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Photosensitized Oxidation of 1,1′-Bi(benzocyclobutenylidene)

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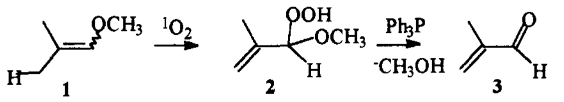
In an attempt to explore whether singlet molecular oxygen reactions could be used to obtain access to antiaromatic species, we carried out the Rose Bengal photosensitized oxygenation of (*E*)- and (*Z*)-1,1′-bi(benzocyclobutenylidene) (**7-*E*** and **7-*Z***). The photooxidation resulted in a facile *E*/*Z* isomerization accompanied by the sluggish uptake of oxygen and formation of benzocyclobutenone **8**, spiroindanone **9**, phthalide **10**, and dione **11**. We found no evidence, however, for the generation of the corresponding benzocyclobutadiene via a $^1O_2$-ene reaction. On the contrary, the data suggests that the isomerization of the diaryl olefin can occur in the absence of sensitizer, while product formation is a free radical autoxidative process, presumably initiated by the interaction of excited dye with molecular oxygen ("type IIc"). The formation of **8-11** may be rationalized in terms of secondary rearrangements (unzipping and cyclization) of the initially formed polyperoxide or polyperoxy radical. The absence of singlet oxygen ene product may reflect the increased activation energy required to generate an antiaromatic product. Alternatively, the inability of the ring methylene hydrogens to attain a pseudoaxial conformation may actually be the controlling factor in inhibiting the ene process.

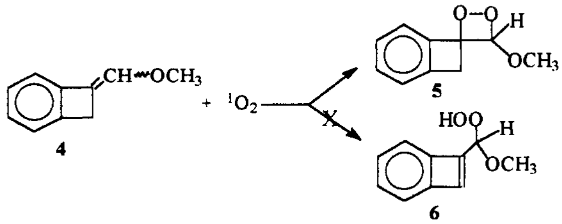
Introduction

Previous research in this laboratory has explored the effect of ring-strain on the mode, rate, and direction of singlet oxygen attack.[1] In particular we have focused on various small ring olefin systems in which ring-strain decreases or develops as we proceed to product. These studies indicate that, in the transition state leading to product, $^1O_2$ is essentially insensitive to strain considerations.[1a,1b] This conclusion is consistent with prior evidence that singlet oxygen reactions have very small activation energies (0.5–8 kcal/mol)[2] and that the product-determining transition state is reactant-like and occurs quite early.[3]

In light of the above, we speculated as to whether singlet molecular oxygen reactions could be used to obtain access to antiaromatic species. One relevant communication by Conia and co-workers[4] reports that enol ethers (**1**, eq 1) undergo photosensitized hydroperoxidation at the vinyl carbon α to the ether group, yielding the corresponding allylic α-hydroperoxy ether **2** or its dehydration product **3**. Nevertheless, 1-(methoxymethylene)benzocyclobutene (**4**, eq 2) upon photooxidation yields only dioxetane **5**.



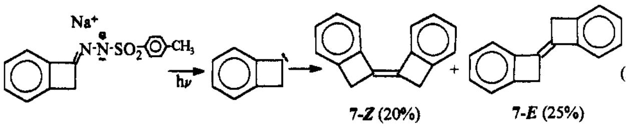
(1)



(2)

Although, Conia argues that the absence of $^1O_2$ ene product **6** stems from its antiaromatic structure, this interpretation is by no means conclusive. Antiaromaticity aside, vinyl aromatics often favor dioxetane formation;[5] a fortiori, if they are electron-rich enol ethers!

To better explore the effect of antiaromaticity on the mode and direction of singlet oxygen attack, we turned to the photosensitized oxygenation of (*E*)- and (*Z*)-1,1′-bi(benzocyclobutenylidene) (**7-*E*** and **-*Z***, see eq 3). It was our hope that the use of these symmetrical tetrasubstituted



(3)

olefins would increase our chances of observing a $^1O_2$ ene reaction. As we shall see, the system opted to react via non-singlet oxygen reaction pathways, but antiaromaticity may not be the determining factor.

Results

A. Photooxidation. The *E*- and *Z*-isomers of the title compound **7** were prepared via the photochemical decomposition of the sodium salt of benzocyclobutenone (*p*-toluenesulfonyl)hydrazone (eq 3)[6] and characterized by their spectral data.[6g] Olefin **7** proved quite stable to autoxidation, and no oxygenation products were observed even after pure samples were allowed to stand in air for 4 years. Samples (2 mmol) of the isomers were photooxidized ($\lambda > 360$ nm) in $CHCl_3$, CH_3CN, C_6H_6, or CH_3OH

[†] The Ethel and David Resnick Chair in Active Oxygen Chemistry.

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(2) a) Koch, E. *Tetrahedron* **1968**, *24*, 6295–6318. b) Ashford, R. D.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1975**, *97*, 3604–3607.

(3) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359–387.

(4) Rousseau, G.; Le Perchec, P.; Conia, J. M. *Synthesis* **1978**, 67–70.

(5) a) Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, A. A., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 173–286; see especially pp 204–214. b) Jiancheng, Z.; Foote, C. S. *Tetrahedron Lett.* **1986**, *27*, 6153–6156 and references cited therein. c) Smonou, I.; Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1988**, *23*, 2769–2772 and refs cited therein.

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Table I. Product Distribution (% Yield) and Solvent Effect in the Photosensitized Oxidation of (*E*)-1,1'-Bi(benzocyclobutenylidene)[a] (7-*E*)

	Chloroform-*d*				CH_3CN	C_6H_6	CH_3OH
photooxid time (h)	0	4[b]	13	30	30	30	30
product (% yield)							
E-olefin 7-***E***	96	56	16				
Z-olefin 7-***Z***	4	37	16				
bicyclobutenone **8**		5	46	68	62	46	38
spiroindanone **9**		2	15	23	24	22	51
phthalide **10**			5	7	6	30	4
dione 11			2	2	8	2	7

[a] A blank space indicates that the product's presence was not observed. [b] In one run, a small amount (ca. 2%) of epoxide **12** was detected after 4 h of irradiation; it was not, however, observed at longer irradiation times.

using polymer-based Rose Bengal (p-RB). The irradiation was followed by TLC, and oxygen uptake proceeded very sluggishly, in sharp contrast to the rapid rate of oxygen uptake (0.5–2 h) generally observed with tetrasubstituted olefins.[7] After about 30 h of irradiation, 1 equiv of O_2 had been absorbed, oxygen uptake had essentially ceased, and no starting material remained. At the same time, the intense red color of the sensitizer had faded to a light pink. No uptake of oxygen occurred when zinc tetraphenylporphyrin (Zn-TPP) replaced p-RB as sensitizer or when the free-radical inhibitor 2,6-di-*tert*-butylphenol[1f,8] was added. The $^1O_2$-quencher DABCO[1f,9] had no effect on the rate or course of the oxygenation reaction.

