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The β-Silicon Effect as a Control Element for the Regioselective Ring Opening of Oxetanes

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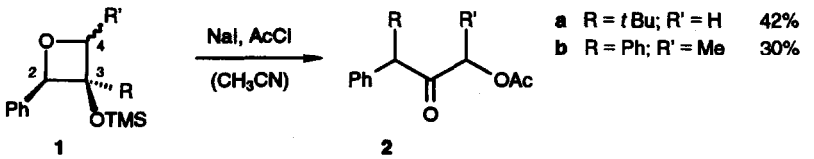
Abstract: The title compound **5** was prepared by a stereoselective photocycloaddition of silyl enol ether **9** and benzaldehyde. In Lewis- and Brönsted-acid promoted ring opening reactions the oxetane is selectively cleaved to yield a 1,2-diol **6** which cyclizes under the reaction conditions to the dihydrofuran **11**. The constitution of the final product was elucidated by reductive degradation to the alcohol **14**.

INTRODUCTION

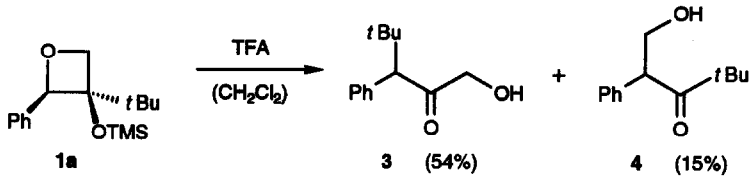
2-Aryl-3-silyloxy-oxetanes like **1** have recently become readily accessible in diastereomerically pure form by the Paternò-Büchi reaction of silyl enol ethers and aromatic aldehydes.[1] The further use of this class of oxetanes in synthesis depends on reliable methods to open the four-membered ring. The most obvious mode of cleavage is the catalytic hydrogenation of the benzylic O-C(2) bond and its application to many substrates has already been demonstrated.[2] A route to selectively open the O-C(4) bond, however, may be considered even more desirable because it leaves the relative configuration which has been established in the photochemical key step untouched. For the ring opening of oxetanes many literature procedures have been developed which are often based on oxygen activation by an electrophile and subsequent nucleophilic attack at carbon.[3] If these methods are applied to our particular case regioselectivity at C(4) was expected difficult to achieve since a positive charge at C(2) is stabilized by the adjacent phenyl group. Indeed, it turned out that a major reaction pathway in many attempted ring openings was a 1,2-alkyl shift with concomitant loss of the TMS group. An example is shown in scheme 1.



1 2

Scheme 1. Rearrangement of oxetanes **1** upon electrophilic oxygen activation

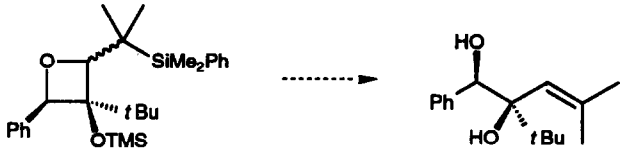
As depicted in scheme 2, acid treatment of 2-phenyl-3-silyloxy-oxetanes gave similar results and it additionally disclosed the migration aptitudes of the substituents at C(3).



1a **3** (54%) **4** (15%)

Scheme 2. Acid catalyzed rearrangement of oxetane **1a**

The introduction of a substituent at C(4) which is a better donor than phenyl appeared to be a reasonable remedy to suppress the undesired mode of ring opening. Carless showed some time ago[4] that a *tert*-butyl substituent at C(4) can effectively compete with a phenyl group at C(2) in stabilizing an adjacent cationic carbon center formed by oxetane ring opening. This type of reaction finally leads to a tetrahydrofuran because a methyl shift from the *tert*-butyl group occurs and the intermediate tertiary carbenium ion is trapped by the former oxetane oxygen. Contrary to that, one may conceive of an electron donating substituent which does not rearrange under the reaction conditions but which is rather cleaved to yield an open chain product. Since silicon is known to stabilize a positive charge in β-position[5] and since the corresponding cations readily eliminate silicon upon nucleophilic attack[6] we intended to construct an oxetane such as **5** suitably substituted for the projected fragmentation to the corresponding diol **6** (scheme 3). A similar rationale for the use of the $TMSCH_2CH_2$ group in O-protection and its cleavage has been put forward by Magnusson et al.[7]



