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McGINNISS, Vincent Daniel, 1942-  
ELECTRONIC EFFECTS OF CYCLOPROPYL  
SUBSTITUENTS IN EXCITED ELECTRONIC STATES.

University of Arizona, Ph.D., 1971  
Chemistry, radiation

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ELECTRONIC EFFECTS OF CYCLOPROPYL SUBSTITUENTS  
IN EXCITED ELECTRONIC STATES

by

Vincent Daniel McGinniss

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A Dissertation Submitted to the Faculty of the  
DEPARTMENT OF CHEMISTRY  
In Partial Fulfillment of the Requirements  
For the Degree of  
DOCTOR OF PHILOSOPHY  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my  
direction by Vincent Daniel McGinniss  
entitled ELECTRONIC EFFECTS OF CYCLOPROPYL SUBSTITUENTS  
IN EXCITED ELECTRONIC STATES  
be accepted as fulfilling the dissertation requirement of the  
degree of DOCTOR OF PHILOSOPHY

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Nov. 2, 1970  
Date

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To Cheryl

## ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation for the assistance and guidance of Dr. Lee B. Jones, research director, during the course of this research.

. Receipt of a Petroleum Research Foundation Grant during the year 1969-1970 is gratefully acknowledged.

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## ABSTRACT

Photolysis of p-cyclopropylbenzyl acetate in a variety of solvent systems, conditions, and concentrations yields polymeric photo-products. These polymeric products arise from isomerization of the cyclopropane ring into a methylstyrene intermediate. Carbene, intermediates were not detected and photoisomerization of the cyclopropane ring is consistent with triplet state molecules.

Photolysis of m-cyclopropylbenzyl acetate in dioxane-water solutions yields m-cyclopropylbenzyl alcohol and a small amount of m-cyclopropylethylbenzene. The cyclopropyl group can effect meta transmission of electron density toward an electron deficient center in benzyl acetate systems and may result in photochemical solvolysis.

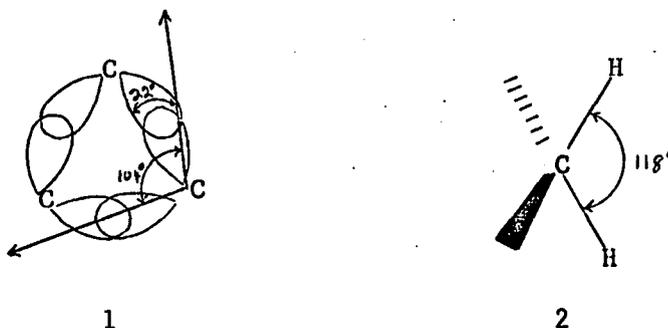
Irradiation of benzyl acetate and p-methylbenzyl acetate in dioxane-water solutions yields free radical products while photolysis of m-methylbenzyl acetate results in ionic products. Solutions of those compounds found to undergo photochemical reactions were stable indefinitely in the dark. A mechanistic scheme is presented which relates the formation of products to certain other photochemical reactions of para- and meta-methoxy substituted benzyl acetate compounds.

## INTRODUCTION

Derivatives of cyclopropane have received considerable attention during the last twenty years. Much of the interest in cyclopropane chemistry is due to the olefinic character of its carbon-carbon single bonds (Ferguson 1969).

### The Structure of the Cyclopropane Ring

A picture of the bonding in cyclopropane is shown below.



The C-C bond is visualized as a bent or "banana" bond with C-C-C bond angles of  $104^\circ$ . Theoretical calculations (Bennett 1967) and experimental verification by nmr spectroscopy (Weigert and Roberts 1967) show the bonding orbitals to be  $sp^5$ -hybridized. The C-H bonds are  $sp^2$ -hybridized with H-C-H bond angles of  $118^\circ$ . The correlation of nmr  $^{13}\text{C}$ - $^{13}\text{C}$  and  $^{13}\text{C}$ -H coupling constants with the S character of the bonding orbitals gives information about the C-C and C-H orbital characteristics.

Table 1 lists for comparison the C-H bond characteristics of olefins, cyclopropanes, and alkanes.

Table 1. C-H bond characteristics.

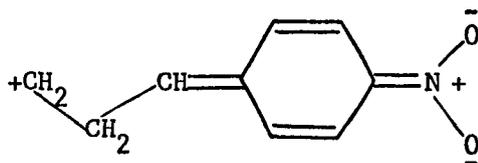
| C-H property        | H-C <sub>sp<sup>2</sup></sub> | H-C  | H-C <sub>sp<sup>3</sup></sub> |
|---------------------|-------------------------------|---------------------------------------------------------------------------------------|-------------------------------|
| H-C-H bond angle    | 120°                          | 118°                                                                                  | 109.5°                        |
| ir νC-H frequency   | 3034                          | 3009                                                                                  | 2853 cm <sup>-1</sup>         |
| C-H length          | 1.086                         | 1.093                                                                                 | 1.102 Å                       |
| C-H force constant  | 5.1                           | 5.5                                                                                   | 4.79x10 <sup>5</sup> dynes/cm |
| J <sup>13</sup> C-H | 156-170                       | 157-166.5                                                                             | 125 Hz                        |
| % s character       | 33                            | 33                                                                                    | 25                            |

Source: Ferguson, 1969.

#### Conjugative Ability of the Cyclopropane Ring

A study on the dipole moments of some para-substituted phenylcyclopropanes (Nishida, Moritani, and Sato 1967) has shown that the cyclopropyl group releases electron density to the benzene ring. Compounds p-chloro- and p-bromophenylcyclopropane have higher moments than those of chlorobenzene and bromobenzene indicating the conjugative ability of the cyclopropane ring. Further comparisons of dipole moments of para-substituted toluene, phenylcyclopropane, and styrene derivatives suggest that the cyclopropyl ring is more electron-releasing than the methyl derivative and behaves more like an alkyl group instead of the unsaturated groups as far as the dipole moment is concerned.

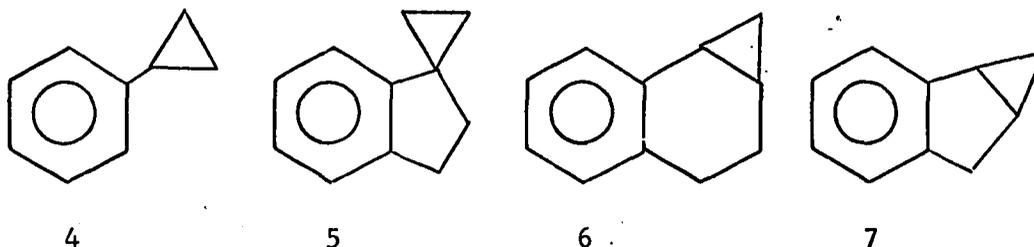
Ultraviolet spectroscopy has been used to indicate cyclopropane ring conjugation with  $\pi$ -electron systems. Strait et al. (1964) examined the ultraviolet spectra of a series of *p*-substituted phenylcyclopropanes with regard to chromophoric enhancement as measured by the effect of the *p*-substitution on the "primary" ( ${}^1A_{1g} \rightarrow {}^1B_{1u}$ ) electronically forbidden transition in benzene. This "primary" band at 210 m $\mu$  is uniquely subject to enhancement such that conjugative effects can be identified and distinguished from inductive effects. The ability to extend conjugation toward higher wavelengths and significant interaction with a nitrobenzene chromophore indicates that the cyclopropyl group is acting primarily as an electron donor. Derivatives of *p*-nitrophenylcyclopropane show a large shift and enhancement of oscillator strength in the 264 m $\mu$  transition of *p*-nitrotoluene to a maximum at 280 m $\mu$ . The 264 m $\mu$  band of *p*-nitrotoluene corresponds with the shifted and enhanced 210 m $\mu$  ( ${}^1A_{1g} \rightarrow {}^1B_{1u}$ ) band of benzene. It was suggested that structures such as 3 might make significant contributions to the ultraviolet spectroscopy of the arylcyclopropane system (Strait et al. 1964).



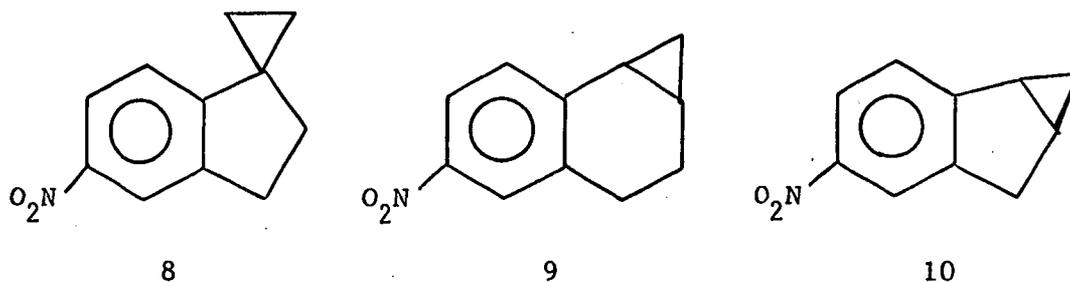
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Goodman and Eastman (1964) studied the ultraviolet spectra of a number of arylcyclopropanes in order to detect a bathochromic shift in

$\lambda_{\max}$  related to increasingly favorable cyclopropane geometries for conjugation with the benzene ring.



The angle made by the methine carbon-hydrogen bond on the cyclopropane ring with the plane of the benzene ring is defined by  $\varnothing$ . In structure 4, the methine carbon-hydrogen bond is arbitrarily placed in the plane of the aromatic nucleus and  $\varnothing$  is equal to  $0^\circ$  (Music and Matsen 1950). In structure 5, the cyclopropane ring is held so that its plane is perpendicular to the plane of the benzene ring. The methine carbon-hydrogen bond has been incorporated into the five-membered ring to effect coplanarity with the benzene ring ( $\varnothing = 0^\circ$ ). In this compound, maximum overlap of the sigma bonds of the cyclopropane ring is obtained with the  $\pi$  cloud of the aromatic nucleus and thus one would expect to see a bathochromic shift and increase in  $\lambda_{\max}$  relative to structures 4, 6, and 7. In structures 6 and 7,  $\varnothing$  is  $10^\circ$  and  $25^\circ$  from coplanarity and therefore maximum overlap of the cyclopropane ring with the phenyl ring is not expected. The absorption spectra of these four compounds were nearly superimposable indicating that there was no preferred geometry for conjugation of the cyclopropane ring with a benzene ring. In contrast to the work of Goodman and Eastman (1964), Hahn et al. (1969) studied the cyclopropyl compounds 8, 9, and 10.



They concluded that the absence of significant ultraviolet spectral differences in cyclopropyl aromatic hydrocarbons, compared with suitable standards (structures 4, 5, 6, and 7), may be regarded as a consequence of the minimal electron-attracting ability of the aromatic chromophore. In the nitro derivatives (structures 8, 9, and 10), large changes in  $\lambda_{\max}$  and increased bathochromic shifts were observed and found to be dependent on the geometrical requirements of the cyclopropane ring. Therefore cyclopropane conjugation in cyclopropyl aromatic systems is a spectroscopically detectable function of cyclopropane geometry if the interacting chromophore is sufficiently electron-attracting.

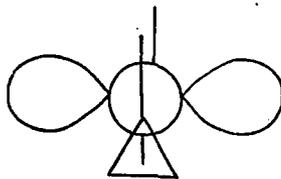
The same type of arguments for geometric dependence of cyclopropane conjugation shown in arylcyclopropanes seems to apply to vinylcyclopropanes (Heathcock and Poulter 1968) as compared to cyclopropylacrylic esters (Jorgenson and Leung 1968). Spectra of cyclopropyl olefins in which free rotation is not likely suggest that there is no conformational preference associated with the donor ability of the cyclopropyl group. This appears contrary to the results observed in cyclopropyl ketones (Dauben and Berezin 1967) and  $\beta$ -cyclopropylacrylic esters, but analogous to the behavior of phenylcyclopropanes (Goodman

and Eastman 1964). In the case of cyclopropyl ketones, the ultraviolet spectra of a series of bicyclo[n.1.o]alkan-2-ones and spiro[n.2]alkan-2-ones were studied and the conjugative ability of the cyclopropane ring with the adjacent carbonyl group was found to be dependent on cyclopropane ring geometry. Beta-cyclopropylacrylic esters also show a geometrical requirement for cyclopropane conjugative orbital overlap and, as in cyclopropyl ketones, the chromophore is sufficiently electron withdrawing to cause this interaction (Hahn et al. 1969). In cyclopropylacrylic esters and cyclopropyl ketones, there exists a charge separation in the ground state which is enhanced during a  $\tilde{\pi} \longrightarrow \tilde{\pi}^*$  transition to an excited electronic state. This charge separation places a partial positive charge next to the cyclopropane ring so that stereochemical factors, which are known to take place in the stabilization of cyclopropylcarbinyl cations (Deno et al. 1962, Pittman and Olah 1965), could effect both the excited state and the ground state. This charge separation of ground and excited states is diminished in pure hydrocarbon compounds, and the differences observed in conformational preference as well as cyclopropane conjugative ability could be due to such electronic factors.

In order to obtain a quantitative measure of the ability of the cyclopropane ring to transmit conjugation in the ground electronic state, Pews and Ojha (1969) studied a series of p-fluoro-m'- and -p'-substituted 1,2-diphenylethanes (bibenzyls), 1,2-diphenylethylenes (stilbenes), and 1,2-diphenylcyclopropanes. The  $^{19}\text{F}$  nmr shielding parameters of these compounds were plotted against Taft's  $\sigma^{\circ}$  constants

and showed that the cyclopropyl ring is 27% as effective as the vinyl moiety (relative to substituted bibenzyls) in its ability to transmit conjugation.

Nuclear magnetic resonance evaluation of geometric requirements for conjugative interaction of a cyclopropane ring with an adjacent chromophore was examined by Monti (1970). Comparison of the chemical-shift behavior of the cyclopropyl protons in conformationally rigid, tricyclic cyclopropyl ketones and corresponding hydrocarbons has shown that the bisected conformation 11 involves equal participation of two cyclopropane  $\sigma$  bonds and is the preferred geometry for maximum conjugative orbital overlap.



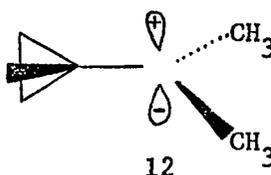
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Recently Clark and Fiato (1970) reported that delocalization of the electrons of carbon-carbon bonds of suitable orientated cyclopropanes in  $\pi$  systems can result in aromatic character.

