Pergamon

Tetrahedron Vol. 50, No. 30, pp. 9009-9024, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $7.00+0.00

0040-4020(94)00496-X

Photooxygenation of Tetramethoxybenzobarrelene: Synthesis and Thermal Decomposition of Bisdioxetane and Endoperoxide

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Key Words: Benzobarrelene/ Singlet Oxygen/ Photooxygenation/ Dioxetanes/ Homo Diels-Alder Cycloadducts

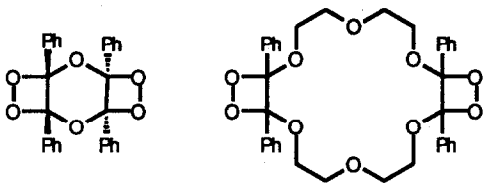
Abstract: Photooxygenation of tetramethoxybenzobarrelene (**2**) afforded endoperoxide **4**, and the diastereomeric bisdioxetanes *syn,syn-* and *syn,anti-***5** in good yields. Thermolysis of the bisdioxetane *syn,syn-***5** and separately of *syn, anti-***5** resulted in the monodioxetane *trans-***6** as major product, whose structure was rigorously established by X-ray analysis. On heating, the monodioxetanes *trans-* and *cis-***6** gave tetraester **7** nearly quantitatively. The *homo* Diels-Alder adduct **4** decomposed at room temperature to the keto ether **9** as the only isolable product. Partial photooxygenation of benzobarrelene **2** gave only the monodioxetane *syn-***3** , no *anti-***3** was observed. Monodioxetane *syn-***3** decomposed at room temperature to the dihydronaphthalene **8**, the naphthalene derivative **10** and dimethyl oxalate. Photooxygenation of dihydronaphthalene **8** gave quantitatively the dioxetane *trans-***6**. The activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$) and excitation yields (Φ^S and Φ^T) for the bisdioxetane **5** were determined by standard chemiluminescence techniques. It is concluded that the two dioxetane rings in the bisdioxetane **5** cleave thermally successively with no evidence for thermally induced intramolecular sensitization to produce upper excited state products. The mechanism of the thermal decomposition of the bisdioxetane **5** and endoperoxide **4** is discussed.

INTRODUCTION

Singlet oxygen serves as an important preparative tool in the synthesis of oxyfunctionalized organic compounds. For example, the sensitized photooxygenation of electron-rich olefins constitutes an effective means of preparing 1,2-dioxetanes through [2+2] cycloaddition.[1] An unique characteristic of such dioxetanes is their thermal decomposition to electronically excited carbonyl products, the latter manifest themselves through chemiluminescence.

Although the chemistry of dioxetanes is well-established,[1] bisdioxetanes are still rarity items. Thus, the first stable authentic bisdioxetane[2] **A** was reported by us in the photooxygenation of tetraphenyl-1,4-dioxin and its structure unequivocally assigned by X-ray analysis.[3] Thermal decomposition of the bisdioxetane **A** derived from the 1,4-dioxin afforded quantitatively benzoic anhydride with efficient chemiluminescence derived from the electronically excited anhydride. An elaborate study of the thermolysis mechanism of such bisdioxetanes derived from substituted tetraphenyl-1,4-dioxins established that they decompose by sequential cleavage of the

two dioxetane rings.[4] A member of a second class of persistent bisdioxetanes, namely **B**, has been isolated in the photooxygenation of a tetraphenyl-substituted crown ether.[5]



A **B**

In this context, tetramethoxybenzobarrelene (**2**) constitutes a suitable precursor for the synthesis of novel bisdioxetanes since the olefinic double bonds are sufficiently electron-rich for [2+2] cycloaddition with $^1O_2$ and ene reaction of the bridgehead allylic hydrogen is for geometrical reasons prohibited. Indeed, it was reported that in the photooxygenation of 2,3-dimethoxy-benzobarrelene the corresponding monodioxetane was formed, while the ene product was not observed in this reaction.[6]

Unlike the 1,4-dioxin bisdioxetanes (dimers of benzoic anhydrides), in which the two carbonyl groups in the fragmentation product compose one common chromophore, namely that of the anhydride functionality, in the benzobarrelene bisdioxetane the two carbonyl groups constitute separate ester chromophores in close proximity. Consequently, it was of interest to assess the thermal behavior of such bisdioxetanes. Presently we report our results on the photooxygenation of benzobarrelene **2** and the thermal decomposition of the resulting bisdioxetanes (Scheme 1).

RESULTS

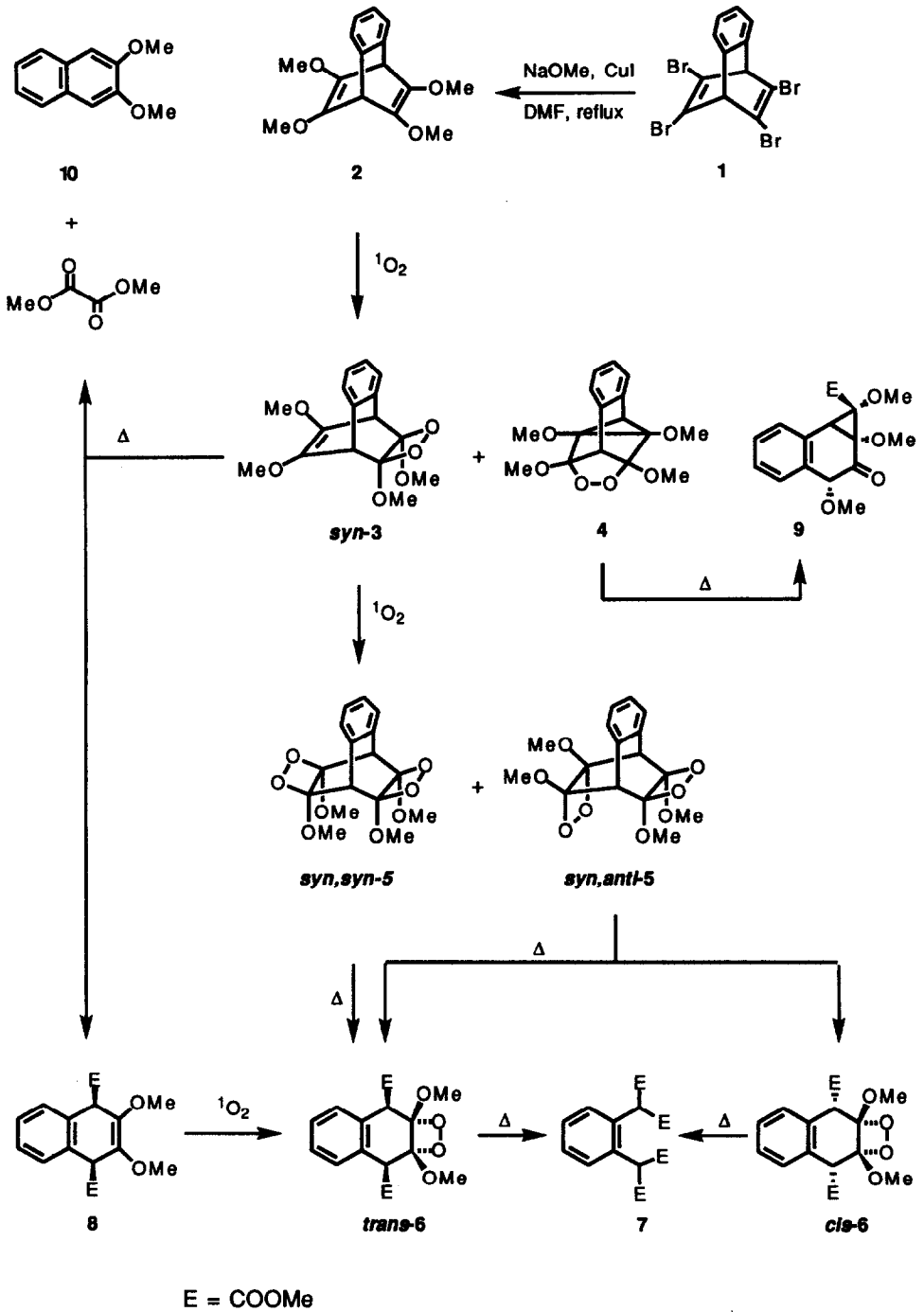
Product Studies of the Photooxygenations and Thermal Decompositions