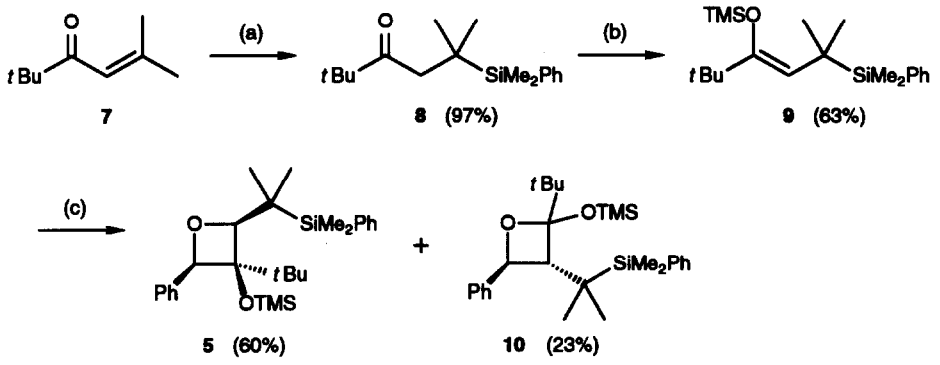
5 **6**

Scheme 3. Projected ring opening of oxetane **5** to the 1,2-diol **6**

RESULTS AND DISCUSSION

***Construction of the Oxetane* 5.** The conjugate addition of $(PhMe_2Si)_2CuLi$ to α,β-unsaturated ketones has been developed by Fleming[8] and we employed his procedure to obtain compound **8**. The mixed cuprate $(PhMe_2Si)(Me)CuLi$ which has also been described for this purpose[8c] gave less satisfactory results. The vinylic dimethylsubstitution of ketone **7**[9] avoids any problems associated with Michael additions of the intermediate enolate to unchanged starting material. An attempt to trap the enolate with TMSCl *in situ* gave product mixtures which were difficult to separate and we therefore carried out the silyl enol ether formation[10] in a second step. The reaction proceeded cleanly but did not go to completion under a broad variety of conditions. Based on our experimental results[11] we attribute this behaviour rather to the steric congestion of the enolate oxygen than to

insufficient deprotonation of the ketone. Since separation of **8** and **9** are simple ketone **8** can be conveniently re-used in the next cycle. With **9** in hand we turned towards the formation of the oxetane nucleus. A high diastereoselectivity was foreseen on the ground of our previous experience with the photocycloaddition of aromatic aldehydes to β-alkylsubstituted silyl enol ethers.[12] Irradiation under standard conditions (30-40°C; Rayonet RPR 3000 Å) gave both the desired compound **5** and its regioisomer **10** in diastereomerically pure form (scheme 4, table 1). The comparably large amount of **10** reflects the bulkiness of the $(PhMe_2Si)Me_2C$ moiety and it underlines the fact that steric bias can effectively compete with electronic factors in these kinds of photocycloadditions. To our surprise the regioselectivity improved with increasing temperature[13] (table 1) and we therefore routinely ran the reaction at 60-70°C (scheme 4).



(a) $(PhMe_2Si)_2CuLi$ (THF), -23°C to 0°C, 2h. (b) LDA, TMSCl (THF), -78°C to rt, 24h. (c) PhCHO, hv (PhH), 60-70°C, 20h.

Scheme 4. Preparation of the target oxetane **5** from the α,β-unsaturated ketone **7**

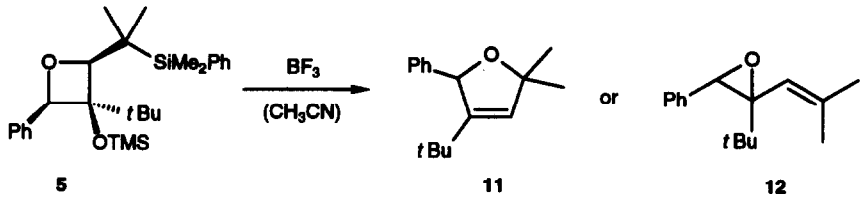
Table 1. The regioselectivity of the photocycloadditon [step (c) in scheme 4] as a function of temperature Θ

Θ [°C]	t [h]	Light Source[a]	Solvent	Regioselectivity (**5**:**10**)[b]
- 25	7	TQ 150	*n* -hexane	44:56
30	20	RPR 3000	benzene	62:38
65	20	RPR 3000	benzene	68:32

[a] See Experimental. [b] Regioselectivities were determined by GC analysis of the crude reaction mixture.

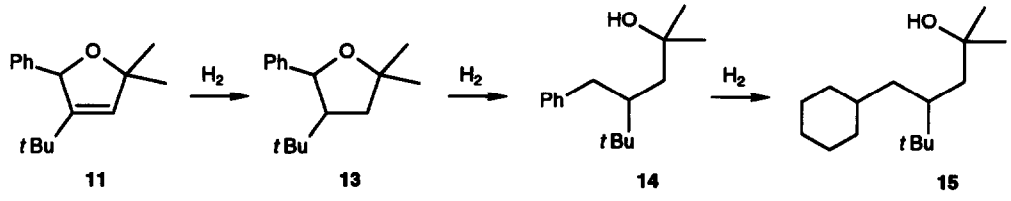
The stereochemical assignment for **5** and **10** as illustrated in scheme 4 was based on analogy to related oxetanes whose configuration had already been elucidated.[12] After separation of the regioisomers the ring opening was attempted.

