Diastereomerically Pure 3-(Silyloxy)oxetanes by a Selective Paternò-Büchi Reaction

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Received May 19, 1993

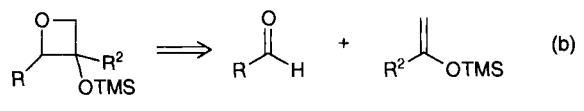
Key Words: Paternò-Büchi reaction / Oxetanes / Diastereoselectivity / Enol silyl ethers / Photocycloaddition

Diastereomerically pure 3-[(trimethylsilyl)oxy]oxetanes **3** were prepared in moderate to good yields (45–72%) by the Paternò-Büchi reaction of silyl enol ethers **2** with benzaldehyde. The photocycloaddition exhibits a high degree of regio- and diastereoselectivity. The substituents R in the silyl enol ether have been varied [R = Me, Et, iPr, *t*Bu, Ph, $CH(OMe)_2$, $CH(OCH_2)_2$, $C(OCH_2)_2Me$], and it was found that steric bulk is mainly responsible for enhanced selectivity (diastereoselectivity from 70:30 up to 95:5). The regiochemical control is perfect (regioselectivity >95:5) except for silyl enol ether **2a** (R = Me) in the case of which a 90:10 ratio of regioisomers was observed. Irradiation of the reaction mixture at lower temperature (−25°C) led to a further improvement of diastereoselectivity. The relative configuration of the products obtained was elucidated both by ^{1}H-NMR spectroscopy and by chemical degradation. As a mechanistic hypothesis to explain the high observed diastereoselectivity we propose that the steric environment in the intermediate diradical **11** determines the selectivity according to two possible reaction pathways, i.e. bond formation and retrocleavage.

The Paternò-Büchi reaction has long been recognized as one of the most important photochemical procedures, and it constitutes a simple and straightforward route to functionalized oxetanes[1]. The variety of substrates employed as carbonyl and alkene components appears to be almost unlimited. Due to their electron rich π-bond, enol ethers quench photoexcited ketones or aldehydes quite efficiently[2]. This fact in combination with the ready availability of the substrates has led to their extensive use in Paternò-Büchi reactions, and many practical applications have been reported[1]. Cases in which the regio- and stereoselectivity of the reaction can be simultaneously controlled are of particular interest[3,4]. Cyclic enol ethers like furans[5] and dihydrofurans[6] undergo in the presence of various carbonyl compounds selective ring closure to 2-alkoxy- and 3-alkoxyoxetanes, respectively. Only the former process, however, the so-called "photoaldolization", has proved to be synthetically valuable[1a], the latter suffers from limited flexibility both in the choice of starting materials and in the further utility of the products.

Nonetheless, 3-alkoxyoxetanes deserve special attention since they may serve as versatile 1,2-functionalized building blocks. In view of a projected ring opening at C-4 (C–O bond cleavage) by nucleophilic attack, acyclic enol ethers which bear no vinylic β substituents are the substrates of choice [equation (a)].

(a)



(b)

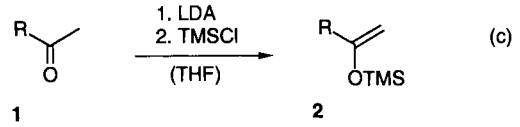
Unfortunately, simple enol ethers of this type, e.g. ethyl vinyl ether, do not fulfill any selectivity requirement. In Paternò-Büchi reactions with various carbonyl compounds they yield 2- and 3-alkoxyoxetanes (ratio from 1:4 to 1:2) almost stereorandomly[7]. In other words, the newly formed oxetane bears partly the desired 1,2- and partly the undesired aldol-like 1,3-substitution pattern. We recently embarked on a project to solve the described selectivity problems by employing silyl enol ethers as alkene components [equation (b)]. An earlier report in this area had already disclosed that regioselective addition to symmetrical ketones (benzophenone) was possible[8]. Our initial study[9], however, confirmed not only the expected regioselectivity of the photocycloaddition to benzaldehyde but it also revealed a surprisingly high diastereoselectivity. The latter observation appears to be of particular synthetic value because there is a lack of umpoled α-alkoxy anion synthons which add stereoselectively to carbonyl compounds[10].

The following account summarizes our results obtained with different silyl enol ethers. The relative stereochemistry of the adducts was unambiguously established. In addition, two optimized irradiation procedures are provided and, based on experimental data, the mechanism of the reaction is briefly discussed.

1. Initial Experiments and Optimization

Several methods for the preparation of silyl enol ethers have been developed during the last two decades[11]. For our purposes a kinetic deprotonation of suitable carbonyl pre-

cursors with subsequent chlorotrimethylsilane (TMSCl) quenching proved most efficient [equation (c)][12].



1 2

	a	b	c	d	e	f	g	h
R	Me	Et	iPr	tBu	Ph	$CH(OMe)_2$		

For the sensitive substrates **1f–h**[13] it was advantageous to add the ketone to a preformed mixture of lithium diisopropylamide (LDA) and TMSCl at −78 °C. By this modification the yet unreported compounds **2f–h** were prepared in good yields (58–72%).

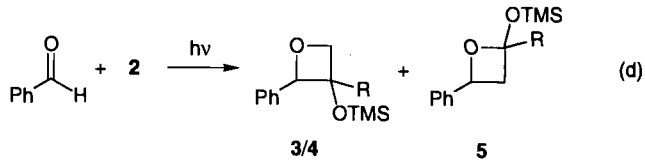
In a series of experiments in order to optimize some parameters (solvent, ratio of starting materials, workup etc.) the photocycloaddition was conveniently performed slightly above room temperature (ca. 30–40 °C) in quartz tubes by employing an air-cooled Rayonet chamber reactor (light source: RPR 3000 Å). This set-up facilitated the irradiation of several samples at a time. A concentration of 0.15 mol l^{-1} was chosen, and the progress of the reaction was monitored by TLC and GC. Benzene emerged as the solvent of choice for this protocol. The major byproducts resulted from benzaldehyde photoreduction and dimerization. An excess of silyl enol ether seemed therefore suited to suppress undesired bimolecular processes. In most cases, however, the yield increased only slightly by raising the amount of enol ether from 1.2 to 2.0 equivalents.

As Table 1 shows, the observed diastereoselectivity roughly parallels the bulkiness of the substituent R. Functionalized R groups (acetals and ketals) cause a remarkably selective ring closure yielding only a single diastereoisomer. The silyl enol ether **2e** reacts less readily than the other alkenes which is likely due to its own photochemical activity. In general, yields are moderate to good, and the products can easily be purified by chromatography. A separation of the diastereoisomers could be mostly achieved except for **3c/4c** and **3e/4e**. In these cases the major isomers **3c** and **3e** could be obtained sufficiently pure after a process of even higher selectivity had been discovered (vide infra).

Table 1. Photocycloaddition reaction of various silyl enol ethers **2** with benzaldehyde at 30–40 °C in benzene (light source: Rayonet RPR 3000 Å)

alkene **2**	t[a] [h]	yield [%]	ds[b] [**3**:**4**]	rs[b] [(**3**+**4**):**5**]
2a	4	51	70/30	90/10
2b	4	51	83/17	> 95/5
2c	6	52	88/12	> 95/5
2d	6	65	91/9	> 95/5
2e	24	46	92/8	> 95/5
2f	4	72	> 95/5	> 95/5
2g	4	54	> 95/5	> 95/5
2h	18	45	> 95/5	> 95/5

[a] Length of irradiation. — [b] ds = diastereoselectivity, rs = regioselectivity; determined by ^{1}H-NMR analysis of the crude reaction mixture.



3/4 **5**

Since we were concerned about the existence of possible regioisomers **5**, we undertook a considerable effort to trace possible products. In a single case (irradiation of benzaldehyde and silyl enol ether **2a**) the ^{1}H-NMR spectrum of the crude material revealed a yet unobserved signal in the characteristic range for the oxetane 2-H (dd) which was shown to be part of an ABX system. Upon hydrolysis the signal disappeared and 4-hydroxy-4-phenyl-2-butanone was identified as the resulting product[14]. Formation of 4-phenyl-4-[(trimethylsilyl)oxy]-2-butanone in a thermal Mukaiyama aldol reaction had been previously ruled out by control experiments and by a comparison of the spectra with its known ^{1}H-NMR data[15]. It is tempting to assign structure **5a** to the elusive side product in particular because all other required ^{1}H-NMR signals were found. The question why only one set of signals, corresponding to a single diastereoisomer, was detected remains unclear at present. In all other irradiation experiments under scrutiny no hint either at the formation of regioisomer **5** or at its hydrolysis product was found by ^{1}H-NMR analysis.

We conclude that the Paternò-Büchi reaction of silyl enol ethers with benzaldehyde proceeds with excellent regioselectivity strongly favoring the formation of the desired 3-[(trimethylsilyl)oxy]-substituted oxetanes. If the size of R is reduced the opposite mode of ring closure may also take place. These results are in accordance with previous studies in this area[8]. On the other hand, the high diastereoselectivity of this process is yet unprecedented, and it was of prime importance to reliably establish the relative configuration of the products.

