THE SENSITIZED PHOTOOXYGENATION OF METHYL SUBSTITUTED 1,2-DIPHENYLCYCLOBUTENES[1a]

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Abstract—A series of Me substituted 1,2-diphenylcyclobutenes was subjected to dye-sensitized photooxidation in the presence of methylene blue. In the case of the 3,3-dimethyl-, 3,3,4-trimethyl- and 3,3,4,4-tetramethyl-1,2-diphenylcyclobutenes, the sensitized oxidations are accompanied by ring-contraction with concomitant *ortho* hydroxylation of one aromatic nucleus. When electron transfer induced photooxidation techniques utilizing 9,10-dicyanoanthracene (DCA) as a sensitizer are employed with the series of Me substituted diphenylcyclobutenes, the reactions take a markedly different course and a broad spectrum of oxidation products are obtained including, most notably, ozonides of the cyclobutenes. The mechanisms of these conversions are addressed and the significance of the results discussed.

INTRODUCTION AND BACKGROUND

In the course of our ongoing studies[1,2] of the reactions of 1,2-diarylcycloalkenes with singlet oxygen ($^1O_2$) generated by dye photosensitization, it was found that C-3 substituents exert a profound and as yet unpredictable effect on the course and reactivity of the 1,2-diphenylcyclopropenes with singlet oxygen.[2a,b,c] Our preliminary studies in this area have revealed that chemiexcitation attends the dye-sensitized photooxidation of the cyclopropene **1a** which is unexceptional and gives the diketone **2a**.[2a,b,3] Emission is also associated with the dye-sensitized oxidation of **1b** although the rate of substrate consumption is considerably slower than that observed for **1a** and is accompanied by structural reorganization which gives **3**.[2a,b,3] No doubt exists that $^1O_2$ is involved in the dye-sensitized conversions of **1a** and **1b** to their respective oxidation products **2a** and the rearrangement product **3**[2b] since the same conversions may be achieved with $^1O_2$ generated by thermal decomposition of triphenylphosphite ozonide[4a] as well as 1-phospha-2,8,9-trioxaadamantane ozonide.[4b] From the equivalence of the emission and Stern–Volmer ratios obtained upon oxidation of **1b** and 1,2,3-triphenylindene with $^1O_2$ it is apparent that a common intermediate, presumably the dioxetane of the indene, is involved in the photooxidation of **1b** as proposed earlier.[2a,3]

encumbered by substituents, dioxetane formation becomes slow relative to rearrangement. In order to test the validity of this premise, 3-methyl-1,2,3-triphenylcyclopropene (**1c**), which embodies structural characteristics which could prove instructive in discerning if steric factors at C-3 are in fact responsible for the observed effect, was subjected to dye-sensitized oxidation. The steric barrier at C-3 in **1c** toward approach of $^1O_2$ at one face should be intermediate in magnitude between that present in **1a** and **1b**, as should the driving force for C—C bond cleavage and rearrangement of the type observed with **1b**.[2c]

The cyclopropene **1c**, however, proved considerably more refractory toward oxidation with $^1O_2$ generated by dye photosensitization and thermal decomposition of triphenylphosphite ozonide[4a] than anticipated and, relative to **1a** (and **1b**), the extent of substrate consumption was dramatically reduced.[2c] Although the diketone **2c** is detectable among the products, the yield is low, and considerable amounts of the cycloalkene **1c** may be recovered (91–99%). The suppressed reactivity of **1c** constitutes a significant departure from the behavior observed with **1a** and **1b**, which could not be accommodated by our original mechanistic rationale. Clearly, substituents in the 3-position may exert a profound influence on the mode of approach and interaction of $^1O_2$ on the strained *pi*-bond of cyclopropenes. This suggests that edge-on-

1a R = H
1b R = Ph
1c R = Me

2a R = H
2b R = Ph
2c R = Me

3
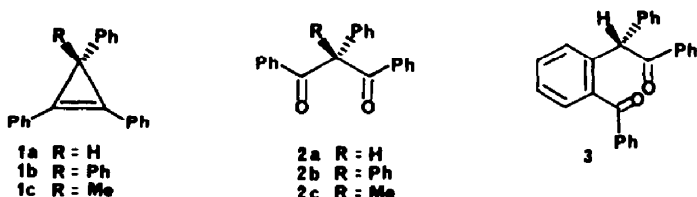
We attributed the disparate reactivities observed for **1a** and **1b** upon dye-sensitized photooxidation to the additional steric interference imposed at C-3 by the introduction of a second phenyl substituent at this site, i.e. if both faces of the cyclopropene ring are

attack (which preserves orbital phase continuity) and/or end-on-attack (to give a perepoxide) by $^1O_2$ on the cyclopropenyl bond is unfavorable and perhaps sterically and electronically encumbered by the 1,2-diaryl substituents, i.e. the approach of $^1O_2$ is
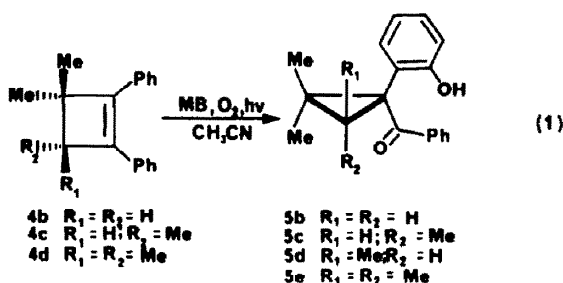
constrained to occur through narrow windows which lie on either face of the 1,2-diarylcyclopropene 1 over the 3-position. As an additional complication, certain of the photooxidations in the 1,2-diphenyl-cyclopropene and cyclobutene series exhibit solvent dependence[2,5] on their course and reactivity whereas others do not. As a result, no self-consistent pattern of chemical behavior has emerged for this class of substrates.

For this reason we initiated a complementary study of the photooxidation of the series of 1,2-diphenyl-cyclobutenes 4a–d with the hope of gaining greater insight with respect to the behavior of 1,2-diphenylcyclopropenes toward $^1O_2$. It was our hope that evaluation of these homologs would clarify the confusion which exists in that area and aid in formulating a mechanistic interpretation capable of reconciling the accumulated data.

4a   4b   4c   4d
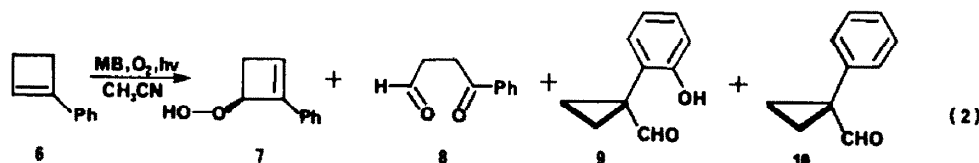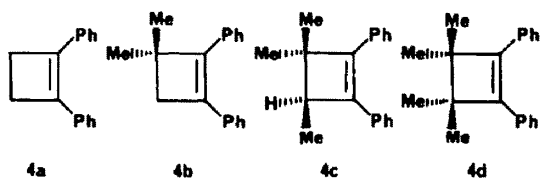
The dye-sensitized photooxidation of 1,2-diphenyl-cyclobutene (4a) was the subject of a previous study by other investigators[5] and the product distribution shown to be solvent dependent, a feature we found in common with 1a and 1b.[2a] The results observed with 4a were rationalized by invoking an "ene" reaction in polar solvents (MeOH, Me_2CO) where the primary product is a cyclic, allylic hydroperoxide 1, while formation of 1,2-dibenzoylethane, presumably by way of a dioxetane, is the dominant product obtained in nonpolar media (CH_2Cl_2, benzene).[5]

As with the cyclopropenes 1, ring substituents dramatically alter the course of the reaction of the dye-sensitized photooxidation of 1,2-diphenylcyclobutene (4b), we found that the ring-contracted product 5b, in addition to secondary oxidation products, are formed upon dye-sensitized photooxidation of this substrate (Eq.1). [4+2] Cycloaddition of $^1O_2$ to the styryl moiety of 4b followed by rearrangement is invoked to

4b $R_1 = R_2 = H$ 5b $R_1 = R_2 = H$
4c $R_1 = H; R_2 = Me$ 5c $R_1 = H; R_2 = Me$
4d $R_1 = R_2 = Me$ 5d $R_1 = Me; R_2 = H$
   5e $R_1 = R_2 = Me$

rationalize the formation of 5b. It was found in a preliminary study[2c] that 1,2-diphenyl-3,3,4,4-tetra-methylcyclobutene (4d) is considerably less reactive toward dye-sensitized oxidation, in dichloromethane, than the dimethyl analog 4b. HPLC analysis revealed that neither the diketone nor epoxide derived from 4d are formed as reaction products. A more detailed discussion of this reaction including more recent data will be presented later.

Jefford and Rimbault[6] report that the ring-contracted cyclopropyl aldehyde 9, incorporating an OH group on the aromatic nucleus is obtained as one of four tractable (non-polymeric) products formed upon dye-sensitized (MB, RB) photooxidation of 1-phenylcyclobutene (6) in polar solvents (CH_3CN, MeOH) (Eq. 2). These investigators[6] invoke a per-epoxide intermediate 11 as the primary intermediate to rationalize the array of photooxidation products (7–10) obtained. Rearrangement of 11 was advanced as the route to the allylic hydroperoxide 7, dioxetane 12 (the precursor for 8, Scheme 1) and the 5-oxabicyclo[2.1.0]pentanes 13 and/or 14, either of which could rearrange to the cyclopropanal 9.[6]

Frimer et al.[7,8] stress the fact that 1-phenylcyclo-butene (6) as well as the cyclopropenes 1 comprise vinyl aromatic systems and suggest that initial [4+2]

6   7   8   9   10   (2)

11

cycloaddition of $^1O_2$ occurs with these substrates, of which 6 is representative, to give an endoperoxide 15. They maintain that this endoperoxide is a more reasonable precursor than 11 for the photooxidation products 7–10. They propose that 15 could rearrange to the dioxetane 12, the phenol 13 as well as the bisepoxide 14 (Scheme 1).