Acid Catalyzed Ring Opening of 5. As the Lewis-acid we initially chose BF_3-OEt_2 because we expected the strong Si-F bond to be an effective driving force for this process. In THF and DMF as solvents no reaction was observed and the starting material was recovered unchanged. In acetonitrile, however, a single product was obtained which - as we had correctly speculated - was formed by regioselective oxetane cleavage at C(4). Disappointingly, this compound was not the desired diol **6** as could be quickly detected by the absence of any OH bands in the IR spectrum. The substance was moderatly stable to chromatography on silica gel and decomposed upon standing at room temperature. Careful analysis of the unknown material which was isolated in improved yields (71%) under acidic conditions (TFA in CH_2Cl_2) led to the possible structure **11**. Epoxide **12** with identical molecular composition was a less likely alternative suggestion (scheme 5).



Scheme 5. The ring opening of **5** under BF_3 catalysis

***Structure Proof of the Ring Opening Product* 11.** Several facts supported the assignment of **11**, among others its ^{1}H-NMR shift data,[14,15] the absence of any allylic $^4J_{HH}$ coupling between the vinylic proton and the methyl groups, a coupling constant of 2.0 Hz between the isolated protons (vinylic H and PhCH) and strong NOE effects of both geminal methyl groups to the vinylic proton. Still, a sound and unambiguous chemical proof was desired. For this purpose the idea to selectively cleave the heterocycle by catalytic hydrogenation appealed to us because it would afford a stable final product which was presumably easy to characterize and it would enable a differentiation between **11** and **12**. Upon treatment with hydrogen at high pressure we isolated the tertiary alcohol **14** in 66% yield (entry 4 in table 2) whose structure correlated with the anticipated dihydrofuran structure **11** (scheme 6). In several runs with two different catalysts and under varying conditions the hydrogenation sequence could be nicely monitored (table 2). As is shown in scheme 6 the double bond is reduced first and a tetrahydrofuran skeleton **13** is formed which is further hydrogenated to the alcohol **14**. Prolonged exposure to a H_2 atmosphere in the presence of $Pd(OH)_2$ (entry 5) finally induced a complete reduction of the phenyl group to afford **15**.



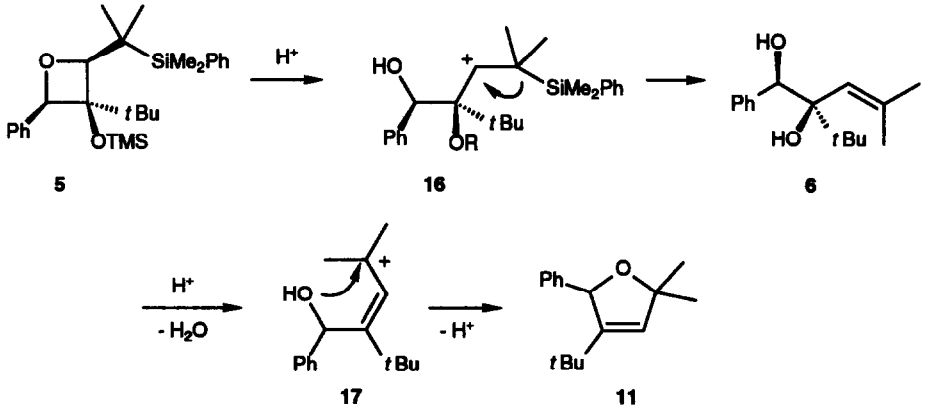
Scheme 6. Hydrogenation of the dihydrofuran **11**

Table 2. The influence of various parameters on the product ratio of the hydrogenation (scheme 6)

Entry	p [bar]	Catalyst[a]	t [h]	Relative Ratio[b]: **11:13:14:15**
1	1	Pd/C	24	78:22:0:0
2	100	Pd/C	24	23:42:33:2
3	100	Pd/C	72	16:29:50:5
4	150	Pd/C	72	0:18:75:7
5	150	$Pd(OH)_2$	96	0:4:55:41

[a] Reaction at room temperature in methanol as solvent. [b] Determined by GC analysis.

Mechanism. With the acquired knowledge about the structure of the oxetane ring opening product the initial mechanistic considerations shall be briefly revisited. The presumed course of the reaction for the acid catalyzed variant is illustrated in scheme 7. Lewis-acid catalysis should proceed in an analogous fashion. It seems likely that the desired diol **6** has indeed been formed via the projected intermediate carbenium ion **16**. The driving force for the regioselectivity in the ring opening has to be attributed to the facile desilylation of this intermediate. There was no hint that 1,2-alkyl shifts occur under the reaction conditions neither to C(2) nor to C(4). Even if the phenyl substituent competed successfully with the silylalkyl group in the stabilization of a carbenium ion, the higher velocity of the nucleophilically assisted desilylation as compared to pinacol type rearrangements would strongly favor the observed reaction pathway. The known instability of the TMSO-protective group under acidic conditions should give rise to the formation of diol **6**. Unfortunately, **6** is not stable under the conditions explored so far and probably yields an allylic cation **17** which cyclizes to the 5-membered dihydrofuran **11**. Literature precedence for similar behaviour of hydroxymethyl-substituted allylic cations stems from acid catalyzed cyclizations of allenic alcohols and 1,4-alkenediols.[14,16]



