Photooxygenation ($^1O_2$) of silyl enol ethers derived from indan-1-ones: competitive formation of tricyclic 3-siloxy-1,2-dioxetane and α-silylperoxy ketone

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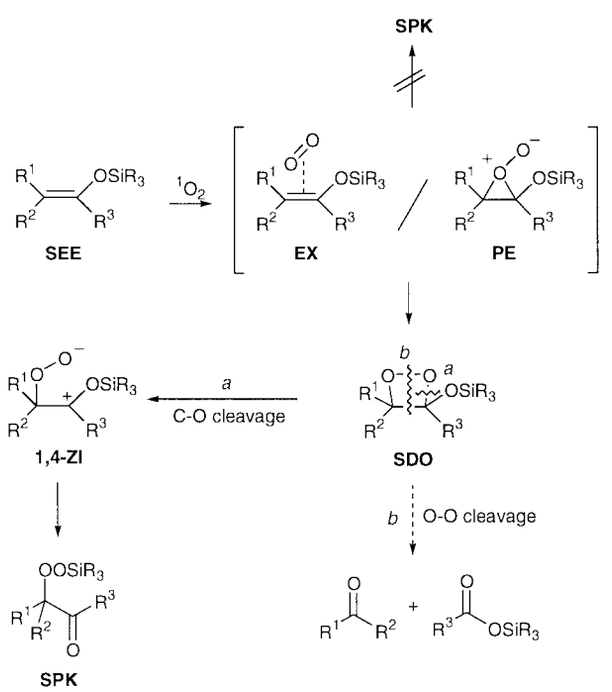
Photooxygenation ($^1O_2$) of silyl enol ethers **1** (X = H) and **2** (X = OMe) derived from indan-1-ones has been investigated. The oxygenation of silyl enol ethers **1** (X = H) was found to give the corresponding tricyclic 3-siloxy-1,2-dioxetanes **3** quantitatively. Alternatively, the silyl enol ethers **2** (X = OMe) gave tricyclic dioxetanes **6** together with α-silylperoxy ketones **7**. The substituent effects of X = OMe on the direct formation of α-silylperoxy ketone **7** are explained by the formation of the 1,4-zwitterion intermediates (**ZI**). Thermolysis of the tricyclic 3-siloxy-1,2-dioxetanes **3** and **6** was observed for the first time to yield the keto esters **4** and **8**, respectively.

Introduction

Photooxygenation of olefins with singlet oxygen ($^1O_2$) has been well investigated from both synthetic and mechanistic points of view.[1] For example, the ene reactions of olefins bearing allylic hydrogens directly produce allylic hydroperoxides *via* hydrogen migration in the perepoxide intermediate.[2] Analogously, silyl enol ethers form α-silylperoxy ketones as the final product.[3] However, the mechanism for the formation of the silatropic ene products, α-silylperoxy ketones, can be distinguished from that for the allylic hydroperoxides. Adam and co-workers have found that the α-(trialkylsilyl)peroxy ketone (**SPK**) is formed not directly from the perepoxide (**PE**) or exciplex (**EX**) intermediate but *via* 3-siloxy-1,2-dioxetanes (**SDO**, Scheme 1).[4]



Scheme 1

Namely, unlike the normal reactivity of 1,2-dioxetanes (O–O cleavage, *b*) **SDO** generates the 1,4-zwitterion (**ZI**) by selective C–O bond cleavage (*a*), and then silyl-migration occurs to give **SPK**.

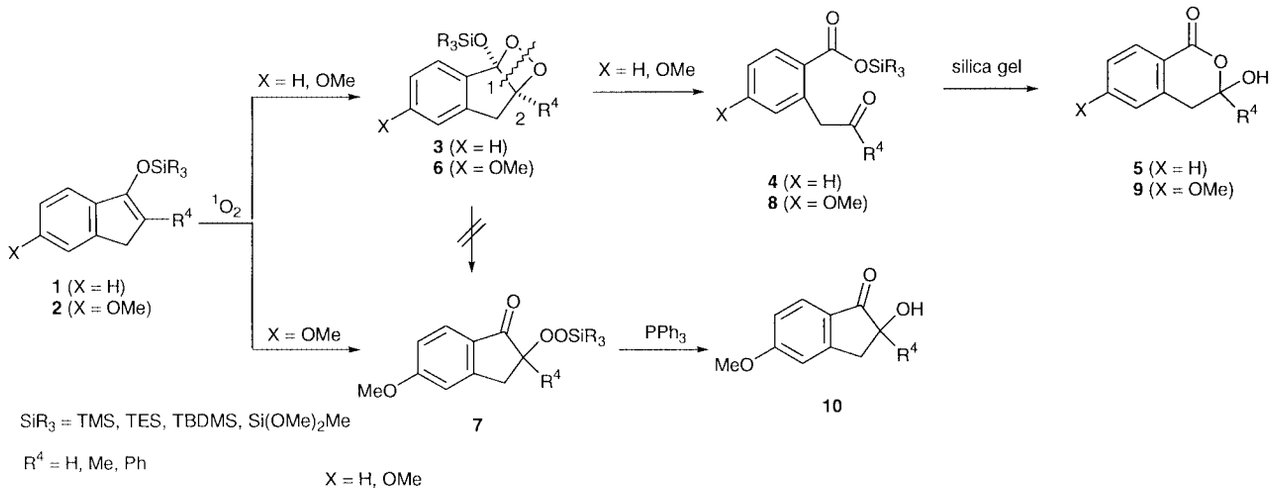
In the present study, we have observed for the first time the competitive formation of 3-siloxy-1,2-dioxetane and α-silylperoxy ketone in the photooxygenation ($^1O_2$) of silyl enol ethers derived from indan-1-ones. The product ratios (dioxetane *vs.* α-silylperoxy ketone) were found to be dependent upon the substituent at silicon (SiR_3 = TMS, TES, TBDMS, methyldimethoxysilyl (DMEOMS)), X (= H or MeO), and R^4 (= H, Me, Ph) (Scheme 2). Furthermore, exclusive O–O bond cleavage (*b*) in the tricyclic 3-siloxy-1,2-dioxetanes has been discovered (Scheme 2).