#### Cyclopropane Ring Stabilization of Electron-Deficient Centers

Deno et al. (1962) and Pittman and Olah (1965) have observed cyclopropylcarbinyl cations in strong acid solutions and have noted that stabilization effects of the cyclopropyl group involve considerable charge dispersal through the ring without extensive skeletal

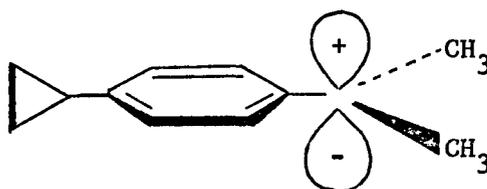
rearrangement. Nuclear magnetic resonance spectra of dimethylcyclopropylcarbiny l carbonium ions generated in  $\text{FSO}_3\text{H}-\text{SO}_2-\text{SbF}_5$  at  $-78^\circ$  indicated that the methyl groups in the ion were separated by 0.54 ppm and are therefore not equivalent. Rotation of the cyclopropyl group was not observed because the methyl peaks did not coalesce upon warming to  $-35^\circ$  at which temperature the ion was destroyed. The cyclopropyl ring can obtain maximum orbital overlap with an electron deficient site when its "banana" bonds lie in a plane perpendicular to the plane of the gem-dimethyl group 12 in a fixed bisected form.



Solvolytic rate studies (Brown and Cleveland 1966) for methyl substituted derivatives of p-cyclopropylcumyl chloride show that as the conformational freedom of the cyclopropane ring was destroyed by steric factors of the methyl groups, the ability to stabilize the carbonium ion in a bisected form similar to 12 was diminished. Another kinetic demonstration of the conjugative ability of the cyclopropane ring, transmitted through an aromatic system, was shown by the high  $\sigma^\ddagger$  value (-0.410) and rate enhancements obtained from solvolysis of p-cyclopropylcumyl chloride relative to other para- and meta-alkyl and cycloalkyl groups (Jones and Jones 1966, Hahn, Corbin, and Shechter 1968). Interestingly, m-cyclopropylcumyl chloride was the slowest to solvolyze ( $\sigma^\ddagger$  - 0.041) and m-cyclopropylbenzoic acid was the strongest acid in

their respective homologous series. These facts indicate that exocyclic cyclopropane orbitals possess considerable "P" character (Bennett 1967) and increased electronegativity. In para-substituted systems the cyclopropyl group becomes less electron-donating when the ring is sterically hindered from assuming the geometry needed for significant overlap of intracyclic orbitals with an electron-deficient system (Brown and Cleveland 1966).

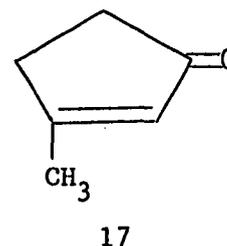
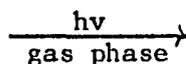
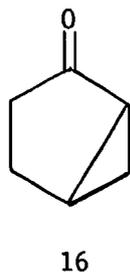
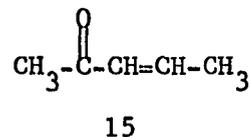
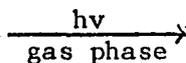
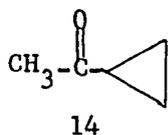
In meta-substituted systems, significant conjugative interaction of the cyclopropane ring is prevented by the inherent nature of the molecular orbital system, rather than by steric effects. The above evidence is consistent with a bisected cyclopropyl ring conformation 13.



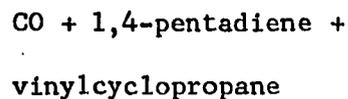
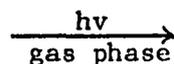
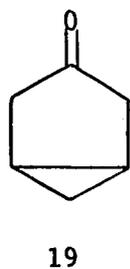
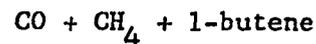
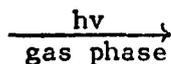
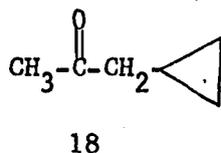
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#### Photolyses of Compounds Containing Cyclopropyl Rings

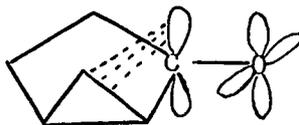
The primary photolytic reactions of compounds containing cyclopropyl rings fall into two distinct categories: those in which the cyclopropyl ring isomerizes to an alkenyl group,



and those in which the cyclopropane ring remains intact while some other bond in the compound is cleaved (Pitts and Norman 1954, Hess and Pitts 1967).



These results are most easily rationalized by assuming that when the cyclopropyl group is adjacent to the carbonyl group (structures 14 and 16), there is interaction between the functional groups and the cyclopropyl ring bonds are weakened (20) allowing easy rupture and formation of the alkenyl derivatives 15 and 17.



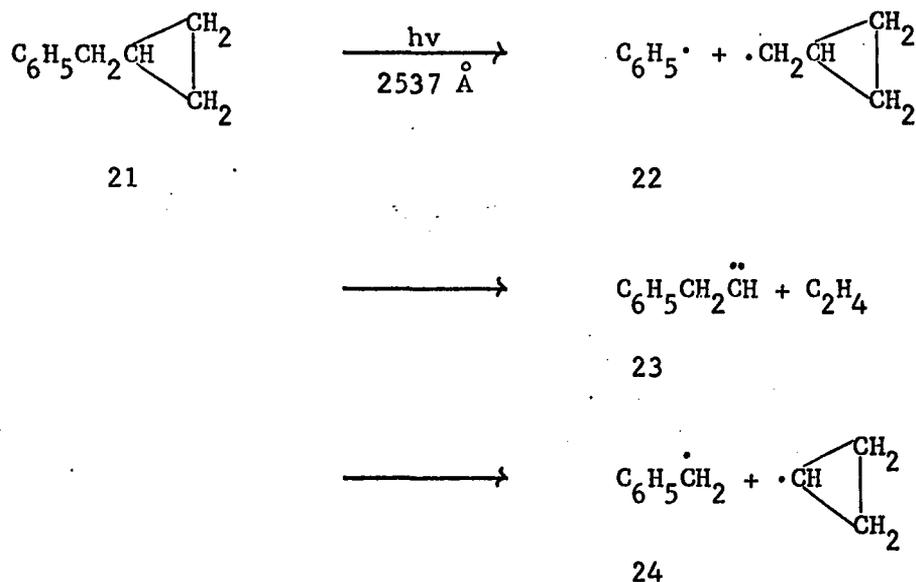
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When there is no interaction of the cyclopropyl rings with the carbonyl group (structures 18 and 19), the carbon-carbon bond  $\alpha$  to the carbonyl is not unlike that in any simple saturated ketone and is the bond that is expected to break under photolytic conditions. Similar results are obtained from unsaturated compounds (Hess and Pitts 1967, Hess et al. 1967). Another factor that might be considered comes from the molecular orbital calculations of cyclopropyl ring bonds. The energies of the cyclopropane ring orbitals are higher than  $\sigma$  orbitals in normal saturated hydrocarbons and almost approach the energies of  $\pi$  and nonbonding orbitals. In some systems one might expect to see  $\Delta \rightarrow \pi^*$  transitions at energies comparable to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions ( $\Delta$  = cyclopropyl bonding orbitals). If  $\Delta \rightarrow \pi^*$  transitions should occur, one would expect them to weaken cyclopropane bonding in the excited state and thus isomerization products would be expected (Hoffman 1965).

The ability of a cyclopropane ring to undergo other types of photolytic rearrangements and fragmentations was demonstrated in the irradiation of ethyl cyclopropylacrylates (Jorgenson 1969). In these compounds the cyclopropane ring can eliminate ethylene to give a carbene intermediate which then undergoes rearrangement to give allenes, furans, and cyclopropenes. The cyclopropane ring in these acrylic esters can

also rearrange to give cyclopentenes and ring expansion to bicyclo-[2.1.0]pentanes.

Leermakers and Vesley (1965) studied the gas phase photochemical decomposition of cyclopropylphenylmethane (21) and their results were explained by the following primary reactions:

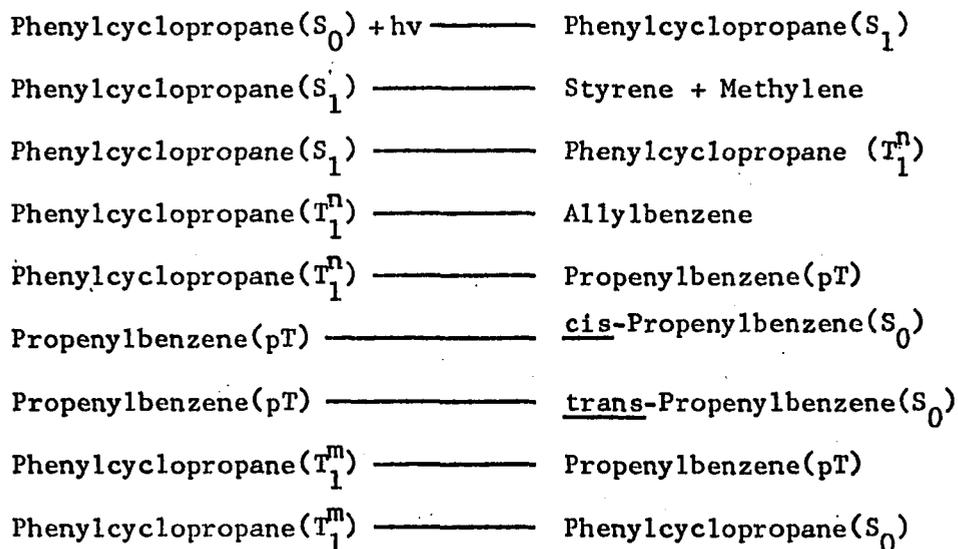


In this case 112 kcal/mole (2537 Å) of energy is absorbed by the phenyl ring and then is transmitted through the molecule as vibrational energy causing the observed fragmentation. The weaker carbon-carbon bonds in the molecule are the ones expected to break and thus intermediates 23 and 24 lead to the major products: styrene, ethylene, toluene, and cyclopropane.

A detailed study of the gas phase photolysis of phenylcyclopropane was undertaken by Foote (1966). The results from this study, compared with those obtained from structurally related ketones,

suggested that relative bond strengths and intramolecular energy transfer in the two systems were similar. Allylbenzene and the cis-trans isomers of propenylbenzene were the only products observed from the photoisomerization of the cyclopropane ring with 2537 Å light. Reactions from the  $S_1$  state of phenylcyclopropane resulted in styrene and a fluorescence quantum yield of 0.23. Quantum yield for the intersystem crossing between the first excited singlet and first triplet state of phenylcyclopropane was 0.65. The isomerization products came from ring opening reactions of vibrationally excited  $T_1$  state molecules. Allylbenzene and propenylbenzene were found to be equally probable at higher vibrational levels of the triplet state, while at lower vibrational levels only propenylbenzene was produced. Low yields of isomerization products at increased pressures indicated that collisional deactivation of the vibrationally excited  $T_1$  state was very efficient.

Mechanism for the Photoisomerization of Phenylcyclopropane

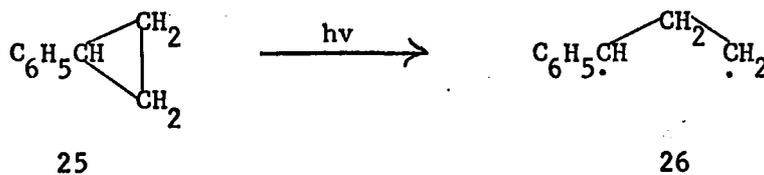


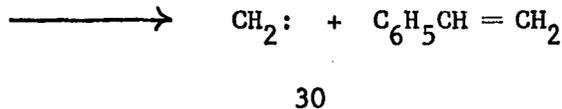
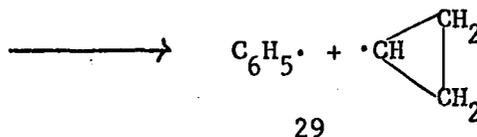
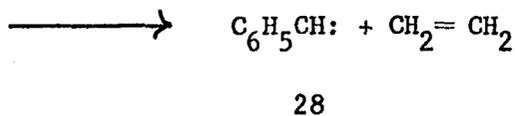
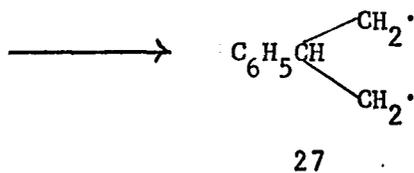
$S_0$ ,  $S_1$ ,  $T_1^n$ , and  $T_1^m$  are the ground singlet, first singlet, first triplet in the  $n^{\text{th}}$  vibrational level, and first triplet in the  $m^{\text{th}}$  vibrational level, respectively ( $n > m$ ) (Foote 1966). The "phantom" triplet pT of the propenylbenzenes is used in the sense of Hammond et al. (1964a). The species M is any molecule capable of removing vibrational energy by collisions.

Two photophysical processes can also occur: Phenylcyclopropane ( $S_1$ ) + M  $\longrightarrow$  Phenylcyclopropane ( $S_0$ ) +  $M^*$  representing internal conversion, and Phenylcyclopropane ( $S_1$ )  $\longrightarrow$  Phenylcyclopropane ( $S_0$ ) +  $h\nu$  representing fluorescence.

Leermakers and Ross (1966) also studied the vapor phase photolysis of phenylcyclopropane (25) with 2537 Å irradiation, but they observed completely different products than did Foote (1966).

In the photolysis, the major liquid products were (in order of decreasing yield) n-propylbenzene,  $\alpha$ -methylstyrene,  $\beta$ -methylstyrene, styrene, ethylbenzene, toluene, and benzene. The gaseous products were methane, ethane, ethylene, and acetylene. Large amounts of polymer were also generated during irradiation. The following reaction scheme was used to explain these products.





The large amount of n-propylbenzene relative to  $\beta$ -methylstyrene indicates hydrogen abstraction is favored over concerted ring opening-hydrogen migration. Intermediate 26 is partially stabilized by the benzene ring and is long-lived enough to abstract a hydrogen atom from some species in the system to give the saturated n-propylbenzene. Intermediate 27 is not stabilized by the phenyl ring. Thus hydrogen migration leading to  $\alpha$ -methylstyrene is favored over hydrogen abstraction products.

