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Synthesis and Fluoride Ion - Triggered Chemiluminescence (CIEEL Mechanism) of Siloxy-Substituted Benzofuran Dioxetanes

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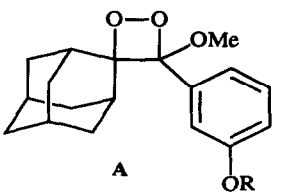
Key Words: Benzofuran Dioxetanes/ CIEEL/ Fluoride Ion Triggering/ Chemiluminescence

Abstract : The dioxetanes **2** with *tert*-butyldimethylsilyoxy-substituted aryl groups have been prepared from the corresponding benzofurans by photooxygenation and their fluoride ion-triggered CIEEL chemiluminescence was investigated; facile saponification by fluoride and even phenoxide ions of the aryl esters **4** is held responsible for the low chemiluminescence efficiencies

Introduction

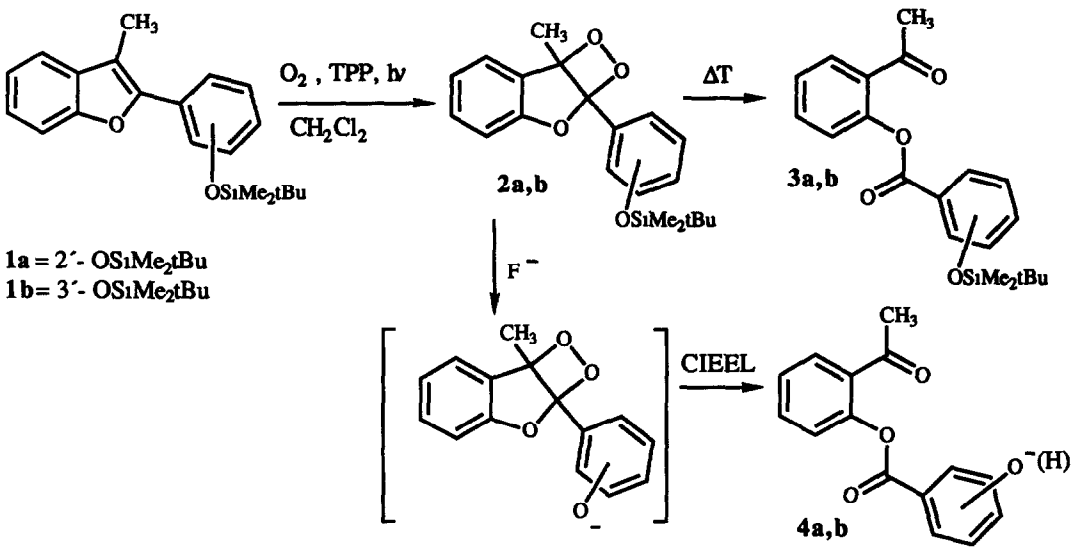
Recently we have demonstrated that the CIEEL mechanism operates in the base-induced decomposition of acetyloxy-protected benzofuran dioxetanes[1] Deprotection of the ester releases the phenolate ion, which serves as an electron donor and leads to rapid decomposition of the dioxetane accompanied with intense light emission This mechanism, originally discovered by Schuster[2] for organic peroxides, was shown to work also for dioxetanes [3] The clinical and biological applications of CIEEL-active substrates have recently been reviewed[4]

In this context, we have been interested in the fluoride ion-triggered CIEEL of siloxy-substituted benzofuran dioxetanes **2** (Scheme 1) This concept was used before in the case of spiroadamantyl-substituted dioxetanes[5] **A**



A

Scheme 1. Synthesis of Benzofuran Dioxetanes **2** and their Thermal and Fluoride Ion-Triggered (CIEEL) Decomposition



1a = 2′- $OSiMe_2tBu$
1b = 3′- $OSiMe_2tBu$

and extended to enzyme-promoted systems, e.g.the action of alkaline phosphatases on the corresponding phosphate esters[6] Since the siloxy-substituted dioxetane A (R=$SiMe_2tBu$) exhibits the highest CIEEL quantum yield ever reported for an dioxetane in DMSO[7], it was our interest to examine the corresponding benzofuran dioxetanes. Such dioxetanes are known to be mutagenic[8] and CIEEL active representatives of this type could serve as potential DNA probes