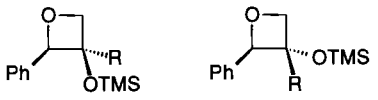
2. Proof of Relative Stereochemistry

All methods employed for this purpose lead to identical conclusions. A first indication was found by comparing the ^{1}H-NMR chemical shift data of the different diastereoisomers (Table 2).

The singlets due to the TMS protons in the major products are shifted roughly by 0.30 ppm upfield relative to comparable TMS ethers ($\delta \cong 0.10$). By contrast, the TMS groups of the minor diastereoisomers exhibit a somewhat weaker downfield shift of ca. 0.10 ppm. This behaviour may be reliably attributed to the ring current of the C-2 phenyl substituent, and the TMS group in **3** must hence be positioned

at the same side as phenyl. If any protons are present at the C-3 substituent R analogous observations can be made: the signals of the alpha and methyl protons of R in **3a–d** are all shifted downfield, whereas they appear at much higher field in the minor diastereoisomers **4a–d**. At this point we have to mention that all configurations represented in the schemes and equations refer to racemic products. One enantiomer is arbitrarily shown.

Table 2. ^{1}H-NMR chemical shift data for the trimethylsilyl protons in the oxetanes **3** and **4**



	a	b	c	d	e	f	g	h
3	-0.16	-0.16	-0.23	-0.28	-0.23	-0.14	-0.11	-0.15
4	0.17	0.23	0.29	0.29	0.06	-	-	-

NOE difference spectroscopy[16] confirmed the assumed relative stereochemistry of the products. For these experiments the isomers **3d** and **4d** were chosen because their ^{1}H-NMR spectra are not obscured by coupling phenomena. After separation by column chromatography each isomer was independently subjected to NOE studies. Due to its lack of nearby protons the 2-H nucleus was most susceptible to induced signal enhancement. Figure 1 illustrates the most prominent results.

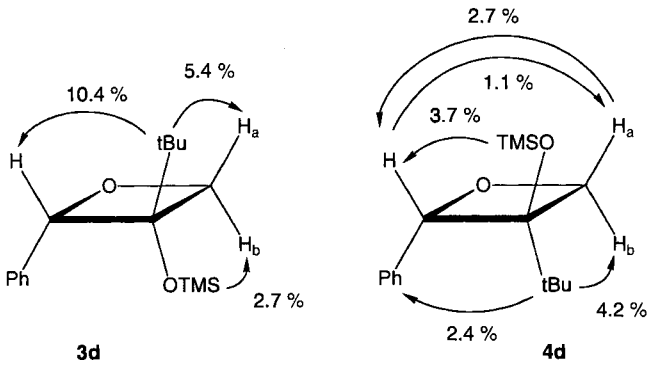
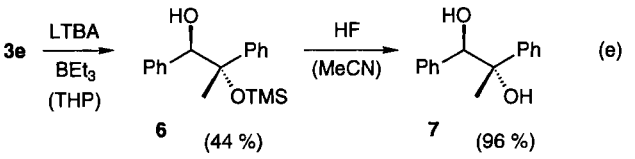


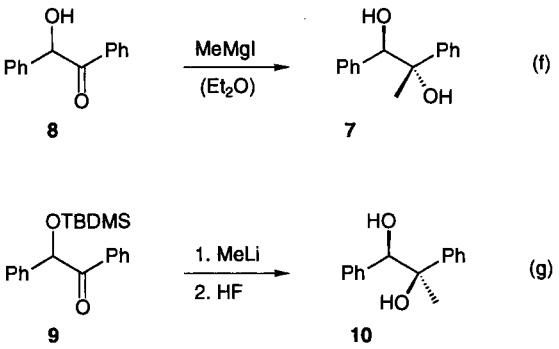
Figure 1. The most prominent signal enhancements observed in NOE difference spectroscopy experiments on **3d** and **4d**

In the major isomer **3d** the *tert*-butyl group and the proton at C-2 appear to be close in space as predicted, whereas in **4d** the TMS group and 2-H are *cis* to each other. All other NOE signals which are comprehensively listed in the experimental section support this assignment.

Finally we sought to prove the relative configuration by a chemical degradation. To this end, the oxetane **3e** with the presumed stereochemistry shown was reductively ring-opened by nucleophilic hydride attack[17]. The selection of this particular oxetane was not accidental. Since one could suppose that the ring current of the 3-phenyl substituent counteracts the effect of the 2-phenyl group, the conclusions drawn from ^{1}H-NMR data above seemed at least slightly ambiguous. An additional confirmation was desirable. The intermediate silyl ether **6** was isolated as a single isomer by flash chromatography and fully characterized. Subsequent deprotection (40% aq. HF, MeCN, 0°C, 2 h) furnished the diol **7** which was identified by a comparison with the known diastereoisomers **7**[18] and **10**[19].



An authentic sample of compound **7** was easily accessible by Grignard addition of methylmagnesium iodide to benzoin (**8**)[18]. Compound **10** was obtained by the non-chelation-controlled addition of methyllithium to TBDMS-protected benzoin **9** (ds = 70:30)[19], followed by desilylation and separation [equations (f) and (g)]. The diol formed by oxetane ring opening and **7** were identical as revealed by all analytical means (^{1}H and ^{13}C NMR, R_f, t_R, MS, m.p.), whereas **7** and **10** unequivocally differed from each other. As one can safely assume that the hydride attack does not interfere with the relative stereochemistry this piece of work lends further support to our initial proposal.



In short, the major diastereoisomer **3** produced in the Paternò-Büchi reaction between silyl enol ethers and benzaldehyde bears the 2-phenyl and the 3-TMSO substituent on the same ring side (*cis*).

3. Temperature Dependence and Mechanism

Comparing the results in Table 1 with our preliminary data[9] one observes different diastereoselectivities for the same reactions. To be precise, the former process appears to be less selective than the latter. This undesired change can be assigned to the differing reaction conditions. Since an air-cooled reactor was employed in the present paper (vide supra) the temperature was markedly increased as compared to the first experiments. We therefore returned to the liquid cooled immersion-well apparatus (light source: Original Hanau TQ 150) previously used (see Experimental). The temperature of the reaction mixture was monitored by a thermocouple. The silyl enol ether **2d** tested as the first sub-

strate showed indeed a significant increase from ds = 91:9 (30 °C) to ds = 95:5 (−25 °C). At 0 °C our earlier result could be reproduced (ds = 93:7, 56% yield). In these experiments *n*-hexane was shown to be superior to other solvents.

Since the seminal work of Scharf and coworkers a deeper understanding of the stereoselectivity in photocycloadditions and its temperature dependence has arisen[4c]. Their studies have been mainly devoted to the facial diastereoselectivity of Paternò-Büchi reactions. It was shown that the photocycloaddition of chiral phenylglyoxylates to various alkenes passes through two selection stages, and it was found that a reversal in the change of diastereoselectivity occurs at a certain temperature, the so-called inversion temperature T_{inv}[20]. In most cases, T_{inv} represented a maximum of diastereoselectivity, and the high-temperature region of the Eyring plot ($T > T_{inv}$) exhibited a decrease of selectivity with *increasing* temperature and was enthalpy-determined, whereas the low-temperature region ($T > T_{inv}$) exhibited a decrease of selectivity with *decreasing* temperature and was entropy-determined. As an extension of our experiments with the selective enol ether **2d** we undertook a brief temperature-dependent study in which the least selective silyl enol ether **2a** was used as the substrate. The possibility that an equilibration of diastereoisomers could intervene was ruled out by irradiation of the pure oxetane **3a** under the reaction conditions. No epimerization to **4a** was detected. Unfortunately, our equipment limited the temperature range under scrutiny to ca. 60 K. Provided that the two diastereoisomers are formed from a single intermediate in a kinetically controlled reaction (vide infra), theory requires that ln k/k' should be directly proportional to T^{-1}. A straight line was indeed obtained from which $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ were calculated to be −3.9 kJ mol^{-1} and −6.2 J mol^{-1} K^{-1}, respectively (Figure 2).

The data reveal that the stereoselectivity of the Paternò-Büchi reaction in the studied temperature range is enthalpy-determined.

Before drawing any conclusions from this result we would like to evaluate several models which may accommodate in particular the stereoselectivity of the studied reactions. For that purpose we start from the generally accepted mechanism of the Paternò-Büchi reaction as it is depicted in Figure 3[21].

