

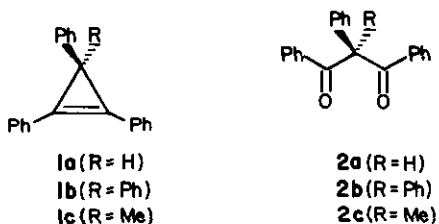
THE ROLE OF CYCLIC PEROXIDES IN THE REACTIONS OF 1,2-DIPHENYLCYCLOPROPENES
AND CYCLOBUTENES WITH SINGLET OXYGEN (1a,b,c,2)

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An array of cyclic peroxy intermediates, including dioxetanes, endo-peroxides and 1,2-dioxoles, are advanced as intermediates in the reactions of 1O_2 with 1,2-diphenylcyclopropenes and cyclobutenes.

We would like to present the results of our continuing studies on the course of the reactions of diarylsubstituted small-ring alkenes with singlet oxygen generated by dye photosensitization (3), chemically (4), as well as through electron transfer (5). As reported earlier, chemexcitation attends the dye-sensitized photooxidation of 1a, which gives the diketone 2a (1b,6), presumably by way of a dioxetane. The oxidation of 1b occurs at a slower rate than that of 1a, is more complex, and is accompanied by structural reorganization: however, emission is also associated with this process. In this case, the 1,3-diketone 2b is conspicuously absent as a product of the oxidation process (1b).



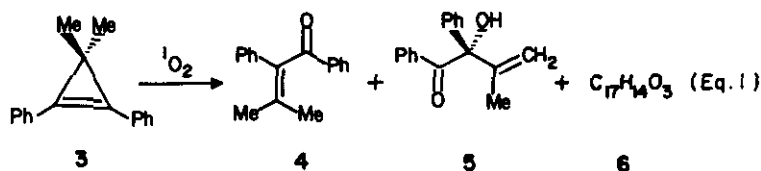
To rationalize the contrasting reaction pathways and disparate reactivities observed for 1a and 1b upon photooxidation, we proposed that introduction of the second phenyl substituent at C-3 in 1b should exert sufficient additional steric interference and/or electronic driving force to render the cyclization to a dioxetane slow relative to rearrangement.

In order to test this premise, we selected 3-methyl-1,2,3-triphenylcyclopropene (1c) (7) as an appropriate and accessible substrate to employ in the next phase of our extended studies in this area. It may be concluded from an examination of conformational free energy barrier data [A-factors (8)(9)] that cyclopropene 1c embodies structural characteristics which could prove instructive in discerning "the" mechanism. The steric barrier at C-3 in 1c toward approach of 1O_2 at one face is intermediate in magnitude between that in 1a and 1b; however, no marked increase in the

enhancement of electronic stabilization, cleavage and rearrangement of the type observed with 1b should be induced.

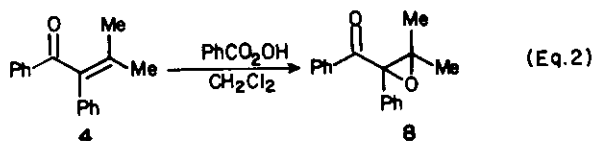
After irradiating (>400 nm) a continuously oxygenated solution of 1c in methylene chloride at -30° for 2.5 h containing methylene blue (MB) as a sensitizer, we found that the extent of substrate consumption was substantially reduced (*i.e.*, relative to 1a). Although the anticipated diketone 2c is detectable, the yield is low (~4%), and a considerable amount of the cycloalkene 1c may be recovered (~91%). Attempts to achieve oxidation with triphenylphosphite ozonide (TPO) (4) also proved unsuccessful with 0.2 as well as 1.0 M ozonide in methylene chloride at -35°. Essentially all (>99%) of the cyclopropene 1c is recovered in this case. The suppressed reactivity of 1c represents a significant departure from the behavior observed with 1a and 1b which cannot be accommodated by our original mechanistic rationale. Based on these limited data, it appears that substituents in the 3-position exert a more profound influence than might be anticipated on the mode of approach and interaction of 1O_2 with the strained *pi*-bond. Clearly this bond is sterically shielded by the 1,2-diaryl substituents from edge-on approach in an antarafacial-suprafacial manner [which preserves orbital phase continuity (10a)] and/or end-on attack to give a perepoxide (10b).