B. Product Identification. The photooxidation mixture was chromatographed, and the products were identified as the known compounds benzocyclobutenone **8**,[10] spiroindanone **9**,[11] phthalide **10**,[12] and dione **11**[13] (Scheme I).

Scheme I

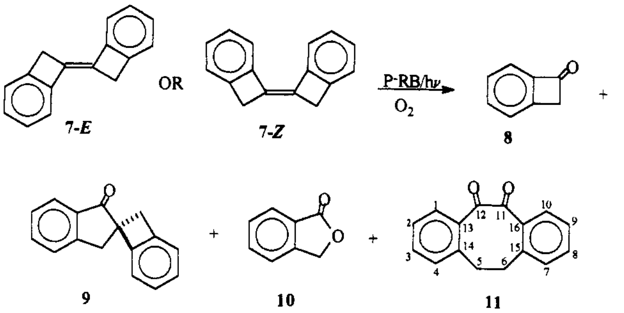

Table II. Product Distribution (% Yield) in the Photosensitized Oxidation of (*Z*)-1,1'-Bi(benzocyclobutenylidene) (7-*Z*) in $CDCl_3$[a]

	% yield of product at photooxidation time			
product	0 h	4 h	13 h	30 h
E-olefin 7-***E***	13	31	16	
Z-olefin 7-***Z***	87	40	17	
bicyclobutenone **8**		14	32	48
spiroindanone **9**		11	26	38
phthalide **10**		3	6	9
dione **11**		2	3	5

[a] A blank space indicates that the product's presence was not detected.

Table III. *E*/*Z* Ratios of Bi(benzocyclobutenylidene) as a Function of Irradiation Conditions in $CDCl_3$

conditions	time (h)	initial *E*/*Z* ratio	final *E*/*Z* ratio
N_2	6	81:19	78:22
N_2/p-RB	6	81:19	61:39
O_2	6	81:19	76:24
O_2	22 ± 4	81:19	63:37
O_2/p-RB	4	96:4	60:40
O_2/p-RB	13	96:4	50:50
O_2/p-RB	4	13:87	44:56
O_2/p-RB	13	13:87	48:52

The product distribution, determined via NMR analysis of the product mixture, varied somewhat with solvent, as shown in Tables I and II. In addition, as shown in Tables I and II, the starting olefins 7-***E*** or 7-***Z*** equilibrate during the early stages of the irradiation. Finally, although hydroperoxides react quite exothermically with triphenylphosphine, no evolution of heat was observed when Ph_3P was added to photooxidized solutions of 7-***E*** and 7-***Z***, nor did its addition affect the product ratio.

To get a better insight into the causes of the isomerization, we irradiated (λ > 360 nm) the substrate under various conditions: N_2 vs O_2 atmosphere, with and without sensitizer, and long vs short irradiation times. A summary of the results are given in Table III. Isomerization occurred both in the presence of DABCO and 2,6-di-*tert*-butylphenol.

Because of our suspicion that isomeric epoxides **12** and/or **13** might be formed during the photooxygenation, we prepared **12** and **13** via the *m*-chloroperbenzoic acid (m-CPBA) epoxidation of 7-***E*** and 7-***Z***, respectively (eq 4). In both cases, varying amounts of spiroindanone **9** are also formed, presumably via a pinacolone-type rearrange-

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(11) Spiro[benzocyclobutene-1(2H),2'-inden]-1'(3'H)-one: Barton, J. W. and Shepherd, M. K. *J. Chem. Soc. Perkin Trans. 1* **1987**, 1561–1565.

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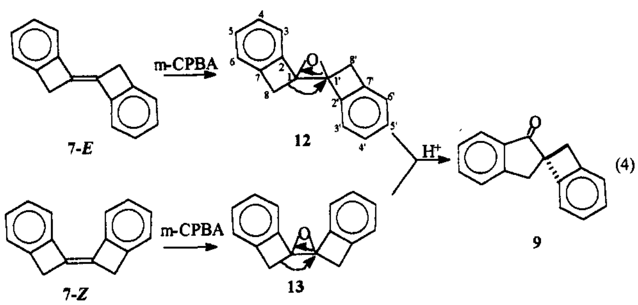

ment,[14] well precedented in strained olefins in general[15] and in the analogous bicyclobutylidene system in particular.[16] Once pure, these epoxides seem relatively stable, but rearrange slowly to **9** upon standing in chloroform solution at room temperature, giving about a 40% yield of the spiroindanone after 2 weeks. No rearrangement was observed, however, when a $CDCl_3$ solution of **12** was exposed to the photosensitized oxidation reaction conditions (O_2, P-RB and visible light) for 7 h.

With authentic samples of the epoxides in hand, we scoured the NMR spectra of the reaction mixtures for evidence of their presence. No epoxide was ever observed during the course of the photooxidation of **7-*Z***. In the case of **7-*E***, however, there was one run in which a small amount of epoxide **12** (ca. 2%), but no **13**, was observed after 4 h of irradiation; but its presence could no longer be detected 9 h later. As noted above, **12** is stable under the reaction conditions.

Discussion

A. Photooxidation Type. There are two major classes of photosensitized oxidative processes, appropriately called "type I" and "type II".[17] The former is characterized by the direct reaction of the triplet sensitizer with a molecule of *substrate*. This interaction can lead down either of two different pathways. The first is hydrogen atom abstraction, which initiates free radical autoxidative processes ("type Ia", eqs 5 and 6). Alternatively, electron transfer from substrate to excited sensitizer may occur, in which case the oxygenation products result from the coupling of the substrate cation radical with superoxide anion radical ("type Ib", eqs 7–9). Irrespective of whether the mechanism of oxygenation is a photoinitiated autoxidation or an electron transfer photooxidation,[18] only ground state triplet molecular oxygen ($^3O_2$) is involved.

type Ia
$$\mathrm{Sens}^3 + \mathrm{RH} \rightarrow {}^{\bullet}\mathrm{SensH} + \mathrm{R}^{\bullet} \tag{5}$$

$$\mathrm{R}^{\bullet} + {}^3\mathrm{O}_2 \rightarrow \mathrm{ROO}^{\bullet} \rightarrow \text{Oxygenation} \tag{6}$$

type Ib
$$\mathrm{Sens}^3 + \mathrm{R} \rightarrow \mathrm{Sens}^{-\bullet} + \mathrm{R}^{+\bullet} \tag{7}$$

$$\mathrm{Sens}^{-\bullet} + {}^3\mathrm{O}_2 \rightarrow \mathrm{Sens} + \mathrm{O}_2^{-\bullet} \tag{8}$$

$$\mathrm{R}^{+\bullet} + \mathrm{O}_2^{-\bullet} \rightarrow \text{Oxygenation} \tag{9}$$