Tetrabromobenzobarrelene (**1**) was prepared according to published procedure[7] by starting from benzonorbornadiene. Copper-assisted nucleophilic substitution[8] by methoxide ion converted tetrabromobenzobarrelene (**1**) into its tetramethoxy derivative **2** in 66% yield (Scheme 1). The structure of benzobarrelene **2** rests on ^1H and ^{13}C NMR spectral data, in which the observed AA'BB' system of the aromatic protons and the singlets for the two bridgehead hydrogen atoms and four methoxy groups confirm the symmetrical structure.

The photooxygenation[6,9] of benzobarrelene **2** at -30 °C gave the bisdioxetanes *syn,syn*-**5** and *syn,anti*-**5** and the *homo* cycloadduct **4** in a ratio of 68:20:12 nearly quantitatively, as determined by ^1H NMR spectroscopy (Scheme 1). Fractional recrystallization at low temperature (-50 °C) afforded the three products in pure form, the endoperoxide **4** as colorless and the separate diastereomeric bisdioxetanes **5** as pale yellow solids.

The characterization of the bisdioxetanes **5** rests on strong peroxide test, IR, ^1H and ^{13}C NMR spectral data, and satisfactory elemental analysis. Thus, ^1H and ^{13}C NMR data for the *syn,anti*-**5** diastereomer exhibit two different sets of resonances for the methoxy groups and dioxetane ring carbons, as expected for the *syn,anti* structure with a symmetry plane which bisects the two dioxetane and the benzo rings.

Scheme 1


NaOMe, CuI
DMF, reflux
10
2
1
$^1O_2$
Δ
syn-3
4
9
syn,syn-5
syn,anti-5
8
trans-6
7
cis-6
E = COOMe

The bisdioxetane diastereomer *syn, syn*-**5** displays six ^{13}C NMR signals (three aromatic and one each for the bridgehead, dioxetane and methoxy carbon atoms). This highly symmetric structure possesses two symmetry planes, of which one bisects the two dioxetane and the benzo rings and the other contains the benzo ring and the bridgehead positions. However, these ^{1}H and ^{13}C NMR data do not allow to distinguish between the *syn,syn* and *anti,anti* stereochemistry of the dioxetane rings. Nonetheless, the assignment of the stereochemistry of the bisdioxetane *syn,syn*-**5** was inferred from its thermal decomposition in that as only product the monodioxetane *trans*-**6** was obtained (Scheme 1), whose structure was rigorously established by X-ray analysis (Figure 1). The stereoisomer *anti,anti*-**5** would give exclusively monodioxetane *cis*-**6** on thermal decomposition.

Indeed, as expected, thermolysis of the bisdioxetane *syn,anti*-**5** afforded some monodioxetane *cis*-**6** (4%), but the major product was *trans*-**6** (92%), together with tetraester **7** (4%) from cleavage of both dioxetane rings (Scheme 1). The configuration of monodioxetane *cis*-**6** was established by comparison of the spectral data with those of *trans*-**6** (cf. X-ray structure in Figure 1).

Partial photooxygenation of tetramethoxybenzobarrelene **2**, i.e. after all the starting material had just been consumed (NMR monitoring), gave a crude product mixture which consisted of monodioxetane *syn*-**3**, endoperoxide **4**, and the bisdioxetanes *syn,syn*- and *syn,anti*-**5** in a ratio of 79:14:4:3. Low-temperature column chromatography afforded the monodioxetane *syn*-**3**, contaminated with some of its decomposition product, the diester **8** (Scheme 1). Indeed, the thermally labile dioxetane *syn*-**3** decomposed on warm-up to room temperature (ca. 20 °C) to the diester **8** as main product, together with 2,3-dimethoxynaphthalene (**10**) and dimethyl oxalate (Scheme 1). The stereochemistry of the monodioxetane *syn*-**3** was assigned by comparison of the spectral data with those of *syn, syn*-**5**, whose configuration was unequivocally established. When the monodioxetane *syn*-**3** was further photooxygenated at -35 °C, ^{1}H NMR analysis of the crude photolysate mixture indicated formation of the bisdioxetanes *syn,syn*- and *syn,anti*-**5** in a ratio of 77:23 (Scheme 1). This is in good agreement with the diastereomeric ratio obtained in the reaction of benzobarrelene **2** with $^{1}O_2$.

The diester **8** gave on photooxygenation quantitatively the monodioxetane *trans*-**6**; not even traces of the diastereomeric *cis*-**6** could be detected by ^{1}H NMR spectroscopy. Interestingly, also autooxidation of diester **8** by exposure to daylight and air resulted slowly in the monodioxetane *trans*-**6**.

The novel endoperoxide **4** derives from *homo* cycloaddition of singlet oxygen to benzobarrelene **2** (Scheme 1). Its ^{1}H NMR spectrum reveals two different singlets for the bridgehead protons (δ 2.71 and 3.93) and the methoxy groups (δ 3.49 and 3.68). Moreover, the twelve signals in the ^{13}C NMR spectrum confirm a symmetrical structure, in which a symmetry plane bisects the peroxide bond and contains the bridgehead carbon atoms and benzo ring (Scheme 1).

On warm-up to room temperature (ca. 20 °C), the endoperoxide **4** rearranged into **9** (93%) as the only isolable product (Scheme 1). Its ^{1}H and ^{13}C NMR spectra indicated a highly unsymmetrical structure. Thus, the ^{13}C NMR spectrum consists of 16 signals with two carbonyl groups at δ 167.4 (ester) and δ 197.0 (ketone). Its stereochemistry has been firmly established by X-ray analysis (Figure 1).