In an attempt to isolate those factors responsible for the diverse reactivities displayed by 1a, 1b, and 1c toward 1O_2 , 3,3-dimethyl-1,2-diphenylcyclopropene (3) (11) was subjected to oxidation under conditions simulating those employed with 1b and 1c (Eq. 1). In contrast to 1c, the cyclopropene 3 is susceptible to oxidation by 1O_2 under similar conditions for reasons yet unclear. The primary products include the cross-conjugated ketone 4 (18%) (11a) and the ketoalcohol 5 (14%) in addition to an unidentified substance 6 (27%), which is assumed to be a secondary oxidation product on the basis of the mass spectrum and elemental analysis. The diketone 2,2-dimethyl-1,3-diphenylpropane dione (7) was also absent in this case as a product as evidenced by thin-layer and high resolution glc in which an authentic sample of 7 was used in control runs. It is noteworthy that ~40% of the starting material was recovered, and thus again the material balance is high (~99%).

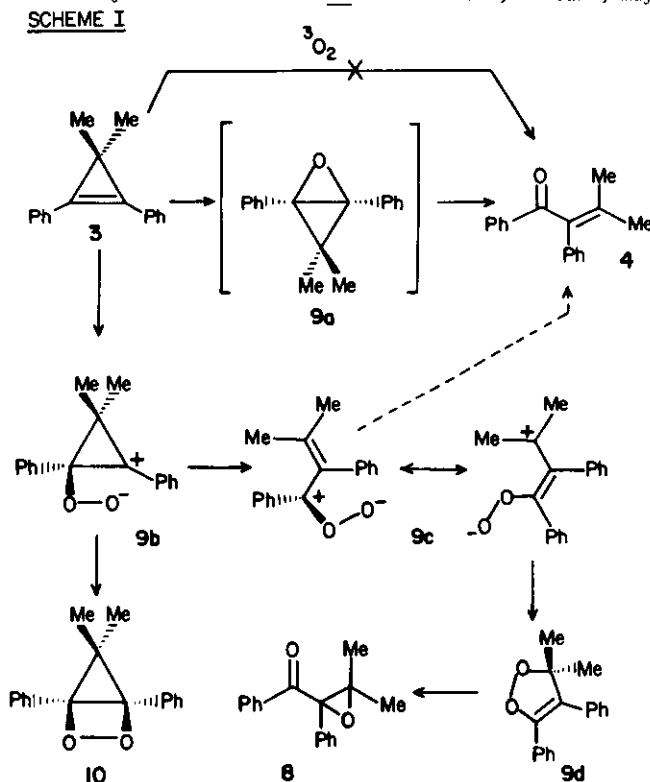


The major product formed upon treatment of 3 with TPO is the ketone 4 (~36%); however, a trace of another product, isolable by tlc, is also produced, which chemiluminesces upon warming. In fact, this substance (*m/e* 252) is isomeric with and rearranges to the epoxyketone 8, which was

synthesized independently by perbenzoic acid oxidation of 4 (Eq. 2). Significantly, neither the ketoalcohol 5 nor 6 is detected as a TPO oxidation product, although they constitute major components obtained upon photosensitized oxidation of 3.



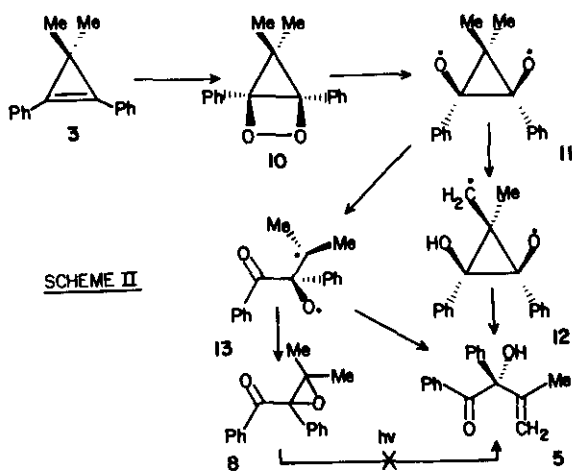
The mechanism by which the cyclopropene 3 undergoes conversion to 4 and the possibility that 9a is implicated as an intermediate has been considered (Scheme I). It had been demonstrated that peracid oxidation of 3 occurs to give 4 (>99%) (11a). Valence isomerization of the transient oxabicyclobutane 9a is invoked to rationalize this transformation (11a). The formation of epoxides as photooxidation products in a variety of systems is not uncommon and is cited as evidence for perepoxide intermediates by advocates of this mechanism (3f). Although the mode of oxirane formation remains a subject of controversy and active research (3f), it is inviting to propose that 9a is also implicated in the photooxidative conversion of 3 to 4. An ionic mechanism (Scheme I) may also be written to rationalize the conversion of 3 to 4. Attack of $^1\text{O}_2$ on 3 may occur to give the dioxetane 10 directly or indirectly *via* a zwitterion 9b. The latter, in turn, may be formed from



an initial peroxide by ring-opening. The cyclopropane ring may then collapse to 9c, which through oxygen transfer or cyclization to 9d provides rational routes to the unsaturated ketone 4 and epoxide 8, respectively.

