to determine whether generation of the α-silyl alkoxyl radicals **23** from α-silyl alcohols **21**[8] (or from their nitrites **25**) leads to carbon radicals **24** (Scheme 1). We also addressed the possibility of forming cyclopropanols **29** by radical cyclization of β-acylsilane carbon radicals **26** and subsequent Brook rearrangement of α-silyl alkoxyl radicals **27** (Scheme 1).[9]

Results and Discussion

A. Synthesis of α-Silyl Alcohols 21. The α-silyl alcohols **21a**−**e**, **21h**, and **21k** (Chart 1) were prepared by treatment of the corresponding aldehydes with dimethylphenylsilyllithium (63−84%, 48% for **21k**),[10,11] as illustrated in eq 2 for **21b**.

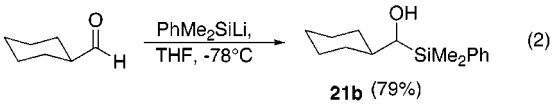
(7) Robertson, J.; Burrows, J. N. *Tetrahedron Lett.* **1994**, *35*, 3777−3780.

(8) Our preliminary results on the reaction of α-hydroxysilanes **21** with lead tetraacetate have recently been published elsewhere: Paredes, M. D.; Alonso, R. *Tetrahedron Lett.* **1999**, *40*, 3973−3976.

(9) At present there is no general radical methodology for the preparation of cyclopropane; see for example Srikrishna, A.; Sharma, G. V. R. *J. Chem. Soc., Perkin Trans. 1* **1997**, 177−181. Journet, M.; Malacria, M. *J. Org. Chem.* **1994**, *59*, 718−719. Weng, W.; Luh, T. *J. Org. Chem.* **1993**, *58*, 5574−5575. Zhang, W.; Dowd, P. *Tetrahedron Lett.* **1992**, *33*, 7307−7310 and references therein. See also Curran, D. P.; Gabarda, A. E. *Tetrahedron* **1999**, *55*, 3327−3336.

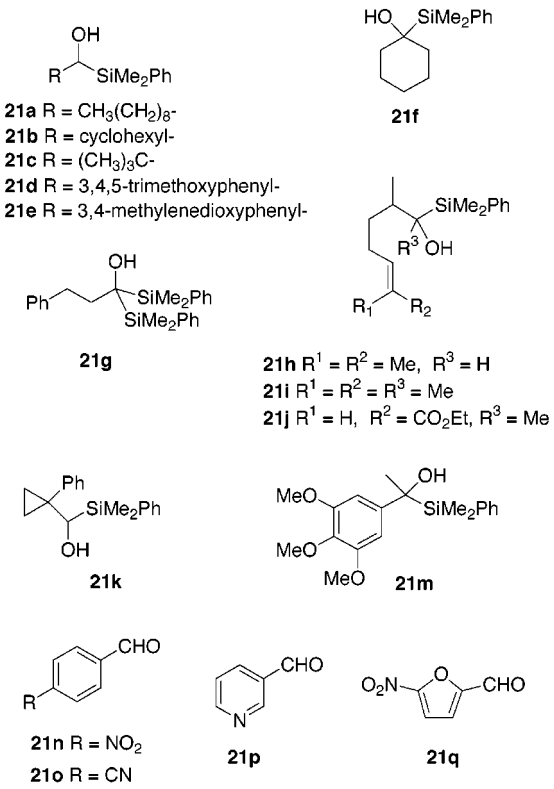
(10) For the preparation of α-silyl alcohols, see Chenede, A.; Abd. Rahman, N.; Fleming, I. *Tetrahedron Lett.* **1997**, *38*, 2381−2382 and references therein. (Dimethylphenylsilyl)lithium was prepared from chlorophenyldimethylsilane as described by: Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527−2532.

(11) Barrett, A. G. M.; Hill, J. *Tetrahedron Lett.* **1991**, *32*, 3285−3288.



The fully α-substituted silyl alcohol **21f** and the α,α-bis-silyl-substituted alcohol **21g**[12] (Chart 1, 60% and 90%)

Chart 1



were prepared analogously starting from cyclohexanone[13] and ethyl 3-phenylpropanoate, respectively. Attempts to apply this transformation to the aldehydes **21n**−**q** resulted in complex mixtures.

The α-methyl-substituted α-silyl alcohols **21i** and **21m** were prepared from **21h** and **21d**, respectively, by oxidation to the acylsilanes[14] followed by treatment with methyllithium,[15] as exemplified for **21i** in Scheme 2. The silyl alcohol **21j** was prepared from **21i** by ozonolysis to the lactol **31** followed by Horner−Emmons olefination (Scheme 2).

B. Treatment of α-Silyl Alcohols with Lead Tetraacetate. The first method we tried to generate carbon radicals **24** from α-silyl alcohols **21** (Scheme 1) consisted in their treatment with lead tetraacetate (LTA).[16] This choice was based on the well-precedented thermal or photochemical generation of α-alkoxyl radicals from alcohols on exposure to LTA in nonpolar solvents.[17]

B1. α-Alkyl- and α-Aryl-Monosubstituted α-Silyl Alcohols. Treatment of α-silyl alcohol **21a** under standard LTA oxidation conditions (110 mol % of LTA, refluxing benzene) gave compound **33a** (73%, Table 2, entry 1). Other monosubstituted alkyl and aryl α-silyl alcohols **21b**−**e** behaved similarly, giving the corresponding mixed acetals **33b**−**e** (Table 2). During these experiments we realized that it was not necessary to run the reaction in refluxing benzene; these transformations took place at room temperature, almost instantaneously, and in essentially quantitative yield with just 1 equiv of LTA. It may also be noted that the mixed acyl-silyl acetals **33**,[18] though rather unusual,[19] have been used to protect aldehyde groups,[20] and their reactions with silyl enol ethers and allyltrimethylsilane in the presence of a Lewis acid have been described.[21] They have also been reduced by DIBALH[22a] and efficiently hydrolyzed under both acidic[23] and basic[22] conditions to the corresponding aldehydes. In this respect, we noted that the aromatic acetals obtained are particularly prone to hydrolysis; in fact, acetals **33d** and **33e** underwent complete conversion to the carbonyl derivatives on filtration through silica gel or alumina.

B2. α,α-Disubstituted-α-Silyl Alcohols. The reaction of LTA with the α,α-disubstituted-α-silyl alcohols **21f** and **21g** proceeded similarly to give the mixed ketals **33f** (88%) and **33g** (94%). In the latter case, addition of silica to the crude reaction mixture resulted in hydrolysis to **34**, completing a synthetic pathway from esters to acylsilanes (**32** → **21g** → **33g** → **34**; Scheme 3).

B3. Trapping Experiments. The efficient conversion of α-silyl alcohols **21** into mixed acetals **33** appeared to indicate that the two well-precedented processes discussed above, the LTA-induced formation of alkoxyl radicals from alcohols (i.e., **21** to **23**, Scheme 4) and the Brook radical rearrangement of α-silyl alkoxyl radicals (i.e., **23** to **24**), could in fact be successfully chained to afford α-silyloxy carbon radicals **24**. To see if these putative intermediates could undergo other synthetically useful transformations, e.g., internal trapping, faster than oxidative transformation to **33**, we selected α-silyl alcohols **21h** and **21j** as suitable precursors of **24h** and **24j**. However, attempts to obtain a cyclized product of type **35** by treatment of **21h** with lead tetraacetate led only to the mixed acetal **33h** in 97% yield. When we tried

Scheme 2

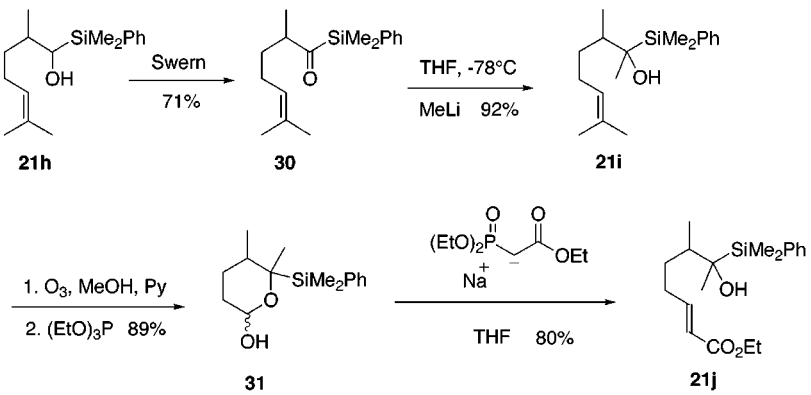
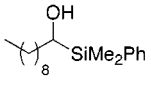
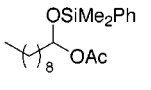
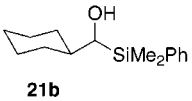
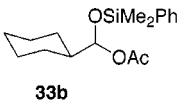
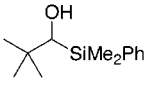
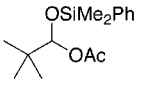
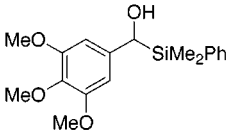
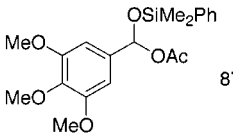
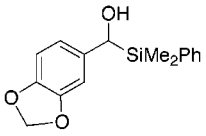
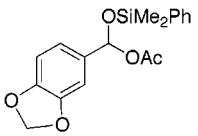


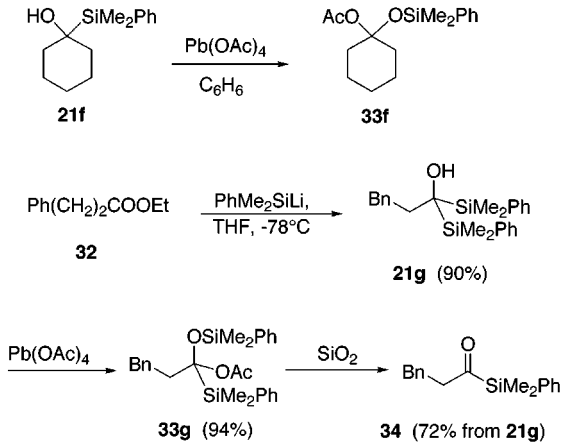
Table 2. Treatment of α-Silyl Alcohols 21 with Lead Tetraacetate

Entry	Substrate	Product	Yield
1	 **21a**	 **33a**	73%[a] 84%[b]
2	 **21b**	 **33b**	71%[a] 93%[b]
3	 **21c**	 **33c**	78%[a] 92%[b]
4	 **21d**	 **33d**	87%[c]
5	 **21e**	 **33e**	92%[b,d]

[a] Yields after isolation by column chromatography. Reactions performed with LTA (110 mol %) in refluxing benzene at the 100 mg scale. [b] To a solution of the α-silyl alcohol (0.04−0.05 mmol) in 0.5 mL of C_6D_6 prepared in an NMR tube were added 1,4-dichlorobenzene (6 mg) and $Pb(OAc)_4$ (100 mol %). The tube was shaken for about 2 min and immediately subjected to proton NMR spectroscopy, which showed complete transformation. Yield was estimated by integration of the well-defined NMR signal of the acetal proton of the product, using 1,4-dichlorobenzene as the internal standard. [c] Standard LTA oxidation conditions, 100 mg scale. The proton NMR of the crude residue obtained by filtration of the reaction mixture and concentration under reduced pressure showed an 87:13 ratio of **33d** versus the corresponding aldehyde. Filtration of this mixture through alumina or silica gel gave the aldehyde in quantitative yield. [d] When the reaction was performed in refluxing benzene (100 mg scale), chromatography isolated piperonal and its monoacetoxy derivative at the methylenedioxy group in 58% and 37% yield, respectively.

the reaction with **21j**, which has a better radical acceptor, we again isolated no cyclized products, but only the silyl enol ether **36j** (9%), the ketone **37j** (47%), and the acetate **38j** (23%). TLC monitoring clearly showed the initial formation of large quantities of the silyl enol ether that upon prolonged heating were hydrolyzed to ketone **37j**. Acetate **38j** was only observed toward the end of the reaction as a result of overoxidation of ketone **37j** on addition of more LTA (up to 150 mol %).