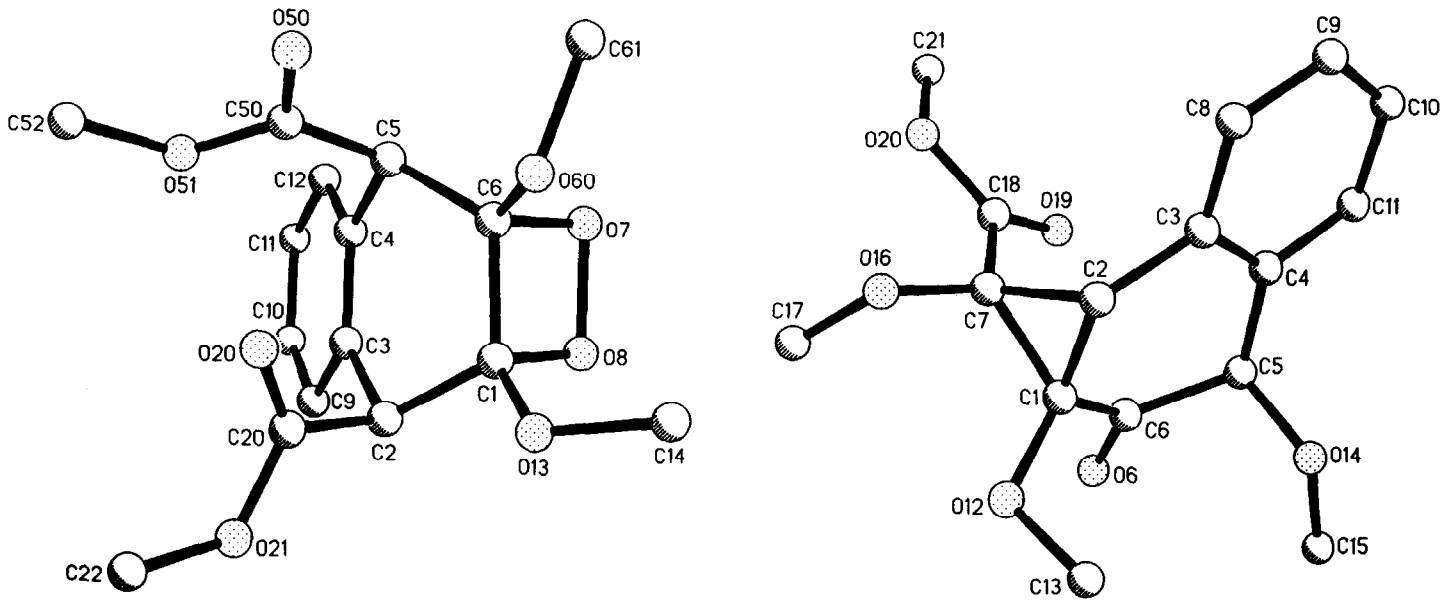


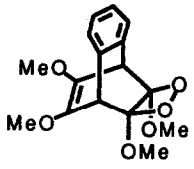
Figure 1. Structures of *trans*-6 and 9 in the Crystal; Selected Bond Lengths [pm] and Angles [°].

***trans*-6**: C1-C2 151.8(15), C1-O8 144.6(14), C3-C4 137.5(13), C4-C5 151.1(14), C6-O7 146.7(14), O7-O8 153.0(14), C1-C6 156.4(15), C6-O60 135.2(13); C2-C1-C6 116.2(7), C6-C1-O8 90.2(6), C6-C1-O13 121.0 (6), C1-C2-C3 108.9(6), C2-C3-C9 117.3(6), C3-C4-C5 120.4(6), C5-C6-O60 116.8 (6), C6-O7-O8 90.8 (6), C2-C1-O8 110.0(6), C2-C1-O13 106.4(6), C1-C2-C20 107.7(6), C2-C3-C4 122.6(6), C1-C6-O60 111.2(6), O7-C6-O60 112.4(7).

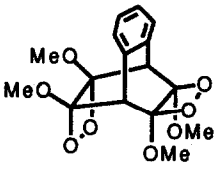
9: C1-C2 149.1(4), C1-C7 151.5(4), C2-C3 150.2(4), C6-O6 121.4(4), C7-C18 150.5(5), C7-C18 149.0(5), C1-C6 150.4(4), C1-O12 140.0(4), C2-C7 151.4(4), C7-O16 138.7(3); C2-C1-C6 118.5(2),C6-C1-C7 119.7(3), C6-C1-O12 114.1(3), C1-C2-C3 118.9(3) C3-C2-C7 120.2(3), C3-C4-C5 121.3(2), C4-C5-O14 106.2(2), C1-C6-C5 117.6(3), C5-C6-O6 120.4(3), C1-C7-O16 117.9(3), C7-C18-O19 122.1(3), C3-C2-C7 118.2(3), C3-C4-C5 121.6(3), C5-C6-O6 120.8(3), C7-C18-O19 123.7(3), C2-C1-C7 60.5(2), C7-C1-O12 113.9(2), C6-C5-O14 105.6(2), C1-C6-O6 121.3(2), C1-C7-C2 59.0(2).

Kinetics and Chemiluminescence Studies of the Dioxetanes

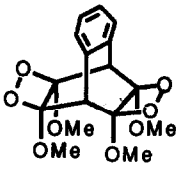
All the mono- and bisdioxetanes are thermally labile and qualitative ^{1}H NMR monitoring of their thermal decomposition gave the following approximate (ca. 10% error) halflives:



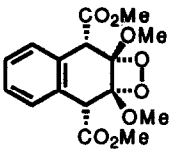
***syn*-3**



***syn,anti*-5**



***syn,syn*-5**



***cis*-6**

T (°C)	ca. 20	ca. 20	ca. 20	ca. 80
$t_{1/2}$ (h)	0.5	6	16	4

As expected, during thermolysis these dioxetanes exhibited chemiluminescence, which comprises a convenient and characteristic property to acquire kinetic data. Thus, for the bisdioxetanes *syn,syn*- and *syn,anti*-**5** (d.r. = 77:23) the activation parameters were determined by chemiluminescence measurements.[4] The rate constants were evaluated according to first-order kinetics and from them the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were computed by means of the Eyring equation. The results in toluene are summarized in Table 1.

Table 1. Rate Constants (k), Activation Enthalpy ($\Delta H^{\ddagger}$), Entropy ($\Delta S^{\ddagger}$) and Free Energy ($\Delta G^{\ddagger}$) of the Thermal Decomposition of the Bisdioxetane **5** [a].

Temp.[b] (K)	k x 10^3 [b] (s^{-1})	$\Delta H^{\ddagger}$ [c] (kcal/mol)	$\Delta S^{\ddagger}$ [c] (e. u.)	$\Delta G^{\ddagger}$ 298 K (kcal/mol)
333	0.750			
333	0.760			
338	1.17	20.4 ± 1.0	-9.1 ± 1.6	23.1 ±1
343	1.70			
343	1.77			
353	3.21			
353	3.40			

[a] A mixture of the diastereomeric bisdioxetanes *syn, syn*- and *syn,anti*-**5** (d.r. 77:23) was used at a concentration of 1x 10^{-3} M in toluene. [b] Temperature was controlled within ca. 0.1 °C. [c]Determined by first-order kinetics through at least three halflives; error ca. 5% of stated values. [d] Determined according to the Eyring equation by plotting lg (k/T) *versus* 1/T.

The excitation parameters were determined by enhanced chemiluminescence as previously described.[4] For the singlet excitation yields (Φ^S) 9,10-diphenylanthracene (DPA) was used as enhancer and for the triplet excitation yields (Φ^T) 9,10-dibromoanthracene (DBA). The relevant data in toluene as solvent are given in Table 2, from which the excitation parameters were calculated to be $\Phi^S = (1.1 \pm 0.4) \times 10^{-4}$ Einstein/mol and $\Phi^T = (6.7 \pm 3) \times 10^{-2}$ Einstein/mol. The large error (ca. 30%) in these excitation yields derives from the fact that only little pure bisdioxetane **5** was available.