Results and discussion

Photooxygenation ($^1O_2$) of silyl enol ethers 1 and 2 in $CDCl_3$

Silyl enol ethers **1** (X = H) and **2** (X = OMe) were prepared from the corresponding indanone derivatives by using the method described previously.[5] Singlet oxygen ($^1O_2$) was photochemically (>400 nm) generated *in situ* in the presence of tetraphenylporphine (TPP) as sensitizer[6] under an oxygen atmosphere and reacted with silyl enol ethers **1**, **2** in CH_2Cl_2 at 0 °C (Scheme 2 and Table 1).

The photooxygenation reactions were directly analyzed by NMR spectroscopy (^1H: 270 MHz and ^{13}C: 67.8 MHz in $CDCl_3$) at low temperature (0 °C), after the solvent (CH_2Cl_2) was removed under reduced pressure at 0 °C. In the photooxygenation of silyl enol ethers **1** (X = H), the quantitative formation of tricyclic 3-siloxy-1,2-dioxetanes **3** was observed independent of the silicon and R^4 substituents (entries 1–6 in Table 1). The dioxetanes **3** were stable at 0 °C and the structural assignment was made from ^{13}C NMR signals, which are characteristic of the dioxetane ring[7] (δ_{C1} = *ca.* 113 ppm and δ_{C2} = *ca.* 92 ppm, see Experimental section). Interestingly, unlike the monocyclic 3-siloxy-1,2-dioxetanes (Scheme 1), the tricyclic dioxetanes **3** (X = H) were not converted to the α-silylperoxy ketones but to the keto esters **4** (X = H) upon warming the solution to room temperature (*ca.* 25 °C). Except for the keto ester **4c** (SiR_3 = TBDMS), the keto esters **4** (SiR_3 = TMS, TES, DMEOMS) were easily converted to the lactone **5** upon treatment with silica gel which was used for separation in column chromatography. To obtain information on the decomposition mechanism of the dioxetanes **3** (SiR_3 = TBDMS), the activation parameters (E_a and ln *A*) were determined from the kinetic measurements of the decomposition by using ^1H NMR (270 MHz; C_6D_6) analysis in the range 25–55 °C (entries 1–3 in Table 2). The values obtained are similar to those for other



Scheme 2

Table 1 Photooxygenation ($^1O_2$) of silyl enol ethers **1** (X = H) and **2** (X = OMe), characteristic ^{13}C NMR (68 MHz) chemical-shifts (δ, ppm) of 3-siloxy-1,2-dioxetanes **3** (X = H) and **6** (X = OMe), and product ratios of dioxetanes and α-silylperoxy ketones[a]

Entry		Silyl enol ether		Product ratios dioxetane : α-silylperoxy ketone[b]	Characteristic ^{13}C NMR chemical shifts of dioxetanes[c]		
		R^4	SiR_3			C1	C2
1	**1a**	H	TMS	>95:5	**3a**	113.05	91.70
2	**1b**	H	TES	>95:5	**3b**	112.90	91.97
3	**1c**	H	TBDMS	>95:5	**3c**	112.96	91.75
4	**1d**	H	$Si(OMe)_2Me$	>95:5	**3d**	111.68	91.50
5	**1e**	Me	TBDMS	>95:5	**3e**	113.21	96.53
6	**1f**	Ph	TBDMS	>95:5	**3f**	113.86	99.50
7	**2a**	H	TBDMS	88:12	**4a**	112.51	92.20
8	**2b**	Me	TBDMS	83:17	**4b**	112.92	96.95
9	**2c**	Ph	TBDMS	>95:5	**4c**	113.55	99.82
10	**2d**	Me	$Si(OMe)_2Me$	66:34	**4d**	112.02	88.09

[a] Photooxygenation ($^1O_2$) was performed in $CDCl_3$ at 0 °C and the reaction was directly analyzed by NMR (^1H: 270 MHz, ^{13}C: 67.8 MHz) spectroscopy at a low temperature (0 °C). [b] Product ratios were determined by the ^1H NMR peak areas (error ± 5%) of dioxetane and α-silylperoxy ketones. >95:5 means that no α-silylperoxy ketone was observed in the NMR spectra. [c] For complete NMR data, ^1H (270 MHz) and ^{13}C (67.8 MHz), in $CDCl_3$, see Experimental section.

Table 2 Activation parameters (E_a and ln A) for the thermolysis of 3-(*tert*-butyldimethylsiloxy)-1,2-dioxetanes **3** (X = H) and **6** (X = OMe) in C_6D_6[a]

Entry		Dioxetanes		E_a/ kcal mol^{-1}	ln A
		X	R^4		
1	**3c**	H	H	21.9	26.7
2	**3e**	H	Me	22.8	27.6
3	**3f**	H	Ph	17.1	19.6
4	**6a**	OMe	H	19.5	23.5
5	**6b**	OMe	Me	21.6	27.6
6	**6c**	OMe	Ph	17.0	18.2

