Paternò−Büchi Photocyclization of 2-Siloxyfurans and Carbonyl Compounds. Notable Substituent and Carbonyl (Aldehyde vs Ketone and Singlet- vs Triplet-Excited State) Effects on the Regioselectivity (Double-Bond Selection) in the Formation of Bicyclic *exo*-Oxetanes

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Paternò−Büchi coupling, photochemical [2 + 2] cycloaddition, of carbonyl compounds **2a**−**f** with 2-siloxyfurans **1a**−**d** has been investigated in detail. The stereoselective formations of *exo*-oxetanes **3** and **4** were observed in high yields. The regioselectivity (double-bond selection, **3** vs **4**) was found to be largely dependent upon the carbonyls, the substituents at the furan ring, and the excited state of the carbonyls (singlet vs triplet). The photoreaction of aldehydes **2a**−**c** gave bicyclic *exo*-oxetanes **3** and **4** at regio-random, independent upon their excited states and the substituents at furan ring. However, the photoreaction of the triplet state of ketones **2d**−**f** was found to give regioselectively *exo*-oxetanes **4**, except for the 4-methyl-2-siloxyfurane **1d** case. The singlet-excited state of acetone **2f** gave both oxetanes **3** and **4** at regio-random. For the singlet-state photochemistry, the approach direction of the electrophilic oxygen of the excited carbonyls to the furan ring is proposed to be an important factor for the exo-stereoselection. The Griesbeck model can rationalize the regio- and exo-selective formation of oxetanes in the triplet-state photoreaction.

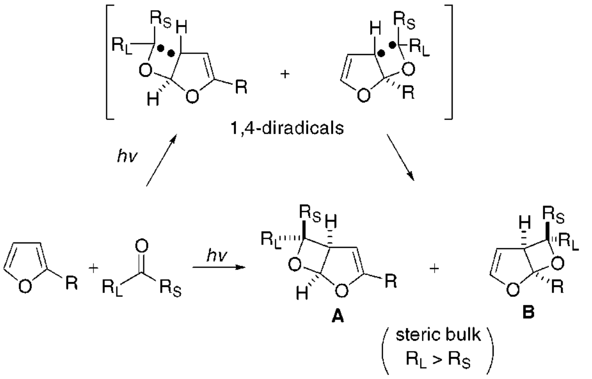
Introduction

Oxetanes formed in the [2 + 2] photocycloaddition of carbonyl compounds with alkenes, the so-called Paternò−Büchi reaction, are now considered as useful building blocks for organic synthesis.[1] The search for the regio- and stereocontrolled photocycloadditions is still a challenging subject.

The photocycloaddition with furans has been recognized as one of the efficient photocycloaddition reactions to give regio- and stereoselectively the bicyclic *exo*-2-alkoxyoxetanes via 1,4 diradicals (R = H, Scheme 1).[2] Schreiber and co-workers have exploited the synthetic utility of the bicyclic 2-alkoxyoxetanes, with success.[3]

However, with respect to the regioselectivity (**A** and/or **B**), i.e., the double-bond selection, for unsymmetrically substituted furans (R ≠ H), only some studies have been done until now. Shima and Sakurai have reported that aldehydes add to 2-methylfuran (R = Me) at regio-random to give a mixture of regioisomers **A** and **B**, while the regioselective formation of type **B** adduct was observed in the photoreaction with benzophenone.[4] Schreiber has found the selective formation of the bicyclic oxetane **A** by the introduction of a bulky trialkylsilyl (R = SiR_3) or trialkylstannyl (R = SnR_3) group.[5] Alternatively, the preferred formation of **B**-type oxetanes (R = Ac, CN) has been discovered by Carless.[6]

Scheme 1. Paternò−Büchi Reaction of Furan Derivatives



In conjunction with our current interest of the Paternò−Büchi reaction of ketene silyl acetals,[7] i.e., stereoselective synthesis of γ-butyrolactone derivatives,[8] we have decided to examine the photochemical reaction of carbonyl compounds **2** with 2-siloxyfuran derivatives **1**

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[1] For reviews, see: (a) Porco, J. A.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, M. M., Ed.; Pergamon Press: New York, 1991; Vol. 5, p 168. (b) Bach, T. *Synthesis* **1998**, 683. (c) Bach, T. *Liebigs Ann./Recueil* **1997**, 1627. (d) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301. (e) Carless, H. A. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 425.

[2] (a) Schenck, G. O.; Hartmann, W.; Steinmetz, R. *Chem. Ber.* **1963**, *96*, 498. (b) Hammond, G. S.; Turro, N. J. *Science* **1963**, *142*, 1541. (c) Gagmaire, D.; Payo-Subiza, E. *Bull. Soc. Chim. Fr.* **1963**, 2623. (d) Toki, S.; Shima, K.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 760. (e) Shima, K.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1806. (f) Evanega, G. R.; Whipple, E. B. *Tetrahedron Lett.* **1967**, 2163. (g) Toki, S.; Sakurai, H. *Tetrahedron Lett.* **1967**, 4119. (h) Leitich, J. *Tetrahedron Lett.* **1967**, 1937. (i) Rivas, C.; Payo, E. *J. Org. Chem.* **1967**, *32*, 2918. (j) Whipple, E. B.; Evanega, G. R. *Tetrahedron* **1968**, *24*, 1299. (k) Schroester, S. H. *J. Chem. Soc., Chem. Commun.* **1969**, 12. (l) Nakano, T.; Rivas, C.; Petez, C.; Tori, K. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2322. (m) Jarosz, S.; Zamojski, A. *Tetrahedron* **1982**, *38*, 1453. (n) Cantrell, T. S.; Allen, A. C.; Ziffer, H. *J. Org. Chem.* **1989**, *54*, 140.