Table 2. Singlet (Φ^S) and Triplet (Φ^T) Excitation Yields of the Bisdioxetane **5** [a] Determined by DPA- and DBA-enhanced Chemiluminescence

DPA chemiluminescence [b]				DBA chemiluminescence [c]			
[DPA] x 10^3 (M)	I (V)	k x 10^3 (s^{-1})	Φ^{-1}_{DPA} x 10^{-4}[d] (Einstein/mol)	[DBA] x10^3 (M)	I (V)	k x 10^3 (s^{-1})	Φ^{-1}_{DBA} [d] (Einstein/mol)
5.00	1.64	1.39	1.45	5.00	8.10	1.21	23.0
5.00	1.57	1.36	1.48	5.00	6.80	1.39	31.5
				3.33	6.60	1.10	25.7
				3.33	6.00	1.09	28.0
1.67	0.930	1.22	2.24	1.67	4.08	1.19	44.9
1.67	0.910	1.22	2.29	1.67	4.01	1.05	40.4
0.83	0.600	1.18	3.37	0.83	2.80	1.20	66.0
0.83	0.600	1.22	3.47	0.83	2.55	1.19	73.9
0.33	0.255	1.16	7.79	0.33	1.30	1.09	129
0.33	0.275	1.23	7.66	0.33	1.24	1.39	172

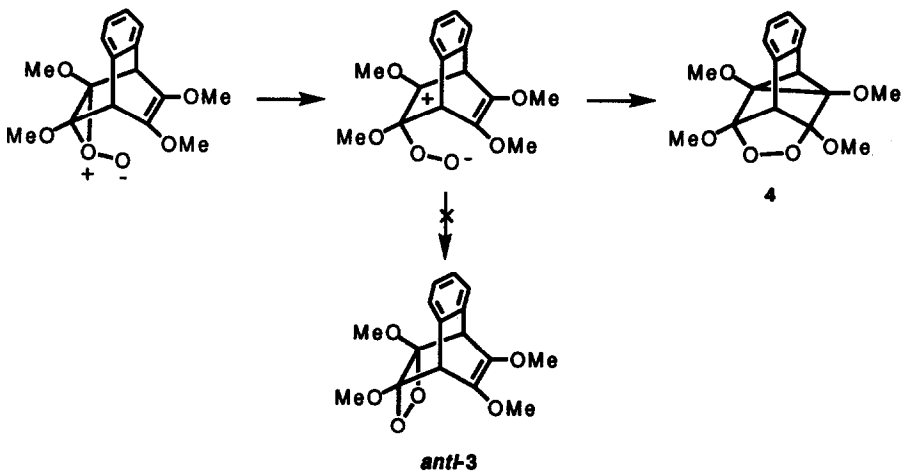
[a] A mixture of diastereomeric bisdioxetanes *syn,syn-* and *syn,anti-***5** was used at a concentration of 2.5 x 10^{-4} M in toluene at 338 K. [b] 9,10-Diphenylanthracene as enhancer for the determination of singlet yields (Φ^S) by singlet-triplet energy transfer. [c] 9, 10 -Dibromoanthracene as enhancer for the determination of triplet yields (Φ^T) by singlet-triplet energy transfer. [d] The procedures described in ref.[4] were followed to determine the enhanced chemiluminescence yields; error ca. 10% of stated values.

DISCUSSION

The photooxygenation of the benzobarrelene **2** proceeds in two discrete stages; first the labile monodioxetane *syn*-**3** is produced, as confirmed by discontinuing the reaction after one mol $^1O_2$ had been consumed (Scheme 1). The *anti*-**3** stereoisomer was not detected by ^1H NMR spectroscopy at low temperatures. Besides some bisdioxetanes **5** (ca. 7%), substantial amounts (ca. 13%) of the endoperoxide **4** were formed by *homo*-[4+2] cycloaddition. Since the diastereomeric bisdioxetanes **5** are subsequent photooxygenation products of the monodioxetane *syn*-**3**, as established by photooxygenation of the latter, the mode selectivity of [2+2] *versus* *homo*-[4+2] cycloaddition is ca. 87:13. Within experimental error, the same (ca. 88:12) mode selectivity was obtained in the exhaustive photooxygenation of benzobarrelene **2**.

The *homo* Diels-Alder cycloaddition mode is rare for singlet oxygen[1], particularly for the bicyclo[2.2.2]octadiene skeleton. A possible mechanistic rationale is that the **2** → **4** transformation is not a *bona fide homo* Diels-Alder cycloaddition; instead, the perepoxide derived from *anti* attack on benzobarrelene **2** (Scheme 2) rearranges to the endoperoxide **4** rather than afford the monodioxetane *anti*-**3**.

Scheme 2



This might also account for the fact that the latter is not observed in the partial photooxygenation of benzobarrelene **2**, although both diastereomeric bisdioxetanes *syn,syn*- and *syn,anti*-**5** are generated in the exhaustive as well as the subsequent photooxygenation of **2** and of *syn*-**3**. In other words, since the bisdioxetane *syn,anti*-**5** is observed, no obvious steric effects appear to operate, which would prevent $^1O_2$ attack from the bottom (opposite to the benzo ring) of benzobarrelene **2** to lead to the monodioxetane *anti*-**3**. In fact, on steric grounds, the first $^1O_2$ molecule should attack preferentially opposite to the benzo ring in the benzobarrelene **2** to give the monodioxetane *anti*-**3** as major diastereomer. Presumably stereoelectronic effects are exercised by the benzo ring, which guide the $^1O_2$ enophile to come in from the *syn* side of **2**. Such stereoelectronically controlled diastereofacial selectivities have been documented.[10]

The bisdioxetanes *syn,syn-* and *syn,anti-***5** are formed in a diastereomeric ratio (d.r.) of ca. 77:23, irrespective of whether monodioxetane *syn-***3** is subsequently or benzobarrelene **2** is exhaustively photooxygenated. Thus, also here the *syn* attack prevails for the second $^1O_2$ molecule. Besides stereoelectronic control by the benzo ring, an appreciable steric effect of the *anti* methoxy substituents in monodioxetane *syn-***3** is expected to play its role. That steric effects can be prominent is displayed in the photooxygenation of diester **8**, the thermal decomposition product of *syn-***3**, which afforded exclusively the monodioxetane *trans-***6** (Scheme 1).

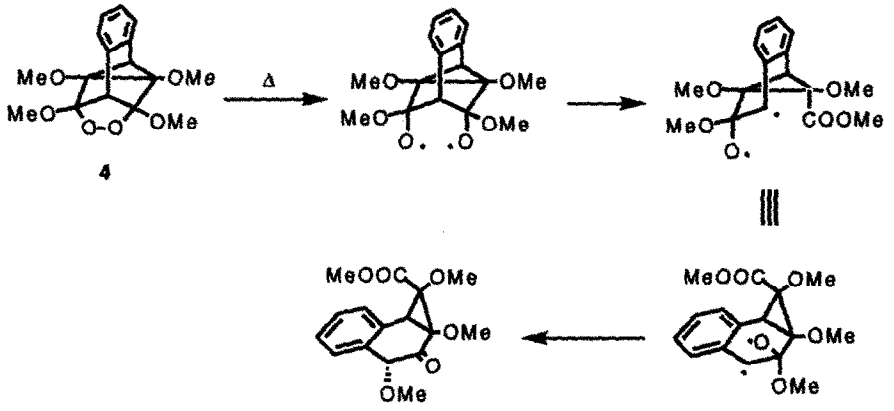
Of the dioxetanes prepared herein, the thermally most labile is the monodioxetane *syn-***3**, which on warm-up to room temperature (ca. 20 °C) decomposed within ca. 1 h to 82:18 mixture of the diester **8** and equal amounts of 2,3-dimethoxynaphthalene (**10**) and dimethyl oxalate (Scheme 1). The major product, diester **8**, is expected from cleavage of the dioxetane ring to generate the two ester functionalities; however, the formation of the naphthalene **10** and oxalate is unusual[1], which arise from fragmentation of the dioxetane ring with preservation of its C-C bond. Cleavage of the lateral C-C bonds is promoted through the gain of aromaticity in the naphthalene **10** product. A precedent has been reported for the thermolysis of the related dioxetane derived from 2,3,5,6-dibenzo-7,8-dimethoxybarrelene, which afforded also anthracene and dimethyl oxalate.[8a]

