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F^--Induced Decomposition of 3-[(*tert*-Butyldimethylsiloxy)phenoxy]-3-phenyl-1,2-dioxetanes without C-C Bond Cleavage of the Dioxetane Ring

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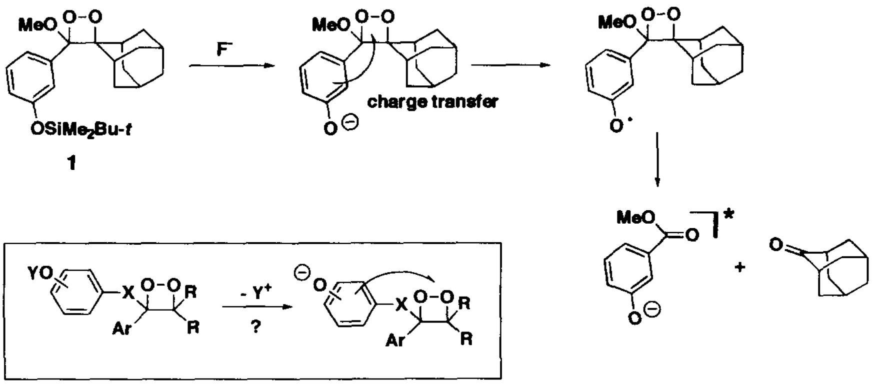
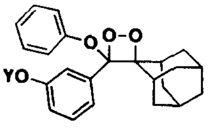
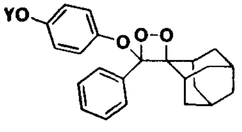
Abstract: F^--induced decomposition of 3-[3-(*tert*-butyldimethylsiloxy)phenoxy]-3-phenyl-1,2-dioxetane (**5c**) yielded an intramolecular redox product (**7b**), whereas 3-phenoxy-3-(3-siloxyphenyl)-1,2-dioxetane (**3**) gave normal carbonyl fragments with intense light emission. An isomer (**5a**) gave light with normal decomposition by CIEEL, though the major process was one to yield an acyloin (**7a**). © 1997 Elsevier Science Ltd.

The chemically induced electron exchange luminescence (CIEEL) has received considerable attention from the viewpoints of the decomposition mechanism of dioxetanes, mechanistic study on bioluminescence, and design of new efficient chemiluminescent substrates.[1] The intramolecular CIEEL occurs effectively for 3-alkoxy-3-aryl-1,2-dioxetanes,[2,3] represented by a 3-[3-(*tert*-butyldimethylsiloxy)phenyl]-3-methoxy-1,2-dioxetane (**1**),[2] in which a siloxyphenyl is attached directly to a dioxetane ring so that the aromatic moiety plays the role of an electron donor as well as of a fluorecer after desilylation. On the other hand, little has been known of the decomposition of dioxetanes induced by a phenoxide anion joining to the dioxetane ring through an atom(s) or atomic group. We investigated here whether for 3-phenyl-3-(siloxyphenoxy)-1,2-dioxetanes (**5**), in which a phenoxide as an electron donor joins to a dioxetane through an oxygen atom, the desilylation causes or does not cause decomposition of the dioxetane, and found that, for **5**, an intramolecular redox reaction takes place preferentially to give an acyloin (**7a**) or its ketal (**7b**) though the CIEEL does occur in part for **5a**.

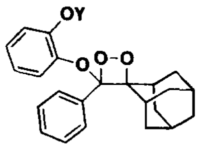




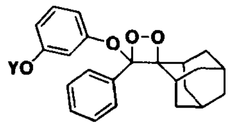
3



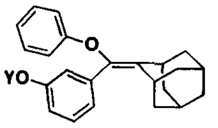
5a



5b



5c



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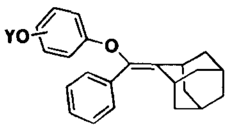