5 16 6

17 11

Scheme 7. Proposed mechanism for the acid-promoted formation of dihydrofuran **11**

Outlook. In summary, we have shown that the concept of silyl directed oxetane ring opening is a viable one. However succeeding acid catalyzed processes have not yet been effectively suppressed. A modified process is required in order to terminate the reaction at the desired diol stage. Preliminary attempts to trigger the reaction by fluoride catalysis have seen no success but the search for proper fragmentation conditions is continued in our laboratory.

EXPERIMENTAL

General. All reactions involving water sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under Ar. Chemicals and solvents for this kind of reactions were distilled from an appropriate drying agent. Irradiation experiments were performed in degassed solvents under argon. Common solvents (cyclohexane, ethyl acetate, pentane, ether) used for chromatography were distilled prior to use. All other reagents and solvents were used as received. - Melting points: Reichert hot bench (uncorrected). - IR: Perkin Elmer 1605 FT or Perkin Elmer 298. - MS: Varian Saturn II ion trap instrument (GC/MS), Finnigan MAT 8230 (GC/MS) or Finnigan MAT 312. - ^1H and ^{13}C NMR: Bruker AM-400, Bruker AM-360 or Bruker WM-300. Chemical shifts are reported relative to tetramethylsilane as an internal reference. $CDCl_3$ was used as solvent unless noted otherwise. The multiplicities of the ^{13}C NMR signals were determined with DEPT puls sequences. - Elemental Analyses: Perkin Elmer 240. - TLC: glass-backed plates (Merck 0.25 mm silica gel 60-F); eluent given in brackets, a cyclohexane (CH) / ethyl acetate (EA) mixture was used unless stated otherwise; detection by UV or by coloration with ceric ammonium molybdate (CAM). - Flash chromatography[17] (FC): Merck silica gel 60 (230-400 mesh) (50 g for 1 g of material to be separated). - Column chromatography (CC): Merck silica gel 60 (70-230 mesh) or Woelm aluminum oxide neutral (activity II).

Rearrangement of Oxetanes upon Treatment with Acetyl Chloride and Sodium Iodide. 1.2 mmol of NaI (180 mg) was suspended in 0.5 ml of acetonitrile and the mixture was cooled to 0°C. 1 mmol of the oxetane[1,12] (**1a**: 278 mg; **1b**: 312 mg) was added first followed by slow addition of a solution of 1 mmol acetyl chloride (79 mg, 71 µl) in 1 ml acetonitrile. After 30 min at 0°C the solution was warmed to room temperature and subsequently stirred for 16 h. It was quenched with 5 ml of a saturated $NaHCO_3$ solution (aq) and the mixture was extracted with Et_2O. The combined organic layers were washed with aqueous $Na_2S_2O_3$ solution and with brine, dried with $MgSO_4$ and filtered. After removal of the solvents *in vacuo* the residue was purified by flash chromatography (CH/EA = 95/5).

1-Acetyloxy-4,4-dimethyl-3-phenyl-2-pentanone (**2a**). 105 mg (42%). R_f = 0.49 (75/25). - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2950 (s, $C_{al}H$), 1750 (vs, CO), 1725 (vs, CO), 1230 (vs, OAc), 730 (m, Ph), 705 (s, Ph). - ^1H NMR (300 MHz): δ = 1.00 [s, 9 H, $C(CH_3)_3$], 2.12 (s, 3 H, $COCH_3$), 3.55 (s, 1 H, C*H*), 4.44 (d, ^2J = 17.0 Hz, 1 H, C*H*H), 4.73 (d, ^2J = 17.0 Hz, 1 H, CH*H*), 7.22-7.38 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 20.3 (q, $COCH_3$), 27.9 [q, $C(CH_3)_3$], 34.7 [s, $C(CH_3)_3$], 63.5 (d, *C*H), 68.7 (t, CH_2), 127.4 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 130.2 (d, $C_{ar}H$), 134.7 (s, C_{ar}), 170.0 (s, *C*OOR), 203.3 (s, *C*O). - MS (EI, 70 eV), *m/z* (%): 192 (57) [M^+ - $(CH_3)_2CCH_2$], 150 (100), 105 (41), 91 (30), 43 (57). - Anal. Calcd. for $C_{15}H_{20}O_3$ (248.322): C, 72.55; H, 8.12. Found: C, 72.53; H, 8.12.