Another aspect of our work concerns the absorption and fluorescence spectral analysis of the dioxetane decomposition products, the phenolate ions of which are the light emitting species in the CIEEL process Due to the lability of the esters under basic conditions, it was so far not possible to determine the fluorescence quantum yields of these compounds in order to calculate singlet excited state efficiencies of the CIEEL reaction[9] Therefore, we decided to use the siloxy-substituted esters, the thermal decomposition products of the presently investigated dioxetanes, and generate the ester phenolate ions by fluoride ion-promoted cleavage of the silyl ethers in aprotic media Herewith we present the results of our investigation of the fluorid ion-induced CIEEL effect of siloxy-substituted benzofuran dioxetanes and the lability of the so generated decomposition products under the experimental conditions

Results

Synthesis and Decomposition of Benzofuran Dioxetanes 2a,b

The siloxy-substituted benzofurans **1a** and **1b** were synthesized according to the literature procedure[10] in 52% and 87% yields Dioxetanes **2a** and **2b** were prepared by photooxygenation of the corresponding benzofurans **1a,b** in methylene chloride with tetraphenylporphine (TPP) as sensitizer at low temperatures (-25 to -40 °C) for several hours (Scheme 1). The *ortho*-substituted dioxetane **2a** was obtained in moderate yield (37%) as yellow needles (m.p 97-99 °C), while the corresponding *meta* isomer **2b** (yellow oil) could only be isolated in 7% yield with decomposition even at -40 °C Besides dioxetane **2b**, 13% of the corresponding allylic hydroperoxide was isolated. Both compounds were sensitve to thermal decomposition.

At elevated temperatures, the dioxetanes **2** cleave to the siloxy-substituted esters **3**, which could also be isolated from the photooxygenation mixture of the benzofurans **1a,b** after silica gel column chromatography The new compounds **1-3** were fully characterized, except dioxetane **2b** and its corresponding hydroperoxide, for which in view of its labile nature only ^{1}H and ^{13}C NMR data are available The NMR spectra of the *ortho*-silcxyphenyl-substituted dioxetane **2a** showed that the methyl groups at the silicon are hindered in their rotation at least at -25°C, for one single signal was obtained for each of them in the proton and carbon NMR spectrum.

Chemiluminescence Measurements of the Benzofuran Dioxetanes 2a,b

Triggering with nBu_4NF in acetonitrile resulted in rapid decomposition of the dioxetanes **2** with intense light emission to afford the corresponding previously reported hydroxy-substituted esters **4** By comparison, the direct thermal chemiluminescence (no fluoride ions) of these dioxetanes **2** was very weak. The quantum yields of the direct chemiluminescence for the CIEEL process was measured as described[9] and the results are listed in Table 1

Table 1 .CIEEL Quantum Yields of the Benzofuran Dioxetanes **2**

Dioxetane [a]	k [sec^{-1}] [b]	Φ^{DC} [x10^7 Einstein/mol]
2a	0 20 ± 0 05	5 30 ±2 0
2b	0 50 ± 0 25	26 0 ±13 0

a) All measurements at 25 °C in CH_3CN, b) tenfold excess of nBu_4NF

As can be seen, the *meta*-substituted dioxetane **2b** emits more efficiently light than its corresponding *ortho* isomer **2a** This is in agreement with earlier results[1,4] , however, the halflife of its light emission is very short (only a

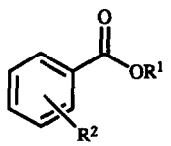
few seconds) Unfortunately, DMSO could not be used as solvent (in such polar aprotic solvents a more efficient fluorescence would be expected[7]), because deoxygenation of the labile benzofuran dioxetanes **2** to the corresponding epoxides and products derived therefrom was observed.

Absorption and Fluorescence Spectral Analysis of the Esters 3-5

For comparison of the optical spectral data of the esters **3** and **4**, the unknown **5a** and the known[11] methyl esters **5b** were prepared. In the case of the ester **5a**, no full conversion could be obtained in the silylation reaction, even when excess of chlorosilane was used.

To determine the fluorescence quantum yields of the phenolate ions of the esters **4**, the siloxy-substituted esters **3** (the thermal decomposition products of the dioxetanes **2**) were desilylated with the help of fluoride ions and the resulting solution of the phenolate ion submitted to absorption and fluorescence spectral analysis by following the procedure described for the corresponding methyl ester **5b** [7,11] The results are given in Table 2 They

Table 2 .Optical Spectral Data of Benzofuran Dioxetane Cleavage Products and Related Compounds