The regioselectivity of the reaction can be explained both on steric and on electronic grounds. The easily accessible unsubstituted olefinic carbon is attacked by the electrophilic oxygen of benzaldehyde in the triplet state to form the mesomerically stabilized triplet diradical. Intersystem crossing (ISC) leads to the singlet 1,4-diradical **11**. At this stage stereoselectivity comes into play. From a simplified point of view the C–C bond formation step may be exclusively responsible for the observed diastereoselectivity. This would require that **11** lives long enough to allow for free rotation; an assumption which seems at least dubious, from what is known about singlet diradicals and their lifetime[22]. An alternative explanation could be put forward if the triplet geometry was considered to be decisive for stereodifferentiation. Free rotation in the triplet diradical is certainly pos-

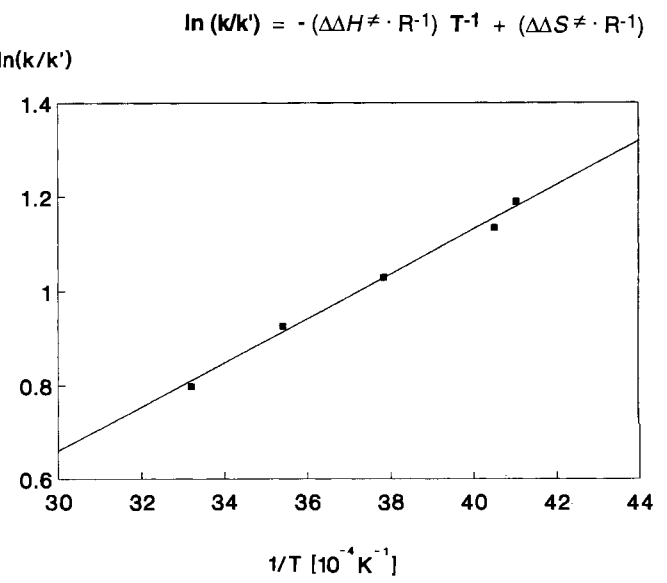


Figure 2. Diastereoselectivity (k/k' = [**3a**]/[**4a**]) observed in the Paternò-Büchi reaction of benzaldehyde with silyl enol ether **2a** as a function of temperature (Eyring plot)

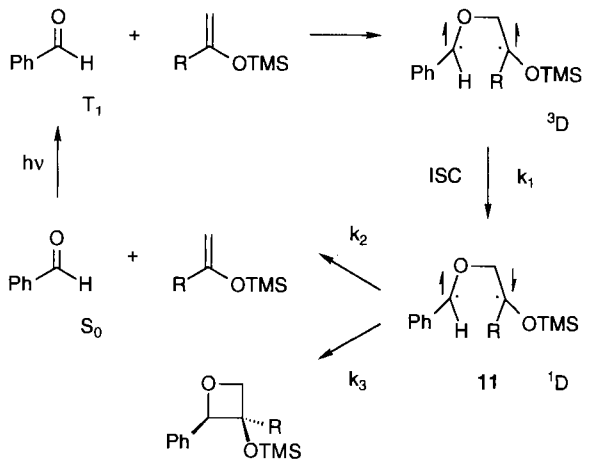


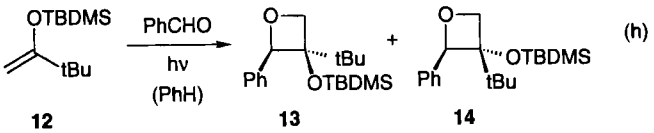
Figure 3. Mechanistic scheme of the Paternò-Büchi reaction: the retrocleavage as decisive selection pathway

sible, and the bulkier substituents could arrange such that they form the less strained C–C bond. This hypothesis, however, neglects the fact that only certain diradical geometries allow effective ISC to occur[23]. The inspection of ISC geometries previously discussed for related cases[6b,c] reveals that the formation of **4** should be favored which is not in accordance with the experiment. The third model which we currently find most satisfactory to explain our results focusses on the competition between the two decay modes of **11**, i.e. retrocleavage and ring closure (Figure 3). For the transformation of **11** into the oxetane **4** bulky substituents are to approach each other. This process is retarded by steric interactions, and retrocleavage is strongly favored ($k_2 \gg k_3$). On the contrary, if the steric environment in **11** is less encumbered, ring closure can take place more readily to yield **3**. In other words, there is one set of conformers of diradical **11** which requires the bulky R group and the phenyl sub-

stituent to be *cis*-oriented for ring closure. In these geometries C–C bond formation is sterically disfavored, and it occurs by far more slowly than cleavage. The other diastereomeric set of conformers enables the more facile approach of R and OTMS, and the oxetane **3** can form irreversibly.

The given explanation implies a stereodifferentiation via tight transition states in which the free activation enthalpy dominates the discrimination step[20,24]. The fact that this prediction can indeed be verified by temperature-dependent studies (vide supra) renders some credibility to our hypothesis. Still we are well aware that a thorough kinetic discussion highly depends on a more precise knowledge of the stability and lifetime of intermediate **11** – if it is an intermediate at all – and this lack severely limits a precise reasoning.

An additional result [equation (h)] obtained with alkene **12** which, in turn, was prepared from ketone **1d** underlines the strong dependence on bulk.



12 **13** **14**

(61 %; ds: 85/15)

Due to its larger silyl group the photocycloaddition of the alkene **12** to benzaldehyde is less selective (ds = 85:15) than that of its TMS counterpart **2d** (ds = 91:9).

4. Irradiation at Low Temperature

With the knowledge we had acquired about temperature dependence and possible side reactions a modified protocol for irradiation was devised. Since benzaldehyde dimerization was to be suppressed the carbonyl compound was slowly added to the silyl enol ether. Furthermore, the reaction was carried out at low temperature (−25 °C) in an immersion-well apparatus, and the consumption of benzaldehyde was monitored by GC analysis. *n*-Hexane was used as the solvent. These modifications led to good yields for almost all silyl enol ether photocycloadditions and to a considerable improvement in diastereoselectivity. The only exception was silyl enol ether **2e** which reacted sluggishly for the reasons described earlier.

The selectivities and yields listed in Table 3 indicate that the Paternò-Büchi reaction of silyl enol ethers with aldehydes has the potential to emerge as a valuable tool for stereocontrolled C–C bond formation. Further studies are under way to extend this methodology to other substrates and to open up new avenues for the ring opening of oxetanes.

Table 3. Photocycloaddition of various silyl enol ethers **2** with benzaldehyde [cf. equation (d)] at −25 °C in *n*-hexane (light source: Original Hanau TQ 150)

alkene **2**[a]	t[b] [h]	yield [%]	ds[c] [3:4]	rs[c] [(3+4):5]
2a	5	48	76/24	90/10
2b	4	60	92/8	> 95/5
2c	4	59	94/6	> 95/5
2d	6	66	> 95/5	> 95/5
2e	8	32	95/5	> 95/5
2f	2	69	> 95/5	> 95/5
2g	4	54	> 95/5	> 95/5

[a] Benzaldehyde was slowly added to a solution of the silyl enol ether in *n*-hexane. – [b] Length of irradiation (including benzaldehyde addition). – [c] Determined by ^{1}H-NMR analysis of the crude reaction mixture.

This work was generously supported by the *Deutsche Forschungsgemeinschaft* (Ba 1372/1-1) and by the *Fonds der Chemischen Industrie*. We thank Priv.-Doz. Dr. *J. Lauterwein* and *K. Busse* for performing the NOE studies and *L. Freund* for skillful technical assistance. The constant encouragement and support of Prof. Dr. *D. Hoppe* is gratefully appreciated.

Experimental

All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under Ar. Irradiation experiments were performed in degassed solvents under Ar. Chlorotrimethylsilane, triethylamine, and diisopropylamine were distilled from calcium hydride. 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. – ^{1}H 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[25] (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 aluminium oxide neutral (activity II).

The silyl enol ethers **2b–e** were conventionally prepared from ketones by quenching the "kinetic" enolate with chlorotrimethylsilane (TMSCl)[12]. Enol ether **2a** was available by a procedure described by Cazeau[26]. For comparison, the most prominent analytical data are briefly provided.

2-[(Trimethylsilyl)oxy]-1-propene (**2a**): B.p. 92–95 °C. – IR (film): $\tilde{\nu}$ = 2945 cm^{-1} (vs, CH), 1635 (s, C=C). – ^{1}H NMR (300 MHz): δ = 0.21 [s, 9H, $Si(CH_3)_3$], 1.77 (s, 3H, CH_3), 4.05 (s, 2H, CH_2). – ^{13}C NMR (75.5 MHz): δ = 0.1 [q, $Si(CH_3)_3$], 22.8 (q, CH_3), 91.2 (t, CH_2), 156.0 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 130 (21) [M$^+$], 115 (74), 75 (100), 73 (38), 45 (39).

2-[(Trimethylsilyl)oxy]-1-butene (**2b**): B.p. 112–114 °C. – IR (film): $\tilde{\nu}$ = 2935 cm^{-1} (vs, b, CH), 1610 (s, C=C). – ^{1}H NMR (300 MHz): δ = 0.23 [s, 9H, $Si(CH_3)_3$], 1.02 (t, ^3J = 7.5 Hz, 3H, CH_3), 2.03 (q, ^3J = 7.5 Hz, 2H, CH_2), 4.03 (s, 1H, CC*H*H), 4.05 (s, 1H, CCH*H*). – ^{13}C NMR (75.5 MHz): δ = 0.1 [q, $Si(CH_3)_3$], 11.6 (q, CH_3), 29.6 (t, CH_2), 88.9 (t, CCH_2), 161.1 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 144 (19) [M$^+$], 129 (31), 75 (100), 73 (40), 45 (25).

