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Synthesis, Thermal Stability, and Chemiluminescence Properties of Bisdioxetanes Derived from *p*-Dioxines

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By elimination of methanol from 2,5-dimethoxy-1,4-dioxanes and 2,3-dihydro-2-methoxy-1,4-dioxines on treatment with *p*-toluenesulfonic acid in acetic anhydride, the new tetrakis(4-methoxyphenyl)-, tetrakis(4-chlorophenyl)-, tetra-*p*-tolyl-, and 2,5-dimethyl-3,6-diphenyl-1,4-dioxines (**1**) were prepared in good yields. Photosensitized singlet oxygenation of these 1,4-dioxines **1** afforded the corresponding bisdioxetanes **2**, the 1,2-diketones, and the enediol diesters **7**. Thermal decomposition of the bisdioxetanes **2** yielded the corresponding anhydrides **4** essentially quantitatively. During the thermolysis of 1,6-dimethyl-3,8-diphenyl-2,4,5,7,9,10-hexaoxatricyclo[6.2.0.0^{3,6}]decane (**2f**) appreciable amounts of (3*R*,4*S*)-3-acetoxy-4-(benzoyloxy)-4-methyl-3-phenyl-1,2-dioxetane (**3f**) were detected. The bisdioxetanes **2** and monodioxetane **3f** exhibited similar thermal stabilities, the free energies of activation ($\Delta G^{\neq}$) at 298 K falling within 25.5 + 1.5 kcal/mol. The singlet excitation yields (Φ^S) ranged between 0.003 and 0.03% and the triplet excitation yields (Φ^T) between 9.5 and 71.5%. Despite the favorable energy balance, it is concluded that no higher excited states of anhydride **4f** are produced during the thermolysis of bisdioxetane **2f**. On thermal activation, the bisdioxetanes decompose by sequential cleavage of the two dioxetane rings.

Synthese, thermische Stabilität und Chemilumineszenz-Eigenschaften von Bisdioxetanen aus *p*-Dioxinen

Durch Eliminierung von Methanol aus 2,5-Dimethoxy-1,4-dioxanen und 2,3-Dihydro-2-methoxy-1,4-dioxinen mit Hilfe von *p*-Toluolsulfonsäure und Acetanhydrid konnten die bisher unbekannten Verbindungen Tetrakis(4-methylphenyl)-1,4-dioxin (**1c**), Tetrakis(4-methoxyphenyl)-1,4-dioxin (**1d**), Tetrakis(4-chlorphenyl)-1,4-dioxin (**1e**) und 2,5-Dimethyl-3,6-diphenyl-1,4-dioxin (**1f**) in guten Ausbeuten erhalten werden. Photosensibilisierte Singulett-Oxygenierung dieser 1,4-Dioxine **1** lieferte die entsprechenden Bisdioxetane **2**, die 1,2-Diketone und die Endioldiester **7**. Durch Thermolyse der Bisdioxetane **2** wurden die jeweiligen Anhydride **4** quantitativ erhalten. Das intermediäre Auftreten von (3*R*,4*S*)-3-Acetoxy-4-(benzoyloxy)-4-methyl-3-phenyl-1,2-dioxetan (**3f**) während der thermischen Zersetzung von 1,6-Dimethyl-3,8-diphenyl-2,4,5,7,9,10-hexaoxatricyclo[6.2.0.0^{3,6}]decan (**2f**) konnte nachgewiesen werden. Die Bisdioxetane **2** und das Monodioxetan **3f** besitzen ähnliche thermische Stabilität. Ihre freien Aktivierungsenthalpien ($\Delta G^{\neq}$) bei 298 K liegen bei 25.5 ± 1.5 kcal/mol. Die Singulett- (Φ^S) und Triplettausbeuten (Φ^T) der Bisdioxetane **2** und des Monodioxetans **3f** liegen zwischen 0.003 und 0.03% bzw. 9.5 und 71.5%. Es wird postuliert, daß beim thermischen Zerfall von Bisdioxetan **2f** trotz günstiger Energiebilanz keine höher angeregten Zustände des Anhydrids **4f** gebildet werden. Der vorherrschende Zerfallsweg von **2f** beinhaltet anscheinend einen stufenweisen Bruch der beiden Dioxetanringe.

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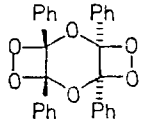
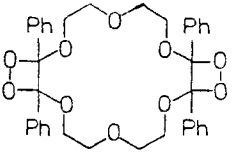
Although the chemistry of dioxetanes is by now well established[1], bisdioxetanes and higher congeners are still rarity items. The first authentic member of this potentially interesting group of compounds, namely the bisdioxetane **A** derived from tetraphenyl-1,4-dioxine, was reported in 1979[2] and its structure rigorously established by *X*-ray analysis[3]. Recently the novel bisdioxetane **B** from the tetraphenyl-substituted crown ether was described[4], which undoubtedly presents interesting opportunities for photomechanistic investigation.

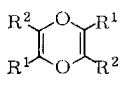
A



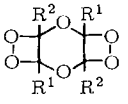


B

What is unusual about the bisdioxetane of tetraphenyl-*p*-dioxine is that it can be considered as a dimer of benzoic anhydride. Indeed, thermal cleavage of the two dioxetane rings in **A** affords quantitatively benzoic anhydride with surprisingly efficient chemiluminescence[2]. Presumably the composite action of the two juxtaposed dioxetane moieties in this bisdioxetane is responsible for the effective chemiexcitation of triplet-excited anhydride. It was therefore the purpose of this study to prepare the diverse series of *p*-dioxines **1**, convert them into the bisdioxetanes **2** via singlet oxygenation, and elucidate their thermal stability and chemiluminescence properties in their thermolysis leading to the monodioxetanes **3** and anhydrides **4**. The specific mechanistic question that we posed was whether such bisdioxetanes, which at least formally can be considered to represent two "bound photons", are capable of generating upper excited states via chemical means. Here we report the full details of this study.



1



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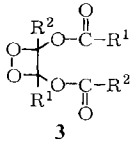

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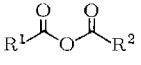
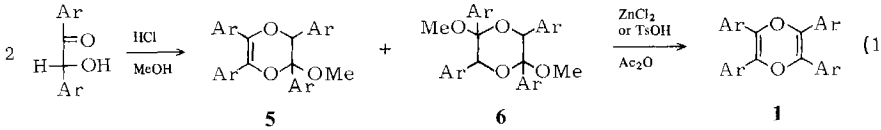


4

	a	b	c	d	e	f
R^1	H	Ph	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	4-ClC_6H_4	Me
R^2	H	Ph	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	4-ClC_6H_4	Ph

Preparation of *p*-Dioxines 1

Relatively few *p*-dioxines were known prior to this work, so that it was essential to improve the synthetic methods. The known parent *p*-dioxine (**1a**) was obtained by chlorination[5] of 1,4-dioxane and subsequent dechlorination[6] with magnesium iodide. The only other known *p*-dioxine **1b** that was used in this research was prepared according to the sequence shown in eq. (1)[7]. Thus, reaction of benzoin with dry HCl gas in methanol afforded a mixture of the monomethoxy- and dimethoxy-substituted dimers **5b** and **6b**, respectively. After treatment of this mixture with zinc chloride in acetic anhydride, the *p*-dioxine **1b** was formed. Better yields of the latter were obtained when instead of $ZnCl_2$ *p*-toluenesulfonic acid (TsOH) was used. This modified method proved successful for the preparation of the hitherto unknown substituted tetraaryl-*p*-dioxines **1c–f**.



5 **6** **1**

Usually the monomethoxy- and dimethoxy-substituted products **5** and **6**, respectively, did not need to be separated and purified and could be used as crude product mixture in the TsOH-Ac_2O elimination step. However, in the case of 4,4′-dimethoxybenzoin the monomethoxy product **5d** was isolated in 22% yield. Treatment with $ZnCl_2$ led besides much intractable material to small amounts of tetrakis(4-methoxyphenyl)furan. Even with TsOH in Ac_2O as catalyst, the *p*-dioxine **1d** contained the above furan as impurity.