Scheme 3



B4. Discussion of the Mechanism. As already indicated above, the reaction of α-silyl alcohols **21** with LTA to give mixed silyl-substituted acetals **33** could be understood as proceeding through the path **21** → **22a** → **23** → **24** → **33** outlined in Scheme 5. The first two steps of this transformation (the formation of alkoxylead derivatives **22a** and of alkoxyl radicals **23**) would be similar to those accepted for the LTA oxidation of nonsilyl-substituted alcohols **39**.[17a] The intermediate alkoxyl radicals **23** would then undergo a radical Brook rearrangement to **24** which would be finally oxidized to **33**. It should be noted that these last two steps are different to those of their nonsilyl-substituted alkoxyl radical analogues **40** which preferentially evolve by 1,5-H abstraction to carbon-radical intermediates **41** in their way to **42**.

In connection with this mechanistic proposal, two facts: (*a) the unexpectedly high speed of the reaction, and* (*b) the failure to obtain cyclized products from **21h** and **21j***, deserve further discussion.

(a) Regarding the speed of the process, it is surprising that the transformation of α-silyl alcohols **21** to acetals **33** occurs so readily, being essentially instantaneous and

(12) This substrate had been prepared before: Fleming, I.; Ghosh, U. *J. Chem. Soc., Perkin Trans. 1* **1994**, 257−262.

(13) Typical examples of the addition of the dimethylphenylsilyllithium to ketones are described in Koreeda, M.; Koo, S. *Tetrahedron Lett.* **1990**, *31*, 831−834; Bishop, P. M.; Pearson, J. R.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1983**, 123−124. Vedejs, E.; Arnost, M. J.; Eustache, J. M.; Krafft, G. A. *J. Org. Chem.* **1982**, *47*, 4384−4386.

(14) Mancuso, A. J.; Huang, S. L.; Swern, D. J. *J. Org. Chem.* **1978**, *43*, 2480−2482.

(15) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1988**, *110*, 4826−4827.

(16) Cekovic, Z.; Mihailovic M. Lj. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley and Sons: Chichester, 1995; Vol. 5; pp 2949−2954 and references therein.

(17) (a) Evidence for the formation of alkoxyl radicals from alcohols on treatment with LTA has been obtained from ESR studies and from the isolation of epimeric products derived from reversible fragmentation of these intermediates; a detailed and well-documented mechanistic description of this reaction is given by Mihailovic M. Lj.; Cekovic, Z.; Lorenc, Lj. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York 1986; Chapter 14, pp 741−816. (b) For another leading review, see Heusler, K.; Kalvoda, J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 525−538.

(18) This is the first reported method for direct conversion of α-silyl alcohols to acetals. It complements the known oxidations of these substrates to aldehydes: (a) Fleming, I.; Ghosh, U. *J. Chem. Soc., Perkin Trans. 1* **1994**, 257−262, and to acylsilanes: (b) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198−2200.

(19) A search of Chemical Abstracts for acyl-silyl acetal substructures found just 23 references between 1967 and mid 1997.

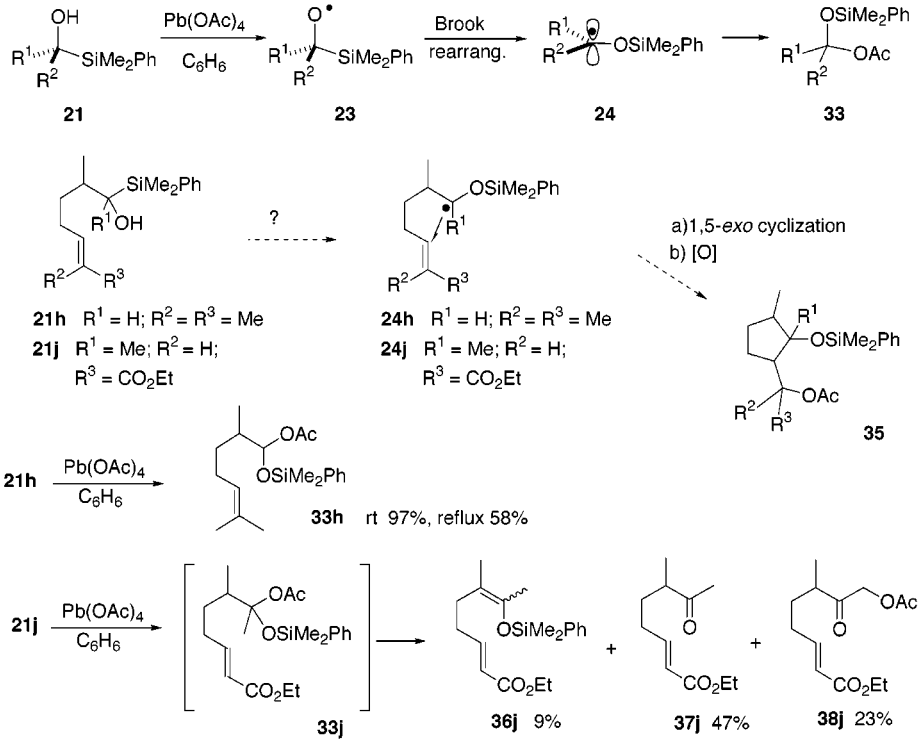
(20) Mander, L. N.; Owen, D. J. *Tetrahedron* **1997**, *53*, 2137−2162.

(21) Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 442−443 and 6706−6707.

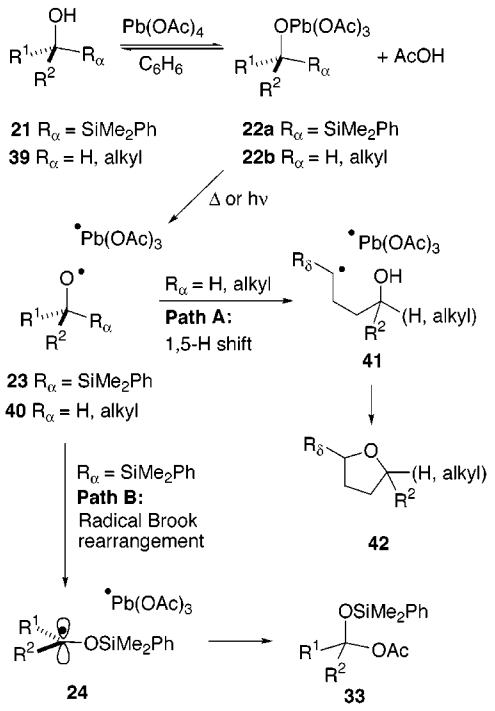
(22) (a) Álvarez, E.; Rico, M.; Rodríguez, R. M.; Zurita, D.; Martín, J. D. *Tetrahedron Lett.* **1992**, *33*, 3385−3388. (b) Deprotection with KF has also been reported: Giese, B.; Horler, H. *Tetrahedron* **1985**, *41*, 4025−4037.

(23) Duff, J. M.; Brook, A. G. *Can. J. Chem.* **1973**, *51*, 2869−2883. Nakatani, S.; Yoshida, J.; Isoe, S. *Tetrahedron* **1993**, *49*, 2011−2024.

Scheme 4



Scheme 5



quantitative even at room temperature and with no excess of LTA. This behavior contrasts with that of non-α-silyl alcohols, significant quantities of which are recovered even after quite lengthy refluxing with up to a 2-fold excess of LTA.[24] Since the reactions of non-α-silyl alcohols **39** seem to be limited by slow homolysis of the alkoxylead(IV) acetate intermediates **22b**,[25] acceptance of the radical mechanism for the conversion of **21** to **33** would require that the formation of alkoxyl radicals **23** from the silylated alkoxylead(IV) acetates **22a** (R_α = $SiMe_2Ph$) would be faster as compared to the nonsilylated analogues **22b** (R_α = H, alkyl). This could well be the case as homolysis of the Pb−O bond in **22a** could be favored by stabilization of the incipient oxygen-radical being formed by the *β*-positioned silyl group as compared to nonsilyl-substituted alcohols.[26]

(b) On the other hand, the nearly quantitative formation of **33h** from **21h** (Scheme 4) could also appear surprising at first sight: the carbon radical intermediate **24h**, because of its 5-hexenyl nature, was expected to undergo quick 1,5-*exo* cyclization and hence afford cyclized products such as **35**. However, preferential oxidation over 1,5-*exo* cyclization of carbon radicals is not without precedent under these reaction conditions. In fact the formation of **33h** by oxidation of **24h** would parallel the behavior previously observed by Cekovic[27] for the carbon radical analogue **41a** (Scheme 6) which, generated under similar conditions, preferentially evolved oxidatively to the tetrahydrofuran **43** instead of giving a cyclopentane derivative by 1,5-*exo* cyclization. Moreover, in the case of **24h**, preference for oxidation would be even higher than for **41a** because of its comparatively higher nucleophilicity due to α-alkoxy substitution. It is inter-

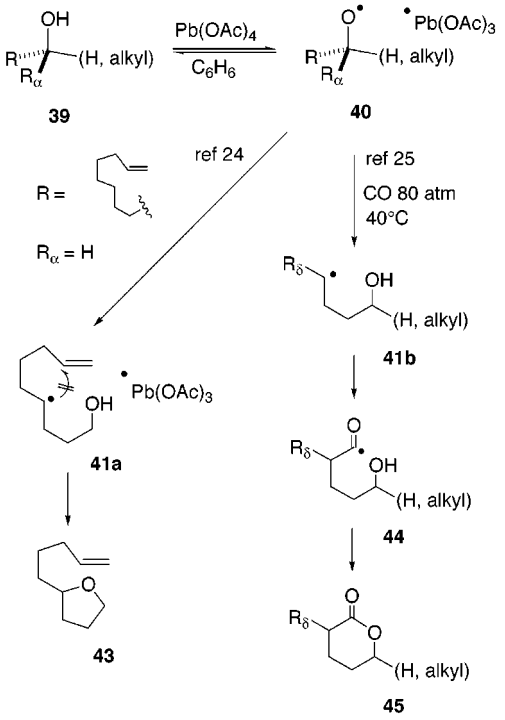
(24) Partch, R. E. *J. Org. Chem.* **1965**, *30*, 2498−2502. Mihailovic, M. Lj.; Cekovic, Z.; Maksimovic, Z.; Jeremic, D.; Lorenc, Lj.; Mamuzic, R. I. *Tetrahedron* **1965**, *21*, 2799−2812.

(25) Tsunoi, S.; Ryu, I.; Okuda, T.; Tanaka, M.; Komatsu, M.; Sonoda, N. *J. Am. Chem. Soc.* **1998**, *120*, 8692−8701.

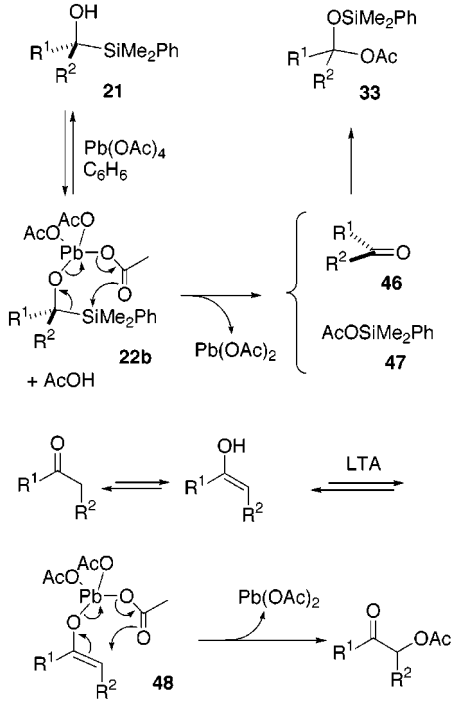
(26) A silyl group can stabilize *β*-carbon radicals through "*σ*−*π* hyperconjugation" and "p−d homoconjugation". See Hwu, J. R.; King, K. Y.; Wu, I.-F.; Hakimelahi, G. H. *Tetrahedron Lett.* **1998**, *39*, 3721−3724. Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819−824. Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644−646. N. Auner, R. Walsh, J. Westrup. *J. Chem. Soc., Chem. Commun.* **1986**, 207−208; Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208−211. Kawamura, T. J.; Kochi. K. *J. Am. Chem. Soc.* **1972**, *94*, 648−650.