3-Acetyloxy-1,1-diphenyl-2-butanone (**2b**). 85 mg (30%). R_f = 0.41 (75/25). - IR (film): $\tilde{\nu}$ = 3030 cm^{-1} (w, $C_{ar}H$), 3020 (w, $C_{ar}H$), 1740 (sh, CO), 1725 (vs, CO), 1230 (vs, OAc), 740 (m, Ph), 700 (s, Ph). - ^1H NMR (300 MHz): δ = 1.33 (d, ^3J = 7.2 Hz, 3 H, $CHCH_3$), 2.01 (s, 3 H, $COCH_3$), 5.30 (q, ^3J = 7.2 Hz, 1 H, $CHCH_3$), 5.37 (s, 1 H, $CHPh_2$), 7.19-7.38 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 16.7 (q, $CHCH_3$), 20.5 (q, $COCH_3$), 60.0 (d, $CHPh_2$), 74.6 (d, CHOAc), 127.2 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 128.8 (d, $C_{ar}H$), 129.0 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 137.3 (s, C_{ar}), 137.9 (s, C_{ar}), 170.0 (s, COOR), 205.6 (s, CO). - MS (EI, 70 eV), *m/z* (%): 282 (0.3) [M^+], 222 (4), 194 (8), 179 (19), 167 (100) [$PhC_7H_7^+$], 165 (33), 152 (19), 115 (56) [M^+ - Ph_2CH], 87 (29), 43 (35). - Anal. Calcd. for $C_{18}H_{18}O_3$ (282.339): C, 76.57; H, 6.43. Found: C, 76.57; H, 6.42.

Rearrangement of Oxetane* 1a *upon Treatment with Trifluoroacetic Acid. 78 mmol (8.9 g, 6.0 ml) Trifluoroacetic acid (TFA) was added to a solution of 0.6 mmol oxetane **1a** (167 mg) in 3 ml CH_2Cl_2 at 0°C. After 2.5 h at this temperature the mixture was diluted with 30 ml of a 2/1 mixture (v/v) of toluene/*n*-propyl acetate and the volatiles were removed *in vacuo*. The residue was treated with 20 ml of toluene and the toluene was removed *in vacuo*. The crude material was purified by flash chromatography (CH/EA = 94/6).

4,4-Dimethyl-1-hydroxy-3-phenyl-2-pentanone (**3**). 67 mg (54%). m.p.: 64-65°C. - R_f = 0.18 (90/10). - IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (s, b, OH), 1750 (vs, CO), 1050 (s, CH_2OH), 720 (m, Ph), 695 (s, Ph). - ^1H NMR (300 MHz): δ = 1.00 [s, 9 H, $C(CH_3)_3$], 3.49 (s, 1 H, OH), 4.11 (d, ^2J = 19.0 Hz, 1 H, CHH), 4.20 (d, ^2J = 19.0 Hz, 1 H, CHH), 7.26-7.30 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 27.9 [q, $C(CH_3)_3$], 34.9 [s, $C(CH_3)_3$], 63.8 (d, CH), 69.4 (t, CH_2), 127.5 (d, $C_{ar}H$), 128.2 (d, $C_{ar}H$), 130.1 (d, $C_{ar}H$), 134.8 (s, C_{ar}), 210.0 (s, CO). - MS (EI, 70 eV), *m/z* (%): 206 (0.3) [M^+], 191 (1), 150 (100) [M^+ - $(CH_3)_2CCH_2$], 147 (44), 105 (67), 104 (37), 91 (97), 57 (29). - Anal. Calcd. for $C_{13}H_{18}O_2$ (206.285): C, 75.69; H, 8.80. Found: C, 75.85; H, 8.74.

4,4-Dimethyl-1-hydroxy-2-phenyl-3-pentanone (**4**). 19 mg (15%). R_f = 0.07 (90/10). - IR (KBr): $\tilde{\nu}$ = 3500 cm^{-1} (s, b, OH), 1690 (vs, CO), 1045 (s, CH_2OH), 725 (m, Ph), 690 (s, Ph). - ^1H NMR (300 MHz): δ = 1.08 [s, 9 H, $C(CH_3)_3$], 1.94 (s, 1 H, OH), 3.70 (dd, ^2J = 11.0 Hz, ^3J = 5.3 Hz, 1 H, CHH), 4.08 (dd, ^2J = 11.0 Hz, ^3J = 8.6 Hz, 1 H, CHH), 4.38 (dd, ^3J = 8.6 Hz, ^3J = 5.3 Hz, 1 H, CH), 7.22-7.40 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 26.6 [q, $C(CH_3)_3$], 45.3 [s, $C(CH_3)_3$], 55.5 (d, CH), 65.8 (t, CH_2), 127.5 (d, $C_{ar}H$), 128.5 (d, $C_{ar}H$), 128.9 (d, $C_{ar}H$), 135.7 (s, C_{ar}), 215.7 (s, CO). - MS (EI, 70 eV), *m/z* (%): 207 (3), 121 (13) [M^+ - $COC(CH_3)_3$], 104 (100), 91 (21), 57 (83). - Anal. Calcd. for $C_{13}H_{18}O_2$ (206.285): C, 75.69; H, 8.80. Found: C, 75.64; H, 8.63.