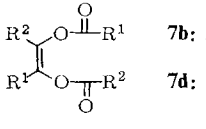
Also with *p*-dioxine **1f** considerable difficulties were encountered in its preparation unless TsOH in Ac_2O was employed. The latter method resulted in a 51% yield of the desired product. Specifically, the readily available dimethoxy-substituted dioxane **6f**, prepared according to literature[8], was used for the TsOH/Ac_2O demethanolation. Tetramethyl-1,4-dioxine could not be obtained via demethanolation of the corresponding dimethoxy-1,4-dioxane, prepared analogously to dioxane **6f**[8].

It should be mentioned that the elimination reaction worked particularly well when on cooling of the reaction mixture the *p*-dioxine **1** directly crystallized. The *p*-dioxines, especially derivative **1e**, are quite unstable in solution and are readily autoxidized into the corresponding α-diketones. For example, on prolonged standing of the tetrachloro-derivative **1e** in methylene chloride even at room temperature, essentially quantitatively 4,4′-dichlorobenzil was obtained.

Preparation of 1,2-Dioxetanes

The bisdioxetanes **2** were conveniently prepared from the *p*-dioxines via photooxygenation in methylene chloride at −78 °C, using tetraphenylporphine (TPP) as sensitizer. TLC-monitoring showed that within 0.5−5 h the *p*-dioxine was consumed. Low temperature (below −60 °C) chromatography on Florisil and final recrystallization afforded the analytically pure bisdioxetanes **2** as relatively stable solids.

In all photooxygenations variable amounts of the corresponding α-diketones were formed[9]. This was especially critical in the case of the tetrakis(4-chlorophenyl)dioxine (**1e**), which, as already mentioned, is readily autoxidized to its benzil derivative with triplet oxygen. Furthermore, in the case of the *p*-dioxines **1b,d** also the corresponding *cis*-enediol esters **7b,d** were isolated. Since **7b**, prepared independently from benzoyl chloride[10], was inert towards singlet oxygen under a great variety of reaction conditions, the monodioxetane **3f**, that was also isolated in the photooxygenation of *p*-dioxine **1f**, was not formed via this route. In this context it is important to mention that enol esters give dioxetanes on singlet oxygenation[11]. On prolonged standing of the pure bisdioxetane **2f** in methylene chloride solution at room temperature the monodioxetane **3f** was formed in sufficient amounts to be isolated.



7b: $R^1 = R^2 = Ph$

7d: $R^1 = R^2 = 4\text{-}CH_3OC_6H_4$

All efforts failed to obtain the bisdioxetane **2a** of the parent *p*-dioxine (**1a**), although singlet oxygenation of 2,3-dihydro-1,4-dioxine afforded the labile monodioxetane[12]. That **2a** was probably formed could be made plausible by means of chemiluminescence emission and carbonyl absorption in the IR of the photooxygenated reaction mixture of **1a**. Attempts to isolate the apparently quite unstable bisdioxetane **2a** failed even at −78 °C.

Thermolysis Products

As expected, the thermal decomposition products of the bisdioxetanes **2b**–**f** and the monodioxetane **3f** were the corresponding anhydrides **4b**–**f**, formed quantitatively as confirmed by ^{1}H NMR. After recrystallization the melting points of the anhydrides matched those reported.

Thermal Stability

To assess the thermal stability of these dioxetanes, the activation parameters were determined by means of isothermal kinetics, monitoring dioxetane consumption with the help of their chemiluminescence[1]. Since the direct chemiluminescence emissions were too weak to record usable intensity versus time profiles, the fluorophor 9,10-dibromoanthracene (DBA) was employed for enhancement of the chemiluminescence by means of energy transfer. Fortunately, these dioxetanes were not nearly as sensitive towards catalytic decomposition as the related dioxetanes derived from benzo-*p*-dioxines and *p*-dioxenes[13]. Even then, all solvents had to be rigorously purified and finally distilled from the disodium salt of ethylenediaminetetraacetic acid (EDTA) to suppress dark catalysis. The kinetic data for the bisdioxetanes **2b**–**f** and monodioxetane **3f** are summarized in Table 1. As the rate constants (k_{obs} at 74 °C) show, these dioxetanes all exhibited quite similar thermal stabilities, falling within a 35-fold range for the most stable (**2f**) and the least stable (**2d**). Even the bisdioxetane **2f** and monodioxetane **3f** decomposed at nearly the same rates, a most unexpected result. Correspondingly, the activation parameters were quite similar, with $\Delta H^{\neq}$ values clustering around 24 ± 1 kcal/mol, $\Delta S^{\neq}$ values at −8 ± 2 e.u., and $\Delta G^{\neq}$ values of 25 ± 1 kcal/mol at 298 K. More significantly, ^{1}H NMR monitoring at 70 °C clearly showed that as the methyl resonance of the bisdioxetane **2f** at δ = 1.53 disappeared, that of the anhydride **4f** at δ = 2.37 appeared, while that of the monodioxetane **3f** at δ = 1.71 and 2.05 passed through a maximum intermediacy (Fig. 1). Clearly the intermediacy of the monodioxetane **3f** was therewith established.

With an activation free energy of $\Delta G^{\neq}$ = 24.2 kcal/mol at 298 K, the methoxy-substituted bisdioxetane **2d** was the least stable. Its stability was principally energy-controlled, because its activation entropy was within the experimental error similar to that of the other bisdioxetanes. In this context it is significant to mention that 4-methoxyphenyl-substituted monodioxetanes show lower thermal stabilities[14].

Table 1. Rate constants (k_{obs}), activation enthalpies ($\Delta H^{\neq}$), entropies ($\Delta S^{\neq}$), and free energies ($\Delta G^{\neq}$) of the thermal decomposition of 1,2-dioxetanes[a]

Dioxetane	Temp. Range (°C)[b]	[Dioxetane] $\cdot 10^4$ (M)	[DBA] $\cdot 10^4$ (M)[c]	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ at 298 K (kcal/mol)	$k_{obs} \cdot 10^5$ (s^{-1})[d]
2b	75.9–99.9	1.18	1.07	23.6±0.3	−8.2±0.7	26.0±0.5	16.0±0.4
2c	72.6–93.6	0.262	4.28	23.2±0.3	−7.8±0.7	25.5±0.5	37.9±0.7
2d	50.0–74.3	1.73	2.14	21.5±0.3	−9.1±0.9	24.2±0.5	220 ±12
2e	80.3–101.5	0.417	1.07	23.1±0.3	−9.4±0.8	25.9±0.5	21.9±0.7
2f	73.8–100.3	2.53	1.07	24.1±0.6	−8.5±1.7	26.6±0.8	6.39±0.3
3f	73.7–100.4	5.00	1.07	25.2±0.6	−5.6±1.7	26.9±0.8	6.41±0.1

[a] Determined in toluene as solvent. – [b] Temperature was controlled to within 0.1 °C. – [c] Since the direct chemiluminescence was too weak for these dioxetanes, DBA (9,10-dibromoanthracene) was used as fluorophor to enhance the light intensity. – [d] Determined independently at 74.0 °C by means of isothermal kinetics.

Table 2. Singlet (Φ^S), triplet (Φ^T), and total (Φ^{T+S}) excitation yields and triplet-singlet ratios (Φ^T/Φ^S) of the 1,2-dioxetanes[a]

Dioxetane	Temp. (°C)[b]	Dioxetane 10^4 (M)	[DBA] $\cdot 10^4$ (M)[c]	[DPA] $\cdot 10^4$ (M)[d]	$k_{obs} \cdot 10^4$ (s^{-1})[e]	Φ^T (%)	$\Phi^S \cdot 10^3$ (%)	Φ^{T+S} (%)	Φ^T/Φ^S
2b	95.4	1.18	1.07–10.7		12.7±0.4	49.7±3		49.7±3	6400±1200
	95.4	1.18		2.18–10.9	10.4±1		7.8±2		
2c	82.8	0.850	1.07–8.56		8.30±0.7	29.5±0.7		29.5±0.7	–
	82.8	0.850			8.13		–[e]		
2d	74.3	0.347	1.07–10.7		23.0±1	10.0±0.5		10.0±0.5	–
	65.1	1.73			8.95		–[e]		
2e	96.6	0.423	1.07–10.7		17.5±0.4	14.7±0.3		14.7±0.3	600±250
	96.6	0.423		2.18–10.9	16.2±2		24.1±10		
2f	95.0	2.53	1.07–10.7		5.46±0.4	71.5±5		71.5±5	11000±2000
	95.0	2.53		1.09–10.9	5.66±1		6.5±2		
3f	95.5	1.00	1.07–10.7		5.75±0.5	9.5±2		9.5±2	2800±1000
	95.3	5.00		1.09–10.9	4.33±1		3.4±2		

[a] Determined in toluene as solvent. – [b] Temperature was controlled within 0.1 °C. – [c] Using DBA (9,10-dibromoanthracene) as fluorophor for triplet excitation yields. – [d] Using DPA (9,10-diphenylanthracene) as fluorophor for singlet excitation yields. – [e] The intensities of the DPA-chemiluminescence were too low to obtain reproducible results.