(27) Cekovic and Ilijev suggested that the hypothesized carbon radical **41a** (Scheme 6) constitutes a tight radical pair with a lead(III) species such as $Pb(OAc)_3$: Cekovic, Z.; Ilijev, D. *Tetrahedron Lett.* **1988**, *29*, 1441−1444.

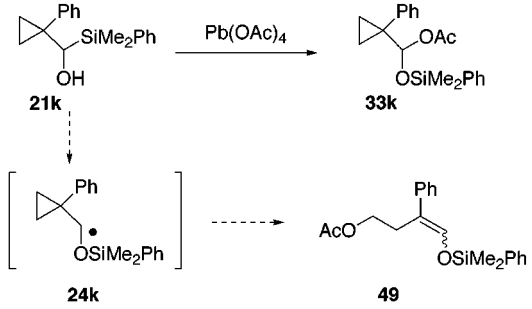
Scheme 6



Scheme 7



Scheme 8



esting to note, however, that under appropriate conditions (CO, 80 atm) carbon radicals generated by treatment of alcohols with LTA can be efficiently trapped before being oxidatively transformed, as recently demonstrated by Ryu[25] which reported the successful synthesis of δ-lactones **45** from primary or secondary alcohols **39** through δ-carbon- and acyl-radical intermediates **41b** and **44**, respectively.

Similarly, preferential oxidation over cyclization of **24j** to acetal **33j** would had taken place starting from **21j** (Scheme 4). In this case, however, the acetal **33j** is $\alpha,\alpha,\beta,\beta$-tetrasubstituted and would have quickly evolved by elimination to the silyl enol ether **36j** (9%) and hence to ketone **37j** (47%) and acetate **38j** (23%).

To explain the conversion of α-silyl alcohols **21** into mixed acetyl-silyl acetals **33**, we alternatively considered nonradical pathways. In a particularly appealing one, alkoxylead(IV) acetates **22b** would evolve to the corresponding carbonyl derivatives **46** by concerted elimination of $Pb(OAc)_2$ and $AcOSiMe_2Ph$ via a seven-membered transition state (Scheme 7), resembling the evolution of enolates **48** in the LTA-promoted α-acetoxylation of carbonyl compounds.[28] Formation of the final mixed acetals **33** would be the result of the direct reaction of **46** with acetoxysilane **47**. This last step is a conceivable process because acetoxysilanes are able to silylate alkoxides, alcohols, and amines.[29] However, both pivalaldehyde and piperonal remained unaltered on treatment with acetoxysilane **47** in benzene, even when $Pb(OAc)_4$ or HOAc were added in variable amounts to reproduce the reaction conditions as close as possible.

Finally, experiments were carried out with silyl alcohol **21k**; the formation of products such as **49** by opening of the cyclopropane ring (Scheme 8) would have given strong support to the radical mechanism hypothesis. In the event, however, LTA treatment of **21k** gave only the mixed acetal **33k** in 92% yield, affording no conclusive evidence.

C. α-Silylated Nitrites. Since alkoxyl radicals formed by photolysis of nitrites are reported to be unassociated with the released nitric oxide,[30] we hypothesized that photolysis of α-silylated nitrites **25** (Scheme 1) might give α-silyl alkoxyl radicals **23** with structures and behaviors resembling those of radicals formed from δ- and ϵ-halogenated acylsilanes (**11**; Table 1, entry 3) and which would therefore evolve by radical Brook rearrangement to the corresponding α-silyloxy carbon radicals **24**. These latter would presumably be liable to further transformations paralleling those undergone by carbon radicals generated by 1,5-H transfer of alkoxyl radicals formed under these conditions.[31]

C1. Synthesis of α-Silylated Aliphatic Nitrites 25. The α-silylated nitrites **25** (Table 3) were prepared from the corresponding α-silyl alcohols **21** by transfer of the

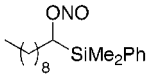
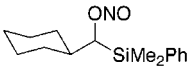
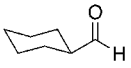
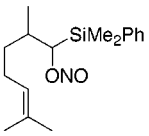
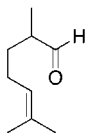
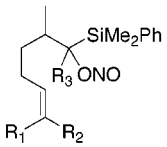
(28) Reference 17a, pp 783−787.

(29) Deardorff, D. R.; Shambayati, S.; Linde II, R. G.; Dunn, M. M. *J. Org. Chem.* **1988**, *53*, 189−191. Hudrlik, P. F.; Feasley, R. *Tetrahedron Lett.* **1972**, *18*, 1781−1784.

(30) Barton, D. H. R.; Beaton, J. M.; Geller, L E.; Pechet, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 2640−2641. Barton, D. H. R.; Beaton, J. M.; Geller, L E.; Pechet, M. M. *J. Am. Chem. Soc.* **1961**, *83*, 4076−4083. Barton, D. H. R. *Pure Appl. Chem.* **1968**, *16*, 1−15.

(31) Akhtar, M.; Barton, D. H. R.; Sammes, P. G. *J. Am. Chem. Soc.* **1965**, *87*, 4601−4607. Akhtar, M.; Barton, D. H. R.; Sammes, P. G. *J. Am. Chem. Soc.* **1964**, *86*, 3394−3395.

Table 3. Photolysis of Aliphatic α-Silyl Nitrites 25

Entry	Nitrite (Yield from α-silyl alcohol)	Product	Yield
1	 **25a** 65%		68% 70,74%[a]
2	 **25b** 62%		[b]
3	 **25h** 20%		[b]
4	 **25i** $R^1 = R^2 = R^3 = Me$[c] **25j** $R^1 = H$, $R^2 = CO_2Et$, $R^3 = Me$[c]		mixtures

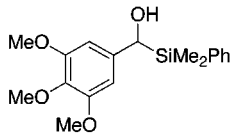
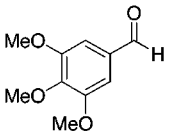
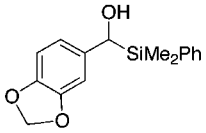
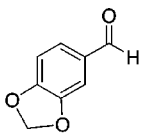
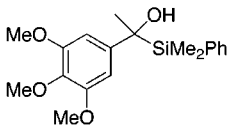
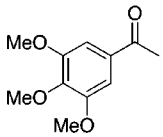
[a] Overall yields for the one-pot conversion from alcohol **21a** by irradiation of a solution of the crude nitrite **25a** in acetonitrile or benzene, respectively. [b] Major product by TLC. [c] Starting nitrites **25i** and **25j** contained variable amounts of the α-silyl alcohol precursors **21i** and **21j**.

nitrosyl group from *tert*-butyl nitrite as reported by Doyle.[32] This method worked reasonably well for the α-monosubstituted derivatives **25a** (65% yield) and **25b** (62%), and poorly for **25h** (20%, one run, unoptimized) and for the α,α-disubstituted nitrites **25i** (20%) and **25j** (20%). These latter could only be obtained as mixtures with the starting α-silyl alcohols, with which they were in equilibrium under the reaction conditions and to which they were partially transformed during attempts at chromatographic purification.

C2. Photolysis of Aliphatic α-Silylated Nitrites. Irradiation of a solution of nitrite **25b** in benzene at 0 °C with a tungsten sun lamp (300 W) or halogen lamp (300 W) surprisingly gave volatile cyclohexanecarbaldehyde as the major product (Table 3). Irradiation at 450 W with a medium-pressure Hanovia Hg lamp, also at 0 °C, gave the same product more quickly, in 30 min instead of several hours. Under these latter conditions, nitrite **25a** also gave the corresponding aldehyde (decanal), in 68% yield. In fact, treatment of **21a** with *tert*-butyl nitrite, dilution of the crude reaction mixture with acetonitrile or benzene, deoxygenation, and irradiation gave decanal in an overall yield of 70% (in CH_3CN) or 74% (in C_6H_6) without intervening purification of the nitrite **25a**.

C3. Trapping Experiments. An aldehyde was also obtained when nitrite **25h** was used in an attempt to trap any radical intermediate with its internal double bond.

Table 4. Treatment of Benzyl α-silyl Alcohols with *t*-BuONO

Benzyl α-silyl alcohol → [Nitrite][a] →	Product, yield[b]
 **21d**	 98%
 **21e**	 75%
 **21m**	 **52** 77%

[a] The benzyl α-silyl nitrite intermediates, inferred by TLC, evolved directly to the carbonyl compounds. [b] Overall yield for the one-pot conversion from the α-silyl-benzyl alcohols **21**.

Photolysis of the α,α-disubstituted nitrites **25i** and **25j**,[33] for which the Brook rearrangement to tertiary α-alkoxy carbon radicals was expected to be easier than for **25h**, gave only complex mixtures.

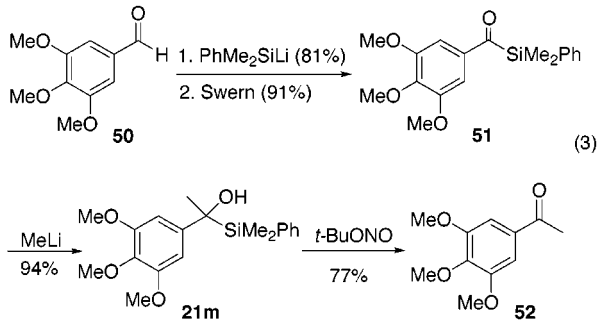
C4. α-Silylated Benzyl Nitrites. Much to our surprise, attempts to make the nitrite of **21d** by treatment with *tert*-butyl nitrite in chloroform at room temperature, either under ordinary light conditions or in the dark, resulted in complete conversion of **21d** to 3,4,5-trimethoxybenzaldehyde (98%, Table 4). TLC analysis showed that the aldehyde was not formed directly from **21d**, but from an intermediate with an R_f in agreement with that expected for the corresponding nitrite. An analogous result was obtained with **21e**, although in this case the reaction was slower.

Since α-silyl-substituted aliphatic nitrites, like the corresponding nonsilyl-substituted benzyl nitrites, are stable at room temperature under ordinary light, it was concluded that the α-silyl substituent and the α-phenyl ring work together to facilitate the evolution of the α-silyl benzyl nitrites to the corresponding carbonyl compounds. The high yields and the mild reaction conditions make α-silyl benzyl alcohols protected precursors of benzyl carbonyls.

tert-Butyl nitrite treatment of the α,α-disubstituted α-silyl alcohol **21m** under nitrosyl exchange conditions gave methyl ketone **52** in 77% yield (Table 4), showing that equilibrium between the fully α-substituted nitrite and its α-silyl alcohol precursor—the main problem in the formation of the aliphatic analogues **25i** and **25j**—is circumvented by in situ conversion to the ketone. The route **50** → **51** → **21m** → **52** from aromatic aldehydes to methyl,aryl-ketones (eq 3), should in principle be applicable to the preparation of other alkyl,aryl- or diaryl-ketones.

(32) Doyle, M. P.; Terpstra, J. W.; Pickering, R. A.; LePoire, D. M. *J. Org. Chem.* **1983**, *48*, 3379−3382.

(33) As indicated, nitrites **25i** and **25j** were obtained as mixtures with their alcohol precursors, **21i** and **21j**, respectively. These mixtures were used in the photolysis experiments.

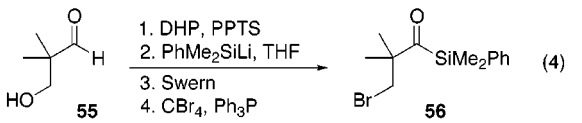


C5. Discussion of the Mechanism. The formation of carbonyl compounds by photolysis of α-silyl aliphatic nitrites **25** ($R^1 = R^2 =$ H, alkyl) can be explained by formation of the alkoxyl radical **23** followed by Brook rearrangement to α-silyloxy carbon radical **24** and final collapse to **46** by interaction with nitric oxide (Scheme 9, path C). Alternatively, in analogy with the proposed evolution of the α-silyl alkoxyl radical **18** (Table 1, entry 5), the carbonyl compound could be formed directly from the intermediate α-silyl alkoxyl radical **23** by *β*-fragmentation with (path D) or without (path E) the assistance of the NO radical. Attempts to differentiate between these pathways by running the reaction with the nitrite derived from the α-silyl alcohol **21k** (Chart **1**) were unavailing, a complex mixture being obtained on photolysis.