***Silylcuprate Addition to the* α,β-*Unsaturated Ketone* 7.** 14 mmol of $PhMe_2SiLi$[8a] in THF (25.0 ml of a 0.56 M solution) were added dropwise to a suspension of 7 mmol CuCN (627 mg) in 4 ml THF at 0°C. After 20 min the ruby red solution was cooled to -23°C and a solution of 6.2 mmol enone **7**[9] (870 mg) in 4 ml THF was slowly added within 15 min. The mixture was stirred at -23°C for 1 h and was subsequently warmed to 0°C within 2 h. 2 ml of a sat. NH_4Cl solution (aq) were injected to quench the reaction. After dilution with pentane the slurry was filtered through a plug of silica gel and dried with $MgSO_4$. Evaporation *in vacuo* gave an oil, which was purified by flash chromatography (pentane/ether = 45/1).

5-(Dimethylphenylsilyl)-2,2,5-trimethyl-3-hexanone (**8**). 1.66 g (97%). R_f = 0.45 (pentane/ether = 45/1). - IR (film): $\tilde{\nu}$ = 3050 cm^{-1} (w, $C_{ar}H$), 2960 (s, $C_{al}H$), 2860 (m, $C_{al}H$), 1705 (s, CO), 1250 (s, $SiMe_2Ph$), 820 (vs,

$SiMe_2Ph$), 770 (s, Ph), 705 (s, Ph). - ^1H NMR (300 MHz): δ = 0.37 [s, 6 H, $Si(CH_3)_2Ph$], 1.03 [s, 9 H, $C(CH_3)_3$], 1.05 [s, 6 H, $C(CH_3)_2$], 2.39 (s, 2 H, CH_2), 7.30-7.55 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -5.0 [q, $Si(CH_3)_2Ph$], 19.3 [s, $C(CH_3)_2$], 24.0 [q, $C(CH_3)_2$], 26.4 [q, $C(CH_3)_3$], 44.4 [s, $C(CH_3)_3$], 45.0 (t, CH_2), 127.4 (d, $C_{ar}H$), 128.8 (d, $C_{ar}H$), 134.4 (d, $C_{ar}H$), 138.0 (s, C_{ar}), 215.7 (s, CO). - MS (EI, 70 eV), *m/z* (%): 276 (4) [M^+], 261 (39) [$M^+ - CH_3$], 219 (28) [$M^+ - C(CH_3)_3$], 135 (100) [$(CH_3)_2SiPh^+$], 105 (8), 75 (10), 40 (13). - Anal. Calcd. for $C_{17}H_{28}OSi$ (276.493): C, 73.85; H, 10.21. Found: C, 73.63; H, 10.11.

***Silyl Enol Ether Formation from Ketone* 8.** TMSCl (4 mmol, 0.43 g, 0.51 ml) was added to a cooled solution of 3.6 mmol of lithium diisopropylamide (LDA) (prepared from 3.6 mmol amine and 3.6 mmol BuLi at 0°C) in 5 ml THF at -78°C. At this temperature 3 mmol ketone **8** (0.83 g) dissolved in 1 ml THF was added dropwise within 20 min. After being kept at -78°C for 10 min the reaction mixture was warmed to ambient temperature and stirred for another 24 h. It was diluted with pentane and filtered through a plug of silica gel. The solvents were removed *in vacuo* and the residue was again treated with pentane and filtered. After removal of the solvent the crude product was purified by flash chromatography (CH to CH/EA = 50/1). 325 mg (39%) of the starting material were recovered.

5-(Dimethylphenylsilyl)-2,2,5-trimethyl-3-[(trimethylsilyl)oxy]-3-hexene (**9**). 428 mg (41%). R_f = 0.73 (pentane/ether = 45/1). - IR (film): $\tilde{\nu}$ = 3040 cm^{-1} (w, $C_{ar}H$), 2940 (s, $C_{al}H$), 2860 (m, $C_{al}H$), 1635 (m, C=C), 1250 (vs, $SiMe_2R$), 1105 (vs, COTMS), 825 (vs, $SiMe_2R$), 765 (m, Ph), 695 (s, Ph). - ^1H NMR (300 MHz): δ = 0.27 [s, 9 H, $Si(CH_3)_3$], 0.32 [s, 6 H, $Si(CH_3)_2Ph$], 1.08 [s, 9 H, $C(CH_3)_3$], 1.13 [s, 6 H, $C(CH_3)_2$], 4.26 (s, 1 H, CCH), 7.3-7.6 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -5.6 [q, $Si(CH_3)_3$], 2.2 [q, $Si(CH_3)_2Ph$], 23.3 [s, $C(CH_3)_2$], 24.9 [q, $C(CH_3)_2$], 29.4 [q, $C(CH_3)_3$], 37.2 [s, $C(CH_3)_3$], 110.4 (d, CCH), 127.2 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 134.7 (d, $C_{ar}H$), 138.1 (s, C_{ar}), 155.0 (s, COTMS). - MS (EI, 70 eV), *m/z* (%): 348 (3) [M^+], 213 (100) [$M^+ - (CH_3)_2SiPh$], 135 (17) [$(CH_3)_2SiPh^+$], 123 (53) [$M^+ - (CH_3)_2SiPh - (CH_3)_3SiOH$], 81 (8), 73 (23) [$(CH_3)_3Si^+$], 43 (7). - Anal. Calcd. for $C_{20}H_{36}OSi_2$ (348.675): C, 68.90; H, 10.41. Found: C, 69.00; H, 10.39.