Despite the fact that no ring-hydroxylation accompanies the dye-sensitized photooxidation of the cyclopropene 1a, Frimer asserts[7,8] that the most probable initial event is still [4+2] cycloaddition of $^1O_2$ to the vinyl aromatic chromophore to give an endoperoxide which then rearranges to a dioxetane, the likely precursor for the observed product, diketone 8.[7a,8] Similarly, Frimer[7a,8] invokes initial endoper-oxide formation to explain the structural reorganiz-ation reported by us[2a,b] in which the dioxetane precursor for the diketone 3 [formally derived from 1,2,3-triphenylindene (1b)] is a probable intermediate formed, to the exclusion of the diketone 2b, upon photosensitized oxidation of 1b. Here again no evidence for aromatic ring functionalization is apparent from the tractable products isolated; however, the extensive polymer formation, which
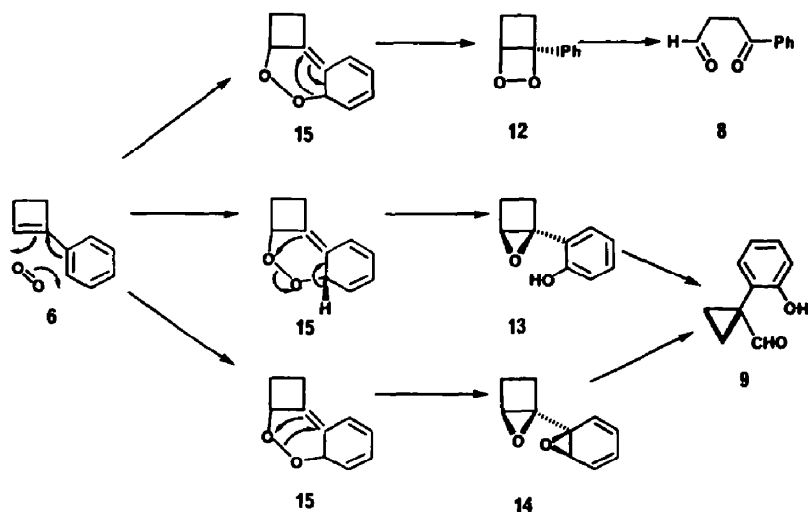
Scheme 1.

accompanies oxidation of **1a** and **1b**, may obscure detection of the reactive endoperoxide.

Photooxygenation of the aromatic ring has also been observed in the case of several other arylalkenes[9] including 9-alkylidenefluorene derivatives[9a] which are hydroxylated in the 1-position. For example, the sensitized (RB) photooxidation of 1-isopropylidene fluorene (**16**) in methanol/benzene (9:1) gives 1-hydroxyfluoren-9-one (**17**) and 9-hydroxy-9-methoxy-9-(1-hydroxy-1-methylethyl)fluorene (**18**) in addition to small amounts of fluorenone (**19**). An endoperoxide **20**, formed by 1,4-cycloaddition of $^1O_2$ to the styryl moiety of **16**, is advanced as a common precursor for **17** and **18**.[9a] An alternative mechanistic formulation is also presented in which ring-oxygenation is achieved by intramolecular attack on the aromatic nucleus via an intermediate perepoxide species.

accommodated solely by a difference in solvent stabilization of common intermediates produced from **6** through interaction with free $^1O_2$. They also observed that addition of DABCO, a $^1O_2$ quencher,[11,12] leads to a pronounced decrease in the yield of **7** and **8** with a concomitant increase in that of **9**. For example, with DABCO present the yield of **9** is increased to 92% in the ZnTPP sensitized photooxidation of **6** in benzene at the expense of **7** and **8** (7 + 8; 8%) and polymer. Clearly, **9** arises through an oxidation mechanism which differs from that involved with **7** and **8** where free $^1O_2$ appears to be implicated. Ground state oxygen was excluded as the species responsible for the conversion of **6** to **9** since only **7** and **10** are formed from **6** under dark autoxidation conditions. While hydroquinone, a radical scavenger, quenches this autoxidation process the formation of **9** by photooxidation is unaffected by
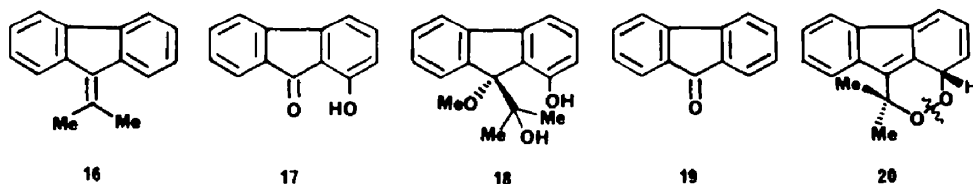
Recently Sakuragi and Sakuragi[10] re-examined the dye-sensitized photooxidation of 1-phenylcyclobutene (**6**) and concluded that singlet oxygen is implicated in the formation of **7** and **8**, but not the ring-contraction products **9** and **10**. This conclusion is based on the changes in the distribution of oxidation products which occur upon variation of the solvent and sensitizer employed. For example, the ratio (7 + 8)/9 varies markedly with the solvent/sensitizer combinations. With MB as the sensitizer the oxidation of **6** to **7** in acetone and acetonitrile proceeds in high yields while in methylene chloride much lower yields of **9** are obtained. Furthermore, the yield of **9** is greatly reduced in acetone and acetonitrile when ZnTPP is the sensitizer. They assert that the observed variation in yields of **9** with different sensitizers in identical solvents cannot be
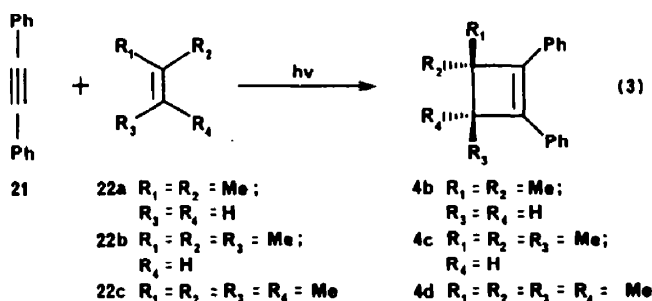
such phenolic radical traps. It is proposed that another reactive oxygen species such as superoxide anion or an adduct of oxygen with the sensitizer is generated together with $^1O_2$ and gives products whose relative ratios vary with changes in solvent sensitizer combinations unlike those derived from $^1O_2$.

In view of these conclusions we initiated a concurrent study of the electron transfer sensitized oxidation of the cyclobutenes **4b–d** which parallels our dye-sensitized investigation in order to test the viability of the proposal that oxidative ring-contraction and ring-functionalization is induced by superoxide radical anion.

*Syntheses of the substituted 1,2-diarylcyclobutenes **4b–d***
Syntheses of the requisite 1,2-diphenylcyclobutenes

was achieved by the crossed [2+2] photocyclo-
addition of diphenylacetylene (tolan) to the ap-
propriately substituted alkene (Eq. 3). This approach
was suggested by the report of Chapman and Adams[13]
that tetramethylcyclobutene **4d** could be prepared by
irradiation of tolan **21** in the presence of 2,3-dimethyl-2-
butene (**22c**) (Eq. 3). This crossed cycloaddition was
extended by Christensen and Griffin to the direct
synthesis of the dimethylcyclobutene **4b** with favorable
results.[2c,14] Application of this crossed cycloaddition
technique to the photocycloaddition of 2-methyl-2-
butene (**22b**) affords high yields of the trimethylcyclo-
butene **4c**.

separation of the reaction mixture is conducted
immediately following termination of irradiation, a
product is observed with a retention time which lies
between that of **4d** and **5e**. TLC analysis of this reaction
mixture, after a delay time of 15 min, indicates that this
product is transient in character. This short-lived
intermediate could in fact be the endoperoxide **23**. That
the endoperoxide mechanism is widely accepted and is
invoked to rationalize this and related conversions
herein does not relieve our anxiety concerning the
validity of this formulation particularly in light of
Sakuragi's observations which may prove to be
general.[10]

$$ (3) $$

21

22a $R_1 = R_2 = Me$; $R_3 = R_4 = H$

22b $R_1 = R_2 = R_3 = Me$; $R_4 = H$

22c $R_1 = R_2 = R_3 = R_4 = Me$

4b $R_1 = R_2 = Me$; $R_3 = R_4 = H$

4c $R_1 = R_2 = R_3 = Me$; $R_4 = H$

4d $R_1 = R_2 = R_3 = R_4 = Me$

RESULTS AND DISCUSSION

*Dye-sensitized photooxygenation of 1,2-diphenyl-
cyclobutenes.* 1,2-Diphenyl-3,3,4,4-tetramethylcyclo-
butene (**4d**) was subjected to photosensitized (MB)
oxygenation in dichloromethane at 0° and proved
relatively unreactive (3 hr, 11% conversion). The ring-
contracted product **5e** was isolated in 5.1% yield in
addition to a mixture of secondary oxidation products
derived from **5e** (ca 5.7%). In accordance with Frimers
suggestion[8] we propose that **5e** is formed through
initial [4+2] cycloaddition of singlet oxygen to the
styryl moiety of **4d** to yield the endoperoxide **23**
followed by isomerization (in a manner described later
for **5b**) to give the cyclopropane (Eq. 4). When the
reaction is conducted in acetonitrile at. −15° the
conversion levels are greater (29%, 2 hr). If the