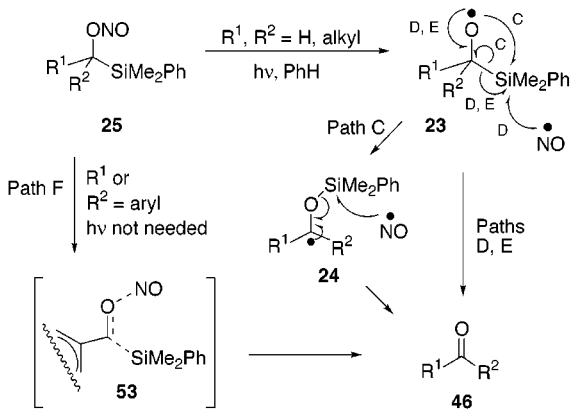
By contrast, the involvement of alkoxyl radical intermediates of type **23** in the conversion of the benzyl nitrite analogues (**25,** R^1 or R^2 = Ar) into their corresponding carbonyl compounds **46** seems unlikely because the process takes place without UV irradiation (even in the dark), and the presence of the phenyl ring is not expected to favor the O−NO bond breaking as an isolated event to any appreciable extent. In this case, the reaction is better explained by a concerted process through a species such as **53**, where C═O bond formation by simultaneous O−NO and C−Si bond breaking would be favored by conjugation with the aromatic ring (path F, Scheme 9).

On the basis of the different behavior of benzyl versus aliphatic nitrites, it is tempting to suggest that stabilization by resonance could similarly be a major factor affecting the evolution of other α-silyl alkoxyl species. In particular, *π*-conjugating substituents in α-silyl alkoxyl radicals **I** could facilitate C═O bond formation by C−Si bond breaking, i.e., they would preferentially evolve to **46** by *β*-silyl fragmentation of the intermediate **54** rather than undergoing the radical Brook rearrangement to **II** (Scheme 10). This would explain the results obtained to date on the evolution of α-silyl alkoxyl radicals **I**; in particular the evolution of **18** to **19** would be attributable to the presence of the double bond.

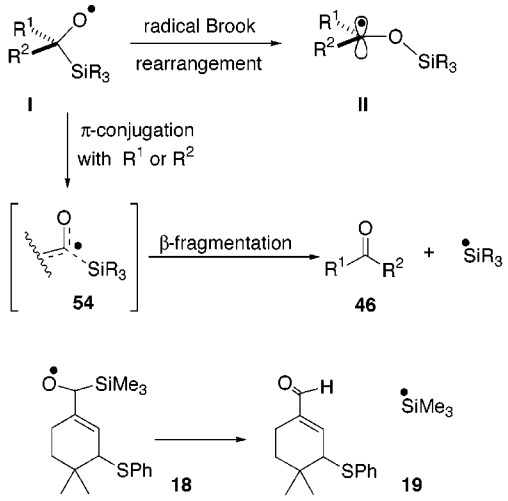
D. *β*-Haloacylsilanes. To evaluate the possibility of forming cyclopropanols **29** by cyclization of *β*-acylsilane carbon radicals **26** to α-silyl alkoxyl radicals **27** and subsequent Brook rearrangement (Scheme 1), we prepared the *β*-bromo acylsilane **56** from commercially available 2,2-dimethyl-3-hydroxypropanal **55** as indicated in eq 4.



Scheme 9



Scheme 10



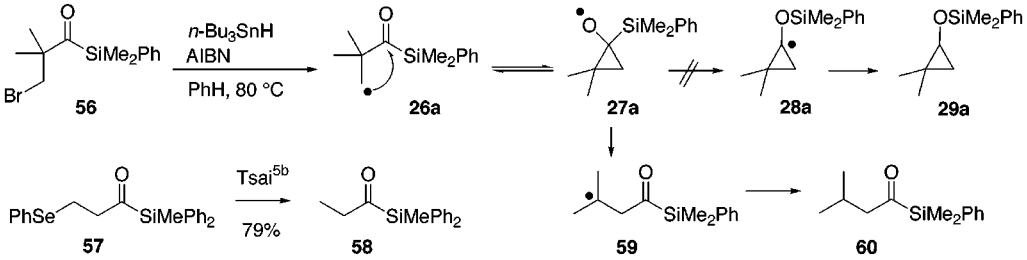
Treatment of a 0.02 M solution of **56** in deoxygenated benzene by slow addition of *n*-Bu_3SnH (150 mol %) and AIBN (10%) in the same solvent failed to afford cyclopropanol **29a** (Scheme 11). This result is in keeping with the recent report on the attempted cyclization of diphenylmethyl(3-phenylselenopropanoyl)silane **57**, which on treatment with *n*-Bu_3SnH gave only the reduced product **58** (79%).[5b] In our case, isolation of the rearranged product **60** (62%) showed that the failure to obtain cyclopropanols was not due to nonoccurrence of 1,3-*exo* radical cyclization (**26a** → **27a**), which appears to be efficient, but to the radical Brook rearrangement of **27a** to **28a** being slower than reopening of **27a** to the tertiary carbon radical **59**, which eventually afforded **60**.[34]

Summary

This work investigated whether radical Brook rearrangement can be reliable induced so as (a) to generate α-silyloxy carbon radicals **24** from α-silyl alcohols **21** and (b) to form cyclopropanols **29** through *β*-acylsilane carbon radicals **26**. For the first goal the formation of α-silyl alkoxyl radical intermediates **23** was attempted by LTA treatment of α-silyl alcohols **21** and by photolysis of their

(34) In line with our result on the acylsilane **56**, Curran observed a similar rearrangement of an α-seleno cyclopropyloxy radical obtained by 1,3-*exo* cyclization of a *β*-acylgermane carbon radical analogous to **26a**: opening was faster than the alternative *β*-elimination of selenyl radicals to the corresponding cyclopropanone: Curran, D. P.; Diederichsen, U.; Palovich, M. *J. Am. Chem. Soc.* **1997**, *119*, 4797−4804.

Scheme 11



nitrites **25**. The second goal was addressed by studying the cyclization of the β-bromoacylsilane **56** under typical *n*-Bu_3SnH conditions.

The most striking result of the first study was the dramatic influence of a geminal silyl group on the reaction of the hydroxy group with LTA: while nonsilyl-substituted alcohols with an accessible δ-hydrogen are converted into cyclic ethers, α-silyl alcohols **21** are efficiently transformed into mixed acyl-silyl acetals.

Silyl substitution also affected the photolysis of α-silyl nitrites, which in this case afforded the corresponding carbonyl compounds. The most surprising observation in these experiments was the clean, efficient, conversion of the presumptive benzyl α-silyl nitrite intermediates (assumed to be formed on treatment of the benzyl α-silyl alcohols with *tert*-butyl nitrite) into the corresponding aromatic aldehydes and ketones without irradiation. Facilitation of the fragmentation process by the aromatic ring is tentatively explained in terms of a concerted process with the resonance-stabilized transition structure **53**. π-Delocalization is similarly put forward as a possible explanation of why some α-silyl alkoxyl radicals **I** appear to undergo Brook rearrangement and others β-fragmentation. Finally we found that the radical Brook rearrangement of α-silyl cyclopropyloxyl radicals **27** is not fast enough to compete with their opening by β-fragmentation, which rules out their use for the preparation of cyclopropanols.

Experimental Section

General. All reactions were carried out under argon with the exclusion of moisture. The reagents were purchased from Sigma-Aldrich Chemical Co. and Fluka Chemical Co. and were used without further purification. THF, Et_2O, and benzene were distilled from sodium benzophenone ketyl; CH_3CN, CH_2Cl_2, $CHCl_3$, and Et_3N from calcium hydride. Anhydrous Na_2SO_4 was used to dry the organic solutions during workups. Flash column chromatography was performed using 230−400 mesh silica gel (Merck). Analytical thin-layer chromatography was done on precoated silica gel aluminum plates containing a fluorescent indicator (GF-254 Merck). ^{1}H NMR spectra were recorded at 250 or 300 MHz; ^{13}C NMR spectra at 63 or 75 MHz. $CDCl_3$ or C_6D_6 were used as solvents. (Dimethylphenylsilyl)-lithium[10] and compounds **21b** and **21g** were synthesized according to literature methods.

General procedure for the Preparation of α-Silyl Alcohols. $PhMe_2SiLi$ (0.375 M in THF, 110−200 mol %) was added dropwise to a 0.2 M solution of the corresponding aldehyde in THF at −78 °C. The reaction mixture was allowed to warm slowly to 0 °C, while being monitored by TLC and then quenched with saturated NH_4Cl. The aqueous layer was extracted with Et_2O (3×), and the combined organic extracts were dried, filtered, and concentrated in vacuo. Column chromatography gave the corresponding α-silyl alcohol.

1-(Dimethylphenylsilyl)decan-1-ol (21a). It was obtained (chromatography: EtOAc−hexane 6:94, 714 mg, 63%) as a colorless oil by treatment of decanal (0.75 mL, 3.83 mmol) with $PhMe_2SiLi$ (18.4 mL, 6.91 mmol, 180 mol %). ^{1}H NMR (300 MHz, $CDCl_3$) 7.58 (m, 2H), 7.37 (m, 3H), 3.52 (dd, J = 6.2 Hz, J = 7.5 Hz, 1H), 1.54 (m, 2H), 1.50−1.20 (m, 15H), 0.90 (t, J = 6.7 Hz, 3H), 0.36 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 136.8, 134.1, 129.2, 127.8, 65.4 (C1), 33.4, 31.9, 29.58, 29.56, 29.46, 29.3, 26.8, 22.6 (C2−C9), 14.1 (C10), −5.4 (CH_3-Si), −5.7 (CH_3Si); IR (neat) 3438 (OH) cm^{-1}; MS *m*/*z* (%) 277 [3, (M − Me)$^+$], 165 [10, ($PhMe_2SiCHOH$)$^+$].

Cyclohexyl(dimethylphenylsilyl)methanol (21b). It was prepared by reaction of $PhMe_2SiLi$ (13.1 mL, 4.90 mmol, 110 mol %) with cyclohexanecarbaldehyde (500 mg, 4.45 mmol). Purification (EtOAc−hexane 6:94) gave **21b** (875 mg, 79%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.61 (m, 2H), 7.40 (m, 3H), 3.37 (d, J = 5.8 Hz, 1H), 1.90−1.56 (m, 6H), 1.31−1.01 (m, 6H), 0.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.8, 134.0, 129.1, 127.8, 70.9 (C−OH), 42.0, 30.7, 29.5, 26.4, 26.3, 26.2, −3.9, −4.3; IR (neat) 3451 (OH) cm^{-1}; MS *m*/*z* (%) 248 [1, M$^+$], 165 [16, ($PhMe_2SiCHOH$)$^+$].

2,2-Dimethyl-1-(dimethylphenylsilyl)propan-1-ol (21c). Treatment of trimethylacetaldehyde (400 mg, 4.64 mmol) with $PhMe_2SiLi$ (24.8 mL, 9.29 mmol, 200 mol %) afforded, after chromatography (EtOAc−hexane 5:95), **21c** as a pale yellow oil (735 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) 7.63 (m, 2H), 7.38 (m, 3H), 3.21 (s, 1H, H1), 1.44 (br s, 1H, OH), 0.94 (s, 9H, H3), 0.45 (s, 6H, $(CH_3)_2$Si); ^{13}C NMR (75 MHz, $CDCl_3$) 138.6, 134.1, 129.0, 127.8, 75.3 (C1), 36.0 (C2), 27.6 (3C, C3), −2.2 (CH_3Si), −3.0 (CH_3Si); IR (neat) 3477 (OH) cm^{-1}; MS *m*/*z* (%) 223 [1, (M+1)$^+$], 222 [1, M$^+$], 165 [18, ($PhMe_2SiCHOH$)$^+$].

