PERKIN 1

A stereoselective, tandem [2+2] photocycloaddition–hydrolysis route to aldol-type adducts

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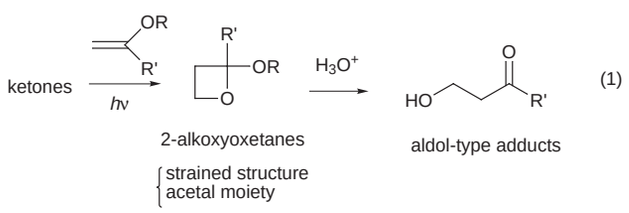
Photocycloadditions of aromatic aldehydes **2a**–**e** with cyclic ketene silyl acetals **1a**–**e** have been investigated. Regio- and *exo*-selective formation of the bicyclic 2-alkoxyoxetanes **3** was observed in high yields. Hydrolysis of the acid-labile oxetanes **3** with neutral water was efficiently achieved to give aldol-type adducts **4** (*threo*-selective formations).

Introduction

2-Alkoxyoxetanes possess inherent potential as precursors of β-hydroxy ketones, aldol-type adducts [eqn. (1)].[1] The synthetic route to aldol-type adducts is attractive, since the transformation can be achieved under mild conditions. However, in general, the procedure has not often been applied for the preparation of aldol-type adducts due to the limited synthetic methods for regioselective formation of 2-alkoxyoxetanes by photochemical cycloaddition of ketones with non-conjugated vinyl ethers.[2–5] Recently, we have found the convenient and regioselective formation of 2-alkoxyoxetanes in photochemical cycloadditions of aromatic ketones with highly electron-rich ketene silyl acetals (KSA).[7] The crucial roles of the silyl group in KSA and the solvent for the exclusive formation of the oxetanes have been revealed in the preceding paper in this issue.



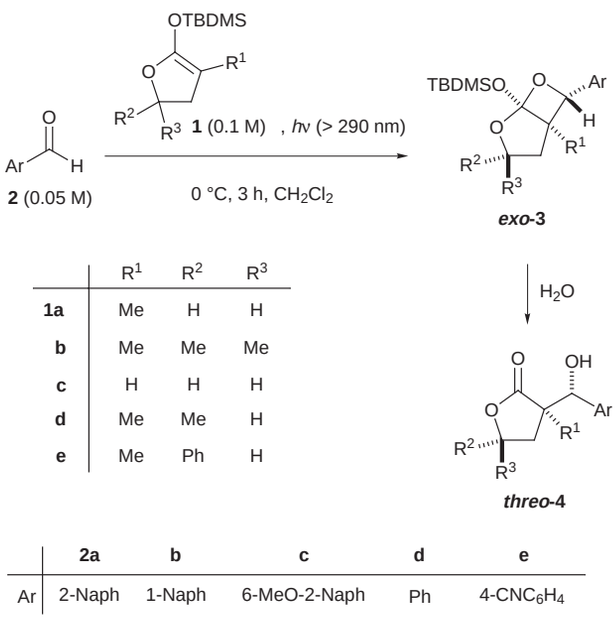
In the present paper, we would like to report the *exo*-selective formation of bicyclic 2-alkoxyoxetanes **3** in the photochemical cycloaddition of aromatic aldehydes **2** with cyclic ketene silyl acetals (*c*-KSA) **1** and their transformation to aldol-type adducts **4** (Scheme 1).

Results and discussion

Based on our previous findings,[7b] we selected the sterically hindered TBDMS as a silyl group in *c*-KSA **1** and non-polar dichloromethane as a solvent for the photochemical cycloaddition reactions.

Photoreactions of 2-naphthaldehyde 2a with *c*-KSA 1a–c

First of all, the photoreactions (>290 nm) of 2-naphthaldehyde **2a** (0.05 M) with *c*-KSA **1a–e** (0.1 M) derived from γ-butyrolactones were performed in dichloromethane at 0 °C (Scheme 1, Table 1). The *exo*-selective formations (86/14 to >95/5) of the bicyclic 2-alkoxyoxetanes **3aa–3ea** were observed in moderate to high yields. The formation of the acid-labile oxetanes **3** was proved by the peculiar ^{13}C-NMR signals of the orthoester carbon (δ_C *ca.* 115) as reported previously (see Table 4 in Experimental section).[7,8] After hydrolysis of the oxetane with wet CH_3CN ($H_2O:CH_3CN = 1:5$), the typical ^{13}C-NMR signals disappeared. The formation of the aldol-type adducts **4** (*threo* major) upon treatment with water proved the intervention of the 2-alkoxyoxetanes. The major configuration of the oxetanes **3** and the hydrolysis products **4** was determined on the basis of the configuration of the acetonides **5**,**6** derived from **4** (Scheme 2, Table 3, *vide infra*).



	R^1	R^2	R^3
1a	Me	H	H
b	Me	Me	Me
c	H	H	H
d	Me	Me	H
e	Me	Ph	H

	2a	**b**	**c**	**d**	**e**
Ar	2-Naph	1-Naph	6-MeO-2-Naph	Ph	4-CNC$_6$H$_4$

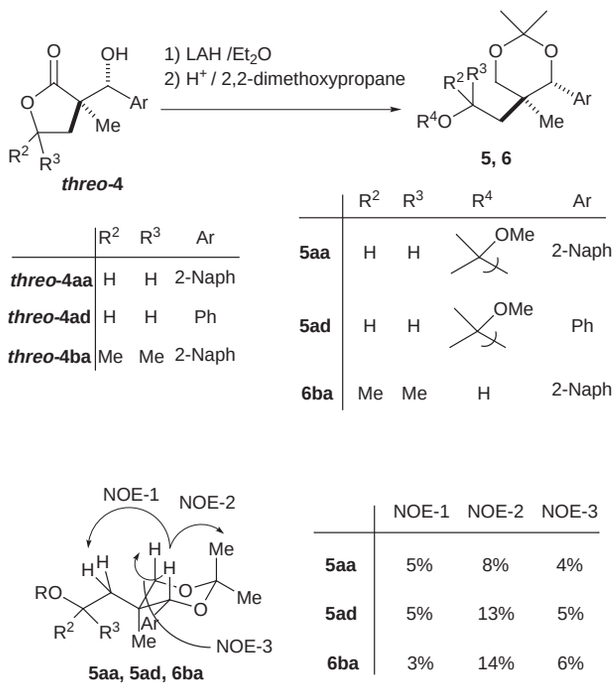
Scheme 1

The introduction of the substituents, R^2 and R^3, on the furan ring induced the *exo*-selectivities (86/14 up to >95/5) (compare entries 1,3 with entry 2 in Table 1). The results suggest that the *exo*-stereochemical outcome mainly arises from the steric repulsion between the naphthyl group and the furan ring. The steric interaction was also an important factor in controlling the face selectivity (entries 4,5). By introducing one methyl or phenyl group on the furan ring in *c*-KSA **1**, preferred formation of the bicyclic 2-alkoxyoxetanes **3da** ($R^1 = R^2 = Me$, $R^3 = H$, Ar = 2-Naph), **3ea** ($R^1 = Me$, $R^2 = Ph$, $R^3 = H$, Ar = 2-Naph) with the *trans* configuration of the substituents (R^2) to the oxetane ring was observed [for Me; *trans*/*cis* = 70/30 (entry 4), for Ph; *trans*/*cis* = 89/11 (entry 5)]. For the *cis* isomers of **3da**,**ea**, exclusive formation of *exo*-**3da**,**ea** was detected (entries 4,5, *exo*/*endo* = >95/5). Good *exo*-selectivities (*ca.* 90/10) were observed for the *trans*-isomer in analogy with the cases of **3aa**,**ba**. The configurations of *trans*- and *cis*-**3da**,**ea** were determined by NOE measurements on the hydrolysis products **4da**,**ea** (Fig. 1). As shown in Fig. 1, for the *trans*-isomers, clear

