91898-22-5; **30**, 91898-23-6; **31**, 91928-34-6; **32**, 91928-35-7; **33**, 87770-97-6; **34**, 51308-90-8; **35**, 91898-24-7; **36**, 4153-24-6; **37**, 91898-25-8; **38**, 91898-26-9; **39**, 4267-13-4; **40**, 91898-27-0; **41**, 91898-28-1; **42**, 71662-03-8; **43**, 91898-29-2; **44**, 51326-52-4; **45**, 91898-30-5; **46**, 91898-31-6; **47**, 91898-32-7; **48**, 91898-33-8; **49**, 91898-34-9; **50**, 53958-71-7; **51**, 91898-35-0; **52**, 14739-10-7; **53**, 91898-36-1; **54**, 91898-37-2; **55**, 91928-36-8; **56**, 91898-38-3; **57**, 69891-85-6; **58**, 91898-39-4; **59**, 91898-40-7; **60**, 91898-41-8; **61**, 91898-42-9; **62**, 22054-14-4; $Ph(CH_2)_2CH_2OH$, 122-97-4; $Me(CH_2)_{10}CH_2OH$, 112-53-8; $Me(CH_2)_6CH(OH)(CH_2)_3Me$, 10203-33-5; $Me(CH_2)_7CHO$, 124-19-6; Me_2BBr, 5158-50-9; Ph_2BBr, 5123-17-1; Menthol, 1490-04-6; 1-butylcyclohexanol, 5445-30-7; 2-naphthalenecarboxaldehyde, 66-99-9; cyclooctanone, 27457-18-7; dibenzo[*a*,*d*]cycloheptenone, 2222-33-5; 2-benzylcyclohexanone, 946-33-8; *trans*-1,2-cycloheptanediol, 13553-19-0.

Supplementary Material Available: Full spectral data (IR, ^1H NMR, and mass spectrum) for compounds studied in the paper (8 pages). Ordering information is given in any current masthead page.

Synthesis, Thermal Stability, and Chemiluminescence Properties of the Dioxetanes Derived from 1,4-Dioxins

Waldemar Adam,*[†,‡] Eva-Maria Peters,[§] Karl Peters,[§] Herbert Platsch,[†,∥] Ernst Schmidt,[†] Hans Georg Von Schnering,[§] and Kiyoshige Takayama[‡]

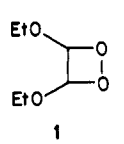
Institut für Organische Chemie, Universität Würzburg, D-8700 Würzburg, West Germany, Departamento de Quimica, Universidad de Puerto Rico, Rio Piedras, Puerto Rico 00931, and the Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, West Germany

Received March 15, 1984

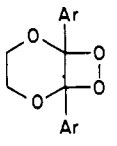
Photosensitized singlet oxygenation of benzo- and naphtho-1,4-dioxins **3** afforded the corresponding 1,2-dioxetanes **4** in moderate to good yields. Ene products **7** were obtained in those cases in which the 1,4-dioxins **3** bear alkyl substituents. Thermal decomposition of the 1,2-dioxetanes **4** afford the corresponding diesters **5** essentially quantitatively. The X-ray crystal structures of the dioxetanes **4g**, **4h**, and **4j** indicate that the four-membered rings are all essentially planar. These dioxetanes exhibit surprisingly similar thermal stabilities; the free energies of activation ($\Delta G^{\ddagger}$) at 298 K fall within 26 ± 1 kcal/mol, the enthalpies of activation ($\Delta H^{\ddagger}$) within 24 ± 1.5 kcal/mol, and the entropies of activation ($\Delta S^{\ddagger}$) within −6 ± 2 eu. In their chemiluminescence properties they are inefficient sources of chemienergized, electronically excited diester products. The singlet excitation yields (ϕ^S) range between 0.0001% and 0.003% and the triplet excitation yields (ϕ^T) between 0.01% and 3.5%. They represent typical dioxetanes in that preferentially triplet excited carbonyl products are chemienergized.

Introduction

The dyestuff-sensitized photooxygenation of electron-rich alkenes such as dialkoxy-substituted ethylenes has proved itself as one of the effective means of preparing 1,2-dioxetanes.[1] In fact, 3,4-diethoxy-1,2-dioxetane (**1**),



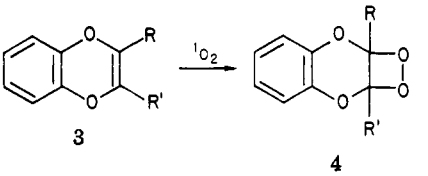
1



2

which was conveniently prepared from 1,2-diethoxyethylene in this way,[2] constituted one of the first fully characterized 1,2-dioxetanes. Similarly, the singlet oxygenation of cyclic analogues, e.g., 2,3-diaryl-1,4-dioxenes, provided an efficient entry into the 1,2-dioxetanes **2**.[3] The latter have been useful substrates for the mechanistic elucidation of the chemiluminescence properties associated with 1,2-dioxetanes.[4]

In this context we have been interested in the related 1,2-dioxetanes **4**, derived from the singlet oxygenation of the corresponding benzo-1,4-dioxins **3** (eq 1).[5] In view of



3 **4** (1)

the fact that the synthetic problem of preparing derivatives of **3** which are mono- and disubstituted in the 2,3-positions was recently solved,[6] a number of interesting 1,2-dioxetanes **4** were in principle accessible via eq 1. Presently we report on the synthesis and characterization of an extensive series of such dioxetanes, together with the elucidation of their thermal stability and chemiluminescence properties.

Results

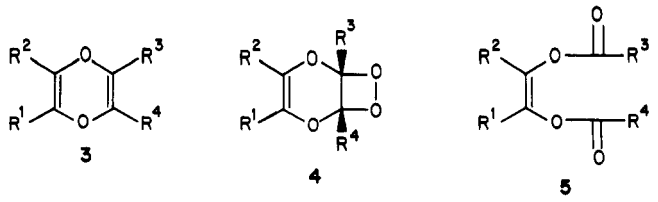
Synthetic Work. 1,4-Dioxins 3. In this study the benzo-1,4-dioxins **3a–k** and the 2,3-naphtho-1,4-dioxin **3l**

* Direct correspondence to the Würzburg address.
† Universität Würzburg.
‡ Universidad de Puerto Rico.
§ Max-Planck-Institut.
∥ Undergraduate research participant, fall 1983.

(1) Adam, W., Cilento, G., Eds. "Chemical and Biological Generation of Electronically Excited States"; Academic Press: New York, 1982.
(2) Bartlett, P. D.; Schaap, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 3223.
(3) Schaap, A. P.; Burns, P. A.; Zaklika, K. A. *J. Am. Chem. Soc.* **1977**, *99*, 1270.
(4) (a) Zaklika, K. A.; Kissel, T.; Thayer, A. L.; Burns, P. A.; Schaap, A. P. *Photochem. Photobiol.* **1979**, *30*, 35. (b) Nakamura, H.; Goto, T. *Ibid.* **1979**, *30*, 27.
(5) Adam, W.; Cueto, O.; Schmidt, E.; Takayama, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1031.
(6) Adam, W.; Schmidt, E.; Takayama, K. *Synthesis* **1982**, 322.

0022-3263/84/1949-3920$01.50/0

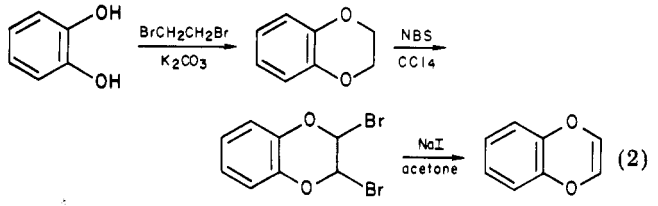
were prepared following literature procedures.[6-8] Thus,



3 **4** **5**

a, $R^1 + R^2$ = benzo; $R^3 = R^4 = H$
b, $R^1 + R^2$ = benzo; R^3 = Me; $R^4 = H$
c, $R^1 + R^2$ = benzo; $R^3 = -(CH_2)_3Br$; $R^4 = H$
d, $R^1 + R^2$ = benzo; $R^3 = -(CH_2)_4Br$; $R^4 = H$
e, $R^1 + R^2$ = benzo; R^3 = Ph; $R^4 = H$
f, $R^1 + R^2$ = benzo; $R^3 = R^4$ = Me
g, $R^1 + R^2$ = benzo; $R^3 + R^4 = -(CH_2)_3$
h, $R^1 + R^2$ = benzo; $R^3 + R^4 = -(CH_2)_4$
i, $R^1 + R^2$ = benzo; R^3 = Me; R^4 = Ph
j, $R^1 + R^2$ = benzo; $R^3 = R^4$ = Ph
k, $R^1 + R^2$ = 3-methoxybenzo; $R^3 = R^4$ = Ph
l, $R^1 + R^2$ = naphtho; $R^3 = R^4$ = Ph

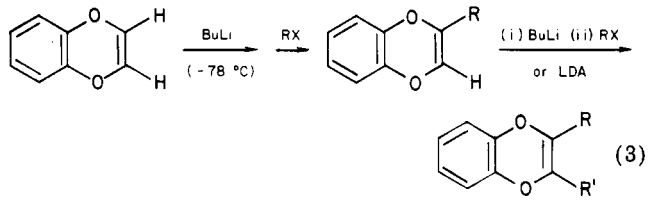
the parent 1,4-dioxin **3a** was obtained by the sequence of reactions shown in eq 2.[7] The bromination step with



(2)

N-bromosuccinimide (NBS) was particularly critical since electrophilic substitution of the benzo ring constituted a menacing side reaction.