(Dimethylphenylsilyl)(3,4,5-trimethoxyphenyl)methanol (21d). It was prepared by reaction of 3,4,5-trimethoxybenzaldehyde (500 mg, 2.55 mmol) and $PhMe_2SiLi$ (10.2 mL, 3.82 mmol, 150 mol %). Purification (CH_2Cl_2 100%) gave **21d** (711 mg, 84%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.44 (m, 2H), 7.35 (m, 3H), 6.21 (s, 2H), 4.60 (s, 1H), 3.80 (s, 3H), 3.60 (s, 6H), 1.88 (br s, 1H), 0.33 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.7, 139.1, 135.83, 135.77, 134.3, 129.3, 127.6, 102.0, 70.1 (C−OH), 60.8 (CH_3O−C4), 55.8 (2C, CH_3O−C3), −5.8, −5.9; IR (neat) 3485 (OH) cm^{-1}; MS *m*/*z* (%) 333 [2, (M + 1)$^+$], 332 [11, M$^+$], 165 [22, ($PhMe_2SiCHOH$)$^+$]; HRMS calcd for $C_{18}H_{24}O_4Si$ *m*/*z* 332.1444, found 332.1442.

Benzo[1,3]dioxol-5-yl(dimethylphenylsilyl)methanol (21e). It was obtained as a colorless oil (chromatography: CH_2Cl_2-hexane 75:25, 447 mg, 78%) by reaction of benzaldehyde (300 mg, 2.00 mmol) and $PhMe_2SiLi$ (8 mL, 3.00 mmol, 150 mol %). ^{1}H NMR (300 MHz, $CDCl_3$) 7.52 (m, 2H), 7.39 (m, 3H), 6.72 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 1.5 Hz, 1H), 6.54 (dd, J = 1.5, 8.0 Hz, 1H), 5.92 (s, 2H), 4.61 (s, 1H), 1.79 (br s, 1H), 0.32 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 147.4, 145.6, 137.6, 136.0, 134.3, 129.4, 127.7, 118.1, 107.8, 106.1, 100.7, 69.8 (*C*-OH), −5.3, −6.3; IR (neat) 3423 (OH) cm^{-1}; MS *m*/*z* (%) 287 [3, (M + 1)$^+$], 286 [11, M$^+$], 165 [8, ($PhMe_2SiCHOH$)$^+$]; HRMS calcd for $C_{16}H_{18}O_3Si$ *m*/*z* 286.1025, found 286.1030.

1-(Dimethylphenylsilyl)cyclohexan-1-ol (21f). Reaction of cyclohexanone (100 mg, 1.02 mmol) with $PhMe_2SiLi$ (4.3 mL, 1.63 mmol, 160 mol %) gave after purification (EtOAc−hexane 5:95), **21f** as a colorless oil (145 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) 7.62 (m, 2H), 7.41 (m, 3H), 1.75−1.64 (m, 5H), 1.51−1.44 (m, 4H), 1.27−1.19 (m, 2H), 0.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 136.9, 135.0, 129.6, 128.2, 65.8 (C1), 33.5, 26.4, 20.5, −5.9; IR (neat) 3472 (OH) cm^{-1}; MS *m*/*z* (%): 234 [0.2,

M^+], 219 [7, $(M - Me)^+$]; HRMS calcd for $C_{14}H_{22}OSi$ *m/z* 234.1440, found 234.1439.

1,1-Bis(dimethylphenylsilyl)-3-phenylpropan-1-ol (21g).[12] ^1H NMR (300 MHz, $CDCl_3$) 7.65 (m, 4H), 7.42 (m, 6H), 7.40−7.19 (m, 3H), 6.99 (d, $J = 7.6$ Hz, 2H), 2.56 (m, 2H), 2.06 (m, 2H), 0.43 (s, 6H), 0.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 142.6, 137.5, 134.6, 129.2, 128.3, 128.1, 127.7, 125.7, 63.5 (C−OH), 39.6, 31.7, −2.9, −3.3; IR (neat) 3560 (OH) cm^{-1}; EM *m/z* (%) 405 [0.4, $(M + H)^+$].

2,6-Dimethyl-1-(dimethylphenylsilyl)hept-5-en-1-ol (21h). It was obtained from 2,6-dimethyl-5-heptenal (5 mL, 24.96 mmol) and $PhMe_2SiLi$ (100 mL, 37.4 mmol, 150 mol %) as a mixture of two diastereomers A:B, 1:1 (5.55 g, 82%). ^1H NMR (250 MHz, $CDCl_3$) 7.57 (m, 4H), 7.40−7.30 (m, 6H), 5.04 (m, 2H), 3.52 (m, 1H), 3.38 (m, 1H), 2.10−1.80 (m, 4H), 1.67 (br s, 6H), 1.58 (br s, 6H), 1.48 (m, 2H), 1.25−1.05 (m, 4H), 1.11 (d, $J = 5.3$ Hz, 1H), 1.06 (d, $J = 5.1$ Hz, 1H), 0.90 (d, $J = 6.8$ Hz, 6H), 0.38 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.7, 134.04, 134.01, 131.43, 131.38, 129.1, 127.86, 127.85, 124.6, 124.5, 71.0, 69.3, 36.8, 35.9, 34.4, 33.1, 25.7, 25.7, 25.4, 17.68, 17.64, 17.1, 16.0, −3.7, −4.0, −4.2; IR (neat) 3448 (OH) cm^{-1}; MS *m/z* (%) 276 [0.2, M^+]; HRMS calcd for $C_{17}H_{28}OSi$ *m/z* 276.1909, found 276.1899.

(Dimethylphenylsilyl)(1-phenylcyclopropyl)methanol (21k). Treatment of 1-phenyl-1-cyclopropanecarbaldehyde (400 mg, 2.74 mmol) with $PhMe_2SiLi$ (10.2 mL, 3.83 mmol, 140 mol %) gave (EtOAc−hexane 10:90) **21k** as a pale yellow oil (370 mg, 48%). ^1H NMR (300 MHz, $CDCl_3$) 7.52−7.21 (m, 10H), 3.14 (s, 1H), 1.65 (br s, 1H), 1.02 (m, 1H), 0.90−0.71 (m, 3H), 0.19 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 142.7, 137.6, 134.0, 130.4, 129.0, 127.9, 127.6, 126.7, 74.4 (C−OH), 30.0 (C−Ph), 12.6 (CH_2), 10.9 (CH_2), −4.5 (CH_3Si), −5.2 (CH_3Si); IR (neat) 3458 (OH) cm^{-1}; MS *m/z* (%) 283 [1, $(M + 1)^+$], 282 [4, M^+]; HRMS calcd for $C_{18}H_{22}OSi$ *m/z* 282.1440, found 282.1448.

Typical Procedure for the Oxidation of α Silyl Alcohols to Acylsilanes. DMSO (400 mol %) in dry CH_2Cl_2 was added to a solution of oxalyl chloride (200 mol %, 0.45 M) in the same solvent at −78 °C. The α-silyl alcohol (0.8 M in dry CH_2Cl_2) and dry Et_3N (500 mol %) were successively added, and the mixture was allowed to warm. After consumption of the starting material as monitored by TLC, water was added, the layers were separated, and the aqueous phase was extracted with additional CH_2Cl_2. The combined organic extracts were dried and concentrated. Purification by flash chromatography afforded the desired acylsilanes.

2,6-Dimethyl-1-(dimethylphenylsilyl)hept-5-en-1-one (30). This compound was obtained as a pale yellow oil (chromatography: EtOAc−hexane 3:97, 980 mg, 71%) by oxidation of **21h** (1380 mg, 4.99 mmol) with oxalyl chloride (0.87 mL, 9.98 mmol, 200 mol %), DMSO (1.43 mL, 19.96 mmol, 400 mol %), and Et_3N (3.48 mL, 24.95 mmol, 500 mol %). ^1H NMR (250 MHz, $CDCl_3$) 7.58−7.55 (m, 2H), 7.43−7.35 (m, 3H), 4.92 (m, 1H), 2.86 (m, 1H), 1.81 (m, 2H), 1.70−1.59 (m, 1H), 1.65 (s, 3H), 1.51 (s, 3H), 1.12 (m, 1H), 0.88 (d, $J = 6.9$ Hz, 3H), 0.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 248.9 (C1), 134.9, 134.0, 131.9, 129.7, 128.0, 123.8, 50.0 (C2), 30.9 (C4), 25.6 (C7), 25.5 (C3), 17.6 (C7), 14.1 (CH_3−C2), −4.2 (CH_3Si), −4.3 (CH_3Si); IR (neat) 1639 (CO) cm^{-1}; MS *m/z* (%) 275 [0.3, $(M + 1)^+$], 274 [1, M^+]; HRMS calcd for $C_{17}H_{26}OSi$ *m/z* 274.1752, found 274.1764.

(Dimethylphenylsilyl)(3,4,5-trimethoxyphenyl)methanone (51). It was obtained as a bright yellow oil (chromatography: EtOAc−hexane 15:85, 182 mg, 91%) from **21d** (202 mg, 0.61 mmol), oxalyl chloride (109 μL, 1.21 mmol, 200 mol %), DMSO (174 μL, 2.43 mmol, 400 mol %), and Et_3N (0.4 mL, 3.04 mmol, 500 mol %). ^1H NMR (300 MHz, $CDCl_3$) 7.63 (m, 2H), 7.41 (m, 3H), 7.00 (s, 2H), 3.85 (s, 3H), 3.66 (s, 6H), 0.61 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 231.5 (CO), 153.0, 142.0, 136.6, 136.5, 134.0, 129.9, 128.4, 105.3, 60.8 (CH_3O−C4), 55.4 (2C, CH_3O−C3), −3.2 (2C, $(CH_3)_2Si$); IR (neat) 1572 (CO) cm^{-1}; MS *m/z* (%) 331 [7, $(M + 1)^+$], 330 [29, M^+]; HRMS calcd for $C_{18}H_{22}O_4Si$ *m/z* 330.1287, found 330.1279.

Reaction of MeLi with Acylsilanes. MeLi (1.5 M in Et_2O, 150−170 mol %) was added to a solution of the corresponding acylsilane (0.48 M) in THF at −78 °C. Once the starting material was completely consumed, saturated NH_4Cl (aq) was added, and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed with saturated $NaHCO_3$ and brine, dried, and filtered, and the volatiles were removed. Column chromatography through silica gel afforded the desired tertiary α-methyl-α-silyl alcohols.

3,7-Dimethyl-2-(dimethylphenylsilyl)oct-6-en-2-ol (21i). Obtained from MeLi (2.20 mL, 3.30 mmol, 170 mol %) and acylsilane **30** (535 mg, 1.95 mmol). Purification (EtOAc−hexane, 6:94) gave **21i** (523 mg, 92%) as a 1:1 mixture of two diastereomers. Higher R_f isomer: ^1H NMR (300 MHz, $CDCl_3$) 7.61 (m, 2H, ArH), 7.38 (m, 3H, ArH), 5.09 (m, 1H, H6), 2.05 (m, 1H, H5), 1.88−1.70 (m, 1H, H5), 1.68 (s, 3H, H8), 1.68−1.58 (m, 2H, H3, H4), 1.58 (s, 3H, H8), 1.15 (s, 3H, H1), 1.05−0.91 (m, 2H, H4, OH), 0.86 (d, $J = 7.0$ Hz, 3H, CH_3−C3), 0.41 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) 137.4 (Ar), 134.5 (Ar), 131.3 (C7), 129.1 (Ar), 127.7 (Ar), 124.7 (C6), 69.5 (C2), 40.7 (C3), 30.0 (C5), 26.4 (C4), 25.6 (C8), 20.0 (C1), 17.6 (C8), 15.6 (CH_3−C3), −3.9 (CH_3Si), −4.3 (CH_3Si). Lower Rf isomer: ^1H NMR (300 MHz, $CDCl_3$) 7.60 (m, 2H, ArH), 7.37 (m, 3H, ArH), 5.02 (m, 1H, H6), 2.06−2.00 (m, 1H, H5), 1.88−1.79 (m, 1H, H5), 1.68 (s, 3H, H8), 1.69−1.57 (m, 1H, H3), 1.59 (s, 3H, H8), 1.46−1.41 (m, 1H, H4), 1.13 (s, 3H, H1), 1.00−0.86 (m, 2H, H4, OH), 0.86 (d, $J = 6.7$ Hz, 3H, CH_3−C3), 0.40 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) 137.4 (Ar), 134.6 (Ar), 131.5 (C7), 129.1 (Ar), 127.7 (Ar), 124.4 (C6), 69.3 (C2), 40.3 (C3), 32.9 (C5), 26.2 (C4), 25.7 (C8), 19.9 (C1), 17.6 (C8), 12.2 (CH_3−C3), −3.8 (CH_3Si), −4.1 (CH_3Si); IR (mixture of diastereomers, neat) 3466 (OH) cm^{-1}; MS (mixture of diastereomers) *m/z* (%) 290 [1, M^+]; HRMS calcd for $C_{18}H_{30}OSi$ *m/z* 290.2066, found 290.2055.