Irradiation of Silyl Enol Ether* 9 *in the Presence of Benzaldehyde. The irradiation was carried out as described elsewhere[1b] either with a Rayonet^R RPR 3000 Å light source (high temperature) or with an Heraeus Original Hanau^R TQ 150 lamp (low temperature). 3 mmol Silyl enol ether **9** (1.05 g) and 1.5 mmol benzaldehyde (160 mg, 154 µl) were employed. In order to achieve a high temperature inside the reaction vessel the Rayonet^R chamber RPR-100 reactor was run without cooling. After complete benzaldehyde consumption the irradiation was stopped and the solvent was removed. The residue was purified by flash chromatography (CH/EA = 400/1). Unchanged silyl enol ether was recovered in varying amounts. The desired major regioisomer could be further purified by recrystallization from acetonitrile.

3-(1,1-Dimethylethyl)-4-[1-(dimethylphenylsilyl)-1-methylethyl]-2-phenyl-3-[(trimethylsilyl)oxy]-oxetane (**5**). 412 mg (60%). R_f = 0.32 (pentane/ether: 45/1). - IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w, $C_{ar}H$), 2950 (s, $C_{al}H$), 2890 (m, $C_{al}H$), 1250 (vs, $SiMe_2R$), 995 (s, C-O-C), 835 (vs, $SiMe_2R$), 755 (s, Ph), 700 (vs, Ph). - ^1H NMR (300 MHz): δ = -0.22 [s, 9 H, $Si(CH_3)_3$], 0.43 (s, 3 H, $SiCH_3$), 0.49 (s, 3 H, $SiCH_3$), 0.97 (s, 3 H, CCH_3), 1.03 [s, 9 H, $C(CH_3)_3$], 1.04 (s, 3 H, CCH_3), 4.77 (s, 1 H, CH), 5.72 (s, 1 H, CHPh), 7.2-7.7 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -5.4 (q, $SiCH_3$), -4.6 (q, $SiCH_3$), 3.2 [q, $Si(CH_3)_3$], 18.2 (q, CCH_3), 20.1 (q, CCH_3), 25.5 [s, $C(CH_3)_2$], 26.9 [q, $C(CH_3)_3$], 36.8 [s, $C(CH_3)_3$], 84.0 (d, CH), 86.7 (d, CHPh), 94.6 (s, COTMS),

127.3 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.8 (d, $C_{ar}H$), 134.8 (d, $C_{ar}H$), 137.5 (s, C_{ar}), 139.8 (s, C_{ar}). - MS (EI, 70 eV), *m/z* (%): 248 (18) [M^+ - $OHCC(CH_3)_2SiMe_2Ph$], 233 (11) [M^+ - $OHCC(CH_3)_2SiMe_2Ph$ - CH_3], 213 (100) [M^+ - PhCHO - $(CH_3)_2SiPh$], 135 (62) [$(CH_3)_2SiPh^+$], 123 (95), 105 (21) [$PhCO^+$], 81 (39), 73 (79) [$Si(CH_3)_3^+$], 57 (28), 44 (32). - Anal. Calcd. for $C_{27}H_{42}O_2Si_2$ (454.799): C, 71.31; H, 9.30. Found: C, 71.33; H, 9.00.

***Acid Catalyzed Ring Opening of Oxetane* 5.**[7] 91 mmol (10.4 g, 7.0 ml) Trifluoroacetic acid (TFA) was added to a solution of 0.7 mmol oxetane **5** (319 mg) in 4 ml CH_2Cl_2 at 0°C. After being kept at this temperature for 2 h the mixture was diluted with 30 ml of a 2/1 (v/v) mixture of toluene/*n*-propyl acetate and the volatiles were removed *in vacuo*. The residue was treated with 20 ml of toluene and the toluene was removed *in vacuo*. The crude material was purified by flash chromatography (CH/EA = 105/1).