Chemiluminescence Properties

The direct chemiluminescence intensities for all of these dioxetanes was too weak to determine singlet excitation yields (Φ^S) directly. Besides, no fluorescence yields for any of the anhydrides were available. However, it is of interest to mention in this connection that the intensity versus time profile of the direct chemiluminescence of bisdioxetane **2f** displayed a maximum. This corresponded approximately to the concentration-time profile of the monodioxetane **3f** in the thermal decomposition of this bisdioxetane **2f** (Fig. 1) if adjustment ist made for the fact that in $CDCl_3$ the decomposition of **2f** is faster than in toluene.

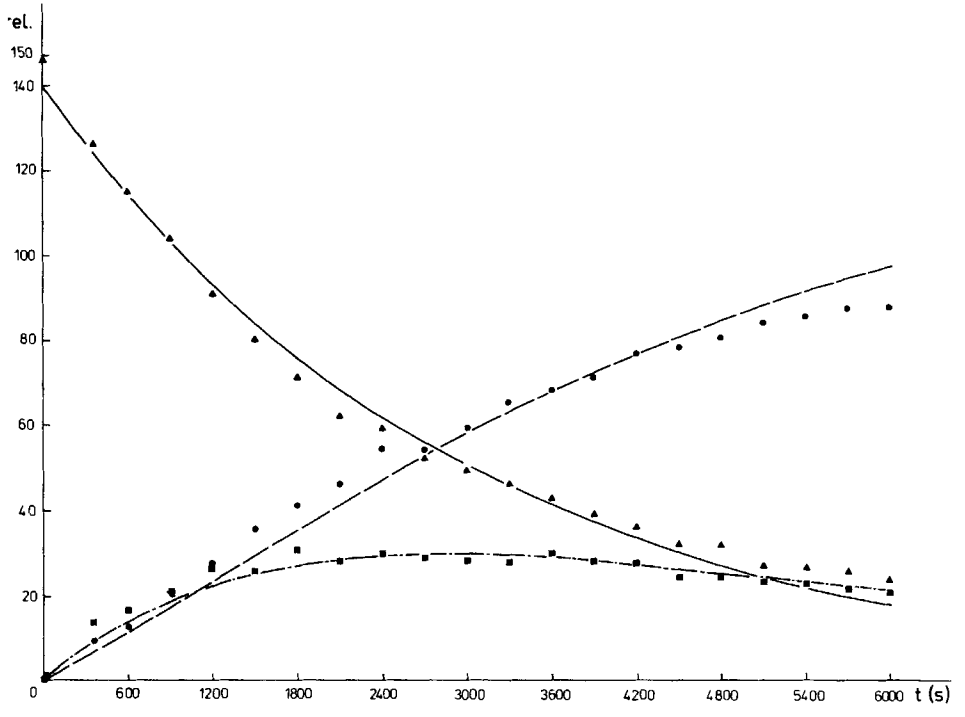


Fig. 1. Concentration-time profile of bisdioxetane **2f** (▲), monodioxetane **3f** (■), and anhydride **4f** (●) determined by means of ^1H NMR at 70.0°C in $CDCl_3$. The curves represent best fit by computer simulation using the kinetic scheme of eq. (2)

In view of the low direct chemiluminescence emission, recourse to the energy transfer chemiluminescence techniques[1] had to be taken in order to determine the excitation yields. 9,10-Diphenylanthracene (DPA) and 9,10-dibromoanthracene (DBA), established and convenient luminescence probes[1], were utilized as fluorophors to acquire singlet (Φ^S) and triplet (Φ^T) excitation yields, respectively. The results are summarized in Table 2. The excitation yields were calculated per mol of dioxetane decomposed for the bisdioxetanes **2**. From the present data it was difficult to assess how many excited states were formed directly from the bisdi-

oxetanes **2** and how many from the intermediary monodioxetanes **3** during the thermolysis of the bisdioxetane **2**.

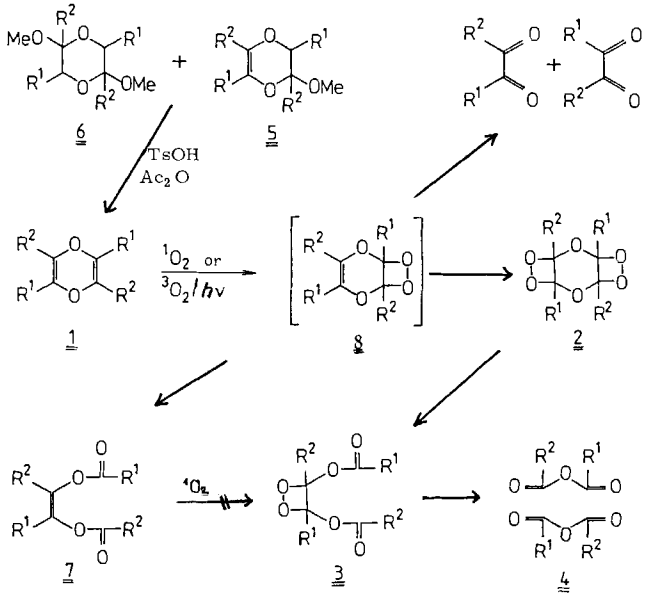
As is typical for simple dioxetanes[1], the triplet yields are high, ranging between ca. 10 and 71%. A control experiment showed that the triplet yields are not significantly influenced whether toluene or chloroform was used as solvent. The singlet yields are usually low, ranging between ca. 0.003 and 0.03%. This is most dramatically brought out in the triplet-singlet ratios (Φ^T/Φ^S), which are as high as ca. 11000. Consequently, these dioxetanes are among the most efficient sources[1] for triplet excited carboxylic anhydrides, as reflected by the total excitation yields (Φ^{T+S}).

Discussion

Synthetic Aspects

The preparative work on the *p*-dioxines **1**, their singlet oxygenation, and the thermal decomposition of their dioxetanes are summarized in Scheme 1. Either starting from 2,5-dimethoxy-1,4-dioxanes **6**, or from 2,3-dihydro-2-methoxy-1,4-dioxanes **5** treatment with TsOH/Ac_2O afforded the tetrasubstituted *p*-dioxines **1** in fair yields (up to ca. 50%). Therewith one can effectively compete with the potential side reaction of furan formation[15] in the demethanolation of products **5** and **6**[16]. In general this *p*-dioxine synthesis is effective for the tetraaryl-substituted derivatives **1b–e** and the diaryl dialkyl derivative **1f**, but fails completely for the tetramethyl derivative. As observed previously for tetraphenyl-1,4-dioxine (**1b**)[9]

Scheme 1. Preparation and singlet oxygenation of *p*-dioxines **1** and thermal decomposition of their dioxetanes



also the *p*-dioxine **1e** is readily autoxidized with triplet oxygen under irradiation affording the corresponding α-diketone. A possible intermediate in this autoxidation is the monodioxetane **8** (Scheme 1). Subsequently, the apparently quite labile monodioxetane **8** decomposes into two molecules of the corresponding benzil, as was previously proposed for the tetraphenyl derivative[9]. The latter cleavage of dioxetanes with retention of the dioxetanyl carbon-carbon bond is unusual, but examples have been reported[1a].

In the photo-oxygenation undoubtedly the monodioxetane **8** is the precursor to the bisdioxetane **2**. Singlet oxygenation of the second double bond leading to **2** competes favorably with cleavage of the labile monodioxetane **8** into α-diketone and enediol diester. In fact, in the case of the chloro-substituted *p*-dioxine **1e**, which is especially prone to autoxidation, its bisdioxetane could only be obtained under the most efficient singlet oxygenation conditions.