[3] (a) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1983**, *105*, 6723. (b) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1984**, *106*, 4186. (c) Schreiber, S. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1984**, *106*, 7200. (d) Schreiber, S. L. *Science* **1985**, *227*, 857.

[4] (a) Sakurai, H.; Shima, K.; Toki, S. *Nippon Kagaku Zasshi* **1968**, *89*, 537. (b) Reference 2e. (c) See also ref 2i.

[5] (a) Schreiber, S. L.; Desmaele, D.; Porco, J. A., Jr. *Tetrahedron Lett.* **1988**, *29*, 6689. (b) Schreiber, S. L. Porco, J. A., Jr. *J. Org. Chem.* **1989**, *54*, 4721.

[6] Carless, H. A. J.; Halfhide, A. F. E. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1081.

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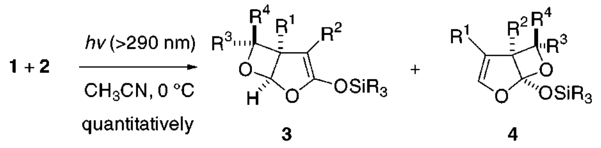
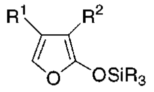
Scheme 2

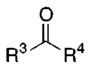


(R = $OSiR_3$), which can be easily prepared from the corresponding 2(5*H*)-furanone derivatives. Herein, we would like to report how the substituents (R^1−R^4) and the excited state of carbonyls (singlet vs triplet) influence the regio- (**A** and/or **B**) and stereoselectivity (exo vs endo) on the oxetane formation.



1

	R^1	R^2	SiR_3
a	H	H	TIPS
b	H	H	TBDMS
c	H	Me	TBDMS
d	Me	H	TBDMS



2

	R^3	R^4
a	Me	H
b	^{n}Pr	H
c	Ph	H
d	Ph	Me
e	Ph	Ph
f	Me	Me

Results

Photoreaction of Aldehydes 2a−c with 2-Siloxyfurans 1a−c. First of all, the photoreactions (>290 nm) of aldehydes **2a**−**c** (0.1 M) with 2-siloxyfurans **1a**−**d** (0.2 M) were performed in a degassed acetonitrile solution (40 mL) at 0 °C (Scheme 2 and Table 1).

After irradiation for 7 h, the photolysate was directly analyzed by NMR (^1H and ^{13}C-DEPT) spectroscopy. The measurements clearly showed the quantitative formation of ca. 1:1 mixtures of A-type bicyclic oxetane **3** (exo/endo = ca. 80/20 to >95/5, the configurational determination is shown below) and B-type adduct **4** (exo/endo = >95/5) at 100% conversion of the aldehyde (Table 1). Although the effects are not so large, it should be noted that for the aliphatic aldehydes **2a**,**b** the product ratios **3**/**4** and their exo/endo ratios of A-type adduct **3** were slightly changed under the diluted conditions, **1** (0.01 M), **2** (0.005 M) (compare entries 2 and 6 with entries 3 and 7), or in the presence of 1,3-pentadiene as a triplet quencher (compare entry 2 and entry 4). In contrast to the efficient formation of the oxetanes **3** and **4** in entry 4, the photoreaction was effectively suppressed in the presence of 1,3-pentadiene under the diluted conditions. The results clearly suggest that the triplet excited state of the aldehydes is crucial for the formation of the oxetanes under the diluted conditions. Alternatively, the singlet excited-state may be important in the presence of 1,3-pentadiene (entry 4), since the additional 1,3-pentadiene (up to 0.5 M) did not affect the selectivities.

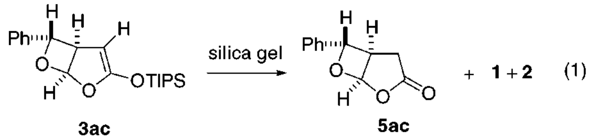
Table 1. Regio- and Stereoselectivity on the Bicyclic Oxetanes 3,4 (3:4) Formed in the Photocycloaddition of Aldehydes 2a−c with 2-Siloxyoxetanes 1a−d[a]

			regio- and stereoselectivity[b]		
entry	**1**	**2**	**3**:**4**	**3** (exo/endo)	**4** (exo/endo)
1	**1a**	**2a**	61:39	87:13	>95:5[c]
2	**1c**	**2a**	54:46	81:19	>95:5[c]
3[d]	**1c**	**2a**	35:65	92:8	>95:5[c]
4[e]	**1c**	**2a**	53:47	74:26	>95:5[c]
5	**1d**	**2a**	69:31	90:10	>95:5[c]
6	**1b**	**2b**	53:47	90:10	>95:5[c]
7[d]	**1b**	**2b**	48:52	>95:5[c]	>95:5[c]
8	**1a**	**2c**	50:50	>95:5[c]	>95:5[c]
9	**1c**	**2c**	40:60	87:13	>95:5[c]
10	**1d**	**2c**	56:44	>95:5[c]	>95:5[c]