"Type II", on the other hand, is characterized by initial interaction between the triplet sensitizer and a molecule of *oxygen*. The traditional "type II" (sometimes called "type IIa")[19] involves transfer of the sensitizer's excitation energy to molecular oxygen generating singlet molecular oxygen ($^1O_2$), which is the oxygenation species (eqs 10 and 11). Recently, however, two additional type II processes

type IIa
$$\mathrm{Sens}^3 + {}^3\mathrm{O}_2 \rightarrow \mathrm{Sens}^1 + {}^1\mathrm{O}_2 \tag{10}$$

$$\mathrm{RH} + {}^1\mathrm{O}_2 \rightarrow \text{Oxygenation} \tag{11}$$

type IIb
$$\mathrm{Sens}^3 + {}^3\mathrm{O}_2 \rightarrow [\mathrm{Sens}^1 + {}^1\mathrm{O}_2] \rightarrow \mathrm{Sens}^{+\bullet} + \mathrm{O}_2^{-\bullet} \tag{12}$$

$$\mathrm{RH} + \mathrm{O}_2^{-\bullet}\ (\text{or HOO}^{\bullet}) \rightarrow \text{Oxygenation} \tag{13}$$

type IIc
$$\mathrm{Sens}^3 + {}^3\mathrm{O}_2 \rightarrow \cdot\mathrm{Sens\text{-}OO}^{\bullet} \tag{14}$$

$$\mathrm{RH} + {}^{\bullet}\mathrm{Sens\text{-}OO}^{\bullet} \rightarrow \text{Oxygenation} \tag{15}$$

have been observed, which result in oxygenation via radical processes. In "type IIb", triplet sensitizer interacts with dioxygen via electron transfer to yield superoxide; the latter, or more likely its derivatives,[20] initiate oxygenation (eqs 12 and 13).[19,21] Research in the case of Rose Bengal has suggested, however, that the source of the superoxide is in fact a reaction between RB and singlet oxygen.[19,22] Finally and most recently, a third "type II" reaction (which we will refer to as "type IIc") has been observed with $n \rightarrow \pi^*$ sensitizers, in which the triplet sensitizer (generally an excited carbonyl) reacts with molecular oxygen generating a diradical peroxy species (e.g., $^{\bullet}OCR_2OO^{\bullet}$). The latter may initiate radical processes itself or via its derivatives (eqs 14 and 15).[23]

There is ample evidence in this study to rule out a "type IIa" oxygenation and demonstrate that a non-singlet oxygen/free-radical mechanism predominates in the photosensitized oxidation of bi(benzocyclobutenylidene): (1)

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(14) March, J. *Advanced Organic Chemistry—Reactions, Mechanisms and Structure*, 3rd ed.; McGraw-Hill: New York, 1985; p 964.

(15) See for example: (a) footnote 1d and refs 15–20 cited therein. (b) Footnote 1b and ref 16 cited therein. (c) Aue, D. H.; Meshishneck, M. J.; Shellhamer, D. F. *Tetrahedron Lett.* **1973**, 4799–4802. (d) Donnely, J. A.; Hoey, J. G. *J. Chem. Soc. Perkin Trans. 1* **1975**, 2364–2368. (e) Crandall, J. K.; Conover, W. W. *J. Org. Chem.* **1978**, *43*, 3533–3535. (f) Erden, I.; de Meijere, A.; Rousseau, G.; Conia, J. M. *Tetrahedron Lett.* **1980**, *21*, 2501–2504. (g) Lechevallier, A.; Huet, F.; Conia, J. M. *Tetrahedron* **1983**, *39*, 3329–3336. (h) de Meijere, A.; Erden, I.; Weber, W.; Kaufmann, D. *J. Org. Chem.* **1988**, *53*, 152–161.

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(20) (a) Superoxide turns out to be a poor radical on all accounts, rarely initiating free radical autoxidative processes via H-abstraction or addition to double bonds.[20b,20c] Its conjugate acid $HOO^{\bullet}$, or another of its derivatives $HO^{\bullet}$, are well-documented radical initiators. (b) Frimer, A. A. In *Superoxide Dismutase*; Oberley, L. W., Ed.; Chemical Rubber Co.: Boca Raton, FL, 1982; Vol. II, pp 83–125. (c) Frimer, A. A. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: Chichester, 1983; pp 429–461.

(21) Neckers, D. C. *J. Photochem. Photobiol., A: Chem.* **1989**, *47*, 1–29.

(22) Jefford, C. W.; Estrada, M. J.; Barchietto, G. *Tetrahedron* **1987**, *43*, 1737–1745 and refs cited therein.

The $^1O_2$-quencher DABCO[1f,9] had no effect on the rate or course of the reaction. (2) On the other hand, no oxygenation occurred when the free-radical inhibitor 2,6-di-*tert*-butylphenol[1f,8] was added. (3) The rate of reaction in "type IIa" processes should be independent of the sensitizer utilized. This is because the sensitizer is not involved in the oxidation of the substrate, but rather only in the generation of $^1O_2$. In the present system, however, no oxygen uptake was observed when zinc tetraphenylporphyrin (Zn-TPP) replaced p-RB as photosensitizer, indicating once more that this is not a $^1O_2$ reaction. We note that Zn-TPP is the sensitizer of choice for the singlet oxygenation of *trans*-stilbene,[24] a compound we a priori thought would be a good model for our substrate 7.[25]

What about the other mechanistic options? After all, the literature is replete with examples in which Rose Bengal, the sensitizer in the present study, initiates "type I" hydrogen or electron transfer processes.[26] Nevertheless, neither of these processes are likely to be the mode of action in our system. Considering the structure of our substrate 7, we see that the only possible candidates for hydrogen atom abstraction are the benzocyclobutenyl ring methylene hydrogens, and a radical formed at this position would formally be both benzylic and allylic. However, in fact it is neither. Antiaromaticity considerations rules out allylic stabilization from the exocyclic double bond, while ring and angle strain would sharply limit the importance of any benzylic resonance stabilization. In addition, we detect no products resulting from hydroperoxide formation at this position, as is generally observed when a "type I"-hydrogen abstraction is observed.[1d]

Regarding the possibility of electron-transfer photooxidation, such oxygenations have been extensively studied[18] and occur generally, and with phenyl-substituted olefins in particular, only in polar solvents such as acetonitrile and methanol.[27] In the present system, we find no substantial change in the rate of reaction or product distribution when the nonpolar solvent benzene is used.[28] In addition, while the dye Methylene Blue succeeded in photosensitizing the slow electron-transfer oxidation of stilbene, a good model for our substrate 7, RB could not.[29]