The structure of **5e** was assigned on the basis of ¹H-
NMR, ¹³C-NMR, IR and mass spectral data. In order
to affirm the assignment of the structure, the ¹H-NMR
spectrum of **5e** was compared to that of the related
compound **24** which lacks the OH substituent on the
aromatic ring[15] as well as that of the ring-contracted
product **5b** produced from the dimethylcyclobutene **4b**
upon MB sensitized photooxygenation (see below). The
structure of **5b**, in turn, is supported by comparison of
spectral data with that of 2,2-dimethyl-1-benzoyl-1-
phenylcyclopropane previously synthesized indepen-
dently.[2c] Marked similarities exist in the spectra
of **5e** and that of **24** and little doubt can exist that
both incorporate common structural characteristics.
Furthermore, the solution IR spectra of **5e** and **5b** are
essentially indistinguishable suggesting that these
compounds have very closely related structures. In

$$ (4) $$

4d   **23**   **5e**

5e   **24**   **5b**
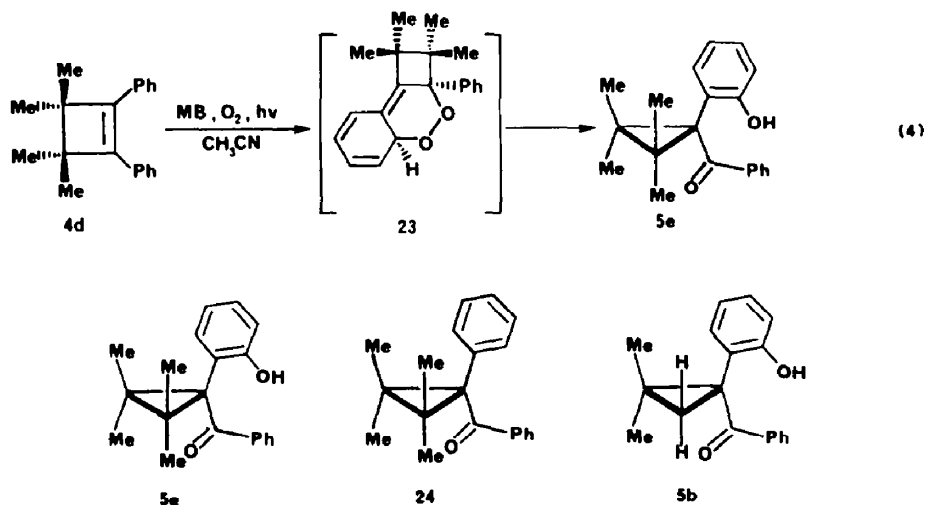
summary, we have relied heavily on previous assignments in characterizing the structure of the product **5e** obtained upon photooxygenation of **4d**. Although we are confident that these assignments of structure are secure, single crystal X-ray data are currently being collected to obtain unequivocal confirmation of the identity of **5e**.

The MB sensitized photooxygenation of 1,2-diphenyl-3,3,4-trimethylcyclobutene (**4c**) under conditions similar to those used with **4d** affords an isomeric pair of ring-contracted products **5c** (13%) and **5d** (14.1%) (38% conversion (Eq. 5). These diastereomers are readily differentiated on the basis of their ^{1}H-NMR spectra which exhibit low and high field Me doublets for **5c** and **5d**, respectively. The oxidation products **5c**

cycloaddition of $^1O_2$ to the styryl function with formation of the endoperoxide **27** (Scheme 2).[2c] Ample precedent exists for endoperoxide formation with styryl systems[7-9] and in this study we extend this process to **4c** and **4d**. Subsequent cleavage of the endoperoxide bond and H-transfer may be anticipated to give **5b** via **28** derived from an arene oxide of type **14**[8] or conceivably the bicyclic intermediate **29**. Regardless of the endoperoxide rearrangement mechanism, the constitutional structure of the unsymmetrically substituted cyclobutene **4b** precludes us from discerning through product structure whether regioselective addition of $^1O_2$ is involved in endoperoxide formation, i.e. whether or not attack occurs in addition to, or exclusively in a manner opposite to

$$(5)$$
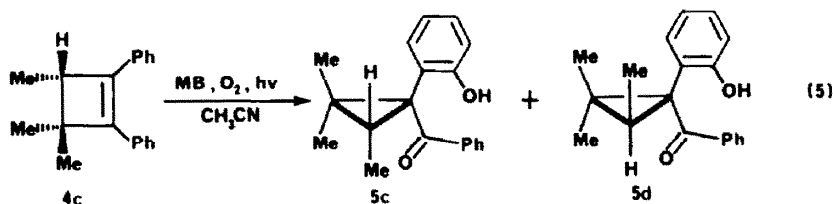
and **5d**, like their tetramethyl counterpart **5e**, are also assumed to arise by initial [4+2] cycloaddition of $^1O_2$ to the two non-equivalent styryl moieties of **4c** followed by isomerization of the intermediate endoperoxides as proposed for **4d** (Eq. 4). The endoperoxide isomerization is addressed in more detail below in connection with the photooxygenation of **4b** (Scheme 2).

The dye-sensitized photooxidation of 3,3-dimethyl-1,2-diphenylcyclobutene **4b** under conditions identical to those employed above for **4c** and **4d**, which was described earlier,[2c] is accompanied by ring-contraction and leads to formation of the cyclopropane **5b** (14%) as a primary product from which **25** (16%) and **26** (14%) are derived (Eq. 6). The mechanism previously advanced for the ring-contraction process accompanying the oxidation of the dimethyl substituted 1,2-diphenylcyclobutene **4b** involved initial [4+2]

that depicted in Scheme 2 to give the isomeric counterpart of **27** formed by interaction of $^1O_2$ with the styryl moiety incorporating the phenyl ring *vicinal* to the dimethyl substituents. A similar restriction applies to cyclobutene **4c** and of course the question is not germane with the symmetrical tetramethylcyclobutene **4d**.

In accordance with the behavior observed for the cyclopropene substrates,[1] a seemingly minor modification in structure at an apparently remote site on the diarylcyclobutene ring of **4a** also has a major influence on the reaction path and rate. It is clear from preliminary studies that the "ene" reaction[5] is the dominant process which occurs in the case of 3-methyl- and *trans*-3,4-dimethyl-1,2-diphenylcyclobutene and the results of these studies will be the subject of a future communication.

Scheme 2.

(6)

4b   5b   25   26
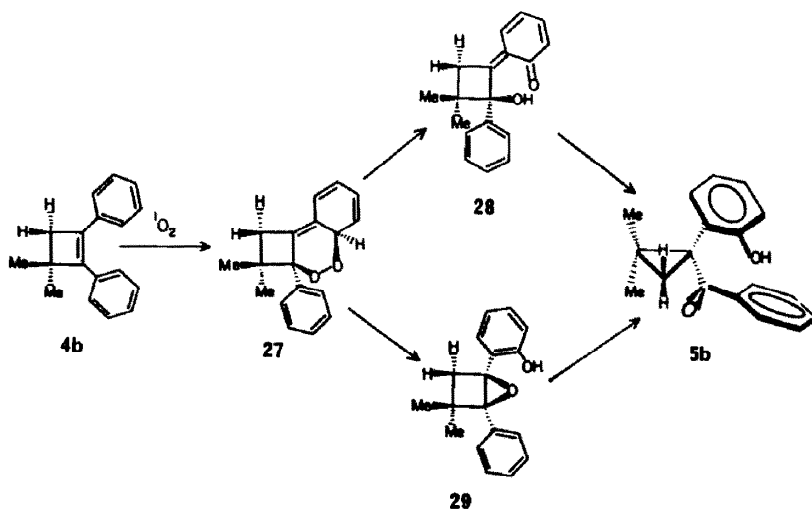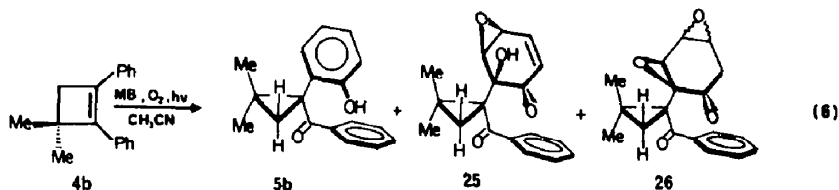
Photooxygenations of 1,2-diphenylcyclobutenes by electron transfer sensitization. Subsequent to publication of the initial results on the photooxidation of 1,2-diphenylcycloalkenes, Foote *et al.*[16] presented evidence that methylene blue (MB), the sensitizer of choice in our studies, may function in the excited state as an electron transfer acceptor in certain applications. In order to evaluate the role of electron transfer processes (if any) in our systems and to test the proposal by Sakuragi[10] that superoxide anion may be implicated in the presumed endoperoxidation leading to the ring-hydroxylation product 9 derived from 6, the initial study was extended to include the DCA photosensitized oxygenation of the Me substituted cyclobutenes 4c and 4d. 1,2-Diphenyl-3,3,4,4-tetramethylcyclobutene (4d) was subjected to DCA sensitized photooxygenation and compelling evidence was obtained that the oxidation affords the stable ozonide 31.[2d] The conversion of 4d to the ozonide 31 constitutes the first report, to our knowledge, of formation of such a product upon sensitized photooxidation of a cycloalkene.