Prolonged thermolysis of the bisdioxetanes **5**, i.e. fragmentation of both dioxetane rings, leads to the tetraester **7** as exclusive decomposition product. On the other hand, partial thermolysis displayed that the dioxetane rings fragment successively. The *syn,anti-***5** diastereomer is ca. three-fold more labile than *syn,syn-***5**, which implies that the *anti* dioxetane ring fragments more readily than the *syn* one. Thus, besides ca. 4% tetraester **7**, the monodioxetanes *trans-* and *cis-***6** are produced in a ratio of ca. 96:4 on partial thermal decomposition of *syn,anti-***5** at room temperature (ca. 20 °C). Presumably, steric interactions of the *anti* methoxy groups with the *anti* dioxetane ring accelerate the fragmentation of the latter. In contrast, the *syn,syn-***5** diastereomer gave exclusively, as expected, the *trans-***6** monodioxetane (*cis-***6** cannot form from *syn,syn-***5**), together with small amounts (ca. 3%) of tetraester. As already mentioned in the Results Section, the selective formation of the monodioxetane *trans-***6** on partial thermal decomposition of *syn,syn-***5** made possible the unequivocal stereochemical assignment of the bisdioxetane stereoisomers *syn,anti-* and *syn,syn-***5**. Of course, thermolysis of the separate diastereomeric monodioxetanes **6** at ca. 80 °C, the thermally most persistent dioxetanes prepared herein, led to the tetraester **7** as the sole fragmentation product.

The endoperoxide **4** is not only unusual in that it constitutes a seldom case of *homo-*[4+2] cycloaddition for singlet oxygen, but also its thermal behavior is surprising. Already on standing at room temperature (ca. 20 °C), this strained endoperoxide rearranged within a day into α-methoxy ketone **9** essentially quantitatively. A plausible mechanism is given in Scheme 3, in which homolysis of the peroxide bondgenerates first a 1,5-dioxyl diradical, followed by C-C bond cleavage to the 1,3 diradical and finally a methoxy 1,2 shift affords **9**. Cyclization of the 1,3 diradical to the epoxide would have been expected; but is presumably thermally too labile to accumulate.

The bisdioxetanes **5** exhibited chemiluminescence on thermal decomposition, which could be substantially enhanced in the presence of 9,10-dibromoanthracene through triplet-triplet energy transfer. Unfortunately, analogous to the bisdioxetane **A** derived from the *para-*dioxin[4], there is no evidence for the production of upper excited states through intramolecular sensitization, i.e. **5**→**6***→**7****. The most pressing evidence for this is the fact that at room temperature the bisdioxetanes **5** decompose essentially quantitatively to the monodioxetanes **6** (isolated in ca. 97% yield), with only small amounts (ca. 3%) of tetraester **7**. This is to be contrasted with the

Scheme 3



bisdioxetanes **A** derived from *para*-dioxins, for which the corresponding monodioxetanes could be merely detected *in situ* by ^{1}H NMR monitoring during the thermolysis.[4] The reason for this is that in the latter case the bisdioxetane **A** and its monodioxetane are of comparable thermal stability, while the monodioxetanes **6** derived from the bisdioxetanes **5** are sufficiently persistent to accumulate nearly quantitatively. The few percent of tetraester **7** presumably arise from *in situ* thermal decomposition of the accumulated monodioxetanes **6**.

Consequently, the cleavage of one of the dioxetane rings in the bisdioxetane **5** leads to electronically excited monodioxetane **6***, but the latter deactivates to its ground state **6** without energizing the decomposition of the remaining dioxetane ring by intramolecular energy transfer to afford the tetraester in an upper excited state **7**** nor even in its lowest excited state **7***. Therefore, despite the fact that two *photon equivalents* are bound in the bisdioxetanes **5** (each dioxetane ring represents formally one *photon equivalent*), each dioxetane ring must be separately thermally activated and not that one dioxetane ring energizes the decomposition of the other; i.e. the sequence **5** → **6*** → **6** → **7*** → **7** applies.

Similar results, but in a more detailed study, were obtained for the bisdioxetane **A** derived from *para*-dioxins. Thus, irrespective of whether the two carbonyl fragments that result from the bisdioxetane decomposition are connected in form of a single chromophore, i.e. the anhydride functionality which results from the cleavage of both dioxetane rings in the *para*-dioxin dioxetane **A**, or constitute separate chromophores as the two malonic ester groups of the tetraester **7** produced from the cleavage of both dioxetane rings in the bisdioxetanes **5**, these more elaborate energy-rich molecules seem not to be advantageous for the generation of upper excited states through thermally activated intramolecular sensitization.

The above conclusions on the decomposition mode of the bisdioxetanes **5** were reached on the basis of product studies rather than by detailed chemiluminescence measurements. Nevertheless, for comparison with the *para*-dioxin dioxetanes **A**, the activation parameters ($\Delta H^{\ddagger}$ $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$) and the excitation yields (Φ^S and Φ^T) were determined by monitoring the enhanced light emission (Table 1 and 2). The activation entropies ($\Delta S^{\ddagger}$ = -9.1 ± 1.6 e.u.) for the bisdioxetanes **5** is comparable to those for bisdioxetane derivatives **A** ($-7.8 \leq \Delta S^{\ddagger} < -9.1$ e.u.)[4], but the activation enthalpies ($\Delta H^{\ddagger}$ = 20.4 ± 1.0 kcal/mol) for **5** are significantly lower than those for **A** ($23.1 \leq \Delta H^{\ddagger} \leq 24.1$ kcal/mol).[4] Thus, the activation free energies at 298 K are for

bisdioxetane **5** ($\Delta G^{\ddagger}$ = 23.1 ± 1 kcal/mol) compared to **A** (25.5 ≤ $\Delta G^{\ddagger}$< 26.6 kcal/mol)[4] by ca. 3 kcal/mol lower. Consequently, the bisdioxetanes **5** are appreciably thermally more labile than the *para*-dioxin derivatives **A**. Presumably, the additional ring strain of the benzobarrelene ring imparts a lower thermal persistence to the bisdioxetane **5**.

In regard to the excitation yields, the singlet yield for the bisdioxetanes **5** (Φ^S = 0.011 ± 0.004%) falls within the range of those for the *para*-dioxin bisdioxetanes **A** (0.0065 ≤ Φ^S ≤ 0.024%)[4]; however, the triplet yields are substantially lower, i.e. Φ^T = 6.7 ± 3% for **5**, since for **A** they cover the range 14.7 ≤ Φ^T ≤ 71.5%.[4] Consequently, the total excitation yield (Φ^T+ Φ^S) is ca. 7% for the bisdioxetanes **5** and the spin state selectivity Φ^T/Φ^S ca. 630. Accordingly, the total yield of excited states is for the bisdioxetane **5** significantly lower than for **A**, but proportionally more triplet excited states are generated for the latter.[4]

In summary, also the bisdioxetanes **5** are *normal* dioxetanes in that on thermal activation the two dioxetane rings cleave separately and in succession. The n,π*-type excited monodioxetanes **6** which are formed (by a wide margin triplet states predominate), prefer to deactivate to their ground states rather than sensitize intramolecularly the decomposition of the remaining dioxetane ring.