Dehydration of an α - or β -ketoalcohol precursor is discounted as a possible route to the conjugated ketone 4 since nmr scrutiny of the crude reaction mixture formed upon TPO oxidation of 3 reveals no evidence for the presence of such ketoalcohol(s) despite the high yield of the conjugated ketone formed.

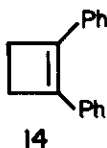
The structure of 5 was established through independent synthesis involving condensation of 2-propenylmagnesium bromide generated in tetrahydrofuran (12) with benzil. The photooxidative formation of such α -hydroxyketones is not unprecedented. Ando and co-workers (13a-c) and Wasserman (13d) report that α -hydroxyketones are generated from dioxetanes produced in turn upon dye-sensitized photooxidation of alkenes. Wasserman (13d), applied the Kornblum-DeLaMare (14) mechanism, which has since been reexamined (15), to explain their results obtained upon enamine oxidation. The reaction involves an ionic, base induced process in which removal of a proton from a dioxetane ring bearing an α -hydrogen is accompanied by β -elimination requiring O-O bond cleavage. Ando and co-workers (13a-c), however, advance an alternate mechanism involving homolysis of a dioxetane peroxide bond followed by intramolecular hydrogen transfer. The latter provides a reasonable route to explain formation of the ketoalcohol 5 from the dioxetane 10 (Scheme II).



Initial homolysis of the O-O bond of 10, if followed by hydrogen transfer from the syn methyl group, should give 12. Collapse of the cyclopropane ring would then afford 5. Alternatively, ring-opening of 11 to form 13 may precede H-transfer, in which case the diradical 13 would be implicated in this mechanism. Further experiments will be required to verify or reject these potential mechanisms and define with certainty the pathway(s) which is/are indeed operative.

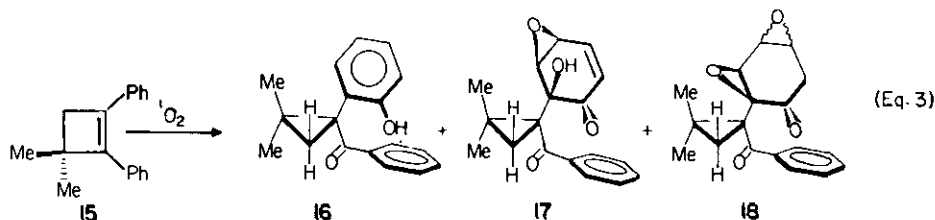
Clearly, however, the resemblance of 5 to an "ene" product derived from 4 is coincidental, since control experiments conducted with 4 exclude the ketoalcohol 5 as a product. Furthermore, the diketone 7 is stable under the reaction conditions and thus is not involved as a precursor for secondary oxidation products. Conversion of 8 to 5 is excluded by appropriate control runs, which indicate that the epoxyketone 8 is unchanged under the reaction conditions.

The absence of a self-consistent pattern of behavior for the series of cyclopropenes 1 and 3 led us to expand our program to include diarylcyclobutenes. The dye-sensitized photooxidation of 1,2-diphenylcyclobutene (14) was the subject of a previous study by other investigators (16) and the product distribution shown to be solvent dependent, a feature we found in common with 1a and 1b (1b). The results observed with 14 were rationalized by invoking an "ene" reaction in polar solvents (methanol, acetone) where the primary product is a cyclic, allylic hydroperoxide, while [2+2]cycloaddition affording a dioxetane and finally diketone is the dominant pathway observed in nonpolar media (methylene chloride, benzene) (16).