3-Methyl-2-[(trimethylsilyl)oxy]-1-butene (**2c**): B.p. 128–131 °C. – IR (film): $\tilde{\nu}$ = 2965 cm^{-1} (s, CH), 1624 (m, C=C). – ^1H NMR (300 MHz): δ = 0.18 [s, 9H, $Si(CH_3)_3$], 1.00 (d, ^3J = 6.8 Hz, 6H, CH_3), 2.18 (sept, ^3J = 6.8 Hz, 1H, CH), 3.94 (d, ^2J = 1.0 Hz, 1H, CC*H*H), 4.01 (d, ^2J = 1.0 Hz, 1H, CCH*H*). – ^{13}C NMR (100 MHz): δ = 0.1 [q, $Si(CH_3)_3$], 20.5 (q, CH_3), 34.5 (d, CH), 87.1 (t, CCH_2), 164.8 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 158 (61) [M^+], 143 (90), 115 (6), 75 (100), 73 (94), 43 (35).

3,3-Dimethyl-2-[(trimethylsilyl)oxy]-1-butene (**2d**): B.p. 141 to 142 °C. – IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (s, CH), 2911 (m, CH), 2871 (m, CH), 1620 (s, C=C). – ^1H NMR (400 MHz): δ = 0.19 [s, 9H, $Si(CH_3)_3$], 1.03 (s, 9H, CH_3), 3.91 (d, ^2J = 1.1 Hz, 1H, CC*H*H), 4.06 (d, ^2J = 1.1 Hz, 1H, CCH*H*). – ^{13}C NMR (100 MHz): δ = 0.2 [q, $Si(CH_3)_3$], 28.5 (q, CH_3), 34.5 [s, $C(CH_3)_3$], 85.8 (t, CCH_2), 167.2 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 172 (6) [M^+], 157 (88), 75 (56), 73 (71), 57 (18), 43 (100).

1-Phenyl-1-[(trimethylsilyl)oxy]ethene (**2e**): B.p. 99 °C/20 Torr. – IR (film): $\tilde{\nu}$ = 3058 cm^{-1} (m, $C_{ar}H$), 2961 (s, $C_{al}H$), 1616 (s, C=C). – ^1H NMR (400 MHz): δ = 0.27 [s, 9H, $Si(CH_3)_3$], 4.43 (d, ^2J = 1.7 Hz, 1H, CC*H*H), 4.91 (d, ^2J = 1.7 Hz, 1H, CCH*H*), 7.27–7.34 (m, 3H, arom. H), 7.56–7.61 (m, 2H, arom. H). – ^{13}C NMR (100 MHz): δ = 0.0 [q, $Si(CH_3)_3$], 91.0 (t, CCH_2), 125.2 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.2 (d, $C_{ar}H$), 137.5 (s, C_{ar}), 155.7 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 192 (52) [M^+], 191 (100), 177 (79), 137 (28), 77 (29), 75 (69).

Modified Procedure for the Preparation of Silyl Enol Ethers from Sensitive Ketones: To a solution of 0.1 mol of lithium diisopropylamide [10.7 g; prepared from 0.10 mol of diisopropylamine (10.1 g; 14.1 ml) and 0.10 mol of *n*BuLi (40 ml of a 2.5 M solution in *n*-hexane) at 0 °C] in 200 ml of THF a solution of 0.12 mol of TMSCl (13.0 g; 15.2 ml) was slowly added by a syringe at −78 °C. At this temperature the freshly distilled ketone[13] (0.10 mol) was added as a solution in 20 ml of THF within 1 h. The mixture was stirred for 30 min at −78 °C and subsequently allowed to reach room temp. It was diluted with 200 ml of pentane and filtered. The solvents were removed in vacuo, and the residue was again treated with pentane (100 ml) and filtered. After removal of the solvent, distillation in vacuo yielded the pure silyl enol ethers.

3,3-Dimethoxy-2-[(trimethylsilyl)oxy]-1-propene (**2f**): Yield: 13.7 g (72%), b.p. 70 °C/20 Torr. – IR (film): $\tilde{\nu}$ = 2961 cm^{-1} (s, CH), 1645 (s, C=C), 1252 (s, $SiMe_3$), 847 (vs, $SiMe_3$). – ^1H NMR (400 MHz): δ = 0.23 [s, 9H, $Si(CH_3)_3$], 3.33 (s, 6H, OCH_3), 4.35 (s, 1H, C*H*H), 4.52 [s, 1H, C*H*$(OMe)_2$], 4.54 (s, 1H, CH*H*). – ^{13}C NMR (100 MHz): δ = 0.1 [q, $Si(CH_3)_3$], 53.0 (q, OCH_3), 91.0 (t, CCH_2), 102.0 (d, CH), 153.1 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 160 (36) [$M^+ - H_2CO$], 159 (14), 89 (22), 75 (100) [$HC(OMe)_2^+$], 73 (21), 59 (29). – $C_8H_{18}O_3Si$ (190.3): calcd. C 50.49, H 9.53; found C 50.45, H 9.58.

1-(2-Methyl-1,3-dioxolan-2-yl)-1-[(trimethylsilyl)oxy]ethene (**2g**): Yield: 12.7 g (63%), b.p. 75 °C/18 Torr. – IR (film): $\tilde{\nu}$ = 2942 cm^{-1} (s, CH), 2875 (m, CH), 1630 (s, C=C), 1252 (s, $SiMe_3$), 840 (vs, $SiMe_3$). – ^1H NMR (300 MHz): δ = 0.23 [s, 9H, $Si(CH_3)_3$], 1.49 (s, 3H, CH_3), 3.95 (m, 4H, OCH_2), 4.19 (d, ^2J = 1.1 Hz, 1H, CC*H*H), 4.91 (d, ^2J = 1.1 Hz, 1H, CCH*H*). – ^{13}C NMR (75.5 MHz): δ = 0.0 [q, $Si(CH_3)_3$], 22.9 (q, CH_3), 64.7 (t, OCH_2), 89.9 (t, CCH_2), 107.1 (s, CCH_3), 156.5 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 202 (1) [M^+], 201 (5), 187 (5), 143 (21), 87 (100) [$MeC(OCH_2)_2^+$], 73 (18), 43 (48). – $C_9H_{18}O_3Si$ (202.3): calcd. C 53.34, H 8.97; found C 53.39, H 9.10.

1-(1,3-Dioxolan-2-yl)-1-[(trimethylsilyl)oxy]ethene (**2h**): Yield: 10.9 g (58%), b.p. 60 °C/20 Torr. – IR (film): $\tilde{\nu}$ = 2938 cm^{-1} (s, CH), 2861 (m, CH), 1628 (s, C=C), 1240 (s, $SiMe_3$), 832 (vs, $SiMe_3$). – ^1H NMR (300 MHz): δ = 0.17 [s, 9H, $Si(CH_3)_3$], 3.82–3.98 (m, 4H, OCH_2), 4.25 (d, ^2J = 1.2 Hz, 1H, CC*H*H), 4.46 (d, ^2J = 1.1 Hz, 1H, CCH*H*), 5.11 (s, 1H, CH). – ^{13}C NMR (75.5 MHz): δ = 0.0 [q, $Si(CH_3)_3$], 65.1 (t, OCH_2), 93.4 (t, CCH_2), 102.4 (d, CH), 154.7 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 188 (2) [M^+], 173 (1), 129 (24), 101 (16), 73 (100) [$HC(OCH_2)_2^+$]. – $C_8H_{16}O_3Si$: calcd. 188.08687; found 188.08649 (MS).

Preparation of 3,3-Dimethyl-2-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-1-butene[27] (**12**): To a stirred solution of 50 mmol of LDA [5.36 g; prepared from 50 mmol of diisopropylamine (5.1 g; 7.0 ml) and 50 mmol of *n*BuLi (20 ml of a 2.5 M solution in *n*-hexane) at 0 °C] in 100 ml of THF a solution of ketone **1d** (50 mmol; 5.01 g, 6.25 ml) in 5 ml of THF was slowly added from a dropping funnel (within 30 min). Then a solution of 52 mmol of *tert*-butylchlorodimethylsilane (TBDMSCl) (7.8 g), dissolved in a mixture of 20 ml of 1,3-dimethyl-2-imidazolidinone (DMI) and 10 ml of THF, was added. The suspension was allowed to reach room temp. and was subsequently stirred for 30 min. The reaction mixture was hydrolyzed with ice-cold water (100 ml) and extracted with cold pentane (2 × 150 ml). The combined organic layers were washed with water (100 ml) and brine (100 ml). After drying with $MgSO_4$ the solvents were removed in vacuo, and the residue was distilled in a kugelrohr apparatus to yield 8.5 g (79%) of a clear colorless liquid; b.p. 100 °C/120 Torr. – IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (vs, CH), 2850 (sh, CH), 1605 (s, C=C). – ^1H NMR (300 MHz): δ = 0.17 [s, 6H, $Si(CH_3)_2$], 0.95 [s, 9H, $SiC(CH_3)_3$], 1.06 (s, 9H, CH_3), 3.89 (d, ^2J = 1.5 Hz, 1H, CC*H*H), 4.04 (d, ^2J = 1.5 Hz, 1H, CCH*H*). – ^{13}C NMR (75.5 MHz): δ = −4.7 [q, $Si(CH_3)_2$], 18.3 (s, SiC), 25.8 [q, $SiC(CH_3)_3$], 28.2 [q, $C(CH_3)_3$], 36.7 [s, $C(CH_3)_3$], 85.1 (t, CCH_2), 167.3 (s, CCH_2). – MS (EI, 70 eV), *m/z* (%): 199 (6) [$M^+ - CH_3$], 157 [$M^+ - t$Bu] (19), 143 (11), 75 (100).