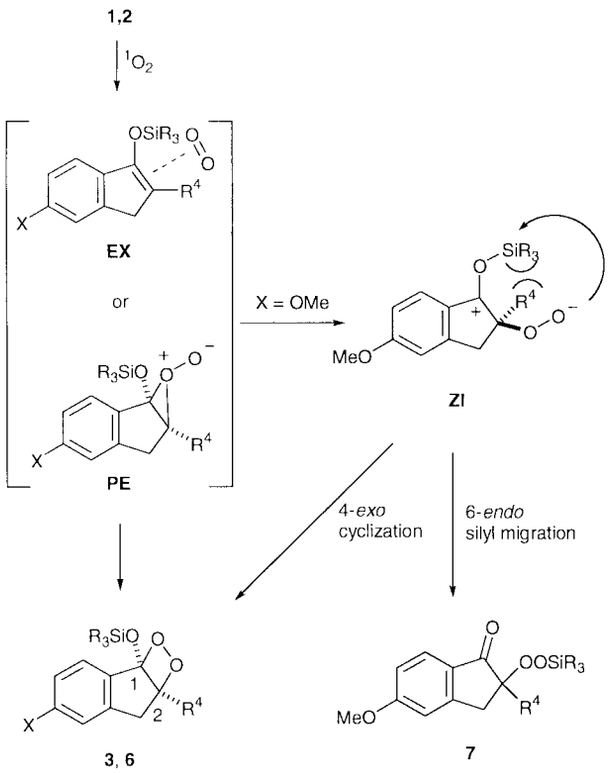
[a] Thermolyses were carried out in C_6D_6 in the range 25–55 °C. For detailed kinetic data, see Experimental section.

1,2-dioxetanes reported previously.[8] It should be noted that a significant drop in the activation energy (E_a *ca.* 3–5 kcal mol^{-1}) is observed with the introduction of the phenyl group (R^4). The results suggest a concerted mechanism (simultaneous cleavage of O–O and C1–C2) for the decomposition of the dioxetane.[9]

In the case of photooxygenation of silyl enol ethers **2** (X = OMe), interestingly, two oxygenated products, dioxetane **6** and α-silylperoxy ketones **7**, were clearly detected by NMR analysis (^1H and ^{13}C) at 0 °C (total yields *ca.* 100% by NMR). Thus, structural assignments of **6** and **7** were feasible (for **6**; δ_{C1} = *ca.* 110 ppm and δ_{C2} = *ca.* 95 ppm: for **7**; $\delta_{C1'}$ = *ca.* 200 ppm and $\delta_{C2'}$ = *ca.* 85 ppm). The structures of the silylperoxy ketones **7** were confirmed by the chemical transformation to α-hydroxy ketones **10** upon treatment with triphenylphosphine (PPh_3). The product ratios (**6** *vs.* **7**) were determined by careful analysis of ^1H NMR (270 MHz) peak areas (error ± 5%) and were found to be dependent on the substituents at the silicon atom and R^4 (entries 7–10 in Table 1). The inductively electron-withdrawing group (OMe) at silicon (SiR_3 = $Si(OMe)_2Me$) increased the yields of the α-silylperoxy ketones **7** (entry 10 in Table 1). Alternatively, decreases in the yields of α-silylperoxy ketones **7** were observed with the introduction of the phenyl ring (R^4) (entry 9 in Table 1). The dioxetanes **6** did not survive above a temperature of 25 °C, and afforded quantitatively the corresponding keto esters **8**. During separation by column chromatography on silica gel, when SiR_3 is $Si(OMe)_2Me$, the ketoester **8d** was unstable and afforded the lactone **9d**. Almost the same ratios of **6**:**7** and **8**:**7** after thermolysis (*ca.* 25 °C, 1 day), analyzed by ^1H NMR (270 MHz) spectra, strongly support the quantitative transformation of dioxetanes **6** to the keto esters **8**. The activation parameters measured in C_6D_6 are summarized in Table 2 (entries 4-6). The values are similar to those for the dioxetanes **3** (X = H) (entries 1–3). Again, a lower activation energy (E_a) was observed for R^4 = Ph (entry 6 in Table 2).

The experimental results for the photooxygenation ($^1O_2$) of silyl enol ethers **1** (X = H) and **2** (X = OMe) can be summarized as follows. (1) For **1** (X = H), the exclusive formation of dioxetanes **3** was observed. (2) For **2** (X = OMe), two oxygenated products, dioxetanes **6** and α-silylperoxy ketones **7**, were

observed, depending upon the substituents (SiR_3 and R^4). (3) The tricyclic 3-silylperoxy-1,2-dioxetanes **3** and **6** were quantitatively converted to the corresponding keto esters **4** and **8** above the temperature of 25 °C. Based on the experimental results, a plausible mechanism for the reactions is shown in Scheme 3.



Scheme 3

The exclusive formation of the tricyclic 1,2-dioxetanes **3** in the photooxygenation of silyl enol ethers **1** (X = H) may be explained by a mechanism, similar to that previously reported, *via* a perepoxide intermediate (**PE**)[10] or exciplex (**EX**) as reported by Adam and co-workers.[4] In the photooxygenation of silyl enol ethers **2** (X = OMe), the competitive formation of dioxetanes **6** (4-*exo* cyclization) and α-silylperoxy ketones **7** (6-*endo* silyl-migration) can be rationalized by assuming the reaction occurs *via* a **PE** or **EX** followed by the formation of the 1,4-zwitterionic intermediate (**ZI**).[11] However, we could not obtain direct evidence for the formation of the zwitterion (**ZI**). The stabilization of the benzyl cation by the MeO substituent on the phenyl ring may be the important factor in the generation of the zwitterion. The effects of the silyl group on the product ratios of dioxetanes **6** and silylperoxy ketones **7** can also be rationalized by the formation of the **ZI**. Namely, the inductively electron-withdrawing group (MeO) may induce the electrophilicity of the silicon to increase the silyl migration pathway affording the α-silylperoxy ketones **7**.[12] The silyl migration pathway may be suppressed by the steric interaction between the silyl group and R^4. In reality, when R^4 is a sterically hindered phenyl group, only the dioxetane was observed (entry 9 in Table 1).