[a] The photoreaction (>290 nm) of aldehydes **1a**−**c** (0.1 M) with 2-siloxyfurans **1a**−**d** (0.2 M) was performed in a degassed acetonitrile (40 mL) at 0 °C. The quantitative formation of the bicyclic oxetanes **3** and **4** was revealed by the NMR analysis of the photolysate. [b] The ratios (**3**:**4**, exo/endo, normalized to 100%) were determined on the basis of ^1H NMR (270 MHz) peak areas; error ±5%. [c] The value, >95:5, means that no minor products were observed by ^1H NMR spectroscopy. [d] The photoreaction was performed under the diluted conditions: **1** (0.01 M), **2** (0.005 M). [e] The photoreaction was run in the presence of 1,3-pentadiene (0.2 M) as a triplet quencher. The total yields of adducts **3** and **4** were ca. 85% from ^1H NMR.

The concentration effect was not observed for the photoreaction of aromatic aldehyde, benzaldehyde **2c** (entries 8−10). Expectedly, the photoreaction of benzaldehyde (E_T = ca. 70 kcal/mol)[9] was effectively quenched by the presence of 1,3-pentadiene (E_T = 59 kcal/mol).[9] The results suggest that the spin-multiplicity of the excited aldehydes **2**, i.e., triplet or singlet, may play an important role for determining the selectivities. Anyway, both the singlet and triplet state of aldehydes gave selectively the *exo*-oxetanes, especially, in the case of B-type adducts **4**.

The adducts **3** and **4** were acid-labile to afford the decomposition products upon treatment with silica gel. For example, A-type adduct **3ac** ($R^1 = R^2$ = H, SiR_3 = TIPS, R^3 = Ph, R^4 = H) was converted to the desilylated bicyclic oxetanes **5ac** (30%) and the corresponding starting materials **1a** and **2c** (eq 1).



Unfortunately, the silica gel induced-decomposition of B-type adducts **4** was rather complex, although we could detect the two starting materials **1** and **2** by the NMR measurements. However, the characteristic ^{13}C NMR signal for the ortho ester carbon in structure **4**, which appears at ca. 120 ppm, supports the structure (for detailed spectroscopic data, see the Experimental Section). The formation of the adducts **4** in the photoreaction with aldehydes **2a**−**c** is also strongly supported by the similarity of the NMR signals with those of B-type adducts **4** ($R^3 = R^4$ = Ph) isolated in the photoreaction with benzophenone **2e** (vide infra).

As judged by the results mentioned above (Scheme 2 and Table 1), the substituent (R^1−R^3, SiR_3) effects on the regioselectivity were quite low (ca. **3**:**4** = ca. 1:1) in the photocycloaddition of aldehydes **2a**−**c** (R^4 = H), although

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(8) γ-Butyrolactones are important precursors for natural products; see, for example: (a) Grieco, P. A. *Synthesis* **1975**, 67. (b) Hoffmann, H. M. R.; Rabe, *J. Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 97. (c) Petragnani, N.; Ferraz, H. M. C.; Silva, G. V. J. *Synthesis* **1986**, 157. (d) Ito, M. *Pure Appl. Chem.* **1991**, *63*, 13. (e) Rassu, G.; Znardi, F.; Battistini, L.; Casiraghi, G. *SynLett* **1999**, 1333. (f) Brinksma, J.; Deen, H.; Oeveren, A.; Feringa, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4159.

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Table 2. Regio- and Stereoselectivity of Bicyclic Oxetane 3,4 (3:4) in the Photocycloaddition of Ketones 2d−f with 2-Siloxyoxetanes 1a−d[a]

			regio- and stereoselectivity[b]			
entry	1	2	3:4	3 (exo/endo)	4 (exo/endo)	Φ[c] (rel)
1	**1a**	**2d**	5:95	*d*	78:22	0.013 (1.0)
2	**1c**	**2d**	7:93	*d*	>95:5[e]	0.016 (1.2)
3	**1d**	**2d**	42:58	95:5	82:18	0.027 (2.1)
4	**1b**	**2e**	7:93			
5	**1c**	**2e**	<5:95[e]			
6	**1d**	**2e**	15:85			
7	**1c**	**2f**	50:50			
8[f]	**1c**	**2f**	57:43			
9[g]	**1c**	**2f**	10:90			

[a] The photoreaction (>290 nm) of ketones **2d**−**f** (0.1 M) with 2-siloxyfurans **1a**−**d** (0.2 M) was performed in a degassed acetonitrile (40 mL) at 0 °C. The quantitative formation of the bicyclic oxetanes **3** and **4** was revealed by the NMR analysis of the photolysate. [b] The ratios (**3**:**4**, exo/endo, normalized to 100%) were determined on the basis of ^{1}H NMR (270 MHz) peak areas; error ±5%. [c] The quantum yields (Φ, the average value after three trials, error ± 10%) were determined on the basis of the Norrish type II photodecomposition of valerophenone ($\Phi_{\mathrm{PhCOCH_3}} = 0.33$ at $\lambda_{\mathrm{e.}} = 313$ nm, ref 15) as an actinometer. [d] The values were not determined due to the low yield of A-type adduct **3**. [e] The values means that no minor products was observed by ^{1}H NMR spectrometer. [f] The photoreaction was performed in the presence of 1,3-pentadiene (0.2 M). [g] The photoreaction was performed under the diluted conditions: **1c** (0.01 M), **2f** (0.005 M).