As already described,[6] the parent 1,4-dioxin **3a** served as a useful precursor in the preparation of the mono- and disubstituted 1,4-dioxins **3b–d** and **3f–h**. The synthetic sequence that was followed is shown in eq 3. In the first



(3)

lithiation leading to the 2-substituted 1,4-dioxins **3b–d** *n*-BuLi was used, followed by alkylation with methyl iodide, 1,3-dibromopropane, and 1,4-dibromobutane, respectively. However, in the second lithiation the use of *n*-BuLi or lithium diisopropylamide (LDA) depended on the nature of the alkyl group in the 1,4-dioxins **3b–d**. Thus, in the case of **3c** and **3d** the terminal bromine substituent obliged employing LDA, leading to the annelated 1,4-dioxins **3g** and **3h**, respectively. For the alkylations **3b** → **3f** and **3e** → **3i** *n*-BuLi served well its purpose. Although all of these 1,4-dioxins have been reported, the previously lacking analytical and spectral data for some of them are given in the Experimental Section.

(7) (a) Coudert, G.; Guillaumet, G.; Loubinoux, B. *Tetrahedron Lett.* **1978**, 1059. (b) Guillaumet, G.; Coudert, G.; Loubinoux, B. *Ibid.* **1979**, 4379.

(8) Katritzky, A. R.; Sewell, M. J.; Topsom, R. D.; Monro, A. M.; Potter, G. W. H.; *Tetrahedron* **1966**, *22*, 931.

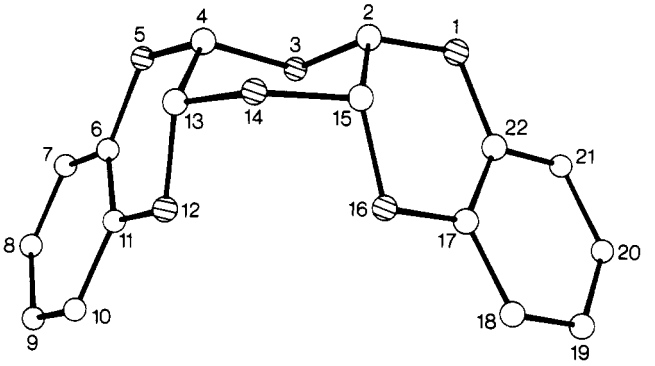
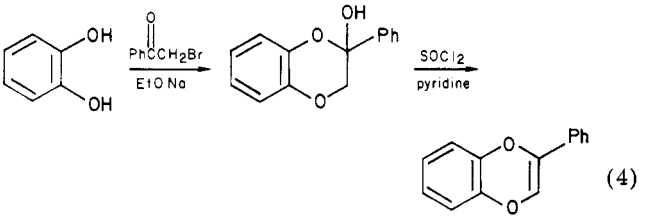


Figure 1. Perspective drawing of dioxane **6**. Hatched circles represent oxygen.

The aryl-substituted 1,4-dioxins **3e** and **3j–l** were prepared according to the sequence shown in eq 4, in which derivative **3e** is illustrated.[8] This procedure was adapted



(4)

for the preparation of the 1,4-dioxins **3j–l**, by using α-bromobenzyl phenyl ketone and 1,2-dihydroxybenzene, 2,3-dihydroxy-1-methoxybenzene, and 2,3-dihydroxynaphthalene, respectively. The yields, physical constants, spectral data, and analytical data are given in the Experimental Section.

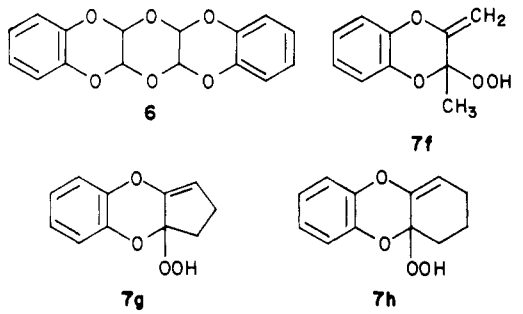
1,2-Dioxetanes 4. These dioxetanes were conveniently prepared[5] via singlet oxygenation of the 1,4-dioxins **3** at −78 °C in methylene chloride using polymer-bound Rose Bengal as sensitizer. TLC monitoring showed that within 2 h the 1,4-dioxin was usually consumed. Removal of the immobilized sensitizer by filtration, rotoevaporation of the solvent, low temperature column chromatography on Florisil, and final recrystallization afforded the analytically pure 1,2-dioxetanes **4**. The experimental details, yields, physical constants, spectral data, and elemental analyses are given in the Experimental Section.

The parent dioxetane **4a** was too unstable for isolation even at low temperatures. At all times only its decomposition product, namely bis(formyloxy)benzene (**5a**), could be isolated and spectroscopically characterized. As main product the unusual substance **6** was isolated in 39% yield, which was fully characterized. An X-ray determination confirms its structure (Figure 1).

The isolation of dioxetane **4b** was also complicated by the fact that singlet oxygenation of 1,4-dioxin **3b** gave mainly ene product similar to **7f**, the latter being derived from the 1,4-dioxin **3f**. In view of these difficulties, no attempts were made to prepare the dioxetanes **4c** and **4d** by singlet oxygenation of the 1,4-dioxins **3c** and **3d**, respectively.

Although the 1,4-dioxins **3g** and **3h** also bear allylic hydrogens and their singlet oxygenation thus beridden by the same problems as **3b**, fortunately sufficient amounts of the respective dioxetanes **4g** and **4h** were produced to permit isolation, purification, and rigorous characterization. The details are given in the Experimental Section, together with the ene products **7g** and **7h**.

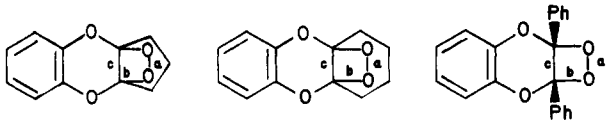
X-ray Structures. Of the 1,2-dioxetanes **4g**, **4h**, and **4j** the crystal structures were determined by X-ray diffraction (for details cf. Experimental Section), primarily



to assess the degree of puckering of the dioxetane ring. As the Figures 2–4 show, the four-membered rings in these dioxetanes are essentially planar within experimental error. The dihedral angles of puckering are ca. 0°, 0°, and 1° respectively for **4g**, **4h**, and **4j**. However, for all three dioxetanes the 1,4-dioxene rings possess a boatlike conformation. Apparently lone pair–lone pair repulsion of the 1,4-dioxene oxygens with the dioxetane oxygen dictates the preferred ring conformations. In fact, even in dioxetane **4h** the annelated cyclohexane ring is obliged to assume a boatlike conformation.

It is of interest to mention that the first attempt to obtain the crystal structure of dioxetane **4h** via X-ray analysis afforded that of its decomposition product, namely catechol adipate (**5h**).

The bond length data for the oxygen–oxygen bond (a), the carbon–oxygen bonds (b), and the carbon–carbon bond (c) of the four-membered rings for the dioxetanes **4g**, **4h**, and **4j** reveal no regularities that can be rationalized in



	(4g)	(4h)	(4j)
a (pm)	158	149	155
b (pm)	144	144	144
c (pm)	158	151	161

terms of structural variations. Nevertheless some interesting features about these data are worthwhile pointing out. Thus, compared to strain-free peroxides, for which the oxygen–oxygen bond length ranges between 148 and 149 pm,[9] expectedly the peroxide bonds in the dioxetanes **4g,j** are significantly elongated. Contrasting the two propellane-type dioxetanes **4g** and **4h**, the former possesses a slightly larger four-membered ring, which could be the consequence of the greater strain in **4g** vs. **4h**. As shall be discussed later, no obvious relationship between bond length and thermal stability can be recognized from the structural data of this series of 1,2-dioxetanes.

Thermal Stability. To assess the thermal stability of these dioxetanes, the activation parameters were determined by means of isothermal kinetics using the chemiluminescence technique to follow dioxetane decomposition.[1] Since the direct chemiluminescence emissions were too weak to record useful intensity vs. time profiles, 9,10-dibromoanthracene (DBA) was employed to enhance the chemiluminescence by means of energy transfer.[1] The first-order decomposition rate constants could be estimated at 97 °C in order to allow comparison of the thermal stability among the various dioxetanes.

A still more serious problem with these dioxetanes was their great propensity for catalytic nonluminescent decomposition by glass wall effects and traces of transition

(9) Hirota, E. *J. Chim. Phys.* **1958**, *28*, 839.
(10) Adam, W.; Cilento, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 529.

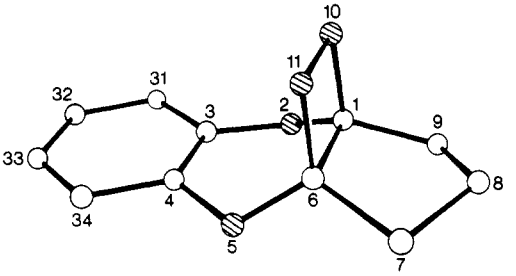


Figure 2. Perspective drawing of dioxetane **4g**. Hatched circles represent oxygen.

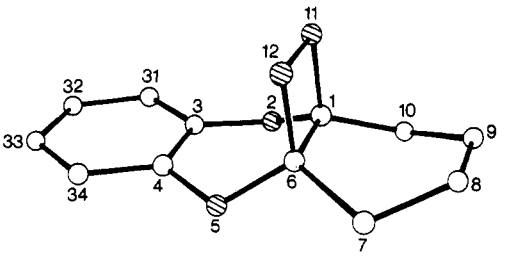


Figure 3. Perspective drawing of dioxetane **4h**. Hatched circles represent oxygen atoms.