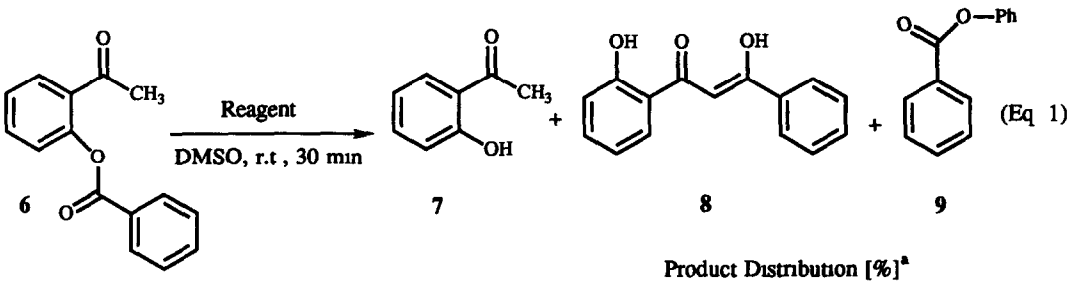


		Conditions	[λ_{max} in nm] Absorption	Fluorescence (Φ^{Fl})
3a	R^1= 2-Acetylphenyl R^2= 2-OSiMe$_2$tBu	DMSO	292	b
		DMSO + nBu$_4$NF	384	451[c]
		CH_3CN + nBu$_4$NF	381	452[c]
4a	R^1= 2-Acetylphenyl R^2= 2-OH	DMSO	308	b
		DMSO + nBu$_4$NF	383	b
3b	R^1= 2-Acetylphenyl R^2= 3-OSiMe$_2$tBu	DMSO	291	b
		DMSO + nBu$_4$NF	378	450[c]
4b	R^1= 2-Acetylphenyl R^2= 3-OH	DMSO	302	b
		DMSO + nBu$_4$NF	376	452[c]
5a	R^1= Me R^2= 2-OSiMe$_2$tBu	CH_3CN	288	b
		DMSO	289	340[c]
		DMSO + nBu$_4$NF	371	421 (0 21±0 02)[d]
5b	R^1= Me R^2= 3-OSiMe$_2$tBu	DMSO	293	b
		DMSO + nBu$_4$NF	380	457(0 31±0 03)[d]
				[lit.[7] 470 (0 44)]

a) Tenfold excess of nBu$_4$NF was employed, concentration of the esters 10^{-4} to 10^{-5}M, b) fluorescence not detected, c) very weak fluorescence, d) corrected fluorescence quantum yields relative to quinine bisulfate (Φ^{Fl}= 0 56)[15] as standard

reveal that hardly any fluorescence emission for the aryl esters **3a,b** could be detected, whereas the methyl esters **5a,b** exhibit intense fluorescence. Treatment of the hydroxy-substituted esters **4a,b** with fluoride ions led to the same results as with the esters **3a,b**. Similar results were obtained by using acetonitrile as a solvent. Therefore, the aryl esters seem to be labile towards fluoride ions and form non-fluorescent products, whereas the methyl esters **5a,b** are not affected under these conditions

This was most convincingly demonstrated in form of a control experiment with the readily hydrolyzable 2-benzoyloxyacetophenone (**6**) as model compound (Eq 1) With fluoride and even phenolate ions the expected 2-hydroxyacetophenone (**7**) was obtained, considerable amounts of the diketone **8** (the aldol product of **7** with the benzoate ester[12]), and phenyl benzoate (**9**).



Reagent	Conv [%]	MB [%] [b]	Product Distribution [%][a] 7	8	9
nBu_4NF (1 5 equiv)	62	82	23	77	-
PhONa (1 0 equiv)	100	63	31	37	32

a) Relative yields of isolated products normalized to 100%, b) after aqueous work up and column chromatography

Discussion

The results presented herein demonstrate that the CIEEL mechanism is also operating in the case of the fluoride ion-induced decomposition of the siloxy-protected benzofuran dioxetanes **2**, as previously presented for the acetyloxy-substituted dioxetanes[1]. Appreciable chemiluminescence was detected when the dioxetanes **2** were treated with fluoride ions in acetonitrile The fluoride ion-triggered light emission was considerably higher than that from the thermal decomposition of these dioxetanes As expected[2], also for this intramolecular electron transfer mechanism (CIEEL) singlet excited carbonyl compounds are being efficiently generated. Dioxetane **2b**, in which the electron donor is located in the *meta* postion to the dioxetane site, gives one of the highest chemiluminescence quantum yield of all CIEEL-active benzofuran dioxetanes investigated so far Unfortunately,

dioxetane **2b** turned out to be much more temperature sensitive than its corresponding acetyloxy-substituted isomer. Furthermore, the cleavage of the silicon-oxygen bond in the silylated dioxetane **2b** takes place much faster than saponification of the ester protection group in the previously used acetylated derivative[1]. Thus, very short bursts of light emission were observed in the fluoride ion-triggered CIEEL decomposition of dioxetane **2b**, which did not obey first order kinetics Therefore, some difficulties were encountered in determining the chemiluminescence quantum yields for the fluoride ion-triggered CIEEL process of **2b**, so that the error is as much as 50%