The presence of oxygen during the photolysis had no effect on the yield of ethylene (arising from intermediate 28), but all other products were totally inhibited except polymer. This suggests that

radical intermediates 26, 27, 29, and 30 are completely scavenged in the presence of oxygen and are incorporated into polymers or peroxides. The fact that oxygen had no effect on the yield of ethylene indicates that its formation does not depend on radical intermediates but is produced through a primary photochemical process.

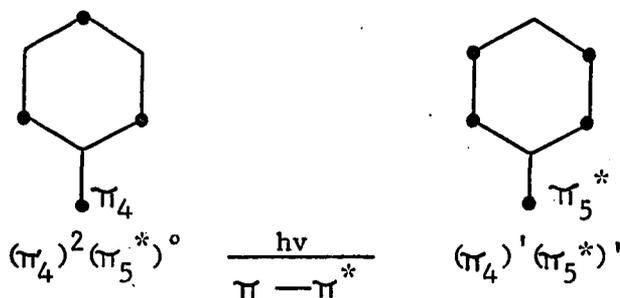
Richardson et al. (1965) studied the photolysis of phenylcyclopropane in cyclohexene and found 4-, 3-, and 1-methylcyclohexenes, polymer, and norcarane. These products and their ratios were the same as those produced by photolysis of diazomethane in cyclohexene (Doering et al. 1956) indicating a singlet carbene intermediate 30.

It is interesting to note that in the gas phase photolysis of phenylcyclopropane the major pathways of decomposition are photoisomerization, ethylene formation, and hydrogen abstraction. The formation of photoisomerization products ( $\beta$ -methylstyrene, allylbenzene, etc.) is pressure-dependent, and as the pressure increases, photoisomerization products decrease (Foote 1966). In solution, however, the only major reaction in the photolysis of phenylcyclopropane is ejection of a singlet carbene intermediate yielding styrene. No photoisomerization, ethylene, or hydrogen abstraction products were observed in the solution photolysis of phenylcyclopropane.

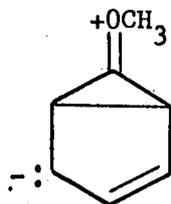
#### Solvolytic Photochemical Reactions

It has been reported that several substituents with nonbonding pairs of electrons show electronic transmission effects in excited electronic states which differ significantly from ground state behavior. Methoxyl substituents in conjugation with a benzene ring are ortho-para

directors in ground state reactions, while in the first excited state they become meta directors, with respect to electrophilic reactions. This latter effect can be explained by simple MO calculations of an aromatic ring with a methoxyl substituent on it. In this case there are eight  $\tilde{\pi}$  electrons which occupy in pairs the  $\tilde{\pi}_1, \tilde{\pi}_2, \tilde{\pi}_3,$  and  $\tilde{\pi}_4$  orbitals. Here promotion of an electron from  $\tilde{\pi}_4$  to  $\tilde{\pi}_5^*$  occurs upon  $\tilde{\pi} \rightarrow \tilde{\pi}^*$  excitation. The excitation removes an electron from  $\tilde{\pi}_4$ , which has no electronic density on the meta position, into  $\tilde{\pi}_5^*$  which does have ortho and meta but no para electron density.

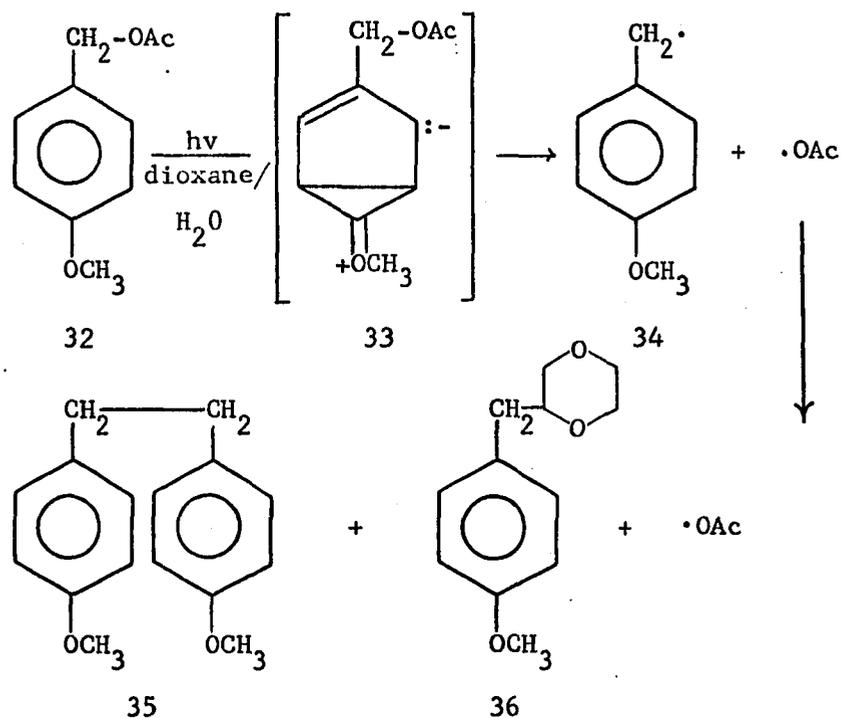


One therefore expects  $\tilde{\pi}, \tilde{\pi}^*$  excitation to lead to enhanced meta electron density. This meta electronic transmission can be represented by valence bond (resonance) structure 31 for the first excited state (Zimmerman and Sandel 1963).

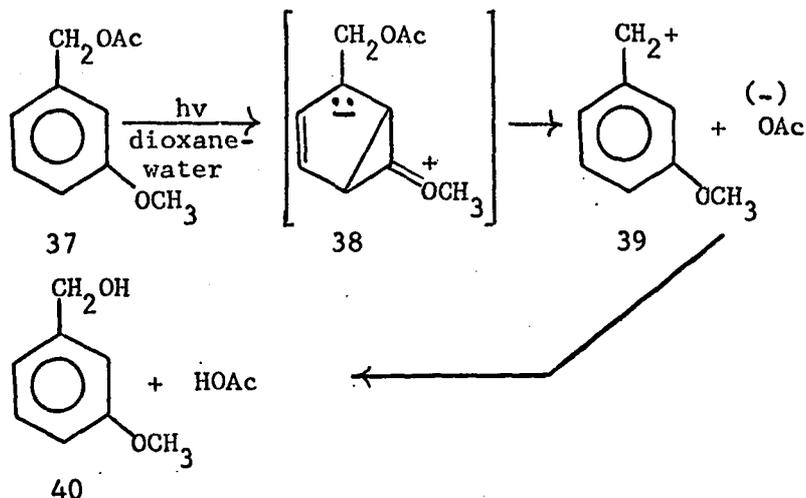


31

In order to substantiate these MO calculations, Zimmerman and Sandel (1963) looked at the solvolysis of meta- and para-methoxybenzyl acetates in the excited state. In the para compound 32 the methoxy group, in the excited state, could not transmit its electron density toward the benzylic carbon in order to assist solvolysis (ionization) and thus only homolytic cleavage was observed.



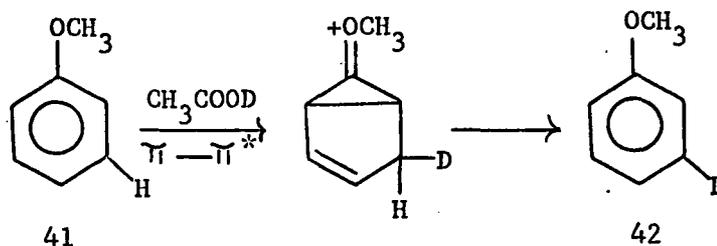
In the meta compound 37 the methoxy group, in the excited state, can transmit its electron density toward the benzylic carbon in order to assist solvolysis and thus heterolytic cleavage was noted.



In addition to 40, small amounts of 3,3'-dimethoxybibenzyl and 3-methoxybenzylidioxane were produced. These compounds arose through a benzyl radical intermediate similar to 34 and are analogous to structures 35 and 36.

The mechanism of excited state solvolysis of these benzyl acetates has not been firmly established. It is not known if a difference in lifetime of excited states has any effect on para versus meta reactivity. It is also possible that unimolecular heterolysis of a singlet excited state competes with unimolecular homolysis. Heterolysis could compete with intersystem crossing to give a triplet which undergoes homolysis. The triplet excited state could also undergo solvolysis and give rise to the observed products.

Consistent with representation 31 is the photochemically induced meta deuteration of anisole (41) (Havinga, de Jongh, and Kronenberg 1967).



Incorporation of deuterium by electrophilic exchange at various positions of anisole showed that the methoxy substituent effected strong meta activation and a relative deactivation at the para position. It was suggested that heterolytic photosubstitution probably starts from the lowest  $\pi \rightarrow \pi^*$  singlet excited state. Evidence cited for direct involvement of the singlet excited state is the lack of the occurrence of triplet states or free radicals and relatively high concentrations of the electrophile ( $10^{-1}$  M) must be present to attain photodeuteration. All efforts to detect a triplet intermediate failed.

It is of interest to look at substituents which do not contain nonbonding pairs of electrons in order to probe  $\pi$ -electron distributions in  $\pi \rightarrow \pi^*$  singlet and triplet excited states in a benzene ring without having to consider the possibility of the nonbonding electrons of a heteroatom interacting with the system via  $n \rightarrow \pi^*$  states. It is also of interest to see if a cyclopropane ring can stabilize an electron deficient center in the excited state as it does in the ground state. For these reasons the photolytic solvolysis of meta- and para-cyclopropylbenzyl acetates were investigated under a variety of reaction conditions.

## EXPERIMENTAL

### General

Melting points were determined with a Mel-Temp capillary apparatus and are uncorrected. Nuclear magnetic resonance spectra were determined in  $\text{CCl}_4$  solutions with Varian A-60 and HA-100 spectrometers using tetramethylsilane as an internal standard. Infrared spectra were obtained with Perkin-Elmer Models 137 and 337 spectrometers, using either neat samples between silver chloride plates or  $\text{CCl}_4$  solutions in sodium chloride cavity cells. Ultraviolet spectra were obtained on a Cary Model 14 spectrometer using ethyl alcohol as the solvent. Gas chromatography was performed on a Varian Model A-90, P-3 chromatograph (5-foot column, 18% GE-SE-30, 20% Carbowax 20-M, suspended on acid-washed 60/80 mesh Chromsorb P). All photoreactions were done in Vycor tubes and irradiations were carried out with a Srinivasan-Griffin Photochemical Chamber Reactor using General Electric G8T5 lamps emitting at 2537 Å. Samples were placed at a distance of 1 inch from the light source and maintained at temperatures of 30-40° during irradiation. Mass spectra were obtained with a Hitachi-Perkin-Elmer Model RMU-6E double focusing mass spectrometer run at an ionization potential of 80 ev. Emission spectra were determined on an Aminco-Bowman Spectrophotofluorometer at room temperature. Thin layer chromatography was used to qualitatively identify products and to follow all photoreactions and column chromatography fractions. Preparative thin layer chromatography was used for quantitative analysis and separation of photoproducts.

### Materials

Dioxane was purified by standard procedure (Fieser and Fieser 1967, p. 333). A mixture of 2 liters of commercial dioxane, 27 ml of concentrated hydrochloric acid, and 200 ml of water was refluxed for 12 hr, during which time a slow stream of nitrogen was bubbled through the solution. The solution was cooled, and potassium hydroxide pellets were added slowly with shaking until they no longer dissolved and a second layer separated out. The dioxane was decanted into a flask and refluxed with sodium for 10 hr. The solvent was then distilled from the sodium to yield material having bp 100-101°. Baker A. R. acetonitrile was stirred over sodium hydroxide pellets, refluxed for 1 hr over phosphorus pentoxide and then distilled. Acidic impurities were removed by further distillation from calcium hydride to yield material having bp 80-81°. Mallinckrodt A. R. benzene was refluxed with sodium metal and then distilled to yield material having bp 78°. Mallinckrodt t-butyl alcohol was refluxed over sodium, distilled, and stored over molecular sieves. Preparative and qualitative thin-layer chromatographic plates were prepared by conventional methods (Randerath 1964, p. 71), using silica gel G for TLC according to Stahl, Kensington Scientific Corporation. Adsorbents used for column chromatography were silica gel (60-200 mesh) Baker Analyzed Reagent, J. T. Baker Chemical Company, and adsorbosil-CAB (60-100 mesh) silica gel, Applied Science Laboratories. Eastman Organic Chemicals benzyl acetate and 1-bromo-3-phenylpropane were used as received. Drying was done with magnesium sulfate unless otherwise specified.

### 1,3-Dibromo-1-phenylpropane

The procedure was as previously described (Corbin, Hahn, and Shechter 1964). A solution of 1-bromo-3-phenylpropane (100 g, 0.5 mole), N-bromosuccinimide (94 g, 0.53 mole), benzoylperoxide (1.5 g, 0.006 mole), and 600 ml of carbon tetrachloride was placed in a 2000-ml three-necked, round-bottomed flask fitted with a stirrer and two reflux condensers. The mixture was heated with a flame to initiate the reaction. After the spontaneous reaction subsided, heating and stirring was continued until most of the N-bromosuccinimide had reacted. The mixture was cooled and filtered. The precipitate was washed with carbon tetrachloride, and the combined carbon tetrachloride layers were concentrated by distillation at water aspirator pressure at 40-50° to give 140 g of crude material.