Table 1 *exo*-Selective synthesis of bicyclic 2-alkoxyoxetanes **3aa**–**ea** in the photoreactions of 2-naphthaldehyde **2a** with cyclic ketene silyl acetals **1a**–**f**[a]

Entry	3	R^1	R^2	R^3	Product ratios[b] **3** (*exo*/*endo*)	Yields (%)[c]
1[d]	**3aa**	Me	H	H	90/10	86
2	**3ba**	Me	Me	Me	>95/5	69
3	**3ca**	H	H	H	86/14	39
4	***trans*-3da**	Me	Me	H	87/13	44
	***cis*-3da**	Me	H	Me	>95/5	19
5	***trans*-3ea**	Me	Ph	H	91/9	77
	***cis*-3ea**	Me	H	Ph	>95/5	9

[a] Unless otherwise noted, photoreactions of **2a** (0.05 M) with **1** (0.1 M) were run in CH_2Cl_2 at 0 °C for 3 h; aldehyde **2a** consumptions were >95%. [b] Product ratios were determined by the direct measurement of ^1H NMR (270 MHz) peak areas of the aldol-type adducts **4**; >95/5 shows no minor product was observed in the reaction mixture. [c] Yields (%) were determined on the basis of the isolated aldol-type adducts **4** after hydrolysis of the oxetanes **3**. [d] Preparative-scale photoreaction of **2a** (5 g, 32 mmol, 1.1 M) with **1a** (2.2 M) in CH_2Cl_2 (30 cm^3) was also done for 15 h to give the aldol-type adduct **4aa** (85%, *threo*/*erythro* = 91/9) after hydrolysis of the oxetane **3aa** (see Experimental section).



Scheme 2

NOE enhancements between the methyl group and R^2 group were detected (NOE 6% for **4da**, 8% for **4ea**), while, for the *cis* isomer, significant NOE enhancements between the methyl protons and the alkoxy proton in the furan ring were observed (NOE 5% for both **4da**,**ea**). Thus, the assignments of the configuration were possible.

As described above, in the case of the photoreaction of 2-naphthaldehyde **2a**, *threo*-selective syntheses of the aldol-type adducts **4aa**–**ea** *via* the bicyclic 2-alkoxyoxetanes **3aa**–**ea** were achieved in good to high yields. We next examined the tandem transformations to the aldol-type adducts for the photoreactions of several aromatic aldehydes **2b**–**e** with *c*-KSA **1a**.

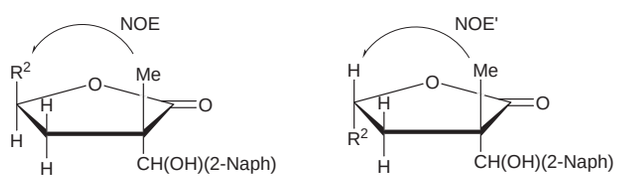
Photoreactions of aromatic aldehydes 2b–e with *c*-KSA 1a

The *exo*-selective formation of the bicyclic 2-alkoxyoxetanes **3ab**–**ae** and their transformation to the aldol-type adducts **4ab**–**ae** were also successful under similar conditions (Table 2). For the naphthaldehyde derivatives **2b** (Ar = 1-Naph), **1c**

Table 2 *exo*-Selective formation of bicyclic oxetanes **3ab**–**ae** in the photoreactions of aromatic aldehydes **2b**–**e** with cyclic ketene silyl acetal **1a** (R^1 = Me, R^2 = R^3 = H) in CH_2Cl_2[a]

Entry	3	Ar	Product ratios[b] **3** (*exo*/*endo*)	Yields (%)[c]
1	**3ab**	1-Naph	93/7	82
2[d]	**3ac**	6-MeO-2-Naph	92/8	47
3[e]	**3ad**	Ph	81/19	19
4	**3ae**	4-CNC_6H_4	78/22	68

[a] Photoreactions of **2b**–**e** (0.05 M) with **1a** (0.1 M) were run at 0 °C for 3 h. [b] Product ratios were determined on the basis of the direct ^1H NMR (270 MHz) peak areas of the aldol-type adducts **4**; >95/5 shows no minor product was observed in the reaction mixture. [c] Yields (%) were determined by the isolated aldol-type adducts **4ab**–**ae**, after hydrolysis of **3**. [d] Pinacol **7c** (17%) was obtained. [e] Pinacol **7d** (42%) was obtained.

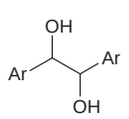


***trans, threo*-4** ***cis,threo*-4**

	NOE	NOE'
4da (R^2 = Me)	6%	5%
4ea (R^2 = Ph)	8%	5%

Fig. 1

(Ar = 6-MeO-2-Naph), highly *exo*-selective formation of the oxetane **3ab**,**ac** (*threo*-selective aldol-type adducts **4ab**,**ac**) was observed (entries 1,2). In the case of the benzaldehyde derivatives **2d** (Ar = Ph), **2e** (Ar = 4-CNC_6H_4), diminished, but significantly *exo*-selective, formation of the 2-alkoxyoxetanes **3ad**,**ae** was detected (entries 3,4), independent of the substituent on the phenyl ring. In the photoreactions of benzaldehyde **2d**, large amounts of pinacol **7d** (42%) were obtained



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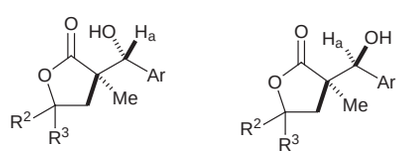
(entry 3). Transformation of the oxetanes **3** was easily accomplished by simple addition of water to afford the aldol-type adducts **4ab**–**4ae** without losing the stereochemistry. Thus, the explored tandem route to the stereoselective synthesis of aldol-type adducts was successfully achieved.

Configurational assignment of the 2-alkoxyoxetanes 3

The stereochemical assignment of the bicyclic 2-alkoxyoxetanes **3** was performed on the basis of the configuration of their hydrolysis products, aldol-type adducts **4**, due to the instability of the oxetanes **3** under the isolation conditions (Scheme 2, Table 3). To determine the configuration of the aldol-type adduct **4**, the major stereoisomers **4aa**,**ad**,**ba** were converted to the acetonide derivatives **5aa**, **5ad** and **6ba** (Scheme 2). When



***threo*-4** ***erythro*-4**

Table 3 Comparison of the ^{1}H NMR chemical shifts of H_a (δ_{Ha}) and protons (δ_{Me}) between the major (*threo*) and minor (*erythro*) isomers in the aldol-type adduct **4**[a]

Entry	**4**	R^2	R^3	Ar	δ_{Ha}		δ_{Me}	
					Major (*threo*)	Minor (*erythro*)	Major (*threo*)	Minor (*erythro*)
1	**4aa**	H	H	2-Naph	5.01	5.06	1.33	1.10
2	**4ab**[a]	H	H	1-Naph	5.75	5.94	1.34	1.03
3	**4ac**	H	H	6-MeO-2-Naph	5.01	5.05	1.33	1.14
4	**4ad**	H	H	Ph	4.87	4.92	1.31	1.12
5	**4ae**	H	H	4-CNC_6H_4	4.94	4.99	1.27	1.11
6[b]	**4ba**	Me	Me	2-Naph	5.06	—	1.40	—
7	**4da**	Me	H	2-Naph	4.98	5.04	1.43	1.31
8	**4ea**	Ph	H	2-Naph	5.08	5.08	1.40	1.19

[a] Chemical shifts were reported on the basis of $CHCl_3$ as an internal standard. [b] The minor adduct, the *erythro* isomer, was not observed by ^{1}H NMR (270 MHz).