Turning now to the remaining "type II" mechanisms, we have already noted above that RB and $^1O_2$ are reported to generate superoxide anion radical ("type IIb") which can in turn initiate radical processes.[19,20,22] Nevertheless, in such cases both DABCO and 2,6-di-*tert*-butylphenol inhibit this oxidation, a situation which is not observed in our system. Having ruled out all the other possibilities, we perforce accept the remaining "type IIc" process as the mode of initiation, in which the carbonyl of RB acts in a fashion analogous to benzophenone.[30] Such a mechanism is only feasible, however, if some cycle for the regeneration of sensitizer is operating. Previous work indicates that this is indeed the case.[23a,23f]

B. Mechanism of *Cis–Trans* Isomerization. Before continuing with our discussion of the mechanism of photooxidation, let us turn for a moment to the mechanism of the *cis–trans* equilibration of the starting olefin observed during the course of the reaction (see Tables I and II). The photoisomerization of aromatic olefins during direct or sensitized irradiation has been extensively studied.[31] This equilibration can clearly result from a direct irradiation since it is observed in the absence of sensitizer and oxygen. Interestingly, the direct isomerization occurs despite our use of a 360-nm cut-off filter and the fact that the highest λ_{max} of 7 occurs at 326 nm (log ϵ 4.75).[32] An end-absorption is presumably involved.[33] The corresponding direct irradiation of stilbene is carried out at ca. 315 nm.[31,33a]

This isomerization does not initiate the concomitant oxidative process; in the absence of sensitizer, isomerization, but not oxygenation, occurs.[33b] However, the sensitizer-initiated autoxidation does seem to play a role in the isomerization. The results indicate that, in the absence of sensitizer, the same isomeric ratios (ca. 60:40 E/Z) are obtained whether the duration of irradiation is 18 or 26 h. We can assume that this ratio is the photostationary state.[33a] However, in the presence of sensitizer this ratio approaches 50:50, suggesting that in the presence of sensitizer an additional equilibration mechanism is involved. Presumably, the peroxy radical-initiating species, generated by the interaction of RB triplet and molecular oxygen, adds reversibly to the olefin bond of the bi(benzocyclobutenylidene), yielding rotamers **14-*E*** and **14-*Z*** (eq 16).

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[23] (a) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193–4200. (b) Mori, A.; Takeshita, H. *Chem. Lett.* **1978**, 395–396. (c) Bartlett, P. D.; Becherer, J. *Tetrahedron Lett.* **1978**, 2983–2986. (d) Koo, J.-Y.; Schuster, G. B. *J. Org. Chem.* **1979**, *44*, 847–851. (e) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2049–2053. (f) Shepherd, J. P. *J. Org. Chem.* **1983**, *48*, 337–342. (g) Clennan, E. L.; Speth, D. R.; Bartlett, P. D. *J. Org. Chem.* **1983**, *48*, 1246–1250. (h) Sawaki, Y.; Foote, C. S. *J. Org. Chem.* **1983**, *48*, 4934–4940. (i) Sawaki, Y.; Ogata, Y. *J. Org. Chem.* **1984**, *49*, 3344–3349.

[24] See, for example, Kwom, B.-M.; Foote, C. S.; Khan, S. I. *J. Org. Chem.* **1989**, *54*, 3378–3382 and refs cited therein. See also note 33c below.

[25] Because of the extreme sluggishness of the reaction of substrate 7 to photooxidation with Rose Bengal and the absence of any reaction with Zn-TPP, we decided against exploring the reaction of 7 with a chemical source of $^1O_2$. The latter are practical only with reactive or at least moderately reactive substrates whose photooxidation reaction time is on the order of a few hours, not days.[1g]

[26] For a review of Rose Bengal and its derivatives as photosensitizers, see: (a) Lamberts, J. J. M.; Neckers, D. C. *Tetrahedron* **1985**, *41*, 2183–2190; see also refs 17–23 cited therein for examples of "type I" initiation. (b) Zakrzewski, A.; Neckers, D. C. *Tetrahedron* **1987**, *43*, 4507–4512. c) Reference 21 *supra*.

[27] Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083–6088.

[28] Foote and co-workers[23h,28b] have used this solvent effect as a diagnostic test for electron transfer photooxidative processes. (b) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221–2227.

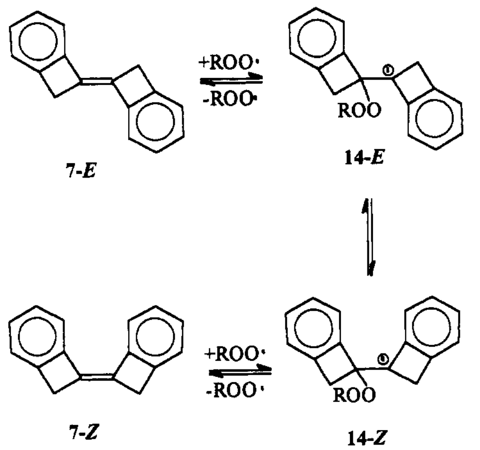
[29] Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275–4277.

[30] (a) Paquette and Carr[30b] have also suggested the involvement of a "type IIc" mechanism in the RB-mediated free-radical epoxidation of certain strained olefins. A similar possibility was raised by Jefford and Boschung, but rejected because, in their bi(adamantylidene) system, epoxide formation is inhibited by DABCO.[19] (b) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553–7559.

[31] (a) Saltiel, J.; D'Agostino, J.; Megarty, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, C. In *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, pp 1–113. (b) Saltiel, J.; Charlton, J. L. In *Rearrangement in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 25–89. (c) Arai, T.; Karatsu, T.; Misawa, H.; Kuriyama, Y.; Okamoto, H.; Hiresaki, T.; Furuuchi, H.; Zeng, H.; Sakuragi, H.; Tokumaru, K. *Pure Appl. Chem.* **1988**, *60*, 989–998. (d) Lednev, I. K.; Alfimov, M. V.; Kuriyama, Y.; Arai, T.; Sakuragi, H. Tokumaru, K. *J. Photochem. Photobiol., A: Chem.* **1992**, *63*, 201–209. (e) Gollnick and Griesbeck[31f] report an example of what they believe to be $^1O_2$ induced *cis–trans* isomerization. Such a process is quite unexpected and surprisingly no diagnostic tests (e.g., DABCO or 2,6-di-*tert*-butylphenol quenching studies) were reported which could have affirmed or ruled out the involvement of $^1O_2$ or free-radical processes. (f) Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1983**, *24*, 3303–3306.

[32] O'Leary, M. A.; Wege, D. *Tetrahedron* **1981**, 801–811.