The exclusive formation of the keto esters **4**,**8** from the tricyclic 3-siloxy-1,2-dioxetanes **3**,**6** may be rationalized by their strained structure. The strain effects on the exclusive formation of the keto esters **5** and **8** are supported by the fact that the significant reduction in the activation energy (E_a) was observed by the introduction of the phenyl group in R^4. Namely, the bond cleavage of the relatively weak C1–C2 bond may be involved in the rate-determining step in the dioxetane decomposition.[9]

We have investigated the photooxygenation ($^1O_2$) of silyl enol ether **1** (X = H) and **2** (X = OMe) derived from indan-1-ones. In the oxygenation of **1**, quantitative formation of tricyclic 3-siloxy-1,2-dioxetanes **3** was found, which were exclusively transformed into the keto esters **4** upon thermolysis (>25 °C). Alternatively, the oxygenation of **2** (X = OMe) gave the dioxetanes **6** with concomitant formation of the α-silylperoxy ketones **7**. The direct formation of the α-silylperoxy ketones **7** suggest the formation of the 1,4-zwitterionic intermediate (**ZI**) which can be stabilized by the substituent X = OMe.

Experimental

General aspects

^1H and ^{13}C NMR spectra were recorded on JEOL JNM-EX-270 spectrometer at 270 and 67.8 MHz, respectively. ^1H NMR chemical shifts were reported in ppm (δ_H) using residual $CHCl_3$ (δ 7.26) in perdeuterated solvent as the internal standard. Mutiplicities were reported with s (singlet), d (doublet), t (triplet) and m (multiplet). ^{13}C NMR chemical shifts were reported in ppm (δ_C) relative to the internal standard $CDCl_3$ (δ 77.00). *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. Photolyses (>400 nm) were conducted with an Eikohsha 500 W high-pressure mercury lamp though a $CuSO_4$ solution in aq. NH_3.

Preparation of silyl enol ethers 1 and 2

Silyl enol ethers **1** and **2** were prepared by a similar method to that previously reported (isolated yields, 60–80%).[5] Silyl enol ether **1a** is a known compound.[13] Spectroscopic data for new compounds **1b**–**f** and **2a**–**d** are as follows.

3-(Triethylsiloxy)indene (1b). An oil, bp 85–87 °C (1.0 mmHg) (Found: C, 72.74; H, 8.96. $C_{15}H_{22}OSi$ requires C, 73.11; H, 9.00); ν_{max} (film)/cm^{-1} 3020–3120, 2850–3000, 1250, 1150; δ_H (270 MHz; $CDCl_3$) 0.84 (q, *J* 7.3, 6 H), 1.07 (t, *J* 7.3, 9 H), 3.30 (d, *J* 2.0, 2 H), 5.46 (t, *J* 2.0, 1 H), 7.24–7.46 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) 4.80, 6.56, 33.75, 105.28, 117.99, 123.58, 125.00, 125.88, 141.78, 142.57, 153.69; HRMS (EI) 246.1445 ($C_{17}H_{19}NOSi$ requires 246.1440).

3-(*tert*-Butyldimethylsiloxy)indene (1c). An oil, bp 90–95 °C (0.6 mmHg) (Found: C, 72.85; H, 8.91. $C_{15}H_{22}OSi$ requires C, 73.11; H, 9.00); ν_{max} (film)/cm^{-1} 3020–3140, 2840–3000, 1260, 1130; δ_H (270 MHz; $CDCl_3$) 0.33 (s, 6 H), 1.11 (s, 9 H), 3.33 (d, *J* 2.4, 2 H), 5.48 (t, *J* 2.4, 1 H), 7.27–7.48 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) −4.71, 18.21, 25.72, 33.89, 105.79, 118.11, 123.70, 125.07, 125.97, 141.89, 142.68, 154.10; HRMS (EI) 246.1445 ($C_{17}H_{19}NOSi$ requires 246.1440).

3-(Methyldimethoxysiloxy)indene (1d). An oil, bp 72–75 (0.25 mmHg) (Found: C, 61.01; H, 6.85. $C_{12}H_{16}O_3Si$ requires C, 60.98; H, 6.82); ν_{max} (film)/cm^{-1} 2850–3120, 1280, 1080; δ_H (270 MHz; $CDCl_3$) 0.33 (s, 3 H), 3.34 (d, *J* 2.3, 2 H), 3.69 (s, 6 H), 5.66 (t, *J* 2.3, 1 H), 7.21–7.46 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) −9.08, 33.89, 50.60, 106.90, 117.95, 123.76, 125.19, 126.00, 140.86, 142.59, 151.81; HRMS (EI) 236.0878 ($C_{12}H_{16}O_3Si$ requires 236.0869).

3-(*tert*-Butyldimethylsiloxy)-2-methylindene (1e). An oil, bp 77–80 °C (0.1 mmHg) (Found: C, 73.65; H, 9.11. $C_{16}H_{24}OSi$ requires C, 73.79; H, 9.29); ν_{max} (film)/cm^{-1} 2800–3100, 1720, 1630, 1460, 1250, 1180; δ_H (270 MHz; $CDCl_3$) 0.22 (s, 6 H), 1.11 (s, 9 H), 2.02 (s, 3 H), 3.21 (s, 2 H), 7.12–7.35 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) −3.84, 12.56, 18.24, 25.82, 38.49, 117.34, 119.73, 123.27, 123.90, 125.88, 140.86, 142.79, 147.46.

3-(*tert*-Butyldimethylsiloxy)-2-phenylindene (1f). White powder, mp 128–130 °C (Found: C, 78.11; H, 8.26. $C_{21}H_{26}OSi$ requires C, 78.21; H, 8.13); ν_{max} (KBr)/cm^{-1} 2800–3100, 1600, 1470, 1260, 1150; δ_H (270 MHz; $CDCl_3$) −0.03 (s, 6 H), 1.06 (s, 9 H), 3.67 (s, 2 H), 7.18–7.71 (m, 9 H); δ_C (67.8 MHz; $CDCl_3$) −3.81, 18.24, 25.82, 36.39, 118.74, 122.25, 123.65, 125.14, 126.09, 126.18, 127.48, 128.10, 140.88; HRMS (EI) 322.1725 ($C_{21}H_{26}OSi$ requires 322.1753).