For the calculation of the singlet excited state efficiencies, it is essential to have available the fluorescence quantum yields of the light-emitting species; therefore, efforts were made to measure them. Our intentions failed in generating the phenolate ions of the aryl esters **3** by deprotecting the siloxy functionality with fluoride ions; the latter are held responsible for the fluorescence in the CIEEL process of the benzofuran dioxetanes **2** Thus, in a control experiment it could be proved that the aryl esters **3** were rapidly decomposed when treated with fluoride ions to yield quite unexpectedly large amounts of the diketone **8**, a product of enolate chemistry. In fact, the aryl esters **3** efficiently transesterified even with phenolate ions to give the corresponding phenyl ester Therefore, contrary to the methyl esters **5**, which are perfectly stable towards fluoride ions and exhibit intense fluorescence in DMSO, the aryl esters **3** are not persistent in the fluoride ion reaction medium and are destroyed by their own aryloxy ions, which are generated through fluoride ion desilylation Consequently, under the experimental conditions employed, fluorescence quantum yields could not be determined These unusual results suggest that the aryloxy ions, necessarily formed in the fluoride ion-promoted desilylation of the dioxetanes **2**, may cause effective *in situ* cleavage of the electronically excited ester products **4** Such a novel chemical quenching process might be responsible for the weak light emissions observed in the fluoride ion-triggered CIEEL process of the dioxetanes **2** This constitutes an inherent difficulty in the determination of fluorescence quantum yields of such aryloxy-substituted esters **4**

In summary, we have demonstrated that the CIEEL mechanism operates also for the siloxy-protected benzofuran dioxetanes **2** through fluoride ion triggering As observed previously[1], the *meta*-substituted isomer **2b** is more effective than the corresponding *ortho* isomer **2a**. A rational design of an efficient CIEEL substrate, desirable especially for chemiluminescent immunoassay applications[4], should make use of the *meta* effect

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Experimental

General Aspects

The IR spectra were taken on a Perkin Elmer 1420 infrared spectrophotometer, the UV spectra were recorded on an Hitachi U-3200 spectrophotometer and the fluorescence spectra were measured on a Perkin Elmer LS 50 spectrofluorimeter.- The ^{1}H and ^{13}C NMR spectra were determined on a Bruker AC 200 (^{1}H. 200 MHz, ^{13}C 50 MHz) or on a Bruker AC 250 spectrometer (^{1}H: 250 MHz, ^{13}C: 63 MHz), with tetramethylsilane or deuterochloroform as internal standards.- Elemental analysis were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg - All melting points were taken on a Reichert Thermovar apparatus - Silica gel (63-200 mesh, Woelm) was used for column chromatography.- TLC analyses were run on silica gel foils Polygram SIL G/UV_{254} (40 x 80) from Macherey & Nagel

Starting Materials

The synthesis of the hydroxy-substituted benzofuran derivatives was described earlier The siloxy-substituted benzofurans **1a.b** were prepared according to the literature procedure[10] by using *tert*-butyldimethylchlorosilane and imidazole in methylene chloride.

2-(2´-tert-Butyldimethylsiloxy)phenyl-3-methylbenzofuran (**1a**) was obtained as a colorless oil in 87% yield after silica gel column chromatography by eluting with 8:1 petroleum ether (30-70 °C)/ ethyl ether.- IR (film) : ν = 3090 cm^{-1}, 2990, 2960, 2880, 1595 (C=C), 1490, 1455, 1390, 1365, 1260, 1210, 1100, 910.- UV (MeOH) λ_{max} (lg ε) = 293 nm (4 00) - ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 0 10 (s, 6H, $SiMe_2$), 0.93 (s, 9H, tBu), 2 35 (s, 3H, CH_3), 6 95 - 7 07 (m, 2H, arom H), 7 20 - 7 35 (m, 3H, aromat H), 7 42 - 7 55 (m, 3H, arom H).- ^{13}C NMR ($CDCl_3$, 63 MHz) δ = - 5 72 (q, $SiMe_2$), 7 89 (q, CH_3), 17 0 (s, tBu), 24 5 (q, tBu), 109 9 (d), 111.8 (s), 118 1 (d), 119 1 (d), 120 3 (d), 121.0 (d), 121 9 (s), 122 8 (d), 129.0 (d), 129.4 (s), 130 4 (d), 148 8 (s, C-2), 152 8 (s, C-7a), 153.2 (s, C-2´) - $C_{21}H_{26}O_2Si$ (338 4) Calcd C 74 54 H 7.74, Found C 74 13 H 8 03