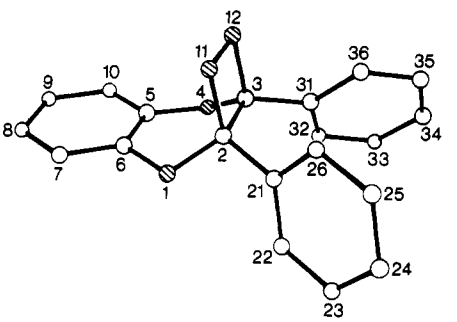


Figure 4. Perspective drawing of dioxetane **4j**. Hatched circles represent oxygen atoms.

metal ions. The latter could be minimized by rinsing the glassware with ethylenediaminetetraacetic acid (EDTA) disodium salt and rigorously purifying the solvents by final distillation from EDTA. However, the menacing and erratic glass wall catalysis was difficult to cope with, matching our experiences with the related dioxetanes **2**. Fortunately, those runs that were badly harassed with such catalytic decomposition could easily be recognized by too fast initial decomposition rates and/or too negative activation entropies ($\Delta S^{\ddagger} < -10$ eu). Sometimes many repetitive runs were necessary to provide the here reported data. In this context it is important to mention that such catalytic decomposition lowers significantly the yields of these dioxetanes, especially during attempted purification by column chromatography. Such decompositions are particularly prone to occur with silica gel as adsorbant, but can be minimized by using Florisil.

The kinetic data for the dioxetanes **4** are summarized in Table I. They are typical for dioxetanes,[1] especially the lack of substituent and structural effects on the activation parameters. Thus, the $\Delta H^{\ddagger}$ values are ca. 24 ± 1 kcal/mol, the $\Delta S^{\ddagger}$ values ca. −6 ± 2 eu, and the $\Delta G^{\ddagger}$ values (at 298 K) ca. 26 ± 1 kcal/mol. In fact, one can state that within the experimental error these activation parameters reveal similar thermal stability for these dioxetanes. For this reason a more sensitive kinetic criterion of stability was sought, namely the less error prone and thus more reliable rate constants (k) of decomposition, all measured at one particular temperature to permit direct comparison. These k values in the last column of Table

Table I. Rate Constants (k_{obsd}), Activation Enthalpies ($\Delta H^{\ddagger}$), Entropies ($\Delta S^{\ddagger}$), and Free Energies ($\Delta G^{\ddagger}$) of the Thermal Decomposition of 1,2-Dioxetanes 4[a]

Dioxetane	Temp. Range,[b] °C	[4]10^4, M	[DBA]10^5,[c] M	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ at 298 K, kcal/mol	$10^3 k_{obsd}$,[d] s^{-1}
4e	79.0–99.0	2.07	3.81	23.8 ± 1	−5.1 ± 1	25.3 ± 1	5.0 ± 0.1
4f	105.0–127.0	2.64	19.1	26.2 ± 1	−3.7 ± 2	27.3 ± 1	0.40 ± 0.02
4g	74.3–97.2	16.7	100	22.5 ± 1	−7.7 ± 1	24.8 ± 1	8.2 ± 0.3
4h	97.0	2.27	100	[e]	[e]	[e]	6 ± 2
4i	104.0–122.0	2.10	3.81	25.1 ± 1	−5.7 ± 2	26.8 ± 1	0.67 ± 0.04
4j	80.3–97.0[f]	3.00	100	24.6 ± 1	−6.3 ± 1	26.5 ± 1	
4j	79.7–103.5[f]	3.36	25.7	24.5 ± 1	−5.4 ± 1	26.1 ± 1	0.99 ± 0.04
4k	82.6–101.8	1.10	10.7	23.6 ± 1	−8.3 ± 2	26.1 ± 1	1.3 ± 0.1
4l	81.1–99.5	20.0	300	25.3 ± 1	−3.8 ± 2	26.4 ± 1	1.4 ± 0.1

[a] Determined in xylene as solvent except **4g** and **4k** for which toluene was used. [b] Temperature was controlled to within 0.1 °C. [c] Since the direct chemiluminescence was too weak for these dioxetanes, 9,10-dibromoanthracene (DBA) was used as fluorophor to enhance the light intensity. [d] Determined independently at 97.0 °C by means of isothermal kinetics. [e] Unreproducible results. [f] Run in duplicate sets to check reproducibility.

Table II. Singlet (ϕ^S), Triplet (ϕ^T), and Total (ϕ^{T+S}) Excitation Yields and Spin-State Selectivities (ϕ^T/ϕ^S) of the Dioxetanes 4[a]

Dioxetane	Temp,[b] °C	[4]10^4, M	[DBA]10^5,[c] M	[DPA]10^4,[d] M	$10^3 k_{obsd}$,[e] s^{-1}	ϕ^T, %	$10^3\phi^S$, %	ϕ^{T+S}, %	ϕ^T/ϕ^S
4e	83.7	1.57	3.54–35.4		1.69 ± 0.1	0.60 ± 0.06			
4e	83.7	1.57		2.41–24.1	2.12 ± 0.3		1.1 ± 0.3	0.60 ± 0.06	500 ± 300
4f	115.5	2.64	3.80–38.0		2.33 ± 0.1	0.012 ± 0.008			
4f	112.7[f]	2.47	35.4–284		2.60 ± 0.4	0.030 ± 0.006		0.012 ± 0.009	400 ± 200
4f	115.5	2.64		3.93–39.3	2.00 ± 0.2		0.12 ± 0.07		
4f	111.8[f]	2.47		3.68–36.8	3.65 ± 0.2		0.07 ± 0.03		
4h	85.8	4.00	10.3–51.7		3.90 ± 0.8	0.013 ± 0.006			
4h	86.1	4.00		8.20–41.0	3.70 ± 0.6		2.6 ± 1.0	0.013 ± 0.006	5 ± 2[g]
4i	115.0	1.07	3.54–28.4		3.70 ● 0.8	3.5 ± 1.3			
4i	115.0	1.07		3.49–34.9	3.60 ± 0.2		1.6 ± 0.2	3.5 ● 1.3	2200 ± 700
4j	95.7	3.36	5.13–51.3		1.95 ± 0.1	1.65 ± 0.23			
4j	96.7	3.36		3.70–37.0	1.95 ± 0.1		1.70 ± 0.18	1.70 ± 0.18	1000 ± 300
4k	96.5	1.12	10.7–107		1.20 ± 0.1	2.50 ± 0.40			
4k	96.5	5.60		21.8–109	1.39 ± 0.2		0.73 ± 0.23	2.5 ± 0.4	3400 ± 1000

[a] Determined in xylene as solvent except **4h** for which toluene was used. [b] Temperature was controlled within 0.1 °C. [c] Using 9,10-dibromanthracene (DBA) as fluorophor for triplet excitation yields. [d] Using 9,10-diphenylanthracene (DPA) as fluorophor for singlet excitation yields. [e] Averaged over the various runs. [f] Duplicate runs to test reproducibility. [g] For such low ϕ^T/ϕ^S ratios corrections of triplet to singlet intersystem crossing is essential (ref 1), but this was not done in view of the difficulties in measuring these data in the first place.

I exhibit a ca. 20-fold range in decomposition rates for these dioxetanes. In view of the substantial variation in substituents and structure of these dioxetanes, the 20-fold range in decomposition rates constitutes a rather small differentiation in thermal stability. It is of interest to point out that these dioxetanes are about as stable as tetramethyl-1,2-dioxetane.[1]

Thermolysis Products. As expected, the thermal decomposition products of the dioxetanes **4** were the diesters **5**, formed essentially quantitatively as confirmed by ^{1}H NMR. These products were purified by silica gel chromatography, followed by crystallization or distillation. The new diesters **5e**, **5g**, and **5h** were fully characterized and the remaining known diesters compared with the reported data. The results are given in the Experimental Section.

Excitation Yields. As pointed out already in the kinetics section, the direct chemiluminescence for all of these dioxetanes was too weak to determine singlet excitation yields (ϕ^S) directly.[1] Besides, the fluorescence yields for none of the diester products **5** were available. For this reason recourse to the energy-transfer chemiluminescence techniques had to be taken in order to determine the excitation yields. For this purpose 9,10-diphenylanthracene (DPA) was employed as fluorophor for the singlet excitation yields (ϕ^S) and 9,10-dibromoanthracene (DBA) as fluorophor for the triplet excitation yields (ϕ^T). These convenient luminescence probes have been described and amply utilized.[1] The results are summarized in Table II. In view of the rather low singlet yields (ϕ^S ranging between 0.0001 and 0.003%) and triplet yields (ϕ^T ranging between 0.01% and 3.5%), the titrimetric probes, e.g., the singlet-sensitized denitrogenation of the azoalkane 7,8-benzo-2,3-diazatricyclo[4.3.0.0^{4,9}]nona-2,7-diene[11] and the triplet-sensitized di-π-methane rearrangement of benzonorbornadiene[12] were not sufficiently sensitive to assess the excitation yields ϕ^S and ϕ^T.

For two dioxetanes, namely **4g** and **4l**, the excitation yields could not be determined even with the luminescence probes DPA and DBA. In the case of the dioxetane **4g** the intensities of the enhanced emissions were too low to obtain reproducible results from the Stern–Volmer plots. In addition to this problem, dioxetane **4l** was also plagued by glass wall catalysis, affording erratic intensities. Despite these difficulties, even the qualitative results reveal that the dioxetanes **4g** and **4l** possess ϕ^S and ϕ^T values near the lower limits of the ranges reported in Table II.

Discussion

Singlet oxygenation of the readily available 1,4-dioxins **3** provides a convenient method for the preparation of the 1,2-dioxetanes **4**. As long as the ene reaction does not predominate, as in those cases in which the 1,4-dioxins **3** bear substituents with allylic hydrogens in the 2- and 3-positions, e.g., **3b** and **3f–h**, the yields of the isolated and purified 1,2-dioxetanes can be quite high (40–80%).