[33] (a) Horspool, W. M. *Aspects of Organic Photochemistry*; Academic Press: London, 1976; p 75ff. (b) R. C. Petterson (*Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 644–645) reports that direct irradiation (λ 300–400 nm) of *cis*- and *trans*-phenylpropenes at 35 °C resulted in rapid interconversion of the isomers and slow (72 h) epoxide formation. Photoepoxidation is also observed with *trans*-stilbene. As noted below, we see no product formation in the absence of sensitizer. (c) Foote and co-workers[24] report isomerization and photoepoxidation in the Zn-TPP photosensitized oxygenation of *trans*-stilbene, despite the use of a 360 nm cut-off filter. As in our case, in which $^1O_2$ is clearly not involved, this probably results from an end absorption.



(16)

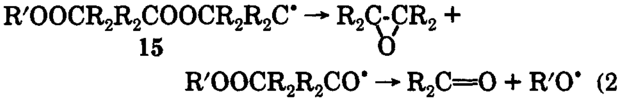
The reversible nature of this addition is certainly not surprising, considering the conjugation regained upon β-elimination of the peroxy radical; nevertheless, the final 1:1 ratio of isomers is. This lack of isomeric preference is consistent, however, with our previous observation[6] of a statistical distribution of ketazines (25% *anti–anti*, 50% *anti–syn* or *syn–anti*, and 25% *syn–syn*) in the reaction of benzocyclobutenone with hydrazines. In both these cases, the 90° angle of the cyclobutyl ring pulls the phenyl ring back, thereby minimizing its steric contribution.

C. Mechanism of Product Formation. Irrespective of the exact mode of initiation, a free radical mode of reaction is clearly indicated. The question now becomes the mechanism of product formation. The autoxidation of olefins initiated by double bond addition has been extensively studied by Mayo and co-workers.[34] Such processes (eqs 17–20; R′ = polyperoxide residue) generally

$$\mathrm{R'OO^{\bullet} + R_2C{=}CR_2 \rightarrow R'OOCR_2R_2C^{\bullet}} \quad (17)$$

$$\mathrm{R'OOCR_2R_2C^{\bullet} + O_2 \rightarrow R'OOCR_2R_2COO^{\bullet}} \quad (18)$$

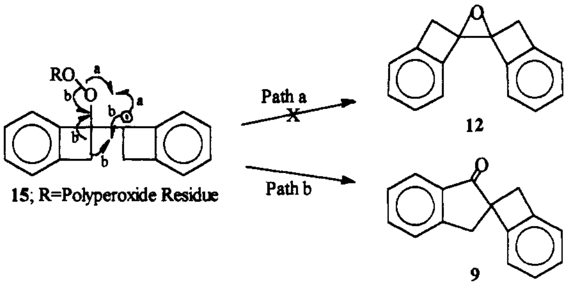
$$\mathrm{R'OOCR_2R_2COO^{\bullet} + R_2C{=}CR_2 \rightarrow R'OOCR_2R_2COOCR_2R_2C^{\bullet}} \quad (19)$$



$$\underset{\mathbf{15}}{\mathrm{R'OOCR_2R_2COOCR_2R_2C^{\bullet}}} \rightarrow \mathrm{R_2\underset{O}{C{-}C}R_2} + \underset{\mathbf{16}}{\mathrm{R'OOCR_2R_2CO^{\bullet}}} \rightarrow \mathrm{R_2C{=}O + R'O^{\bullet}} \quad (20)$$

lead to polyperoxides which "unzip" to epoxides (via carbon-centered radicals of type **15**) and oxidative cleavage products (via oxygen-centered radicals of type **16**).

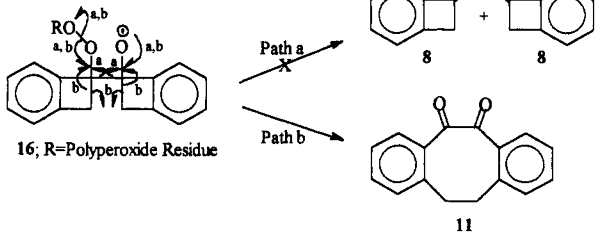
Surveying the products of our reaction, it is clear that the major product bicyclobutenone **8** is the oxidative cleavage product. In addition, we have shown above that spiroindanone **9** is the expected rearrangement product of epoxide **12**. We have also demonstrated, however, that this rearrangement is slow, and that the epoxide is stable under the reaction conditions; hence it is unlikely that **12** is the precursor of the **9** in this reaction.[35] Nevertheless, we believe that **9** is generated from the same carbon-centered radical (**15**) as expected for **12**; but, in light of the additional ring strain that would accrue in epoxide formation, **15** prefers β-cleavage (ring opening; path b in eq 21) over cyclization (path a).[36]



(21)

We note that in methanol the yield of spiroindanone **9** increased dramatically at the expense of oxidative cleavage product **8**. This indicates that the chain length of the polyperoxide is much shorter in hydroxylic solvents than it is in aprotic media. Consistent with this observation, Sawaki and Foote[23h] have observed a greater yield of epoxides in type IIc processes in hydroxylic solvents.

As in the case of indanone **9**, ring strain is also the driving force for the formation of dione **11**. We suggest that the latter is formed from oxygen-centered radical **16** (cf. eq 20) by a variation of the oxidative cleavage process in which ring opening β-cleavage (eq 22, path b) competes with the usual "unzipping" mechanism (path a).



(22)

We are not sure as to the mechanism of phthalide formation, but considering the presence of peroxidic species, a Baeyer–Villiger oxidation of benzocyclobutanone would not be surprising. However, we are at a loss to explain the dramatic rise in the yield of this product in benzene at the expense of oxidative cleavage product.

D. Absence of $^1O_2$ Product. We have thus demonstrated that the photooxidation of bi(benzocyclobutenylidenes) **7-*E*** and **-*Z*** occurs via a free-radical process resulting in rapid *cis–trans* isomerization, as well as, the slow formation of a polyperoxide which "unzips" yielding the observed products **8–11**. The question remains, however, as to why no $^1O_2$ ene reaction is observed, particularly since this mode of action has been reported for the corresponding non-benzo analog, bicyclobutylidene.[16c] The loss of conjugation is certainly not a consideration; the singlet oxygenation of the analogous *cis-* and *trans*-2,3-diphenyl-2-butenes has been well documented.[37] While the latter isomers react, respectively,

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[34] (a) Mayo, F. R. *J. Am. Chem. Soc.* **1958**, *80*, 2465–2480. (b) Mayo, F. R.; Miller, A. A.; Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 2500–2507. (c) Van Sickle, D. E.; Mayo, F. R.; Gould, E. S.; Arluck, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 977–984. (d) Mayo, F. R. *Acc. Chem. Res.* **1968**, *7*, 193–201. (e) Howard, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 3–62; see especially p 25ff. (f) Filippova, T. V.; Blyumberg, E. A. *Russ. Chem. Rev.* **1982**, *51*, 582–591.

