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Chemiluminescence of Spiro[1,2-dioxetane-3,1′-dihydroisobenzofuran]s, Spiro[1,2-dioxetane-3,1′-isochroman]s and a Spiro[1,2-dioxetane-3,1′-(2-benzoxepane)]

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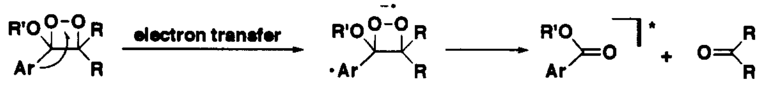
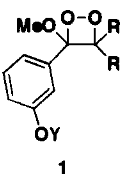
Abstract: Spiro[1,2-dioxetane-3,1'-dihydroisobenzofuran]s (**3**), spiro[1,2-dioxetane-3,1'-isochroman]s (**5**) and a spiro[1,2-dioxetane-3,1'-(2-benzoxepane)] (**7**) were synthesized by singlet oxygenation of the corresponding ethylenes (**2**, **4** and **6**). Treatment of **3** and **5** with TBAF in DMSO induced light emission with half-life far longer than those of the parent dioxetanes (**1**). The phenomenon is most likely attributed to the suppression of free rotation of an aromatic substituent as an electron donor.

Deprotonation or deprotection of a thermally stable dioxetane bearing a phenolic substituent under basic conditions can generate an unstable phenoxide-substituted dioxetane which decomposes rapidly to emit light by CIEEL mechanism, where an electron (charge) transfer from the phenoxide anion to the dioxetane induces its decomposition.[1, 2, 3] The electronic character of an electron donor has been known to influence significantly the rate of decomposition (half-life of emission) for CIEEL-active dioxetanes.[2a, 4] On the other hand, the conformation of an aromatic electron donor relative to the dioxetane ring would also affect the ease of the electron (charge) transfer.[5] We report here that, for spirodioxetanes (**3** and **5**), the rotation of the aromatic ring of which is suppressed, to some extent, by joining it to a *geminal* alkoxyl in **1**, the half-life of emission becomes far longer than that of dioxetanes (**1a**)[2f] and (**1b**)[2a] in which an aromatic ring can formally rotate freely.





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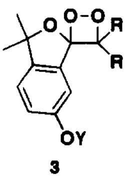

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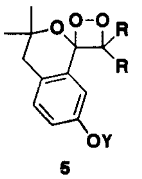

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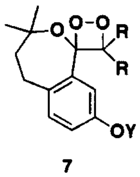

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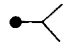
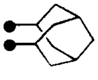
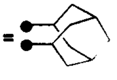
a: Y = t-Bu(Me)$_2$Si-, R = 

b: Y = t-Bu(Me)$_2$Si-, R = 

c: Y = H, R = 

A solution of a dihydroisobenzofuran (**2a**) (100 mg) and tetraphenylporphin (5 mg) in dichloromethane (10 mL) was externally irradiated with a 940 W sodium vapor lamp under an oxygen atmosphere at -78 °C for 2 h. After concentrating the solution, the mixture was chromatographed on silica gel with hexane to give a spiro[1,2-dioxetane-3,1'-dihydroisobenzofuran] (**3**) as a pale yellow viscous oil in 89 % yield.[6] When a solution of **3a** in DMSO (1.0×10^{-5} mol dm^{-3}, 1 mL) was added to a solution of tetrabutylammonium fluoride (TBAF) (1.0×10^{-2} mol dm^{-3}, 2 mL) at 25 °C, **3a** emitted light[7] with λ_{max} = 456 nm, Φ_{CL} = 0.15,[8] and half-life $t_{1/2} = 1.5 \times 10^2$ s. Comparing the half-life of chemiluminescence with those of dioxetanes **1a** and **1b**, in which an aromatic substituent can formally rotate freely, one realizes that **3a** exhibits far longer half-life emission than **1a-b** ($t_{1/2}$ = 6.3 s for **1a**,[2f] $t_{1/2}$ = 5 s for **1b**[2a]). To know whether the phenomenon described above is particular or not for the diisopropyldioxetane (**3a**), we synthesized dioxetane (**3b**) bearing an adamantylidene instead of two isopropyls, and examined its F^--induced chemiluminescence. Treatment of **3b** with TBAF under the conditions similar to the case of **3a** induced chemiluminescence with $t_{1/2} = 1.7 \times 10^2$ s. The prolonged light emission was also observed for an unprotected phenolic dioxetane (**3c**) as shown in Table 1, where chemiluminescent properties of the other dioxetanes synthesized here were also summarized. These results showed that the decomposition induced by an electron transfer from the phenoxide is impeded appreciably for all the dioxetanes (**3a**, **b** and **c**) bearing an electron donor (phenoxide) fused with a carbon of alkoxyl attached to the same carbon of the dioxetane ring, though the efficiency (Φ_{CL}) is considerably affected by the substituent **R**.