2-(3´-tert-Butyldimethylsiloxy)phenyl-3-methylbenzofuran (**1b**) was obtained in 52% yield as colorless oil after silica gel column chromatography by eluting with 2 1 petroleum ether (30-70 °C)/ ethyl ether - IR(film): ν = 3080 cm^{-1}, 2980, 2950, 2880, 1580 (C=C), 1455, 1370, 1300, 1245, 1205, 1115, 1090, 950, 840, 790, 750 - ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 0 23 (s, 6H, $SiMe_2$), 1 00 (s, 9H, tBu), 2 45 (s, 3H, CH_3), 6.79 - 6 86 (m,

1H, arom H), 7 18 - 7 53 (m, 7H, aromat. H) - ^{13}C NMR ($CDCl_3$, 63 MHz). δ = -5.73 (q, $SiMe_2$), 8.47 (q, CH_3), 17.2 (s, tBu), 24 7 (q, tBu), 109 9 (d), 110 3 (s), 117 3 (d), 118 2 (d), 118 7 (d), 118.8 (d), 121 3 (d), 123 3 (d), 128 6 (d), 130 1 (s), 131 6 (s), 149 4 (s, C-2), 152 7 (s, C-7a), 154 8 (s, C-3').- $C_{21}H_{26}O_2Si$ (338 4). Calcd C 74.54 H 7.74, Found C 74.28 H 7.58

Methyl 2-tert-butyldimethylsiloxybenzoate **(5a)** was obtained in only 39% yield as colorless liquid after silica gel column chromatography by eluting with 6·1 petroleum ether (30-70^{0}C)/ ethyl ether. Full conversion of the starting material could not be achieved even with an excess of chlorosilane after 24 h in boiling methylene chloride under a nitrogen gas atmosphere - IR(film): ν = 3080 cm^{-1} , 2960, 2930, 2860, 1735 (C=O), 1600 (C=C), 1575 (C=C), 1485, 1450, 1300, 1250, 1080, 920, 830 - ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 0 19 (s, 6H, $SiMe_2$), 0 99 (s, 9H, tBu), 3 84 (s, 3H, OMe), 6.85 (dd, J_{34} = 8 3 Hz, J_{35} = 1 0 Hz, 1H, 3-H), 6 95 (dt, J_{43} = J_{45} = 7 5 Hz, J_{46} = 0.8 Hz, 1H, 4-H), 7.32 (m, 1H, 5-H), 7 75 (dd, J_{65} = 7 8 Hz, J_{64} = 0.8 Hz, 1H, 6-H).- ^{13} C NMR ($CDCl_3$, 63 MHz) δ = -4.15 (q, $SiMe_2$), 18 5 (s, tBu), 25 9 (q, tBu), 52 0 (q, OMe), 121.1 (d), 121 4 (d), 123 1 (s, C-1), 131 8 (d), 133 2 (d), 155 3 (s, C-2), 167 5 (s, C=O) - $C_{14}H_{22}O_3Si$ (266 3) Calcd. C 63 14 H 8 33, Found C 63 50 H 8 61

Methyl 3-tert-butyldimethylsiloxybenzoate **(5b)** was prepared as previously described[11] in 76% yield and was purified by destillation (bp 85-90 ^{o}C/0.1 Torr) The spectral and analytical data are in accord with those reported[11]

Preparation of the Benzofuran Dioxetanes **2** *by Photooxygenation of the Benzofurans* **1** - *General Procedure* Into a 100-ml test tube, equipped with a gas inlet and outlet, was placed a solution of the corresponding benzofuran **1** (0 30 - 0 90 mmol) and 2 - 10 mg of tetraphenylphorphine (TPP) as sensitizer in metal-free (distilled from EDTA) methylene chloride The solution was cooled to the appropiate temperature (-20 to -40 ^{o}C) by means of a methanol bath with the help of a MGW Lauda Cryomat A gentle stream of dry oxygen gas was bubbled through the solution while irradiating with two 150-W sodium lamps (Philips G/98/2 SON 150-W) The reaction progress was monitored by TLC After complete consumption of the starting material, the solution was concentrated on a rotary evaporator at 0^{o}C and 15 Torr and the residue chromatographed on silica gel (63-200 mesh) at - 25 ^{0}C.