One of the limiting features of these dioxetanes is their great tendency toward nonluminescent decomposition by

(11) Adam, W.; Hannemann, K. *J. Am. Chem. Soc.* **1983**, *105*, 714.
(12) Adam, W.; Cheng, C.-C.; Cueto, O.; Sakanishi, K.; Zinner, K. *J. Am. Chem. Soc.* **1979**, *101*, 1324.

glass wall catalysis. In that respect they are akin to the related dioxetanes **2** derived from 1,4-dioxenes.[3]

In their chemiluminescence properties they are typical dioxetanes in that they exhibit high preference for triplet-state excitation. Thus, with the only exception of dioxetane **4h**, Table II reveals high spin-state selectivities ϕ^T/ϕ^S. Although no spectroscopic evidence exists in view of the weak fluorescence properties of the electronically excited diester products **5**, presumably n,π^* excited states are chemienergized in the decomposition of these dioxetanes.[1]

The total excitation yields (ϕ^{T+S}) are not impressive for dioxetanes **4** (Table II). Clearly, phenyl substitution as in the derivatives **4e**, **4i**, and **4j** provides for more efficient total excitation yields. Thus, dioxetane **4i** is the most efficient in this series. 3-Methoxybenzo substitution as in the dioxetane **4k** does not alter significantly the total excitation yield nor the spin-state selectivity compared to dioxetane **4j**. Unfortunately, for the naphtho-annelated dioxetane **4l**, which also bears phenyl substituents, the excitation yields could not be determined due to surface catalysis. However, as stated already in the Results section, qualitative intensity data show convincingly that the excitation yields are relatively low. Therefore, 3-methoxybenzo- or naphtho- vs. benzo-annelation provides no increase in the excitation efficiencies.

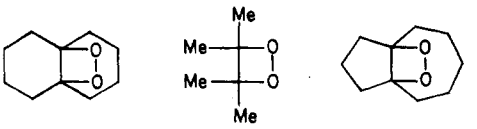
Annelation at the dioxetane carbons, as in the propellane-type dioxetanes **4g** (trimethylene bridging) and **4h** (tetramethylene bridging), causes significant reduction in the excitation efficiencies (Table II). In fact, for dioxetane **4g** the enhanced emissions were so weak that no reproducible intensity values could be extrapolated from the Stern–Volmer plots; but the fact that the qualitative intensities were weak confirms that the excitation yields must be very low. Furthermore, when comparing the total efficiencies of **4h** and the dimethyl-substituted dioxetane **4f** (Table II), we note that they possess identical ϕ^{T+S} values within the experimental error. In view of the empirical trend that annelation usually increases the yields of excited carbonyl products,[1] the poor ability of dioxetanes **4g** and **4h** to energize excited states is surprising. Also unusual is the rather low spin-state selectivity for dioxetane **4h**, i.e., ϕ^T/ϕ^S ca. 5. Since the triplet yields for the dioxetanes **4f** and **4h** are the same within experimental error (Table II), the low spin-state selectivity derives from the fact that the singlet yield is abnormally high in comparison. However, it must be stressed that the absolute singlet yields are at best very small even for dioxetane **4h**, i.e., ϕ^S is only ca. 0.003% or ca. 100-fold less than for tetramethyl-1,2-dioxetane.[1]

In view of the analytical problems of measuring low excitation yields, it behooves us not to place too much confidence in such results and excercise some restraint in their interpretation. Yet, the qualitative conclusion that the 1,4-dioxin-derived dioxetanes **4** are inefficient sources of chemienergized excited diester products is unquestionably valid on the basis of the excitation yield data of Table II.

In regard to the thermal stability of these dioxetanes, the activation parameters of Table I show that they are about as stable as tetramethyl-1,2-dioxetane.[1] In fact, as already pointed out in the Results section, the $\Delta G^{\ddagger}$ values at 298 K fall all within 26 ± 1 kcal/mol. Thus, irrespective of phenyl vs. alkyl substitution, mono- vs. disubstitution, benzo- vs. 3-methoxybenzo- or naphtho-substitution, and even propellane-type annelation, the activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are too insensitive to differentiate thermal stability trends in terms of such structural variations. For this purpose the set of decomposition rate constants (k) measured at one common temperature is more revealing and reliable. However, even for this diverse set of related dioxetanes the differention in decomposition rates is only ca. 20-fold, the most stable dioxetane being the dimethyl derivative **4f** and the least stable being the trimethylene-annelated derivative **4g**.

Despite the small differentiation in thermal stabilities, the k values of Table I bring out some interesting trends. For example, comparing dioxetanes **4e** vs. **4j** as expected[1] disubstitution stabilizes the dioxetane toward thermal cleavage by ca. 5-fold. On the other hand, comparing dioxetanes **4j** vs. **4l**, benzo vs. naphtho substitution causes insignificant changes in the thermal stability.

The largest destabilization is caused by annelation, e.g., the propellane-type dioxetanes **4g** and **4h**, which constitute the least stable members in this series, with the dimethyl derivative **4f** representing the most stable (Table I). Depending on the length of the annelating bridge, the stability can be increased or decreased with respect to the acyclic derivative. For example, taking propellane-type cases for ease of comparison, the dioxetane **8** is much less



	8	**9**	**10**
E_a, kcal/mol	22.7	27.6	29.8

stable than tetramethyl-1,2-dioxetane (**9**),[13] while dioxetane **10** is significantly more stable.[14] Such stability trends have been rationalized in terms of degree of puckering of the dioxetane ring, dictated by conformational effects of the annelated rings.[15] It was argued that six-membered ring annelation as in **8** obliges the most puckered dioxetane ring and hence lowest stability, while five- and/or seven-membered ring annelation as in **10** obliges a planar dioxetane ring and hence highest stability.

On this basis we would have expected that the six-membered ring annelated dioxetane **4b** should be less stable than the acyclic derivatives **4f** or **4j**, but that the five-membered ring annelated dioxetane **4g** should be more stable than **4f** or **4j**. The experimental results (Table I), however, display that **4g** and **4h** are equally stable within experimental error and both only slightly less stable than the acyclic cases **4f** and **4j**. Since the X-ray structures of the dioxetanes **4g**, **4h**, and **4j** (none is available for dioxetane **4f**) all exhibit essentially planar four-membered rings (cf. Figures 2–4), the similar decomposition rates of the dioxetanes **4g**, **4h**, and **4j** is not surprising. Presumably the annelated benzo-1,4-dioxene ring in these dioxetanes controls the conformation of the four-membered ring in these dioxetanes. It urges, therefore, to determine the X-ray structures of dioxetanes such as **8** and **10** and to test the validity of the hypothesis[15] that the thermal stability of annelated dioxetanes depends on the degree of puckering of the four-membered ring.

Experimental Section

Boiling points and melting points are uncorrected and the latter were determined on a Reichert Thermovar apparatus. Infrared spectra were run on a Beckman Acculab 4 spectrometer, ^{1}H NMR at 60 MHz on a Hitachi-Perkin-Elmer R-24B, at 90 MHz on a

(13) Kopecky, K. R.; Filby, J. E.; Mumford, C.; Lockwood, P. A. and Ding, J.-Y. *Can. J. Chem.* **1975**, *53*, 1103.
(14) Kopecky, K. R.; Lockwood, P. A.; Gomez, R. R.; Ding, J.-Y. *Can. J. Chem.* **1981**, *59*, 851.
(15) Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* **1981**, *22*, 4363.

Varian EM 390 spectrometer, and at 400 MHz and at 100.61 MHz for ^{13}C NMR on a Bruker WM 400 spectrometer. Mass spectra were taken on a Varian CH-7 mass spectrometer. Elemental analyses were kindly run for us by Professor G. Maier's staff of the University of Giessen. Solvents were purified according to standard literature procedures. Known compounds were either purchased from commercial suppliers or prepared according to published methods and purified to match reported physical constants and spectral data. Unless stated, solvent removal was conducted by rotoevaporation at 20–30 °C and 20 torr, but in the case of dioxetanes at 0 °C and 20 torr. Column chromatography was run at room temperature on silica gel (70–230 mesh, Brockmann activity grade I) using a 1:30 substrate–adsorbent ratio. Room temperature is unless specified ca. 20–25 °C. The dioxetanes, however, were chromatographed on Florisil (1:60 substrate to adsorbent ratio) at –60 to –70 °C, eluting with CH_2Cl_2 or a 1:1 petroleum ether/CH_2Cl_2 mixture. Drying of reaction mixtures after aqueous workup was conducted over anhydrous sodium sulfate. Unless stated, stirring was performed magnetically. Peroxide tests and titrations 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 EDTA disodium salt and freshly distilled before use.

General Procedure for the Preparation of Alkyl-Substituted Benzo-1,4-dioxins 3b–d, 3f, and 3i.[6] Into a 50-mL, 3-necked flask, provided with a rubber septum, nitrogen gas inlet and outlet, and magnetic spinbar were placed 10 mmol of the corresponding 1,4-dioxin precursor, dissolved in 30 mL of absolute THF. The solution was cooled to –78 °C by means of a Dry Ice bath and with the help of a syringe 9.5 mL of 1.6 N (15.2 mmol) *n*-butyllithium in hexane was added. The reaction mixture turned instantly yellow. After the solution stirred 1 h at –78 °C, 50 mmol of the freshly distilled alkyl halide or α,ω-dihalide was syringed into the lithiated reaction mixture and allowed to warm up to room temperature. After 8 h stirring the volatile materials were removed by rotoevaporation. To the residue were added 10 mL of water and the solution was acidified to pH <3 with 2 N hydrochloric acid. Extraction with ether (4 × 15 mL), washing of the combined ether extracts with saturated aqueous sodium bicarbonate (2 × 10 mL) and with water (1 × 10 ml), drying, and rotoevaporation of the ether afforded the crude product. Silica gel chromatography of the crude product, eluting with a 4:1 petroleum ether/methylene chloride mixture or fractional distillation gave the pure benzo-1,4-dioxins. The details for the individual cases have already been reported.[6] Here we shall give only some additional data that were not available previously.