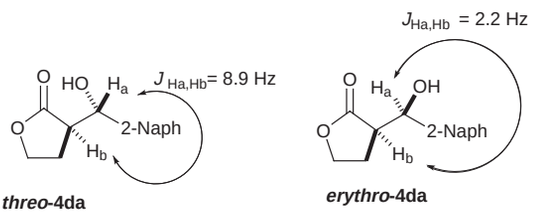


Fig. 2

the aryl methyl proton was irradiated, NOE enhancements (NOE-1, -2, -3), as shown in Scheme 2, were observed. The NOE observation indicated that the configuration between the aryl methyl proton and the carbon tethered group is located as a *cis* relationship. Thus, the obtained major isomer of the aldol-type adduct **4aa**,**ad**,**ba** should have a *threo*-configuration. The stereochemical assignment of the aldol-type adducts **4** enabled the configurational determination of the major diastereomers in the bicyclic-2-alkoxyoxetanes **3aa**,**ad**,**ba** as *exo*-isomers. As shown in Table 3, entries 1,4, the ^{1}H-NMR chemical shifts (δ_{Me}) of the methyl group in the major isomers (*threo*) were clearly observed at lower field than those of the minor isomers (*erythro*). In the cases of the aryl methyl protons (δ_{Ha}), the opposite tendency was observed, although the differences are small. Thus, the stereochemical assignments for the other aldol-type adducts **4**, except for **4ca** ($R^1 = R^2 = R^3 = H$, Ar = 2-Naph), were determined by their chemical-shift comparisons of both the arylmethyl protons and the methyl protons (Table 3). The major isomers with the lower-field chemical shift (δ_{Me}) of the methyl protons and the higher-field chemical shift (δ_{Ha}) of the arylmethyl proton were determined as having a *threo* configuration. In the case of the adduct **4ca**, the stereochemistry was determined on the basis of the ^{1}H-NMR coupling constants (J) between the arylmethyl proton and the α-proton of the ester group (Fig. 2). As established in the case of Ar = Ph,[9] the clear trend of $J_{threo} > J_{erythro}$ was observed for **4da**. Thus, the stereoisomer with the large coupling constant (J 8.9 Hz) was assigned to the *threo*-configuration (for the *erythro* isomer; J 2.2 Hz, see Experimental section). All of the above-mentioned stereochemical assignments of the aldol-type adducts **4** clearly suggest that the primary photo-adducts, bicyclic-2-alkoxyoxetanes **3**, were formed as *exo*-isomers.

Conclusion

Photochemical cycloadditions of the aromatic aldehydes **2** with *c*-KSA **1** derived from γ-butyrolactones were performed. The regio- (>95/5) and *exo*-selective (86/14) formation of the acid-labile bicyclic 2-alkoxyoxetanes **3** occurred in moderate to high yields. The oxetanes **3** were successfully converted to the aldol-type adducts **4** with no loss of the stereochemistry. The tandem photocycloaddition–hydrolysis route to the aldol-type adducts **4** is synthetically useful, since general Lewis-acid ($TiCl_4$, $BF_3{\cdot}OEt_2$) promoted reaction of the *c*-KSA **1** with the aromatic aldehydes gave stereorandom adducts **4**.[7a]

Experimental

General aspects

^{1}H and ^{13}C spectra were measured on a JEOL JNM-EX-270 (^{1}H; 270 MHz, ^{13}C; 67.8 MHz) spectrometer with deuteriochloroform as internal standard. J values are given in Hz. IR spectra were recorded on a Hitachi 260-30 spectrophotometer. Mass spectrometric data were obtained by using a JEOL JNS-BX 303-HF mass spectrometer. Elemental analyses were carried out by Analytical Division of the Faculty of Engineering, Osaka University. Melting points are not corrected. Flash column chromatography was performed by using silica gel (Wakogel C-300) as absorbent.

Materials

The solvents used were dried and distilled prior to use. Cyclic ketene silyl acetals (*c*-KSA) **1** were prepared from the corresponding γ-butyrolactone derivatives (*vide infra*).[10] Aromatic aldehydes **2** are commercially available and used without further purification. Pinacol **7c** (Ar = 6-MeO-2-Naph) is a known compound.[11] Pinacol **7d** (Ar = Ph) is commercially available.

Photolyses

Photolyses were conducted with an Eikohsha 500 W high-pressure mercury lamp.

Preparation of the *c*-KSA 1a–e

To a solution of LDA (31.5 mmol) in THF (60 cm^3) was slowly added a solution of the corresponding γ-butyrolactone derivative (30 mmol) in THF (10 cm^3) at −78 °C under argon atmosphere. After stirring for 10 min, a solution of HMPA (30 mmol) in THF (10 cm^3) was added. And then, a solution of TBDMSCl (30 mmol) in THF (10 cm^3) was added dropwise to the mixture. The reaction mixture was allowed to warm up to room temperature (*ca*. 20 °C). After stirring for 10 h, 100 cm^3 of *n*-hexane and 300 cm^3 of water were added and the organic layer was separated. The organic phase was dried over $MgSO_4$ and removed under reduced pressure. The desired *c*-KSA **1** was distilled under reduced pressure. Derivative **1c**[8c] is a known compound.

2-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-4,5-dihydrofuran 1a. Colorless oil (3.8 g, 59%), bp 83–89 °C/9 mmHg (Found: C, 61.70; H, 10.48. $C_{11}H_{22}O_2Si$ requires C, 61.63; H, 10.34%); ν_{max}(liquid film)/cm^{-1} 2850–3000, 1740, 1260, 1110; δ_H(270 MHz; $CDCl_3$) 0.17 [s, 6 H, $OSi(CH_3)_2(Bu^t)$], 0.94 (s, 9 H, Bu^t), 1.53 [s, 3 H, C(3)CH_3], 2.52 [t, J 8.9, 2 H, C(4)H_2], 4.17 [t, J 8.9, 2 H,

C(5)H_2]; δ_C(67.8 MHz; $CDCl_3$) −4.26, 10.32, 18.24, 25.81, 33.44, 66.04, 75.84, 152.70; *m*/*z* (EI) 214.1398 (M^+, 79%, $C_{11}H_{22}O_2Si$ requires 214.1389), 157 (17), 129 (64), 115 (32), 99 (16), 89 (17), 73 (100).