2a,7b-Dihydro-2a-(2'-tert-butyldimethylsiloxy)phenyl-7b-methyl-1,2-dioxeto[3,4-b]benzofuran(**2a**) Photooxygenation of 125 mg (0 369 mmol) of **1a** in 25 ml methylene chloride at -30°C for 7 h gave 50 0 mg (37%) of **2a** as yellow needles after silica gel column chromatography of the crude product by eluting with 5 1 pentane/ ethyl ether. Recrystallization from 10 1 pentane/ methylene chloride afforded yellow needles, m.p 97-99°C.- IR (CCl_4): ν = 2960 cm^{-1}, 2950, 2850, 1600, 1580 (C=C), 1490, 1285, 1185, 1110, 1080, 1050, 1000, 920 - ^1H NMR ($CDCl_3$, -25°C, 200 MHz) δ = -0.27 (s, 3H, SiMe), 0 09 (s, 3H, SiMe), 0.68 (s, 9H, tBu), 1 74 (s, 3H, CH_3), 6 89 - 7.15 (m, 4H, arom H), 7 31 - 7 48 (m, 3H, arom H), 7.78 (dd, J = 7 7 Hz, J = 1 8 Hz, 1H, arom H) - ^{13}C NMR ($CDCl_3$, -25°C, 50 MHz) δ = -4 61 (q, SiMe), -3 85 (q, SiMe), 17.5 (q, CH_3), 18 6 (s, tBu), 25 6 (q, tBu), 96 4 (s, C-7b), 112 1 (d), 117 6 (s), 118 2 (d), 120 3 (d), 122.3 (d), 122 4 (s), 123 6 (d), 128 4 (s), 128.6 (d), 131 2 (d), 131 6 (d), 153 1 (s, C-2'), 160 7 (s, C-3a) - $C_{21}H_{26}O_4Si$ (370 4) Calcd C 68 07 H 7 07, Found C 67 71 H 7 05

2a,7b-Dihydro-2a-(3'-tert-butyldimethylsiloxy)phenyl-7b-methyl-1,2-dioxeto[3,4-b]benzofuran(**2b**) Photooxygenation of 300 mg (0 886 mmol) of **1b** in 30 ml methylene chloride at -40°C for 19 h gave 20 0 mg (7%) of **2b** as yellow oil and 40 0 mg (13%) of the corresponding 2-hydroperoxy-2-(3'-tert-butyldimethylsiloxy)phenyl-3-methylenebenzofuran after silica gel column chromatography of the crude product by eluting with 10 1 pentane/ ethyl ether Both compounds were too labile for elemental analysis Spectral and analytical data for dioxetane **2b** ^1H NMR ($CDCl_3$, -40°C, 200 MHz)· δ = 0 20 (s, 6H, $SiMe_2$), 0.98 (s, 9H, tBu), 1 56 (s, 3H, CH_3), 6 97 - 7 56 (m, 8H, arom H) - ^{13}C NMR ($CDCl_3$, -40 °C, 50 MHz) δ = - 4.52 (q, $SiMe_2$), 18 1 (s, tBu), 18 3 (q, CH_3), 25 5 (q, tBu), 96 6 (s, C-7b), 111 9 (d), 118.0 (s), 119 1 (d), 120 0 (d), 122 0 (d), 122 9 (d), 123 8 (d), 124.0 (s), 129 8 (d), 132 0 (d), 133 4 (s), 155 7 (s, C-3'), 160 7 (s, C-3a) Spectral and analytical data for the hydroperoxide IR(CCl_4) ν = 3540 cm^{-1} (OOH), 2995, 2980, 2880, 1600 (C=C), 1575 (C=C), 1500 (C=C), 1480, 1450, 1290, 1270, 1220, 1105, 1015, 920, 640 - ^1H NMR ($CDCl_3$, -25°C, 200 MHz) δ = 0 18 (s, 6H, $SiMe_2$), 0 95 (s, 9H, tBu), 5 32 (s, 1H, =CH), 5 84 (s, 1H, =CH), 6 86 - 7 47 (m, 8H, arom H), 8 80 (s, 1H, OOH) - ^{13}C NMR ($CDCl_3$, -25 °C, 50 MHz) δ = -4 56 (q, $SiMe_2$), 18 1 (s, tBu), 25 5 (q, tBu), 109 5 (t, $=CH_2$), 110 4 (d), 114 2 (s, C-2), 117 6 (d), 118 5 (d), 120 7 (d), 121 3 (d), 121 9 (d), 124 0 (s), 129 7 (d), 130 9 (d), 138 0 (s), 143 2 (s, C-3), 155 5 (s, C-3'), 155 6 (s, C-7a)