[35] Footnote a of Table I records the observation of a low yield of epoxide **12**, in one instance, undoubtedly via path a. This occurrence did not repeat itself.

[36] For related reasons, we now believe that, in the previously reported photosensitized oxygenation of cyclopropenes,[1d] no actual epoxide need be formed in order to obtain the related epoxide rearrangement products.

10 and 100 times more slowly than tetramethylethylene, they both react at least 10 times more rapidly than 2-butene itself.[37d]

Another common cause for low reactivity in $^1O_2$ reactions is a substrate's high ionization potential (IP);[37d,38] however, the IP of 7 is certainly not the source of its inertness to $^1O_2$. The IP of the analogous *cis*- and *trans*-2,3-diphenyl-2-butenes is reported[37c] to be 8.00 and 8.26 eV, respectively, lower than the values 8.30[39] or 8.42[40] eV determined for tetramethylethylene (TME). In addition, we have carried out a cyclic voltametric measurement of the irreversible peak potential of 7-*E* and find it to be 1.4 V vs SCE. Following the lead of Miller and co-workers,[41] this value can be corrected to give an approximate $E_{1/2}$ which can in turn be correlated with IP, using eq 23. The two

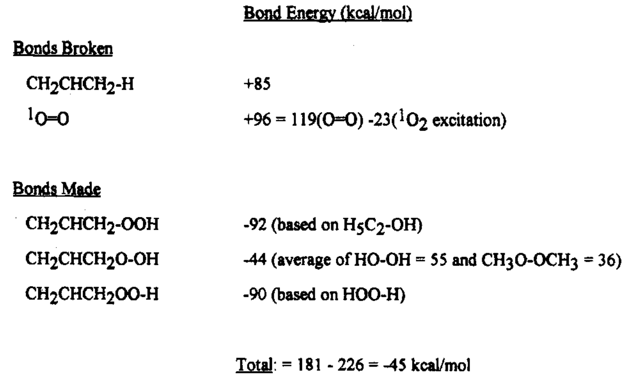
$$E_{1/2} = 0.89(\mathrm{IP}) - 6.20 \tag{23}$$

corrections are as follows: (1) 0.30 V needs to be deducted to compensate for the use of SCE instead of Ag/$AgNO_3$, Miller's reference; (2) a further 0.15 V is deducted to adjust for the irreversible nature of the oxidation. This gives an approximate $E_{1/2}$ of 0.95 and a corresponding IP of 7.85. This again reaffirms that the IP of 7 is lower than that of TME and certainly not the source of 7's lack of $^1O_2$ reactivity.

We have already noted Conia's[4] suggestion that the antiaromatic structure of the expected product is the controlling factor. In order to properly evaluate this proposal, we must first determine two thermodynamic quantities: (a) the heat of reaction for a typical $^1O_2$ ene reaction; and (b) the amount of destabilization engendered in the formation of a benzocyclobutadiene moiety.

Regarding the former, Gollnick and Kuhn[42] have calculated that the singlet oxygen ene reaction of propene to give allyl hydroperoxide should be exothermic by about 45 kcal/mol (see Figure 1). Their value seems to be in error, however, by about 22 kcal. This is because they approximate the energy released in the formation of the C–O bond in HOO–$CH_2CH{=}CH_2$ as 92 kcal/mol, based on HO–C_2H_5. However, Benson and Shaw[43] evaluate the C–O bond energy in HOO–C_2H_5 as only 70 kcal/mol. Hence, the actual heat of reaction should be closer to −23 kcal/mol.

As to the second quantity, theoretical calculations have given a wealth of values for the negative resonance energy of cyclobutadiene,[44] though the most oft quoted numbers are 18 kcal/mol (calculated by Dewar[45] using sophisticated MO methods) and 33 kcal/mol (calculated by Schaad and Hess[46] using a modified HMO approach). Dewar's value has apparently been confirmed by Breslow in several ingenious experiments.[44b,47] Based on Dewar's data, Baird calculates the destabilization in benzocyclobutadiene to be somewhat lower, ca. 11 kcal/mol.[44a] The corresponding value using Schaad and Hess' numbers would be ca. 22 kcal/mol.[48]



	Bond Energy (kcal/mol)
Bonds Broken	
CH_2CHCH_2-H	+85
^{1}O=O	+96 = 119(O=O) -23($^1O_2$ excitation)
Bonds Made	
CH_2CHCH_2-OOH	-92 (based on H_5C_2-OH)
CH_2CHCH_2O-OH	-44 (average of HO-OH = 55 and CH_3O-OCH_3 = 36)
CH_2CHCH_2OO-H	-90 (based on HOO-H)
	Total: = 181 - 226 = -45 kcal/mol

Figure 1. Gollnick and Kuhn's[42] calculation of the heat of reaction for the singlet oxygen ene reaction of 1-propene to allyl hydroperoxide

Schaad and Hess' value would lead us to the conclusion that a singlet oxygen ene reaction of 7 in which the antiaromatic benzocyclobutadiene moiety would be generated would essentially be a thermoneutral process.[49] On the basis of the Hammond postulate, we would expect the transition state for this reaction to occur substantially along the way to product, in contradistinction to the aforementioned early transition state so typical of $^1O_2$ reactions. We would also expect a considerable activation energy which might well disfavor a $^1O_2$ pathway as compared to a free radical process.

However, Dewar's results indicate that the destabilization engendered in forming a benzocyclobutadiene is only 11 kcal/mol. This would still leave the singlet oxygenation of 7 about 12 kcal/mol exothermic, still sufficient to permit an early transition state. Indeed, earlier work from this laboratory[1a,1b] has demonstrated that $^1O_2$ is essentially insensitive to strain considerations, even in cases where the strain energy developed is as high as 11.5 kcal/mol. Clearly, these results require a very different scenario.

It has been well documented that in the $^1O_2$ ene reaction, there is a strong preference for the abstraction of those allylic hydrogens aligned in a 90° dihedral angle with respect to the plane of the double bond *in the low-energy conformations* of the olefin.[38,50] Similarly, in cyclic

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(37) (a) Schulte-Elte, K. H. Ph.D. Dissertation, Gottingen University, Germany, 1961; cited in Gollnick, K.; Schenck, G. O. *Pure Appl. Chem.* **1964**, *9*, 507–525. (b) Kopecky, K. R.; van de Sande, J. H. *Can. J. Chem.* **1972**, *50*, 4034–4049. (c) Adam, W.; Carballiera, N.; Cheng, C.-C.; Sakanishi, K.; Gleiter, R. *J. Org. Chem.* **1979**, *44*, 851–853. (d) Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*, Wasserman, A. A., Murray, R. W., Ed.; Academic Press: New York, 1979; pp 287–427; see especially pp 291 and 298.