2-(3-Bromopropyl)benzo-1,4-dioxin (3c): $C_{11}H_{11}BrO_2$, calcd 253.9942, found 253.9944 (MS).

2-(4-Bromobutyl)benzo-1,4-dioxin (3d): $C_{12}H_{13}BrO_2$, calcd 268.0099, found 268.0098 (MS).

2,3-Dimethylbenzo-1,4-dioxin (3f): ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 14.39 (q), 115.49 (d), 123.25 (d), 128.13 (s), 143.10 (s).

2-Methyl-3-phenylbenzo-1,4-dioxin (3i): ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 15.79 (q), 115.39 (d), 115.62 (d), 123.42 (d), 123.61 (d), 127.96 (d), 128.06 (d), 131.73 (s), 131.89 (s), 132.93 (s), 142.65 (s), 143.27 (s); MS (70 eV), *m/e* 224 (100%, M^+), 209 (59%, $M^+ - CH_3$), 181 (32%).

General Procedure for the Preparation of Annelated Benzo-1,4-dioxins 3g and 3h.[6] A 50-mL, 3-necked flask, provided with a rubber septum, nitrogen gas inlet and outlet, and magnetic spin bar, was charged with 133 mg (1.30 mmol) of diisopropylamine in 10 mL of absolute THF and cooled to –78 °C by means of a Dry Ice bath. Into this solution was first syringed 0.8 mL of 1.6 N (1.3 mmol) *n*-butyllithium in hexane and the solution was allowed to warm to room temperature. After 30 min at room temperature, the solution was cooled to –60 °C and while stirring 1 mmol of the corresponding benzo-1,4-dioxins **3c** and **3d** in 5 mL of absolute THF was added by means of a syringe. The reaction mixture was brought to room temperature and worked up as described above. The details for the individual cases have already been reported.[6] Here we shall give only some additional data that were not available previously.

2,3-Dihydro-1*H*-benzo[*b*]cyclopenta[*e*][1,4]dioxin (3g): ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 16.28 (t), 26.54 (t), 116.69 (d), 123.84 (d), 130.50 (s), 142.91 (s).

1,2,3,4-Tetrahydrodibenzo[1,4]dioxin (3h): ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 22.42 (t), 25.08 (t), 115.78 (d), 123.29 (d), 130.34 (s), 143.10 (s).

General Procedure for the Preparation of the Aryl-Substituted 1,4-Dioxins 3e and 3j–l.[8] Into a 250-mL, 3-necked flask, provided with a mechanical stirrer and a dropping funnel were placed under a nitrogen atmosphere 21.8 mmol of 1,2-dihydroxybenzene or naphthalene-2,3-diol or 2,3-dihydroxy-1-methoxybenzene dissolved in 100 mL of dry ethanol. At 0 °C 0.57 g of sodium (25 mmol) was added in portions within 1.5 h. When the hydrogen evolution had finished, 21.8 mmol of α-bromoacetophenone or α-bromobenzyl phenyl ketone dissolved in 100 mL of dry ethanol was added within 1.5 h at room temperature and stirred for 3 h. After neutralization with aqueous ammonium chloride solution, the ethanol was rotoevaporated, and the residue extracted with ether (3 × 50 mL). The combined ether extracts were dried, rotoevaporated, and chromatographed on silica gel, eluting with methylene chloride.

Without further purification 13.8 mmol of the crude products dissolved in 30 mL of pyridine and 1.9 g of thionyl chloride were heated at 90 °C in a 50-mL round-bottomed flask while stirring for 4 h. After cooling to room temperature, 70 mL of ether was added and the reaction mixture washed with 2 N hydrochloric acid (4 × 20 mL) and water (2 × 20 mL). The ether layer was dried and rotoevaporated and the residue chromatographed on silica gel, eluting with a 4:1 petroleum ether (50–70 °C)/methylene chloride mixture affording the pure 1,4-dioxins. Dioxin **3e** has already been fully characterized,[8] but dioxin **3j**, although reported,[16] required like the new dioxins **3k** and **3l** complete characterization. The details for these dioxins are given below.

2,3-Diphenylbenzo-1,4-dioxin (3j)[16] was prepared according to the above procedure starting with 2.40 g (21.8 mmol) of catechol and 6.00 g (21.8 mmol) of α-bromobenzyl phenyl ketone, affording 2.60 g (42%) of pure product: mp 95–96 °C (colorless needles from petroleum ether); IR (CCl_4) 3050, 1610, 1500, 1280, 1045, 1030, 1015, 950 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.80 (s, 4 H, benzo), 7.1–7.4 (m, 10 H, phenyl); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 115.65 (d), 123.74 (d), 127.96 (d), 128.26 (d), 128.48 (d), 132.77 (s), 134.14 (s), 142.97 (s); MS (70 eV), *m/e* 286 (100%, M^+), 257 (19%), 209 (45%, $M^+ - Ph$), 181 (26%, $M^+ - PhCO$), 105 (46%, $PhCO^+$), 77 (22%, Ph^+). Anal. Calcd for $C_{20}H_{14}O_2$ (286.3): C, 83.90; H, 4.93. Found: C, 83.81; H, 4.80.

2,3-Diphenyl-5-methoxybenzo-1,4-dioxin (3k) was prepared according to the above procedure starting with 3.05 g (21.8 mmol) of 2,3-dihydroxy-1-methoxybenzene and 6.00 g (21.8 mmol) of α-bromobenzyl phenyl ketone, affording 1.24 g (18%) of pure product: mp 137 °C (colorless needles from petroleum ether/CH_2Cl_2); IR (KBr) 3050, 2830, 1690, 1605, 1505, 1475, 1335, 1295, 1255, 1205, 1105, 1015, 975, 765, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 3.76 (s, 3 H, OCH_3), 6.43–6.51 (2 H, AB part of an ABX system, J_{AB} = 1.1 Hz), 6.74–6.79 (1 H, X part of an ABX system, J_{AX} = 8.4 Hz, J_{BX} = 8.3 Hz), 7.11–7.18 (m, 6 H, ar), 7.28–7.34 (m, 4 H, ar); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 56.31 (q), 108.00 (d), 108.34 (d), 122.86 (d), 128.05 (d), 128.34 (d), 128.57 (d), 128.66 (d), 132.82 (s), 132.87 (s), 134.11 (s), 134.63 (s), 144.00 (s), 147.86 (s); MS (70 eV), *m/e* 316 (100%, M^+), 239 (60%, $M^+ - Ph$), 211 (21%, $M^+ - PhCO$), 178 (33%), 105 (81%, $PhCO^+$), 77 (33%, Ph^+). Anal. Calcd for $C_{21}H_{16}O_3$ (316.2): C, 79.73; H, 5.10. Found: C, 79.79; H, 5.00.

2,3-Diphenylnaphtho[2,3-*b*][1,4]dioxin (3l) was prepared according to the above procedure starting with 0.58 g (3.60 mmol) of 2,3-dihydroxynaphthalene and 1.00 g (3.60 mmol) of α-bromobenzyl phenyl ketone, affording 0.27 g (22%) of pure product: mp 120–121 °C (colorless needles from ethanol/benzene); IR (CCl_4) 3055, 1670, 1510, 1475, 1360, 1280, 1170, 1040, 1020, 960, 870 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 7.14 (s, 2 H, ar), 7.20–7.24 (m, 6 H, ar), 7.24–7.29 (2 H, AA′ part of an AA′XX′ system, J_{AX} = 8 Hz), 7.31–7.35 (m, 4 H, ar), 7.54–7.59 (2 H, XX′ part of an AA′XX′ system); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 111.38 (d), 125.09 (d), 126.80 (d), 128.15 (d), 128.46 (d), 128.73 (d), 131.27 (s), 132.97 (s), 134.09 (s), 142.92 (s); MS (70 eV), *m/e* 336 (100%, M^+), 307 (18%), 259 (88%, $M^+ - Ph$), 231 (54%, $M^+ - PhCO$), 105 (41%, $PhCO^+$), 77 (25%, Ph^+). Anal. Calcd for $C_{24}H_{16}O_2$

(16) Dagaut, J.; Dizabo, P.; Pompon, A.; Fillaux, J. *OMS* **1975**, *10*, 905.

(336.4): C, 85.69; H, 4.79. Found: C, 85.67; H, 4.66.

General Procedure for the Photooxygenation of the 1,4-Dioxins 3.[5] Photosensitized singlet oxygenation of ca. 0.03 M methylene chloride solutions of the 1,4-dioxins **4** at −78 °C, using polymer-bound Rose Bengal as sensitizer and a 150-W sodium street lamp as radiation source,[17] led to complete consumption of the dioxins within 2 h, as evidenced by TLC. After removal of the polymer-bound Rose Bengal by filtration, the methylene chloride was rotoevaporated and the residue chromatographed on Florisil, affording the dioxetanes **4** and in some cases the hydroperoxides **7**. The details of the individual systems are given below.

1,2-Bis(formyloxy)benzene (5a) (colorless oil, 50 mg (7%)) and **5a,6a,12a,13a-tetrahydro[1,4]benzodioxino[2,3-*b*]-*syn*-[1,4]benzodioxino[2,3-*e*][1,4]dioxin (6)** (colorless prisms, 245 mg (39%) mp 151–153 °C (from petroleum ether/methylene chloride)) were obtained in the photooxygenation of 1.00 g (7.46 mmol) dioxin **3a** following the above procedure, except that the photooxygenation time was prolonged to 8 h and the chromatographic isolation was performed on silica gel.