Tetramethylcyclobutene 4d quenches the fluorescence of DCA at a rate near the diffusion controlled limit. The linear Stern–Volmer plot has a slope of 217 l mol^{-1} which corresponds to a quenching rate of 1.43×10^{10} l mol^{-1} sec^{-1} in nitrogen saturated acetonitrile.[17]

Thus, when an oxygen saturated acetonitrile solution of 4d containing DCA (10^{-4} M) is irradiated at 400–430 nm (CuSO$_4$ filter) for 1 hr the following products are obtained: the oxirane 30 (6.7%), the ozonide 31 (31.2%), the diketone 32 (13.5%), benzil 33 (10.5%), a trace of the ring-contracted product 5e, as well as a mixture of benzoic anhydride and as yet unidentified products (18.5%) (Eq. 7).[2d]

A study of the evolution of the reaction products as a function of time by HPLC analysis indicates that the oxirane 30, the ozonide 31, the dione 32 and benzil 33 are products formed initially whereas benzoic anhydride and a complex mixture of highly polar materials are formed more slowly and are perhaps secondary in nature. Trace quantities of the ring-contraction product 5e obtained with $^1O_2$ may be detected among the products at an early stage of the reaction.[17] Although the presence of 5e at low levels is observable by means of the sensitive HPLC UV detector, insufficient quantities are present to be isolated by preparative TLC.[17]

The structure of the diketone 32 was established by comparison with an authentic sample[18] while the oxirane 30, a known compound,[15a] was identified by independent synthesis through peracid oxidation of 4d. A sample of the ozonide 31 was obtained independently by ozonolysis of 4d according to published procedures (Eq. 8).[18] Comparison of the ^{1}H-NMR, ^{13}C-NMR, IR and mass spectral data of the ozonolysis product with those of the adduct obtained by photooxidation of 4d provides confirmation of their identity. No depression in m.p. was observed in a mixture m.p. determination.

Once the structure of the ozonide 31 was established, it was of interest to obtain information regarding the origin of this unexpected product. That photogenerated ozone is the oxidant in the conversion of 4d to 31 was excluded by an appropriate control experiment. A solution (10^{-4} M) of DCA in acetonitrile was irradiated as oxygen was continuously passed through the solution. The effluent oxygen stream potentially containing photogenerated ozone was conducted to a dark reaction zone consisting of a flask, surrounded by an opaque shield, containing 4d dissolved in dichloromethane at $-78°$. No ozonide formation was

(7)

4d   30   31   32   33   5e

+ Benzoic Anhydride

(8)

4d   31   32
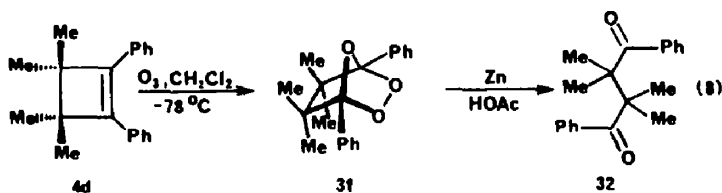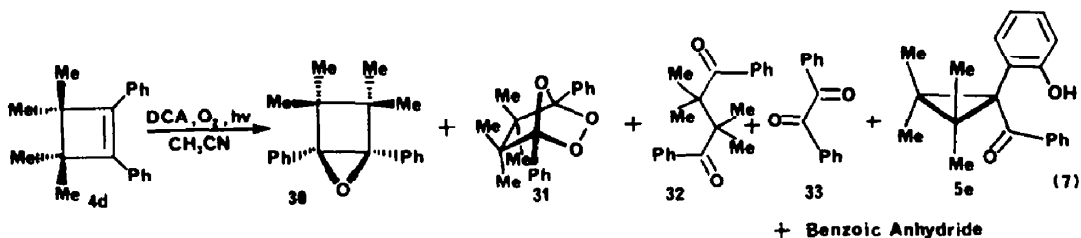
detected after 4 hr of irradiation. Similarly, no ozonide was formed in a second control experiment in which biphenyl was added to the DCA solution to promote the formation of superoxide radical anion.[19,20]

The isolation of small quantities of the oxirane **30** upon oxidation of **4d** led us to speculate that the oxirane **30** is formed in the primary photooxidation step, but is efficiently oxidized to ozonide **31** under the reaction conditions. This contention is in accord with the recent reports by Schaap and Ohta and their respective co-workers[19,20] of the DCA sensitized oxidation of tetraphenyloxirane to the corresponding ozonide and similar conversions of stilbene oxides bearing electron donor groups to their respective ozonides to be discussed later.

To test the plausability of this mechanistic scheme in our system, a sample of oxirane **30** was prepared and subjected to DCA sensitized photooxidation. Under the conditions employed, the oxirane **30** is converted to the ozonide **31** in 88% yield thus demonstrating the feasibility of the proposed process (Eq. 9).

saturated acetonitrile is reportedly 15.2 nsec which translates to a quenching rate (k_q) of 6.96×10^9 l mol^{-1} sec^{-1} which is slightly below the diffusion controlled rate limit in acetonitrile at 20°. In summary, the formation of the ozonide **31** from **30** is conveniently rationalized by the sequence of events depicted in Scheme 3. Electron transfer from **30** to singlet excited DCA gives the DCA radical anion and the radical cation **34**. The oxirane radical cation **34** may undergo ring-opening to **35** followed by direct addition of superoxide radical anion to produce the ozonide **31**. Alternatively, electron transfer from superoxide radical anion to **35** may occur to form the ylide **36** and $^1O_2$. Ground state and/or $^1O_2$ may then add to the ylide **36** to yield the ozonide **31** (Scheme 3). That ground state oxygen is capable of oxidizing the ylide **36** to the ozonide **31** was confirmed by generating the ylide **36** photochemically followed by introducing oxygen into the purple colored solution after irradiation (254 nm) had been discontinued. Upon addition of oxygen, the color of the ylide is immediately bleached. Analysis of

In experiments conducted in collaboration with Professor A. P. Schaap,[17] the rate of DCA fluorescence quenching by the oxirane **30** was subjected to Stern–Volmer kinetic analysis, and a linear plot was obtained $(r = 0.989)$ with the slope $(k_q \times \tau^*_{DCA})$ equal to 106 l mol^{-1}. The singlet lifetime of DCA in nitrogen

this solution by 300 MHz ^{1}H-NMR[17] revealed the presence of singlet resonance signals at 0.75 and 1.29 ppm corresponding to the *endo* and *exo* Me substituents, respectively, of the ozonide **31** (Eq. 10). Prior to this experimental result, it was tacitly assumed that $^1O_2$ was required for the conversion of ylides to


Scheme 3.

(10)
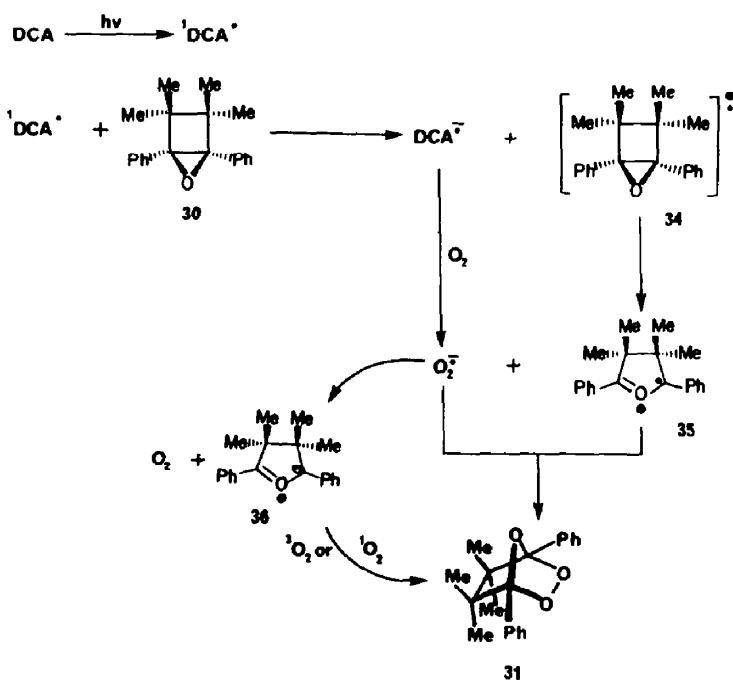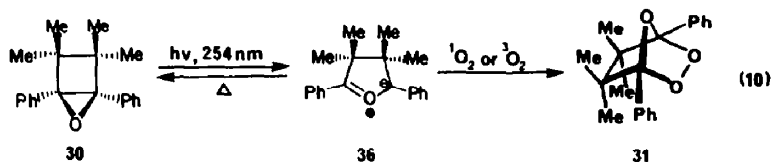
ozonides; however, interception of **35** with superoxide anion and/or **36** with $^1O_2$ may occur more efficiently and constitute the dominant route to the ozonide **31**.

It is widely accepted that DCA sensitized photooxygenations involve the formation of superoxide radical anion which subsequently reacts with the radical cations of alkene substrates.[21] It is of interest in the context of this work to establish whether or not the intermediacy of superoxide radical anion is implicated in the formation of the oxirane **30** as well as the other products such as the ozonides.