*Acknowledgement.*We thank the *Deutsche Forschungsgemeinschaft* (SFB 172 "Molekulare Mechanismen Kanzerogener Primärveränderungen") and the *Fonds der Chemischen Industrie* for their generous financial support. O.C. expresses his gratitude to the *Alexander von Humboldt Foundation* for a postdoctoral fellowship.

EXPERIMENTAL SECTION

Materials. Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. All solvents for preparative work were distilled from EDTA. The starting material 2,3,5,6-tetrabromobenzobarrelene (**1**) was prepared according to the literature procedure[7] starting from benzobarrelene.

Apparatus. Melting points were taken on a Reichert Thermovar hot stage apparatus. The chemiluminescence measurements were carried out on a Mitchell-Hastings photometer. Infrared spectra: Perkin-Elmer 1420 infrared spectrophotometer. ^{1}H NMR spectra: Bruker AC 200 (200 MHz), Bruker AC 250 (250 MHz), tetramethylsilane as internal standard; ^{13}C NMR spectra: Bruker AC 200 (50 MHz), Bruker AC 250 (63 MHz), [D]chloroform, [D_6]acetone, tetramethylsilane and hexamethyldisiloxane as internal standard. Combustion analyses for elemental composition were performed by the Analytical Division of the Institute of Inorganic Chemistry, University of Würzburg (Carlo Erba 1106). For thin-layer chromatography (TLC) Polygram SIL G/UV_{254} (40x80 mm) foils from Macherey & Nagel Co. were employed. Column chromatography was conducted on silica gel (63-200 mesh; Woelm).

2,3,5,6-Tetramethoxybenzobarrelene **2**. Freshly cut sodium (1.38 g, 60.0 mmol) was added under nitrogen gas to dry methanol (30 ml). When dissolution was complete, the warm solution was diluted with 30 ml of dry dimethylformamide (DMF), followed by the addition of vacuum-dried cuprous iodide (480 mg, 2.50 mmol). After dissolution, 1.88 g (4.00 mmol) of benzobarrelene **1** in 60 ml of dry DMF was added. The

reaction mixture was stirred magnetically for 10 h under a nitrogen gas atmosphere at reflux (ca. 99 °C). After cooling to room temperature, 100 ml of H_2O and 150 ml of diethyl ether were added to the reaction mixture. The organic layer was separated, washed with H_2O (4 x 60 ml), and dried over $MgSO_4$ for 1 h. The solvent was removed (0 °C/17 Torr) and the crude product was passed through a short column packed with Al_2O_3 (7 g). Recrystallization from a 1:3 mixture of CH_2Cl_2/petroleum ether (b.p. 30-50 °C) in the refrigerator yielded 720 mg (66%) of benzobarrelene **2** as colorless needles, m.p. 125 - 126 °C; TLC (2:1 pentane/Et_2O, R_f 0.57). - IR (KBr): ν = 3020 cm^{-1}, 2990, 2950, 2845, 2830, 1690, 1680, 1470, 1460, 1320, 1290, 1230, 1210, 1170, 1150, 1120.- ^1H NMR (250 MHz, $CDCl_3$): δ = 3.65 (s, 12 H, OCH_3), 3.93 (s, 2H, CH), 6.91 (AA'BB' system, part of A, 2H, arom. H), 7.17 (part of B, 2H, arom. H). - ^{13}C NMR (63 MHz, $CDCl_3$): d = 50.7 (q), 58.8 (d), 121.2 (d), 124.1 (d), 145.8 (s), 148.8 (s).- $C_{16}H_{18}O_4$ (274.3): calcd. C 70.00, H 6.61; found C 70.44, H 6.50.

Tetramethoxybenzobarrelene Endoperoxide **4** and *Tetramethoxybenzobarrelene Bisdioxetane* **5**. A solution of **2** (274 mg, 1.00 mmol) in 6 ml of dry CH_2Cl_2, which contained ca. 1 mg of TPP as sensitizer, was irradiated with a 150-W sodium lamp at -30 °C while passing a gentle stream of dry oxygen gas through the reaction mixture. The reaction progress was monitored by TLC and within 15 min the starting material was consumed. ^1H NMR analysis of the crude reaction mixture at low temperature (-30 °C) by using hexamethyldisiloxane as internal standard, indicated the presence of the endoperoxide **4**, and the diastereomeric bisdioxetanes *syn,syn*-**5** and *syn,anti*-**5** in a ratio of 12:68:20 (mass balance ca. 95%). Fractional recrystallization from a 7:3 mixture of ether/pentane at -50 °C in the freezer afforded the individual products in pure form. First **4** crystallized as yellow needles, 30.2 mg (10%), m.p. 79 - 80 °C (dec.). To the mother liquor from **4** was added 2 ml of pentane and on standing in the freezer at -50 °C overnight, the bisdioxetane *syn,anti*-**5** separated as yellow needles, 47.0 mg (14%). Finally, when the mother liquor from *syn,anti*-**5** was allowed to stand in the refrigerator at -50 °C for ca. three days, the bisdioxetane *syn,syn*-**5** (164 mg, 48%) was obtained as yellow needles, m.p. 130 - 132 °C.

4: IR (CH_2Cl_2): ν = 3090 cm^{-1}, 3020, 2920, 1500, 1380, 1250, 1180, 1160, 1140, 1050. - ^1H NMR (200 MHz, - 20 °C, $CDCl_3$): δ = 2.71 (s, 1H, cyclopropane H), 3.49 (s, 6H, OCH_3), 3.68 (s, 6H, OCH_3), 3.93 (s, 1H, bridgehead H), 7.28 - 7.47 (m, 4H, arom. H). - ^{13}C NMR (50 MHz, -20 °C, $CDCl_3$): δ = 29.7 (d), 47.2 (d), 52.6 (q), 60.1 (q), 68.9 (s), 107.8 (s), 124.9 (s), 126.5 (d), 126.8 (d), 127.3 (s), 128.2 (d,2c), 134.2 (s).- $C_{16}H_{18}O_6$ (306.3): calcd. C 62.74, H 5.92; found C 62.39, H 5.96.

syn,syn-**5**: IR (CH_2Cl_2): ν = 3040 cm^{-1}, 2990, 1410, 1360, 1150, 1010. - ^1H NMR (200 MHz, -20 °C, $CDCl_3$): δ = 3.76 (s, 12H, OCH_3), 3.84 (s, 2H, bridgehead H), 7.38 - 7.58 (AA'BB' system, 4H, arom. H).- ^{13}C NMR (50 MHz, -20 °C, $CDCl_3$): δ = 52.6 (q), 52.8 (d), 108.5 (s), 126.5 (d), 128.2 (d), 134.0 (s).- $C_{16}H_{18}O_8$ (338.3): calcd. C 56.80, H 5.36; found C 57.70; H 5.50.

syn,anti-**5**: IR (CH_2Cl_2): ν = 3040 cm^{-1}, 2980, 1410, 1350, 1270, 1260, 1240, 1150, 1140, 1000, 890.- ^1H NMR (200 MHz, -20 °C, [d_6]acetone): δ = 3.54 (s, 6H, OCH_3), 3.73 (s, 6H, OCH_3), 4.06 (s, 2H, bridgehead H), 7.33 - 7.44 (AA'BB' system, 4H, arom. H).- ^{13}C NMR (50 MHz, -20 °C, [d_6]acetone): δ = 49.7 (q), 51.5 (q), 52.4 (d), 109.5(s, 2C), 127.6 (d), 128.7 (d), 134.5 (s).- $C_{16}H_{18}O_8$ (338.3): calcd. C 56.80, H 5.36; found C 55.96, H 5.37.