3-(*tert*-Butyldimethylsiloxy)-6-methoxyindene (2a). White powder, mp 58–60 °C (Found: C, 69.16; H, 8.52. $C_{16}H_{24}O_2Si$ requires C, 69.52; H, 8.75); δ_H (270 MHz; $CDCl_3$) 0.23 (s, 6 H), 1.01 (s, 9 H), 3.23 (d, *J* 1.9 H, 2 H), 3.83 (s, 3 H), 5.28 (t, *J* 1.9, 1 H), 6.85–7.27 (m, 3 H); δ_C (67.8 MHz; $CDCl_3$) −4.78, 18.17, 25.66, 33.75, 55.42, 103.67, 110.14, 111.64, 118.42, 134.93, 144.49, 153.35, 158.26; HRMS (EI) 276.1551 ($C_{15}H_{24}O_2Si$ requires 276.1546).

3-(*tert*-Butyldimethylsiloxy)-2-methyl-6-methoxyindene (2b). An oil, bp 115–117 (0.4 mmHg); ν_{max} (film)/cm^{-1} 2800–3100, 1710, 1630, 1470, 1250, 1160; δ_H (270 MHz; $CDCl_3$) 0.30 (s, 6 H), 1.19 (s, 9 H), 2.06 (s, 3 H), 3.26 (s, 3 H), 6.90–7.24 (m, 3 H); δ_C (67.8 MHz; $CDCl_3$) −3.88, 12.47, 18.22, 25.82, 38.35, 55.46, 110.28, 111.12, 117.27, 117.57, 135.90, 142.66, 147.03, 157.38; HRMS (EI) 290.1712 ($C_{15}H_{24}O_2Si$ requires 290.1702).

3-(*tert*-Butyldimethylsiloxy)-6-methoxy-2-phenylindene (2c). White powder, mp 97–99 °C (Found: C, 75.01; H, 7.97. $C_{22}H_{28}O_2Si$ requires C, 74.95; H, 8.00); ν_{max} (KBr)/cm^{-1} 2800–3100, 1700, 1590, 1450, 1230, 1120; δ_H (270 MHz; $CDCl_3$) −0.01 (s, 6 H), 1.05 (s, 9 H), 3.63 (s, 2 H), 3.85 (s, 3 H), 6.84–7.68 (m, 8 H); δ_C (67.8 MHz; $CDCl_3$) −3.79, 18.24, 25.82, 36.23, 55.53, 110.17, 111.86, 119.26, 120.04, 125.70, 127.19, 128.07, 135.96, 136.41, 142.80, 149.01, 158.31.

3-(Methyldimethoxysiloxy)-6-methoxy-2-methylindene (2d). An oil (Found: C, 59.84; H, 7.21. $C_{14}H_{20}O_4Si$ requires C, 59.97; H, 7.19); ν_{max} (film)/cm^{-1} 2800–3100, 1710, 1640, 1480, 1260, 1100; δ_H (270 MHz; $CDCl_3$) 0.25 (s, 3 H), 2.02 (s, 3 H), 3.18 (s, 2 H), 3.65 (s, 6 H), 3.83 (s, 3 H), 6.81–7.24 (m, 3 H); δ_C (67.8 MHz; $CDCl_3$) −7.80, 11.84, 38.28, 50.64, 54.46, 110.32, 111.23, 117.32, 117.66, 135.02, 142.39, 145.32, 157.48; HRMS (EI) 280.1147 ($C_{14}H_{20}O_4Si$ requires 280.1130).

Photooxygenation ($^1O_2$) of silyl enol ethers 1 and 2

General procedure. A solution of silyl enol ether (0.2 mmol) in CH_2Cl_2 (20 cm^3) was irradiated (>400 nm) in the presence of TPP (1–3 mg) at 0 °C under oxygen atmosphere. After irradiation for *ca.* 30 min, the photolysate was directly analyzed by NMR (^{1}H: 270 MHz, ^{13}C: 67.8 MHz) spectroscopy at 0 °C. After confirmation of the formation of 3-siloxy-1,2-dioxetanes **3** and **6** (from both **1** and **2**) and α-silylperoxy ketone **7** (from **2**) by NMR analyses, the solution was warmed up to 25 °C. After standing the solution for *ca.* 24 h, the decomposition of the 1,2-dioxetane was found to afford the keto ester **4** and **8**. The products were isolated by column chromatography on silica gel. Except for the case of SiR_3 = TBDMS, the ketoesters **4** and **8** were unstable under the isolation conditions and afforded the corresponding lactones **5** and **9** in reasonable yields. Lactone **5a** (X = H, R^4 = H) is known.[14] The α-silylperoxy ketones **7** were also unstable under the isolation conditions (silica gel), thus, the peroxides were treated with triphenylphosphine and the α-hydroxy ketones **10** were obtained in reasonable yield. Compound **10a** (R^4 = H) is known.[15] The NMR data for the oxygenated products are as follows.

1-Trimethylsiloxy-10,11-dioxatricyclo[7.2.0.0^{2,7}]undeca-2,4,6-triene (3a). δ_H (270 MHz; $CDCl_3$) 0.41 (s, 9 H), 3.23 (dd, *J* 4.6 and 16.9, 1 H), 3.33 (d, *J* 16.9, 1 H), 5.93 (d, *J* 4.6, 1 H), 7.37–7.41 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) 1.26, 37.52, 91.70, 113.05, 122.70, 125.93, 127.67, 130.53, 140.92, 142.03.