Foote et al.[22] observed that the DCA sensitized photooxidation of trans-stilbene is modified upon addition of benzoquinone (BQ). They attribute the change in reaction course to efficient interception of superoxide radical anion by BQ: When the photooxidation of **4d** was conducted in the presence of BQ (2×10^{-3} M), no significant changes in product distribution and relative conversion levels were observed. This result led us to speculate that the photooxidation of **4d** sensitized by DCA does not proceed via a mechanism involving superoxide radical anion as a reactive intermediate. On this basis we proposed that the oxirane **30** is formed initially and subsequently oxidized to the ozonide **31** in the absence of superoxide radical anion, conceivably through the intermediate carbonyl ylide **36**.[24] This proved to be at variance with the initial mechanism advanced by Schaap and associates[19a] for the photooxidation of tetraphenyloxirane to the corresponding ozonide in which the radical cation of tetraphenyloxirane is proposed to react directly with superoxide radical anion to yield the ozonide. We now realize, as a result of collaborative efforts conducted with Professor Schaap,[17] that our conclusions reported initially were reached on the basis of recommended, albeit low, concentrations of BQ and, therefore, are incorrect. With enhanced concentration levels of BQ (10^{-2} M), the observed oxidation is completely suppressed even upon prolonged irradiation provided that precautions are taken to insure that the concentration of BQ is maintained at sufficiently high levels to allow efficient trapping of superoxide radical anion. When these conditions are met, the only products observed are the ring-contracted product **5e** and traces of a more polar product also observed in the MB sensitized reaction (Eq. 11), i.e. no oxirane **30** or ozonide is formed. These results suggest that superoxide ion is indeed involved under the conditions originally employed; however, BQ is rapidly depleted by reaction with superoxide after which the reaction proceeds in the usual manner.
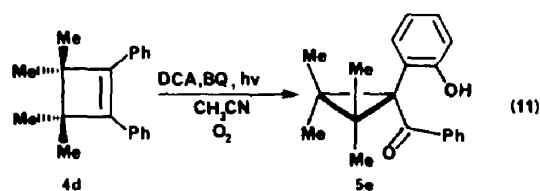
Once we had established that superoxide radical anion is a reactive intermediate in the conversion of **4d** to oxirane **30**, it was of interest to determine if this reactive species is implicated in the conversion of oxirane **30** to ozonide **31** as well. The DCA sensitized photooxygenation of oxirane **30** was conducted in the presence of BQ (10^{-2} M) and the formation of the products monitored by HPLC.[17] The oxirane **30** is largely consumed after 2 hr of irradiation and peaks corresponding to the ozonide **31** and benzoic anhydride were observed. Thus a pathway exists for the conversion of **30** to **31** in which superoxide is not required although we have not excluded the possibility that superoxide anion may react with the radical cation(s) **34** and/or **35** in the absence of the BQ trapping agent. Oxirane **30** exhibits behavior strikingly different from that of the cis- and trans-stilbene oxides **37** and **38**, respectively, studied by Schaap and associates.[20] The co-sensitizer biphenyl (BP) is required in addition to DCA in order to achieve conversion of oxiranes **37** and **38** to the ozonide **39**, i.e. **37** and **38** unlike **30** do not quench DCA fluorescence (Eq. 12). Furthermore,

(12)
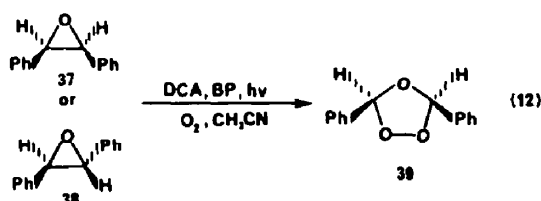
BQ completely inhibits the co-sensitized photooxygenation of these substrates. These contrasting results are attributed to the ability of oxirane **30** to quench the fluorescence of DCA with concomitant electron transfer to give **34** while the stilbene oxides lack this capability. The BP co-sensitizer is required in the case of **37** and **38** to achieve radical cation formation while superoxide is required to form $^1O_2$ and a carbonyl ylide which they suggest react to give the observed ozonide **39**.

The DCA sensitized photooxygenation of trimethylcyclobutene **4c** produces a spectrum of products analogous to those observed for **4d** (Eq. 13). An isomeric pair of ozonides **40** and **41** is obtained, presumably by secondary oxygenation of an initially formed pair of oxiranes. The ozonides **40** and **41** were differentiated on the basis of their ^{1}H-NMR spectra which exhibit low and high field Me doublets assigned to the endo and exo Me-substituents, respectively. In addition to the ozonides **40** and **41**, the dione **42** (37.3%) and benzil (4.3%) were isolated from the mixture. The structures of the ozonides **40** and **41** were confirmed by comparison with the two products formed upon conventional ozonolysis of **4c** in dichloromethane at $-78°$ (Eq. 14). An authentic sample of the diketone **42** was prepared by reduction of the ozonides **40** and **41** with Zn in acetic acid. The structure of the ozonide **40** has been confirmed by X-ray crystallography.[23]

(11)

(13)

(14)
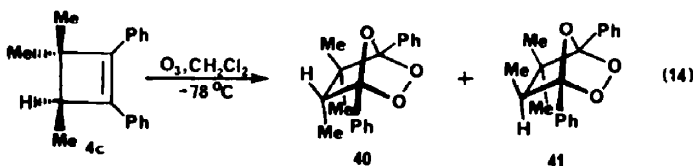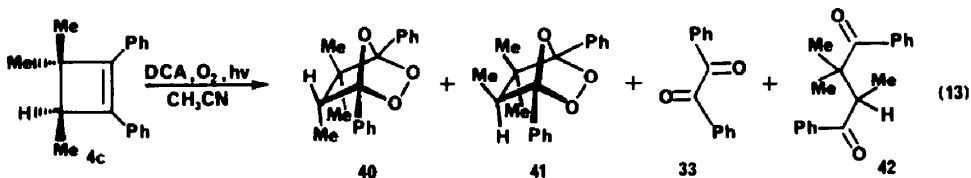
Several significant points regarding the work described herein should be stressed. Firstly, the methylene blue dye-sensitized photooxidations of the 1,2-diphenylcyclobutenes **4a–d** parallel the corresponding oxidations of the cyclopropenes **1a–c** in that a diversity of products, reaction rates and yields are observed in each series. Furthermore, the results of the present study confirm that steric interference toward the approach of singlet oxygen apparent in the cyclopropene series extends to the 1,2-diphenylcyclobutenes **4a–d** albeit to different degrees. Secondly, significantly different product distributions are observed in the photoinduced electron transfer sensitized photooxidations of **4b–d** than that found in the corresponding photooxidations employing methylene blue as an energy transfer sensitizer. Clearly, the ring contracted cyclobutenes, which appear as major photooxidation products in the methylene blue dye-sensitized photooxidation of **4b–d**, are either absent or constitute minor photooxidation products in the electron transfer sensitized process where the involvement of superoxide radical anion would be expected (Scheme 3). These oxidations provide strong evidence that the involvement of superoxide radical anion in the methylene blue sensitized oxidations of 1-phenylcyclobutene (6) to 9 (and presumably **4b–d** to **5b–e**), as proposed by Sakuragi and Sakuragi,[10] is not operative. Quenching studies are currently in progress to affirm or refute our proposal that the functionalized cyclopropanes **5b–e** emanate from endoperoxidation of the 1,2-diphenylcyclobutenes **4b–d** with $^1O_2$. The involvement of a reactive oxidizing species in which $^1O_2$ is bound to the sensitizer is also suggested by the Sakuragis and cannot presently be excluded as the oxidizing species leading to **5b–e**. Clearly, however, methylene blue does *not* function as an electron transfer sensitizer in the reactions described here. In the absence of data to the contrary, we still believe that the most plausible mechanism for the methylene blue sensitized photooxidation of the 1,2-diphenylcyclobutenes **4b–d** to the ring functionalized cyclopropanes **5b–e** remains initial [4+2] cycloaddition to the styryl unit in each case to give an endoperoxide as formulated in Schemes 1 and 2.

EXPERIMENTAL

General procedures. Routine 60 MHz ^{1}H-NMR spectra were obtained on a Varian A-60, Hitachi Perkin–Elmer R-20B or Varian EM-360A spectrometer. CDCl$_3$ with 1% TMS as an internal standard was utilized as the solvent. High resolution ^{1}H- or ^{13}C-NMR spectra were determined on a Jeol FX90Q spectrometer. Mass spectra were obtained on a Hitachi Perkin–Elmer RMU-6E spectrometer employing an ionization potential of 70 eV. All m.p. determinations were performed utilizing a Thomas–Hoover capillary m.p. apparatus and are uncorrected.

Analytical separations were conducted on Eastman Chromagram sheets (silica gel). Silica Gel G (PF 254; Brinkman Co.) coated on glass plates was employed in all preparative thick-layer chromatographic separations. The resolved bands were visualized using a hand-held short-wavelength UV lamp (Black-Ray UVL-21). Elemental combustion analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

All [2+2] photocycloaddition reactions were conducted in either Griffin–Worden quartz pressure vessels (Kontes Glass Co., Vineland, NJ) or serum capped quartz test tubes. Solutions to be irradiated were degassed by sparging with argon or N$_2$ for 15 min prior to use. A Srinivasan–Griffin Rayonet Photochemical Reactor (RPR-100; The Southern N.E. Ultraviolet Co., Hamden) equipped with sixteen 8W, G8T5 low pressure lamps was employed as a UV source.

Preparation of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**4d**). The crossed photocycloaddition of 2,3-dimethyl-2-butene to tolan to give **4d** was achieved using the method of Chapman and Adams.[13] The physical and spectral properties of the cyclobutene **4d** thus prepared proved identical to those reported previously: m.p. 92–93° (lit.[13] m.p. 92–93°); ^{1}H-NMR (CDCl$_3$) δ 1.28 (s, 12H), 7.12–7.25 (m, 10H, ArH); IR (CHCl$_3$, KBr) 2950, 1595, 1475, 1440, 1360, 1250, 1220, 1075, 1040, 1010, 950, 915, 695 cm^{-1}; mass spectrum *m/e* (relative intensity) 262 (M$^+$, 100), 247 (41), 232 (20), 219 (94), 205 (17), 204 (17), 178 (16), 143 (22), 119 (32), 115 (21), 105 (12), 91 (39), 77.