2-[(*tert*-Butyldimethylsilyl)oxy]-3,5,5-trimethyl-4,5-dihydrofuran 1b. Colorless oil (3.7 g, 52%), bp 50–55 °C/1 mmHg (Found: C, 64.70; H, 10.73. $C_{13}H_{26}O_2Si$ requires: C, 64.41; H, 10.81%); ν_{max}(liquid film)/cm^{-1} 2850–3000, 1740, 1340, 1260, 1110; δ_H(270 MHz; $CDCl_3$) 0.16 [s, 6 H, OSi(CH_3)$_2$(Bu^t)], 0.93 (s, 9 H, *Bu*^{t}), 1.30 [s, 6 H, C(5)(CH_3)$_2$], 1.49 [s, 3 H, C(3)CH_3], 2.31 [s, 2 H, C(3)H_2]; δ_C(67.8 MHz; $CDCl_3$) −3.61, 10.25, 18.03, 25.61, 28.68, 46.52, 75.63, 81.96, 148.01; *m*/*z* (EI) 242.1707 (M^+, 88%, $C_{13}H_{26}O_2Si$ requires 242.1702), 226 (27), 185 (75), 130 (25), 110 (79), 73 (100).

2-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dimethyl-4,5-dihydrofuran 1d. Colorless oil (2.9 g, 41%), bp 50–52 °C/1 mmHg (Found: C, 63.01; H, 10.65. $C_{12}H_{24}O_2Si$ requires: C, 63.10; H, 10.59%); ν_{max}(liquid film)/cm^{-1} 2850–3000, 1720, 1460, 1250; δ_H(270 MHz; $CDCl_3$) 0.16 [s, 6 H, OSi(CH_3)$_2$(Bu^t)], 0.94 (s, 9 H, *Bu*^{t}), 1.28 [d, *J* 6.3, 3 H, C(5)CH_3], 1.49 [s, 3 H, C(2)CH_3], 2.10 [dd, *J* 6.6 and 13.2, 1 H, C(4)*H*], 2.65 [dd, *J* 9.6 and 13.2, 1 H, C(4)H_2], 4.49 [qdd, *J* 6.3, 6.6 and 9.6, 1 H, C(5)*H*]; δ_C(67.8 MHz; $CDCl_3$) −4.47, 10.14, 17.94, 22.32, 25.54, 40.54, 73.30, 75.96, 151.05; *m*/*z* (EI) 228.1551 (M^+, 67%, $C_{12}H_{24}O_2Si$ requires 228.1546), 171 (44), 159 (13), 130 (26), 115 (16), 103 (20), 97 (17), 73 (100).

2-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-5-phenyl-4,5-dihydrofuran 1e. Colorless oil (4.9 g, 69%), bp 90–91 °C/1 mmHg (Found: C, 70.38; H, 8.87. $C_{17}H_{26}O_2Si$ requires: C, 70.29; H, 9.02%); ν_{max}(liquid film)/cm^{-1} 3000–3100, 2850–3000, 1740, 1260; δ_H(270 MHz; $CDCl_3$) 0.21 [s, 6 H, OSi(CH_3)$_2$(Bu^t)], 0.97 (s, 9 H, *Bu*^{t}), 1.56 [s, 3 H, C(3)CH_3], 2.55 [dd, *J* 8.3 and 13.5, 1 H, C(4)*H*], 2.95 [dd, *J* 10.2 and 13.5, 1 H, C(4)*H*], 5.38 [dd, *J* 8.3 and 10.2, 1 H, C(5)*H*], 7.28–7.37 (m, 5 H, Ph); δ_C(67.8 MHz; $CDCl_3$) −4.36, −4.33, 10.03, 17.99, 25.55, 41.92, 76.21, 78.26, 125.50, 127.35, 128.37, 143.45, 151.41; *m*/*z* (EI) 290.1964 (M^+, 39%, $C_{17}H_{26}O_2Si$ requires 290.1702), 233 (100), 158 (37), 131 (14), 115 (12), 91 (20), 73 (71).

Photolyses of aldehydes 2a–e with *c*-KSA 1a–e

General procedure. A test tube shaped reaction flask was flushed with dry argon. The reaction mixture of *c*-KSA **1** (0.1 M, 1.28 mmol) and aromatic aldehyde **2** (0.05 M, 0.64 mmol) in degassed dichloromethane (13 cm^3) was irradiated with a high-pressure mercury lamp through a Pyrex filter (>290 nm). After the aldehyde **2** was consumed (3 h), the solvent was removed under reduced pressure by using a rotary evaporator. After the formation of the oxetane **3** was checked by NMR (Table 4), the crude mixture was treated with wet CH_3CN (H_2O:CH_3CN = 1:5, 25 cm^3). The organic layer was extracted with diethyl ether and the solvent was removed. The products were separated by silica gel chromatography. The yields and product ratios (*exo*:*endo*) of **3** were determined on the basis of the isolated aldol-type adducts **4** (Tables 1,2).

4,5-Dihydro-3-(hydroxy-2-naphthylmethyl)-3-methylfuran-2(3*H*)-one (*threo*-4aa). An oil (Found: C, 75.23; H, 6.43. $C_{16}H_{16}O_3$ requires: C, 74.98; H, 6.29%); ν_{max}(liquid film)/cm^{-1} 3200–3650, 3000–3200, 2850–3000, 1770, 1400, 1220, 1040; δ_H(270 MHz; $CDCl_3$) 1.33 (s, 3 H, CH_3), 1.70 [ddd, *J* 3.8, 7.0 and 13.0, 1 H, C(4)H], 2.48 (ddd, *J* 8.6, 8.6 and 13.0, 1 H, C(4)H], 3.96 (s, 1 H, OH), 3.98 [ddd, *J* 3.8, 8.6 and 8.9, 1 H, C(5)H], 4.12 [ddd, *J* 7.0, 8.6 and 8.9, 1 H, C(5)H], 5.01 [s, 1 H, C*H*OH(2-Naph)], 7.43–7.50 (m, 3 H, 2-Naph), 7.78–7.83 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 17.47, 32.54, 47.30, 65.86, 76.78, 124.85, 126.09, 126.18, 126.23, 127.62, 127.81, 128.12, 132.90, 133.15, 136.30, 182.30; *m*/*z* (EI) 256.1096 (M^+, 20%, $C_{16}H_{16}O_3$ requires 256.1100), 157 (56), 129 (56), 100 (100).

Table 4 ^{13}C-NMR chemical shifts (δ_C) of the ratio of the orthoester carbon in the bicyclic 2-alkoxyoxetanes **3**[a]

3	R^1	R^2	R^3	Ar	δ_C[b]
3aa	CH_3	H	H	2-Naph	113.40
3ba	CH_3	CH_3	CH_3	2-Naph	116.35
3ca	H	H	H	2-Naph	119.94
***trans*,*exo*-3da**	CH_3	CH_3	H	2-Naph	116.41
***trans*,*exo*-3ea**	CH_3	Ph	H	2-Naph	114.11
3ab	CH_3	H	H	1-Naph	113.48
3ac	CH_3	H	H	6-MeO-2-Naph	118.76
3ad	CH_3	H	H	Ph	113.44
3ae	CH_3	H	H	4-CNC_6H_4	114.21

[a] NMR measurements ^{13}C-NMR (67.8 MHz; $CDCl_3$) were quickly performed after the solvent was removed under reduced pressure. [b] Chemical shifts (ppm) were reported relative to the internal standard ($CDCl_3$; δ 77.0).