1-(Dimethylphenylsilyl)-1-(3,4,5-trimethoxyphenyl)-ethanol (21m). Obtained as a yellow oil (EtOAc−hexane 20:80, 157 mg, 94%) from (dimethylphenylsilyl)-3,4,5-trimethoxyphenyl)methanone (**51**) (160 mg, 0.48 mmol) and MeLi (0.48 mL, 0.73 mmol, 150 mol %). ^1H NMR (300 MHz, $CDCl_3$) 7.40−7.34 (m, 5H), 6.29 (s, 2H), 3.82 (s, 3H), 3.69 (s, 6H), 1.60 (s, 3H), 1.41 (s, 1H), 0.32 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.4, 143.1, 135.8, 135.6, 134.7, 129.4, 127.5, 102.0, 70.0 (C−OH), 60.8 (CH_3O−C4), 55.8 (2C, CH_3O−C3), 26.1 (CH_3COH), −5.9 (CH_3Si), −6.2 (CH_3Si); IR (neat) 3478 (OH) cm^{-1}; MS *m/z* (%) 346 [2, M^+]; HRMS calcd for $C_{19}H_{26}O_4Si$ *m/z* 346.1600, found 346.1619.

5,6-Dimethyl-6-(dimethylphenylsilyl)tetrahydropyran-2-ol (31). Ozone was passed through a solution of **21i** (higher R_f isomer, 700 mg, 2.41 mmol) and dry pyridine (1 mL) in MeOH (30 mL) kept at −78 °C. When a blue color appeared, the solution was purged with N_2, and $(EtO)_3P$ (2 mL) was added. The reaction was allowed to warm to room temperature, the solvents were rotary evaporated, and the residue was partitioned between Et_2O and water. The organic layer was washed with 1% HCl, dried, filtered, and concentrated. Purification through silica gel (EtOAc−hexane, 15:85 → 20:80) afforded **31** as a white and volatile oil (565 mg, 89%, 4.7:1 mixture of isomers A:B). ^1H NMR (250 MHz, $CDCl_3$) 7.63 (m, 4H), 7.37 (m, 6H), 5.25 (m, 1H), 4.90 (m, 1H), 2.49 (m, 1H), 2.44 (m, 1H), 1.91−1.44 (m, 8H), 1.30−1.14 (m, 2H), 1.25 (s, 6H), 0.72 (d, $J = 6.5$ Hz, 3H), 0.64 (d, $J = 6.5$ Hz, 3H), 0.38 (s, 6H), 0.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.5, 134.8, 134.7, 128.94, 128.87, 127.5, 92.0, 89.8, 74.0, 72.0, 34.1, 33.6, 30.7, 27.0, 21.2, 18.6, 18.3, 17.5, 13.3, −4.3, −4.6, −5.0; IR (neat) 3411 (OH) cm^{-1}; MS *m/z* (%) 265 [0.3, $(M + 1)^+$], 264 [1, M^+]; HRMS calcd for $C_{15}H_{24}O_2Si$ *m/z* 264.1545, found 264.1549.

Ethyl (*E*)-7-Hydroxy-6-methyl-7-(dimethylphenylsilyl)-oct-2-enoate (21j). Triethylphosphonoacetate (509 mg, 2.27 mmol, 150 mol %) was added to a suspension of sodium hydride (91 mg, 2.27 mmol, 150 mol %) in THF (3.8 mL) at 0 °C. After the evolution of hydrogen stopped, the reaction was cooled to −78 °C and a solution of the lactol **31** (400 mg, 1.51 mmol) in THF (0.5 mL) was added. The reaction was allowed to warm slowly until no starting material was detected by TLC. The solvent was removed and the residue redisolved in EtOAc. The organic layer was washed with water, saturated $NaHCO_3$, and

brine. Purification by chromatography (silica gel, EtOAc−hexane, 15:85) afforded the α,β-unsaturated ester **21j** (403 mg, 80%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.58 (m, 2H), 7.37 (m, 3H), 6.93 (dt, J = 15.6 Hz, J = 6.8 Hz, 1H), 5.78 (dt, J = 15.6 Hz, J = 1.5 Hz, 1H), 4.17 (c, J = 7.1 Hz, 2H), 2.31−2.20 (m, 1H), 2.08−1.99 (m, 1H), 1.90−1.79 (m, 1H), 1.66−1.60 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.14 (s, 3H), 1.14−1.01 (m, 1H), 0.93 (br s, 1H), 0.84 (d, J = 6.9 Hz, 3H), 0.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.7 (CO), 149.4, 137.1, 134.5, 129.2, 127.8, 121.1, 69.3 (C7), 60.0 (OCH_2CH_3), 40.6 (C6), 30.7, 28.2, 19.8 (C8), 15.5 (OCH_2CH_3), 14.2 (CH_3−C6), −3.9 (CH_3-Si), −4.5 (CH_3Si); IR (neat) 3493 (OH), 1712 (CO)cm^{-1}; MS m/z (%) 334 [0.1, M$^+$]; HRMS calcd for $C_{19}H_{30}O_3Si$ m/z 334.1964, found 334.1940.

Treatment of α-Silyl alcohols with Lead Tetraacetate. Method A: A mixture of the α-silyl alcohol (0.14 M in degassed benzene) and $Pb(OAc)_4$ (110 mol %) was refluxed in a light protected vessel until no starting material was detected by TLC. The suspension was filtered and the solid washed with EtOAc. The resulting filtrate was concentrated and purified by chromatography. **Method B:** To a solution of the α-silyl alcohol (0.04−0.05 mmol) in 0.5 mL of C_6D_6 prepared in an NMR tube were added 1,4-dichlorobenzene (6 mg) and $Pb(OAc)_4$ (100 mol %). The tube was shaken for a few minutes (held vertically with a cloth and moved rapidly to and fro in this "sheath", measured internal temperature 35 °C) and immediately subjected to proton NMR spectroscopy, which showed complete transformation. Yield was estimated by integration of the defined signal of the acetal proton of the product, using dichlorobenzene as the internal standard.

1-Acetoxy-1-(dimethylphenylsilyloxy)decane (33a). Method A: Treatment of **21a** (150 mg, 0.51 mmol) with $Pb(OAc)_4$ (250 mg, 0.56 mmol, 110 mol %) afforded **33a** (chromatography: EtOAc−hexane 3:97, 130 mg, 73%) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.59 (m, 2H), 7.38 (m, 3H), 6.01 (t, J = 5.4 Hz, 1H), 1.90 (s, 3H), 1.65 (m, 2H), 1.26 (m, 14H), 0.89 (t, J = 6.7 Hz, 3H), 0.444 (s, 3H), 0.439 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 170.0 (CH_3COO), 137.1, 133.4, 129.7, 127.7, 92.8 (C1), 36.6, 31.8, 29.4, 29.2, 29.1, 23.9, 22.6, 21.1, 14.1, −1.4, −1.5; IR (neat) 1741 (CO) cm^{-1}; MS m/z (%) 335 [2, (M − Me)$^+$], 291 [4, (M − AcO)$^+$]. **Method B: 33a** was obtained in 84% yield from **21a** (20 mg, 0.07 mmol) and $Pb(OAc)_4$ (32 mg, 0.07 mmol, 100 mol %). ^{1}H NMR (250 MHz, C_6D_6) 7.68 (m, 2H), 7.26 (m, 3H), 6.30 (t, J = 5.3 Hz, 1H), 1.76 (m, 2H), 1.64 (s, 3H), 1.39−1.10 (m, 14H), 0.94 (t, J = 6.5 Hz, 3H), 0.49 (s, 6H).

Acetoxycyclohexyl(dimethylphenylsilyloxy)methane (33b). Method A: It was obtained as a colorless oil (chromatography: EtOAc−hexane 4:96, 99 mg, 71%) by treatment of **21b** (113 mg, 0.45 mmol) with $Pb(OAc)_4$ (221 mg, 0.5 mmol, 110 mol %). ^{1}H NMR (300 MHz, $CDCl_3$) 7.60 (m, 2H), 7.39 (m, 3H), 5.80 (d, J = 5.6 Hz, 1H), 1.89 (s, 3H), 1.88−1.53 (m, 6H), 1.25−0.98 (m, 5H), 0.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 170.2 (CH_3COO), 137.2, 133.5, 129.6, 127.7, 95.1 (OCHO), 43.4, 27.2, 27.0, 26.2, 25.62, 25.59, 21.0, −1.4, −1.6; IR (neat) 1738 (CO) cm^{-1}; MS m/z (%) 291 [0.5, (M − Me)$^+$], 247 [16, (M − AcO)$^+$]. **Method B:** Prepared in 93% yield from **21b** (12 mg, 0.05 mmol) and $Pb(OAc)_4$ (23 mg, 0.05 mmol, 100 mol %). ^{1}H NMR (250 MHz, C_6D_6) 7.69 (m, 2H), 7.26 (m, 3H), 6.07 (d, J = 5.3 Hz, 1H), 1.94 (m, 1H), 1.67−1.08 (m, 5H), 1.63 (s, 3H), 0.74−0.48 (m, 5H), 0.50 (s, 3H), 0.48 (s, 3H).

1-Acetoxy-2,2-dimethyl-1-(dimethylphenylsilyloxy)-propane (33c). Method A: Reaction of **21c** (150 mg, 0.67 mmol) with $Pb(OAc)_4$ (299 mg, 0.67 mmol, 100 mol %) gave **33c** as a transparent oil (chromatography: EtOAc−hexane 3:97, 148 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) 7.62 (m, 2H), 7.39 (m, 3H), 5.76 (s, 1H), 1.91 (s, 3H), 0.92 (s, 9H), 0.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 170.4 (CH_3COO), 137.3, 133.5, 129.6, 127.7, 96.7 (C1), 36.0 (C2), 24.2 (3C, C3), 21.0 (CH_3-COO), −1.4 (CH_3Si), −1.6 (CH_3Si); IR (neat) 1742 (CO) cm^{-1}; MS m/z (%) 221 [4, (M − OAc)$^+$]. *Method B*: Obtained in 92% yield by reaction of **21c** (11 mg, 0.05 mmol) and $Pb(OAc)_4$ (23 mg, 0.05 mmol, 100 mol %). ^{1}H NMR (250 MHz, C_6D_6) 7.69 (m, 2H), 7.26 (m, 3H), 5.97 (s, 1H, H1), 1.58 (s, 3H, CH_3COO), 0.97 (s, 9H, H3), 0.48 (s, 3H, CH_3Si), 0.47 (s, 3H, CH_3Si).

Acetoxy(dimethylphenylsilyloxy)(3,4,5-trimethoxyphenyl)methane (33d). Method A: From α-silyl alcohol **21d** (105 mg, 0.31 mmol) and $Pb(OAc)_4$ (154 mg, 0.35 mmol, 110 mol %). After workup, the ^{1}H NMR of the crude showed **33d** and 3,4,5-trimethoxybenzaldehyde in a ratio 87:13. Attempts to separate these two compounds by filtration through silica gel or alumina gave the aldehyde in quantitative yield. **33d**: ^{1}H NMR (250 MHz, $CDCl_3$) 7.58 (m, 2H), 7.37 (m, 3H), 6.85 (s, 1H), 6.65 (s, 2H), 3.84 (s, 3H), 3.82 (s, 6H), 1.98 (s, 3H), 0.49 (s, 3H), 0.47 (s, 3H).