1-Triethylsiloxy-10,11-dioxatricyclo[7.2.0.0^{2,7}]undeca-2,4,6-triene (3b). δ_H (270 MHz; $CDCl_3$) 0.78–0.85 (m, 6 H), 0.88–1.01 (m, 9 H), 3.21 (dd, *J* 3.5 and 15.7, 1 H), 3.30 (d, *J* 15.7, 1 H), 5.81 (d, *J* 3.5, 1 H), 7.26–7.35 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) 5.77, 6.69, 37.58, 91.97, 112.90, 122.73, 125.97, 127.58, 127.71, 130.49, 141.19, 142.05.

1-(*tert*-Butyldimethylsiloxy)-10,11-dioxatricyclo[7.2.0.0^{2,7}]-undeca-2,4,6-triene (3c). δ_H (270 MHz; $CDCl_3$) 0.42 (s, 6 H), 0.98 (s, 9 H), 2.57 (dd, *J* 5.0 and 18.1, 1 H), 2.94 (d, *J* 18.1, 1 H), 5.48 (d, *J* 5.0, 1 H), 6.94–7.43 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) −3.70, −3.59, 17.81, 25.54, 37.67, 91.75, 112.96, 122.71, 125.98, 127.73, 130.35, 141.24, 142.03.

1-(Methyldimethoxysiloxy)-10,11-dioxatricyclo[7.2.0.0^{2,7}]-undeca-2,4,6-triene (3d). δ_H (270 MHz; $CDCl_3$) 0.29 (s, 3 H), 3.22 (dd, *J* 3.0 and 18.1, 1 H), 3.35 (d, *J* 18.1, 1 H), 3.58 (s, 3 H), 3.60 (s, 3 H), 6.03 (d, *J* 3.0, 1 H), 7.29–7.37 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) −6.43, 37.41, 50.60, 91.50, 111.68, 122.77, 125.97, 127.69, 130.67, 140.18, 142.28.

1-(*tert*-Butyldimethylsiloxy)-9-methyl-10,11-dioxatricyclo-[7.2.0.0^{2,7}]undeca-2,4,6-triene (3e). δ_H (270 MHz; $CDCl_3$) 0.22 (s, 3 H), 0.38 (s, 3 H), 0.90 (s, 9 H), 1.61 (s, 3 H), 3.00 (d, *J* 18.2, 1 H), 3.43 (d, *J* 18.2, 1 H), 7.23–7.31 (m, 4 H); δ_C (67.8 MHz; $CDCl_3$) −2.73, −2.21, 17.95, 19.16, 25.54, 43.78, 96.59, 113.23, 122.84, 125.86, 127.55, 130.30, 141.33, 142.21.

1-(*tert*-Butyldimethylsiloxy)-9-phenyl-10,11-dioxatricyclo-[7.2.0.0^{2,7}]undeca-2,4,6-triene (3f). δ_H (270 MHz; $CDCl_3$) −0.23 (s, 3 H), 0.13 (s, 3 H), 0.77 (s, 9 H), 3.45 (d, *J* 18.1, 1 H), 3.71 (d, *J* 18.1, 1 H), 7.34–7.52 (m, 9 H); δ_C (67.8 MHz; $CDCl_3$) −3.77, −2.32, 17.79, 25.54, 46.58, 99.50, 113.86, 123.20, 125.77, 127.87, 127.96, 128.12, 128.21, 130.49, 137.84, 141.51, 142.14.

***tert*-Butyldimethylsilyl *o*-(formylmethyl)benzoate (4c).** An oil. ν_{max} (film)/cm^{-1} 2800–3100, 1730, 1700, 1260; δ_H (270 MHz; C_6D_6) 0.29 (s, 6 H), 0.92 (s, 9 H), 3.76 (s, 2 H), 6.70–6.74 (m, 1 H), 6.98–7.07 (m, 2 H), 8.07–8.11 (m, 1 H), 9.58 (s, 1 H); δ_C (67.8 MHz; C_6D_6) −4.72, 17.92, 25.77, 49.64, 127.42, 130.78, 131.81, 132.64, 132.85, 136.61, 166.99, 197.45.

***tert*-Butyldimethylsilyl *o*-(2-oxopropyl)benzoate (4e).** An oil. ν_{max} (film)/cm^{-1} 2800–3100, 1740, 1700, 1280; δ_H (270 MHz; $CDCl_3$) 0.28 (s, 6 H), 0.95 (s, 9 H), 2.20 (s, 3 H), 4.08 (s, 2 H), 7.16–7.19 (m, 1 H), 7.25–7.38 (m, 1 H), 7.41–7.49 (m, 1 H), 8.03–8.09 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) −4.83, 17.74, 25.61, 29.94, 49.51, 127.15, 130.28, 131.57, 132.81, 135.89, 137.39, 166.83, 205.95; HRMS (EI) 292.1492 ($C_{16}H_{24}O_3Si$ requires 292.1495).

***tert*-Butyldimethylsilyl *o*-(benzoylmethyl)benzoate (4f).** An oil. ν_{max} (film)/cm^{-1} 2800–3100, 1680, 1270; δ_H (270 MHz; $CDCl_3$) 0.27 (s, 6 H), 0.98 (s, 9 H), 4.79 (s, 2 H), 7.21–7.23 (m, 1 H), 7.31–7.60 (m, 5 H), 8.03–8.10 (m, 3 H); δ_C (67.8 MHz; $CDCl_3$) −4.83, 17.77, 25.56, 44.76, 127.10, 128.18, 128.46, 131.07, 131.52, 132.18, 132.33, 132.81, 137.25, 167.03, 197.18; HRMS (EI) 354.1653 ($C_{21}H_{26}O_3Si$ requires 354.1651).