Mechanistic Aspects

As already alluded to in the introductory remarks, the novel feature of such bisdioxetanes is the possibility of making sufficient energy available to generate

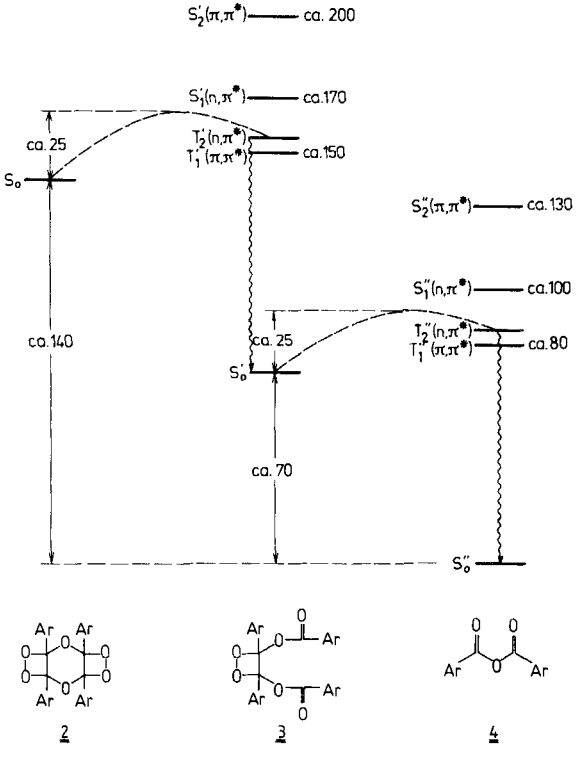


Fig. 2. Reaction enthalpies, activation energies, and triplet and singlet energies of n,π* and π,π* excited states for the thermal decompositions of the bisdioxetanes **2** and monodioxetanes **3** into anhydrides **4** (in kcal/mol)

chemically upper excited states[17]. This energy sufficiency is most convincingly demonstrated in the energy diagram of Fig. 2. Unfortunately, no thermochemical data are available for the ground states nor spectroscopic data for the excited states of the actual molecules involved, so that we were obliged to estimate these using known simpler model compounds. Since for the tetramethyldioxetane decomposition into acetone the reaction enthalpy is ca. 68 kcal/mol[18], a conservative value of ca. 70 kcal/mol is assumed for the cleavage of the bisdioxetane **2** into the monodioxetane **3**. Similarly, this reasonable value of ca. 70 kcal/mol is adopted for the reaction enthalpy of the conversion of **3** into anhydride **4**. Since the experimental activation energies (cf. Table 1) for the decompositions of the bisdioxetane **2f** and its monodioxetane **3f** are each ca. 25 kcal/mol, we estimate that for the double cleavage **2** → **4** ca. 165 kcal/mol of energy are released, while for the single cleavages **2** → **3** and **3** → **4** each ca. 95 kcal/mol of energy are made available.

In view of the precarious situation on the photophysics of aryl esters and anhydrides[19], our estimates of the singlet and triplet energies of the respective n,π* and π,π* states are merely qualitative guides. For methyl benzoate[20], a reasonable model compound for the aryl carbonyl functions in the monodioxetane **3** and anhydride **4**, the ^{3}π,π* and ^{1}n,π* excited states are located at ca. 80 and 100 kcal/mol, respectively. Since apparently the ^{3}π,π* triplet state is that of lower energy, ^{3}n,π* must lie between 80 and 100 kcal/mol, presumably closer to the lower limit. More dubious is the placement of the ^{1}π,π* singlet states of aryl carbonyl functions. The triplet-singlet energy gap for aromatic hydrocarbons is large (ca. 30–40 kcal/mol), but usually the triplet energy is less than half of the singlet energy for π,π* states[21]. For carbonyl chromophores, e.g. benzophenone, the triplet-singlet energy gap for π,π* states is still less, ca. 26 kcal/mol[22]. Therefore, even conservatively speaking, the ^{1}π,π* singlet states of the carbonyl chromophore of aryl esters and anhydrides cannot be more than 40 kcal/mol above their ^{3}π,π* triplet states. This brackets the ^{1}π,π* singlet states between 120 and 130 kcal/mol for the aryl carbonyl chromophores in the monodioxetane **3** and anhydride **4**.

These qualitative estimates are summarized in Fig. 2. Admittedly that our energy diagram is crude, nevertheless it bears out some clear features about the chemical excitation of upper excited states. Only the double cleavage process **2** → **4** has sufficient energy (ca. 165 kcal/mol) to energize upper excited states, namely the π,π* singlet, of the anhydride product. Neither of the single cleavages **2** → **3** and **3** → **4** make sufficient energy (only ca. 95 kcal/mol) available to energize the corresponding upper excited states. In fact, not even the respective n,π* singlet states can be reached efficiently, only the two possible ^{3}n,π* and ^{3}π,π* triplet states.

What are the experimental effects? For convenience we shall briefly reiterate the essential points referring only to the bisdioxetane **2f**, since this derivative is mechanistically the most informative and relevant. The facts are:

a) The transient monodioxetane **3f** accumulates and traverses a maximum (Fig. 1) in the thermal decomposition of the bisdioxetane **2f** into anhydride **4f**.

b) The direct chemiluminescence (albeit of weak intensity) vs. time profile in the thermolysis of the bisdioxetane **2f** displays a maximum which qualitatively coincides with the maximum of accumulated monodioxetane **3f**.

c) The rate constants and activation energies (Table 1) for the thermal decomposition of the dioxetanes **2f** and **3f** are nearly the same.

d) The triplet excitation yields (Table 2) for the bisdioxetane **2f** is with 71% one of the highest[1], while for the monodioxetane **3f** it is only 9.5%.

e) The singlet excitation yields (Table 2) are very low, i.e. 0.0065 and 0.0034%, respectively, for **2f** and **3f**, quite typical for dioxetanes[1].

The fact that the monodioxetane **3f** accumulates (point a) unquestionably indicates successive single cleavages of the dioxetane units, i.e. **2f** → **3f** → **4f**. Fortunately, the thermal stabilities of the bisdioxetane **2f** and monodioxetane **3f** are sufficiently similar (point c), so that the latter can be kinetically monitored by ^{1}H NMR during the thermolysis of **2f**. Moreover, the fact that **2f** and **3f** have within experimental error the same activation energies, i.e. 25 kcal/mol (point c), a rather typical value for simple dioxetanes[1], definitively dispenses with the possibility of direct double cleavage **2f** → **4f**, without trespassing monodioxetane **3f** or excited states thereof. The thermal activation of breaking both dioxetane rings at once in the bisdioxetane **2f** is energetically and mechanistically not feasible[23]. However, the question still obtains whether double cleavage of the bisdioxetane **2f** into anhydride **4f** is channelled via electronically excited monodioxetane **3f**? In other words, how competitive is the "double cleavage" pathway **2f** → ^{S,T}[**3f**]* → ^{S,T}[**4f**]* → **4f** with the successive "single cleavage" route **2f** → ^{S,T}[**3f**]* → **3f** → ^{S,T}[**4f**]* → **4f**, as depicted in Scheme 2? From energy sufficiency considerations (Fig. 2) only the "double cleavage" pathway could generate upper excited states of the anhydride **4f**.