Irradiation Procedure A (Irradiation in an Air-Cooled Chamber Reactor): A quartz tube was charged with 1.5 mmol of benzaldehyde (159 mg, 150 µl), 3.0 mmol of silyl enol ether **2** (or **12**) and 10 ml of benzene. The samples were irradiated at 300 nm (RPR 3000 Å) in a merry-go-round unit. The reaction was monitored by TLC. After complete consumption of benzaldehyde irradiation was stopped. The solvent was evaporated in vacuo, and the residue was analyzed by ^1H-NMR spectroscopy to determine the diastereo- and regioselectivity. Purification was carried out by flash chromatography with the solvent mixture indicated below. Yields and diastereomeric ratios are given in Table 1.

Irradiation Procedure B (Irradiation at Low Temperature): A Duran glass jacket (ca. 50 ml volume) directly attached to a liquid cooled immersion lamp (Original Hanau TQ 150) and equipped with a septum-capped joint was charged with 20 ml of *n*-hexane and 4.0 mmol of silyl enol ether **2**. The mixture was stirred by a continuous Ar stream which was introduced through a bent gas inlet on the bottom of the glass jacket. After cooling to −25 °C, irradiation was started and a solution of 2.0 mmol of benzaldehyde (212 mg, 202 µl) in 10 ml of *n*-hexane was slowly added by a syringe (within ca. 1.5 h). The reaction was subsequently monitored by GC. After complete consumption of benzaldehyde the mixture was filtered, and the solvent was evaporated from the filtrate in vacuo. Further workup was carried out as outlined in procedure A. Yields and diastereomeric ratios are given in Table 3.

(2RS,3RS)-(±)-3-Methyl-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**3a**): Purification by FC (CH/EA = 50:1), R_f = 0.59 (75:25). – IR (film): $\tilde{\nu}$ = 3018 cm^{-1} (w, $C_{ar}H$), 2940 (m, $C_{al}H$), 2860 (m, $C_{al}H$), 1243 (s, $SiMe_3$), 973 (s, COC), 833 (vs, $SiMe_3$). – ^1H NMR (300 MHz): δ = −0.16 [s, 9H, $Si(CH_3)_3$], 1.68 (s, 3H, CH_3), 4.55 (d, ^2J = 6.0 Hz, 1H, CC*H*H), 4.68 (d, ^2J = 6.0 Hz, 1H, CCH*H*), 5.39 (s,

1H, C*H*Ph), 7.20–7.41 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 1.4 [q, Si(CH$_3$)$_3$], 27.5 (q, CH$_3$), 75.6 (s, *C*OTMS), 83.8 (t, CH$_2$), 94.8 (d, *C*HPh), 127.0 (d, C$_{ar}$H), 127.2 (d, C$_{ar}$H), 127.6 (d, C$_{ar}$H), 138.5 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 219 (18) [M$^+$ – OH], 206 (22) [M$^+$ – H$_2$CO], 191 (23), 130 (54) [M$^+$ – PhCHO], 115 (100), 105 (40), 75 (51) [SiMe$_2$OH$^+$], 73 (36). – $C_{13}H_{20}O_2Si$ (236.4): calcd. C 66.05, H 8.53; found C 65.86, H 8.43.

(2RS,3SR)-(±)-3-Methyl-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**4a**): Purification by FC (CH/EA = 50:1), R_f = 0.64 (75:25). – IR (film): ṽ = 3010 cm^{-1} (w, C$_{ar}$H), 2940 (m, C$_{al}$H), 2860 (m, C$_{al}$H), 1245 (s, SiMe$_3$), 960 (s, COC), 832 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = 0.17 [s, 9H, Si(CH$_3$)$_3$], 1.08 (s, 3H, CH$_3$), 4.28 (d, ^2J = 5.6 Hz, 1H, CC*H*H), 4.69 (d, ^2J = 5.6 Hz, 1H, CCH*H*), 5.67 (s, 1H, C*H*Ph), 7.28–7.35 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 1.9 [q, Si(CH$_3$)$_3$], 22.8 (q, CH$_3$), 77.2 (s, *C*OTMS), 82.0 (t, CH$_2$), 94.2 (d, *C*HPh), 125.4 (d, C$_{ar}$H), 127.5 (d, C$_{ar}$H), 128.1 (d, C$_{ar}$H), 138.5 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 219 (19) [M$^+$ – OH], 206 (31) [M$^+$ – H$_2$CO], 191 (23), 130 (53) [M$^+$ – PhCHO], 115 (100), 105 (33), 75 (52) [SiMe$_2$OH$^+$], 73 (36). – $C_{13}H_{20}O_2Si$ (236.4): calcd. C 66.05, H 8.53; found C 66.12, H 8.28.

(2RS,3RS)-(±)-3-Ethyl-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**3b**): Purification by FC (CH/EA = 150:1), R_f = 0.60 (75:25). – IR (film): ṽ = 3018 cm^{-1} (w, C$_{ar}$H), 2930 (vs, C$_{al}$H), 2865 (sh, C$_{al}$H), 1243 (vs, SiMe$_3$), 978 (s, COC), 832 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = –0.16 [s, 9H, Si(CH$_3$)$_3$], 1.04 (t, ^3J = 7.2 Hz, 3H, CH$_3$), 1.92 (dq, ^2J = 14.4, ^3J = 7.2 Hz, 1H, C*H*HMe), 2.08 (dq, ^2J = 14.4, ^3J = 7.2 Hz, 1H, CH*H*Me), 4.53 (d, ^2J = 6.4 Hz, 1H, CC*H*H), 4.70 (d, ^2J = 6.4 Hz, 1H, CCH*H*), 5.44 (s, 1H, C*H*Ph), 7.21–7.39 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 1.3 [q, Si(CH$_3$)$_3$], 7.6 (q, CH$_3$), 33.3 (t, *C*H$_2$Me), 77.9 (s, *C*OTMS), 81.7 (t, CH$_2$), 92.6 (d, *C*HPh), 126.6 (d, C$_{ar}$H), 127.2 (d, C$_{ar}$H), 127.7 (d, C$_{ar}$H), 138.7 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 220 (29) [M$^+$ – H$_2$CO], 205 (21), 144 (100) [M$^+$ – PhCHO], 129 (93), 91 (21), 75 (88) [SiMe$_2$OH$^+$], 73 (68). – $C_{14}H_{22}O_2Si$ (250.4): calcd. C 67.15, H 8.85; found C 67.38, H 8.97.

(2RS,3SR)-(±)-3-Ethyl-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**4b**): Purification by FC (CH/EA = 150:1), R_f = 0.64 (75:25). – IR (film): ṽ = 3018 cm^{-1} (w, C$_{ar}$H), 2935 (vs, C$_{al}$H), 2865 (sh, C$_{al}$H), 1242 (s, SiMe$_3$), 972 (s, COC), 832 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = 0.23 [s, 9H, Si(CH$_3$)$_3$], 0.61 (t, ^3J = 7.1 Hz, 3H, CH$_3$), 1.24–1.36 (m, 1H, C*H*HMe), 1.40–1.52 (m, 1H, CH*H*Me), 4.33 (d, ^2J = 6.2 Hz, 1H, CC*H*H), 4.69 (d, ^2J = 6.2 Hz, 1H, CCH*H*), 5.70 (s, 1H, C*H*Ph), 7.23–7.40 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 2.0 [q, Si(CH$_3$)$_3$], 6.6 (q, CH$_3$), 28.4 (t, *C*H$_2$Me), 80.0 (t, CH$_2$), 80.2 (s, *C*OTMS), 93.9 (d, *C*HPh), 125.8 (d, C$_{ar}$H), 127.6 (d, C$_{ar}$H), 128.0 (d, C$_{ar}$H), 138.4 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 220 (36) [M$^+$ – H$_2$CO], 205 (19), 144 (97), 129 (95) [M$^+$ – PhCHO], 91 (16), 75 (100) [SiMe$_2$OH$^+$], 73 (82). – $C_{14}H_{22}O_2Si$ (250.4): calcd. C 67.15, H 8.85; found C 67.23, H 9.02.