### Phenylcyclopropane

A zinc-copper couple (66 g, 1 mole), as was previously described by Hennion and Sheehan (1949), and 250 ml of dimethylformamide were placed in a 500-ml, three-necked, round-bottomed flask fitted with a mechanical stirrer, addition funnel, and thermometer. The mixture was cooled in ice water, and 1,3-dibromo-1-phenylpropane (140 g, 0.5 mole) obtained from the preceding experiment without purification was added at a rate to maintain the temperature at 7-9°. The highly exothermic reaction has an induction period, the end of which is characterized by a rapid temperature rise. At this point, the addition of the 1,3-dibromo-1-phenylpropane was stopped and was resumed only after the temperature had stopped rising. The mixture was stirred for 30 min

after addition was completed, poured into 500 ml of water, and steam distilled until the condensate was homogeneous. The organic layer was extracted with ether, washed with water, dried, concentrated, and distilled to give 48.3 g (81%) of material: bp 170-173°;  $n_D^{26.5}$  1.5288; lit. bp 170-175°;  $n_D^{26}$  1.5306-1.5318 (Corbin, Hahn, and Shechter 1964); nmr ( $CCl_4$ ),  $\tau$  9.0-9.5 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 7.85-8.45 (one-hydrogen multiplet, tertiary cyclopropyl hydrogen), 2.4-2.8 (five-hydrogen multiplet, aromatic hydrogens); analysis of this product by gas liquid chromatography (18% GE-SE-30, 115°) showed it to be 99% pure; mass spec,  $m/e$  118 ( $C_9H_{10}^+$ ) (57), 117 ( $C_9H_9^+$ ) (100), 91 ( $C_7H_7^+$ ) (35), 77 ( $C_6H_5^+$ ) (8); ir ( $CCl_4$ ), 3060, 3040, and 3020  $cm^{-1}$  (aromatic CH), 1600, 1580, 1500 (aromatic C=C). Increased yields and simplified procedures have been reported by use of copper(I) chloride (Rawson and Harrison 1970).

#### p-Bromophenylcyclopropane

The procedure was as previously described (Levina et al. 1964). A solution of phenylcyclopropane (16.6 g, 0.14 mole) in 85 ml of chloroform was placed in a 1000-ml, three-necked, round-bottomed flask fitted with a mechanical stirrer, condenser, and addition funnel. The mixture was cooled in Dry Ice-acetone, and bromine (22 g, 0.275 mole) in 55 ml of chloroform was added dropwise with stirring to the phenylcyclopropane solution. After the completion of addition, the mixture was stirred at Dry Ice-acetone temperatures for an additional 6 hr, then washed with aqueous sodium sulfite, followed by aqueous sodium bicarbonate. Drying, concentration, and distillation yielded 21.7 g (78%) of

material: bp 157-158° (65 mm);  $n_D^{25}$  1.5747; lit. bp 116° (15 mm);  $n_D^{20}$  1.5752 (Levina et al. 1964); nmr ( $CCl_4$ ),  $\tau$  8.90-9.6 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 7.9-8.4 (one-hydrogen multiplet, tertiary cyclopropyl hydrogen), 2.44 and 2.80 (two two-hydrogen doublets,  $J = 8.5$  Hz, aromatic hydrogens, further split by the benzylic proton,  $J = 1-2$  Hz); analysis of this product by gas liquid chromatography (18% GE-SE-30, 205°) showed it to be 99% pure.

#### p-Cyclopropylbenzyl Alcohol

The procedure used was similar to Gilman and Catlin (1967). Magnesium turnings (5.3 g, 0.22 mole) and 20 ml of absolute ethyl ether was placed in a dry 500-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and addition funnel. A crystal of iodine and 0.5 ml of 1,2-dibromoethane were added to activate the magnesium. When reaction had set in, p-bromophenylcyclopropane (42 g, 0.22 mole) in 200 ml of ether was added to the activated magnesium. When all the halide had been added, stirring and refluxing were continued for 30 min. After this period of time, the dropping funnel was replaced by a wide glass tube connected directly with a 200-ml round-bottomed flask containing 50 g of paraformaldehyde which had been previously dried for two days in a vacuum desiccator over phosphorus pentoxide. This 200-ml flask contained an inlet tube for admitting dry nitrogen. The stirrer was started, and the flask containing the paraformaldehyde was heated in an oil bath to 180-200°. At the end of 3 hr the reaction was complete. The mixture was poured onto ice, decomposed with ammonium chloride, and extracted with ether. The ether

layer was washed with aqueous sodium bicarbonate, dried, concentrated down, and distilled to give 9.6 g (30%) of material: bp 76-78° (0.1-0.15 mm);  $n_D^{26}$  1.5539; nmr ( $CCl_4$ ),  $\tau$ 9.0-9.5 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 7.85-8.45 (one-hydrogen multiplet, tertiary cyclopropyl hydrogen), 5.50-5.70 (two-hydrogen singlet, benzyl hydrogens attached to OH), 5.80-6.00 (one-hydrogen singlet, alcohol proton), 2.70-2.90 and 2.90-3.20 (two two-hydrogen doublets,  $J = 7-8$  Hz, aromatic hydrogens); analysis of this product by gas liquid chromatography (18% GE-SE-30, 200°) showed it to be 95% pure; ir (neat), 3350-3400  $cm^{-1}$  (alcohol), 3090, 3040, and 3020  $cm^{-1}$  (aromatic CH); 2960-2870  $cm^{-1}$  (aliphatic CH), 1613, 1595, and 1500  $cm^{-1}$  (aromatic ring), 801  $cm^{-1}$  (para-substituted phenyl).

#### p-Cyclopropylbenzyl Acetate

A solution of p-cyclopropylbenzyl alcohol (32 g, 0.21 mole) in 150 ml of pyridine was placed in a 500-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and addition funnel. The mixture was cooled in ice-water, and acetyl chloride (26 g, 0.32 mole) was added slowly with stirring. The solution was warmed up to room temperature overnight and 200 ml of water was then added to the reaction flask. The organic layer was extracted with ether, dried, concentrated down, and distilled to give 36 g (90%) of material: bp 82-83° (0.1-0.15 mm);  $n_D^{29.9}$  1.5275; nmr ( $CCl_4$ ),  $\tau$ 9.0-9.5 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 8.10-8.25 (one-hydrogen multiplet, tertiary cyclopropyl hydrogen), 8.0-8.1 (three-hydrogen singlet,  $CH_3-C(=O)-$ ), 5.0-5.1 (two-hydrogen singlet, benzyl hydrogens attached to

an acetate), 2.70-2.90 and 2.90-3.20 (two two-hydrogen doublets,  $J = 7-8$  Hz, aromatic hydrogens characteristic of para-substituted phenyl); analysis of this product by gas liquid chromatography (18% GE-SE-30, 200°) showed it to be 95% pure; mass spec,  $m/e$  190 ( $C_{12}H_{14}O_2^+$ ) (29), 148 ( $C_{10}H_{12}O^+$ ) (35), 131 ( $C_{10}H_{11}^+$ ) (63), 130 ( $C_{10}H_{10}^+$ ) (36), 129 ( $C_{10}H_9^+$ ) (53), 117 ( $C_9H_9^+$ ) (32), 116 ( $C_9H_8^+$ ) (25), 115 ( $C_9H_7^+$ ) (88), 107 ( $C_7H_7O^+$ ) (32), 91 ( $C_7H_7^+$ ) (79), 77 ( $C_6H_5^+$ ) (24), 43 ( $C_2H_3O^+$ ) (100); ir ( $CCl_4$ ), 3080, 3040, and 3020  $cm^{-1}$  (aromatic CH), 2950-2840  $cm^{-1}$  (aliphatic CH), 1745  $cm^{-1}$  (C=O of the acetate), 1600, 1580, and 1500  $cm^{-1}$  (aromatic ring), 1240  $cm^{-1}$  (asymmetric stretching of acetate =C-O-C, "acetate band");  $\lambda_{max}$  ( $C_2H_5OH$ ), 2850 Å ( $\epsilon = 660$ ); TLC (benzene)  $R_f = 0.5$ .

The distilled acetate was chromatographed on a 6 x 3 in column of silica gel, and benzene was used as the eluting solvent. The acetate was then further purified and collected by gas chromatography (18% GE-SE-30, 200°) before using in photolytic reactions. A purity check on this material showed it to be 99% pure.

#### m-Bromobenzaldehyde

The procedure used was similar to Pearson, Stamper, and Suthers (1963). Powdered anhydrous aluminum chloride (335 g, 2.5 mole) was placed in a 2000-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and addition funnel. The free-flowing catalyst was stirred and benzaldehyde (106 g, 1 mole) was added in a slow stream over a period of 20 to 60 min. Considerable heat was evolved and, if the drops of aldehyde were not dispersed, darkening or

charring occurred. When one-third of the benzaldehyde had been added, the mixture became a viscous ball-like mass that was difficult to stir. Turning the stirrer by hand or a more rapid addition of aldehyde was necessary at this point. Near the end of the addition, the mass became molten and could be stirred easily. The color of the aldehyde-aluminum chloride complex ranges from brown to tan. After the addition of benzaldehyde was completed, bromine (160 g, 1 mole) was added dropwise to the well-stirred mixture over a period of 40 min. After all of the bromine had been added, the molten mixture was stirred at 80-85° on a steam bath for 2 hr. The complex was then added in portions to a well-stirred mixture of 2000 ml of cracked ice and 200 ml of concentrated hydrochloric acid in a 3000-ml beaker. Part of the cold aqueous layer was added to the reaction flask to decompose the reaction mixture remaining there, and the resulting solution was added to the beaker. A dark oil settled out and was extracted from the mixture with four 150-ml portions of ether. The extracts were combined, washed consecutively with 100 ml of water, 100 ml of 5% sodium bicarbonate, and dried with anhydrous sodium sulfate. Concentration and distillation yielded 108 g (59% of material: bp 230-232° (750 mm); *p*-nitrophenylhydrazone derivative mp 219-220°; lit. bp 234° (760 mm); *p*-nitrophenylhydrazone derivative mp 220° (Vogel 1962, p. 723);  $n_D^{20}$  1.5935; nmr (CCl<sub>4</sub>),  $\tau$  0.0-0.3 (one-hydrogen singlet, aldehyde proton), 2.0-2.8 (four-hydrogen multiplet, aromatic hydrogens); analysis of this product by gas liquid chromatography (18% GE-SE-30, 150°) showed it to be 99% pure; ir (neat) 2950 cm<sup>-1</sup> (aromatic C-H),

2820 and 2730  $\text{cm}^{-1}$  (aldehyde C-H), 1690-1700  $\text{cm}^{-1}$  (aromatic CHO), 1610, 1580, 1520, 767, and 700  $\text{cm}^{-1}$  (meta-substituted phenyl).

Ethyl  $\beta$ -(m-Bromophenyl)- $\beta$ hydroxypropionate

The procedure used was similar to Hauser and Breslow (1967). Powdered zinc (40 g, 0.62 mole) was placed in a dry 500-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and addition funnel. The zinc dust was purified by washing it rapidly with dilute sodium hydroxide solution, water, dilute acetic acid, water, ethanol, acetone, and ether. It was then dried in a vacuum oven at 100°. A solution of ethyl bromoacetate (83.5 g, 0.5 mole) and m-bromobenzaldehyde (108 g, 0.59 mole) in 80 ml of dry benzene and 20 ml of absolute ether was placed in the addition funnel. About 10 ml of this solution was added to the zinc, and the flask was warmed until the reaction started. The mixture was then stirred and the rest of the solution added at such a rate that the reaction mixture refluxed. The reaction mixture was refluxed for 30 min on a steam bath after the addition of the solution was complete. The flask was then cooled in an ice bath and the reaction mixture hydrolyzed by the addition of 200 ml of cold 10% sulfuric acid. The acid layer was drawn off and the benzene solution extracted twice with 50 ml-portions of 5% sulfuric acid. The benzene solution was washed once with 25 ml of 10% aqueous sodium carbonate, then with 25 ml of 5% sulfuric acid, and finally with two 25 ml-portions of water. The combined acid solutions were extracted with two 50 ml portions of ether, and the combined ether and benzene solutions were dried with 5 g of magnesium sulfate. The solution was filtered, the

solvent removed by distillation from a steam bath, and the residue was distilled, yielding 91.3 g (67%) of material: bp 154-155° (0.2 mm); nmr (CCl<sub>4</sub>),  $\tau$  8.7-9.0 (three-hydrogen triplet, J = 7-8 Hz, methyl group split by adjacent methylene hydrogens characteristic of ethyl esters), 7.4-7.5 (two-hydrogen doublet, J = 8 Hz, methylene hydrogens attached to the carbonyl of the ester and split by one benzylic hydrogen), 6.4 (one-hydrogen singlet, alcohol proton attached to the benzylic carbon), 6.0 (two-hydrogen quartet, J = 7-8 Hz, methylene hydrogens attached to the ester and split by a methyl group characteristic of ethyl esters), 5.0 (one-hydrogen triplet, J = 8 Hz, benzylic hydrogen split by adjacent methylene), 2.7-3.0 (four-hydrogen multiplet, aromatic hydrogens); analysis of this product by gas liquid chromatography (18% GE-SE-30, 190°) showed it to be 99% pure; ir (CCl<sub>4</sub>), 3550 cm<sup>-1</sup> (alcohol), 3020, 1600, 1580, and 1490 cm<sup>-1</sup> (aromatic), 1745 and 1190 cm<sup>-1</sup> (ethyl ester).

#### 1,3-Dihydroxy-1-m-bromophenylpropane

A solution of lithium aluminum hydride (14 g, 0.38 mole) in 200 ml of dry ether was placed in a 1000-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and addition funnel. The flask was cooled in ice water, and a solution of ethyl  $\beta$ -(m-bromophenyl)- $\beta$ -hydroxypropionate (102 g, 0.38 mole) in 50 ml of dry ether was added slowly to the hydride. After the addition had been completed, the solution was refluxed for 1 hr. The procedure of Mićović and Mihailović (1953) was used to destroy the excess hydride. To the reaction flask were added 14 ml of water, 14 ml of 15% sodium hydroxide, and 50 ml of water. A white precipitate formed which was

then filtered, washed with ether, and the ether solution concentrated down to give 70 g (80%) of crude material.

### 1,3-Dibromo-1-m-bromophenylpropane

A solution of 1,3-dihydroxy-1-m-bromophenylpropane (70 g, 0.31 mole), obtained from the preceding experiment without purification, in 500 ml of dry ether was placed in a 1000-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and addition funnel. The flask was cooled in ice water, and phosphorus tribromide (70 g, 0.26 mole) was added slowly to the stirring mixture. The solution was warmed up to room temperature overnight and 250 ml of water was added slowly, with cooling, to the reaction flask to destroy the excess phosphorus tribromide. The organic layer was extracted with ether and the ether layer was washed with aqueous sodium bicarbonate, water, dried, and concentrated down to give 100 g (90%) of crude material.