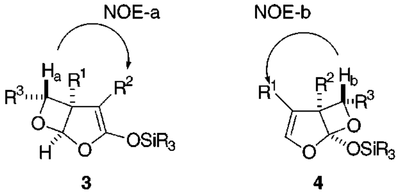


Figure 1.

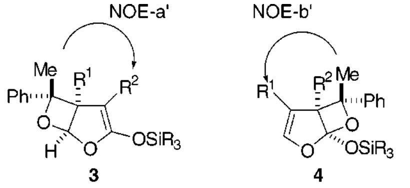


Figure 2.

the high exo selectivity of the bicyclic oxetanes **3** and **4** was observed (exo/endo = > 80:20).

Photoreaction of Ketones 2d−f with 2-Siloxyfurans 1a−d. Next, we examined the regioselectivity (**3**:**4**) in the photocycloaddition of ketones **2d**−**f** (0.1 M) and 2-siloxyfurans **2a**−**c** (0.2 M) under similar irradiation conditions (Scheme 2 and Table 2). As judged by the NMR analyses of the photolysate, again, the quantitative formation of the bicyclic oxetanes **3** and **4** was clearly observed at 100% conversion of the ketones (**3** + **4**:**1** = ca. 1:1). As mentioned before, B-type adducts **4be** ($R^1 = R^2 = H$, $R^3 = R^4 = Ph$, SiR_3 = TBDMS) and **4de** (R^1 = Me, R^2 = H, $R^3 = R^4$ = Ph, SiR_3 = TBDMS) derived from benzophenone **2e** could be isolated by quick column chromatography on silica gel and fully characterized (entries 4 and 6, see the Experimental Section). Unfortunately, the isolation of other adducts **4** failed even when alumina (Al_2O_3) was used for the column chromatography to give the starting materials. The observation of the characteristic ^{13}C NMR signal of the ortho ester carbon in **4**, which appears at ca. 120 ppm in the photolysate, strongly supports the structure.

Interestingly, the highly regioselective formation of B-type adducts **4** was observed for the photoreaction of **1a**−**c** (entries 1, 2, and 4−5) with aromatic ketones **2d**−**e**. However, for the photoreaction of **1d** (R^1 = Me, R^2 = H), the decrease of the formation of the B-type adducts **4** were observed with increasing A-type adducts **3** (entries 3and 6). In the photoreactions of acetophenone **2d**, the major isomer of the adducts **3** and **4** possesses the exo configuration, which is similar to the cases for the photoreaction of aldehydes **2a**−**c** (the configurational determination was discussed below).

Surprisingly, in the photoreaction of acetone **2f** (0.1 M) with **1c** (0.2 M), the formation of a 1:1 mixture of oxetanes **3** and **4** was observed (entry 7). The product ratio (**3**/**4**) did not change in the presence of 1,3-pentadiene as a triplet quencher (entry 8). To understand the sharp contrast results on the regioselectivity between the aromatic ketones **2d**,**e** and aliphatic ketone **2f**, the photoreaction of acetone **2f** with **1c** was performed at low concentration of furan **1c** (0.01 M) under the similar irradiation conditions (entry 9). Consequently, the dramatic concentration effect was also observed to give regioselectively the B-type adduct **4cf** (R^1 = H, R^2 = Me, $R^3 = R^4$ = Me, SiR_3 = TBDMS, **3cf**/**4cf** = 10/90). The results clearly suggest that the singlet excited state of the aliphatic ketone gives the oxetanes at regio-random, while the triplet states of both the aromatic and aliphatic ketones result in the selective formation of the B-type adduct **4** (see, Discussion).

To get the information for the notable substituent effects at the furan ring on the regioselectivity (**3** vs **4**), the quantum yields (Φ, error < 10%) for the formation of the adducts **3** and **4** were measured in the photoreactions of acetophenone **2d** with **1a**,**c**,**d** (entries 1−3). The quantum yield ($\Phi_{\mathbf{1d}}$ = 0.027, **3dd**:**4dd** = 42:58, entry 3) for the photoreaction with **1d** was roughly twice as high as those for **1a**,**c** ($\Phi_{\mathbf{1a}}$ = 0.013 and $\Phi_{\mathbf{1c}}$ = 0.016, **3**:**4** = ca. 5:95). Namely, the higher quantum yield was observed for the photoreaction with lower regioselectivity. The results suggest that triplet excited acetophenone can attack both double bonds equally, while, in the case of the photoreaction with **1a**,**c** the A-type attack producing **3** is not productive but goes back to starting materials.

Configurational Determination of Bicyclic Oxetanes 3 and 4. The configuration (exo and endo) of the two types of adducts **3** and **4** from aldehydes **2a**−**c** were determined on the basis of their NOE measurements (Figure 1). Namely, the isomer with the clear NOE-a (5−7%) enhancement between H_a and R^1 was assigned as an exo isomer of the A-type adduct **3**. Similarly, the isomer with the NOE-b enhancement (5−7%) between H_b and R^2 was determined as an exo diastereoisomer of the B-type adduct **4** (see the Experimental Section).