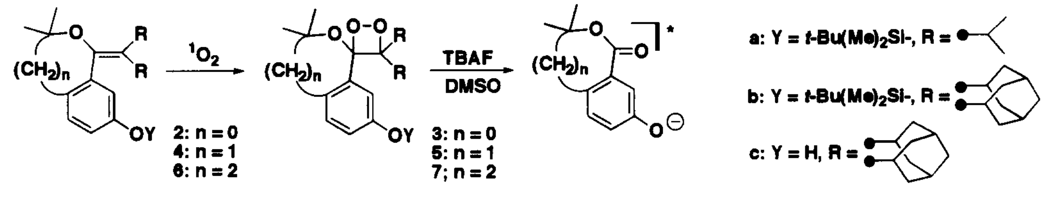
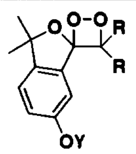
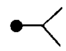
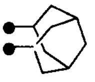
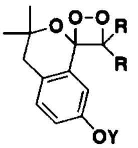
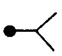
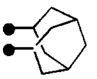
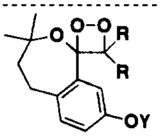
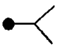


Table 1 F^--Induced chemiluminescence of spirodoxetanes (3), (5), and (7)[a)]

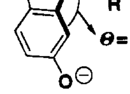
Dioxetane		R	Y	λmax / nm	Φ_{CL}[b)]	$t_{1/2}$ / s
(3a)			t-Bu(Me)2Si-	456	0.15	1.5×10^2
(3b)			t-Bu(Me)2Si-	456	0.04	1.7×10^2
(3c)			H	456	0.03	1.7×10^2
(5a)			t-Bu(Me)2Si-	476	0.1	4.5×10^3
(5b)			t-Bu(Me)2Si-	477	0.02	5.3×10^3
(5c)			H	478	0.01	5.3×10^3
(7a)			t-Bu(Me)2Si-	464	0.002	9.4

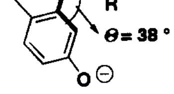
a) Measured at 25 °C. b) Relative quantum yield based on the value for 1b.[2a]

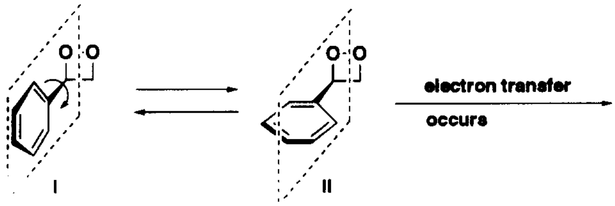
Next, we attempted to examine F$^-$-induced chemiluminescence of dioxetanes bearing a phenolic substituent fixed with a six-membered ring. Singlet oxygenation of an alkylideneisochroman (**4a**) gave a spiro[1,2-dioxetane-3,1'-isochroman] (**5a**) in 61 % yield. On treatment with excess TBAF similarly to the case of **3**, **5a** afforded blue light with extremely long half-life $t_{1/2} = 4.5 \times 10^3$ s. An adamantylidene- analogue (**5b**) and its unprotected phenolic form (**5c**) were also synthesized from the corresponding olefins (**4b** and **4c**) (**5b**: 89 %, **5c**: 30 % yields). These dioxetanes gave also blue light with long half-lives. The results summarized in Table 1 showed that, for isochromans (**5**), F$^-$-induced decomposition occurs far more sluggishly than for dihydroisobenzofurans (**3**). Considering that the electronic characters of an electron donor (aromatic π-system) in isobenzofurans (**3**) are probably similar to those in isochromans (**5**), the difference in chemiluminescent half-lives between **3** and **5** is likely attributed to difference in a conformation of the aromatic ring relative to the dioxetane ring for **3** and for **5**, though there is, at present, little experimental evidence to clarify which conformation(s) of the aromatic ring is the most preferred for the electron transfer to the dioxetane ring. An MM2 calculation showed that a rotational angle of the aromatic ring (a dihedral angle θ illustrated as a bold line) is $\theta = 68°$ at an energy minimum for an oxy anion of **3c** and is $\theta = 38°$ for an oxy anion of **5c**.