Distillation of ethyl  $\beta$ -(m-bromophenyl)- $\beta$ -hydroxypropionate (273 g, 1 mole) in the presence of a trace amount of acid produced 133 g (52%) of ethyl  $\beta$ -(m-bromophenyl)-acrylate: bp 130-132° (0.1 mm);  $n_D^{24}$  1.5862; nmr ( $CCl_4$ ),  $\tau$  8.5-8.9 (three-hydrogen triplet,  $J = 7$  Hz, methyl hydrogens split by adjacent methylene characteristic of an ethyl ester), 5.8-5.9 (two-hydrogen quartet,  $J = 7$  Hz, methylene hydrogens split by adjacent methyl group characteristic of ethyl esters), 3.75 and 3.40 (two one-hydrogen singlets, vinyl hydrogens), 2.2 (one-hydrogen multiplet, aromatic hydrogen); 2.5 (three-hydrogen multiplet, aromatic hydrogens); ir ( $CCl_4$ ), 3080 and 3020  $cm^{-1}$  (aromatic CH), 2960  $cm^{-1}$  (aliphatic CH), 1720  $cm^{-1}$  ( $\alpha$ ,  $\beta$ -unsaturated ester carbonyl), 1640  $cm^{-1}$

(double bond), 1600, 1560, and 1480  $\text{cm}^{-1}$  (aromatic), 1300, 1250, and 1180  $\text{cm}^{-1}$  (ethyl ester); TLC (benzene),  $R_f = 0.52$ .

This  $\alpha, \beta$ -unsaturated ester (133 g, 0.52 mole) was then reduced with lithium aluminum hydride (22 g, 0.57 mole) and yielded 100 g (90%) of 1-hydroxy-1-m-bromophenylpropane: bp 125-127° (0.1-0.2 mm);  $n_D^{23.5}$  1.5684; nmr ( $\text{CCl}_4$ ),  $\tau$  8.3 (two-hydrogen multiplet,  $J = 8$  Hz, methylene hydrogens split by adjacent methylene and benzylic hydrogens), 7.35 (two-hydrogen triplet,  $J = 7-8$  Hz, benzylic hydrogens split by adjacent methylene), 6.5 (two-hydrogen triplet,  $J = 7$  Hz, methylene hydrogens attached to alcohol split by adjacent methylene hydrogens), 7.4 (one-hydrogen singlet, alcohol hydrogen), 2.7 (two-hydrogen multiplet, aromatic hydrogens), 2.9 (two-hydrogen multiplet, aromatic hydrogens); ir ( $\text{CCl}_4$ ), 3650 and 3350  $\text{cm}^{-1}$  (alcohol), 3080  $\text{cm}^{-1}$  (aromatic CH), 2960 and 2880  $\text{cm}^{-1}$  (aliphatic CH), 1600, 1580, and 1480 (aromatic), 692  $\text{cm}^{-1}$  (meta-substituted phenyl ring); TLC (benzene),  $R_f = 0.22$ ; analysis of this material by gas liquid chromatography showed it to be 90% pure (18%, GE-SE-30, 185°).

This alcohol (100 g, 0.47 mole) was then reacted with phosphorus tribromide (50 g, 0.16 mole) to yield 75 g (79%) of 1-bromo-1-m-bromophenylpropane:  $n_D^{28.5}$  1.5761; nmr ( $\text{CCl}_4$ ),  $\tau$  7.9 (two-hydrogen multiplet, methylene hydrogens split by adjacent methylene and benzylic hydrogens), 7.4-7.5 (two-hydrogen triplet,  $J = 8$  Hz, benzylic hydrogens split by adjacent methylene), 6.7 (two-hydrogen triplet,  $J = 7-8$  Hz, methylene hydrogens adjacent to a bromine atom and split by adjacent methylene hydrogens), 2.7 (four-hydrogen multiplet, aromatic hydrogens); analysis

of this material by gas liquid chromatography showed it to be 99% pure (20% Carbowax 20-M, 205°).

The 1-bromo-1-m-bromophenylpropane (75 g, 0.37 moles) was then reacted with *N*-bromosuccinimide (59 g, 0.42 mole) to yield 90 g (67%) of 1,3-dibromo-1-m-bromophenylpropane: nmr (CCl<sub>4</sub>),  $\tau$  7.4 (two-hydrogen multiplet, methylene hydrogens split by adjacent methylene group and benzylic hydrogen), 6.6 (two-hydrogen triplet, methylene attached to a bromine atom and split by adjacent methylene), 4.9 (one-hydrogen triplet,  $J = 7-8$  Hz, benzylic hydrogen split by adjacent methylene hydrogens), 2.4-2.8 (four-hydrogen multiplet, aromatic hydrogens).

#### m-Bromophenylcyclopropane

Meta-bromophenylcyclopropane was prepared by the same procedure previously described for phenylcyclopropane. After normal work-up procedures, the organic layer was distilled to give 39 g (80%) of material: bp 48-50° (0.1-0.8 mm);  $n_D^{30.5}$  1.5588; lit. bp 63-64° (1-2 mm);  $n_D^{25}$  1.5735 (Hahn, Corbin, and Shechter 1968); nmr (CCl<sub>4</sub>),  $\tau$  8.9-9.4 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 7.8-8.2 (one-hydrogen multiplet, cyclopropyl methine hydrogen), 2.4 (two-hydrogen multiplet, aromatic hydrogens), 2.7-2.9 (two-hydrogen multiplet, aromatic hydrogens); analysis by gas liquid chromatography showed this material to be 99% pure (20% Carbowax 20-M, 180°).

#### m-Cyclopropylbenzyl Alcohol

Meta-cyclopropylbenzyl alcohol was prepared by the same procedure previously described for the para isomer. After normal work-up

procedure, the organic layer was distilled to give 15 g (50%) of material: bp 72-73° (0.15 mm);  $n_D^{29.8}$  1.5519,  $n_D^{25.9}$  1.5542; nmr ( $CCl_4$ ),  $\tau$  9.0-9.5 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 8.1-8.4 (one-hydrogen multiplet, cyclopropyl methine hydrogen), 5.9 (one-hydrogen singlet, alcohol hydrogen), 5.7 (two-hydrogen singlet, benzyl hydrogens attached to OH), 2.8-3.3 (four-hydrogen multiplet, aromatic hydrogens); analysis by gas liquid chromatography showed this material to be 99% pure (18% GE-SE-30, 205°); mass spec,  $m/e$  148 ( $C_{10}H_{12}O^+$ ) (68), 117 ( $C_9H_9^+$ ) (100), 115 ( $C_9H_7^+$ ) (48), 91 ( $C_7H_7^+$ ) (79), 77 ( $C_6H_5^+$ ) (24), 41 ( $C_3H_5^+$ ) (29); ir ( $CCl_4$ ), 3640 and 3450  $cm^{-1}$  (alcohol), 3090, 3040, and 3020  $cm^{-1}$  (aromatic CH), 2940 and 2880  $cm^{-1}$  (aliphatic CH), 1600, 1580, and 1490  $cm^{-1}$  (aromatic), 692  $cm^{-1}$  (meta-substituted phenyl); TLC (chloroform),  $R_f$  = 0.60.

#### m-Cyclopropylbenzyl Acetate

Meta-cyclopropylbenzyl acetate was prepared by the same procedure previously described for the para isomer. After normal work-up procedure, the organic layer was distilled to give 16 g (85%) of material: bp 75-76° (0.15 mm);  $n_D^{29}$  1.5198; nmr ( $CCl_4$ ),  $\tau$  9.0-9.5 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 8.10-8.25 (one-hydrogen multiplet, tertiary cyclopropyl hydrogen), 8.0-8.1 (three-hydrogen singlet, methyl group adjacent to the carbonyl of the ester), 5.0-5.1 (two-hydrogen singlet, benzyl hydrogens attached to an acetate), 2.9-3.2 (four-hydrogen multiplet, aromatic hydrogens); analysis by gas liquid chromatography showed this product to be 98% pure (18% GE-SE-30, 200°); mass spec  $m/e$  190 ( $C_{12}H_{14}O_2^+$ ) (36), 148 ( $C_{10}H_{12}O^+$ ) (90), 131

( $C_{10}H_{11}^+$ ) (39), 130 ( $C_{10}H_{10}^+$ ) (39), 129 ( $C_{10}H_9^+$ ) (70), 117 ( $C_9H_9^+$ ) (33), 115 ( $C_9H_7^+$ ) (90), 107 ( $C_7H_7O^+$ ) (66), 91 ( $C_7H_7^+$ ) (88), 77 ( $C_6H_5^+$ ) (38), 43 ( $C_2H_3O^+$ ) (100), ir (neat), 3080, 3040, and 3020  $cm^{-1}$  (aromatic CH), 2960  $cm^{-1}$  (aliphatic CH), 1745  $cm^{-1}$  (carbonyl of the acetate), 1600, 1580, and 1490  $cm^{-1}$  (aromatic ring), 1240  $cm^{-1}$  ("acetate band"), 780 and 695  $cm^{-1}$  (meta-substituted phenyl ring);  $\lambda_{max}$  ( $C_2H_5OH$ ), 2630 Å ( $\epsilon = 500$ ); TLC (benzene),  $R_f = 0.65$ .

This acetate was also chromatographed on a 6 x 3 inch silica gel column using benzene and chloroform as the eluting solvents and then was further purified by preparative GLC (18% GE-SE-30, 200°) before using in photolytic reactions.

### $\beta$ -Methylstyrene

Normal Grignard reaction procedures for the addition of bromoethane (45 g, 0.42 mole) to benzaldehyde (44 g, 0.42 mole) were used to obtain 50 g (88%) of 1-hydroxy-1-phenylpropane. The alcohol (50 g, 0.37 mole) and 25 ml of 85% phosphoric acid were added to a 200-ml round-bottomed boiling flask. The solution was distilled to half volume and the contents of the receiver flask were extracted with ether, washed with a sodium chloride solution, dried, and distilled to give 31 g (70%) of  $\beta$ -methylstyrene (Fieser 1964, p. 63): bp 170° (750 mm);  $n_D^{20}$  1.5485; lit. bp 176-177 (760 mm);  $n_D^{16}$  1.5903 (Cheronis and Entrikin 1961, p. 658); nmr ( $CCl_4$ ),  $\tau$  8.1-8.2 (three-hydrogen doublet,  $J = 7$  Hz, methyl group split by a vinyl hydrogen), 3.9-4.2 (one-hydrogen multiplet, vinyl hydrogen split by adjacent vinyl and methyl hydrogens), 3.8 (one-hydrogen doublet,  $J = 15-16$  Hz, vinyl hydrogen, adjacent to the

aromatic ring, split by a vinyl hydrogen), 2.7 (five-hydrogen singlet, aromatic hydrogens); gas liquid chromatography analysis showed this material to be 99% pure (18% GE-SE-30, 110°); ir (neat), 3080 and 3040  $\text{cm}^{-1}$  (aromatic CH), 2950  $\text{cm}^{-1}$  (aliphatic CH), 1650  $\text{cm}^{-1}$  (double bond), 1600, 1580, and 1490  $\text{cm}^{-1}$  (aromatic).

### Norcarane

The procedure was as previously described (LeGoff 1964). A solution of cupric acetate monohydrate (0.1 g,  $5 \times 10^{-4}$  mole) in 10 ml of glacial acetic acid was placed in a 200-ml three-necked, round-bottomed flask fitted with a reflux condenser, glass stopper, addition funnel, and a magnetic stir bar. The mixture was heated to reflux and granular zinc (6 g, 0.1 mole, 30 mesh) was added to the flask. The mixture was then stirred with a magnetic stirrer for 1 to 3 min, after which the acetic acid was decanted and the zinc-copper couple was washed with a 10-ml portion of glacial acetic acid, then with three 10-ml portions of ether. To this couple were added 20 ml of ether and 2 ml of dibromomethane. Warming up the mixture on a steam bath initiated the reaction so that it could be maintained at a gentle reflux. At this time a solution of cyclohexene (4.1 g, 0.05 mole) and dibromomethane (12.2 g, 0.07 mole) was added dropwise over a period of 2 hr. The reaction mixture was stirred at reflux for 40 hr; at the end of this time, the entire solution was filtered and the ether layer was put into a separatory funnel containing a mixture of ice and one normal hydrochloric acid. The ether layer was separated, washed with a second portion of chilled hydrochloric acid, washed four times with 20 ml of water, dried,

concentrated, and distilled to give 3.8 g (80%) of norcarane: bp  $110^{\circ}$  (750 mm);  $n_D^{25}$  1.4540; lit. bp 115-116 (760 mm);  $n_D^{25}$  1.4542 (LeGoff 1964); nmr ( $CCl_4$ ),  $\tau$  8.9-9.5 (four-hydrogen multiplet, cyclopropyl hydrogens), 8.7-8.9 (four-hydrogen multiplet, cyclohexane methylene hydrogens), 8.2-8.4 (four-hydrogen multiplet, cyclohexane methylene hydrogens adjacent to the cyclopropyl ring).

#### p-Methylbenzyl Alcohol

A solution of lithium aluminum hydride (11 g, 0.28 mole) in 200 ml of dry ether was placed in a 1000-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and addition funnel. The flask was cooled in ice water, and a solution of para-toluic acid (50 g, 0.37 mole) in 500 ml of dry ether was added slowly to the hydride. After the addition had been completed, the solution was refluxed for 1 hr. The procedure of Mićović and Mihailović (1953) was used to destroy the excess hydride and the ether solution was concentrated down to give 29 g (65%) of p-methylbenzyl alcohol: mp  $59^{\circ}$  (after recrystallizing from methanol and water); bp  $210^{\circ}$  (750 mm); lit. mp  $60^{\circ}$ ; bp  $217^{\circ}$  (760 mm) (Cheronis and Entrikin 1961, p. 576); gas liquid chromatography showed this material to be 99% pure (18% GE-SE-30,  $163^{\circ}$ ); ir ( $CCl_4$ ), 3640 and 3400  $cm^{-1}$  (alcohol), 3040  $cm^{-1}$  (aromatic CH), 2940 and 2880  $cm^{-1}$  (aliphatic CH), 1600, 1580 and 1500 (aromatic), 1040  $cm^{-1}$  (alcohol); TLC (chloroform),  $R_f = 0.67$ , (benzene)  $R_f = 0.23$ .