Synthesis of 1,2-diphenyl-3,3,4-trimethylcyclobutene (**4c**). The Chapman and Adams photocycloaddition procedure[13] was extended to prepare **4c**. A soln of tolan (0.50 g, 2.8 mmol) dissolved in 15 ml of 2-methyl-2-butene was introduced into a serum-capped quartz tube and the mixture deoxygenated with N$_2$ for 15 min. The resulting soln was then irradiated for 72 hr. Subsequent removal of the volatile solvent afforded a green oil which was chromatographed on silica to give **4c** as a pale yellow liquid (0.43 g, 63%): ^{1}H-NMR (CDCl$_3$) δ 1.16 (d, 3H, J = 7 Hz), 1.28 (s, 6H), 2.83 (q, 1H, J = 7 Hz), 7.08–7.61 (m, 10H, ArH); IR (CHCl$_3$, KBr) 2950, 1595, 1484, 1440, 1360, 1320, 1250, 1160, 1065, 1025, 1005, 970, 910, 690, 640, 600 cm^{-1}; mass spectrum *m/e* (relative intensity) 248 (M$^+$, 100), 233 (83), 219 (77), 218 (41), 205 (70), 178 (52), 143 (56), 128 (25), 105 (27), 91 (52), 77 (23).

Synthesis of 3,3-dimethyl-1,2-diphenylcyclobutene (**4b**). As with **4c**, a modification of the method of Chapman and Adams[13] was used to prepare **4b**. Tolan (0.5 g, 2.8 mmol) in pure dry hexane (50 ml) was placed in a quartz Griffin–Worden reaction vessel. Isobutylene gas was bubbled through the soln

for 0.5 hr after which the tube was immersed in a dry-ice/acetone bath until 30–40 ml of isobutylene had condensed in the tube. The tube was then capped and the mixture irradiated for 36 hr at 254 nm in a Rayonet Photochemical Reactor. The tube was cooled in an ice bath, uncapped and N_2 bubbled through the liquid as it was allowed to warm to room temp. Once the isobutylene was removed, the hexane was evaporated under reduced pressure, leaving a green solid-liquid mixture. The mixture was dissolved in a small amount of hexane and spotted on two chromatography thick-layer plates (30 g, silica gel). The plates were eluted with hexane. The cyclobutene and tolan separated as one large band from the azulene and other reaction by-products which remain near the bottom of the plate. The cyclobutene appeared as a noticeably fluorescent band which when removed from the plate contained tolan as an impurity. The tolan was removed by rechromatographing the appropriate band, once isolated, on a new plate and developing that plate twice. A yield of 100–200 mg (15–30%) was obtained. IR (neat) 3080 (W), 3060 (W), 3030 (W), 2950 (M), 2930 (M), 2850 (W), 2830 (W), 1600 (W), 1500 (W), 1440 (M), 1270 (W), 1210 (W), 1180 (W), 1070 (W), 1030 (W), 1000 (W), 950 (W), 915 (W), 780 (M), 755 (S), 690 (S), 640 (M); ^{1}H-NMR (CDCl$_3$) δ 1.35 (s, 6H, methyl), 2.55 (s, 2H methylene), 7.1–7.4 (m, 10H, phenyl).

Photooxygenations sensitized by methylene blue

Photooxygenation of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**4d**). A double-walled concentric cylindrical pyrex vessel with a fritted gas entry tube attached near the bottom was utilized for the photosensitized oxygenations employing MB. The light source consisted of an EHC-500W tungsten-halogen lamp in conjunction with a uranyl glass filter built into the pyrex immersion well. This lamp/filter combination provides radiation ($\lambda > 400$ nm) with the maximum output occurring in the 500–550 nm region of the visible spectrum. Irradiation of **4d** (262 mg, 1.00 mmol) in 100 ml of oxygen saturated acetonitrile containing MB (10^{-4} M) for 2 hr at $-15°$ results in the slow oxidation of **4d** (186 mg recovered, 29% conversion). In addition to unreacted **4d**, separation of the mixture on a silica gel plate provided the ring-contracted product **5e** (24 mg, 8.2%) as a white solid: m.p. 178–179°, MeOH; ^{1}H-NMR (CDCl$_3$) δ 0.944 (s, 3H), 1.015 (s, 3H), 1.302 (s, 3H), 1.365 (s, 3H), 6.883–7.498 (m, 7H, ArH), 8.043–8.15 (m, 2H), 8.214 (s, 1H, ArOH); ^{13}C-NMR (CDCl$_3$) δ 18.74 (q), 20.48 (q), 23.30 (q), 27.74 (s), 41.3 (s), 117.78 (d), 119.94 (d), 121.9 (s), 128.23 (d), 128.83 (d), 129.80 (d), 131.81 (d), 133.49 (d), 135.35 (s), 156.1 (s), 201.2 (s); IR (CHCl$_3$, KBr) 3325, 2925, 1635, 1600, 1585, 1485, 1455, 1385, 1315, 1280, 1230, 1185, 1130, 1025, 1000, 890, 840, 710, 640 cm^{-1}; mass spectrum m/e (relative intensity) 294 (M$^+$, 28), 279 (100), 264 (9), 237 (28), 236 (24), 221 (29), 201 (7), 185 (9), 181 (8), 173 (7), 165 (8), 159 (14), 157 (11), 153 (9), 145 (13), 131 (13), 121 (12), 115 (17), 105 (78), 91 (22), 77 (63). (Found: C, 81.27; H, 7.63. Calc for $C_{20}H_{22}O_2$: C, 81.60; H, 7.52%.) In a similar run utilizing CH$_2$Cl$_2$ as the solvent at 0°, the ring-contracted product **5e** was isolated in 5.1% yield in addition to 89% recovered starting material after irradiation for 3 hr.

Photooxygenation of 1,2-diphenyl-3,3,4-trimethylcyclobutene (**4c**). In addition to recovered **4c** (90.2 mg, 36.3%), the following products were isolated upon irradiation of an oxygen saturated acetonitrile soln of **4c** (248 mg, 1.00 mmol) in the presence of MB for 2.5 hr as described above followed by silica gel chromatography. The ring-contracted product **5c** (39.4 mg, 14.1%) was isolated as a yellow oil: ^{1}H-NMR (CDCl$_3$) δ 0.98 (s, 3H), 1.04 (d, 3H, J = 6 Hz), 1.19 (s, 3H), 1.58 (q, 1H, J = 6 Hz), 6.8–7.5 (m, 7H, ArH), 7.95–8.16 (m, 2H), 8.18 (s, 1H, ArOH); IR (CHCl$_3$, KBr) 3310, 2935, 1635, 1600, 1580, 1485, 1455, 1380, 1325, 1290, 1230, 1160, 1030, 975, 890, 840, 705, 635 cm^{-1}; mass spectrum m/e (relative intensity) 280 (M$^+$, 28), 265 (16), 237 (11), 222 (5), 207 (8), 175 (24), 159 (7), 133 (17), 121 (11), 115 (12), 105 (100), 91 (12), 77 (73). The epimeric ring-contracted product **5d** (36.3 mg, 13.0%) was obtained as a yellow oil as well: ^{1}H-NMR (CDCl$_3$) δ 1.08 (s, 3H), 1.20 (s, 3H), 1.22 (d, 3H, J = 6 Hz), 1.51 (q, 1H, ArOH); IR (CHCl$_3$, KBr)

3285, 2950, 1635, 1600, 1580, 1485, 1450, 1380, 1320, 1290, 1235, 1185, 1160, 1125, 1075, 1035, 995, 960, 885, 840, 710, 640 cm^{-1}; mass spectrum m/e (relative intensity) 280 (M$^+$, 30), 265 (17), 237 (66), 222 (25), 207 (12), 175 (52), 159 (20), 133 (23), 121 (18), 115 (23), 105 (100), 91 (24), 77 (85).

Photooxidation of 3,3-dimethyl-1,2-diphenylcyclobutene (**4b**). The following compounds were obtained upon dye (MB) photosensitized oxidation of **4b** in the manner described above. Compound **5b**; yield 14%; ^{1}H-NMR (CDCl$_3$) δ 0.97 (3H, s), 1.21 (3H, s), 1.42 (2H, d, J = 5.3 Hz), 1.50 (1H, d, J = 5.3 Hz), 6.78–8.13 (9H, ArH), 9.01 (br s, OH); ^{13}C-NMR (CDCl$_3$) 21.7 (CH$_3$), 26.5 (CH$_3$), 24.1 (C$_2$), 24.6 (C$_3$), 40.8 (C$_1$), 203.0 (C(O)Ph) ppm; IR (CHCl$_3$) 3265, 1645, 1600, 1580, 1475, 1450, 1380, 1330, 1300, 1158, 1127, 1040, 967 cm^{-1}; mass spectrum m/e 266, 248, 223, 208, 167, 145, 105, 91, 77. 2-(1-Benzoyl-2,2-dimethylcyclopropyl)-2-hydroxy-7-oxabicyclo[4.1.0]hept-4-en-3-one **25**; yield 16%; ^{1}H-NMR (CDCl$_3$) δ 0.96 (3H, s), 1.25 (1H, d, J = 6.0 Hz), 1.53 (3H, s), 1.72 (1H, d, J = 6.0 Hz), 3.26 (1H, dd, J = 2.1, 3.7 Hz), 3.45 (br s, OH), 3.84 (1H, dd, J = 2.7, 3.7 Hz), 5.80 (1H, dd, J = 10.6, 2.7 Hz), 6.92 (1H, dd, J = 10.6, 2.1 Hz), 7.3–8.00 (5H, ArH); ^{13}C-NMR (CDCl$_3$) 21.1 (CH$_3$), 26.4 (CH$_3$), 21.6 (C$_2$), 23.4 (C$_3$), 43.9 (C$_1$), 53.3 (C$_6$), 59.4 (C$_1$), 69.3 (C$_2$), 112.2 (C$_4$), 148.5 (C$_5$), 193.3 (C$_3$), 199.6 (C(O)Ph) ppm (double irradiation experiments were carried out to aid in the determination of the proton assignments); IR (CHCl$_3$) 3425, 1682, 1602, 1585, 1450, 1380, 1298, 1162, 1128, 1022, 962 and 910 cm^{-1}; mass spectrum m/e 298 (M$^+$), 280, 268, 251, 174, 159, 123, 115, 105, 77.