A benzoxepane ring would be more flexible than a dihydroisobenzofuran or an isochroman ring, so that the decomposition induced by an electron transfer was expected to occur more effectively for a spiro[1,2-dioxetane-3,1'-(2-benzoxepane] (**7**) than for **3** and **5**. Thus, we finally examined F$^-$-induced chemiluminescence of a dioxetane (**7a**) as a representative, which was easily synthesized from the corresponding olefin (**6a**) (87 % yield). On treatment with TBAF in DMSO, **7a** emitted light (λ_{max} = 464 nm, Φ_{CL} = 0.002) with half-life ($t_{1/2}$ = 9.4 s) far shorter than those of **3** and **5** and slightly longer than those of **1a** and **1b**, as expected. Here, it should be noted that the efficiency of luminescence is significantly lower for **7a** than those for **3a** and **5a**, though the reason is obscure at present.

The present work suggests that, for a CIEEL-active dioxetane bearing a phenolic moiety, an electron transfer occurs preferentially from a donor to the dioxetane ring, when the aromatic ring is in a certain conformation(s). An idea, that the aromatic ring may lie in or near a plane perpendicular to a plane comprising of 2-O, 3-C of the dioxetane, and a carbon of the aromatic ring attached to 3-C for a preferable conformation(s) as **II** illustrated below, is likely consistent with the facts that a) for F$^-$-induced chemiluminescence[2f] of a series of 3-alkoxy-3-(3-tert-butyldimethylsiloxy)phenyl-4,4-diisopropyl-1,2-dioxetanes (3-alkoxyl = MeO: **1a**), half-lives of emission are prolonged as the 3-alkoxyl group becomes bulkier, and b) 1-aryl-2,6,7-trioxabicyclo[3.2.0]heptanes[9] possess remarkable thermal stability, whereas dioxetanes of benzofurans[10] and indenes[11] are not so stable thermally.[12]







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5 The ease (rate) of intramolecular electron transfer are known to be influenced by the donor-acceptor attachment geometry; Closs, G. L.; Calcaterra, L. H.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673 - 3683.
6. All the dioxetanes synthesized here gave satisfactory spectral data, and were stable enough to permit handling at room temperature and could be stored with little decomposition at -20 °C for > 1 y.
7. For all the dioxetanes synthesized here, TBAF induced luminescence occurred by a pseudo-first order process under the conditions described here, and the chemiluminescence spectra from them were identical to the fluorescence spectra of the corresponding spent reaction mixture.
8. All the efficiencies of Φ_{CL} measured here were based on the value for the Φ_{CL} of **1a**.[2a]
9. Matsumoto, M.; Watanabe, N.; Kasuga, N. C.; Hamada, F.; Tadokoro, K. *Tetrahedron Lett.* **1997**, *38*, 2863 - 2866.
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12. For dioxetanes of benzofurans and indenes, an aromatic ring is probably fixed in the conformation as **II**, whereas a single crystal X-ray analysis of a certain 1-aryl-2,6,7-trioxabicyclo[3.2.0]heptane has been reported to show that an aryl lies in the conformation as **I**.[9]

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