In the case of the acetophenone adducts **3** and **4**, the isomer with the clear NOE-a′ or NOE-b′ enhancements (2−3%) between the methyl protons and R^2 or R^1 substituents was determined as the exo isomer of **3** or **4** (Figure 2). The assignment based on the NOE measurements was consistent with the observation of the ^{1}H NMR upfield shift of the R^1 in **3** and R^2 in **4**, which are cis to the phenyl ring.

Discussion

The important findings from our experiments in the photocycloaddition of carbonyl compounds **2** with 2-siloxyfurans **1** are as follows: (1) when the aldehydes

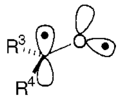


Figure 3. Electronic configuration of nπ* carbonyls, perpendicular orientation.

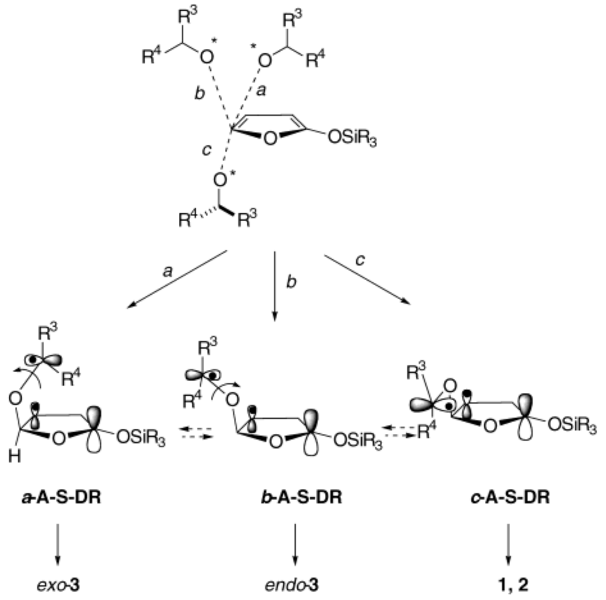
2a−**c** (R^4 = H) were used for the photoreaction, the low regioselectivity (**3**:**4** = ca. 1:1) was observed independent upon the excited of carbonyls and the substituents R^1−R^3 (Table 1); (2) the exo-selective formation of both the bicyclic oxetanes **3** and **4** was observed independent upon the excited state of carbonyls (Table 1). (3) the selective formation of B-type adducts **4** (**3**:**4** = ca. 5:95) was observed in the photoreaction of the triplet excited state of ketones **2d**−**f** (R^4 = Me, Ph), except for the case of the reaction with furan **1d**, while the singlet excited carbonyls gave oxetanes at regio-random (Table 2); (4) the quantum yields for the photoreaction of acetophenone **2d** were largely dependent upon the used furans **1**, $\Phi_{\mathbf{1a}}$ = 0.013 for **1a** (R^1 = R^2 = H, SiR_3 = TIPS, **3**:**4** = 5:95), $\Phi_{\mathbf{1c}}$ = 0.016 for **1c** (R^1 = H, R^2 = Me, SiR_3 = TBDMS, **3**:**4** = 7:93), $\Phi_{\mathbf{1c}}$ = 0.027 for **1d** (R^1 = Me, R^2 = H, SiR_3 = TBDMS, **3**:**4** = 42:58) (entries 1−3 in Table 2).

Singlet-State Photochemistry. As mentioned above, the singlet nπ* carbonyls gave both oxetanes **3** and **4** at regio-random, but exo-selectively. Since the singlet excited-state reaction does not involve the intersystem crossing (ISC) step to produce the ground-state compounds, the initial geometries of 1,4-diradicals **A-** and **B-S-DR** formed in the nπ* singlet carbonyls with furans **1** may influence the stereoselectivity of the final oxetanes. As judged by the electronic configuration of the nπ* carbonyls (Figure 3), the three directions *a*−*c* of the perpendicular approach[10] to the furan ring are assumed to be important (Schemes 3 and 4), where they may generate (*a*) inside-gauche, (*b*) outside-gauche, and (*c*) outside-trans conformations of **A-** and **B-S-DR** (Scheme 3).

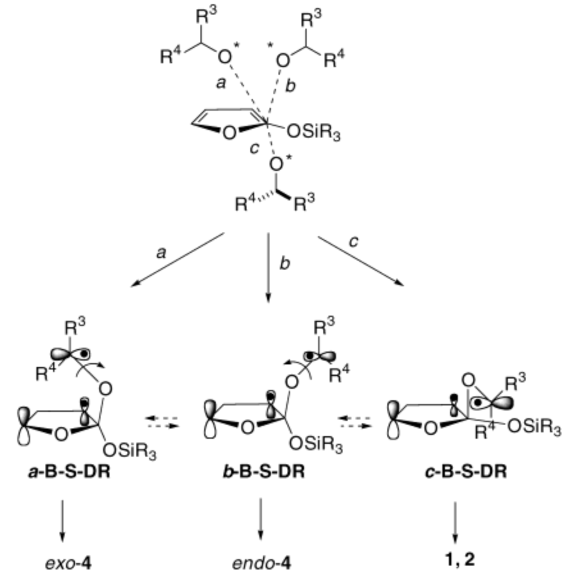
The inside-gauche geometries ***a*-A- and *a*-B-S-DR** will mainly produce the *exo*-oxetanes **3** and **4**, while the outside-gauche structures ***b*-A-** and ***b*-B-S-DR** may preferentially give the *endo*-oxetanes **3** and **4**. The outside-trans geometries ***c*-A-** and ***c*-B-S-DR** will go back to the starting materials due to the spatially separated orientation of the two radical sites. The experimental results, i.e., preferred formation of *exo*-oxetanes, suggest the *a* approach selectively occurred to produce "inside-gauche" structure ***a*-A-S-DR** and ***b*-B-S-DR**, if the equilibration between the conformers is negligible. The reason is rather unclear, but, at this point, we propose the electrostatic attraction between the electrophilic oxygen and π-electrons of another double bond (Scheme 4).