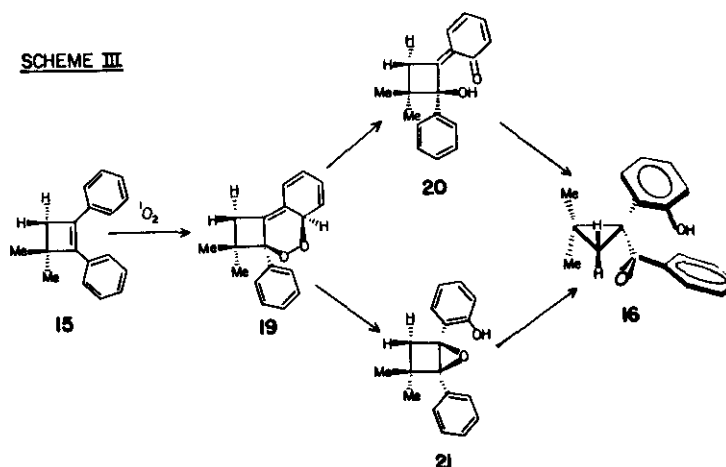
In accordance with the behavior observed for the cyclopropene substrates, a seemingly minor modification in structure at an apparently remote site on the diarylcyclobutene ring of 14 also exerts a major influence on the reaction path and rate. The course of the photooxidation of 3,3-dimethyl-1,2-diphenylcyclobutene (15), for example, departs markedly from that observed for the unsubstituted counterpart 14. The cyclobutene 15 was prepared by photoaddition of diphenylacetylene to isobutylene in a modification of a procedure described for the photocycloaddition of toluene to 2,3-dimethyl-2-butene (17).

Dye-sensitized photooxidation of 15 under conditions identical to those employed above for 1c, 3, and 14 is accompanied by ring contraction and leads to formation of the cyclopropane 16 (14%) as the primary product from which 17 (16%) and 18 (14%) are presumably derived (Eq. 3).



The ring contraction process accompanying the oxidation of the dimethyl substituted 1,2-diphenylcyclobutene 15 may be explained by invoking initial [4+2]cycloaddition of $^1\text{O}_2$ to the styryl moiety with formation of the endoperoxide 19 (Scheme III). Ample precedent exists for endoperoxide

formation from sytryl systems (18, 19, 20, 21a). Subsequent homolysis of the endoperoxide bond and H-transfer may be anticipated to give 16 via the bicyclic intermediate 21 (19) or conceivably

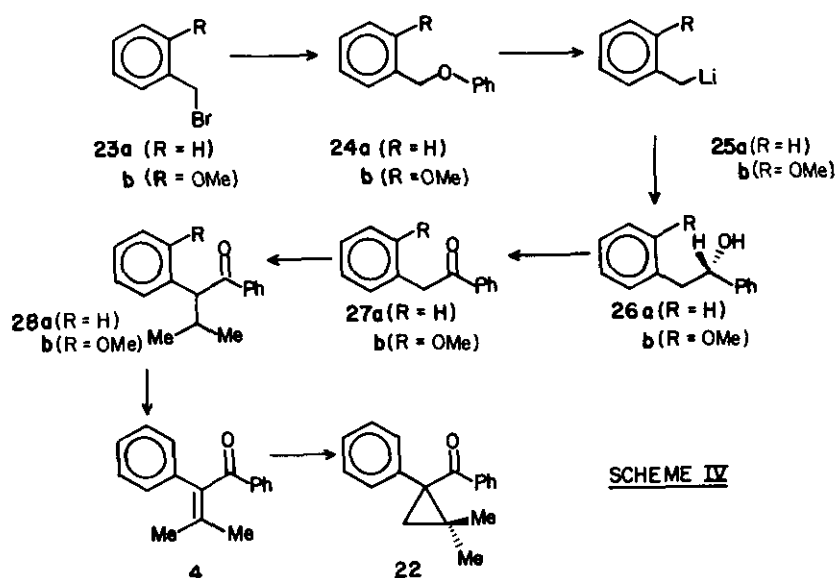


20 may be implicated (20). The constitutional structure of the cyclopropane 16 precludes us from discerning whether attack occurs in addition to or solely in the alternate manner to give the isomeric counterpart of 19 involving interaction of 1O_2 with the reverse phenyl ring *vicinal* to the dimethyl substituents. Frimer (21a) has argued that the photooxidation of cyclopropenes, including 1a and 1b with 1O_2 involves initial [4+2]cycloaddition to give an endoperoxide (21b).

The requisite ring-contraction is also not without precedent and is also observed in the case of 1-phenylcyclobutene (19). This process is dominated by other modes of reaction, as evidenced by the fact that the analog of 16 obtained also incorporates an *ortho*-hydroxy substituent on phenyl (a remnant of initial endoperoxy ring) and is formed in low yields relative to other products (19).

To date, attempts to confirm the structure of 16 by independent synthesis of the corresponding methyl ether by techniques which proved successful for the model synthesis of the less complex analog, 2,2-dimethyl-1-phenyl-1-benzoylcyclopropane (22), have failed (Scheme IV).