1,4-Dihydronaphthalene Dioxetane **6**. A sample of 210 mg (0.621 mmol) of *syn,anti*-**5** was dissolved in 2 ml of $CHCl_3$ and allowed to stand at room temperature in the dark. After 14 h, the bisdioxetane was completely consumed and the monodioxetanes *trans*- and *cis*-**6** and the tetraester **7** were observed in a ratio of 92:4:4 by ^1H NMR spectroscopy relative to hexamethyldisiloxane as internal standard (mass balance ca. 95%). The halflife of the bisdioxetane was found to be ca. 6 h at ca. 20 °C (room temp.), as determined by ^1H NMR spectroscopy.

The pure products were isolated by fractional recrystallization from CH_2Cl_2/pentane. As first product monodioxetane *trans*-**6** (major stereoisomer; 189 mg, 90%) was obtained as yellow needles, m.p. 133 - 34 °C. Subseqeuently, *cis*-**6** (minor stereo-isomer; 5.6 mg, 3%) was isolated as yellow needles, m.p. 107 - 108 °C. As third product tetraester **7** (5.6 mg, 3%) crystallized in the form of colorless needles, m.p. 99 - 100 °C.

trans-**6**: IR ($CHCl_3$): ν = 3040 cm^{-1}, 2990, 1755, 1510, 1450, 1365, 1330, 1270, 1220, 1165, 1110.- ^1H NMR (200 MHz, - 20 °C, $CDCl_3$): δ = 3.61 (s, 6H, OCH_3), 3.83 (s, 6H, OCH_3), 4.10 (s, 2H, bridgehead H), 7.36 (AA'BB' system, 4H, arom. H).- ^{13}C NMR (50 MHz, -20 °C, $CDCl_3$): δ = 51.9 (q), 52.3 (q), 53.5 (d), 108.7 (s), 128.5 (d), 130.9 (d), 131.7 (s), 167.8 (s).- $C_{16}H_{18}O_8$ (338.3): calcd. C 56.80, H 5.36; found C 56.24; H 5.34.

The crystallographic data and refinement parameters of *trans*-**6** are given at the end of the Experimental Section.

cis-**6**: IR ($CHCl_3$): ν = 2980 cm^{-1}, 1750, 1440, 1360, 1250, 1200, 1160.- ^1H NMR (200 MHz, -20 °C, $CDCl_3$): δ = 3.85 (s, 6H, OCH_3), 3.89 (s, 6H, OCH_3), 4.15 (s, 2H, bridgehead H), 7.08 (AA'BB' system, part of A, 2H, arom. H), 7.34 (part of B, 2H, arom. H).- ^{13}C NMR (50 MHz, - 20 °C, $CDCl_3$): δ = 52.5 (q), 53.0 (q), 53.3 (d), 107.7 (s), 126.5 (d), 128.4 (d), 131.2 (s).- $C_{16}H_{18}O_8$ (338.3): calcd. C 56.80, H 5.36; found C 56.22, H 4.98.

7: IR ($CHCl_3$): ν = 2980 cm^{-1}, 1750, 1440, 1270, 1160. - ^1H NMR (200 MHz, $CDCl_3$): δ = 3.75 (s, 12H, OCH_3), 4.93 (s, 2H, CH), 7.34 - 7.49 (AA'BB' system, 4H, arom. H). - ^{13}C NMR (50 MHz, $CDCl_3$): δ = 53.2 (q), 55.0 (d), 129.0 (d), 130.9 (d), 132.9 (s), 168.5 (s).- $C_{16}H_{18}O_8$ (338.3): calcd. C 56.80, H 5.36; found C 56.34 H 5.16.

Thermal Decomposition of Bisdioxetane syn,syn-**5**. A solution of 33.1 mg (0.100 mmol) of *syn,syn*-**5** in 0.5 ml of $CDCl_3$ was placed into a NMR tube, which contained hexamethyldisiloxane as internal standard, and allowed to stand at ca. 20 °C (room temp.) in the dark. The progress of decomposition was monitored by ^1H NMR spectroscopy and conversion to monodioxetane *trans*-**6** (97%) was complete after 34 h. The halflife of *syn,syn*-**5** was found to be 16 h at ca. 20 °C. The crude product was recrystallized from a 2:3 Et_2O/pentane mixture to afford *trans*-**6** as yellow needles, m.p. 133 - 134 °C. Its spectral data matched those obtained in the thermolysis of *syn,anti*-**5**.

Thermal Decomposition of Monodioxetanes cis- and trans-**6**. A solution of *trans*-**6** (30.0 mg, 0.090 mmol) in 0.5 ml $CDCl_3$ was placed into an NMR tube and heated at 55 °C for 15 h. After this time the starting material was completely consumed as monitored by peroxide test (KI, AcOH). The crude product was recrystallized from a 1:3 Et_2O/pentane mixture to give 29.0 mg (98%) of tetraester **7** as colorless needles, m.p. 99 - 100 °C. The spectral data were identical with those obtained in the thermal decomposition of *syn,anti*-**5**.

The same procedure was employed for *cis*-**6** and after 9 h at 55 °C the tetraester **7** was obtained nearly quantitatively. The halflife of *cis*-**6** was determined to be 3.75 h at 80 °C by chemiluminescence measurements.

Benzo[d]cyclopropa[b]cyclohexanone **9**. A sample of 20.2 mg (0.066 mmol) **4** was dissolved in 4 ml of dry CH_2Cl_2 and the solution was allowed to stand at ca. 20 °C (room temp.) in the dark. After 24 h, as monitored by ^1H NMR, the conversion was complete. On exposure to daylight the starting material was consumed within 5 h. Removal of the solvent and recrystallization of the residue from a 1:1 mixture of Et_2O/pentane afforded 18.8 mg (93%) **9** as colorless plates, m.p. 116 - 117 °C.

9: IR (KBr): ν = 3000 cm^{-1}, 2970, 2860, 1760, 1740, 1480, 1360, 1220, 1150, 1110, 1100, 1010, 920.- ^1H NMR (250 MHz, $CDCl_3$): δ = 3.29 (s, 1H, cyclopropane H), 3.47 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 4.31 (s, 1H, CH), 7.25-7.35 (m, 4H, arom. H). - ^{13}C NMR (63 MHz, $CDCl_3$): δ = 39.4 (d), 52.7 (q), 57.6 (q), 58.3 (q), 58.9 (q), 72.9 (s), 76.6 (s), 80.0 (d), 127.8 (s), 128.0 (d), 128.9 (d), 129.1 (d), 135.7 (s), 167.4 (s), 197.0 (s). - $C_{16}H_{18}O_6$ (306.30): calcd. C 62.74, H 5.92; found C 62.47, H 5.92.

The crystallographic data and refinement parameters of **9** are given at the end of the Experimental Section.

Synthesis of Monodioxetane syn-**3**. A solution of benzobarrelene **2** (80.0 mg, 0.292 mmol) in 4 ml of dry CH_2Cl_2 at -30 °C was photooxygenated by irradiation with a 150-W sodium lamp and TPP (0.5 mg) as sensitizer. The reaction was monitored by TLC and after consumption of the starting material (ca. 6 min) the solvent was removed (-35 °C/0.1 Torr). Low-temperature (-35 °C) NMR analysis of the crude product mixture indicated the presence of *syn*-**3**, **4** and *syn,syn*- and *syn,anti*-**5** in a ratio of 79:14:4:3 at a conversion of ca. 95%. Mass balance was ca. 85% as established by NMR spectroscopy by using hexamethyldisiloxane as internal standard. The mixture was recrystallized from 2:3 Et_2O/pentane mixture at -50 °C to afford 8.0 mg (9%) endoperoxide **4** as yellow needles, m.p. 79 - 80 °C (dec.).