Diester 5a: IR (CCl_4) 3080, 1785, 1760, 1495, 1235, 1175, 1115, 1085 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 7.24–7.28 (2 H, AA′ part of an AA′BB′ system), 7.30–7.33 (2 H, BB′ part of an AA′BB′ system), 8.24 (s, 2 H, HCOO); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 123.36 (d), 127.39 (d), 141.31 (s), 158.00 (d).

Dioxane 6: IR (KBr) 3070, 3040, 2930, 2900, 1605, 1500, 1460, 1360, 1325, 1290-1260, 1210, 1175, 1150, 1115, 1100, 1045, 1030, 930, 880, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 5.48 (s, 4 H, HCOO), 6.8–7.0 (tm, 8 H, ar); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 88.20 (d), 116.95 (d), 122.70 (d), 139.46 (s); MS (70eV), *m/e* 300 (29%, M^+), 242 (12%), 134 (100%, $C_8H_6O_2^+$), 121 (34%, $C_7H_5O_2^+$). Anal. Calcd for $C_{16}H_{12}O_6$ (300.3): C, 64.00; H, 4.03. Found: C, 63.94; H, 3.81.

2a-Phenyl-2a,8a-dihydrobenzo[*b*][1,2]dioxeto[3,4-*e*][1,4]-dioxin (4e) was prepared according to the above procedure starting with 200 mg (0.95 mmol) 1,4-dioxin **3e** affording 94 mg (41%) pure product: mp 70–72 °C (yellow prisms from petroleum ether/methylene chloride); peroxide content >98% by iodometry; IR (CCl_4) 3055, 3000, 2980, 1760, 1615, 1505, 1460, 1265, 1205, 1180, 1110, 1015, 700 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 6.33 (s, 1 H, dioxetane), 7.16 (s, 4 H, benzo), 7.4–7.6 and 7.8–8.0 (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 105.67 (d), 108.11 (s), 118.72 (d), 118.96 (d), 124.56 (d), 125.94 (d), 128.85 (d), 130.69 (d), 134.00 (s), 140.31 (s), 141.62 (s). Anal. Calcd for $C_{14}H_{10}O_4$ (242.2): C, 69.42; H, 4.16. Found: C, 69.28; H, 4.15.

2a,8a-Dimethyl-2a,8a-dihydrobenzo[*b*][1,2]dioxeto[3,4-*e*][1,4]dioxin (4f) was prepared according to the above procedure starting with 255 mg (1.57 mmol) of dioxin **3f**, resulting in 102 mg (33%) of pure product: mp 118–122 °C dec. (yellow needles from petroleum ether/methylene chloride); IR (CCl_4) 3040, 3000, 2930, 1610, 1495, 1385, 1265, 1135, 975, 895 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.81 (s, 6 H, CH_3), 6.99 (s, 4 H, benzo); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.50 (q), 110.59 (s), 118.29 (d), 124.07 (d), 141.98 (s). Anal. Calcd for $C_{10}H_{10}O_4$ (194.2): C, 61.85; H, 5.19. Found: C, 62.25; H, 5.30.

2,3-Dihydro-1*H*-3a,9a-epidioxybenzo[*b*]cyclopenta[*e*]-[1,4]dioxin (4g) was prepared according to the above procedure starting with 400 mg (2.30 mmol) of dioxin **3g** resulting in 60 mg (13%) pure product: mp 90–95 °C (yellow prisms from petroleum ether/methylene chloride); IR (CCl_4) 3050, 2950, 2930, 1490, 1355, 1250, 1220, 1180, 1120, 1110, 945 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.9–2.6 (m, 6 H, CH_2), 7.08 (s, 4 H, benzo); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.17 (t), 33.85 (t), 112.92 (s), 118.75 (d), 124.33 (d), 141.04 (s). Anal. Calcd for $C_{11}H_{10}O_4$ (206.2): C, 64.07; H, 4.89. Found: C, 64.33; H, 5.05.

1,2,3,4-Tetrahydro-4a,10a-epidioxydibenzo[1,4]dioxin (4h) was prepared according to the above procedure starting with 170 mg (0.90 mmol) dioxin **3h**, affording 100 mg (50%) pure product: mp 170 °C (yellow prisms from petroleum ether/methylene chloride); IR (CCl_4) 3050, 2950, 2870, 1610, 1495, 1360, 1260, 1000 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.7–2.2 (m, 8 H, CH_2), 6.98 (s, 4 H, benzo); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 18.67 (t), 30.99 (t), 108.78 (s), 118.28 (d), 123.97 (d), 142.01 (s). Anal. Calcd for $C_{12}H_{12}O_4$ (220.2): C, 65.45; H, 5.49. Found: C, 65.59; H, 5.48.

2a,8a-Dihydro-2a-methyl-8a-phenylbenzo[*b*][1,2]dioxeto-[3,4-*e*][1,4]dioxin (4i) was prepared according to the above procedure starting from 300 mg (1.34 mmol) of dioxin **3i**, isolating 120 mg (35%) pure product: mp 72–76 °C (yellow plates from petroleum ether/methylene chloride); peroxide content 98% by iodometry; IR (CCl_4) 3065, 2875, 1780, 1750, 1610, 1495, 1450, 1390, 1260, 1205, 1190, 1170, 1125, 1060, 1010 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.41 (s, 3 H, CH_3), 7.06 (s, 4 H, benzo), 7.4–7.6 and 7.7–7.9 (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.81 (q), 111.68 (s), 112.32 (s), 118.45 (d), 118.72 (d), 124.27 (d), 124.36 (d), 126.69 (d), 128.72 (d), 130.51 (d), 133.49 (s), 141.89 (s), 142.24 (s). Anal. Calcd for $C_{15}H_{12}O_4$ (256.3): C, 70.31; H, 4.72. Found: C, 70.55; H, 4.73.

2a,8a-Dihydro-2a,8a-diphenylbenzo[*b*][1,2]dioxeto[3,4-*e*][1,4]dioxin (4j) was prepared according to the above procedure starting with 210 mg (0.73 mmol) of dioxin **3j**, obtaining 186 mg (80%) pure product: mp 113–116 °C (yellow prisms from *n*-pentane); IR (CCl_4) 3065, 1495, 1450, 1300, 1260, 1175, 1110, 1030, 1005, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.1–7.6 (m, 14 H, ar); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 113.35 (s), 118.87 (d), 124.46 (d), 126.84 (d), 128.06 (d), 129.91 (d), 133.79 (s), 142.38 (s). Anal. Calcd for $C_{20}H_{14}O_4$ (318.3): C, 75.46; H, 4.43. Found: C, 75.49; H, 4.34.

2a,8a-Dihydro-2a,8a-diphenyl-4-methoxybenzo[*b*][1,2]dioxeto[3,4*e*][1,4]dioxin (4k) was prepared according to the above procedure starting with 250 mg (0.79 mmol) dioxin **3k**, obtaining 110 mg (40%) pure product: mp 100–101 °C (yellow needles from petroleum ether/methylene chloride); IR (CCl_4) 3080, 3050, 3010, 2960, 2900, 2850, 1620, 1505, 1480, 1455, 1330, 1300, 1280, 1250, 1215, 1180, 1110, 1075, 1035, 1005, 940, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 3.88 (s, 3 H, OCH_3), 6.80 (d, $J_{5,6}$ = 8.3 Hz, 1 H, 5-H), 6.85 (d, $J_{6,7}$ = 8.3 Hz, 1 H, 7-H), 7.11 (t, 1 H, 7-H), 7.20–7.23 (m, 6 H, ar), 7.54–7.57 (m, 4 H, ar); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 56.17 (q), 107.73 (d), 111.13 (d), 113.23 and 113.47 (s, C-2a and C-8a), 123.66 (d), 126.66 (d), 126.78 (d), 128.03 (d), 129.89 (d), 133.31 (s), 133.42 (s), 142.97 (s), 149.84 (s). Anal. Calcd for $C_{21}H_{16}O_5$ (348.4): C, 72.41; H, 4.63. Found: C, 72.63; H, 4.82.

2a,10a-Dihydro-2a,10a-diphenyl[1,2]dioxeto[3,4-*b*]-naphtho[2,3-*e*][1,4]dioxin (4l) was prepared according to the above procedure starting with 430 mg (1.28 mmol) of dioxin **3l**, affording 210 mg (45%) pure product: mp 125–130 °C dec (yellow prisms from petroleum ether/methylene chloride); IR (CH_2Cl_2) 1600, 1510, 1470, 1360, 1220, 1175, 1060, 1025, 1005, 875 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 7.24–7.35 (m, 6 H, ar), 7.47–7.53 (2 H, AA′ part of an AA′XX′ system, J_{AX} = 8.5 Hz), 7.59–7.64 (m, 4 H, ar), 7.66 (s, 2 H, ar), 7.82–7.87 (2 H, XX′ part of an AA′XX′ system); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 113.16 (s), 115.56 (d), 125.57 (d), 126.72 (d), 127.21 (d), 128.12 (d), 129.97 (d), 130.91 (s), 133.43 (s), 141.71 (s). Anal. Calcd for $C_{24}H_{16}O_4$ (368.4): C, 78.25; H, 4.38. Found: C, 78.32; H, 4.28.