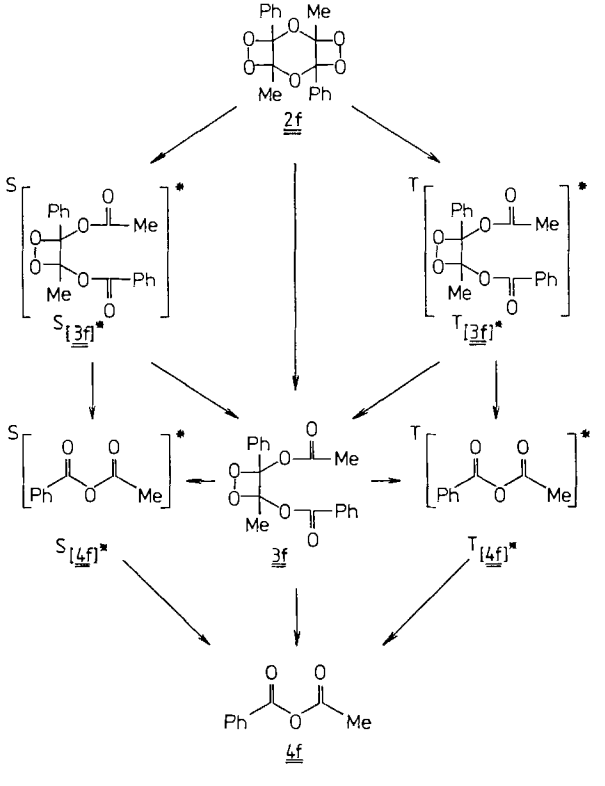
The singlet excitation mode (Scheme 2) shall be considered first. Although this process has low priority from the point of view of excitation yields (point e), it is mechanistically the more interesting and significant one in view of the possibility of chemi-energizing upper excited single states, i.e. S_2'' (π,π^*) versus S_1'' (n,π^*), of the anhydride **4f** (Fig. 2). Assuming that the "double cleavage" adiabatic process **2f** → S_1' (n,π^*)-**3f** → S_2'' (π,π^*)-**4f** → **4f** + $h\nu$ is the only course of action (Fig. 2), the peculiar intensity maximum in the direct chemiluminescence-time profile (point b) can hardly be rationalized. A steady decrease, the usual behavior of simple dioxetanes[1], in the direct chemiluminescence intensity should be observed under these mechanistic circumstances. Even population of the S_2'' (π,π^*) singlet state of the anhydride **4f** via the T_1' (π,π^*) and T_2' (n,π^*) triplet states of the monodioxetane **3f** by intersystem-crossing cannot reconcile the unusual maximum of the direct chemiluminescence intensity (point b).

The fact that the direct chemiluminescence intensity builds up and diminishes with time in the thermolysis of the bisdioxetane **2f** implies that a labile transient intervenes, which on thermal decomposition chemiluminesces comparatively efficiently. Of course, this could be the monodioxetane **3f**, which accumulates in the **2f** → **4f** thermolysis (point a). Presumably the anhydride **4f** fluoresces more efficiently than the monodioxetane **3f**, so that a maximum in the direct chemi-

luminescence intensity can be observed at all. Consequently, we allege that the principal direct chemiluminescent pathway in the thermolysis of the bisdioxetane **2f** entails **3f** $\rightarrow S_1''$ (n,π*)-**4f** $\rightarrow$ **4f** + $h\nu$ (Fig. 2). The precursors to the monodioxetane **3f**, i.e. via the dark channel from the bisdioxetane **2f** or via deactivation of the intermediary excited states S_1' (n,π*), T_1' (π,π*), and T_2' (n,π*) of **3f** is open to debate. What can be said at this point is that some additional singlet excited states, presumably S_1' (n,π*) of the monodioxetane **3f** must be involved in the thermolysis of the bisdioxetane **2f** because the singlet excitation yield (determined by energy transfer with DPA) for the **2f** $\rightarrow$ **4f** conversion is about double that for the **3f** $\rightarrow$ **4f** conversion (point e). However, on a comparative basis, no significant amount of the upper excited S_2'' (π,π*) singlet of anhydride **4f** appears to be formed in the thermolysis of the bisdioxetane **2f**, despite the fact that the energy sufficiency condition applies (Fig. 2)[24]. Therefore, we postulate that the "double cleavage" pathway **2f** $\rightarrow$ **3f*** $\rightarrow$ S_2''(π,π*)-**4f** is unlikely. Consequently, bisdioxetanes derived from *p*-dioxines are ineffective precursors for the chemical generation of upper excited singlet states.

It remains to analyze whether the exceedingly high triplet yield (point d) of the thermolysis of the bisdioxetane **2f** can be explained in terms of the "double cleav-

Scheme 2. Possible decomposition pathways of bisdioxetane **2f** leading to anhydride **4f**



age" pathway **2f** → ^{T}[**3f**]* → ^{T}[**4f**]* → **4f** (Scheme 2). Alternatively, as for the singlet excitation channel, does also for the triplet excitation the successive "single cleavage" route **2f** → ^{T}[**3f**]* → **3f** → ^{T}[**4f**]* → **4f** apply? That the second cleavage **3f** → ^{T}[**4f**]* → **4f** cannot be the major source of triplet states in the **2f** → **4f** thermolysis is clearly documented by the fact (point d) that for the authentic **3f** → **4f** thermolysis the triplet yield is only one-sevenths that of the **2f** → **4f** process. Clearly, the **2f** → **4f** conversion is responsible for the high triplet yield; but is "double cleavage" or successive "single cleavage" the dominating source (Scheme 2)?

Also for the triplet excitation channel we propose that the present set of data is better accounted for in terms of the successive "single cleavage" route. The most pressing feature is the accumulation of the monodioxetane **3f** in the **2f** → **4f** thermolysis (point a). The adiabatic "double cleavage" process **2f** → T_2' (n,π*)-**3f** → T_2'' (n,π*)-**4f** → **4f** (Fig. 2) cannot be the principle source of triplet states[25] (point d) because how could the monodioxetane **3f** accumulate and trespass even a maximum (point a)? In fact, using the experimental rate constants and the experimental triplet excitation yields and assuming consecutive first-order kinetics, we found by simulation (cf. Exp. Part) that the successive "single cleavage" route **2f** → **3f** → **4f** accounts for ca. 60% of the decomposition channel of bisdioxetane **2f** and the "double cleavage" pathway **2f** → **4f** ca. 40%. Assuming that the dark channel corresponds to the "double cleavage" route and the **2f** → **3f** conversion affords almost exclusively triplet states of **3f**, the expected triplet yields (ca. 68%) is in good agreement with the observed one (ca. 72%). Therefore, it is concluded that the successive "single cleavage" route S_0-**2f** → T_2' (n,π*)-**3f** → S_0'-**3f** → T_2'' (n,π*)-**4f** → S_0''-**4f** is the principle reaction channel. The adiabatic "double cleavage" pathway **2f** → T_2' (n,π*)-**3f** → T_2'' (n,π*)-**4f** → **4f** appears to be of secondary importance.

In conclusion, despite the large amount of energy (ca. 165 kcal/mol) that is stored in the bisdioxetanes **2** investigated here, the prevailing decomposition mode entails the successive singlet cleavages **2** → **3** → **4**, both for the singlet and the triplet excitation modes. The electronically excited monodioxetanes **3** that are produced in the thermolysis of the bisdioxetane **2** prefer to deactivate to their ground states rather than generate upper excited states via adiabatic pathways. This is surprising, especially since it is known[26] that on direct irradiation dioxetanes readily cleave to produce high yields of excited states. However, in the latter cases the dioxetane chromophore is being excited while in the present case it is the carbonyl chromophore of the ester substituent. It should be of photomechanistic interest to investigate singlet and triplet sensitization of dioxetanes with and without additional chromophores.

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Experimental Part

Melting points: uncorrected, Reichert Thermovar. – IR spectra: Beckman Acculab 4. – ^{1}H NMR: 90 MHz Varian EM 390 and 400 MHz Bruker WM 400. – ^{13}C NMR: 100 MHz Bruker WM 400 and 22.6 MHz Bruker WH 90. – Mass spectra (MS): Varian CH-7. – Elemental analyses: done in-house. – Solvents were purified according to standard literature procedures. Known compounds were either purchased or prepared according to published methods and purified to match reported physical constants and spectral data. Unless stated otherwise, solvent removal was conducted by roto-evaporation at 20–30°C and 20 Torr, but in the case of the dioxetanes at 0°C/20 Torr. Column chromatography was run at 20–25°C on silica gel (70–230 mesh, Brockmann, activity grade 1), using a 1:50 substrate-adsorbent ratio. The dioxetanes, however, were chromatographed on Florisil (1:60 substrate to adsorbent ratio) at –60 to –70°C. TLC analysis was performed on silica gel plates 40 × 80 mm with fluorescence indicator. Usually the same solvent system as for the column chromatography was used. Drying of reaction mixtures after aqueous work-up was usually conducted over anhydrous sodium sulfate. Stirring was performed magnetically. Peroxide tests were carried out with potassium iodide in acetic acid. Solvents that were used in the synthesis of dioxetanes and for chemiluminescence measurements were stirred for 24 h over the disodium salt of EDTA and freshly distilled before use. Unless stated, recrystallizations of dioxetanes were performed in methylene chloride/petroleum ether mixtures.