Preparation of the Thermal Decomposition Products **3a,b** The unknown siloxy-substituted aryl esters **3a,b** were isolated from the photooxygenation mixture of the benzofurans **1a,b** by silica gel column chromatography

2-(2´-tert-Butyldimethylsiloxy)benzoyloxyacetophenone (**3a**) was obtained in 37% yield as yellow oil by eluting with 5 1 pentane / ethyl ether and on standing at -25°C for several days crystallized as yellow plates, m p. 53-55 °C - IR(film). ν = 3080 cm^{-1}, 2960, 2860, 1755 (C=O), 1690 (C=O), 1600 (C=C), 1575 (C=C), 1490, 1450, 1250, 1195, 1025, 920 - UV(MeCN) λ_{max}(lg ε) = 292 nm (4 19) - ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 0.17 (s, 6H, $SiMe_2$), 0 90 (s, 9H, tBu), 2 47 (s, 3H, CH_3), 6 87 (dd, J = 8 3 Hz, J = 0 9 Hz, 1H, arom H), 6 99 (dt, J = 7 6 Hz, J = 1 1 Hz, 1H, arom H), 7 14 (dd, J = 8 1 Hz, J = 1 1 Hz, 1H, arom H), 7 27 (dt, J = 7.6 Hz, J = 1 1 Hz, 1H, arom. H), 7 35 - 7 42 (m, 1H, arom H), 7 46 - 7 53 (m, 1H, arom H), 7 77 (dd, J = 7.8 Hz, J = 1 7 Hz, 1H, arom H), 8.01 (dd, J = 7 9 Hz, J = 1.8 Hz, 1H, arom. H) - ^{13}C NMR ($CDCl_3$, 63 MHz) δ = - 4 18 (q, $SiMe_2$), 18 3 (s, tBu), 25 7 (q, tBu), 29 8 (q, CH_3), 121.0 (d), 121.1 (s), 121 1 (d), 123.9 (d), 125 9 (d), 130 1 (d), 131 6 (s), 132.4 (d), 133.3 (d), 134 1 (d), 149 4 (s, C-2), 156 4 (s, C-2´), 163.9 (s, C=O), 197 7 (s, C=O) - $C_{21}H_{26}O_4Si$ (370 4). Calcd C 68.07 H 7 07, Found C 67.80 H 7 45

2-(3´-tert-Butyldimethylsiloxy)benzoyloxyacetophenone (**3b**) was obtained as colorless oil in 40% yield from the photooxygenation mixture of benzofuran **1b** by eluting with 3 1 pentane/ ether - IR(film)· ν = 3080 cm^{-1}, 2960, 2940, 2860, 1750 (C=O), 1695 (C=O), 1605 (C=C), 1590 (C=C), 1490, 1440, 1360, 1290, 1210, 960, 865 - UV(MeOH): λ_{max}(lg ε) = 238 nm (4 45), 291 (3 75).- ^{1}H NMR ($CDCl_3$, 250 MHz)· δ = 0 16 (s, 6H, $SiMe_2$), 0 93 (s, 9H, tBu), 2 47 (s, 3H, CH_3), 7 05 (ddd, J = 8.1 Hz, J = 2 5 Hz, J = 1 0 Hz, 1H, arom H), 7 16 (dd, J = 8 1 Hz, J = 1.0 Hz, 1H, arom H), 7 25 - 7 34 (m, 2H, arom H), 7 50 (dt, J = 7 9 Hz, J = 1 7 Hz, 1H, arom H), 7 57 (t, J = 2 0 Hz, 1H, 2´-H), 7 74 (td, J = 7.7 Hz, J = 1 2 Hz, 1H, arom. H), 7 80 (dd, J = 7 8 Hz, J = 1 7 Hz, 1H, arom H) - ^{13} C NMR ($CDCl_3$, 63 MHz) δ = - 4 15 (q, $SiMe_2$), 18 5 (s, tBu), 25 9 (q, tBu), 30.2 (q, CH_3), 121 9 (d), 123 5 (d), 124 1 (d), 126 0 (d), 126.4 (d), 130 0 (d),130 5 (d), 130 7 (s), 131 6 (s), 133 6 (d), 149 7 (s, C-2), 156 2 (s, C-3´), 165 2 (s, C=O), 197 8 (s, C=O) - $C_{21}H_{26}O_4Si$ (370 4) Calcd C 68 07 H 7 07, Found C 67 61 H 7 27