2-Acetoxy-[1,3]-benzodioxol-5-carbaldehyde. Method A: Reaction of α-silyl alcohol **21e** (100 mg, 0.35 mmol) with $Pb(OAc)_4$ (170 mg, 0.38 mmol, 110 mol %) afforded after purification (CH_2Cl_2−hexane, 45:55 → 65:35) piperonal (31 mg, 58%) and 2-acetoxy-[1,3]-benzodioxol-5-carbaldehyde (27 mg, 37%): ^{1}H NMR (250 MHz, $CDCl_3$) 9.88 (s, 1H, CHO), 7.78 (s, 1H), 7.57 (dd, J = 8.0 Hz, J = 1.4 Hz, 1H), 7.51 (d, J = 1.4 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) 190.1 (CHO), 168.5 (CH_3COO), 150.0, 146.0, 132.6, 128.5, 113.4, 109.3, 108.3, 20.9 (CH_3COO); IR (neat) 1762 (COO), 1686 (CHO) cm^{-1}; MS m/z (%) 209 [2, (M + 1)$^+$], 208 [12, M$^+$]. HRMS calcd for $C_{10}H_8O_5$ m/z 208.0372, found 208.0368.

Acetoxy(benzo[1,3]dioxol-5-yl)(dimethylphenylsilyloxy)methane (33e). Method B: Treatment of **21e** (21 mg, 0.07 mmol) and $Pb(OAc)_4$ (48 mg, 0.11 mmol, 150 mol %) afforded **33e** in 92% yield. ^{1}H NMR (250 MHz, C_6D_6) 7.63 (m, 2H), 7.23 (m, 3H), 7.14 (s, 1H), 6.93 (dd, J = 8.0 Hz, J = 1.7 Hz, 1H), 6.78 (m, 1H), 6.60 (d, J = 8.0 Hz, 1H), 5.29 (s, 2H), 1.57 (s, 3H), 0.46 (s, 3H), 0.45 (s, 3H); ^{13}C NMR (63 MHz, C_6D_6) 169.6 (CH_3COO), 148.5−128.1 (Ar), 120.3, 108.0, 107.0, 101.1, 91.9, 20.7, −1.2, −1.4.

Acetoxy(dimethylphenylsilyloxy)cyclohexane (33f). Method B: 33f was obtained in 88% yield from α-silyl alcohol **21f** (15 mg, 0.06 mmol) and $Pb(OAc)_4$ (50 mg, 0.11 mmol, 170 mol %). ^{1}H NMR (250 MHz, C_6D_6) 7.72 (m, 2H), 7.28 (m, 3H), 2.45 (m, 2H), 1.77 (m, 2H), 1.63 (s, 3H), 1.60−1.37 (m, 4H), 1.25 (m, 2H), 0.49 (m, 6H); ^{13}C NMR (63 MHz, C_6D_6) 168.5 (CH_3COO), 139.3−127.9 (6C), 37.3, 25.2, 23.7, 22.0, 0.7.

1-Acetoxy-1-(dimethylphenylsilyl)-1-(dimethylphenylsilyloxy)-3-phenylpropane (33g). Method B: It was obtained from **21g** (12 mg, 0.03 mmol) and $Pb(OAc)_4$ (13 mg, 0.03, 100 mol %) in 94% yield. ^{1}H NMR (250 MHz, C_6D_6) 7.75 (m, 2H), 7.67 (m, 2H), 7.61−7.01 (m, 11H), 2.77 (m, 2H), 2.60 (m, 1H, 2.26 (m, 1H), 1.51 (s, 3H), 0.71 (s, 3H), 0.62 (s, 3H), 0.49 (s, 3H), 0.48 (s, 3H); ^{13}C NMR (63 MHz, C_6D_6) 169.1 (CH_3COO), 142.1−126.1 (18C), 108.0 (OCO), 41.9, 30.6, 20.6, 1.11, 1.07, −2.1, −2.5.

1-(Dimethylphenylsilyl)-3-phenylpropan-1-one (34). Treatment of the crude mixture of **33g** in the NMR tube with silica (230−400 mesh) afforded the acylsilane **34** in 72% overall yield from **21**. ^{1}H NMR (250 MHz, C_6D_6) 7.59−6.96 (m, 10H), 2.86−2.70 (m, 4H), 0.32 (s, 6H); ^{13}C NMR (63 MHz, C_6D_6) 242.7 (CO), 142.0−126.0 (12C), 50.5, 28.6, −4.9.

1-Acetoxy-2,6-dimethyl-1-(dimethylphenylsilyloxy)-hept-5-ene (33h). Method A: Reaction of α-silyl alcohol **21h** (100 mg, 0.36 mmol, 1:1 diastereomeric mixture) and $Pb(OAc)_4$ (160 mg, 0.36 mmol, 100 mol %) gave **33h** (chromatography: EtOAc−hexane 3:97, 1:1 mixture of diastereomers, 70 mg, 58%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.59 (m, 4H, ArH), 7.38 (m, 6H, ArH), 5.90 (m, 2H, H1), 5.06 (m, 2H, H5), 2.06−1.87 (m, 4H, H4), 1.90 (s, 3H, CH_3COO isom B), 1.89 (s, 3H, CH_3COO isom A), 1.74−1.63 (m, 2H, H2), 1.69 (s, 6H, H7), 1.59 (s, 6H, H7), 1.57−1.44 (m, 2H, H3), 1.21−1.08 (m, 2H, H3), 0.93 (d, J = 5.3 Hz, 3H, CH_3−C2 isom A), 0.91 (d, J = 5.3 Hz, 3H, CH_3−C2 isom B), 0.43 (s, 12H, $(CH_3)_2$Si); ^{13}C NMR (isom A, 75 MHz, $CDCl_3$) 170.0 (CO), 137.1 (Ar), 133.5 (Ar), 131.5 (C6), 129.6 (Ar), 127.7 (Ar), 124.4 or 124.3 (C5), 94.7 (C1), 38.4 (C2), 31.0 (C3), 25.7 (C7), 25.3 (C4), 21.1 or 21.0 (CH_3COO), 17.6 (C7), 13.6 (CH_3−C2), −1.6 (2C, $(CH_3)_2$-Si); ^{13}C NMR (isom B, 75 MHz, $CDCl_3$) 170.0 (CO), 137.1 (Ar), 133.5 (Ar), 131.5 (C6), 129.6 (Ar), 127.7 (Ar), 124.4 or 124.3 (C5), 94.1 (C1), 38.2 (C2), 31.3 (C3), 25.7 (C7), 25.3 (C4), 21.1 or 21.0 (CH_3COO), 17.6 (C7), 13.3 (CH_3−C2), −1.4 (2C, $(CH_3)_2$-Si); IR (neat) 1730 (CO) cm^{-1}; MS m/z (%) 275 [9, (M − AcO)$^+$],

223 [5, $(PhMe_2SiOCHOAc)^+$], 137 (92), 135 [100, $(PhMe_2Si)^+$], 123 (55), 117 (46), 103 (76). **Method B:** Obtained in 97% yield from **21h** (13 mg, 0.05 mmol) and $Pb(OAc)_4$ (22 mg, 0.05 mmol, 100 mol %). ^{1}H NMR (250 MHz, C_6D_6) 7.68 (m, 2H), 7.26 (m, 3H), 6.20 (m, 1H), 5.19 (m, 1H), 2.29−1.92 (m, 2H), 1.88−1.58 (m, 11H), 1.40−1.22 (m, 1H), 1.04 (m, 3H), 0.49 (s, 3H), 0.48 (s, 3H).

Treatment of 21j with $Pb(OAc)_4$. Method A: Reaction of **21j** (56 mg, 0.17 mmol) with $Pb(OAc)_4$ (111 mg, 0.24 mmol, 150 mol %) gave, after purification (EtOAc−hexane 10:90 → 20:80), silyl enol ether **36j** (5 mg, 9%), ketone **37j** (15 mg, 47%) and α-acetoxyketone **38j** (10 mg, 23%). **Ethyl (2*E*)-6-methyl-7-(dimethylphenylsilyloxy)octa-2,6-dienoate (36j).** ^{1}H NMR (300 MHz, $CDCl_3$) 7.59 (m, 2H, ArH), 7.37 (m, 3H, ArH), 6.92 (m, 1H, H3), 5.79 (m, 1H, H2), 4.18 (c, J = 7.1 Hz, 2H, OCH_2-CH_3), 2.26−2.04 (m, 4H, H4, H5), 1.72 (m, 3H, H8), 1.57 (m, CH_3−C6), 1.29 (m, 3H, OCH_2CH_3), 0.42 (s, 6H, $(CH_3)_2Si$); IR (neat) 1720 (CO) cm^{-1}; MS *m*/*z* (%) 332 [2, M$^+$]. **Ethyl (*E*)-6-methyl-7-oxooct-2-enoate (37j).** ^{1}H NMR (250 MHz, $CDCl_3$) 6.91 (dt, J = 15.5 Hz, J = 7.0 Hz, 1H), 5.82 (dt, J = 15.5 Hz, J = 1.5 Hz, 1H), 4.18 (c, J = 7.2 Hz, 2H), 2.53 (m, 1H), 2.26−2.14 (m, 2H), 2.14 (s, 3H), 1.84 (m, 1H), 1.49 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.11 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.8 (C7), 166.4 (COO), 147.9, 121.9, 60.1, 46.2, 30.7, 29.6, 28.1, 16.2, 14.2; IR (neat) 1717 (2CO) cm^{-1}; MS *m*/*z* (%) 199 [1, (M + 1)$^+$], 198 [5, M$^+$]; HRMS calcd for $C_{11}H_{18}O_3$ *m*/*z* 198.1256, found 198.1270. **Ethyl (*E*)-8-acetoxy-6 methyl-7-oxooct-2-enoate (38j).** ^{1}H NMR (250 MHz, $CDCl_3$) 6.90 (dt, J = 15.7 Hz, J = 7.0 Hz, 1H, H3), 5.83 (br d, J = 15.7 Hz, 1H, H2), 4.74 (d, J = 17.0 Hz, 1H, H8), 4.66 (d, J = 17.0 Hz, 1H, H8), 4.18 (c, J = 7.1 Hz, 2H, OCH_2CH_3), 2.62 (m, 1H, H6), 2.25−2.16 (m, 2H, H4), 2.17 (s, 3H, CH_3COO), 1.89 (m, 1H, H5), 1.54 (m, 1H, H5), 1.28 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.14 (d, J = 6.9 Hz, 3H, CH_3−C6); ^{13}C NMR (75 MHz, $CDCl_3$) 206.6 (C7), 170.2, 166.1, 147.6, 122.1, 67.1, 60.3, 41.8, 30.7, 29.4, 20.4, 16.3, 14.2; IR (neat) 1752, 1721 (3CO) cm^{-1}; MS *m*/*z* (%) 211 [9, (M − EtO)$^+$].

Acetoxy(dimethylphenylsilyloxy)(1-phenylcyclopropyl)methane (33k). Method B: Obtained by reaction of **21k** (11 mg, 0.04 mmol) and $Pb(OAc)_4$ (19 mg, 0.04 mmol, 100 mol %) in 92% yield. ^{1}H NMR (250 MHz, C_6D_6) 7.60 (m, 2H), 7.41 (d, J = 7.1 Hz, 2H), 7.25−7.08 (m, 6H), 6.27 (s, 1H), 1.54 (s, 3H), 1.07 (m, 2H), 0.75 (m, 2H), 0.42 (s, 3H), 0.41 (s, 3H); ^{13}C NMR (63 MHz, C_6D_6) 169.6 (CH_3COO), 141.3−127.1 (12C), 94.6, 30.7, 20.5, 9.8, 9.2, −1.3, −1.4.

Preparation of Aliphatic α-Silyl Alcohol Nitrite Esters 25 by Nitrosyl Exchange. Typical Procedure. A solution of the α-silyl alcohol (0.2 M in dry $CHCl_3$) and excess *t*-BuONO (150−300 mol %) was stirred at room temperature in the darkness until TLC showed total consumption of the starting material. The volatiles were then rapidly removed, and the resulting residue was chromatographed.