### p-Methylbenzyl Acetate

Para-methylbenzyl acetate was prepared from the alcohol (29 g, 0.24 mole) by the same procedure previously described for p-cyclopropylbenzyl acetate. After normal work-up procedure, the organic layer was distilled to give 33 g (83%) of material: bp 52-53° (0.15 mm);  $n_D^{27.5}$  1.4970; nmr ( $CCl_4$ ),  $\tau$  8.0-8.1 (three-hydrogen singlet, methyl hydrogens adjacent to the carbonyl of the ester), 7.7 (three-hydrogen singlet, methyl hydrogens adjacent to the aromatic ring), 5.1 (two-hydrogen singlet, benzyl hydrogens adjacent to the aromatic ring and the ester), 2.9 (two two-hydrogen singlets, para-substituted aromatic ring); gas liquid chromatography showed this material to be 99% pure (18% GE-SE-30, 165°); ir (neat), 3040  $cm^{-1}$  (aromatic CH), 2950  $cm^{-1}$  (aliphatic CH), 1745  $cm^{-1}$  (carbonyl of the acetate), 1600, 1580 and 1500 (aromatic), 1240  $cm^{-1}$  ("acetate band"), 805  $cm^{-1}$  (para-substituted phenyl ring); TLC (benzene),  $R_f = 0.5$ .

### m-Methylbenzyl Alcohol

Meta-methylbenzyl alcohol was prepared by the same procedure previously described for the para isomer and yielded 33 g (73%) of material: bp 211° (750 mm); lit. bp 217° (760 mm) (Cheronis and Entrikin 1961, p. 572);  $n_D^{26}$  1.5201; gas liquid chromatography showed this material to be 99% pure (18% GE-SE-30, 165°) ir (neat), 3640 and 3400  $cm^{-1}$  (alcohol), 3040  $cm^{-1}$  (aromatic CH), 2950 and 2895  $cm^{-1}$  (aliphatic CH), 1600, 1580, and 1500  $cm^{-1}$  (aromatic), 1040  $cm^{-1}$  (alcohol), 692  $cm^{-1}$  (meta-substituted phenyl ring); TLC (benzene),  $R_f = 0.28$ .

### m-Methylbenzyl Acetate

Meta-methylbenzyl acetate was also prepared by the same procedure previously described for the para isomer and yielded 41 g (89%) of material: bp 44-45° (0.1-0.15 mm);  $n_D^{30}$  1.4980; nmr ( $CCl_4$ ),  $\tau$  8.0-8.1 (three-hydrogen singlet, methyl hydrogens adjacent to the carbonyl of the ester), 7.7 (three-hydrogen singlet, methyl group adjacent to the aromatic ring), 5.1 (two-hydrogen singlet, benzyl hydrogens adjacent to the aromatic ring and the ester), 2.9 (four-hydrogen singlet, aromatic hydrogens); gas liquid chromatography showed this material to be 99% pure (18% GE-SE-30, 165°); ir (neat), 3040  $cm^{-1}$  (aromatic CH), 2950  $cm^{-1}$  (aliphatic CH), 1745  $cm^{-1}$  (carbonyl of the acetate), 1600, 1580 and 1500  $cm^{-1}$  (aromatic), 1240  $cm^{-1}$  ("acetate band"), 780 and 692  $cm^{-1}$  (meta-substituted phenyl ring); TLC (benzene),  $R_f$  = 0.5.

### 2,2'-Bicyclohexenyl

The procedure was as previously described (Bradshaw 1966). A solution of acetone (25 g, 0.4 mole) and cyclohexene (25 g, 0.3 mole) was placed in a 100-ml Pyrex tube and irradiated, in the presence of air, with a Srinivasan-Griffin Photochemical Reactor for five days. The following products from this reaction were separated and collected by gas liquid chromatography (18% GE-SE-30, 150-180°; Carbowax 20-M, 170°): 2-cyclohexen-1-ol (49% of the mixture as determined by integrating each GLC peak by cutting and weighing each GLC cutout with an analytical balance) was identified by its nmr spectrum which contained a broadened singlet at  $\tau$  7.9-8.1 (two methylene hydrogens adjacent to the double bond), 8.1-8.8 (four-hydrogen multiplet, two adjacent

methylene groups), 6.5 (alcohol hydrogen, broad singlet), 5.9 (one-hydrogen multiplet, methine hydrogen adjacent to the alcohol and split by adjacent methylene and vinyl hydrogens), 4.3 (two-hydrogen singlet, vinyl hydrogens); lit. nmr (Chapman and Magnus 1966, p. 81 and 87); mass spec,  $\underline{m/e}$  98 ( $C_6H_{10}O^+$ ); ir ( $CCl_4$ ), 3640 and 3400  $cm^{-1}$  (alcohol), 3050  $cm^{-1}$  (alkene CH), 2950 and 2880  $cm^{-1}$  (aliphatic CH), 1650  $cm^{-1}$  (double bond); bp 160°;  $n_D^{25}$  1.4795. The second product, 2-cyclohexen-1-one (33% of the mixture as determined by integration of the GLC trace), was identified by its mass spectrum [parent  $\underline{m/e}$  96 ( $C_6H_8O^+$ )], nmr ( $CCl_4$ ),  $\uparrow$  7.5-8.2 (six-hydrogen multiplet, three adjacent methylene groups), 4.1-4.3 (one-hydrogen doublet,  $J = 6$  Hz vinyl hydrogen adjacent to the carbonyl split by the adjacent vinyl hydrogen), 3.1-3.2 (one-hydrogen multiplet, vinyl hydrogen adjacent to vinyl and methylene hydrogens); bp 164° (750 mm);  $n_D^{20}$  1.4900; lit. nmr ( $CCl_4$ ); bp 168° (760 mm);  $n_D^{20}$  1.4896 [(Sadtler NMR Spectra Catalogue 1966) Spectrum No. 9880]; ir ( $CCl_4$  and neat), 3050  $cm^{-1}$  (alkene CH), 2950  $cm^{-1}$  (aliphatic CH), 1690-1680  $cm^{-1}$  (carbonyl of the  $\alpha, \beta$ -unsaturated ketone), 1618  $cm^{-1}$  (double bond of  $\alpha, \beta$ -unsaturated ketones); lit. ir (Sadtler IR Spectra Catalogue, Spectrum No. 19138). The third product, oxetane (8% of the mixture as determined by integration of the GLC trace) was identified by its mass spectrum [parent  $\underline{m/e}$  140 ( $C_9H_{16}O^+$ )]. The fourth product was the desired 2,2'-bicyclohexenyl (10% of the mixture as determined by integration of the GLC trace) and identified by its mass spectrum [parent  $\underline{m/e}$  162 ( $C_{12}H_{18}^+$ )]; nmr ( $CCl_4$ ),  $\uparrow$  8.3-8.9 (eight-hydrogen multiplet, two two-adjacent methylene groups), 8.0-8.2

(six-hydrogen broad singlet, allylic hydrogens), 4.5 (four-hydrogen broad singlet, vinyl hydrogens); ir ( $\text{CCl}_4$ ),  $3030\text{ cm}^{-1}$  (alkene CH),  $2950\text{-}2940\text{ cm}^{-1}$  (aliphatic CH),  $1650\text{ cm}^{-1}$  (double bond).

#### Irradiation of Phenylcyclopropane

The procedure was as previously described (Richardson et al. 1965). A solution of phenylcyclopropane (3 g, 0.025 mole) and cyclohexene (100 g, 1.22 mole) was placed in a Vycor tube, purged for 5 min with deoxygenated nitrogen, and irradiated for 8 days. Five components were collected by GLC (18% GE-SE-30,  $110^\circ$ ) and identified by coinjection and comparative retention times of authentic samples on two GLC columns (18% GE-SE-30,  $110^\circ$ ; 20% Carbowax 20-M,  $115^\circ$ ) as well as comparative ir and nmr spectra with authentic samples. These compounds were norcarane (12% of the mixture as determined by integration of the GLC trace, styrene (63%), and three methylcyclohexene isomers (25%).

#### Purification of Nitrogen

The system utilized was as previously described (Fieser 1924). All irradiations degassed and purged with nitrogen were conducted with commercial tank nitrogen purified by the following procedure. A solution was prepared by dissolving 20 g of potassium hydroxide in 100 ml of water and adding 2 g of sodium anthraquinone- $\beta$ -sulfonate and 15 g of sodium hydrosulfite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to the warm solution. The mixture was stirred until a clear, blood-red solution was obtained and then was allowed to cool to room temperature. Traces of oxygen in commercial tank nitrogen were removed by passage through two wash bottles

containing the anthraquinone- $\beta$ -sulfonate solution and then into a wash bottle containing a saturated solution of lead acetate. Traces of hydrogen sulfide formed are readily removed by the lead acetate. The sulfonated anthrahydroquinone dianion absorbs oxygen rapidly and is continually regenerated by the hydrosulfite. Since the reagent operates on a catalytic principle, the original efficiency was retained to the point of exhaustion of the hydrosulfite. When the color changed to brown and a precipitate appeared, the solution was replaced.

#### Product Studies From p-Cyclopropylbenzyl Acetate Irradiations

A  $9.4 \times 10^{-2}$  M solution of p-cyclopropylbenzyl acetate was prepared by dissolving (1.43 g,  $7.5 \times 10^{-3}$  moles) in 80 ml of a 60/40 volume percent dioxane-water mixture. The solution was placed in a Vycor tube and degassed at 0.05 mm pressure using three freeze-thaw cycles at Dry Ice temperatures or by purging with deoxygenated nitrogen for 5 min. The solution was then irradiated for 100 hr in the photochemical chamber reactor containing 2537 Å lamps. The irradiation was monitored using TLC analysis for detection of the disappearance of the starting material ( $R_f = 0.50$  in benzene) and the appearance of photoproducts ( $R_f = 0.00$ , and 0.12 in benzene). After the irradiation was completed, the photolysis mixture was extracted with ether. The ether layer was dried, concentrated to one-half volume, and analyzed by GLC. No liquid photoproducts could be detected other than the starting material (p-cyclopropylbenzyl acetate). The ether was removed at reduced pressure and yielded 1.25 g of a yellow-brown oil. A small sample (0.22 g)

of this photoproduct mixture was dissolved in benzene and chromatographed over a 33 x 1.5 cm column of silica gel. Benzene was used to elute the starting material from the photoproducts. Removal of the solvent afforded 0.06 g of *p*-cyclopropylbenzyl acetate.

The photoproducts were eluted with a 10% methanol-benzene solution. Removal of the solvent afforded 0.10 g of a yellow-brown oil. Analytical TLC in a variety of solvents showed that this oil contained at least two photoproducts ( $R_f = 0.00$  and  $0.12$  in benzene), but they could not be separated by column chromatography. Thus preparative TLC was used to separate these products. The oil (0.10 g) was dissolved in a small amount of methanol and placed on an 8 x 8-inch glass plate containing 20 g of silica gel (TLC grade). The preparative TLC plate was eluted with benzene followed by extraction of the photoproducts from the silica gel. Removal of the solvent afforded 0.09 g of photoproduct having a  $R_f = 0.00$  in benzene, and 0.01 g of photoproduct having a  $R_f = 0.12$  in benzene. Both of these photoproducts were polymeric solids having melting points greater than  $200^\circ$ . Photoproduct  $R_f = 0.00$  in benzene has a mp greater than  $200^\circ$ : nmr ( $\text{CCl}_4$  and  $\text{CDCl}_3$ ),  $\tau$  8.7-9.2 (four or five-hydrogen broad multiplet, methyl and methine hydrogens or methyl, and methylene hydrogens. It was difficult to get exact ratios of hydrogens by integration because the sample was polymeric):  $\tau$  8.0 (three-hydrogen broad singlet, methyl hydrogens adjacent to the carbonyl of the ester), 6.4 (seven-hydrogen broad singlet, dioxane hydrogens), 4.9-5.0 (two-hydrogen broad singlet, benzyl hydrogens adjacent to the acetate), 2.8 (four-hydrogen broad multiplet, aromatic

hydrogens); ir ( $\text{CCl}_4$ ),  $3040\text{ cm}^{-1}$  (aromatic CH),  $2950\text{ cm}^{-1}$  (aliphatic CH),  $1745\text{ cm}^{-1}$  (carbonyl of the acetate), 1600, 1580, and 1500 (aromatic),  $1240\text{ cm}^{-1}$  ("acetate band"); mass spec,  $m/e$  218 ( $\text{C}_{14}\text{H}_{18}\text{O}_2^+$ ) (7), 190 ( $\text{C}_{12}\text{H}_{14}\text{O}_2^+$ ) (11), 148 ( $\text{C}_{10}\text{H}_{12}\text{O}^+$ ) (14), 131 ( $\text{C}_{10}\text{H}_{11}^+$ ) (68), 117 ( $\text{C}_9\text{H}_9^+$ ) (29), 91 ( $\text{C}_7\text{H}_7^+$ ) (53), 87 ( $\text{C}_4\text{H}_7\text{O}_2^+$ ) (78), 43 ( $\text{C}_2\text{H}_3\text{O}^+$ ) (100).

Photoproduct having a  $R_f = 0.12$  in benzene showed the identical nmr and ir spectrum as photoproduct having a  $R_f = 0.00$  in benzene. The only noticeable difference between these two products was shown in their mass spectrum analysis. Photoproduct having a  $R_f = 0.12$  in benzene has the following mass spec  $m/e$  values: 218 ( $\text{C}_{14}\text{H}_{18}\text{O}_2^+$ ) (6), 190 ( $\text{C}_{12}\text{H}_{14}\text{O}_2^+$ ) (14), 148 ( $\text{C}_{10}\text{H}_{12}\text{O}^+$ ) (23), 131 ( $\text{C}_{10}\text{H}_{11}^+$ ) (27), 117 ( $\text{C}_9\text{H}_9^+$ ) (20), 91 ( $\text{C}_7\text{H}_7^+$ ) (48), 87 ( $\text{C}_4\text{H}_7\text{O}_2^+$ ) (100), 43 ( $\text{C}_2\text{H}_3\text{O}^+$ ) (89).

The water layer from the photolysis reaction contained a small amount of water soluble polymer (a polymeric benzylic alcohol with dioxane incorporated in the polymer chain) and the solution was weakly acidic. There was also large amounts of polymer deposited on the sides of the phototube.