Reaction of 2-Benzoyloxyacetophenone (**6**) *with Fluoride Ions*

To a solution of 500 mg (2 08 mmol) 2-benzoyloxyacetophenone (**6**) in 20 ml of DMSO was added 984 mg (3 12 mmol) nBu_4NF $3H_2O$ and stirred for 30 min at room temperature 50 ml of water was added to the orange solution and the latter with 0 5 N HCl adjusted to pH 7 After extraction with ether (2x50 ml) and silica gel column chromatography (2 1 petroleum ether/ ethyl ether) 32 0 mg (18%) of 2-hydroxyacetophenone (**7**) and 190 mg (61%) of 1-(2´-hydroxy)phenyl-3-phenylpropane-1,3-dione (**8**) were obtained Only 62% of conversion was achieved, based on reisolated starting material Spectral and analytical data for the known[12] diketone **8** IR(KBr)·

1610 cm^{-1}(C=O), 1575 (C=C), 1490, 1300, 1200, 1185, 1020, 895, 730, 620 - UV(MeOH): λ_{max}(lg ε) = 252 nm (4.01), 364 (4 44) - ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 4 63 (s, 2H, CH_2, 11% diketo tautomer), 6 84 (s, 1H, =CH, 89% enol tautomer), 6 91 (dt, J = 7 3 Hz, J = 1 2 Hz, 1H, arom. H), 7 00 (dd, J = 8 4 Hz, J = 1 0 Hz, 1H, arom H), 7.41 - 7 55 (m, 3H, arom H), 7 77 (dd, J = 8 1 Hz, J = 1 0 Hz, 1H, arom H), 7 88 - 7 94 (m, 2H, arom H), 11 92 (s, 1H, OH, 11% diketo tautomer), 12 09 (s, 1H, OH, 89% enol tautomer), 15 54 (s, 1H, OH) - ^{13}C NMR ($CDCl_3$, 63 MHz) δ = 92 5 (d, =CH), 119 1 (s), 119.2 (d), 119 4 (d), 127 1 (2 d), 128 8 (d), 129 0 (2 d), 132 7 (d), 133 9 8s), 136.1 (d), 162 8 (s, C-2'), 177 8 (s, C-3), 195 9 (s, C-1) -

Reaction of 2-Benzoyloxyacetophenone (**6**) *with Sodium Phenolate*

To a solution of 242 mg (2 08 mmol) sodium phenolate in 30 ml DMSO was added a solution of 500 mg (2 08 mmol) 2-benzoyloxyacetophenone (**6**) in 10 ml of DMSO and the mixture stirred at room temperature for 1 h To the reaction mixture was added 30 ml of water and the latter with 0 5 N HCl adjusted to a pH 7 After extraction with ethyl ether (50 ml) and methylene chloride (50 ml) and silica gel column chromatography (1 1 petroleum ether (30-70 ^{0}C)/ methylene chloride) 161 mg (20%) of phenyl benzoate (**9**) was obtained, m p 68-69^{o}C Also diketone **8** (23%) and 2-hydroxyacetophenone (**7**) (19%) were isolated The spectral and analytical data of these compounds matched those reported[12,13]

CIEEL Measurements of the Benzofuran Dioxetanes **2** - *General Procedure* All measurements were performed on a Mitchell-Hastings photometer[14] From a 0 01 M stock solution of the dioxetane in acetonitrile were transferred 3 ml into a scintillation tube and the latter placed into the photometer, which was thermostated with the help of a MGW Lauda Cryomat at 25 ^{o}C After 5 to 7 min an appropriate amount of 0.1 M tetra-n-butylammonium fluoride in acetonitrile was added by means of a syringe through the rubber septum under rigorous exclusion of light, with the photomultiplier open for immediate measurement The light emission was recorded with a Servogor Z10 recorder and the intensity-time traces processed according to first-order kinetics The light intensity was calibrated by means of the scintillation "cocktail" of Hastings and Weber[14] as light standard The CIEEL results are summarized in Table 1

Recording of the UV/VIS and Fluorescence Spectra

To a sample of the esters **3-5**, disolved in DMSO or acetonitrile (c = 1 10^{-4} to 1 10^{-5} M), was added a solution of nBu_4NF in the correponding solvent, so that a tenfold excess of fluoride resulted The absorption spectrum was recorded immediately and subsequently the fluorescence spectrum of the same sample was measured As

standard for the determination of the fluorescence quantum yields a 5 10^{-6} M solution of quinine bisulfate in 1 N sulfuric acid was used [Φ^{fl}(QBS) = 0 56] The calculation of the fluorescence quantum yields was performed as described in the literature[15]

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