***erythro*-4aa.** Obtained in admixture with 51% ***threo*-4aa**. An oil; δ_H(270 MHz; $CDCl_3$) 1.10 (s, 3 H, CH_3), 1.68 [ddd, *J* 4.1, 7.3 and 12.4, 1 H, C(4)H], 1.90 (s, 1 H, OH), 2.88 [ddd, *J* 8.9, 8.9 and 12.4, 1 H, C(4)H], 4.17 [ddd, *J* 7.3, 8.9 and 8.9, 1 H, C(5)H], 4.31 [ddd, *J* 4.1, 8.9 and 8.9, 1 H, C(5)H], 5.06 [s, 1 H, C*H*OH(2-Naph)], 7.42–7.52 (m, 3 H, 2-Naph), 7.77–7.82 (m, 4 H, 2-Naph).

4,5-Dihydro-3-(hydroxy-2-naphthylmethyl)-3,5,5-trimethylfuran-2(3*H*)-one (*threo*-4ba). Viscous oil (Found: C, 76.07; H, 7.13. $C_{18}H_{20}O_3$ requires: C, 76.03; H, 7.09%); ν_{max}(liquid film)/cm^{-1} 3200–3600, 3000–3100, 2800–3000, 1730, 1200; δ_H(270 MHz; $CDCl_3$) 1.18 [s, 3 H, C(5)Me], 1.40 [s, 3 H, C(3)Me], 1.49 [s, 3 H, C(5)Me], 1.68 [d, *J* 13.5, 1 H, C(4)H], 2.36 [d, *J* 13.5, 1 H, C(4)H], 3.93 (s, 1 H, OH), 5.06 [s, 1 H, C*H*OH(2-Naph)], 7.47–7.54 (m, 3 H, 2-Naph), 7.80–7.87 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 21.46, 29.71, 29.87, 43.70, 50.12, 77.23, 82.37, 125.19, 126.02, 126.06, 126.43, 127.49, 127.62, 128.03, 132.76, 132.99, 136.57, 181.42; *m*/*z* (EI) 284.1425 (M^+, 12%, $C_{18}H_{20}O_3$ requires 284.1413), 156 (56), 128 (100), 113 (15), 69 (8), 59 (12), 43 (15).

4,5-Dihydro-3-(hydroxy-2-naphthylmethyl)furan-2(3*H*)-one (*threo*-4ca). An 83:17 mixture of ***threo*-4ca** and ***erythro*-4ca** isomers. Viscous oil, ν_{max}(liquid film)/cm^{-1} 3150–3600, 3000–3070, 2800–3000, 1740; δ_H(270 MHz, $CDCl_3$) 1.87–2.05 [m, 2 H, C(4)H_2], 3.02 [ddd, *J* 8.9, 8.9 and 11.2, 1 H, C(3)H], 4.16 [ddd, *J* 6.6, 8.9 and 8.9, 1 H, C(5)H], 4.31 [ddd, *J* 2.3, 8.9 and 8.9, 1 H, C(5)H], 4.46 (s, 1 H, OH), 4.99 [d, *J* 8.9 Hz, 1 H, C*H*(OH)(2-Naph)], 7.48–7.53 (m, 3 H, 2-Naph), 7.83–7.89 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 25.93, 46.17, 67.06, 74.86, 123.90, 125.88, 126.27, 126.36, 127.73, 128.01, 128.73, 131.79, 137.32, 137.59, 172.52; *m*/*z* (EI) 242.0941 (M^+, 40%, $C_{15}H_{14}O_3$ requires 242.0943), 157 (100), 129 (57), 86 (21).

***erythro*-4ca.** Viscous oil; readable signals δ_H(270 MHz; $CDCl_3$) 1.86–1.98 (m, 1 H), 2.40–2.55 (m, 1 H), 2.83 (s, 1 H), 3.03 (m, including *J* 2.2, 1 H), 4.16 (m, 1 H), 4.36 (ddd, 1 H), 5.56 [d, *J* 2.2, 1 H, C*H*(OH)(2-Naph)].

4,5-Dihydro-3,5-dimethyl-3-(hydroxy-2-naphthylmethyl)-furan-2(3*H*)-one (*trans*,*threo*-4da). Obtained in admixture with 7% ***trans*,*erythro*-4da** isomers. Viscous oil; ν_{max}(liquid film)/cm^{-1} 3200–3650, 3000–3100, 2850–3000, 1750, 1210, 1060; δ_H(270 MHz; $CDCl_3$) 1.22 [d, *J* 5.9, 3 H, C(5)CH_3], 1.43 [s, 3 H, C(3)CH_3], 1.50 [dd, *J* 8.4, 13.7, 1 H, C(4)H], 2.70 [dd, *J* 7.1, 13.7, 1 H, C(4)H], 3.05 (s, 1 H, OH), 3.81 [qdd, *J* 5.9, 7.1 and 8.4, 1 H, C(5)H], 4.98 [s, 1 H, C*H*(OH)(2-Naph)], 7.47–7.52 (m, 3 H, 2-Naph), 7.79–7.86 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 21.93, 22.21, 39.27, 50.66, 74.52, 76.59, 124.67, 125.89,

126.22, 126.25, 127.64, 127.96, 128.16, 132.87, 133.17, 137.00, 180.83; *m*/*z* (EI) 270.1265 (M^+, 22%, $C_{17}H_{18}O_3$ requires 270.1256), 157 (41), 129 (34), 114 (100), 69 (10).

***trans*,*erythro*-4da.** Obtained in admixture with 93% ***trans*, *threo*-4da** isomers. Viscous oil; readable signals δ_H(270 MHz, $CDCl_3$) 1.25 [d, *J* 2.0, 3 H, C(5)CH_3], 1.28–1.39 [m, 1 H, C(4)H], 1.70–1.74 [m, 1 H, C(4)H], 2.84 (br s, 1 H, OH), 4.52–4.58 [m, 1 H, C(5)H], 5.04 [s, 1 H, C*H*(OH)(2-Naph)].

***cis*,*threo*-4da.** Viscous oil; ν_{max}(liquid film)/cm^{-1} 3250–3650, 3000–3100, 2800–3000, 1740, 1200, 1050; δ_H(270 MHz; $CDCl_3$) 1.31 [s, 3 H, C(3)CH_3], 1.40 [d, *J* 5.9, 3 H, C(5)CH_3], 1.72 [dd, *J* 5.3 and 12.9, 1 H, C(4)H], 2.01 [dd, *J* 10.6 and 12.9, 1 H, C(4)H], 4.51 (br s, 1 H, OH), 4.58 [dqd, *J* 5.3, 5.9 and 10.6, 1 H, C(5)H], 5.07 [s, 1 H, C*H*(OH)(2-Naph)], 7.46–7.52 (m, 3 H, 2-Naph), 7.80–7.87 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 15.85, 20.79, 41.49, 48.88, 74.70, 77.00, 125.00, 126.06, 126.13, 126.20, 127.58, 127.64, 128.09, 132.90, 133.10, 135.99, 182.46; *m*/*z* (EI) 270.1263 (M^+, 26%, $C_{17}H_{18}O_3$ requires 270.1256), 157 (35), 129 (32), 114 (100), 69 (10).