General Procedure for the Preparation of 1,4-Dioxines **1b–e** *Starting from the Corresponding Benzoins*[7]: Through the stirred solution of 50 mmol of the corresponding benzoin and 150 ml of absol. methanol for 6–8 h dry hydrogen chloride gas was passed at a moderate rate at 20–30°C. After standing at 20°C for 48 h, the precipitate, consisting of compounds **5** and **6**, was collected on a Büchner funnel and dried. The solid product was heated with *p*-toluenesulfonic acid (TsOH) in acetic anhydride to 160°C. The amounts and reaction times are given in the individual experiments below. After cooling to 0°C, the precipitated dioxine was collected on a Büchner funnel.

Tetraphenyl-1,4-dioxine (**1b**): With 10.6 g of benzoin, leading to ca. 3.9 g of a precipitate, which was allowed to react with 0.511 g (2.97 mmol) of TsOH in 25 ml of acetic anhydride for 20 min, yielding 3.15 g (32%) of dioxine, m.p. 214–217°C (lit.[7] 214°C), yellow needles from toluene/petroleum ether.

Tetrakis(4-methylphenyl)-1,4-dioxine (**1c**): From 12.0 g of toluoin, leading to ca. 7.3 g of a precipitate which was allowed to react with 5.23 g (30.4 mmol) of TsOH in 50 ml of acetic anhydride for 5 min; yield 4.86 g (44%), m.p. 216–220°C, yellow needles from toluene/petroleum ether. – IR (KBr): 3025, 2915, 1655, 1610, 1520, 1275, 1185, 1115, 1075, 1020, 1000, 830, 720 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 2.30 (s; 12H, CH_3), 7.20 (AA'BB'-system; 16H, aromat.). – ^{13}C NMR ($CDCl_3$, 22.6 MHz): δ = 21.28 (q; CH_3), 128.13 (d), 128.74 (d), 130.17 (s), 135.57 (s), 137.90 (s). – MS (70 eV): *m/e* = 444 (8%, M^+), 341 (2, $M^+ - H_3CC_6H_4C$), 325 (3, $M^+ - H_3CC_6H_4CO$), 206 (17, $CH_3C_6H_4C{\equiv}CC_6H_4CH_3^+$), 119 (100, $H_3CC_6H_4CO^+$), 91 (31, $H_3CC_6H_4^+$).

$C_{32}H_{28}O_2$ (444.6) Calcd. C 86.45 H 6.35 Found C 86.60 H 6.24

Tetrakis(4-methoxyphenyl)-1,4-dioxine (**1d**): From 13.6 g of anisoin, leading to ca. 7.5 g of a precipitate, which was allowed to react with 1.43 g (8.29 mmol) of TsOH in 50 ml of acetic anhydride for 3 min, yielding after column chromatography, eluting with petroleum ether/methylene chloride (2:1) ($R_F \approx 0.2$), 3.71 g (29%) of dioxine, m.p. 175–177°C, yellow prisms from toluene/petroleum ether. – IR (KBr): 3080, 3000, 2950, 2930, 2900, 2840, 1650, 1605, 1570, 1515, 1465, 1440, 1360, 1295, 1250, 1175, 1075, 1035, 995, 835 cm^{-1}. – ^{1}H NMR

($CDCl_3$, 400 MHz): δ = 3.77 (s; 12H, OCH_3), 6.77 (AA'-part of an AA'XX'-system; 8H, aromat.), 7.31 (XX'-part of an AA'XX'-system; 8H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.22 (q; OCH_3), 113.56 (d), 125.66 (s), 129.57 (d), 134.90 (s), 159.31 (s). – MS (70 eV): *m/e* = 508 (13%, M^+), 238 (15, $H_3COC_6H_4C{\equiv}CC_6H_4OCH_3^+$), 223 (15), 135 (100, $H_3COC_6H_4CO^+$), 107 (4, $H_3COC_6H_4^+$).

$C_{32}H_{28}O_6$ (508.6) Calcd. C 75.57 H 5.55 Found C 75.28 H 5.51

Tetrakis(4-methoxyphenyl)furan: A 3.00 g sample of the precipitate obtained in the preparation of **1d**, was heated with 0.30 g (2.20 mmol) of zinc chloride in 30 ml of acetic anhydride for 2 min at 160°C. After removal of the solvent by distillation at 60°C/20 Torr, the residue was chromatographed on silica gel eluting with methylene chloride, affording 100 mg of the furan ($R_F \cong 0.4$), m.p. 216–218°C, colorless prisms from benzene/petroleum ether. – IR (KBr): 3060, 3030, 2980, 2920, 2830, 1615, 1595, 1580, 1570, 1515, 1500, 1460, 1440, 1300, 1290, 1250, 1175, 1110, 1035, 945, 835, 805 cm^{-1}. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 3.80 (s; 12H, OCH_3), 6.7–7.6 (m; 16H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.11 (q; OCH_3), 55.23 (q; OCH_3), 113.95 (d), 123.39 (s), 124.32 (s), 125.97 (s), 127.21 (d), 131.63 (d), 147.23 (s; C-2 and -5), 158.72 (s), 158.90 (s). – MS (70 eV): *m/e* = 492 (100%, M^+), 477 (18, $M^+ - CH_3$), 357 (12, $M^+ - H_3COC_6H_4CO$), 135 (40, $H_3COC_6H_4CO^+$), 107 (5, $H_3COC_6H_4^+$).

$C_{32}H_{28}O_5$ (492.6) Calcd. C 78.03 H 5.73 Found C 77.85 H 5.57

Tetrakis(4-chlorophenyl)-1,4-dioxine (**1e**): From 14.1 g of 4,4'-dichlorobenzoin, affording ca. 3.5 g of a precipitate, which was allowed to react with 1.88 g (10.9 mmol) of TsOH in 30 ml of acetic anhydride for 45 min, yielding after passing through a short column of basic aluminium oxide with methylene chloride as eluant 1.73 g (13%) of dioxine, m.p. 248–251°C, yellow needles from toluene/petroleum ether. – IR (KBr): 3060, 1665, 1595, 1500, 1405, 1355, 1280, 1175, 1100, 1075, 1020, 835, 760 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.20 (AA'BB'-system; 16H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 128.86 (d), 129.74 (d), 130.89 (s), 134.80 (s), 135.37 (s). – MS (70 eV): *m/e* = 526 (8%, M^+), 246 (18, $ClC_6H_4C{\equiv}CC_6H_4Cl^+$), 176 (14), 139 (100, $ClC_6H_4CO^+$), 111 (10, $ClC_6H_4^+$).

$C_{28}H_{16}Cl_4O_2$ (526.3) Calcd. C 63.91 H 3.06 Found C 64.13 H 3.10

2,3-Dihydro-2-methoxy-2,3,5,6-tetrakis(4-methoxyphenyl)-1,4-dioxine (**5d**): Through the stirred solution of 6.67 g (24.5 mmol) of anisoin and 80 ml of absol. methanol for 6 h dry hydrogen chloride gas was passed at a moderate rate at 20–30°C. After standing at 20°C for 48 h, the precipitate was collected by filtration and chromatographed on silica gel with methylene chloride as eluent affording 1.50 g (22%) of **5d** ($R_F \approx 0.3$), m.p. 223–227°C, colorless prisms from petroleum ether/methylene chloride. – IR (KBr): 3035, 2995, 2930, 2900, 2835, 1655, 1610, 1510, 1460, 1440, 1300, 1245, 1175, 1140, 1105, 1070, 1030, 1005, 980, 940, 835 cm^{-1}. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 3.33 (s; 3H, OCH_3), 3.7–3.8 (m; 12H, OCH_3), 4.68 (s; 1H, 3-H), 6.7–7.4 (m; 16H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 50.17 (q; OCH_3), 55.21 (q; OCH_3), 82.48 (d; C-3), 99.82 (s; C-2), 112.79 (d), 113.19 (d), 113.38 (d), 113.50 (d), 127.45 (s), 127.87 (s), 128.09 (s), 128.73 (s), 129.57 (d), 129.94 (d), 130.12 (s), 130.28 (d), 130.58 (d), 134.79 (s), 158.85 (s), 159.08 (s), 159.48 (s), 159.73 (s). – MS (70 eV): *m/e* = 540 (2%, M^+), 492 (9), 270 (100), 227 (38), 135 (52, $H_3COC_6H_4CO^+$).