(2RS,3RS)-(±)-3-(1-Methylethyl)-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**3c**): Purification by FC (CH/EA = 120:1), R_f = 0.60 (75:25). – IR (film): ṽ = 3019 cm^{-1} (m, C$_{ar}$H), 2934 (vs, C$_{al}$H), 2862 (s, C$_{al}$H), 1247 (s, SiMe$_3$), 978 (s, COC), 833 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = –0.23 [s, 9H, Si(CH$_3$)$_3$], 0.96 (d, ^{3}J = 6.7 Hz, 3H, CH$_3$), 1.10 (d, ^3J = 6.8 Hz, 3H, CH$_3$), 2.23 (sept, ^3J = 6.8 Hz, 1H, C*H*Me$_2$), 4.59 (d, ^2J = 6.8 Hz, 1H, CC*H*H), 4.67 (d, ^2J = 6.8 Hz, 1H, CCH*H*), 5.49 (s, 1H, C*H*Ph), 7.22–7.41 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 1.4 [q, Si(CH$_3$)$_3$], 16.0 (q, CH$_3$), 16.3 (q, CH$_3$), 36.4 (d, *C*HMe$_2$), 79.9 (t, CH$_2$), 80.3 (s, *C*OTMS), 91.1 (d, *C*HPh), 125.9 (d, C$_{ar}$H), 126.9 (d, C$_{ar}$H), 127.7 (d, C$_{ar}$H), 138.9 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 234 (52) [M$^+$ – H$_2$CO], 219 (28), 158 (47) [M$^+$ – PhCHO], 143 (100), 75 (65) [SiMe$_2$OH$^+$], 73 (72). – $C_{15}H_{24}O_2Si$ (264.4): calcd. C 68.13, H 9.15; found C 68.17, H 9.25.

(2RS,3SR)-(±)-3-(1-Methylethyl)-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**4c**): The compound was not isolated in diastereomerically pure form. Purification by FC (CH/EA = 120:1), R_f = 0.60 (75:25). – ^{1}H NMR (300 MHz): δ = 0.29 [s, 9H, Si(CH$_3$)$_3$], 0.72 (d, ^3J = 6.4 Hz, 3H, CH$_3$), 1.09 (d, ^3J = 6.6 Hz, 3H, CH$_3$), 1.92 (sept, ^3J = 6.6 Hz, 3H, C*H*Me$_2$), 4.48 (d, ^2J = 6.8 Hz, 1H, CC*H*H), 4.67 (d, ^2J = 6.8 Hz, 1H, CCH*H*), 5.64 (s, 1H, C*H*Ph), 7.22–7.39 (m, 5H, arom. H).

(2RS,3RS)-(±)-3-(1,1-Dimethylethyl)-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**3d**): Purification by FC (CH/EA = 150:1), R_f = 0.27 (95:5). – IR (film): ṽ = 3018 cm^{-1} (w, C$_{ar}$H), 2940 (vs, C$_{al}$H), 2890 (sh, C$_{al}$H), 1245 (s, SiMe$_3$), 983 (s, COC), 832 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = –0.28 [s, 9H, Si(CH$_3$)$_3$], 1.10 (s, 9H, CH$_3$), 4.61 (d, ^2J = 7.0 Hz, 1H, CC*H*H), 4.68 (d, ^2J = 7.0 Hz, 1H, CCH*H*), 5.63 (s, 1H, C*H*Ph), 7.20–7.39 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 1.4 [q, Si(CH$_3$)$_3$], 24.4 (q, CH$_3$), 35.9 (s, *C*Me$_3$), 77.4 (t, CH$_2$), 82.4 (s, *C*OTMS), 88.3 (d, *C*HPh), 125.7 (d, C$_{ar}$H), 126.7 (d, C$_{ar}$H), 127.7 (d, C$_{ar}$H), 139.5 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 248 (9) [M$^+$ – H$_2$CO], 233 (12), 172 (13) [M$^+$ – PhCHO], 157 (100), 75 (22) [SiMe$_2$OH$^+$], 73 (43). – $C_{16}H_{26}O_2Si$ (278.5): calcd. C 69.01, H 9.41; found C 68.85, H 9.37.

(2RS,3SR)-(±)-3-(1,1-Dimethylethyl)-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**4d**): Purification by FC (CH/EA = 150:1), R_f = 0.30 (95:5). – IR (film): ṽ = 3015 cm^{-1} (w, C$_{ar}$H), 2940 (vs, C$_{al}$H), 2900 (sh, C$_{al}$H), 1243 (s, SiMe$_3$), 980 (s, COC), 830 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = 0.29 [s, 9H, Si(CH$_3$)$_3$], 0.79 (s, 9H, CH$_3$), 4.61 (d, ^2J = 6.9 Hz, 1H, CC*H*H), 4.65 (d, ^2J = 6.9 Hz, 1H, CCH*H*), 5.88 (s, 1H, C*H*Ph), 7.20–7.38 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 2.1 [q, Si(CH$_3$)$_3$], 24.8 (q, CH$_3$), 36.8 (s, *C*Me$_3$), 76.4 (t, CH$_2$), 85.7 (s, *C*OTMS), 94.9 (d, *C*HPh), 126.1 (d, C$_{ar}$H), 127.1 (d, C$_{ar}$H), 127.8 (d, C$_{ar}$H), 139.2 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 248 (9) [M$^+$ – H$_2$CO], 233 (12), 172 (10) [M$^+$ – PhCHO], 157 (100), 75 (28) [SiMe$_2$OH$^+$], 73 (52). – $C_{16}H_{26}O_2Si$ (278.5): calcd. C 69.01, H 9.41; found C 68.94, H 9.38.

(2RS,3RS)-(±)-2,3-Diphenyl-3-[(trimethylsilyl)oxy]oxetane (**3e**): Purification by FC (CH/EA = 100:1), R_f = 0.60 (75:25). – IR (film): ṽ = 3015 cm^{-1} (w, C$_{ar}$H), 2939 (m, C$_{al}$H), 1243 (s, SiMe$_3$), 982 (s, COC), 833 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = –0.23 [s, 9H, Si(CH$_3$)$_3$], 4.96 (d, ^2J = 6.8 Hz, 1H, CC*H*H), 5.18 (d, ^2J = 6.8 Hz, 1H, CCH*H*), 5.75 (s, 1H, C*H*Ph), 7.33–7.46 (m, 8H, arom. H), 7.53–7.58 (m, 2H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 1.1 [q, Si(CH$_3$)$_3$], 79.2 (s, *C*OTMS), 82.1 (t, CH$_2$), 95.2 (d, *C*HPh), 125.3 (d, C$_{ar}$H), 127.1 (d, C$_{ar}$H), 127.7 (d, C$_{ar}$H), 127.8 (d, C$_{ar}$H), 128.5 (d, C$_{ar}$H), 137.9 (s, C$_{ar}$), 144.4 (s, C$_{ar}$). – MS (EI, 70 eV), *m/z* (%): 297 (1) [M$^+$ – H], 268 (19) [M$^+$ – H$_2$CO], 253 (9), 192 (63) [M$^+$ – PhCHO], 191 (100), 177 (65), 167 (29), 105 (19), 75 (21) [SiMe$_2$OH$^+$], 73 (19). – $C_{18}H_{22}O_2Si$ (264.4): calcd. C 72.43, H 7.44; found C 72.21, H 7.44.

(2RS,3SR)-(±)-2,3-Diphenyl-3-[(trimethylsilyl)oxy]oxetane (**4e**): The compound was not isolated in diastereomerically pure form. Purification by FC (CH/EA = 100:1), R_f = 0.60 (75:25). – ^{1}H NMR (300 MHz): δ = 0.06 [s, 9H, Si(CH$_3$)$_3$], 4.99 (d, ^2J = 6.8 Hz, 1H, CC*H*H), 5.10 (d, ^2J = 6.8 Hz, 1H, CCH*H*), 6.00 (s, 1H, C*H*Ph), 7.10–7.95 (m, 10H, arom. H).

(2RS,3RS)-(±)-3-(Dimethoxymethyl)-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**3f**): Purification by FC (CH/EA = 95:5), R_f = 0.44 (75:25). – IR (film): ṽ = 3015 cm^{-1} (m, C$_{ar}$H), 2935 (s, C$_{al}$H), 2820 (m, C$_{al}$H), 1241 (vs, SiMe$_3$), 981 (s, COC), 832 (vs, SiMe$_3$). – ^{1}H NMR (300 MHz): δ = –0.14 [s, 9H, Si(CH$_3$)$_3$], 3.52 (s, 3H,

OCH_3), 3.58 (s, 3H, OCH_3), 4.41 [s, 1H, $CH(OMe)_2$], 4.57 (d, $^2J = 6.8$ Hz, 1H, CCHH), 4.82 (d, $^2J = 6.8$ Hz, 1H, CCHH), 5.71 (s, 1H, CHPh), 7.21–7.39 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = 1.4$ [q, $Si(CH_3)_3$], 55.9 (q, OCH_3), 57.1 (q, OCH_3), 78.3 (t, CH_2), 79.5 (s, COTMS), 89.0 (d, CHPh), 106.5 [d, $CH(OMe)_2$], 126.6 (d, $C_{ar}H$), 127.5 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 138.1 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 235 (3) [$M^+ - H_2CO - CH_3O$], 160 (53), 145 (11), 131 (12), 89 (18), 75 (100) [$HC(OMe)_2^+$]. – $C_{15}H_{24}O_4Si$ (296.4): calcd. C 60.78, H 8.16; found C 60.69, H 8.17.