4,5-Dihydro-3-(hydroxy-2-naphthylmethyl)-3-methyl-5-phenylfuran-2(3*H*)-one (*trans*,*threo*-4ea). Obtained in admixture with 7% ***trans*,*erythro*-4ea** isomers. White powder, mp 137–139 °C (Found: C, 79.00; H, 6.03. $C_{22}H_{20}O_3$ requires C, 79.40; H, 6.07%): ν_{max}(KBr)/cm^{-1} 3150–3600, 3000–3100, 2850–3000, 1760, 1460, 1200; δ_H(270 MHz; $CDCl_3$) 1.40 [s, 3 H, C(3)CH_3], 1.92 [dd, *J* 8.2 and 13.5, 1 H, C(4)H], 3.01 [dd, *J* 7.9 and 13.5, 1 H, C(4)H], 3.09 (br s, 1 H, OH), 4.81 [dd, *J* 7.9 and 8.2, 1 H, C(5)H], 5.08 [s, 1 H, C*H*(OH)(2-Naph)], 7.14–7.18 (m, 2 H, Ph), 7.27–7.35 (m, 3 H, Ph), 7.47–7.59 (m, 3 H, 2-Naph), 7.81–7.90 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 21.71, 40.38, 50.15, 65.41, 78.37, 124.60, 124.96, 125.86, 126.02 126.15, 126.33, 126.36, 127.67, 128.09, 128.59, 132.87, 133.24, 136.84, 139.91, 180.54; *m*/*z* (EI) 332.1403 (M^+, 13%, $C_{22}H_{20}O_3$ requires 332.1413), 176 (100), 157 (28), 131 (37), 107 (8).

***trans*,*erythro*-4ea.** Obtained in admixture with 3% ***trans*, *threo*-4ea** isomers. Viscous oil; ν_{max}(liquid film)/cm^{-1} 3150–3600, 3000–3100, 2850–3000, 1760, 1460, 1200; δ_H(270 MHz; $CDCl_3$) 1.19 [s, 3 H, C(3)CH_3], 1.75 [dd, *J* 7.9 and 13.5, 1 H, C(4)H], 2.60 (s, 1 H, OH), 3.20 [dd, *J* 7.9 and 13.5, 1 H, C(4)H], 5.16 [s, 1 H, C*H*(OH)(2-Naph)], 5.61 [dd, *J* 7.9 and 7.9, 1 H, C(5)H], 7.29–7.40 (m, 5 H, Ph), 7.47–7.55 (m, 3 H, 2-Naph), 7.82–7.92 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 23.24, 38.21, 50.32, 65.86 78.94, 124.85, 125.10, 126.18, 126.33, 126.40, 126.51, 127.64, 128.07, 128.34, 128.66, 132.92, 133.23, 137.18, 140.56, 181.51; *m*/*z* (EI) 332.1408 (M^+, 12%, $C_{22}H_{20}O_3$ requires 332.1413), 176 (100), 157 (25), 131 (38), 107 (7).

***cis*,*threo*-4ea.** White powder, mp 114–115 °C; ν_{max}(KBr)/cm^{-1} 3150–3600, 3000–3100, 2850–3000, 1760, 1460, 1200; δ_H(270 MHz; $CDCl_3$) 1.45 [s, 3 H, C(3)CH_3], 2.05 [dd, *J* 5.9 and 12.9, 1 H, C(4)H], 2.37 [dd, *J* 10.6 and 12.9, 1 H, C(4)H], 4.39 (br s, 1 H, OH), 5.16 [s, 1 H, C*H*(OH)(2-Naph)], 5.45 [dd, *J* 5.9 and 10.6, 1 H, C(5)H], 7.21–7.29 (m, 3 H, Ph), 7.30–7.38 (m, 2 H, Ph), 7.45–7.53 (m, 3 H, 2-Naph), 7.79–7.88 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 21.71, 40.36, 50.15, 65.43, 78.37, 124.60, 124.96, 125.86, 126.02, 126.33, 126.36, 127.67, 128.09, 128.14, 128.28, 128.59, 132.87, 136.84, 139.91, 180.54; *m*/*z* (EI) 332.1403 (M^+, 13%, $C_{22}H_{20}O_3$ requires 332.1413), 176 (100), 157 (23), 131 (39), 107 (8).

4,5-Dihydro-3-(hydroxy-1-naphthylmethyl)-3-methylfuran-2(3*H*)-one (*threo*-4ab). Viscous oil (Found: C, 74.68; H, 6.27. $C_{16}H_{16}O_3$ requires: C, 74.98; H, 6.29%); ν_{max}(liquid film)/cm^{-1} 3200–3650, 3000–3100, 2850–3000, 1760, 1390, 1210, 1070, 1030; δ_H(270 MHz; $CDCl_3$) 1.34 [s, 3 H, C(3)CH_3], 1.53 [ddd, *J* 4.8, 7.3 and 13.2, 1 H, C(4)H], 2.47 [ddd, *J* 7.9, 8.3 and 13.2, 1 H, C(4)H], 3.93–4.16 [m, 3 H, OH + C(5)H_2], 5.75 [s, 1 H, C*H*(OH)(2-Naph)], 7.40–7.59 (m, 3 H, 1-Naph), 7.72–7.89 (m, 3 H, 1-Naph), 8.12–8.17 (m, 1 H, 1-Naph); δ_C(67.8 MHz; $CDCl_3$) 17.49, 32.96, 47.51, 65.84, 71.52, 123.25, 124.92, 125.34, 125.86, 126.02, 128.64, 128.82, 130.91, 133.57, 134.56, 182.14; *m*/*z* (EI) 256.1084 (M^+, 32%, $C_{16}H_{16}O_3$ requires 256.1100), 157 (80), 129 (53), 100 (100).

4,5-Dihydro-3-[hydroxy-2-(6-methoxynaphthyl)methyl]-3-methylfuran-2(3*H*)-one (*threo*-4ac). An 87 : 13 mixture of ***threo*-4ac** and ***erythro*-4ac** isomers. White powder, mp 93–96 °C (Found: C, 70.99; H, 6.30. $C_{17}H_{18}O_4$ requires: C, 71.31; H, 6.34%); ν_{max}(KBr)/cm^{-1} 3200–3650, 3000–3100, 2800–3000, 1760, 1610, 1490, 1390, 1270, 1030; δ_H(270 MHz; $CDCl_3$) 1.33 [s, 3 H, C(3)CH_3], 1.71 [ddd, *J* 4.0, 7.3 and 12.9, 1 H, C(4)H], 2.46 [ddd, *J* 8.2, 8.6 and 12.9, 1 H, C(4)H], 3.90 (s, 3 H, OCH_3), 3.98 [ddd, *J* 4.0, 8.2 and 8.9, 1 H, C(5)H], 4.14 [ddd, *J* 7.3, 8.6 and 8.9, 1 H, C(5)H], 5.01 [s, 1 H, C*H*(OH)(6-MeO-2-Naph)], 7.12–7.19 (m, 2 H, 6-MeO-2-Naph), 7.44–7.47 (m, 1 H, 6-MeO-2-Naph), 7.69–7.77 (m, 3 H, 6-MeO-2-Naph); δ_C(67.8 MHz; $CDCl_3$) 17.94, 32.24, 47.50, 55.24, 65.79, 76.66, 105.45, 119.01, 125.32, 125.79, 126.54, 128.30, 129.54, 134.12, 134.27, 157.79, 182.16; *m*/*z* (EI) 286.1218 (M^+, 21%, $C_{17}H_{18}O_4$ requires 286.1205), 187 (100), 159 (16), 144 (14), 127 (5), 115 (5), 100 (9).