$C_{33}H_{32}O_7$ (540.6) Calcd. C 73.32 H 5.97 Found C 73.62 H 6.23

2,5-Dimethyl-3,6-diphenyl-1,4-dioxine (**1f**): A mixture of 1.00 g (3.05 mmol) of 2,5-dimethoxy-2,5-dimethyl-3,6-diphenyl-1,4-dioxane[8] and 150 mg (0.87 mmol) of TsOH in 7 ml of acetic anhydride was heated for 2 min at 160°C. After cooling to 0°C, the precipitate was collected by filtration and recrystallized; yield 0.41 g (51%), m.p. 153–155°C, yellow

plates from petroleum ether/methylene chloride. – IR (KBr): 3040, 3000, 1680, 1495, 1445, 1390, 1335, 1315, 1285, 1245, 1140, 1075, 1050, 1020, 920, 770, 750, 700 cm^{-1}. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 1.95 (s; 6H, CH_3), 7.23–7.53 (m; 10H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.71 (q; CH_3), 127.64 (d), 127.68 (d), 128.05 (d), 132.04 (s), 133.18 (s), 133.26 (s). – MS (70 eV): *m/e* = 264 (14%, M^+), 249 (2, $M^+ - CH_3$), 116 (100, $C_6H_5C{\equiv}CCH_3^+$), 105 (37, $C_6H_5CO^+$), 77 (30, $C_5H_5^+$), 43 (16, CH_3CO^+).

$C_{18}H_{16}O_2$ (264.3) Calcd. C 81.79 H 6.10 Found C 81.79 H 5.96

General Procedure for the Photooxygenation of the 1,4-Dioxines **1**: Photosensitized singlet oxygenation of ca. 0.01 M methylene chloride solutions of the 1,4-dioxines **1** at –78°C, using tetraphenylporphine as sensitizer and a 150-W sodium street lamp as radiation source[1b], led to complete consumption (monitored by TLC) of the dioxines within the time stated for the individual experiments. The methylene chloride was roto-evaporated and the residue chromatographed on Florisil, affording the corresponding bisdioxetanes **2** together with other products. The details of the individual derivatives are given below.

1,3,6,8-Tetraphenyl-2,4,5,7,9,10-hexaoxatricyclo[6.2.0.0^{3,6}]decane (**2b**): Photooxygenation of 420 mg (1.08 mmol) of **1b**[2] afforded after 2.5 h and Florisil chromatography, eluting with petroleum ether/methylene chloride (2:1), 110 mg (22%) of **2b** as first fraction (R_F ≈0.4), m. p. 111°C (lit.[2] 103–104°C), yellow prisms from petroleum ether/methylene chloride, as second fraction (R_F ≈0.1) 103 mg (21%) of benzil, m. p. 96°C (lit.[27a] 95–96°C), and as third fraction (R_F ≈0.03) 210 mg (43%) of *cis*-stilbenediol dibenzoate (**7b**), m. p. 160–162°C (lit.[10] 159°C).

2b: ^1H NMR ($CDCl_3$, 90 MHz): δ = 7.1–7.4 (m; 12H, aromat.), 7.5–7.8 (m; 8H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 107.80 (s; C-1, -3, -6, -8), 127.65 (d), 128.02 (d), 129.99 (d), 133.65 (s).

$C_{28}H_{20}O_6$ (452.5) Calcd. C 74.33 H 4.46 Found C 74.43 H 4.33

1,3,6,8-Tetrakis(4-methylphenyl)-2,4,5,7,9,10-hexaoxatricyclo[6.2.0.0^{3,6}]decane (**2c**): Photooxygenation of 400 mg (0.90 mmol) of **1c** afforded after 1.5 h and Florisil chromatography, eluting with petroleum ether/methylene chloride (3:1), 120 mg (26%) of **2c** as first fraction (R_F ≈0.8; petroleum ether/methylene chloride 1:1), m. p. 117–122°C (yellow prisms from petroleum ether/methylene chloride), and as second fraction (R_F ≈0.1) 60 mg (14%) of 4,4′-dimethylbenzil, m. p. 102–104°C (lit.[27b] 104–105°C).

2c: ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.28 (s; 12H, CH_3), 7.08 (d, *J* = 8.2 Hz; 8H, aromat.), 7.51 (d, *J* = 8.2 Hz; 8H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.34 (q; CH_3), 107.89 (s; C-1, -3, 6-, -8), 127.48 (d), 128.60 (d), 130.79 (s), 139.81 (s).

$C_{32}H_{28}O_6$ (508.6) Calcd. C 75.58 H 5.55 Found C 75.49 H 5.49

1,3,6,8-Tetrakis(4-methoxyphenyl)-2,4,5,7,9,10-hexaoxatricyclo[6.2.0.0^{3,6}]decane (**2d**): Photooxygenation of 120 mg (0.24 mmol) of **1d** afforded after 40 min and Florisil chromatography, eluting with petroleum ether/ethyl acetate/methylene chloride (2:1:2), 43 mg (32%) of **2d** as first fraction, m. p. 105–106°C (dec.), yellow prisms from petroleum ether/methylene chloride, as second fraction (R_F ≈0.3) 7 mg (6%) of 4,4′-dimethoxybenzil, m. p. 128–130°C (lit.[28] 133°C), and as third fraction (R_F ≈0.2) 42 mg (33%) of 1,2-bis(4-methoxyphenyl)-1,2-ethendiyl bis(4-methoxybenzoate) (**7d**), m. p. 192–194°C (lit.[10] 187°C).

2d: ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.81 (s; 12H, OCH_3), 6.81 (d, *J* = 8.3 Hz; 8H, aromat.), 7.57 (d, *J* = 8.3 Hz; 8H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.19 (q; OCH_3), 107.95 (s; C-1, -3, -6, -8), 113.03 (d), 125.65 (s), 129.14 (d), 160.07 (s).

$C_{32}H_{28}O_{10}$ (572.6) Calcd. C 67.12 H 4.93 Found C 67.45 H 4.93

1,3,6,8-Tetrakis(4-chlorophenyl)-2,4,5,7,9,10-hexaoxatricyclo[6.2.0.0^{3,6}]decane (**2e**): Photooxygenation of 300 mg (0.57 mmol) of **1e** afforded after 2.5 h and Florisil chromatography, eluting with petroleum ether/methylene chloride (1:1), 50 mg (15%) of **2e** as first fraction ($R_F \approx 0.7$), m.p. 195–197°C (dec.), yellow prisms from petroleum ether/methylene chloride, and as second fraction ($R_F \approx 0.4$) 200 mg (63%) of 4,4'-dichlorobenzil, m.p. 199–200°C (lit.[29] 200°C).

2e: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.29 (d, J = 8.6 Hz; 8H, aromat.), 7.55 (d, J = 8.6 Hz; 8H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 107.40 (s; C-1, -3, -6, -8), 128.68 (d), 129.10 (d), 131.91 (s), 136.76 (s).

$C_{28}H_{16}Cl_4O_6$ (590.2) Calcd. C 56.98 H 2.73 Found C 57.27 H 2.68

1,6-Dimethyl-3,8-diphenyl-2,4,5,7,9,10-hexaoxatricyclo[6.2.0.0^{3,6}]decane (**2f**): Photooxygenation of 360 mg (1.36 mmol) of **1f** afforded after 5 h and Florisil chromatography, eluting with petroleum ether/methylene chloride (1:1), 240 mg (54%) of **2f** as first fraction ($R_F \approx 0.7$), m.p. 90–98°C, yellow prisms from petroleum ether/methylene chloride, and as second fraction ($R_F \approx 0.2$) 60 mg (13%) (3*R*,4*S*)-3-acetoxy-4-(benzoyloxy)-4-methyl-3-phenyl-1,2-dioxetane (**3f**), m.p. 100–109°C, colorless needles from petroleum ether/methylene chloride.

2f: IR (CCl_4): 3070, 3030, 2940, 1500, 1460, 1395, 1275, 1210, 1185, 1170, 1150, 1125, 1050, 1035, 1020, 920, 885, 700 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 1.53 (s; 6H, CH_3), 7.4–7.6 (m; 6H, aromat.), 7.8–8.0 (m; 4H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.92 (q; CH_3), 106.08 (s), 108.23 (s), 127.33 (d), 128.60 (d), 130.30 (d), 134.36 (s).