Triplet-State Photochemistry. Unlike the singlet-state photochemistry, in the triplet-state, the intersystem crossing process (ISC) is indispensable to form the ground-state materials. The triplet-1,4-diradicals **T-DR** involved in the triplet reactions should have lifetimes. Therefore, the sharp contrast regioselectivity (**3** vs **4**) between the singlet and triplet state should be originated in the ISC process, rather than (1) the product stability (**3** vs **4**) or (2) relative stability of 1,4-diradical intermediates (**A-T-DR** vs **B-T-DR**) without considering the geometry. Thus, to rationalize our experimental results in the triplet-state photochemistry, the preferred geometries of the triplet 1,4-diradicals **T-DR** for the ISC process should be considered, as reported by Griesbeck (Griesbeck model), which is originally proposed for rationalizing the stereoselectivity (exo/endo) in the Paternò−Büchi reaction.[11] Before going to the mechanistic discussion for our regioselectivity (**3** vs **4**) in the triplet-state photochemistry, we would like to introduce the "Griesbeck model" briefly.

Scheme 3. Proposed Mechanism for the Exo-Selective Formation of Oxetanes 3 in the Singlet-State Photochemistry



Scheme 4. Proposed Mechanism for the Exo-Selective Formation of Oxetanes 4 in the Singlet-State Photochemistry



Griesbeck has proposed that the preferred geometry in triplet 1,4-diradicals for the ISC process, which is induced by the spin−orbit coupling (SOC),[12] governs the

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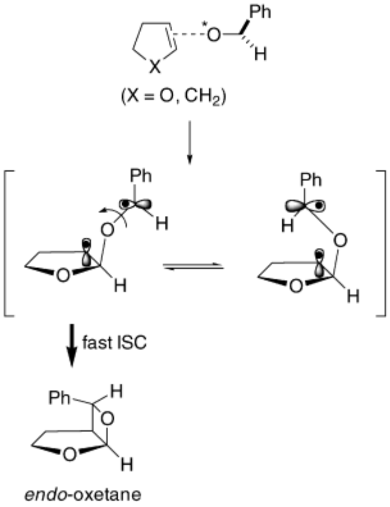
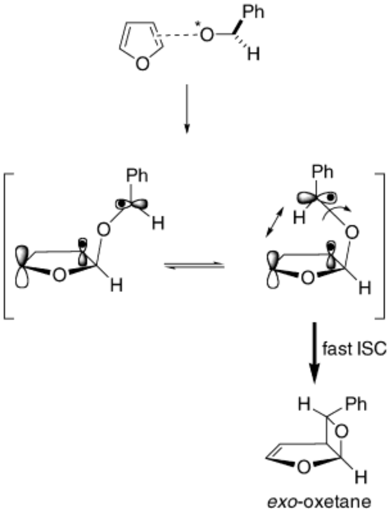
[10] For the nucleophilic attack, perpendicular approach, of excited carbonyl to electron-rich alkenes, see: (a) Turro, N. J.; Dalton, J. C.; Farrington, G.; Niemczyk, M.; Pond, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 6978. (b) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. (c) Bigot, B.; Devaquet, A.; Turro, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 6. (d) Turro, N. J. In *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co., Inc.: Menlo Park, 1978; p 446. (e) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727. (f) Palmer, I. J.; Ragazos, I. N.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 2121.

Scheme 5. Griesbeck Model for Endo-Selective Formation of Oxetanes Derived from Dihydrofuran



Scheme 6. Griesbeck Model for Exo-Selective Formation of Oxetanes Derived from Furan



stereochemical outcome of oxetanes. Namely, the perpendicular orientation of the two radical *p*-orbitals,[13] which increase the rate of ISC process, plays an important role for the diastereoselection (Scheme 5).

The idea excellently explains the preferred formation of the thermodynamically less-favored *endo*-oxetanes derived from cyclic monoalkenes. Very recently, he has also reported that the idea is applicable for the exo-selective formation of bicyclic oxetanes formed in the photoreaction of benzaldehyde derivatives with furan, considering the additional orbital interaction caused by the allylic radical moiety (Scheme 6).[14] The second model seems to be valuable for our case.