(38) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133–336.

(39) Nishida, S.; Moritani, I.; Teraji, T. *J. Chem. Soc., Chem. Commun.* **1972**, 1114–1114.

(40) Fuss, W.; Bock, H. J. *J. Chem. Phys.* **1974**, *61*, 1613–1617.

(41) a) Miller, L. L.; Nordbloom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916–918. (b) See also Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503–2504.

(42) Reference 37d, p 298 and the footnote *ad locum*.

(43) Benson, S. W.; Shaw, R. In *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1, p 132, Table 12.

(44) For reviews on the antiaromaticity of cyclobutadiene see: a) Baird, N. C. *J. Chem. Ed.* **1971**, *48*, 509–514. b) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393–398. c) Maier, G. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 425–4900. d) Masamune, S.; Bally, T. *Tetrahedron* **1980**, *36*, 343–370.

(45) Dewar, M. J. S.; Kohn, M. C.; Trinajstic, N. *J. Am. Chem. Soc.* **1971**, *93*, 3437–3440.

(46) a) Schaad, L. J.; Hess, Jr., B. A. *J. Am. Chem. Soc.* **1972**, *94*, 3068–3074. b) These same authors[46c] have carried out *ab initio* calculations which give an even larger negative resonance energy (−55 to −62 kcal/mol) for bicyclobutadiene. c) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500–7505.

(47) See, however, Bauld, N. L.; Welsher, T. L.; Cessac, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6920–6924.

(48) a) More recent calculations of Moyano and Panniagua[48b] leave cyclobutadiene essentially as before, but find benzocyclobutadiene to be about 2.5 kcal/mol less destabilizing. b) Moyano, A.; Panniagua, J. C. *J. Org. Chem.* **1986**, *51*, 2250–2257.

(49) a) Strain considerations have been ignored in our discussion of the transformation of 4 to 6. This is because cyclobutene and methylenecyclobutane differ by only 0.9 kcal/mol in strain energy, with the former actually less strained.[49b,49c] b) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395–3397. c) Turner, R. B.; Goebel, P.; Mallon, R. J.; Von E. Doering, W.; Coburn, Jr., J. F.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315–4322.

systems, the abstraction of pseudoaxial hydrogens are greatly preferred over pseudoequitorial ones. Even the more rigid systems, e.g. cyclobutenes and alkylidenecyclobutanes[1e], can react via an $^1O_2$ ene process presumably because they are flexible enough to permit even a normally equatorial hydrogen to attain a pseudoaxial position (via "flipping" or "puckering"), if necessary. There are, however, systems in which a pseudoaxial position is completely precluded, and indeed no singlet oxygen *ene* reaction is observed. For example, the allylic ring hydrogens of both alkylidenecyclopropanes[51] and cyclopropenes[52] are displaced ca. 33° from the perpendicular and both resist abstraction in a singlet oxygen process.[53–55]

Turning now to the case at hand, cyclobutyl rings containing three trigonal carbons are constrained to be planar, with the remaining ring methylene hydrogens displaced ca. 36° from the perpendicular.[56] Hence, there is no way the allylic/benzylic ring hydrogens of bi(benzocyclobutylidene) can attain anything even approximating a pseudoaxial position. The lack of reactivity of this system in a $^1O_2$ ene reaction should, therefore, not be surprising.

Conclusion

We have thus demonstrated that the photooxidation of bi(benzocyclobutenylidenes) **7-*E*** and **7-*Z*** occurs via a sensitizer-initiated free-radical process and that the formation of the observed products **8–11** may be rationalized in terms of secondary rearrangements (unzipping and cyclization) of the initially formed polyperoxide or polyperoxy radical. The absence of singlet oxygen ene product may reflect the increased activation energy required to generate an antiaromatic product. Alternatively, the inability of the ring methylene hydrogens to attain a pseudoaxial conformation may actually be the controlling factor in inhibiting the ene process. Further work on the effect of antiaromaticity on singlet oxygenations is presently in progress.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker AM 300 Fourier transform spectrometer. Assignments were facilitated by correlating proton and carbon chemical shifts through analysis of residual couplings in off-resonance decoupled spectra. In all cases, TMS served as the internal standard. In the case of known compounds, the previously published NMR spectral data were often obtained on a 60-MHz instrument and/or lacking the corresponding ^{13}C data and are, therefore, recorded below. IR spectrometers used were generally Perkin-Elmer Models 457 and 621, though spectra designated "FTIR" were taken with the Nicolet 60 SXB FTIR. Mass spectra were run on a Finnigan-4000 GC/MS machine. High-resolution mass spectra (HRMS) for the determination of exact masses were performed at the Mass Spectroscopy Center at the Technion, Haifa. UV-visible spectra were taken with a Varian DMS-100 spectrometer. Preparative thin-layer chromatography (TLC) was carried out on Merck silica gel F_{254} precoated plates, while analytical runs were performed using Riedel-De Haen microcards. The retention times given are for the analytical runs.

Photooxidation of (*E*)- and (*Z*)-1,1′-Bi(benzocyclobutenylidene) (7-*E* and -*Z*). The photooxidation apparatus previously described[57] was charged with 3 mL of solvent ($CHCl_3$, CH_3CN, C_6H_6, or CH_3OH) containing 2.0 mmol of **7-*E*** or **7-*Z***,[6] as well as polymer-based Rose Bengal (p-RB, Dye Tel Inc., POB 23, Perrysburg, OH) to serve as photosensitizer. The photooxidation ($\lambda > 360$ nm) was followed by TLC and after about 30 h of irradiation, a little less than 1 equiv of O_2 had been absorbed, oxygen uptake had essentially ceased, and no starting material remained. At the same time, the intense red color of the sensitizer had faded to a light pink. The product solution was filtered and evaporated, and the residue was dissolved in a minimal amount of $CHCl_3$ and thin-layer or column chromatographed on silica eluting with hexane/acetone 95:5. The products were identified by their spectral data as the known compounds benzocyclobutenone **8**,[10] spiroindanone **9**,[11] phthalide **10**,[12] and dione **11**.[13] The ^{13}C NMR data of **11** is not reported in the literature and is given below with the numbering of the carbons as shown in eq 3.

Product yields (Tables I–III) were determined by NMR analysis of reactions. In the case of $CHCl_3$, $CDCl_3$ was used directly; however, in the case of CH_3CN, C_6H_6, and CH_3OH, the deuterated solvents presented integration problems. As a result, the protiated solvent was utilized, the photooxidized solution was then filtered and evaporated, and the residue was weighed and dissolved in $CDCl_3$ for NMR analysis.