1-(Dimethylphenylsilyl)decyl Nitrite (25a). It was obtained as a yellow oil (chromatography: hexane 100%, 142 mg, 65%) from **21a** (200 mg, 0.68 mmol) and *t*-BuONO (125 mg, 1.16 mmol, 170 mol %). ^{1}H NMR (250 MHz, $CDCl_3$) 7.53 (m, 2H), 7.39 (m, 3H), 5.36 (dd, J = 3.3 Hz, J = 9.5 Hz, 1H), 1.64 (m, 2H), 1.20 (m, 14H), 0.88 (t, J = 6.0 Hz, 3H), 0.36 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 135.6, 134.0, 129.6, 127.9, 31.8, 31.2, 29.5, 29.4, 29.3, 29.1, 26.9, 22.6, 14.1, −4.9, −5.2; IR (neat) 1637 (NO) cm^{-1}; MS *m*/*z* (%) 291 [0.5, (M − NO)$^+$], 275 [1, (M − ONO)$^+$].

1-Cyclohexyl-1-(dimethylphenylsilyl)methyl Nitrite (25b). Treatment of **21b** (250 mg, 1.01 mmol) with *t*-BuONO (0.375 mL, 3.02 mmol, 300 mol %) gave **25b** (chromatography: hexane 100%, 173 mg, 62%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.54 (m, 2H), 7.38 (m, 3H), 5.29 (d, J = 6.1 Hz, 1H), 1.67−1.52 (m, 6H), 1.29−0.85 (m, 5H), 0.39 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 136.5, 133.9, 129.4, 127.8, 40.7, 31.0, 29.9, 26.2, 26.1, 26.0, −3.6, −3.9; IR (neat) 1637 (NO) cm^{-1}; MS *m*/*z* (%): 247 [1, (M − NO)$^+$].

2,6-Dimethyl-1-(dimethylphenylsilyl)hept-5-enyl Nitrite (25h). It was obtained as a pale yellow oil (chromatography: 100% hexane, 58 mg, 20%) from **21h** (258 mg, 0.93 mmol) and *t*-BuONO (0.25 mL, 2.10 mmol, 225 mol %). ^{1}H NMR (300 MHz, $CDCl_3$): 7.52 (m, 4H), 7.36 (m, 6H), 5.40 (d, J = 4.2 Hz, 1H), 5.29 (d, J = 6.2 Hz, 1H), 4.95 (m, 2H), 1.94−1.82 (m, 6H), 1.64 (s, 6H), 1.56 (s, 3H), 1.55 (s, 3H), 1.28−1.21 (m, 2H), 1.21−1.05 (m, 2H), 0.83 (d, J = 6.9 Hz, 6H), 0.37 (s, 6H), 0.34 (s, 6H). UV (EtOH) λ_{max}: 226 nm.

Photolysis of Aliphatic α-Silyl Alcohol Nitrite Esters 25. A solution of the corresponding nitrite in degassed benzene (0.03 M) was irradiated at 0 °C with a 450 W Hanovia mercury lamp for 30 min. The solvent was concentrated and the residue chromatographed through silica gel. In this way the known aldehydes decanal (41 mg, 68%), cyclohexanecarbaldehyde, and 2,6-dimethyl-5-heptenal (9 mg, 40%) were obtained from **25a** (124 mg, 0.38 mmol), **25b**, and **25h** (50 mg, 0.16 mmol), respectively.

One-Pot Procedure for the Formation and Photolysis of α-Silyl Nitrite 25a. To a solution of the α-silyl alcohol **21a** (150 mg, 0.51 mmol) in 2.5 mL of dry benzene was added *t*-BuONO (127 μL, 1.02 mmol, 200 mol %). After consumption of the starting material, additional benzene (14.5 mL) was added, the solution was degassed with a stream of argon and irradiated at 0 °C with a Hanovia lamp (450 W) for 30 min. Removal of the volatiles and purification (EtOAc−hexane 4:96) gave decanal (59 mg, 74% overall) as a colorless oil.

Treatment of Benzyl α-Silyl Alcohols 21d, 21e, and 21m with *t*-BuONO. Following the procedure described above to form nitrite esters from aliphatic α-silyl alcohols, 3,4,5-trimethoxybenzaldehyde (**50**) (116 mg, 98%), piperonal (71 mg, 75%), and methyl (3,4,5-trimethoxyphenyl) ketone **52** (chromatography: EtOAc−hexane 15:85, white solid, 65 mg, 77%) were obtained from **21d** (200 mg, 0.60 mmol), **21e** (180 mg, 0.63 mmol), and **21m** (140 mg, 0.40 mmol), respectively, on treatment with *t*-BuONO (410 μL, 3.3 mmol, 550 mol % for **21d**; 117 μL, 0.94 mmol, 150 mol % for **21e**; and 75 μL, 0.061 mmol, 150 mol % for **21m**). TLC indicated the initial formation of a less-polar compound, which directly evolved in situ to the final carbonyl compounds. Methyl (3,4,5-trimethoxyphenyl) ketone **52**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.18 (s, 2H), 3.89 (s, 9H), 2.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.9 (CO), 153.0, 142.6, 132.4, 105.8, 60.9, 56.3, 26.4); IR (neat) 1680 (CO) cm^{-1}; MS *m*/*z* (%) 211 [7, (M + 1)$^+$], 210 [57, M$^+$]; HRMS calcd for $C_{11}H_{14}O_4$ *m*/*z* 210.0892, found 210.0886.

2,2-Dimethyl-3-(tetrahydropyran-2-yloxy)propanal. A mixture of 2,2-dimethyl-3-hydroxy-propanal (**55**) (500 mg, 4.89 mmol), DHP (617 mg, 7.34 mmol, 150 mol %), and PPTS (123 mg, 10 mol %) in dry CH_2Cl_2 (34 mL) was stirred at room temperature overnight. The solution was diluted with Et_2O and washed with brine. The organic layer was dried, filtered, and concentrated. Purification of the residue (EtOAc−hexane, 25:75) gave the protected aldehyde (733 mg, 80%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) 9.54 (s, 1H, CHO), 4.55 (m, 1H), 3.75 (d, J = 9.7 Hz, 1H), 3.49 (m, 2H), 3.32 (d, J = 9.7 Hz, 1H), 1.52 (m, 6H), 1.08 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) 204.5 (C1), 98.3 (OCHO), 71.8, 61.2, 46.2 29.9, 29.8, 25.0, 18.5; IR (neat) 1730 (CO) cm^{-1}; MS *m*/*z* (%) 187 [8, (M + H)$^+$], 186 [0.3 M$^+$].

2,2-Dimethyl-1-(dimethylphenylsilyl)-3-(tetrahydropyran-2-yloxy)propan-1-ol. It was obtained (2076 mg, 60%, eluent for chromatography: EtOAc−hexane, 12:88) as a mixture of diastereomers (A:B, 1:1.3) from 2,2-dimethyl-3-(tetrahydropyran-2-yloxy)propanal (2 g, 10.73 mmol) and $PhMe_2SiLi$ (43 mL, 16.10 mmol, 150 mol %), following the general procedure indicated above to transform aldehydes into α-silyl alcohols. ^{1}H NMR (250 MHz, $CDCl_3$): 7.61 (m, 4H), 7.36 (m, 6H), 4.47 (m, 1H), 4.17 (m, 1H), 3.85−3.70 (m, 2H), 3.66 (d, J = 9.4 Hz, 1H), 3.59 (d, 1H), 3.48−3.43 (m, 4H), 3.21 (d, 1H), 3.19 (d, J = 9.1 Hz, 1H), 3.10 (d, J = 9.4 Hz, 1H), 2.92 (d, J = 6.7 Hz, 1H), 1.83−1.44 (m, 12H), 1.00 (s, 3H), 0.89 (s, 3H), 0.84 (s, 3H), 0.79 (s, 3H), 0.42 (s, 6H), 0.41 (s, 6H); IR (neat): 3478 (OH) cm^{-1}.

2,2-Dimethyl-1-(dimethylphenylsilyl)-3-(tetrahydropyran-2-yloxy)propan-1-one. It was obtained as a pale yellow oil (740 mg, 75%, eluent for chromatography: EtOAc−hexane 10:90) from 2,2-dimethyl-1-(dimethylphenylsilyl)-3-(tetrahydropyran-2-yloxy)propan-1-ol (995 mg, 3.08 mmol), oxalyl chloride (0.58 mL, 6.17 mmol, 200 mol %), DMSO (0.87 mL,

12.34 mmol, 400 mol %), and Et_3N (2.15 mL, 15.42 mmol, 500 mol %), following the general procedure indicated above for the oxidation of α-silyl alcohols to acylsilanes. ^{1}H NMR (250 MHz, $CDCl_3$) 7.56 (m, 2H), 7.35 (m, 3H), 4.39 (m, 1H), 3.73 (m, 1H), 3.64 (d, J = 9.6 Hz, 1H), 3.46 (m, 1H), 3.35 (d, J = 9.6 Hz, 1H), 1.52 (m, 6H), 1.06 (s, 3H), 0.97 (s, 3H), 0.53 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) 247.5 (CO), 136.1, 134.1, 129.6, 128.0, 98.7 (O*C*HO), 73.2, 61.7, 53.3, 30.3, 25.3, 19.0, 20.5, 20.4, −2.5, −2.7; IR (neat) 1633 (CO) cm^{-1}; MS *m*/*z* (%) 320 [0.2, M^+].

3-Bromo-2,2-dimethyl-1-(dimethylphenylsilyl)propan-1-one (56). CBr_4 (188 mg, 0.57 mmol, 280 mol %) was added to a solution of 2,2-dimethyl-1-(dimethylphenylsilyl)-3-(tetrahydropyran-2-yloxy)propan-1-one (65 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) at room temperature. After 10 min the mixture was cooled to 0 °C and Ph_3P (298 mg, 1.13 mmol, 560 mol %) was added, allowing the reaction to warm to room temperature overnight. The mixture was concentrated to ca. half its volume and filtered through silica gel. After evaporation of the solvent, the residue was purified by PTLC (EtOAc−hexane 8:92) affording the β-bromoacylsilane **56** (25 mg, 41%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) 7.61 (m, 2H), 7.40 (m, 3H), 3.36 (s, 2H), 1.10 (s, 6H), 0.56 (s, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) 245.4 (CO), 135.6, 134.4, 130.2, 128.5, 53.6, 40.7, 22.4, −2.5; IR (neat) 1634 (CO) cm^{-1}; MS *m*/*z* (%) 135 [51, $(PhMe_2Si)^+$].

1-(Dimethylphenylsilyl)-3-methylbutan-1-one (60). To a refluxed solution of **56** (72 mg, 0.24 mmol) in 12 mL of degassed benzene, a solution of *n*-Bu_3SnH (97 μL, 0.36 mmol, 150 mol %) and AIBN (10.5 mg, 0.06 mmol, 25 mol %) in the same solvent was slowly added (syringe pump, 1h). The reaction was monitored by TLC (Et_2O−hexane, 10:90) until consumption of the starting material was observed. Removal of the solvent and chromatographic purification (PTLC, Et_2O−hexane, 10:90) afforded **60** (32 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) 7.55 (m, 2H), 7.40 (m, 3H), 2.46 (d, J = 6.6 Hz, 2H), 2.13 (m, 1H), 0.80 (d, J = 6.7 Hz, 6H), 0.49 (s, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) 246.9 (CO), 134.5, 133.9, 129.8, 128.1, 57.7, 22.9, 22.6, −4.8; IR (neat) 1640 (CO) cm^{-1}; MS *m*/*z* (%) 221 [0.2, $(M + 1)^+$], 220 [2, M^+]; HRMS calcd for $C_{13}H_{20}OSi$ *m*/*z* 220.1283, found 220.1277.

Acknowledgment. We thank the Xunta de Galicia and the DGES for funding this work under projects (XUGA 20902B97) and (PB95-0824), respectively. M.D.P. also thanks the Xunta de Galicia and the Fundación Benéfico-Docente Segundo Gil Dávila for fellowships.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for **33a**−**h**,**k**, **36j**, **37j**, **38j**, **25a**,**b**,**h**, **56**, and **60**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9912855