$C_{18}H_{16}O_6$ (328.3) Calcd. C 65.85 H 4.91 **2f**: Found C 65.82 H 4.67
3f: Found C 66.06 H 4.94

3f: IR (CCl_4): 3060, 2930, 1775, 1740, 1450, 1380, 1270, 1215, 1145, 1020, 905, 865, 705 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.71 (s; 3H, CH_3), 2.05 (s; 3H, $COCH_3$), 7.49–7.60 (m; 5H, aromat.), 7.70–7.74 (m; 1H, aromat.), 7.77–7.81 (m; 2H, aromat.), 8.20–8.21 (m; 2H, aromat.). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.16 (q; CH_3), 21.48 (q; CH_3), 109.46 (s), 112.44 (s), 126.24 (d), 128.70 (d), 128.81 (d), 129.06 (s), 129.94 (d), 134.04 (d), 134.85 (s), 163.97 (s), 167.61 (s).

3f was also obtained by allowing a solution of 300 mg (0.91 mmol) of **2f** in 20 ml of methylene chloride to stand for 14 d at ca. 25°C. Florisil chromatography, eluting with petroleum ether/methylene chloride (1:1) afforded 50.0 mg (17%) of **3f**.

Thermolysis of Dioxetanes: Samples (0.02–0.1 mmol) of the dioxetanes in 5 ml of tetrachloromethane were heated at ca. 75°C until the peroxide test was negative (5–10 h). After roto-evaporation of the solvent, the anhydride products were purified by recrystallization.

Benzoic Anhydride (**4b**): 7.0 mg (70%) colorless prisms from ether, m.p. 41–42°C (lit.[27a] 42–43°C), obtained from 10.0 mg (0.02 mmol) **2b**.

Bis(4-methylbenzoic) Anhydride (**4c**): 17.0 mg (80%) colorless needles from ethanol, m.p. 93–95°C (lit.[30] 95°C), obtained from 21.0 mg (0.04 mmol) **2c**.

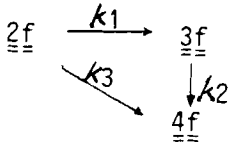
Bis(4-methoxybenzoic) Anhydride (**4d**): 11.0 mg (73%) colorless needles from petroleum ether/ether, m.p. 97–99°C (lit. [31] 99°C), obtained from 15.0 mg (0.026 mmol) **2d**.

Bis(4-chlorobenzoic) Anhydride (**4e**): 7.5 mg (75%) colorless prisms from aqu. acetone, m.p. 190–192°C (lit.[32] 193–194°C), obtained from 10.0 mg (0.017 mmol) **2e**.

Acetic Benzoic Anhydride (**4f**) (lit.[33] m.p. 10°C) was obtained quantitatively from **2f** and **3f**. – IR (CCl_4): 3060, 1820, 1745, 1600, 1455, 1370, 1265, 1150, 1075, 1060, 1040, 1020,

730 cm^{-1}. – ^1H NMR (CCl_4, 90 MHz): δ = 2.37 (s; 3H, CH_3), 7.3–7.7 (m; 3H, aromat.), 7.9–8.2 (m; 2H, aromat.).

^1H NMR Kinetics of the Thermal Decomposition of the Bisdioxetane **2f**: The decomposition of a ca. 0.2 M **2f** solution in $CDCl_3$ was monitored directly in the Perkin Elmer Hitachi R-24 B NMR spectrometer using dimethyl sulfone (δ = 3.1) as internal standard. The sample was heated at 70.0°C for 100 min and every 5 min a ^1H NMR spectrum was recorded. As the methyl resonance of **2f** at δ = 1.5 disappeared, those of the monodioxetane **3f** at δ = 1.7 and 2.1 and of the anhydride **4f** at δ = 2.4 appeared. The signals were integrated three times and the relative concentrations (I_{rel}) calculated accordingly. The concentration-time curves of **2f**, **3f**, and **4f** are shown in Fig. 1. A computer simulation of these data, using the kinetic scheme[34] of eq. (2) and taking the experimental rate constant $k_{obs} = k_1 + k_3 = 3.4 \cdot 10^{-4} s^{-1}$ for the decay of **2f**, the best agreement (full lines in Fig. 1) was obtained when $k_1 = 2.1 \cdot 10^{-4} s^{-1}$, $k_2 = 5.3 \cdot 10^{-4} s^{-1}$, and $k_3 = 1.3 \cdot 10^{-4} s^{-1}$.



(2)

Chemiluminescence Measurements: The total chemiluminescence intensities were determined with a Mitchell Hastings photometer[35a], equipped with a RCA PF 1006A photomultiplier tube and a Servogor Model 210 recorder. Constant temperature in the photomultiplier compartment was maintained within 0.1 °C of the desired temperature by means of a thermostated variable temperature circulating bath (MGW Lauda). A Packard scintillation glass vial was charged with 3.0 ml of the fluorophor solution (enhanced chemiluminescence), placed into the cell compartment, and allowed to equilibrate thermally (ca. 5 min). The required amount of the dioxetane was added directly by means of a calibrated glass pipette and the chemiluminescence signal (in volts) recorded vs. time, covering usually at least three half-lives. The voltage signals were converted to luminescence units (Einstein/sL) using an experimentally established conversion factor, which was determined with the help of a calibrated POPOP-PPO scintillation mixture[35b], kindly supplied by Professor *J. W. Hastings*, Harvard University. From the intensity vs. time plots the total chemiluminescence intensities were extrapolated to zero time (t_0), affording the initial intensities (I_0). A first-order rate analysis of the intensity decay with time afforded the observed rate constants (k_{obs}).

Determination of Activation Parameters: Solutions (ca. 10^{-3}–10^{-4} M) of the dioxetanes **2** and **3** in toluene and appropriate concentrations (10^{-3}–10^{-5} M) of 9,10-dibromoanthracene (DBA) as fluorophor were placed into the cell compartment of the Mitchell Hastings photometer and the enhanced chemiluminescence intensity vs. time profile was monitored on a Servogor 210 recorder under isothermal conditions as described under chemiluminescence measurements. Rate constants were acquired at five to six temperatures, covering a temperature range of ca. 20°C, and processed according to the Eyring equation (3). The results are summarized in Table 1.

$$\ln(k_{obs}/T) = -\Delta H^{\neq}/R \cdot T + \ln(k/h) + \Delta S^{\neq}/R \qquad (3)$$

Determination of Excitation Yields[1]: The interception of a double reciprocal plot of the enhanced chemiluminescence intensity (I^{EC}) and fluorophor concentration (Stern Volmer

plot) afforded the intensity (I_{∞}^{EC}) at infinite fluorophor (F) concentration. The enhanced chemiluminescence quantum yield (Φ_F^{EC}) was calculated via eq. (4), in which $[Diox]_0$ is the initial dioxetane concentration; the remaining terms are already defined.

$$\Phi_F^{EC} = I_{\infty}^{EC}/k_{obs}[Diox]_0 \quad (4)$$

The singlet (Φ^S) and triplet (Φ^T) excitation yields were calculated from eq. (5), where Φ_{ET} is the quantum yield for energy transfer from the chemi-energized excited ketone to the

$$\Phi^{S,T} = \Phi_F^{EC}/\Phi_{ET} \cdot \Phi_F^{fl} \quad (5)$$

fluorophor, Φ_F^{fl} the fluorescence yield of the fluorophor (F), and the Φ_F^{EC} term as already defined. For the singlet excitation yields (Φ^S), 9,10-diphenylanthracene (DPA) was used as fluorophor, for which $\Phi_{DPA}^{fl} = 1.00$[36] and $\Phi_{ET} = \Phi_{DPA}^{SS} = 1.00$. For the triplet excitation yields (Φ^T) 9,10-dibromoanthracene (DBA) was used as fluorophor, for which $\Phi_{ET} = \Phi_{DBA}^{TS} = 0.25$[37]. Since the fluorescence yield of DBA (Φ_{DBA}^{fl}) is temperature dependent, it was corrected according to eq. (6), using $\Phi_{DBA}^{fl} = 0.1$[38] for 20°C (T_1) and $E_a = -4.5$ kcal/mol[36]. The enhanced chemiluminescence data were processed on a Tektronix 4051 computer and the results are summarized in Table 2.

$$\ln \Phi_{DBA}^{fl}(T_2) = E_a/R \cdot (T_2 - T_1)/(T_1 \cdot T_2) + \ln \Phi_{DBA}^{fl}(T_1) \quad (6)$$

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**) Dissertation, Universität Würzburg, July 1984.

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