11: ^{13}C NMR ($CDCl_3$) δ 188.55 (C_{11} and C_{12}), 151.24 and 147.97 (C_{13} and C_{16}, C_{14} and C_{15}), 135.09 (C_3 and C_8), 128.65 (C_2 and C_9), 123.64 (C_4 and C_7), 120.53 (C_1 and C_{10}), 52.36 (C_5 and C_6).

1,1′-Epoxy-(*E*)-1,1′-Bi(benzocyclobutenylidene) (12) and 1,1′-Epoxy-(*Z*)-1,1′-Bi(benzocyclobutenylidene) (13). m-CPBA (0.89 mmol) dissolved in 50 mL of CH_2Cl_2 was added dropwise to CH_2Cl_2 solutions (100 mL) of **7-*E*** (165 mg, 0.81 mmol; 95% pure containing 5% of the ***Z***-isomer). The reaction mixture was stirred overnight and was then washed with 10% Na_2SO_3, 5% $NaHCO_3$, H_2O and saturated NaCl, and dried over $MgSO_4$. Rotary evaporation gave a yellow oil (155 mg) which contained the desired epoxide contaminated with small amounts of starting material and the isomeric epoxide as well as ca. 25% spiroindanone **9**. The resulting oil spontaneously crystallized partially to give clear needles of relatively pure epoxide **12** (100 mg, 0.45 mmol, 56% yield). A similar reaction carried out on **7-*Z*** (32 mg, 0.16 mmol; 95% pure) yielded epoxide **13** which was purified by preparative TLC eluting with hexane/acetone 95:5. Epoxides **12** and **13** were identified by their spectral data (numbering as shown in eq 4).

12: ^{1}H NMR ($CDCl_3$) δ 7.34 (dt, $J_{3,4}$ and $J_{4,5}$ = 7.5 Hz, $J_{4,6}$ = 1 Hz, 2H, H_4 and $H_{4'}$), 7.28 (dt, $J_{4,5}$ and $J_{5,6}$ = 7.5 Hz, $J_{3,5}$ = 1 Hz,

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(50) a) Reference 37d, pp 318–327. b) See ref 1c for a recent application of this rule.

(51) Laurie, V. W.; Stiglani, W. M. *J. Am. Chem. Soc.* **1970**, *92*, 1485–1488.

(52) Allen, F. H. *Tetrahedron* **1982**, *38*, 645–655.

(53) a) If an exocyclic allylic hydrogen is unavailable, methylenecyclopropanes generally prefer to remain unreactive.[1b,1e,53b] In the case of bi(cyclopropylidene)[53c,53d] and adamantylidenecyclopropane[53e–53g] singlet oxygen reactions are observed, but none involving abstraction of the ring allylic hydrogen. b) Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1981**, *22*, 91–94. c) Erden, I.; de Meijere, A.; Rousseau, G.; Conia, J. M. *Tetrahedron Lett.* **1980**, *21*, 2501–2504. d) de Meijere, A.; Erden, I.; Weber, W.; Kaufmann, D. *J. Org. Chem.* **1988**, *53*, 152–156. e) van den Heuvel, C. J. M.; Steinberg, H.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 145–152. f) Akasaka, T.; Ando, Wataru *Tetrahedron Lett.* **1987**, *28*, 217–220. g) Akasaka, T.; Ando, Wataru, *J. Org. Chem.* **1987**, *109*, 1260–1262.

(54) We have previously suggested that the abnormally large interatomic distance between the α-olefinic carbon and the γ-allylic hydrogen may be a pivotal consideration in determining the lack of reactivity of the ring hydrogens of alkylidenecyclopropanes to ene reaction.[1b,1e] While we have no reason to abandon this novel suggestion, we have found no hard evidence supporting it either. We believe that the inability of the allylic ring hydrogens of alkylidenecyclopropanes and related small-ring olefins to attain a pseudoaxial position may be of greater importance. As is clear from this discussion, the conformational consideration certainly has greater application.

(55) (a) In the case of 1,2-diarylcyclopropenes, singlet oxygen interacts with the olefinic system.[55b–55e] In the case of the dialkyl analogs, ring hydrogen abstraction is indeed observed, but this is clearly a radical process.[1d,1e] Methylcyclopropene is reported to be inert.[53b] b) Politzer, I. R.; Griffin, G. W. *Tetrahedron Lett.* **1973**, 4775–4778. c) Griffin, G. W.; Politzer, I. R.; Ishikawa, K.; Turro, N. J.; Chow, M.-F. *Tetrahedron Lett.* **1977**, 1287–1290. d) Vaz, C.; Griffin, G.; Christensen, S.; Lankin, D. *Heterocycles* **1981**, *15*, 1643–1658. e) See also the introduction to Griffin, G. W.; Kirschenheuter, G. P.; Vaz, C.; Umrigar, P. P.; Lankin, D.; Christensen, S. *Tetrahedron* **1985**, *41*, 2069–2080.

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2H, H_5 and $H_{5'}$), 7.20 (dt, $J_{3,4} = 7.5$ Hz, $J_{3,5} = 1$ Hz, 2H, H_3 and $H_{3'}$), 7.12 (dt, $J_{5,6} = 7.5$ Hz, $J_{4,6} = 1$ Hz, 2H, H_6 and $H_{6'}$), 3.72 and 3.56 (ABq, $J_{gem} = 14.5$ Hz, 4H, methylenes); ^{13}C NMR ($CDCl_3$) δ 144.95 (C_2), 143.09 (C_7), 129.96 (C_4), 127.79 (C_5), 122.66 (C_6), 121.03 (C_3), 69.93 (C_1), 39.94 (C_8); MS (CI, 70 ev) m/z 221 (MH^+, 100%), 203 ($MH^+ - O$, 13.4%); HRMS m/z (M^+) calcd for $C_{16}H_{12}O$ 220.0888, obsd 220.0918.

13: ^1H NMR ($CDCl_3$) δ 7.44–7.31 (m, 6 H, aromatic), 7.18 (bd, $J = 7$ Hz, 2H), 4.11 (s, 4H, methylene); ^{13}C NMR ($CDCl_3$) δ 148.32 (C_2), 137.37 (C_7), 131.86 (C_4), 128.96 (C_5), 123.89 (C_6), 120.40 (C_3), 78.96 (C_1), 57.32 (C_8); MS (CI, 70 ev) m/z 221 (MH^+, 100%).

Cyclic Voltammetry of 7-*E*. Cyclic voltammetry was carried out with a PAR Potentiostat Model 179 and PAR Function Generator Model 173 with a sweep rate of 20 mV/s. The measurement was carried out with a Pt electrode immersed in 50 mL of 0.1 M Bu_4NClO_4 in acetonitrile solution containing 80 mg (0.39 mmol; 7.8 mM) of **7**. The oxidation was irreversible with a peak potential at 1.4 V.