Compound **26** is also formed in overall yield of 14%. Both ^{1}H- and ^{13}C-NMR spectra indicate this to be a mixture of diastereomers (oxirane ring about C$_1$C$_2$). IR 1675 cm^{-1}; mass spectrum m/e 298 (M$^+$), 282, 211, 201, 165, 141, 123, 115, 105. A 41% recovery of **4b** was achieved.

Electron transfer photooxygenations sensitized by 9,10-dicyanoanthracene (DCA)

Photooxygenation of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene **4d**. A pyrex vessel similar to that utilized for the MB sensitized photooxygenations was constructed. In this case a 1.0 cm wide cylindrical chamber was interposed between the cooling well and the reaction chamber. This modification allowed the introduction of a filter soln between the light source and reaction medium. The light source consisted of a 500W Hanovia medium pressure mercury vapor lamp employed in conjunction with a band pass filter soln composed of 27 g of CuSO$_4$, 30 g of NaNO$_2$ and 50 ml of conc NH$_4$OH diluted to 1 l with distilled water. This filter soln transmits and isolates the 404–408 and 436 nm spectral bands of the emission spectrum of mercury.[23] A soln of **4d** (262 mg, 1.0 mmol) and DCA (2.3 mg, 0.01 mmol) in 100 ml of O$_2$ saturated acetonitrile was irradiated as described above for 1 hr. Separation of the components of the crude mixture by TLC techniques applied previously permitted recovery of 100 mg (38.1%) of **4d** as well as **30** (19 mg, 7.2%): ^{1}H-NMR (CDCl$_3$) δ 1.14 (s, 6H), 1.18 (s, 6H), 7.23 (s, 10H, ArH) identified by comparison with an authentic sample obtained upon peracid oxidation of **4d**;[15] the ozonide **31** (40.8 mg, 13.2%) as white needles from MeOH: m.p. 150–151° (lit.[18] m.p. 150–151°); ^{1}H-NMR (CDCl$_3$) δ 0.75 (s, 6H), 1.29 (s, 6H), 7.23–7.64 (m, 10H, ArH); ^{13}C-NMR (CDCl$_3$) δ 20.21 (q), 23.62 (q), 49.97 (s), 115.23 (s), 126.17 (d), 127.96 (d), 129.04 (d), 131.6 (s); IR (CHCl$_3$, KBr) 2950, 1440, 1395, 1370, 1290, 1150, 1120, 1100, 1070, 1040, 1020, 985, 920, 700 cm^{-1}; mass spectrum m/e (relative intensity) (M$^-$ not observed), 278 (8), 263 (7), 262 (7), 248 (27), 233 (20), 219 (28), 205 (29), 178 (16), 143 (15), 105 (100), 91 (25), 77 (47). (Found: C, 77.41; H, 7.4. Calc for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14%); benzil **33** (22.1 mg, 10.5%): ^{1}H-NMR (CDCl$_3$) δ 7.23–7.62 (m, 6H, ArH), 7.85–8.15 (m, 4H); mass spectrum m/e (relative intensity) 210 (M$^+$), 105 (100); and finally 38.3 mg (13%) of diketone **32** as white needles from MeOH: m.p. 113–114° (lit.[18] m.p. 113–114°); ^{1}H-NMR (CDCl$_3$) δ 1.40 (s, 12H), 7.14–7.73 (m, 10H, ArH); IR (CHCl$_3$, KBr) 2960, 1655, 1460, 1440, 1380, 1360, 1255, 1140, 1000, 960, 955, 910, 695, 660, 620

cm^{-1}; mass spectrum m/e (relative intensity) 294 (M$^+$, 3), 189 (6), 172 (10), 157 (6), 105 (100), 84 (8), 77 (45).

The evolution of products as a function of irradiation time was monitored by HPLC. HPLC analysis was performed on a Varian 5000 Liquid Chromatograph (Model No. 5020LC) equipped with an Alltech C18 reverse phase column (25 cm × 4.6 mm, 5 microns). A 50:50 acetonitrile/water mixture ramped to 100% acetonitrile over a period of 12 min was used for the elution process. The identity of each peak was determined by comparison with standards of known composition. It was determined that the oxirane **30**, the ozonide **31**, benzil **33** and the diketone **32** are the products formed initially. Benzoic anhydride (and benzoic acid) are formed at a somewhat slower rate.

Photooxygenation of 1,2-diphenyl-3,3,4-trimethylcyclobutene (**4c**). Irradiation of **4c** (248 mg, 1.00 mmol) as described above in the presence of DCA for 3.5 hr in O$_2$ saturated acetonitrile results in consumption of 77% of **4c**. Chromatographic separation of the oxidation products provided 15 mg (5.1%) of **41** as a white solid from MeOH : m.p. 83–84°; ^{1}H-NMR (CDCl$_3$) δ 0.65 (d, 3H, J = 7 Hz), 0.72 (s, 3H), 1.45 (s, 3H), 2.65 (q, 1H, J = 7 Hz), 7.23–7.52 (m, 10H, ArH); ^{13}C-NMR (CDCl$_3$) δ 12.0 (q), 21.0 (q), 23.6 (q), 48.6 (s), 51.4 (d), 114.1 (s), 115.1 (s), 126.1 (d), 128.0 (d), 128.3 (d), 129.1 (d), 129.4 (d), 130.6 (s); IR (CHCl$_3$, KBr) 2955, 1450, 1390, 1360, 1330, 1300, 1180, 1135, 1105, 1065, 1040, 1010, 980, 950, 910, 700, 665 cm^{-1}; mass spectrum m/e (relative intensity) (M$^+$ not observed), 280 (1), 264 (19), 249 (10), 255 (metastable peak), 226 (2), 198 (3), 174 (3), 159 (9), 148 (4), 131 (5), 122 (5), 105 (100), 91 (3), 77 (45); in addition to 19 mg (6.4%) of **40** as a white solid from MeOH m.p. 77–78°; ^{1}H-NMR (CDCl$_3$) δ 0.875 (s, 3H), 1.15 (d, 3H, J = 4.8 Hz), 1.22 (s, 3H), 2.30 (q, 1H, J = 4.8 Hz), 7.25–7.57 (m, 10H, ArH); ^{13}C-NMR (CDCl$_3$) δ 9.81 (q), 17.77 (q), 29.04 (q), 45.89 (s), 50.27 (d), 113.0 (s), 115.5 (s), 126.2 (d), 126.9 (d), 128.0 (d), 128.5 (d), 129.1 (d), 129.8 (d), 130.7 (s), 131.10 (s); IR (CHCl$_3$, KBr) 2960, 1450, 1390, 1365, 1330, 1300, 1180, 1140, 1110, 1070, 1045, 1015, 990, 950, 920, 705, 670 cm^{-1}; mass spectrum m/e (relative intensity) (M$^+$ not observed), 280 (1), 264 (32), 249 (15), 255 (metastable), 226 (3), 198 (3), 174 (4), 159 (10), 148 (8), 131 (6), 122 (7), 105 (100), 91 (4), 77 (66) as well as 9.1 mg (4.3%) of benzil; and finally 104.5 mg (37.3%) of **42**; ^{1}H-NMR (CDCl$_3$) δ 1.20 (d, 3H, J = 7 Hz), 1.42 (s, 3H), 1.48 (s, 3H), 4.16 (q, 1H, J = 7 Hz), 7.25–8.13 (m, 10H, ArH); IR (CHCl$_3$, KBr) 2950, 1670, 1600, 1580, 1450, 1360, 1270, 1225, 1180, 1010, 960, 920, 705, 620 cm^{-1}.

Photooxygenation of 1,4-diphenyl-2,2,3,3-tetramethyl-5-oxabicyclo[2.1.0]pentane (**30**). The oxirane **30** (49 mg, 0.18 mmol) and DCA (0.4 mg, 0.002 mmol) were dissolved in 20 ml of acetonitrile. The soln was saturated with O$_2$ and irradiated for 1.5 hr in the usual manner. Separation of the mixture on a silica plate provided 48 mg (88%) of **31** identical in all respects to that obtained previously by direct ozonolysis of **4d**.

Synthesis of 1,4-diphenyl-2,2,3,3-tetramethyl-5-oxabicyclo-[2.1.0]pentane (**30**). The method described by Arnold and Karnischky[15a] was utilized to convert **4d** to **30**. To a stirred mixture of **4d** (200 mg, 0.763 mmol) in 50 ml of CH$_2$Cl$_2$ and 50 ml of sat NaHCO$_3$ aq was added *m*-chloroperoxybenzoic acid (186 mg, 0.77 mmol). After stirring for 9 hr the reaction was quenched by adding 5 ml of 0.1 M Na$_2$S$_2$O$_3$. The organic layer was separated and washed successively with sat NaHCO$_3$ aq, sat NaCl aq and distilled water. The solvent was removed and the residue chromatographed on a silica plate to provide **30** as a white solid. Recrystallization from MeOH afforded white needles (199 mg, 94%): m.p. 116–177° (lit.[15a] m.p. 116–177°); ^{1}H-NMR (CDCl$_3$) δ 1.14 (s, 6H), 1.18 (s, 6H), 7.18–7.53 (m, 10H, ArH).