Deoxybenzoin (27a) may be synthesized from benzaldehyde upon treatment with benzylmagnesium bromide and subsequent oxidation of the alcohol 26a with dilute sodium hypobromite (22) or with pyridinium chlorochromate in methylene chloride (23). Difficulties were encountered in generating 2-methoxy benzylmagnesium bromide in the above manner, and it was necessary to resort to an alternate pathway to circumvent the adverse effects exerted by the methoxy substituent on the generation of the Grignard reagent and subsequent oxidation. It was found, however, that the synthetically equivalent organolithium reagent 25b could be generated efficiently by cleavage of 2-methoxybenzyl phenyl ether (24b) with lithium (24). The diether 24b, in turn, was generated in high yield by treatment of 2-methoxy benzyl bromide (23b) with sodium phenoxide in dioxane. Sodium hypobromite oxidation (22) of 26b proved undesirable because concomitant aromatic substitution by bromine

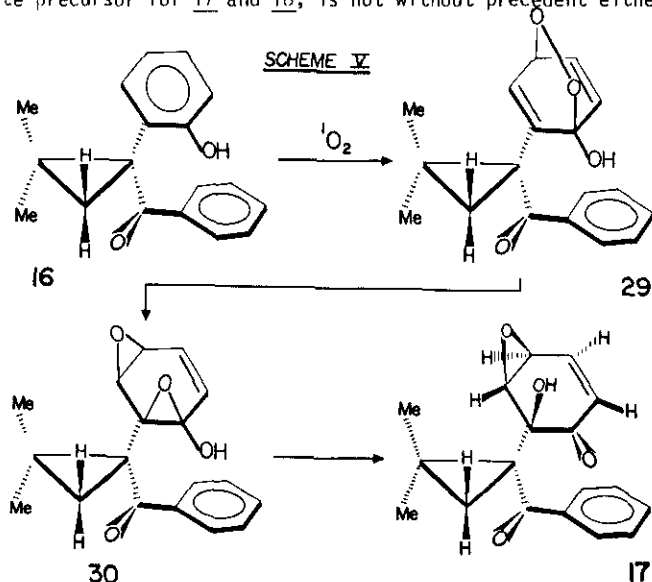


accompanies the oxidation process. This restriction on the utility of the reaction could not be avoided under a variety of conditions.

On the other hand, the oxidative conversion of the alcohol 26b to the deoxybenzoin 27b was achieved using pyridinium chlorochromate (23) as the oxidizing agent. Several obvious direct routes for the conversion of 27a to the conjugated ketone 4 were attempted, including the crossed aldol condensation of 27a with acetone, and proved futile. Treatment of 27a with 1,2-dibromo-2-methylpropane and base (25) in an attempt to obtain 22 directly also failed. Conversion of deoxybenzoin 27a to 4 was finally achieved in two steps by initial alkylation of the deoxybenzoin anion, generated from potassium *t*-butoxide in *t*-butanol with 2-bromopropane. The C-alkylated ketone 28a obtained in high yield was then readily transformed to the unsaturated ketone 4 by bromination in carbon disulfide and dehydrohalogenation with lithium chloride in dimethylformamide and proved identical to that obtained upon treatment of 3 with $^1\text{O}_2$ generated by photosensitization or from TPO. Unfortunately, attempts to extend this procedure to the accessible analog 28b proved ineffective because of the facile competitive electrophilic bromination of the aromatic nucleus. Cyclopropanation of 4 employing the Corey method (26) gives the cyclopropane 22, which proved indispensable in characterizing the hydroxy analog 16 by spectroscopic means.

Precedent may also be cited for the formation of the secondary oxidation products 17 and 18. Addition of $^1\text{O}_2$ in the [4+2] manner to phenols such as 16 to give endoperoxides of the type 29 is a very facile process (Scheme V). Since the phenol 16 is consumed at rates comparable to its precursor 15, it is not unexpected that the secondary oxidation products are formed in high yield. Subsequent homolysis of the peroxide bond and rearrangement of the resulting diradical to give such

products as 17 and 18 has been observed (27). The proposed rearrangement of 29 to the bis epoxide 30, the immediate precursor for 17 and 18, is not without precedent either (28)

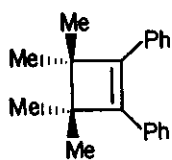
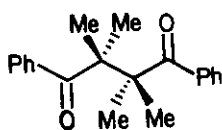
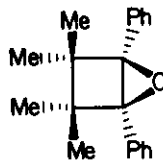


The structures assigned to 16, 17, and 18 rest largely on ms, pmr, cmr, and ir spectroscopic data. For example, the proton nmr spectra of 16, 18 and 22 prove very similar in the sense that all exhibit isolated AB patterns for the cyclopropyl protons. In addition, the presence of the benzoyl group in 16-18 and 22 is consistent with the presence of a low-field multiplet centered at $\sim \delta$ 8.0-8.2 assigned to the aromatic protons *ortho* to the carbonyl group. The aromatic patterns in the proton spectra of 16 and 22 (Fig. 1) are very similar and may be distinguished on the basis of the exchangeable OH signal at δ 9.01.