2,3-Dihydro-2-methyl-3-methylenebenzo[1,4]dioxin-2-yl hydroperoxide (7f) was obtained as a byproduct in the preparation of dioxetane **4f**: 60 mg (20%); colorless oil after Florisil chromatography at −60 °C, eluting with methylene chloride; IR (CCl_4) 3520, 3040, 3005, 2945, 1665, 1605, 1495, 1305, 1275, 1180, 1120, 870 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.76 (s, 3 H, CH_3), AB system (δ_A 4.66, δ_B 4.82, J = 2.4 Hz), 6.87 (br s, 4 H, benzo), 8.03 (br s, 1 H, OOH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.37 (q), 93.69 (t), 100.42 (s), 115.93 (d), 117.33 (d), 122.60 (d), 122.94 (d), 139.86 (s), 142.09 (s), 150.01 (s). Anal. Calcd for $C_{10}H_{10}O_4$ (194.2): C, 61.85; H, 5.19. Found: C, 62.22; H, 5.25.

2,3-Dihydro-3a*H*-benzo[*b*]cyclopenta[*e*][1,4]dioxin-3a-yl hydroperoxide (7g) was obtained as a byproduct in the preparation of dioxetane **4g**: 200 mg (42%); colorless oil after Florisil chromatography at −60 °C, eluting with methylene chloride; IR (CCl_4) 3530, 3080, 3040, 2830, 1685, 1490, 1360, 1260, 1105, 1045, 925, 840 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.9–2.9 (m, 4 H, CH_2), 5.3–5.4 (m, 1 H, olefinic), 6.85 (s, 4 H, benzo), 8.30 (br s, 1 H, OOH); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 23.20 (t), 31.38 (t), 107.56 (s), 108.18 (d), 116.53 (d), 117.96 (d), 122.86 (d), 140.63 (s), 141.58 (s), 144.47 (s). Anal. Calcd for $C_{11}H_{10}O_4$ (206.2): C, 64.07; H, 4.89. Found: C, 63.53; H, 4.81.

3,4-Dihydro-2*H*-dibenzo[1,4]dioxin-4a-yl hydroperoxide (7h) was obtained as a byproduct in the preparation of dioxetane **4h**: 40 mg (20%); colorless oil after Florisil chromatography at

(17) Adam, W.; Eggelte, H. J. *J. Org. Chem.* **1977**, *42*, 3987.

–60 °C, eluting with methylene chloride; IR (CCl_4) 3525, 3040, 2980, 2940, 2835, 1690, 1605, 1495, 1275, 1155, 1065, 950, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.7–2.9 (m, 6 H, CH_2), 5.57 (t, 1 H, olefinic), 6.92 (s, 4 H, benzo), 8.15 (br s, 1 H, OOH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 18.89 (t), 23.80 (t), 29.60 (t), 99.23 (s), 109.45 (d), 116.09 (d), 117.37 (d), 122.25 (d), 122.92 (d), 139.54 (s), 141.45 (s), 142.36 (s). Anal. Calcd for $C_{12}H_{12}O_4$ (220.2): C, 65.45; H, 5.49. Found: C, 65.25; H, 5.38.

Thermolysis of Dioxetanes. Samples (0.5 mmol) of the dioxetanes in 20 mL of carbon tetrachloride were thermolyzed at ca. 75 °C until the peroxide test was negative (5–10 h). After rotoevaporation of the solvent the diester products were purified either by fractional distillation or recrystallization. The details of the individual cases are summarized below.

1-(Benzoyloxy)-2-(formyloxy)benzene (5e) (74 mg (82%); bp ca. 200 °C (0.1 Torr); n^{20}_D 1.5701) was obtained from 90 mg (0.37 mmol) dioxetane **4e**: IR (CCl_4) 3060, 2940, 2920, 1780, 1755, 1495, 1450, 1260, 1240, 1170, 1115, 1090, 1055, 1025, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 7.16–7.29 (m, 4 H, benzo), 7.39–7.44 (m, 2H, *m*-phenyl), 7.53–7.57 (m, 1 H, *p*-phenyl), 8.11 (s, 1 H, HCOO), 8.12–8.15 (m, 2 H, *o*-phenyl); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 123.09 (d), 123.90 (d), 126.86 (d), 127.27 (d), 128.71 (d), 130.33 (d), 133.92 (d), 141.71 (s), 142.38 (s), 158.22 (d), 164.14 (s); MS (70 eV), *m/e* 242 (0.2%, M^+), 214 (2%, $M^+ - CO$), 197 (4%, $M^+ - HCO_2$), 105 (100%, $PhCO^+$). Anal. Calcd for $C_{14}H_{10}O_4$ (242.2): C, 69.42; H, 4.16. Found: C, 69.35; H, 4.19.

1,2-Diacetoxybenzene (5f) (110 mg (73%); mp 62–64 °C (lit.[18] mp 64 °C); colorless prisms from petroleum ether/methylene chloride) was obtained from 150 mg (0.77 mmol) dioxetane **4f**: IR (KBr) 3080, 3020, 2980, 2930, 1760, 1600, 1495, 1435, 1375, 1245, 1210, 1175, 1100, 1035, 1015, 955, 920, 910, 860, 835, 805, 770 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 2.20 (s, 6 H, CH_3), 7.17 (s, 4 H, benzo); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 20.53 (q), 123.45 (d), 126.57 (d), 142.19 (s), 168.18 (s); MS (70 eV), *m/e* 194 (3%, M^+), 152 (19%), 110 (100%), 43 (69%, $MeCO^+$).

4,5-Dihydro-3*H*-benzo[*b*][1,4]dioxonin-2,6-dione (5g) (110 mg (85%); mp 150–152 °C; colorless prisms from petroleum ether/methylene chloride) was obtained from 130 mg (0.63 mmol) dioxetane **4g**: IR (KBr) 3070, 2980, 2950, 2920, 1760, 1600, 1485, 1450, 1350, 1315, 1225, 1140, 1095, 1035, 950, 890, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.1–2.5 (m, 2 H, CH_2), 2.6–2.8 (m, 4 H, CH_2), 7.27 (s, 4 H, benzo); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 23.81 (t), 34.49 (t), 122.48 (d), 126.59 (d), 144.41 (s), 173.00 (s); MS (70 eV), *m/e* 206 (16%, M^+), 110 (78%), 55 (100%). Anal. Calcd for $C_{11}H_{10}O_4$ (206.2): C, 64.07; H, 4.89. Found: C, 63.96; H, 4.75.

3,4,5,6-Tetrahydrobenzo[*b*][1,4]dioxecin-2,7-dione (5h) (23 mg (86%); mp 170 °C; colorless needles from petroleum ether/methylene chloride) was obtained from 27 mg (0.12 mmol) of dioxetane **4h**: IR (KBr) 3030, 2980, 2940, 2870, 1760, 1745, 1490, 1460, 1440, 1365, 1335, 1265, 1245, 1230, 1160, 1125, 1100, 1045, 980, 915, 875, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.9–2.2 (m, 4 H, CH_2), 2.5–2.7 (m, 4 H, CH_2), 7.1–7.4 (m, 4 H, benzo); ^{13}C NMR ($CDCl_3$, 22.6 MHz) 23.07 (t), 35.61 (t), 122.77 (d), 126.73 (d), 142.68 (s), 171.37 (s); MS (70 eV), *m/e* 220 (12%, M^+), 111 (100%), 83 (23%), 55 (59%). Anal. Calcd for $C_{12}H_{12}O_4$ (220.2): C, 65.45; H, 5.49. Found: C, 65.37; H, 5.86.

1-(Acetoxy)-2-(benzoyloxy)benzene (5i) (120 mg (80%); mp 46–48 °C; colorless prisms from petroleum ether/acetone (lit.[18] mp 78 °C)) was obtained from 150 mg (0.59 mmol) of dioxetane **4i**: IR (KBr) 3060, 3010, 2980, 1770, 1735, 1600, 1495, 1455, 1375, 1245, 1210, 1170, 1105, 1060, 1030, 910, 850, 765, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.11 (s, 3 H, CH_3), 7.2–7.7 and 8.1–8.3 (m, 5 H, phenyl), 7.27 (s, 4 H, benzo); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.43 (q), 123.49 (d), 123.57 (d), 126.61 (d), 128.70 (d), 129.11 (s), 130.15 (d), 133.79 (d), 142.53 (s), 142.65 (s), 164.03 (s), 168.16 (s); MS (70 eV), *m/e* 214 (12%, M^+), 105 (100%, $PhCO^+$), 77 (38%, Ph^+). Anal. Calcd for $C_{15}H_{12}O_4$ (256.3): C, 70.30; H, 4.72. Found: C, 70.51; H, 4.89.

1,2-Bis(benzoyloxy)benzene (5j) (410 mg (73%); mp 86–87 °C (lit.[19] mp 84 °C); colorless plates from petroleum ether/methylene chloride) was obtained from 500 mg (1.57 mmol) of dioxetane **4j**: IR (KBr) 3070, 3055, 1740, 1605, 1500, 1460, 1280, 1250, 1180, 1110, 1085, 1065, 1030, 950, 855, 760, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.2–7.7 (m, 10 H, ar), 8.0–8.2 (m, 4, ar); ^{13}C NMR ($CDCl_3$, 22.6 MHz) δ 123.58 (d), 126.66 (d), 128.45 (d), 128.78 (s), 130.08 (d), 133.58 (d), 142.58 (s), 164.19 (s); MS (70 eV), *m/e* 318 (3%, M^+), 105 (100%, $PhCO^+$), 77 (40%, Ph^+).