Let us start the discussion for the regioselectivity, **3** vs **4** (Schemes 7 and 8). As predicted by Griesbeck, in reality, the exo-selective formation of the bicyclic oxetanes **3** and **4** was also found in our triplet photoreaction of 2-siloxyfurans **1** (Tables 1 and 2). Thus, like the singlet-state photochemistry, the geometries **A1-** and **B1-T-DR**, where the fast ISC is expected instead of the other conformations, may be important for the formation of the *exo*-oxetanes **3** and **4**.

In the photoreaction of aldehydes ($R^4 = H$), the proportion of the **A1**- and **B1-T-DR** structures in each three conformers may be almost the same, since the steric effects of R^4 group is very small. Thus, the regio-random formation of *exo*-oxetanes **3** and **4** may be expected. In reality, this was the case, as shown in Table 1.

In the case of the photoreaction of ketones, the highly regioselective formation of B-type adduct *exo*-**4** was observed except for the case of **1d** ($R^1 = Me$, $R^2 = H$, $SiR_3 = TBDMS$). Based on the quantum yields measured for the reaction of acetophenone (entries 1−3 in Table 1), the triplet-state of ketones can also attack both double bonds equally to generate the two types of diradicals **A-** and **B-T-DR**, like the singlet-state reactions. However, for the case of **1a**−**c** ($R^1 = H$), the proportion of **B1-T-DR** in the possible B-type conformations should be higher than that of **A1-T-DR** in A-type conformations, since steric repulsion between R^4 (= Me, Ph) and R^2 and $OSiR_3$ can be expected in B-type diradicals. Alternatively, in the photoreaction with **1d** ($R^1 = Me$), the content of **A1-T-DR** geometry may be increased due to the steric repulsion between R^4 and R^1. Thus, the competitive formation of *exo*-**3** and **4** has been observed.

In summary, we have investigated the Paternò−Büchi-ype reaction of 2-siloxyfuran derivatives **1** in conjunction with our interest in the short-step synthesis of stereocontrolled γ-butyrolactones. We have found the following points in this study: (1) the excited state of carbonyls, singlet vs triplet, largely influence the regioselectivity, i.e. **3** vs **4**; (2) the regioselectivity has also been found to be largely dependent upon the substituents at the furan-ring for the reaction of ketones; (3) the exo-selective formation of both oxetanes has been discovered independent upon the carbonyls and their excited states (singlet vs triplet). On the basis of the findings of this study, further synthetic work is now ongoing.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz, respectively. ^1H NMR chemical shifts were reported in ppm (δ) using residual $CHCl_3$ (δ 7.26) in $CDCl_3$. ^{13}C NMR chemical shifts were reported in ppm (δ) relative to the internal standard $CDCl_3$ (δ 77.00). Elemental analyses were performed by the Analytical Center of the Faculty of Engineering, Osaka University. Melting points are not corrected. Flash column chromatography was performed using silica gel (Wakogel C-300) as absorbent.

Preparative Photolyses. Photolyses (>290 nm) were conducted with an Eikohsha 500 W high-pressure mercury lamp though a Pyrex filter.

Determination of Quantum Yields of Oxetane Formation. The quantum yields of the oxetane formations from the photoreaction of acetophenone **2d** were measured by Xenon lamp (500 W) focused at 313 nm at room temperature. The absorbance at 313 nm of a solution of furan **1** and acetophe-

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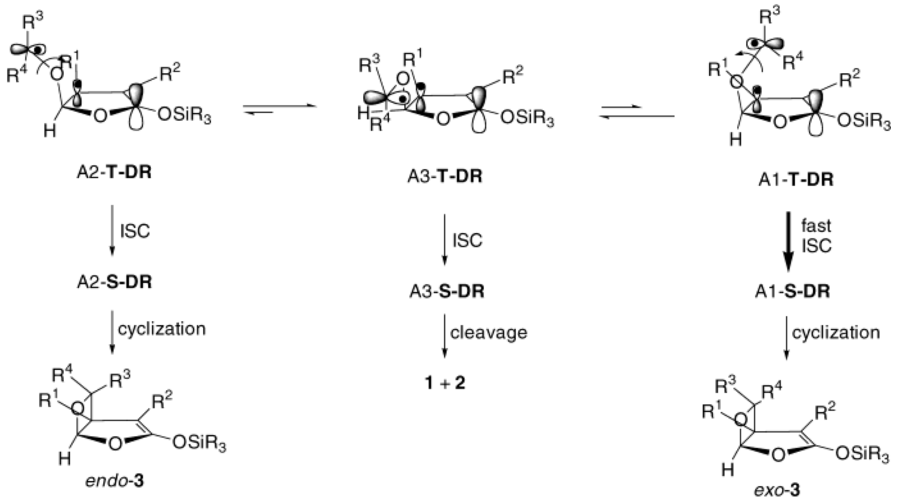
[11] (a) Griesbeck, A. G.; Stadtmüller, S. *Chem. Ber.* **1990**, *123*, 357. (b) Griesbeck, A. G.; Mauder, H.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Chem. Ber.* **1991**, *124*, 407. (c) Griesbeck, A. G.; Stadtmüller, S. *J. Am. Chem. Soc.* **1990**, *112*, 1281. (d) Griesbeck, A. G.; Stadtmüller, S. *J. Am. Chem. Soc.* **1991**, *113*, 6923. (e) Griesbeck A. G.; Stadtmüller, S.; Bringmann, G.; Busse, H.; Buddrus, J. *Chem. Ber.* **1992**, *125*, 933. (f) Griesbeck, A. G.; Mauder, H.; Stadtmüller, S. *Acc. Chem. Res.* **1994**, *27*, 70.