#### Product Studies From *m*-Cyclopropylbenzyl Acetate Irradiations

A  $4.3 \times 10^{-2}$  M solution of *m*-cyclopropylbenzyl acetate was prepared by dissolving (0.09 g,  $4.75 \times 10^{-4}$  mole) in 11 ml of a 60/40 volume percent dioxane-water mixture and irradiated for 48 hr. The same irradiation and work-up procedure was followed as previously described for the *para* isomer. Analysis of the ether layer by GLC (18% GE-SE-30,  $150^\circ$ ; Carbowax 20-M,  $145^\circ$ ) showed the following liquid

photoproducts: m-cyclopropylbenzyl alcohol (70.5% as determined by integration of the GLC trace) and was identified by coinjections and retention times, ir, and nmr comparison with an authentic sample; m-cyclopropylethylbenzene (17.2% as determined by integration of the GLC trace) was identified by its nmr spectrum which contained a broad multiplet at  $\tau$  9.1-9.5 (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 8.7-8.8 (three-hydrogen triplet,  $J = 8-10$  Hz, methyl group split by adjacent benzyl hydrogens), 8.2 (one-hydrogen multiplet, cyclopropyl tertiary hydrogen), 7.5 (two-hydrogen quartet,  $J = 8-10$  Hz, benzyl hydrogens split by adjacent methyl group), 2.8-3.3 (four-hydrogen multiplet, aromatic hydrogens); mass spec,  $m/e$  146 ( $C_{11}H_{14}^+$ ) (33), 131 ( $C_{10}H_{11}^+$ ) (39), 117 ( $C_9H_9^+$ ) (100), 115 ( $C_9H_7^+$ ) (26), 105 ( $C_8H_9^+$ ) (18), 91 ( $C_7H_7^+$ ) (31), 77 ( $C_6H_5^+$ ) (19).

The ether layer was then chromatographed over a 46 x 1.5 cm column of silica gel, and benzene and chloroform were used to elute the m-cyclopropylbenzyl alcohol ( $R_f = 0.60$ , in chloroform) and m-cyclopropylethylbenzene ( $R_f = 1$ , benzene). Removal of the solvent afforded a 0.05 g mixture of these photoproducts.

The polymeric photoproducts having a  $R_f = 0.00$  in benzene were eluted with methanol and after removal of the solvent afforded 0.02 g of a yellow-brown solid. This polymeric solid was analyzed by its nmr spectrum which contained a broad multiplet at  $\tau$  9.0-9.2 (methyl or methylene hydrogens, the exact ratio could not be obtained because this material is polymeric), 8.7-8.9 (three-hydrogen broad triplet,  $J = 8$  Hz, methyl group split by adjacent methylene), 6.4 (seven-hydrogen broad

singlet, dioxane hydrogens), 5.4-5.5 (two-hydrogen broad singlet, benzyl hydrogens adjacent to an alcohol), 2.75-3.0 (four-hydrogen multiplet, aromatic hydrogens). This polymer could arise from secondary photolysis reactions of the meta-cyclopropylethylbenzene or the alcohol and will be discussed later. The water layer from the photolysis reaction contained a small amount of water soluble polymer and the water solution was strongly acidic (pH = 2-3). There was very little polymer deposited on the walls of the phototube.

The same procedure for isolation of photoproducts was used for the other compounds studied. In general only slight variations in solvent composition were necessary to elute the various products from silica gel columns and silica gel (TLC grade) preparative TLC plates. The extent of reaction and stoichiometric determination of products from irradiated samples of varying concentrations were monitored by GLC and TLC analysis. Solid and polymeric photoproducts were isolated quantitatively by preparative TLC and liquid photoproducts were quantitatively analyzed by GLC.

The product distributions obtained from irradiation of p-cyclopropylbenzyl, m-cyclopropylbenzyl, and various other substituted benzyl acetates are listed in Tables 5, 6, and 7, respectively (see Results). Spectral identification of these products are listed in Tables 2, 3, and 4 (see p. 51 through 59).

Difference Spectra Analysis  
of Irradiated Samples

Samples of *p*-cyclopropylbenzyl acetate of various concentrations were prepared in various solvents and irradiated for suitable time intervals. The irradiated samples were diluted to concentrations appropriate for spectral analysis and analyzed on a Cary Model 14 spectrophotometer. In all cases the solution used as a reference consisted of starting material which had been diluted by the same factor as the irradiated sample. Base lines were determined from unirradiated samples which had been diluted appropriately. In all cases it was necessary to maintain slit openings of not more than 1.5 mm in order to obtain reproducible results.

A  $5.33 \times 10^{-5}$  M solution of *p*-cyclopropylbenzyl acetate in a 50/50 mixture of dioxane-ethanol was irradiated for 18 hr. A difference spectra analysis showed a positive absorption band at 2800 Å. An absorption spectra showed that the starting material,  $\lambda_{\text{max}}$  at 2650 Å, had decreased and that a shoulder started to appear at 2800 Å due to a photoproduct or an intermediate. After 41 hr, a difference spectra showed an increased positive absorption at 2800-2900 Å and an absorption spectra showed no starting material and a weak 2800 Å band. The loss of the 2650 Å band could be due to the fact that the starting material was polymerized out of the solution. Large amounts of solid polymeric materials were deposited on the sides of the photoreaction tube.

Irradiation of *m*-Cyclopropylbenzyl  
Acetate-2-norbornene Mixture

Analytical reagent grade 2-norbornene (Aldrich Chemical Co.) (1 g, 0.0106 mole) and *m*-cyclopropylbenzyl acetate (0.057 g,  $3.3 \times 10^{-4}$  mole) was added to 0.6 ml of tertiary butyl alcohol affording a solution of  $5.5 \times 10^{-3}$  M in acetate and 17.7 M in 2-norbornene. The solution was placed in a Vycor tube, purged with deoxygenated nitrogen for 5 min, and irradiated at 2537 Å for 24 hr. Analysis of this solution by gas liquid chromatography (18% GE-SE-30, 180°; 20% Carbowax 20-M, 180°) showed the following products: *m*-cyclopropylethylbenzene (31% as determined by integration of the GLC trace) was identified by coinjections and comparative retention times with authentic samples; seven unidentified photoproducts (41% as determined by integration of the GLC trace); pentacyclo[8.2.1.1<sup>4,7</sup>.0<sup>2,9</sup>.0<sup>3,8</sup>]tetradecane(endo-trans-exo dimer of 2-norbornene) (28% of the photoproduct mixture as determined by integration of the GLC trace) was identified by its mass spectrum,  $m/e$  188 (C<sub>14</sub>H<sub>20</sub><sup>+</sup>) (33), 160 (C<sub>12</sub>H<sub>16</sub><sup>+</sup>) (31), 159 (C<sub>12</sub>H<sub>15</sub><sup>+</sup>) (58), 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>) (100); lit. mass spec (Meisels and Arnold 1968).

This compound was also identified by GLC comparison with an authentic sample, prepared by the irradiation of 2-norbornene in tertiary butyl alcohol using xylene as the sensitizer (Kropp 1969).

A control sample containing 2-norbornene (1 g, 0.0106 mole) in 0.6 ml of tertiary butyl alcohol was also irradiated for 24 hr and analysis of this mixture by gas liquid chromatography (18% GE-SE-30, 180°; 20% Carbowax 20-M, 180°) showed the following products: seven unidentified photoproducts (79% of the photoproduct control mixture

as determined by integration of the GLC trace). These seven photoproducts were the same unidentified products obtained from the photolysis of 2-norbornene with *p*-cyclopropylbenzyl acetate (as determined by comparative GLC retention times and coinjections). The other product in the control sample was the endo-trans-exo dimer of 2-norbornene (21% of the photoproduct control mixture as determined by integration of the GLC trace) which was identified by GLC comparison with an authentic sample.

A comparison of the seven unidentified photoproducts (79%) and dimer (21%) in the control irradiation with the seven unidentified photoproducts (59%) and dimer (41%) of the *p*-cyclopropylbenzyl acetate sensitized reaction shows that the *p*-cyclopropylbenzyl acetate increased the dimer concentration by a factor of two compared with the control reaction. These results will be discussed later.

The dimerization of a conjugated diolefin, such as piperylene, was attempted but the absorption of piperylene extends far enough into the near ultraviolet to absorb significantly at 2537 Å, thus making its use here difficult.

#### Attempted Photodeuteration of Cyclopropylbenzene

A 1-2 ml solution of cyclopropylbenzene (1.6 g, 0.0137 mole) and deuterated acetic acid (10 g, 0.156 mole) was placed in a quartz nmr tube (Wilmad Glass Company) and sealed. The nmr spectrum of this sample showed that the cyclopropyl ring was stable to acidic conditions at temperatures ranging from 30-40°. This sample was then irradiated

at 2537 Å for 600 hr and nmr spectra were recorded at intervals. Analysis of the nmr spectra showed no large, noticeable difference in the cyclopropyl and aromatic regions (compared with a blank sample) but there was evidence of hydrogen-deuterium exchange which was represented by the appearance of an acid proton at  $-1\tau$ . Polymeric absorptions also appeared in various regions of the spectra and polymer was found on the inside of the nmr tube. The cyclopropylbenzene in the irradiated solution was separated by gas liquid chromatography (18% GE-SE-30, 130°) and collected for mass spectra analysis. The irradiated cyclopropylbenzene showed a parent  $m/e$  value of 118 (100) and no significant enrichment of the P-1, 117 (99) and P+1, 119 (22) peaks as compared with the mass spectrum of unirradiated cyclopropylbenzene, 118 (88), 117 (100), and 119 (12).

Table 2. Spectral identification of photoproducts resulting from the irradiation of *p*-cyclopropylbenzyl acetate.

| Product                                                                                                                 | Mass spectrum                                                           | N.M.R.                                                                                                                    | Infrared                               |
|-------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|----------------------------------------|
| Polymer (Rf=0.12, benzene)<br>from irradiation of<br><i>p</i> -cyclopropylbenzyl<br>acetate in dioxane-water<br>(60/40) | 218 (C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> <sup>+</sup> ) (6)  | 8.7-9.2 4-5 H(m) (CH <sub>3</sub> -CH or<br>CH <sub>3</sub> CH <sub>2</sub> )                                             | cm <sup>-1</sup><br>3040 (Aromatic CH) |
|                                                                                                                         | 190 (C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> <sup>+</sup> ) (14) |                                                                                                                           |                                        |
|                                                                                                                         | 148 (C <sub>10</sub> H <sub>12</sub> O <sup>+</sup> ) (23)              | 8.0 3 H(s) (CH <sub>3</sub> -C <sup>o</sup> -O-)                                                                          | 2950 (Aliphatic CH)                    |
|                                                                                                                         | 131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (27)                | 6.4 7 H(s) (Dioxane)                                                                                                      | 1745 (Acetate)                         |
|                                                                                                                         | 117 (C <sub>9</sub> H <sub>9</sub> <sup>+</sup> ) (20)                  | 4.9-5.0 2 H(s) (φ-CH <sub>2</sub> -O-C <sup>o</sup> -)                                                                    | 1240 (Acetate)                         |
|                                                                                                                         | 91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (48)                   | 2.8 4 H(m) (Aromatic)                                                                                                     | 1600 )<br>)                            |
|                                                                                                                         | 87 (C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup> ) (100)   |                                                                                                                           | 1580 ) (Aromatic)<br>)                 |
| 43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (89)                                                                 |                                                                         | 1500 )                                                                                                                    |                                        |
| Polymer (Rf=0.00, benzene)<br>from irradiation of<br><i>p</i> -cyclopropylbenzyl<br>acetate in dioxane-water<br>(60/40) | 218 (C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> <sup>+</sup> ) (7)  | N.M.R. and Infrared are the same as polymer<br>(Rf=0.12, benzene) except for trace amounts<br>of alcohol (less than 1-2%) |                                        |
|                                                                                                                         | 190 (C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> <sup>+</sup> ) (11) |                                                                                                                           |                                        |
|                                                                                                                         | 148 (C <sub>10</sub> H <sub>12</sub> O <sup>+</sup> ) (14)              |                                                                                                                           |                                        |
|                                                                                                                         | 131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (68)                | 5.5 3 H(m) (φ-CH <sub>2</sub> -OH)                                                                                        | 3450 (Alcohol)                         |
|                                                                                                                         | 117 (C <sub>9</sub> H <sub>9</sub> <sup>+</sup> ) (29)                  |                                                                                                                           |                                        |
| 91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (53)                                                                   |                                                                         |                                                                                                                           |                                        |

Table 2.--Continued.

| Product                                                                                                                      | Mass spectrum                                                                                                                                                                                                                                                                                                          | N.M.R.                                                                                                                                                                                                                                            | Infrared                                                                                                                       |
|------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
|                                                                                                                              | 87 (C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup> ) (78)                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                   |                                                                                                                                |
|                                                                                                                              | 43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (100)                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                   |                                                                                                                                |
| Polymer (Rf=0.14, benzene)<br>from irradiation of<br><i>p</i> -cyclopropylbenzyl acetate<br>in acetonitrile-water<br>(60/40) | 190 (C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> <sup>+</sup> ) (100)<br>148 (C <sub>10</sub> H <sub>12</sub> O <sup>+</sup> ) (56)<br>131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (40)<br>91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (36)<br>43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (71) | 8.7-8.9 4-5 H(m) (CH <sub>3</sub> -CH or<br>CH <sub>3</sub> -CH <sub>2</sub> -)<br>8.0-8.1 5 H(s) (CH <sub>3</sub> -C <sup>O</sup> =O<br>and -CH <sub>2</sub> -CN)<br>5.0 2 H(s) (φ-CH <sub>2</sub> -O-C <sup>O</sup> -)<br>2.8 4 H(m) (Aromatic) | 3040 (Aromatic CH)<br>2950 (Aliphatic CH)<br>2220 (C≡N)<br>1745 (Acetate)<br>1240 (Acetate)<br>1600<br>1580 (Aromatic)<br>1500 |
| Polymer (Rf=0.00, benzene)<br>from irradiation of<br><i>p</i> -cyclopropylbenzyl acetate<br>in acetonitrile-water<br>(60/40) | 190 (C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> <sup>+</sup> ) (20)<br>148 (C <sub>10</sub> H <sub>12</sub> O <sup>+</sup> ) (16)<br>131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (28)<br>91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (32)<br>43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (100) | N.M.R. and Infrared are the same as<br>polymer (Rf=0.14, benzene)                                                                                                                                                                                 |                                                                                                                                |

Table 2.--Continued.