***erythro*-4ac.** Viscous oil; readable signals δ_H(270 MHz; $CDCl_3$) 1.14 [s, 3 H, C(3)CH_3], 1.55–1.64 (m, 1 H), 1.83 (s, 1 H), 2.80–2.97 (m, 1 H), 4.07–4.15 (m, 2 H), 5.05 [s, 1 H, C*H*(OH)-(6-MeO-2-Naph)].

4,5-Dihydro-3-[hydroxy(phenyl)methyl]-3-methylfuran-2(3*H*)-one (*threo*-4ad). White powder, mp 78–81 °C (Found: C, 69.59; H, 6.91. $C_{12}H_{14}O_3$ requires: C, 69.89; H, 6.84%); ν_{max}(KBr)/cm^{-1} 3200–3700, 3000–3150, 2900–3000, 1770, 1470, 1400, 1210, 1200; δ_H(270 MHz; $CDCl_3$) 1.31 [s, 3 H, C(3)CH_3], 1.71 [ddd, *J* 4.1, 7.3 and 13.1, 1 H, C(4)H], 2.43 [ddd, *J* 8.6, 8.6 and 13.1, 1 H, C(4)H], 3.81 (br s, 1 H, OH), 3.97 [ddd, *J* 4.1, 8.6 and 8.9, 1 H, C(5)H], 4.10 [ddd, *J* 7.3, 8.6 and 8.9, 1 H, C(5)H], 4.87 [s, 1 H, C*H*(OH)Ph], 7.32–7.37 (m, 5 H, Ph); δ_C(67.8 MHz; $CDCl_3$) 17.41, 32.40, 47.13, 65.79, 76.62, 126.94, 128.16, 128.28, 138.69, 182.22; *m*/*z* (CI) 207.1006 (M^+ + 1, 1%, $C_{12}H_{15}O_3$ requires 207.1021), 189 (1), 107 (29), 100 (100), 79 (19), 56 (10), 41 (12).

***erythro*-4ad.** Obtained in admixture with 67% ***threo*-4ad** isomer. Viscous oil; δ_H(270 MHz; $CDCl_3$) 1.12 [s, 3 H, C(3)CH_3], 1.61 [ddd, *J* 4.1, 7.6 and 12.4, 1 H, C(4)H], 1.92 (s, 1 H, OH), 2.80 [ddd, *J* 8.6, 8.9 and 12.4, 1 H, C(4)H], 4.19 [ddd, *J* 7.6, 8.9 and 8.9, 1 H, C(5)H], 4.29 [ddd, *J* 4.1, 8.6 and 8.9, 1 H, C(5)H], 4.92 [s, 1 H, C*H*(OH)(Ph)], 7.31–7.37 (m, 5 H, Ph).

4,5-Dihydro-3-(hydroxy-4-cyanophenylmethyl)-3-methylfuran-2(3*H*)-one (*threo*-4ae). An 85 : 15 mixture of ***threo*-4ae** and ***erythro*-4ae** isomers. White powder, mp 93–96 °C (Found: C, 67.19; H, 5.81. $C_{13}H_{13}NO_3$ requires: C, 67.52; H, 5.67%); ν_{max}(KBr)/cm^{-1} 3200–3600, 3000–3100, 2850–3000, 2240, 1760, 1620, 1390, 1200, 1100; δ_H(270 MHz; $CDCl_3$) 1.27 [s, 3 H, C(3)CH_3], 1.57 [ddd, *J* 3.3, 7.2 and 12.9, 1 H, C(4)H], 2.40 [ddd, *J* 8.9, 8.9 and 12.9, 1 H, C(4)H], 4.05 (s, 1 H, OH), 4.08–4.27 [m, 2 H, C(5)H_2], 4.94 [s, 1 H, C*H*(OH)(4-CNC_6H_4)], 7.46–7.54 (m, 2 H, 4-CNC_6H_4), 7.63–7.68 (m, 2 H, 4-CNC_6H_4); δ_C(67.8 MHz; $CDCl_3$) 18.19, 31.88, 47.21, 65.72, 75.94, 111.54, 118.40, 127.71, 131.68, 144.51, 181.31.

***erythro*-4ae.** Viscous oil, readable signals δ_H(270 MHz; $CDCl_3$) 1.11 [s, 3 H, C(3)CH_3], 1.74 [ddd, *J* 3.3, 6.9 and 12.9, 1 H, C(4)H], 2.75 [ddd, *J* 8.9, 8.9 and 12.9, 1 H, C(4)H], 4.08–4.27 [m, 1 H, C(5)H], 4.35 [ddd, *J* 3.3, 8.9 and 8.9, 1 H, C(5)H], 4.99 [s, 1 H, C*H*(OH)(4-CNC_6H_4)]; δ_C(67.8 MHz; $CDCl_3$) 20.52, 28.11, 48.72, 65.63, 75.22, 111.54, 118.40, 127.78, 131.75, 145.30, 181.08.

Preparative-scale photoreaction of 2-naphthaldehyde 2a with *c*-KSA 1a

A test tube shaped reaction flask was flushed with dry argon. The reaction mixture of *c*-KSA **1a** (2.2 M, 64 mmol) and 2-naphthaldehyde **2a** (1.1 M, 32 mmol) in degassed dichloromethane (30 cm^3) was irradiated with a high-pressure mercury lamp through a Pyrex filter (>290 nm). After the aldehyde **2a** was consumed (15 h), the solvent was removed under reduced pressure by using a rotary evaporator. The crude mixture was treated with wet CH_3CN (H_2O:CH_3CN = 1:5, 50 cm^3) for 12 h to afford the aldol-type adduct **4aa** (27 mmol, 85%) after column chromatography on silica gel.

Transformation to acetonides 5aa, 5ad, 6ba

General procedure. To a suspension of LAH (0.8 mmol) in dry Et_2O (15 cm^3) was added a solution of *threo*-**4** (0.4 mmol) in dry Et_2O (2 cm^3). After 5 h at reflux temperature, aq. Na_2SO_4 (20 cm^3) was added carefully. After separation of the organic phase, the solvent was removed under reduced pressure. The organic material obtained was dissolved in 2,2-dimethoxypropane (5 cm^3) and a catalytic amount of camphorsulfonic acid (0.04 mmol) was added. After stirring for 12 h, 50 cm^3 each of aq. $NaHCO_3$ and Et_2O were added and the organic layer was separated. The desired acetonides **5aa** (23%), **5ad** (28%), **6ba** (14%) were obtained by basic alminium oxide chromatography with EtOAc–*n*-hexane as eluent.