The proton spectrum of 17 displayed in Figure 2a reveals the presence of two epoxy proton multiplets in addition to another pair. The results of decoupling experiments and coupling constants are depicted in Figure 2b. Such unusual coupling patterns have been documented in the literature, and the nature and magnitude of coupling in our system is very similar to that previously reported for related types (29).

Analysis of the carbon-13 nmr spectra of 16, 17 and 22 (Fig. 3), coupled with additional literature results (30) provides self-consistent data in support of the structural assignments. It is noteworthy that the data collated for 16 indicate that the phenolic OH is intramolecularly hydrogen bonded to the aryl carbonyl, *i.e.* downfield shift (3.9 ppm) of the carbonyl carbon of 16 relative to 22

1,2-Diphenyl-3,3,4,4-tetramethylcyclobutene (31) prepared by [2+2] photoaddition of tolan to 2,3-dimethyl-2-butene (17) was also subjected to photosensitized oxidation under conditions similar to those employed with the cyclobutenes 14 and 15. This substrate proved even less reactive than the dimethyl analog 15 under the standard conditions employed throughout this study. In fact, 95%

**31****32****33**

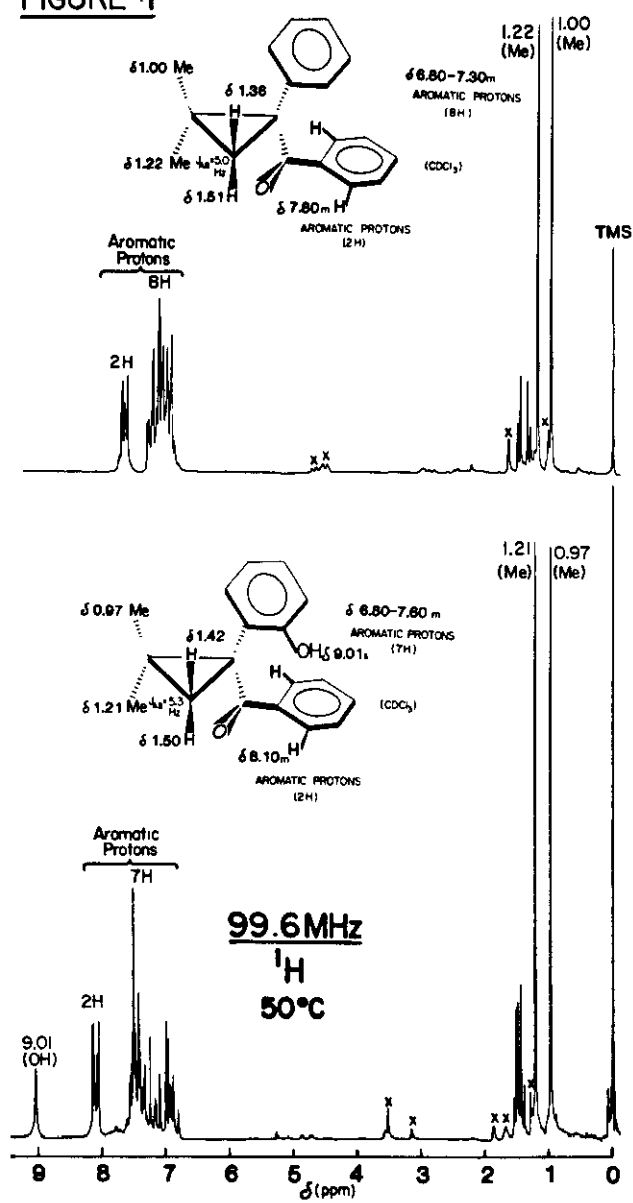
of the cyclobutene 31 was recovered. An examination of the trace quantities of products which are obtained from cyclobutene 31 employing high pressure liquid chromatographic techniques, and standard authentic samples of the diketone 32 (31) and the oxabicyclobutane 33 (32) confirmed that these are not formed as oxidation products.