1-(*tert*-Butyldimethylsiloxy)-5-methoxy-10,11-dioxatricyclo-[7.2.0.0^{2,7}]undeca-2,4,6-triene (6a). δ_H (270 MHz; $CDCl_3$) 0.36 (s, 3 H), 0.39 (s, 3 H), 1.00 (s, 9 H), 3.27 (dd, *J* 3.5 and 18.3, 1 H), 3.35 (d, *J* 18.3, 1 H), 3.85 (s, 3 H), 5.86 (d, *J* 3.5, 1 H), 6.71–6.72 (m, 1 H), 6.83–6.88 (m, 1 H), 7.25–7.33 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) −3.72, −2.86, 17.81, 25.55, 37.68, 55.47, 92.20, 110.21, 112.51, 114.57, 123.79, 134.21, 144.04, 161.76.

1-(*tert*-Butyldimethylsiloxy)-5-methoxy-9-methyl-10,11-dioxatricyclo[7.2.0.0^{2,7}]undeca-2,4,6-triene (6b). δ_H (270 MHz; $CDCl_3$) 0.30 (s, 3 H), 0.47 (s, 3 H), 1.00 (s, 9 H), 1.70 (s, 3 H), 3.06 (d, *J* 18.1, 1 H), 3.49 (d, *J* 18.1, 1 H), 3.83 (s, 3 H), 6.83–6.90 (m, 2 H), 7.18–7.24 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) −2.78, −2.28, 17.92, 19.16, 25.54, 43.78, 55.38, 96.95, 110.10, 112.92, 114.32, 123.88, 133.73, 144.13, 161.53.

1-(*tert*-Butyldimethylsiloxy)-5-methoxy-9-phenyl-10,11-dioxatricyclo[7.2.0.0^{2,7}]undeca-2,4,6-triene (6c). δ_H (270 MHz; $CDCl_3$) −0.23 (s, 3 H), 0.12 (s, 3 H), 0.78 (s, 9 H), 3.42 (d, *J* 18.5, 1 H), 3.67 (d, *J* 18.5, 1 H), 3.87 (s, 3 H), 6.82–6.95 (m, 2 H), 7.25–7.44 (m, 6 H); δ_C (67.8 MHz; $CDCl_3$) −3.83, −2.39, 17.74, 25.41, 46.51, 55.46, 99.82, 109.85, 114.86, 124.15, 125.70, 127.80, 128.05, 128.16, 133.85, 137.90, 144.01, 161.71.

1-(Methyldimethoxysiloxy)-5-methoxy-9-methyl-10,11-dioxatricyclo[7.2.0.0^{2,7}]undeca-2,4,6-triene (6d). δ_H (270 MHz; $CDCl_3$) 0.16 (s, 3 H), 1.61 (s, 3 H), 3.21 (d, *J* 18.2, 1 H), 3.43 (s, 3 H), 3.45 (s, 3 H), 3.56 (d, *J* 18.2, 1 H), 3.73 (s, 3 H), 6.86–6.90 (m, 2 H), 7.23–7.34 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) −8.75, 20.85, 37.43, 50.96, 55.53, 88.09, 109.54, 112.02, 115.25, 118.19, 126.27, 140.40, 165.91.

2-(*tert*-Butyldimethylsilylperoxy)-5-methoxyindan-1-one (7a). δ_H (270 MHz; $CDCl_3$) readable signals 0.16 (s, 6 H), 1.08 (s, 9 H), 2.25 (dd, *J* 4.8 and 16.5, 1 H), 2.75 (dd, *J* 4.8 and 16.5, 1 H), 3.88 (s, 3 H), 5.81 (t, *J* 4.8, 1 H).

2-(*tert*-Butyldimethylsilylperoxy)-5-methoxy-2-methylindan-1-one (7b). δ_H (270 MHz; $CDCl_3$) 0.12 (s, 3 H), 0.15 (s, 3 H), 0.83 (s, 9 H), 1.36 (s, 3 H), 2.96 (d, *J* 17.2, 1 H), 3.68 (d, *J* 17.2, 1 H), 3.88 (s, 3 H), 6.86–6.91 (m, 2 H), 7.68–7.71 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) readable signals, 87.51 (C2), 201.72 (CO).

2-(Methyldimethoxysilylperoxy)-5-methoxy-2-methylindan-1-one (7d). δ_H (270 MHz; $CDCl_3$) 0.22 (s, 3 H), 1.25 (s, 3 H), 2.51 (d, *J* 16.5, 1 H), 2.91 (d, *J* 16.5, 1 H), 3.43 (s, 3 H), 3.35 (s, 3 H), 3.77 (s, 3 H), 6.68–6.91 (m, 2 H), 7.67–7.88 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) readable signals, 97.04 (C2), 201.00 (CO).

***tert*-Butyldimethylsilyl *p*-methoxy-*o*-(formylmethyl)benzoate (8a).** An oil. ν_{max} (film)/cm^{-1} 2800–3100, 1720, 1690, 1250; δ_H (270 MHz; C_6D_6) 0.32 (s, 6 H), 0.97 (s, 9 H), 3.21 (s, 3 H), 3.83 (s, 2 H), 6.45–6.58 (m, 2 H), 8.08–8.12 (m, 1 H), 9.66 (s, 1 H); δ_C (67.8 MHz; C_6D_6) −4.61, 17.96, 25.86, 49.91, 54.83, 112.53, 118.40, 122.88, 139.39, 163.13, 166.65, 197.34; HRMS (CI) 309.1537 ($C_{16}H_{25}O_4Si$ requires 309.1523).