5-[2-(1-Methoxy-1-methylethoxy)ethyl]-4-naphthyl-2,2,5-trimethyl-1,3-dioxane 5aa. An oil; ν_{max}(liquid film)/cm^{-1} 3000–3100, 2800–3000, 1460, 1380, 1360, 1250, 1200, 1150, 1090, 1040; δ_H(270 MHz; $CDCl_3$) 1.05 [s, 3 H, C(5)CH_3], 1.31 (s, 6 H, 2 × CH_3), 1.58 [s, 6 H, 2 × C(2)CH_3], 1.51–1.65 (m, 2 H, CH_2CH_2O), 3.16 (s, 3 H, OCH_3), 3.30–3.40 (m, 2 H, CH_2CH_2O), 3.72 [d, *J* 11.7, 1 H, C(6)H], 4.02 [d, *J* 11.7, 1 H, C(6)H], 4.93 [s, 1 H, OC*H*(2-Naph)], 7.45–7.53 (m, 3 H, 2-Naph), 7.78–7.86 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 16.28, 18.87, 24.30, 24.33, 29.69, 35.67, 36.66, 48.48, 55.80, 70.30, 79.41, 98.92, 99.82, 125.66, 125.71, 125.80, 126.15, 127.04, 127.48, 127.98, 132.72, 132.92, 135.67; *m*/*z* (EI) 327.2289 (M^+, 1%, $C_{23}H_{32}O_4$ requires 372.2301), 340 (11), 241 (17), 225 (13), 156 (59), 126 (17), 98 (40), 84 (11), 73 (100).

5-[2-(1-Methoxy-1-methylethoxy)ethyl]-4-phenyl-2,2,5-trimethyl-1,3-dioxane 5ad. Viscous oil (Found: C, 70.51; H, 9.54. $C_{19}H_{30}O_4$ requires: C, 70.78; H, 9.38%); ν_{max}(liquid film)/cm^{-1} 3000–3050, 2850–3000, 1740, 1460, 1390, 1260, 1210; δ_H(270 MHz; $CDCl_3$) 0.99 [s, 3 H, C(5)CH_3], 1.25 (s, 6 H, 2 × CH_3), 1.30 [s, 3 H, C(2)CH_3], 1.53 [s, 3 H, C(2)CH_3], 1.54–1.65 (m, 2 H, CH_2), 3.13–3.24 (m, 1 H, CH_2CH_2O), 3.16 (s, 3 H, OCH_3), 3.30–3.40 (m, 1 H, CH_2CH_2O), 3.67 [d, *J* 11.6, 1 H, C(6)H], 4.00 [d, *J* 11.6, 1 H, C(6)H], 4.74 [s, 1 H, C(4)H], 7.28–7.42 (m, 5 H, Ph); δ_C(67.8 MHz; $CDCl_3$) 16.09, 18.82, 24.37, 29.36, 29.69, 32.78, 36.35, 48.56, 55.81, 70.32, 77.20, 98.85, 99.88, 127.58, 127.62, 127.94, 128.09, 128.23, 138.04.

5-(2-Hydroxy-2-methylpropyl)-4-naphthyl-2,2,5-trimethyl-1,3-dioxane 6ba. Viscous oil (Found: C, 76.45; H, 8.41. $C_{21}H_{28}O_3$ requires: C, 76.79; H, 8.59%); δ_H(270 MHz; $CDCl_3$) 1.23 (s, 9 H, 3 × CH_3), 1.33 (d, *J* 14.8, 1 H, CH) 1.57 (s, 6 H, 2 × CH_3), 1.65 (d, *J* 14.8, 1 H, CH), 4.03 [d, *J* 11.7, 1 H, C(5)H], 4.20 [d, *J* 11.7, 1 H, C(5)H], 4.93 [s, 1 H, C(3)H], 7.45–7.53 (m, 3 H, 2-Naph), 7.79–7.87 (m, 4 H, 2-Naph); δ_C(67.8 MHz; $CDCl_3$) 17.81, 19.01, 29.69, 31.18, 33.97, 38.47, 48.39, 70.39, 72.01, 79.93, 98.89, 125.77, 125.84, 126.45, 126.99, 127.30, 127.49, 128.07, 132.72, 132.90, 135.83.

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References

1 (*a*) S. L. Schreiber, A. H. Hoveyda and H. Wu, *J. Am. Chem. Soc.*, 1983, **105**, 660; (*b*) S. L. Schreiber and K. Satake, *J. Am. Chem. Soc.*, 1983, **105**, 6723; (*c*) J. A. Porco and S. L. Schreiber, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon Press, New York, 1991, vol. 5, pp. 168–188; (*d*) A. Zamojeski and S. Jarosz, *Tetrahedron Lett.*, 1982, **38**, 1447.

2 Paternó–Büchi reactions (ref. 6) with non-conjugated vinyl ethers (3-alkoxyoxetanes are major isomer), see (*a*) S. H. Schroeter and C. M. Orlando, *J. Org. Chem.*, 1969, **34**, 1181; (*b*) N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, 1970, **92**, 320; (*c*) S. H. Schroeter, *J. Chem. Soc.*, *Chem Commun.*, 1969, 12; (*d*) T. Bach, *Tetrahedron Lett.*, 1991, **32**, 7037; (*e*) H. A. J. Carless and D. J. Haywood, *J. Chem. Soc.*, *Chem. Commun.*, 1980, 1067; (*f*) A. G. Griesbeck and S. Stadtmüller, *J. Am. Chem. Soc.*, 1990, **112**, 1281.

3 Regioselective formation of 2-alkoxyoxetanes with conjugated vinyl ethers, see ref. 1.

4 Regioselective formation of 2-alkoxyoxetanes of α,β-diketones with vinyl ethers, see (*a*) H. A. J. Carless and G. K. Fekarurhobo, *Tetrahedron Lett.*, 1985, **26**, 4407; (*b*) J. Mattay, J. Gersdorf and K. Buchkremer, *Chem. Ber.*, 1987, **120**, 307.

5 Lewis-acid catalyzed formation of 2-alkoxyoxetanes, see W. W. Ellis and B. Bosnich, *Chem. Commun.*, 1998, 193.

6 For review, see (*a*) A. G. Griesbeck, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 522–535; (*b*) C. Rivas and F. Vargas, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 536–549; (*c*) A. G. Griesbeck, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 550–559; (*d*) H. A. J. Carless, in *Organic Photochemistry and Photobiology*, eds. W. M. Horspool and P. Song, CRC Press, New York, 1995, pp. 560–569; (*e*) H. A. J. Carless, in *Synthetic Organic Photochemistry*, ed. W. M. Horspool, Plenum Press, New York, 1984, pp. 425–488; (*f*) N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Inc., Menlo Park, 1978, pp. 432–452.

7 (*a*) M. Abe, M. Ikeda, Y. Shirodai and M. Nojima, *Tetrahedron Lett.*, 1996, **37**, 5901; (*b*) M. Abe, Y. Shirodai and M. Nojima, *J. Chem. Soc.*, *Perkin Trans. 1*, preceding paper in this issue.

8 J. Mattay and J. Runsink, *J. Org. Chem.*, 1985, **50**, 2815.

9 (*a*) H. O. House, D. S. Crumrine, A. Y. Teranishi and H. D. Olmstead, *J. Am. Chem. Soc.*, 1973, **95**, 3310; (*b*) T. Mukaiyama, K. Banno and K. Narasaka, *J. Am. Chem. Soc.*, 1974, **96**, 7503; (*c*) C. H. Heathcock, S. K. Davidson, K. T. Hug and L. A. Flippin, *J. Org. Chem.*, 1986, **51**, 3027.

10 R. E. Ireland, P. Wipf and J. D. Armstrong, *J. Org. Chem.*, 1991, **56**, 650.

11 R. Chenevert and G. Ampleman, *Synthesis*, 1987, 739.

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