A comparison of the reactivities and products generated by electron transfer sensitized oxidation using dicyanoanthracene in acetonitrile as a solvent-sensitizer system and a 400-450 nm band pass filter was conducted. It is evident from the results that the reactivity increases and the products differ. For example, oxidation of 31 under these conditions affords the diketone 32 (~22%), benzil (14%), and conceivably the 1,2-diol (8%) whose stereochemistry remains to be established. These results provide an indication that the methylene blue sensitized processes are proceeding *via* $^1\text{O}_2$ rather than electron transfer, as recently suggested could be the case under certain conditions (33). These preliminary results suffer from the disadvantage that a solvent of high dielectric constant must be employed in the electron-transfer experiments (acetonitrile) which differs from that used with methylene blue (methylene chloride), and it is recognized that the course of $^1\text{O}_2$ reactions is solvent sensitive (1b,16) at least in certain cases (34).

In summary, the results of this study confirm that the course of oxidation of the cyclopropenes 1c, 3 and the cyclobutenes 14, 15 and 31 by singlet oxygen generated by photosensitization and chemical means show no consistent or predictable behavior and is highly sensitive to substituent effects. In most cases, product structure has been confirmed by independent synthesis. Furthermore, the essential details necessary to expand this project and evaluate these substrates for chemiluminescent behavior have been accumulated. The requisite samples are available in a state of purity sufficient to expand our ongoing spectroscopic investigations in this area (1c). Preliminary total luminescence studies and product analysis in the case of 3,3-dimethyl-1,2-diphenylcyclopropene (3) and 1,2-diphenylcyclobutene (14) confirm that these two compounds merit further study as potential lumophores.

Furthermore, we have demonstrated that in the case of the cyclobutenes, the introduction of methyl substituents at an allylic position drastically affects both the course and extent of photo-sensitized oxidation. The different reactivities displayed by the cyclobutenes studied provides