2,2-Dimethyl-4-(1,1-dimethylethyl)-5-phenyl-2,5-dihydrofuran (**11**). 115 mg (71%). R_f = 0.30 (95/5). - IR (film): $\tilde{\nu}$ = 3065 cm^{-1} (w, $C_{ar}H$), 3029 (w, $C_{ar}H$), 2966 (vs, $C_{al}H$), 2868 (m, $C_{al}H$), 1014 (s, C-O-C), 758 (s, Ph), 700 (s, Ph). - ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 [s, 9 H, $C(CH_3)_3$], 1.32 (s, 3 H, CCH_3), 1.45 (s, 3 H, CCH_3), 5.60 (d, ^4J = 2.0 Hz, 1 H, CC*H*), 5.69 (d, ^4J = 2.0 Hz, 1 H, PhC*H*), 7.2-7.4 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 28.6 (q, CCH_3), 28.9 (q, CCH_3), 30.1 [q, $C(CH_3)_3$], 31.9 [s, $C(CH_3)_3$], 86.1 (s, CCO), 88.0 (d, CHPh), 127.9 (d, CCH), 128.2 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 142.5 (s, C_{ar}), 149.4 [s, $CC(CH_3)_3$]. - MS (EI, 70 eV), *m/z* (%): 215 (58) [M^+ - CH_3], 173 (12) [M^+ - $C(CH_3)_3$], 159 (94) [M^+ - CH_3 - $CH_2C(CH_3)_2$], 91 (11), 77 (20), 57 (100) [$C(CH_3)_3^+$], 43 (66). - HRMS Calcd. for $C_{15}H_{19}O$: 215.1436. Found: 215.1440.

NOE experiments. The experiments were performed with a Bruker AM-360 instrument by employing a known pulse sequence.[18] By irradiation of the indicated proton(s) the following intensity enhancements were detected: H(PhC*H*) (5.69): H_{ar}(ortho) [2.7 %]; H(CC*H*) (5.63): $H(C_aH_3)$ [0.3 %], $H(C_bH_3)$ [0.3 %]; $H(C_bH_3)$ (1.45): H(CCH) [3.1 %], H_{ar}(ortho) [1.3 %]; $H(C_aH_3)$ (1.32): H(CCH) [3.7 %], H(PhCH) [1.8 %]; H[$C(CH_3)$] (0.88): H(CCH) [5.3 %], H(PhCH) [3.4 %].

***Hydrogenation of Dihydrofuran* 11.** Dihydrofuran **11** (0.2 mmol, 43.4 mg) was dissolved in 2.5 ml of MeOH. 50 mg Pd/C (10% w/w) were added and the mixture was hydrogenated at 150 bar for 3 d. The crude reaction mixture was filtered through a plug of cotton and the solvent was removed *in vacuo*. The oily residue (68 mg) was purified by flash chromatography (CH/EA = 115/1).

3-Phenylmethyl-2,2,5-trimethyl-5-hexanol (**14**). 30 mg (66%). m.p. = 45°C. - R_f = 0.15 (90/10). - IR (KBr): $\tilde{\nu}$ = 3420 (s, b, OH) cm^{-1}, 3010 (w, $C_{ar}H$), 2940 (vs, $C_{al}H$), 1385 (w, *t* Bu), 1360 (s, *t* Bu), 1140 (m, COH), 735 (m, Ph), 695 (s, Ph). - ^1H NMR (300 MHz): δ = 0.93 [s, 9 H, $C(CH_3)_3$], 0.98 (s, 3 H, CCH_3), 1.05 (s, 3 H, CCH_3), 1.40 (dd, ^2J = 15.0 Hz, ^3J = 5.8 Hz, 1 H, CC*H*H), 1.67-1.73 (m, 1 H, C*H*tBu), 1.74 (dd, ^2J = 15.0 Hz, ^3J = 2.2 Hz, 1 H, CCH*H*), 2.40 (dd, ^2J = 13.8 Hz, ^3J = 8.2 Hz, 1 H, PhC*H*H), 2.98 (dd, ^2J = 13.8 Hz, ^3J = 4.5 Hz, 1 H, PhCH*H*), 7.14-7.31 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 28.1 [q, $C(CH_3)_3$], 29.4 (q, CH_3), 31.0 (q, CH_3), 34.4 [s, $C(CH_3)_3$], 39.7 (t, CCH_2), 44.0 (t, $PhCH_2$), 45.3 (d, CH), 70.5 [s, $C(CH_3)_2$] 125.9 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 129.4 (d, $C_{ar}H$), 142.8 (s, C_{ar}). - MS (EI, 70 eV), *m/z* (%): 219 (1) [M^+ - CH_3], 201 (9) [M^+ - H_2O - CH_3], 160 (60) [M^+ - H_2O - $(CH_3)_2CCH_2$], 145 (100), 91 (45), 57 (32). - Anal. Calcd. for $C_{16}H_{26}O$ (234.381): C, 81.99; H, 11.18. Found: C, 81.97; H, 11.08.

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