[12] Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

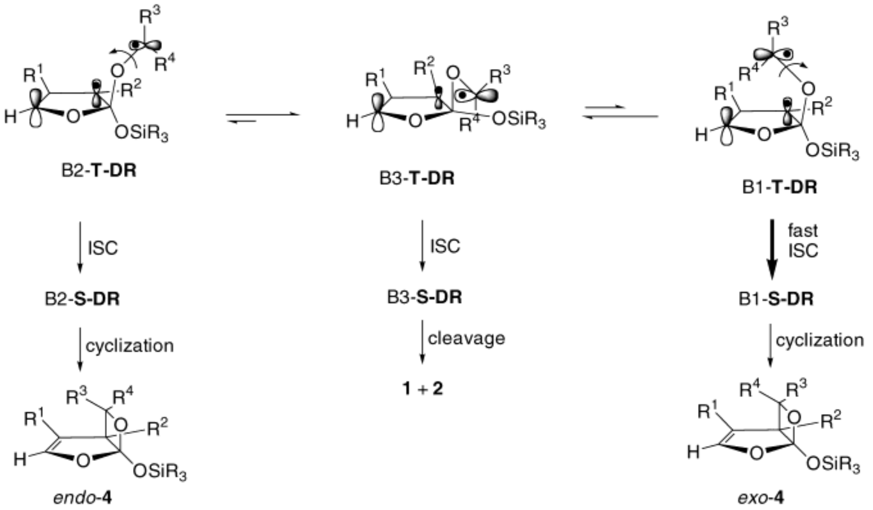
[13] For the semiempirical formula for magnitude of SOC, see: (a) Furlani, T. R.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577. (b) Carlacci, L.; Doubleday, C., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323. (c) Caldwell, R. A. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990, p 77.

[14] Griesbeck, A. G.; Buhr, S.; Fiege, M.; Schmickler, H.; Lex, J. *J. Org. Chem.* **1998**, *63*, 3847.

Scheme 7. Proposed Mechanism for the Exo-Selective Formation of Oxetanes 3 in the Triplet-State Photochemistry



Scheme 8. Proposed Mechanism for the Exo-Selective Formation of Oxetanes 4 in the Triplet-State Photochemistry



none **2d** remained above 1.5 through the irradiation, and thus no correction for transmitted light was necessary. The intensity of the lamp was determined on the basis of the Norrish type-II photodecomposition of valerophenone ($\Phi_{PhCOCH_3} = 0.33$ at 313 nm)[15] as an actinometer. The values listed in Table 2 are the average after three trials, error ± 10%.

Preparation of 2-Siloxyfuran Derivatives 1a−d. 2-Siloxyfurans **1a**−**d** (60−80%) were prepared by the method reported by Ireland et al.[16] The 2-siloxyfurans **1a**,**b** are known compounds.[17,18] Spectroscopic data for new compounds **1b**−**d** are given in the Supporting Information.

General Procedure for Photocycloaddition of Carbonyl Compounds 2a−f with 2-Siloxyfurans 1a−d. A degassed solution of 2-siloxyfuran **1** (0.2 M, 8 mmol) and carbonyl compound **2** (0.1 M, 4 mmol) in acetonitrile (40 mL) was irradiated with a high-pressure Hg lamp through a Pyrex filter at 0 °C. After the carbonyl compound **2** was consumed (typically for 7 h), the solvent was removed by using a rotary evaporator. The photolysate was analyzed by ^{1}H NMR spectroscopy. The spectra revealed the quantitative formation of the bicyclic oxetanes **3** and **4** together with the excess amounts of 2-siloxyfuran **1** (**3** + **4**/**1** = ca. 1/1). After 2-siloxyfuran **1** was removed from the photolysate under reduced pressure (50−60 °C/0.1 mmHg) by using Kugelrohl distillation apparatus, the bicyclic oxetanes **3** and **4** were carefully analyzed by NMR spectroscopy (^{1}H, ^{13}C, NOE, DEPT). The benzophenone adducts **4be**, **4ce**, and **4de** were isolated by the quick column chromatography on silica gel (*n*-hexane as an eluent). All of the spectroscopic data for compounds **3** and **4** are listed in the Supporting Information. The spectroscopic data for **5ac** formed by silica gel-induced decomposition of **3ac** are also listed in the Supporting Information.

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Supporting Information Available: Copies of the ^{1}H (270 MHz) and ^{13}C NMR (67.8 MHz) spectra for acid-labile bicyclic oxetanes **3** and **4**; listed spectroscopic data for compounds **1**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896.

[16] Ireland, R. E.; Wipf, P.; Armstrong, J. D. *J. Org. Chem.* **1991**, *56*, 650.

[17] Martin, S. F.; Barr, K. J.; Smith, D. W.; Bur, S. K. *J. Am. Chem. Soc.* **1999**, *121*, 6990.

[18] Casiraghi, G.; Colombo, L.; Rassu, G.; Spanu, P. *J. Org. Chem.* **1991**, *56*, 2135.