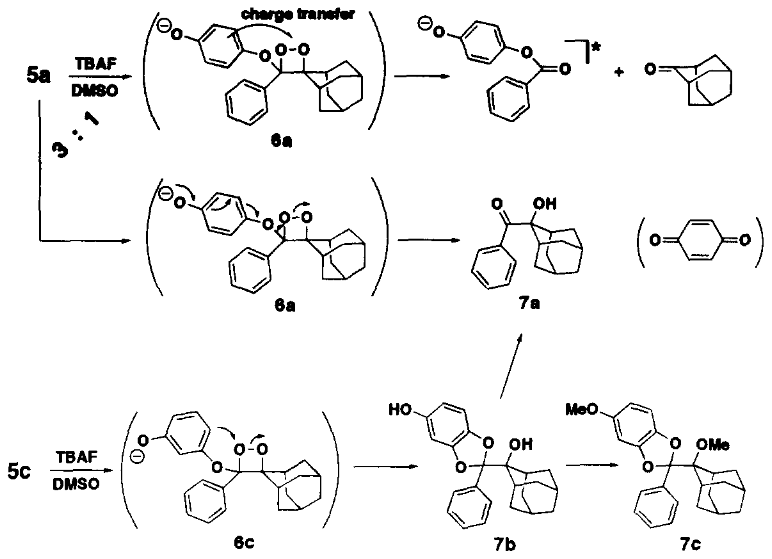
4a: *para*-YO
4b: *ortho*-YO
4c: *meta*-YO

Y = *t*-BuMe$_2$Si-

Before examining F$^-$-induced reaction of dioxetanes (**5**), we attempted to synthesize isomeric 3-[3-(*t*-butyldimethylsiloxy)phenyl]-3-phenoxy-1,2-dioxetane (**3**)[4] to find out whether **3** acts, or not, as a chemiluminescent substrate similarly to 3-[3-(*t*-butyldimethylsiloxy)phenyl]-3-methoxy-1,2-dioxetane (**1**). A solution of an ethylene (**2**) (73 mg) and tetraphenylporphin (0.8 mg) in dichloromethane (2 mL) was externally irradiated with a Na vapor lamp (940 W) under an oxygen atmosphere at -78 °C for 2 h. The photolysate was concentrated *in vacuo* and the residue was chromatographed on silica and eluted with hexane to give a dioxetane (**3**) in a 77 % yield. When a solution of **3** in DMSO (1.0 x 10^{-4} mol dm^{-3}, 1mL) was added to a solution of tetrabutylammonium fluoride (TBAF) in DMSO (1.0 x 10^{-1} mol dm^{-3}, 2mL) at 25 °C, **3** emitted light with λ_{max} = 504 nm, Φ_{CL} = 0.007, and half-life $t_{1/2}$ = 0.86 s. The results revealed that a phenoxydioxetane (**3**) is CIEEL-active as well after triggering by F$^-$, though its chemiluminescent properties are considerably different from those of **1**; for **3**, half-life ($t_{1/2}$) of chemiluminescence was shorter, while the efficiency (Φ_{CL}) was lower than that for **1** (λ_{max} = 470 nm, Φ_{CL} = 0.25, $t_{1/2}$ = 5 s).[2]

Similar singlet oxygenation of an ethylene (**4a**) took place[5] smoothly at 0 °C to afford the corresponding dioxetane (**5a**) as colorless crystals (m. p. 114.4 - 115.1 °C) in a 75 % yield. On treatment with TBAF similarly to the cases of **3**, **5a** afforded light (λ_{max} = 460 nm, $t_{1/2}$ = 5.5 s) though the efficiency was markedly low (Φ_{CL} = 7 x 10^{-6}). The emission spectrum was in agreement with the fluorescence spectrum of an anion prepared *in situ* by treatment of a *p*-(*t*-butyldimethylsiloxy)phenyl benzoate with TBAF in DMSO. These results disclosed that even a phenoxide anion unattached to the dioxetane ring of an intermediate (**6a**) is most likely capable of inducing decomposition of the dioxetane with light emission. At this stage, the low efficiency of emission was thought to be attributed to the low yield of an excited species at a singlet state and/or its low fluorescent quantum yield. However, the analysis of the spent reaction mixture clarified that normal fragmentation to form an ester and adamantanone was a minor process for **5a**. The spent reaction mixture included *p*-hydroxyphenyl benzoate, adamantanone, and an acyloin (**7a**) with a ratio 1 : 1 : 3;[6] **7a** was isolated as colorless crystals (m.p. 162.5 - 163.3 °C) in a 74 % yield. The acyloin (**7a**) might be produced by an intramolecular reaction between a phenoxide anion and a dioxetane, though another expected product, *p*-benzoquinone, was not isolable.[7] These results suggested that an intermediary dioxetane (**6a**) decomposes through two concurrent processes; an intramolecular oxidation of a phenolic moiety occurs preferentially, while a part of **6a** (25 %) decomposes into two carbonyl fragments with light emission by the intramolecular CIEEL. Next, we examined F$^-$-induced reaction of an *ortho*-isomer (**5b**), which was synthesized from an ethylene (**4b**); the singlet oxygenation of **4b** was less effective than the case of **4a** (yield of **5b** = 37 %). Similar treatment of a dioxetane (**5b**) with TBAF in DMSO gave no detectable light emission, but afforded the acyloin (**7a**) exclusively.