1,2-Bis(benzoyloxy)-3-methoxybenzene (5k) (70 mg (70%), mp 94–96 °C (lit.[20] mp 83 °C); colorless needles from petroleum ether/methylene chloride) was obtained from 100 mg (0.29 mmol) of dioxetane **4k**: IR (KBr) 3070, 3010, 2970, 2940, 2840, 1750, 1735, 1610, 1500, 1480, 1450, 1320, 1290, 1270, 1240, 1200, 1180, 1095, 1080, 1055, 1025, 845, 770, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 3.84 (s, 3 H, OCH_3), 6.94 (dd, $J_{4,5}$ = 8.5 Hz, $J_{4,6}$ = 1.3 Hz, 1 H, 4-H), 6.98 (dd, $J_{5,6}$ = 8.3 Hz, 1 H, 6-H), 7.28 (t, 1 H, 5-H), 7.34–7.40 (m, 4 H, ar), 7.49–7.55 (m, 2 H, ar), 8.05–8.11 (m, 4 H, ar); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 56.35 (q), 110.07 (d), 115.26 (d), 126.25 (d), 128.42 (d), 128.93 (s), 128.99 (s), 130.15 (d), 130.26 (d), 132.45 (s), 133.43 (d), 133.52 (d), 144.07 (s), 152.98 (s), 163.81 (s), 164.22 (s). Anal. Calcd for $C_{21}H_{16}O_5$ (348.4): C, 72.41; H, 4.63. Found: C, 72.70; H, 4.74.

2,3-Bis(benzoyloxy)naphthalene (5l) (220 mg (79%); mp 154–155 °C (lit.[21] mp 150–151 °C); colorless needles from petroleum ether/methylene chloride) was obtained from 280 mg (0.76 mmol) of dioxetane **4l**: IR (KBr) 3050, 1740, 1595, 1510, 1470, 1450, 1245, 1150, 1100, 1060, 1045, 1020, 955, 900, 740, 720, 705, 655 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.2–7.6 (m, 8 H, ar), 7.7–7.9 (m, 4 H, ar), 8.0–8.2 (m, 4 H, ar); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 121.04 (d), 126.37 (d), 127.54 (d), 128.45 (d), 128.81 (s), 130.14 (d), 131.67 (s), 133.65 (d), 141.41 (s), 164.51 (s); MS (70 eV), *m/e* 368 (6%, M^+), 105 (100%, $PhCO^+$), 77 (33%, Ph^+). Anal. Calcd for $C_{24}H_{16}O_4$ (368.4): C, 78.25; H, 4.38. Found: C, 78.36; H, 4.23.

Chemiluminescence Measurements. The total chemiluminescence intensities were determined with a Mitchell-Hastings photometer,[22a] 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/s L) using an experimentally established conversion factor, which was determined with the help of a calibrated POPOP-PPO scintillation cocktail,[22b] 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_{obsd}).

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

$$\ln (k_{obsd}/T) = -\Delta H^*/RT + \ln (k/h) + \Delta S^*/R \qquad (5)$$

Determination of Excitation Yields.[1] The intercept 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 ($\phi_F{}^{EC}$) was calculated via eq 6, in which $[4]_0$ is the initial dioxetane con-

(18) Green, A. *J. Chem. Soc.* **1927**, 500.
(19) Döbner, O. *Liebigs Ann. Chem.* **1881**, *210*, 261.
(20) Loudon, J. D.; Scott, J. A. *J. Chem. Soc.* **1953**, 269.
(21) Prajer-Janczewska, L. *Roczniki Chem.* **1961**, *35*, 553; *Chem. Abstr.* **1962**, *56*, 11509b.
(22) (a) Mitchell, G. W.; Hastings, J. W. *Anal. Biochem.* **1971**, *39*, 243. (b) Hastings, J. W.; Weber, G. *J. Opt. Soc. Am.* **1963**, *53*, 1410.

centration and the remaining terms are already defined.

$$\phi_F^{EC} = I_\infty^{EC}/k_{obsd}[4]_0 \quad (6)$$

The singlet (ϕ^S) and triplet (ϕ^T) excitation yields were calculated from eq 7, where ϕ_{ET} is the quantum yield for energy transfer

$$\phi^{S,T} = \phi_F^{EC}/\phi_{ET}\phi_F^{fl} \quad (7)$$

from the chemienergized excited ketone to 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 $\phi_{DPA}^{fl} = 1.00$[23] 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 $\phi_{DBA}^{fl} = 0.10$[24] and $\phi_{ET} = \phi_{DBA}^{TS} = 0.25$.[25] The enhanced chemiluminescence data were processed on a Tektronix 4051 Computer and the results are summarized in Table II.

X-ray Crystallography. The orientation matrix and the cell parameters were determined from all clear colorless crystals of given dimensions on a SYNTHEX-P3 four circle diffractometer. Measurement of intensities: ω scan, 1° range, Mo Kα, 2θ maximum = 55°. The structures were solved by direct-phase determination. Positional and thermal parameters could be refined by anisotropic least-squares cycles to the given R values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Perspective drawings are given in Figures 1-4.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support. We thank Dr. D. Scheutzow for measuring the 400-MHz ^{1}H NMR and the 100.61-MHz ^{13}C NMR spectra and Dr. G. Lange for measuring the mass spectra.

Registry No. **3a**, 255-37-8; **3b**, 4345-55-5; **3c**, 82912-44-5; **3d**, 82912-45-6; **3e**, 5770-58-1; **3e** (alcohol), 5770-68-3; **3f**, 79792-92-0; **3g**, 82912-48-9; **3h**, 82912-49-0; **3i**, 79792-91-9; **3j**, 75694-46-1; **3j** (alcohol), 91201-75-1; **3k**, 91201-56-8; **3l**, 91201-57-9; **3l** (alcohol), 91201-76-2; **4e**, 91201-58-0; **4f**, 91201-59-1; **4g**, 91201-60-4; **4h**, 91201-61-5; **4i**, 91201-62-6; **4j**, 91201-63-7; **4k**, 91201-64-8; **4l**, 91201-65-9; **5a**, 91201-66-0; **5e**, 79792-93-1; **5f**, 635-67-6; **5g**, 91201-67-1; **5h**, 91201-68-2; **5i**, 79792-94-2; **5j**, 643-94-7; **5k**, 91201-69-3; **5l**, 91201-70-6; **6**, 91201-71-7; **7f**, 91201-72-8; **7g**, 91201-73-9; **7h**, 91201-74-0; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $PhCOCH_2Br$, 70-11-1; PhCHBrCOPh, 1484-50-0; 1,2-dihydroxybenzene, 120-80-9; 2,3-dihydroxy-1-methoxybenzene, 934-00-9; naphthalene-2,3-diol, 92-44-4.

Supplementary Material Available: Positional and thermal parameters of the atoms of the dioxetanes **4g**, **4h**, and **4j**, diester **5h**, and dioxane **6** are given in Tables I-X; details of the crystallographic parameters in Table XI; perspective drawing of diester **5h**; labeling of the atoms in the Figures 1-4 corresponds to that given in Tables I-X (13 pages). Ordering information is given on any current masthead page.

(23) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4136.
(24) Wu, K.-C.; Ware, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 5906.
(25) Berenfeld, V. M.; Chumaevesky, E. V.; Grinev, M. P.; Kuryatnikow, Yu. J.; Artmev, E. T.; Dzhagatspanyan, R. V. *Izv. Acad. Nauk. SSSR Ser. Fiz* **1970**, *34*, 678.

Substitution Reactions of Secondary Halides and Epoxides with Higher Order, Mixed Organocuprates, $R_2Cu(CN)Li_2$: Synthetic, Stereochemical, and Mechanistic Aspects

Bruce H. Lipshutz,*† Robert S. Wilhelm, Joseph A. Kozlowski, and David Parker

Department of Chemistry, University of California, Santa Barbara, California 93106

Received January 9, 1984

Higher order cuprates, represented by the general formula $R_2Cu(CN)Li_2$, are readily prepared from copper cyanide and 2 equiv of an organolithium. These novel reagents react readily and efficiently with secondary unactivated iodides and bromides affording products of substitution. Likewise, mono-, di-, and trisubstituted epoxides undergo ring opening leading to the corresponding alcohols in excellent yields. The effects of solvent, temperature, gegenion, and variations in ligands are discussed. Replacement of the second equivalent of RLi by CH_3Li strongly encourages transfer of R over CH_3 in $R(CH_3)Cu(CN)Li_2$ with halides. Use of PhLi as R_RLi in place of one R_TLi (i.e., $R_T(Ph)Cu(CN)Li_2$) is suggested for oxirane cleavage. The stereochemical implications associated with both couplings are also addressed.

Introduction

Among the vast array of methodologies available to the organic chemist, organocopper based reagents have provided one of the most consistently popular tools for carbon–carbon bond construction.[1] This is not surprising as copper salts are available in quantity, and reactions of reagents derived therefrom tend to be efficient and conditions mild.[2] As with most useful methodologies, however, there are limitations which require alternative strategies for effecting the same net overall synthetic transformation. Thus, in the case of organocuprates R_2CuLi, **1**, displacement processes at secondary unactivated centers bearing halogen are quite rare due to highly competitive reduction and elimination pathways.[2,3] Likewise, substitution reactions of these "lower order" species **1** with, in particular, di- and trisubstituted epoxides are oftentimes problematic as both products of rearrangement and elimination are commonly encountered.[2,4] These pitfalls notwithstanding, interest in the applications of cuprate chemistry have continued unabated.[5]

† A. P. Sloan Foundation Fellow, 1984–1986.

(1) Collman, J. P.; Hegedus, L. S. In "Principles and Applications of Organotransition Metal Chemistry"; University of Science Books: Mill Valley, CA, 1980; pp 544–565.
(2) Posner, G. H. *Org. React.* **1975**, *22*, 253.
(3) Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Boshe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871.
(4) Hartman, B. C.; Livinghouse, T.; Rickborn, B. *J. Org. Chem.* **1973**, *38*, 4346. Johnson, C. R.; Herr, R. W.; Wieland, D. M. *Ibid.* **1973**, *38*, 4263, *J. Am. Chem. Soc.* **1970**, *92*, 3813.

0022-3263/84/1949-3928$01.50/0