(2RS,3RS)-(±)-3-(2-Methyl-1,3-dioxolan-2-yl)-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**3g**): Purification by FC (CH/EA = 95:5), $R_f = 0.41$ (75:25). – IR (film): $\tilde{\nu} = 3017$ cm^{-1} (w, $C_{ar}H$), 2940 (s, $C_{al}H$), 2870 (m, $C_{al}H$), 1242 (s, $SiMe_3$), 985 (s, COC), 831 (vs, $SiMe_3$). – ^1H NMR (300 MHz): $\delta = -0.11$ [s, 9H, $Si(CH_3)_3$], 1.33 (s, 3H, CH_3), 4.03–4.22 (m, 4H, OCH_2), 4.58 (d, $^2J = 7.0$ Hz, 1H, CCHH), 4.82 (d, $^2J = 7.0$ Hz, 1H, CCHH), 5.73 (s, 1H, CHPh), 7.31–7.39 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = 1.4$ [q, $Si(CH_3)_3$], 18.7 (q, CH_3), 65.3 (t, OCH_2), 65.5 (t, OCH_2), 77.3 (t, CCH_2), 81.5 (s, COTMS), 89.1 (d, CHPh), 110.1 [s, CCH_3], 126.6 (d, $C_{ar}H$), 127.3 (d, $C_{ar}H$), 127.6 (d, $C_{ar}H$), 138.3 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 278 (2) [$M^+ - H_2CO$], 263 (2), 202 (7) [M^+ – PhCHO], 143 (10), 87 (100) [$MeC(OCH_2)_2^+$], 73 (14), 43 (24). – $C_{16}H_{24}O_4Si$ (308.5): calcd. C 62.30, H 7.84; found C 62.50, H 7.95.

(2RS,3RS)-(±)-3-(1,3-Dioxolan-2-yl)-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (**3h**): Purification by FC (CH/EA = 95:5), $R_f = 0.35$ (75:25). – IR (film): $\tilde{\nu} = 3005$ cm^{-1} (w, $C_{ar}H$), 2940 (s, $C_{al}H$), 2865 (s, $C_{al}H$), 1245 (s, $SiMe_3$), 978 (s, COC), 832 (vs, $SiMe_3$). – ^1H NMR (300 MHz): $\delta = -0.15$ [s, 9H, $Si(CH_3)_3$], 4.00–4.06 (m, 2H, OCH_2), 4.10–4.16 (m, 2H, OCH_2), 4.63 (d, $^2J = 6.8$ Hz, 1H, CCHH), 4.79 (d, $^2J = 6.8$ Hz, 1H, CCHH), 5.14 [s, 1H, $CH(OCH_2)_2$], 5.70 (s, 1H, CHPh), 7.24–7.39 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = 1.2$ [q, $Si(CH_3)_3$], 65.6 (t, OCH_2), 65.8 (t, OCH_2), 77.6 (t, CCH_2), 77.8 (s, COTMS), 88.5 (d, CHPh), 105.0 [d, $CH(OCH_2)_2$], 126.7 (d, $C_{ar}H$), 127.3 (d, $C_{ar}H$), 127.6 (d, $C_{ar}H$), 137.8 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 264 (3) [$M^+ - H_2CO$], 205 (6), 188 (7) [M^+ – PhCHO], 129 (18), 73 (100) [$HC(OCH_2)_2^+$], 45 (21). – $C_{15}H_{22}O_4Si$ (294.4): calcd. C 61.19, H 7.53; found C 61.06, H 7.62.

(2RS,3RS)-(±)-3-(1,1-Dimethylethyl)-3-{[(1,1-dimethylethyl)-dimethylsilyl]oxy}-2-phenyloxetane (**13**): Purification by FC (CH/EA = 200:1), $R_f = 0.37$ (95:5). – IR (film): $\tilde{\nu} = 3020$ cm^{-1} (w, $C_{ar}H$), 2930 (vs, $C_{al}H$), 2870 (sh, $C_{al}H$), 1250 (s, $SiMe_2R$), 987 (s, COC), 832 (s, $SiMe_2R$). – ^1H NMR (300 MHz): $\delta = -0.61$ (s, 3H, $SiCH_3$), –0.13 (s, 3H, $SiCH_3$), 0.69 [s, 9H, $SiC(CH_3)_3$], 1.14 [s, 9H, $C(CH_3)_3$], 4.64 (d, $^2J = 6.8$ Hz, 1H, CCHH), 4.70 (d, $^2J = 6.8$ Hz, 1H, CCHH), 5.67 (s, 1H, CHPh), 7.20–7.38 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = -2.9$ (q, $SiCH_3$), –2.4 (q, $SiCH_3$), 18.5 [s, $SiC(CH_3)_3$], 24.5 [q, $SiC(CH_3)_3$], 26.0 [q, $C(CH_3)_3$], 36.3 (s, CMe_3), 77.3 (t, CH_2), 82.0 (s, COTMS), 88.4 (d, CHPh), 125.8 (d, $C_{ar}H$), 126.7 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 139.2 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 290 (1) [$M^+ - H_2CO$], 233 (6), 214 (2) [M^+ – PhCHO], 207 (11), 159 (21), 75 (100) [$SiMe_2OH^+$], 73 (19), 57 (27). – $C_{19}H_{32}O_2Si$ (320.5): calcd. C 71.19, H 10.06; found C 71.10, H 10.07.

(2RS,3SR)-(±)-3-(1,1-Dimethylethyl)-3-{[(1,1-dimethylethyl)-dimethylsilyl]oxy}-2-phenyloxetane (**14**): Purification by FC (CH/EA = 200:1), $R_f = 0.33$ (95:5). – IR (film): $\tilde{\nu} = 3020$ cm^{-1} (w, $C_{ar}H$), 2925 (vs, $C_{al}H$), 2845 (sh, $C_{al}H$), 1250 (s, $SiMe_2R$), 985 (s, COC), 830 (s, $SiMe_2R$). – ^1H NMR (300 MHz): $\delta = 0.22$ (s, 3H, $SiCH_3$), 0.38 (s, 3H, $SiCH_3$), 0.78 [s, 9H, $SiC(CH_3)_3$], 0.99 [s, 9H, $C(CH_3)_3$], 4.63 (s, 2H, CH_2), 5.89 (s, 1H, CHPh), 7.20–7.39 (m, 5H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = -2.2$ (q, $SiCH_3$), –2.4 (q, $SiCH_3$), 18.5 [s, $SiC(CH_3)_3$], 24.9 [q, $SiC(CH_3)_3$], 25.8 [q, $C(CH_3)_3$], 37.1 (s, CMe_3), 76.5 (t, CH_2), 85.6 (s, COTMS), 94.9 (d, CHPh), 126.1 (d, $C_{ar}H$), 127.2 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 139.2 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 233 (9) [$M^+ - H_2CO - t$Bu], 207 (7), 159 (20), 157 (20), 75 (100) [$SiMe_2OH^+$], 73 (19), 57 (18). – $C_{19}H_{32}O_2Si$ (320.5): calcd. C 71.19, H 10.06; found C 70.96, H 10.06.

NOE Investigations: The experiments were performed with a Bruker AM-360 instrument by employing a known pulse sequence[16]. By irradiation of the indicated proton(s) the following intensity enhancements were detected:

Major diastereoisomer **3d**: H_{ar} (7.28): H [3.1%], H (TMS) [0.3%]; H (5.63): H_{ar} (*ortho*) [1.8%], H (*t*Bu) [0.5%]; H_a (4.68): H (*t*Bu) [0.5%]; H_b (4.61): H_{ar} (*ortho*) [0.8%], H (TMS) [0.6%]; H (*t*Bu) (1.10): H [10.4%], H_a [5.4%]; H (TMS) (–0.28): H_{ar} (*ortho*) [0.8%], H_b [2.7%].

Minor diastereoisomer **4d**: H_{ar} (7.34): H [3.5%], H (*t*Bu) [0.7%]; H (5.88): H_{ar} (*ortho*) [1.6%], H_a [1.1%]; H_a (4.65): H [2.7%], H (TMS) [0.4%]; H_b (4.61): H (*t*Bu) [0.5%]; H (*t*Bu) (0.79): H_{ar} (*ortho*) [2.4%], H_b [4.2%]; H (TMS) (0.29): H [3.7%], H_a [1.4%].

Preparation of Diol **7** *by MeMgI Addition to Benzoin* (**8**). – *(1RS,2SR)-(±)-1,2-Diphenyl-1,2-propandiol* (**7**)[18]: 10 mmol of **8** (2.12 g) was suspended in 5 ml of anhydrous ether. Upon cooling to 0°C 11 mmol of methylmagnesium iodide (11.0 ml of a 1.0 M solution in ether) was added to the stirred reaction mixture by a syringe. The solution was allowed to reach room temp. The reaction was quenched with 20 ml of 1 N HCl (aq), and the aqueous layer was extracted with ether (4 × 50 ml). The combined organic extracts were washed with a satd. $NaHCO_3$ solution (30 ml) and brine (30 ml). After drying with $MgSO_4$ the solvents were evaporated in vacuo, and the residue was purified by flash chromatography (CH/EA = 90:10). Thus, 1.95 g (86%) of the diastereomerically pure diol **7** was obtained as a white solid with m.p. 102–104°C (ref.[18a] 103–104°C). $R_f = 0.35$ (60:40). – IR (film): $\tilde{\nu} = 3250$ cm^{-1} (vs, b, OH). – ^1H NMR (300 MHz): $\delta = 1.62$ (s, 3H, CH_3), 2.40 (s, b, 2H, OH), 4.75 (s, 1H, CH), 6.96–7.02 (m, 2H, arom. H), 7.13–7.23 (m, 8H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = 25.5$ (q, CH_3), 76.8 (s, C), 80.9 (d, CH), 126.0 (d, $C_{ar}H$), 126.9 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 127.5 (d, 2C, $C_{ar}H$), 127.6 (d, $C_{ar}H$), 139.4 (s, C_{ar}), 143.6 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 228 (5) [M^+], 209 (6), 194 (14), 179 (23), 121 (100) [M^+ – PhCHOH], 107 (29) [$PhCHOH^+$], 107 (29), 106 (39), 105 (83), 77 (91), 51 (43).