"Scheme 1"



A *meta*-isomer (**5c**) was expected to behave in ways different from **5a** and **5b** under TBAF / DMSO, because a resorcinol moiety of **5c** would not, at least, lead to an unsubstituted benzoquinone which is active to various nucleophilic reactions, even if **5c** undergoes an intramolecular reaction as in the cases of **5a** and **5b**. Thus, we synthesized a *meta*-isomer (**5c**) (colorless crystals melted at 101.1 - 102.0 °C) by the singlet oxygenation of an ethylene (**4c**) (77 % yield). On treatment of **5c** with TBAF similarly to the cases of **3** and **5a**, no light emission was observed. A ^1H NMR analysis of the reaction mixture showed that the F^--induced reaction of **5c** took place also effectively to produce a sole decomposition product, which was isolated in 85 % yield as colorless crystals (m.p. 216.5 - 217.5 °C) and whose structure was determined as a ketal (**7b**)[8] of **7a** by NMR, IR, and Mass spectral analyses. The ketal **7b** gave a dimethyl ether **7c** on treatment with MeI / NaH / THF, while the acyloin **7a** was obtained in good yield after hydrolysis of **7b** in acidic aqueous acetone. The ketal (**7b**) might be produced through an intramolecular nucleophilic attack of a proximal carbon (*para*-position) of a phenoxide anion to O-O of a dioxetane as shown in **Scheme 1**. These results showed that, for an intermediary dioxetane (**6c**), an intramolecular redox reaction surpassed completely an electron transfer from a phenoxide anion to O-O of a dioxetane. It should be noted that the oxidation of a phenolic functionality with a dioxetane as shown here has been little known, though a dioxetane is well known to oxidize various substrates such as amines, sulfides, and phosphines,[9] and that, from the mechanistic viewpoint, the present acyloin (or its ketal) formation is likely different from the so-called Kornblum-DeLaMare reaction,[10] or decomposition of singlet oxygenation products of enamines[11] and vinylic sulfides.[12,13,14]

In conclusion, the work described here disclosed that a phenoxide attached to a dioxetane through an oxygen is preferentially oxidized by O-O of the dioxetane (**5**) rather than acting as an electron donor for the intramolecular CIEEL, though the CIEEL takes place in part for **5a**.

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4. A pivaloyl analogue of **3** has very recently been synthesized; Akhavan-Tafti, H.; Eickholt, R. A.; Arghavani. Z.; Schaap, A. P. *J. Amer. Chem. Soc.* **1997**, *119*, 245 - 246.
5. The singlet oxygenation of **4a** proceeded sluggishly at -78 °C.
6. The ratio was measured by ^{1}HNMR analysis of a mixture after treatment of **5a** with TBAF in DMSO-d_6.
7. To isolate a fragment (quinone) derived from a phenoxide part of **5**, we attempted to synthesize an analogue bearing a *t*-butyl-substituted phenoxide in place of an unsubstituted phenoxide in **5a**. However, the singlet oxygenation of the corresponding ethylene gave a complex mixture including little of the desired dioxetane.
8. ^{1}HNMR (400 MHz in $CDCl_3$) δ 1.47 - 1.95 (m, 10H), 1.95 (s, 1H), 2.19 - 2.40 (m, 2H), 2.45 - 2.55 (m, 2H), 4.38 (s, 1H), 6.18 (dd, J = 8.3 and 2.9 Hz, 1H), 6.41 (d, J = 2.9 Hz, 1H), 6.62 (d, J = 8.3 Hz, 1H), 7.32 - 7.36 (m, 3H), and 7.64 (dd, J = 7.6 and 1.7 Hz, 2H) ppm; IR (KBr) 3358, 3058, 2911, 2865, 1498, and 1206 cm^{-1}; Mass (m/z, %) 364 (M^+, 0.7), 214 (100), 150 (23), 105 (47).
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