***tert*-Butyldimethylsilyl *p*-methoxy-*o*-(2-oxopropyl)benzoate (8b).** An oil. ν_{max} (film)/cm^{-1} 2800–3100, 1730, 1690, 1260; δ_H (270 MHz; $CDCl_3$) 0.32 (s, 6 H), 0.99 (s, 9 H), 3.83 (s, 3 H), 4.11 (s, 2 H), 6.66–6.70 (m, 1 H), 6.84–6.85 (m, 1 H), 8.00–8.04 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) −4.74, 17.76, 25.66, 29.98, 49.83, 55.33, 112.02, 117.99, 122.44, 134.00, 140.04, 162.48, 166.38, 205.93; HRMS (CI) 323.1678 ($C_{17}H_{27}O_4Si$ requires 323.1679).

***tert*-Butyldimethylsilyl *p*-methoxy-*o*-(benzoylmethyl)benzoate (8c).** An oil. ν_{max} (film)/cm^{-1} 2800–3100, 1730, 1700, 1260; δ_H (270 MHz; $CDCl_3$) 0.28 (s, 6 H), 0.99 (s, 9 H), 3.82 (s, 3 H), 4.78 (s, 2 H), 6.70–6.81 (m, 1 H), 6.82–6.95 (m, 1 H), 7.44–7.55 (m, 3 H), 8.01–8.20 (m, 3 H); δ_C (67.8 MHz; $CDCl_3$) −4.81, 17.72, 25.57, 45.02, 55.22, 111.93, 117.86, 123.02, 128.12, 128.39, 132.72, 133.85, 137.22, 139.91, 162.37, 197.14; HRMS (CI) 385.1825 ($C_{22}H_{28}O_4Si$ requires 385.1824).

3,4-Dihydro-3-hydroxy-3-methyl-4-methoxy-1*H*-2-benzopyran-1-one (9). White powder, mp 102–105 °C (Found: C, 63.31; H, 5.81. $C_{11}H_{12}O_4$ requires C, 63.46; H, 5.81); ν_{max} (film)/cm^{-1} 3220, 3050–3000, 3000–2900, 1700, 1260; δ_H (270 MHz; $CDCl_3$) 1.32 (s, 3 H), 3.01 (d, *J* 17.0, 1 H), 3.65 (d, *J* 17.0, 1 H), 3.84 (s, 3 H), 6.81–6.84 (m, 2 H), 7.60–7.63 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) 20.79, 37.56, 55.56, 88.09, 109.58, 115.80, 126.42, 127.24, 154.63, 166.24, 203.83; HRMS (EI) 208.0736 ($C_{11}H_{12}O_4$ requires 208.0728).

2-Hydroxy-2-methyl-5-methoxyindan-1-one (10b). White powder, mp 86–88 °C (Found: C, 68.42; H, 6.30. $C_{11}H_{12}O_3$ requires C, 68.74; H, 6.29); ν_{max} (film)/cm^{-1} 3430, 3100–3000, 3000–2800, 1690, 1260; δ_H (270 MHz; $CDCl_3$) 1.41 (s, 3 H), 3.13 (d, *J* 17.3, 1 H), 3.21 (d, *J* 17.3, 1 H), 3.86 (s, 3 H), 6.83–6.91 (m, 2 H), 7.65–7.70 (m, 1 H); δ_C (67.8 MHz; $CDCl_3$) 25.61, 42.28, 55.62, 109.76, 115.85, 126.40, 126.65, 154.25, 166.13, 206.16; HRMS (EI) 192.0787 ($C_{11}H_{12}O_3$ requires 192.0798).

Kinetic measurements of the thermal decomposition of tricyclic 3-(*tert*-butyldimethylsiloxy)-1,2-dioxetanes 3c,f,g and 6a–c in C_6D_6

General procedure. A solution of dioxetane, which was prepared by the above-mentioned photooxygenation, was heated in C_6D_6 at 25 (or 30), 40 and 55 °C. The monomeric decomposition was monitored by NMR analysis and the ratios of dioxetane and keto ester were determined by their peak areas (error ± 5%) at least five points at such a temperature. The obtained first-order kinetic data (k_{dec}) are as follows. The activation parameters (E_a and ln *A*), calculated by an Arrhenius plot are shown in Table 2.

For **3c** (SiR_3 = TBDMS, R^4 = H, X = H): $k_{dec,\ 25} = 3.3 \times 10^{-5}$, $k_{dec,\ 40} = 2.2 \times 10^{-4}$, $k_{dec,\ 55} = 9.6 \times 10^{-4}$ s^{-1}. For **3e** (SiR_3 = TBDMS, R^4 = Me, X = H): $k_{dec,\ 25} = 3.3 \times 10^{-5}$, $k_{dec,\ 40} = 1.2 \times 10^{-4}$, $k_{dec,\ 55} = 6.0 \times 10^{-4}$ s^{-1}. For **3f** (SiR_3 = TBDMS, R^4 = Ph, X = H): $k_{dec,\ 30} = 3.3 \times 10^{-5}$, $k_{dec,\ 40} = 8.3 \times 10^{-5}$, $k_{dec,\ 55} = 5.5 \times 10^{-4}$ s^{-1}. For **6a** (SiR_3 = TBDMS, R^4 = H, X = OMe): $k_{dec,\ 25} = 3.1 \times 10^{-5}$, $k_{dec,\ 40} = 4.1 \times 10^{-4}$, $k_{dec,\ 55} = 1.6 \times 10^{-3}$ s^{-1}. For **6b** (SiR_3 = TBDMS, R^4 = Me, X = OMe): $k_{dec,\ 30} = 3.3 \times 10^{-5}$, $k_{dec,\ 40} = 2.0 \times 10^{-4}$, $k_{dec,\ 55} = 1.1 \times 10^{-3}$ s^{-1}. For **6c** (SiR_3 = TBDMS, R^4 = Ph, X = OMe): $k_{dec,\ 30} = 3.3 \times 10^{-5}$, $k_{dec,\ 40} = 8.3 \times 10^{-5}$, $k_{dec,\ 55} = 4.8 \times 10^{-4}$ s^{-1}.

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