FIGURE 1



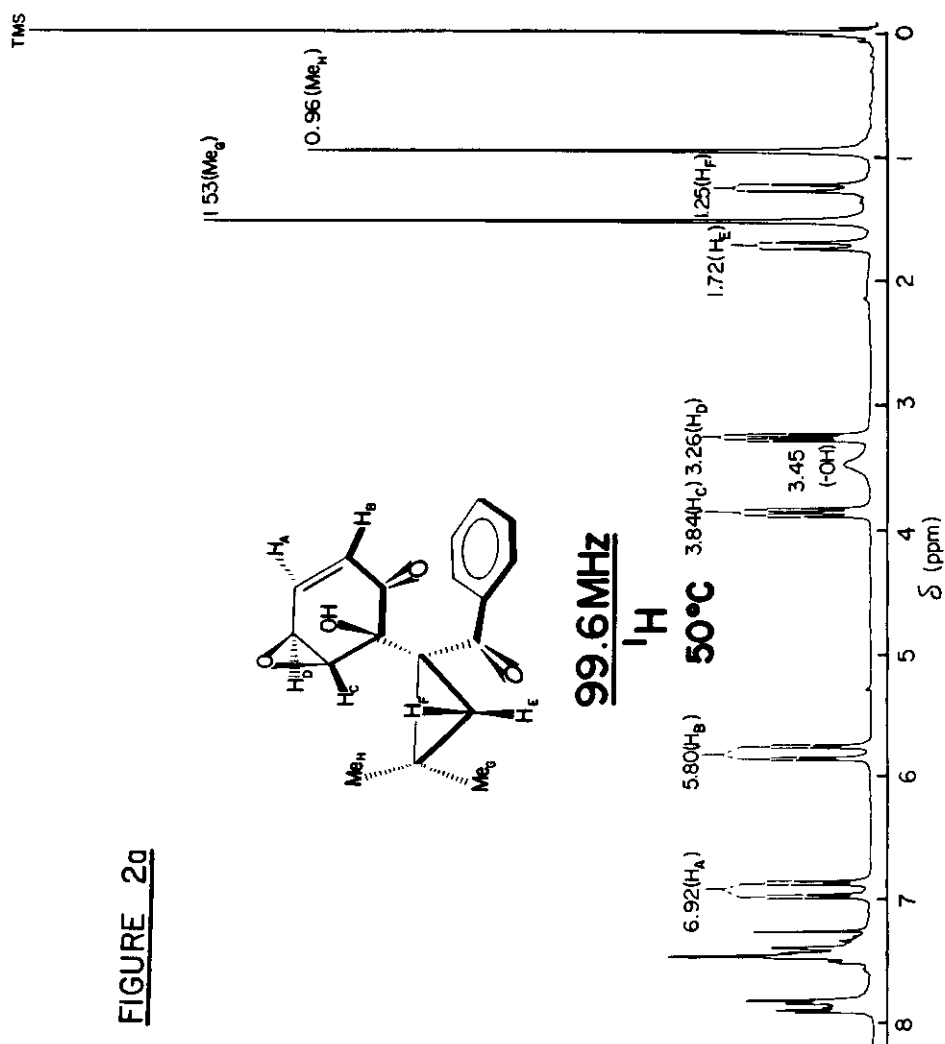
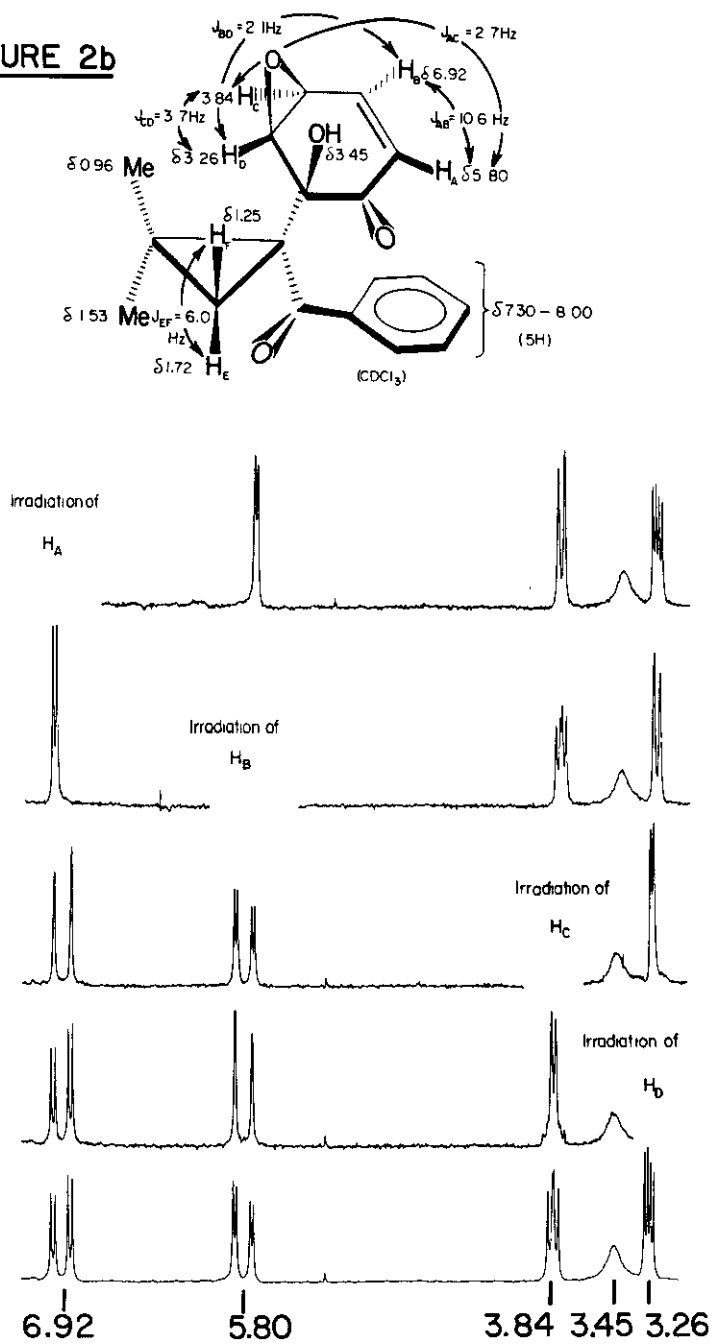


FIGURE 2b



evidence that the steric factors play a significant role in dictating the nature of the transition state for the photooxidation reactions. Further studies, both theoretical and experimental, are required to define the nature of the interaction(s) of singlet molecular oxygen with cyclopropenes and cyclobutenes.

Acknowledgments:

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- 6) The phosphorescence quantum yields for 2a and 2b were found to be exceedingly low under the reaction conditions. Therefore, indirect probes ["energy transfer acceptors" (3e)] were employed to monitor production of excited states.
- 7) We wish to thank Prof. A. Padwa for an authentic sample of 1c and a bulk quantity of the immediate precursor, which proved invaluable in expediting our experimental work. (b)

Structural assignments based upon spectroscopic data were corroborated by independent syntheses of the compounds which gave satisfactory elemental analyses.

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proposal is in contradiction to that advanced by us (1b) which leads directly to the same zwitterion and does not suffer from the disadvantage that cleavage of an endoperoxide C-O bond is required in an additional step under conditions where otherwise O-O bond homolysis is generally the preferred process.

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