TBDMS Silylation of Benzoin. – *(2RS)-(±)-2-{[(1,1-Dimethylethyl)dimethylsilyl]oxy}-1,2-diphenylethanone* (**9**): A solution of 5 mmol of benzoin (**8**) (1.06 g), 10 mmol of TBDMSCl (1.51 g), and 20 mmol of imidazole (1.36 g) in 15 ml of anhydrous DMF was stirred for 24 h at room temp. As TLC showed the reaction to be complete it was quenched with 50 ml of a satd. $NaHCO_3$ solution, and this mixture was extracted with ether (4 × 50 ml). The combined organic layers were washed with brine and dried with $MgSO_4$. After removal of the solvent in vacuo the residue was purified by flash chromatography (CH/EA = 100:1) to afford 1.42 g (86%) of a colorless oil. $R_f = 0.62$ (75:25). – IR (film): $\tilde{\nu} = 1672$ cm^{-1} (C=O). – ^1H NMR (300 MHz): $\delta = 0.00$ (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.89 [s, 9H, $SiC(CH_3)_3$], 5.74 (s, 1H, CH), 7.22–7.53 (m, 8H, arom. H), 7.96–8.02 (m, 2H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = -5.1$ (q, $SiCH_3$), –5.0 (q, $SiCH_3$), 18.3 [s, $SiC(CH_3)_3$], 25.7 [q, $SiC(CH_3)_3$], 80.4 (d, CH), 125.7 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.5 (d, $C_{ar}H$), 129.9 (d, $C_{ar}H$), 132.7 (d, $C_{ar}H$), 134.5 (s, C_{ar}), 138.9 (s, C_{ar}), 198.9 (CO). – MS (EI, 70 eV), *m/z* (%): 311 (5) [$M^+ - CH_3$], 269 (49) [$M^+ - t$Bu], 221 (100) [M^+ – PhCO], 165 (21), 105 (21), 77 (25), 73 (88).

Preparation of Diol **10** *by MeLi Addition to* **9** *and Subsequent Desilylation.* – *(1RS,2RS)-(±)-1,2-Diphenyl-1,2-propandiol* (**10**): A solution of 1.75 mmol of ketone **9** (570 mg) in 10 ml of ether was cooled to 0°C. 1.8 mmol of methyllithium (1.13 ml of a 1.6 M

solution in ether) was slowly added by a syringe, and the solution was stirred for 1 h at 0°C. It was subsequently treated with 10 ml of a satd. NH_4Cl solution and extracted with ether (3 × 20 ml). The combined extracts were washed with a satd. $NaHCO_3$ solution (20 ml) and brine (20 ml) and dried with $MgSO_4$. After removal of the solvent in vacuo a colorless oil remained (605 mg) which was dissolved in 10 ml of acetonitrile. After cooling of the resulting solution to 0°C, 1 ml of aq. HF (40%) was slowly added. The reaction mixture was allowed to reach room temp. and stirred for another 12 h. It was then poured carefully into 20 ml of a satd. $NaHCO_3$ solution and extracted with ether (4 × 20 ml). The combined extracts were washed with brine (20 ml). After drying ($MgSO_4$) the solvents were removed in vacuo, and the residue was purified by FC (CH/EA = 75:25). The obtained oil (315 mg; 79%) was shown to be a mixture of diastereoisomers (70:30) from which the desired diol **10** could finally be isolated by FC (CH/EA = 90:10) in 55% (220 mg) yield; m.p. 93–94°C (ref.[18a] 94–95°C), $R_f = 0.38$ (60:40). – IR (film): $\tilde{\nu} = 3350\ cm^{-1}$ (vs, b, OH). – ^1H NMR (300 MHz): $\delta = 1.36$ (s, 3H, CH_3), 2.56 (s, b, 2H, OH), 4.81 (s, 1H, CH), 7.05–7.16 (m, 2H, arom. H), 7.20–7.38 (m, 8H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = 24.0$ (q, CH_3), 77.0 (s, C), 80.8 (d, CH), 125.8 (d, $C_{ar}H$), 127.2 (d, $C_{ar}H$), 127.6 (d, 2C, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 139.1 (s, C_{ar}), 145.0 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 228 (5) [M^+], 194 (21), 179 (29), 165 (18), 121 (80) [M^+ – PhCHOH], 107 (21) [$PhCHOH^+$], 106 (34), 105 (87), 77 (100), 51 (47).

Reductive Ring Opening of Oxetane **3e** *by LTBA/BEt_3 in THP. – (1RS,2SR)-(±)-1,2-Diphenyl-2-[(trimethylsilyl)oxy]-1-propanol* (**6**): 2.0 mmol of lithium tri-*tert*-butoxyaluminium hydride (LTBA) was suspended in 1 ml of tetrahydropyran (THP). Then 0.5 mmol of a solution of oxetane **3e** (150 mg) in 1.5 ml of THP was added, and the stirred mixture was cooled to 0°C. Subsequently, 2.0 mmol of BEt_3 (2.0 ml of a 1.0 M solution in THP) was slowly added by a syringe (within 15 min). The solution was allowed to reach room temp. and stirred for another 3 h. Then 5 ml of a satd. $NaHCO_3$ solution was added, and the resulting slurry was extracted with ether (4 × 10 ml). The organic layers were combined and dried with $MgSO_4$. The solvents were removed in vacuo, and the residue was purified by flash chromatography (CH/EA = 98:2). The silyl ether (55 mg) was obtained as a colorless oil (37%). In addition, 30 mg of starting material was recovered (20%). $R_f = 0.25$ (75:25). – IR (film): $\tilde{\nu} = 3450\ cm^{-1}$ (m, b, OH), 1242 (s, $SiMe_3$), 829 (vs, $SiMe_3$). – ^1H NMR (300 MHz): $\delta = 0.00$ [s, 9H, $Si(CH_3)_3$], 1.63 (s, 3H, CH_3), 2.71 (d, $^3J = 2.9$ Hz, 1H, OH), 4.64 (d, $^3J = 2.9$ Hz, 1H, CH), 7.01–7.06 (m, 2H, arom. H), 7.14–7.26 (m, 8H, arom. H). – ^{13}C NMR (75.5 MHz): $\delta = 2.1$ [q, $Si(CH_3)_3$], 23.6 (q, CH_3), 79.8 (s, C), 82.1 (d, CH), 126.7 (d, $C_{ar}H$), 127.0 (d, $C_{ar}H$), 127.3 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 139.4 (s, C_{ar}), 144.1 (s, C_{ar}). – MS (EI, 70 eV), *m/z* (%): 283 (5) [M^+ – OH], 193 (100) [M^+ – PhCHOH], 177 (11), 75 (17), 73 (56). – $C_{18}H_{24}O_2Si$ (300.5): calcd. C 71.96, H 8.05; found C 71.73, H 8.14.

Preparation of Diol **7** *by Desilylation of Silyl Ether* **6**: 0.16 mmol of **6** (48 mg) was dissolved in 2 ml of acetonitrile. Upon cooling to 0°C, 0.5 ml of aq. HF (40%) was slowly added. The reaction mixture was stirred at this temp. for 2 h. It was carefully poured in 5 ml of a satd. $NaHCO_3$ solution and extracted with ether (4 × 10 ml). The organic layers were combined and washed with brine (10 ml). After drying ($MgSO_4$) the solvents were removed in vacuo, and the residue was purified by FC (CH/EA = 85:15). The product so obtained (35 mg; 96%) was identical with the diol **7** previously described.

Rate Studies at Low Temperatures: The photoreactor described in procedure B was charged with 30 ml of *n*-hexane. The degassed solvent was cooled, and the irradiation source was turned on in order to balance the thermal conditions of the reaction medium. After ca. 15 min the temp. remained within a constant range (±2 K). Then 2.0 mmol of benzaldehyde (212 mg, 202 µl) and 4.0 mmol of silyl enol ether **2a** (521 mg) were added rapidly by a syringe. The temperature was permanently monitored by means of a thermocouple. After 2.5 h the irradiation was interrupted and the mixture worked up as outlined in procedure B. The diastereomeric ratio (ds) was determined by integration of suitable ^1H-NMR signals. For the Eyring plot k/k' was set equal to [**3a**]/[**4a**], and the error was estimated from experimental uncertainties and deviations to be $\Delta T \pm 2$ K; $\Delta(k/k') \pm 0.05$.

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