Ozonolysis of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**4d**). The procedure of William and Dolbier[18] was employed for the conversion of **4d** to **31**. O$_3$ was passed through a soln of **4d** (186 mg, 0.710 mmol) in 50 ml CH$_2$Cl$_2$ at −78° until the blue color persisted. The soln was purged with N$_2$ and the volatile solvent removed under vacuum. The residual oil was chromatographed on silica gel to give a white solid which was recrystallized from MeOH to furnish **31** (230 mg, 92%) as white

needles: m.p. 150–151° (lit.[18] m.p. 150–151°). This substance was identical in all respects to the ozonide obtained upon DCA sensitized photooxygenation of **4d** and **30**.

Preparation of 2,3-dibenzoyl-2,3-dimethylbutane (**32**). The ozonide **31** (31 mg, 0.1 mmol) in 2 ml of glacial AcOH was treated with excess Zn powder. The mixture was filtered, diluted with water and extracted with ether. The solvent was removed under vacuum and the residue chromatographed on a silica gel plate (benzene) to afford 14 mg (48%) of **32**: ^{1}H-NMR (CDCl$_3$) δ 1.40 (s, 12H), 7.21–7.62 (m, 10H, ArH); IR (CHCl$_3$, KBr) 2960, 1660, 1460, 1440, 1380, 1360, 1255, 1140, 1000, 945, 905, 695 cm^{-1}; mass spectrum m/e 294 (M$^+$), 283, 281, 252, 237, 189, 172, 157, 148, 147, 105 (100), 91, 84, 77; IR (CHCl$_3$, KBr) 2960, 1660, 1460, 1440, 1380, 1360, 1255, 1210, 1140, 1000, 960, 950, 910, 695, 660, 620 cm^{-1}.

Ozonolysis of 1,2-diphenyl-3,3,4-trimethylcyclobutene (**4c**). O$_3$ was introduced into a soln of **4c** (100 mg, 0.40 mmol) dissolved 100 ml CH$_2$Cl$_2$ at −78° until the blue color persisted. The soln was purged with N$_2$, the solvent removed *in vacuo* and the residue chromatographed on silica gel (benzene) to afford two isomeric ozonides. Ozonide **40** (least polar) eluted first and was recrystallized from MeOH to afford 51 mg (43%) of white crystals: m.p. 77–78°; ^{1}H-NMR (CDCl$_3$) δ 0.88 (s, 3H), 1.15 (d, 3H, J = 4.8 Hz), 1.22 (s, 3H), 2.30 (q, 1H, J = 4.8 Hz), 7.25–7.57 (m, 10H, ArH); ^{13}C-NMR (CDCl$_3$) δ 9.81 (q), 17.77 (q), 29.04 (q), 45.89 (s), 50.27 (d), 113.0 (s), 115.5 (s), 126.2 (d), 126.9 (d), 128.0 (d), 128.5 (d), 129.1 (d), 129.8 (d), 130.7 (s), 131.0 (s); mass spectrum m/e (relative intensity) (M$^+$ not observed), 280, 264, 249, 255 (metastable), 226, 198, 174, 159, 148, 122, 105, 77. (Found: C, 77.24; H, 6.88. Calc for C$_{19}$H$_{20}$O$_3$: C, 77.00; H, 6.80%.) Ozonide **41** (58 mg, 47%) is obtained as white plates from MeOH: m.p. 83–83.5°; ^{1}H-NMR (CDCl$_3$) δ 0.65 (d, 3H, J = 7 Hz), 0.72 (s, 3H), 1.45 (s, 3H), 2.65 (q, 1H, J = 7 Hz), 7.23–7.52 (m, 10H, ArH); ^{13}C-NMR (CDCl$_3$) δ 12.0 (q), 21.0 (q), 23.6 (q), 48.6 (s), 51.4 (d), 114.1 (s), 115.1 (s), 126.1 (s), 128.0 (d), 128.3 (d), 129.1 (d), 129.4 (d), 130.6 (s); mass spectrum m/e (M$^+$ not observed), 280, 264, 249, 255 (metastable), 266, 198, 174, 159, 148, 122, 105, 77. (Found: C, 77.30; H, 6.84. Calc for C$_{19}$H$_{20}$O$_3$: C, 77.00; H, 6.80%.) These two diastereomeric ozonides were identical to those obtained from the DCA sensitized photooxygenation of **4c**.

*Reduction of the ozonide **40** to 2,3-dibenzoyl-2-methylbutane* **42**. To a soln of **40** (50 mg, 0.17 mmol) in 10 ml of glacial AcOH was added excess Zn powder (∼ 2 g). The mixture was filtered and concentrated under reduced pressure and the resulting residue chromatographed on a silica gel plate (benzene) to give **42** (16 mg, 34%) as a yellow oil: ^{1}H-NMR (CDCl$_3$) δ 1.20 (d, 3H, J = 7 Hz), 1.42 (s, 3H), 1.48 (s, 3H), 4.16 (q, 1H, J = 7 Hz), 7.20–7.66 (m, 8H, ArH), 7.87–8.08 (m, 2H); IR (CHCl$_3$, KBr) 2960, 1670, 1595, 1575, 1450, 1360, 1270, 1225, 1180, 1010, 970, 920, 705, 625 cm^{-1}.

REFERENCES

[1a]Taken in part from the Doctoral Dissertation of G. P. Kirschenheuter, University of New Orleans, New Orleans, LA, 1983; [b]presented in part at the 15th Mardi Gras Symposium in Organic Chemistry, Louisiana State University, Chemistry Department, Baton Rouge, LA, February 14, 1983 and at the 15th Midwest Regional Meeting, St. Louis, MO, November 8–9, 1979, poster session B, No. 616; see also G. W. Griffin, G. P. Kirschenheuter and P. P. Umugar, Proc. of the COSMO 84 Conference on Singlet Molecular Oxygen, Clearwater Beach, FL, U.S.A., January 4–7 (1984), p. 548.

[2a]I. R. Politzer and G. W. Griffin, *Tetrahedron Lett.* 4775 (1973); [b]G. W. Griffin, I. R. Politzer, K. Ishikawa, N. J. Turro and M.-F. Chow, *Ibid.* 1287 (1977); [c]C. Vaz, G. W. Griffin, S. Christensen and D. Lankin, *Heterocycles* 15, 1643 (1981); [d]G. P. Kirschenheuter and G. W. Griffin, *J. Chem. Soc. Chem. Commun.* 596 (1983).

[3]The phosphorescence quantum yields for 2a and 2b were exceedingly low. Thus indirect probes were employed as energy transfer acceptors to monitor production of excited states; see K. A. Horn, J. Koo, S. P. Schmidt and G. B. Schuster, *Mol. Photochem.* 9, 1 (1978–79).

[4a]R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.* 91, 5358 (1969); [b]A. P. Schaap, K. Kees and A. L. Thayer, *J. Org. Chem.* 40, 1185 (1975).

[5]A. G. Schultz and R. H. Schlessinger, *Tetrahedron Lett.* 2731 (1970).

[6]C. W. Jefford and C. G. Rimbault, *Tetrahedron Lett.* 2479 (1976).

[7a]A. A. Frimer, *Isr. J. Chem.* 21, 194 (1981); [b]A. A. Frimer and A. Antebi, *J. Org. Chem.* 45, 2334 (1980); [c]A. A. Frimer and D. Rot, *J. Org. Chem.* 44, 3882 (1979); [d]A. A. Frimer, T. Farkash and M. Sprecher, *J. Org. Chem.* 44, 989 (1979); [e]A. A. Frimer, D. Rot and M. Sprecher, *Tetrahedron Lett.* 1927 (1977).

[8]A. A. Frimer, *Chem. Rev.* 79, 359 (1979).

[9a]W. Ando and S. Kohmoto, *J. Chem. Soc. Chem. Commun.* 120 (1978); [b]J. Rigaudy, M. Maumy, P. Capdevielle and L. Breton, *Tetrahedron* 33, 53 (1977); [c]C. W. Jefford, A. F. Boschung and C. G. Rimbault, *Helv. Chim. Acta* 59, 2542 (1976).

[10]M. Sakuragi and H. Sakuragi, *Chem. Lett.* 1017 (1980).

[11]C. Quannes and T. Wilson, *J. Am. Chem. Soc.* 90, 6527 (1968).

[12]R. S. Davidson and K. R. Trethewey, *J. Am. Chem. Soc.* 98, 4008 (1976).

[13]O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.* 90, 2333 (1968).

[14]G. W. Griffin and S. Christensen, unpublished results.

[15a]D. R. Arnold and L. A. Karnischky, *J. Am. Chem. Soc.* 92, 1404 (1970); [b]D. R. Arnold and Y. C. Chang, *J. Heterocyclic Chem.* 8, 1097 (1971).

[16]L. E. Manring, J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.* 102, 4275 (1980).

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[18]W. M. Williams and W. R. Dolbier, Jr., *J. Am. Chem. Soc.* 94, 3955 (1972).

[19a]A. P. Schaap, L. Lopez and S. D. Gagnon, *J. Am. Chem. Soc.* 105, 663 (1983); [b]S. Futamura, S. Kusunose, H. Ohta and Y. Kamiya, *J. Chem. Soc. Chem. Commun.* 1223 (1982).

[20]A. P. Schaap, S. Siddiqui, S. D. Gagnon and L. Lopez, *J. Am. Chem. Soc.* 105, 5149 (1983); A. P. Schaap, S. Siddiqui, G. Prasad, A. F. M. Magusuder Rahman and J. P. Oliver, *J. Am. Chem. Soc.* 106, 6087 (1984).

[21]J. Eriksen, C. S. Foote and T. L. Parker, *J. Am. Chem. Soc.* 99, 6455 (1977).

[22]L. E. Manring, M. K. Kramer and C. S. Foote, *Tetrahedron Lett.* 2523 (1984).

[23]A. Syed, G. P. Kirschenheuter, V. Jain, G. W. Griffin and E. D. Stevens, *Acta Cryst.* (1985), in press.