The mother liquor was chromatographed on silica gel (30 g) at -30 °C with a 4:1 petroleum ether (b.p. 35-40 °C)/Et_2O mixture as eluent. The first fraction contained the monodioxetane *syn*-**3** as main product. After removal of the solvent by distillation (ca. -30 °C/0.03 Torr), 30.0 mg (33%) of monodioxetane *syn*-**3** was obtained as a yellow oil (TLC, 2:1 pentane/Et_2O, R_f 0.45), which contained ca. 7% of diester **8** as decomposition product.

syn-**3**: ^1H NMR (200 MHz, -35 °C, $CDCl_3$): δ = 3.62 (s, 6H, OCH_3), 3.78 (s, 6H, OCH_3), 3.93 (s, 2H, bridgehead H), 7.27 (AA'BB' system, 4H, arom. H).- ^{13}C NMR (50 MHz, -35 °C, $CDCl_3$): δ = 49.2 (q), 51.9 (q), 58.9 (d), 110.8 (s), 124.4 (d), 127.1 (d), 137.1 (s), 138.7 (s).

Photooxygenation of Monodioxetane syn- **3**. A solution of 15.3 mg (0.050 mmol) dioxetane **3** in 0.5 ml of $CDCl_3$ and TPP (0.5 mg) as sensitizer was placed into an NMR tube and irradiated with a 150-W sodium lamp at -35 °C for 10 min while passing a slow stream of dry oxygen gas. Reaction progress was monitored by TLC. NMR analysis (hexamethyldisiloxane as internal standard) of the crude reaction mixture at -30 °C indicated total consumption of the starting material and formation of the bisdioxetanes *syn,syn*-**5** and *syn,anti*-**5** in a ratio of 77:23 in nearly quantitative yield.

Thermal Decomposition of Monodioxetanes syn-3. A solution of 92.0 mg (0.300 mmol) monodioxetane *syn-3* in $CDCl_3$ was allowed to warm up to ca. 20 °C and kept at this temperature for 1 h. 1H NMR analysis of the crude thermolysate indicated that the expected diester **8**, but also 2,3-dimethoxynaphthalene (**10**) and dimethyl oxalate, were formed in a ratio of 70:15:15. Conversion was ca. 100% and mass balance was 85%. The halflife of *syn-3* at ca. 20 °C (room temp.) was determined to be 25 min. Naphthalene **10** (6.7 mg, 12%) was isolated as first fraction by silica gel (45 g) column chromatography with petroleum ether (b.p. 30-50 °C)/Et_2O (3:1) as eluent. As a second fraction, a mixture of diester **8** and naphthalene **10** was isolated. Recrystallization from Et_2O/pentane gave 5.0 mg (5.4%) of diester **8**.

8: IR ($CHCl_3$): ν = 3020 cm^{-1}, 2920, 1750, 1460, 1280, 1250, 1230, 1040.- ^1H NMR (200 MHz, $CDCl_3$): δ = 3.70 (s, 6H, OCH_3), 3.79 (s, 6H, OCH_3), 4.51 (s, 2H, CH), 7.30 (AA'BB' system, part of A, 2H, arom. H), 7.41 (part of B, 2H, arom. H).- ^{13}C NMR (50 MHz, $CDCl_3$): δ = 49.6 (q), 52.6 (q), 59.2 (d), 127.6 (d), 128.4 (d), 131.7 (s), 137.6 (s), 171.3 (s).- $C_{16}H_{18}O_8$ (338.3): calcd. C 56.80, H 5.36; found C 56.34, H 5.16.

The known naphthalene **10**[11] and dimethyl oxalate were identified by comparison of their spectral data with those reported.

Photooxygenation of Diester **8.** A sample (10.0 mg, 0.033 mmol) of diester **8** and TPP (0.5 mg) was dissolved in 0.5 ml $CDCl_3$, transfered into an NMR tube, and irradiated with a 150-W sodium lamp at -15 °C for 13 min while passing a slow stream of dry oxygen gas. ^1H NMR analysis indicated that the dioxetane *trans-6* was formed quantitatively.

Autooxidation of Diester **8.** A solution of 7.0 mg (0.023 mmol) diester **8** in 10 ml of pentane was stirred at 20 °C (room temp.) in daylight while exposed to air for five days. The solvent was removed under reduced pressure (20 °C/17 Torr) and the residue was analyzed by ^1H NMR, which indicated the presence of dioxetane *trans-6* and its decomposition product tetraester **7** in a ratio of 80:20.

X-Ray Crystal Stucture Analysis[12] *of trans-6* and **9**

The measurements were made on a STOE Stadi4 diffractometer; Mo-Kα radiation; graphite monochromator; the structures were solved by the direct-phase determination method and refined by the full-matrix least squares method; Siemens SHELXTL PLUS program (Micro VAX II) was used; hydrogen atom positions: riding model with fixed isotopic U.

Crystallographic Data for the Monodioxetane trans-6. $C_{16}H_{18}O_8$ (338.3); Crystal size 0.45 x 0.6 x 0.35 mm; triclinic; $P\bar{1}$; 200 K; a = 824.9 (2), b = 1369.9 (3), c = 797.6 (2) pm; α = 105.71 (2)°, β = 115.59 (2)°, γ =78.60 (2)°; V = 779.2 (6) · 10^6 pm^3; Z = 2; d (calcd.) = 1.442 g·cm^{-3}. - Data collection: ω/Θ -Scan; Θ = 1.75 - 27.5°; h = -10→9; k = -17→11; l = 0→11; number of reflections: 4118 measured, 3336 unique; 2775 with $F > 3\sigma(F)$; μ = 0.11 mm^{-1}; absorption correction: none. - Structural analysis and refinement: data-to-parameter ratio: 12.73; R = 0.095; R_W = 0.084; $w=1/\sigma^2(F)$; largest difference peak: 0.67 e$Å^{-3}$; largest difference hole: 0.47 $Åe^{-3}$.

Crystallographic Data for the α-Methoxy Ketone **9**. $C_{16}H_{18}O_6$ (306.3); crystal size 0.75 x 1.6 x 0.15 mm; triclinic, P_1; a = 1282.5 (2), b = 1496.2 (3), c = 815.4 (1) pm; α = 101.78 (1)°, β = 90.38 (1)°, γ = 91.97 (2)°; V = 1530.6 (4) $\cdot 10^6$ pm^3; Z = 4; d (calcd.) = 1.329 $g\cdot cm^{-3}$.- Data collection: ω/Θ-scan; Θ = 1.75 - 22.50; h = -13→13; k = -16 →15; l = 0→8; number of reflections: 4015 measured, 4015 unique; 3594 with $F > 3\sigma(F)$; $\mu = 0.10$ mm^{-1}; absorption correction: Ψ-scan.- Structural analysis and refinement: data-to-parameter ratio: 9.03; R = 0.048; $R_w = 0.043$; $w = 1/\sigma^2$ (F); largest difference peak: 0.5 $eÅ^{-3}$; largest difference hole: 0.47 $eÅ^{-3}$.

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(*Received in Germany* 9 *May* 1994; *accepted* 3 *June* 1994)