| Product                                                                                                    | Mass spectrum                                                           | N.M.R.                                                                                        | Infrared                      |
|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-------------------------------|
| Polymer (Rf=0.00, benzene)<br>from irradiation of<br><i>p</i> -cyclopropylbenzyl acetate<br>in benzene     | 190 (C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> <sup>+</sup> ) (2)  |                                                                                               | 3040 (Aromatic CH)            |
|                                                                                                            | 131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (6)                 |                                                                                               | 1745<br>) (Acetate)           |
|                                                                                                            | 91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (32)                   |                                                                                               | 1240)                         |
|                                                                                                            | 77 (C <sub>6</sub> H <sub>5</sub> <sup>+</sup> ) (29)                   |                                                                                               | 1600<br>)                     |
|                                                                                                            | 43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (100)                |                                                                                               | 1580<br>) (Aromatic)<br>1500) |
| Polymer (Rf=0.00, benzene)<br>from irradiation of<br><i>p</i> -cyclopropylbenzyl<br>acetate in cyclohexene | 190 (C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> <sup>+</sup> ) (17) | 8.2-9.0 7 H(m) (Cyclohexene)                                                                  |                               |
|                                                                                                            | 131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (35)                | 8.0 3 H(s) (CH <sub>3</sub> -C(=O)-)                                                          |                               |
|                                                                                                            | 117 (C <sub>9</sub> H <sub>9</sub> <sup>+</sup> ) (30)                  | 5.2 2 H(s) (φ-CH <sub>2</sub> -O-C(=O)-)                                                      |                               |
|                                                                                                            | 91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (53)                   | 2.8 4 H(m) (Aromatic)                                                                         |                               |
|                                                                                                            | 81 (C <sub>6</sub> H <sub>9</sub> <sup>+</sup> ) (26)                   |                                                                                               |                               |
|                                                                                                            | 43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (100)                |                                                                                               |                               |
| 2-Cyclohexen-1-ol (49)                                                                                     | 98 (C <sub>6</sub> H <sub>10</sub> O <sup>+</sup> ) (15)                | Infrared and N.M.R. spectra were previously<br>described on page 39 under 2,2'-bicyclohexenyl |                               |
|                                                                                                            | 70 (C <sub>5</sub> H <sub>10</sub> <sup>+</sup> ) (100)                 |                                                                                               |                               |

Table 2.--Continued.

| Product                           | Mass spectrum                                                                                                                                                                                                                                                       | N.M.R.                                                                                               | Infrared                                                                                   |
|-----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| 2-Cyclohexen-1-one ( <u>50</u> )  | 96 (C <sub>6</sub> H <sub>8</sub> O <sup>+</sup> ) (51)<br>68 (C <sub>5</sub> H <sub>8</sub> <sup>+</sup> ) (100)                                                                                                                                                   |                                                                                                      | Infrared and N.M.R. spectra were previously described on page 39 under 2,2'-bicyclohexenyl |
| 2,2'-Bicyclohexenyl ( <u>48</u> ) | 162 (C <sub>12</sub> H <sub>18</sub> <sup>+</sup> ) (14)<br>81 (C <sub>6</sub> H <sub>9</sub> <sup>+</sup> ) (100)                                                                                                                                                  | (Same as above)                                                                                      |                                                                                            |
| 2-Cyclohexen-1-dioxane            | 168 (C <sub>10</sub> H <sub>16</sub> O <sub>2</sub> <sup>+</sup> ) (2)<br>87 (C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup> ) (78)<br>81 (C <sub>6</sub> H <sub>9</sub> <sup>+</sup> ) (39)<br>44 (C <sub>2</sub> H <sub>4</sub> O <sup>+</sup> ) (100) | 7.8-8.4 7 H(m) (CH <sub>2</sub> and CH of cyclohexene)<br>6.4 7 H(s) (Dioxane)<br>4.2 2 H(s) (Vinyl) |                                                                                            |

Table 3. Spectral identification of photoproducts resulting from the irradiation of m-cyclopropylbenzyl acetate.

| Product                                                                                      | Mass spectrum                                                                                                                                                                                                                                                                                            | N.M.R.                                                                                                                                                                                       | Infrared                                                                                                      |
|----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| <u>m</u> -Cyclopropylmethyl<br>benzene ( <u>55</u> )                                         | 132 (C <sub>10</sub> H <sub>12</sub> <sup>+</sup> ) (37)<br>117 (C <sub>9</sub> H <sub>9</sub> <sup>+</sup> ) (100)<br>91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (34)                                                                                                                             |                                                                                                                                                                                              |                                                                                                               |
| <u>m</u> -Cyclopropylethyl<br>benzene ( <u>53</u> )                                          |                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                              | (Previously described on page 45 under product studies from <u>m</u> -cyclopropylbenzyl acetate irradiations) |
| Polymer from the irradiation of <u>m</u> -cyclopropylbenzyl acetate in dioxane-water (60/40) |                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                              | (Previously described on page 45 under product studies from <u>m</u> -cyclopropylbenzyl acetate irradiations) |
| Methyl <u>m</u> -cyclopropylbenzyl ether ( <u>58</u> )                                       | 162 (C <sub>11</sub> H <sub>14</sub> O <sup>+</sup> ) (100)<br>147 (C <sub>10</sub> H <sub>11</sub> O <sup>+</sup> ) (22)<br>131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (79)<br>117 (C <sub>9</sub> H <sub>9</sub> <sup>+</sup> ) (88)<br>91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (77) | 9.0-9.5 4 H(m) (Cyclopropyl methylenes)<br>8.1 1 H(m) (Cyclopropyl methine)<br>6.7 3 H(s) (O-CH <sub>3</sub> )<br>5.6-5.7 2 H(s) ( $\phi$ -CH <sub>2</sub> -O-)<br>2.8-2.9 4 H(m) (Aromatic) |                                                                                                               |

Table 4. Spectral identification of photoproducts resulting from the irradiation of various acetates and related compounds.

| Product <sup>a</sup>               | Mass spectrum                                                        | N.M.R.  | Infrared                                  |
|------------------------------------|----------------------------------------------------------------------|---------|-------------------------------------------|
| <u>m</u> -Cyclopropyl- $\alpha$ -  | 234 (C <sub>14</sub> H <sub>18</sub> O <sub>3</sub> ) (5)            | 9.0-9.4 | 4 H(m) (Cyclopropyl                       |
| hydroxy- $\alpha$ -dioxanyl-       | 148 (C <sub>10</sub> H <sub>12</sub> O <sup>+</sup> ) (26)           |         | methylene)                                |
| toluene (54)                       | 117 (C <sub>9</sub> H <sub>9</sub> <sup>+</sup> ) (42)               | 8.1-8.2 | 1 H(m) (Cyclopropyl                       |
|                                    | 91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (25)                |         | methine)                                  |
|                                    | 87 (C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup> ) (23) | 6.4     | 7 H(m) (Dioxane)                          |
|                                    | 44 (C <sub>2</sub> H <sub>4</sub> O <sup>+</sup> ) (100)             | 5.5     | 1 H(s) ( $\phi$ -CH-O-)                   |
|                                    |                                                                      | 3.0     | 4 H(m) (Aromatic)                         |
|                                    |                                                                      | 5.6     | 1 H(m) (OH)                               |
| <hr/>                              |                                                                      |         |                                           |
| Polymer from the irradi-           |                                                                      | 8.8-9.2 | 4 or 5 H(m) (CH <sub>3</sub> CH           |
| ation of <u>m</u> -cyclopropyl-    |                                                                      |         | or CH <sub>3</sub> CH <sub>2</sub> )      |
| benzyl alcohol in                  |                                                                      | 6.4     | 7 H(m) (Dioxane)                          |
| dioxane-water (60/40)              |                                                                      | 5.5     | 2 or 3 H(s) ( $\phi$ -CH <sub>2</sub> -OH |
|                                    |                                                                      |         | or $\phi$ -CH-OH)                         |
|                                    |                                                                      | 2.8     | 4 H(m) (Aromatic)                         |
| <hr/>                              |                                                                      |         |                                           |
| Polymer from the irradi-           |                                                                      | 8.7-9.3 | 4 or 5 H(m) (CH <sub>3</sub> -CH or       |
| ation of $\beta$ -methylstyrene in |                                                                      |         | CH <sub>3</sub> -CH <sub>2</sub> -)       |
| dioxane-water (60/40)              |                                                                      | 6.4     | 7 H(m) (Dioxane)                          |
|                                    |                                                                      | 2.8     | 5 H(m) (Aromatic)                         |

Table 4.--Continued.

| Product <sup>a</sup>                              | Mass spectrum                                                                                                         | N.M.R.                          | Infrared                                                  |
|---------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|---------------------------------|-----------------------------------------------------------|
| Polymer I from the irradiation of benzyl acetate  | 87 (C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup> )                                                       | 8.9-9(m) (CH <sub>3</sub> -) )  | Corresponds to Polymer I                                  |
|                                                   |                                                                                                                       | 7.5 (m) (φ-CH <sub>2</sub> -) ) |                                                           |
|                                                   |                                                                                                                       | 6.4 (s) (Dioxane) )             |                                                           |
|                                                   |                                                                                                                       | 2.8 (m) (Aromatic) )            |                                                           |
| Polymer II from the irradiation of benzyl acetate | 87 (C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup> )<br>43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) | corresponds to Polymer II       | ( 1745 (Acetate)                                          |
|                                                   |                                                                                                                       |                                 | ( 1600 )<br>( )<br>( 1580 ) (Aromatic)<br>( )<br>( 1500 ) |
| <u>p</u> -Methylethylbenzene (64)                 | 120 (C <sub>9</sub> H <sub>12</sub> <sup>+</sup> ) (75)                                                               |                                 |                                                           |
|                                                   | 105 (C <sub>8</sub> H <sub>9</sub> <sup>+</sup> ) (100)                                                               |                                 |                                                           |
| <u>p</u> -Methylbenzyl dioxane (67)               | 192 (C <sub>12</sub> H <sub>16</sub> O <sub>2</sub> <sup>+</sup> ) (44)                                               |                                 |                                                           |
|                                                   | 105 (C <sub>8</sub> H <sub>9</sub> <sup>+</sup> ) (62)                                                                |                                 |                                                           |
|                                                   | 87 (C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup> ) (100)                                                 |                                 |                                                           |

Table 4.--Continued.

| Product <sup>a</sup>                                                                                                            | Mass spectrum                                                           | N.M.R.                                                                                                                           | Infrared       |
|---------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|----------------|
|                                                                                                                                 | 86 (C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> <sup>+</sup> ) (85)    |                                                                                                                                  |                |
|                                                                                                                                 | 44 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (24)                 |                                                                                                                                  |                |
| 1,2-di-(4-methylphenyl)-<br>ethane ( <u>66</u> )                                                                                | 210 (C <sub>16</sub> H <sub>18</sub> <sup>+</sup> ) (84)                |                                                                                                                                  |                |
|                                                                                                                                 | 105 (C <sub>8</sub> H <sub>9</sub> <sup>+</sup> ) (100)                 |                                                                                                                                  |                |
| Polymer I from the<br>irradiation of <u>p</u> - and<br><u>m</u> -methylbenzyl acetate<br>in dioxane-water (60/40) <sup>b</sup>  |                                                                         | 8.7-9.2 3 H(m) (CH <sub>3</sub> )<br>7.7 3 H(s) ( $\phi$ -CH <sub>3</sub> )<br>6.4 7 H(s) (Dioxane)<br>2.8-3.0 4 H(m) (Aromatic) |                |
| Polymer II from the<br>irradiation of <u>p</u> - and<br><u>m</u> -methylbenzyl acetate<br>in dioxane-water (60/40) <sup>c</sup> | 190 (C <sub>12</sub> H <sub>14</sub> O <sub>2</sub> <sup>+</sup> ) (84) |                                                                                                                                  |                |
|                                                                                                                                 | 148 (C <sub>10</sub> H <sub>12</sub> O <sup>+</sup> ) (92)              |                                                                                                                                  |                |
|                                                                                                                                 | 131 (C <sub>10</sub> H <sub>11</sub> <sup>+</sup> ) (84)                |                                                                                                                                  | 1745 (Acetate) |
|                                                                                                                                 | 117 (C <sub>9</sub> H <sub>9</sub> <sup>+</sup> ) (78)                  |                                                                                                                                  | 1240 (Acetate) |

Table 4.--Continued.

| Product <sup>a</sup>                                                       | Mass spectrum                                           | N.M.R.                                                                                               | Infrared |
|----------------------------------------------------------------------------|---------------------------------------------------------|------------------------------------------------------------------------------------------------------|----------|
|                                                                            | 91 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> ) (100)  |                                                                                                      |          |
|                                                                            | 43 (C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ) (57) |                                                                                                      |          |
| Polymer from the irradiation of ethylbenzene in dioxane-water <sup>c</sup> |                                                         | 8.9-9(m) (CH <sub>3</sub> )<br>7.5(m) (φ-CH <sub>2</sub> -)<br>6.4(s) (Dioxane)<br>2.8(m) (Aromatic) |          |

- Ethylbenzene and benzyl alcohol were identified by comparative GLC analysis with authentic samples.
- Polymers I and II from the irradiation of *p*-methylbenzyl acetate were almost identical with polymers I and II from the *m*-methylbenzyl acetate irradiations.
- Polymer from the irradiation of ethylbenzene had the identical N.M.R. spectrum as polymer I from the benzyl acetate irradiation.

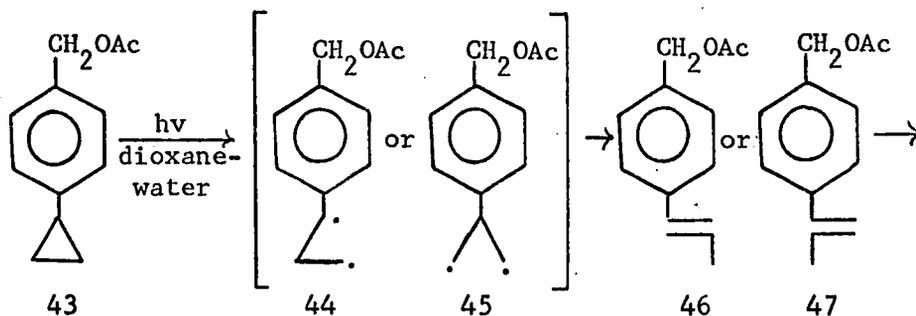
## RESULTS

The compounds used in this study were easily synthesized and proved suitable for use after standard purification procedures.

A full range of solvent systems were looked at but dioxane-water was of major interest in this study. Dioxane-water was used as the major solvent system in order to correlate experimental results with similar studies in the literature.

Integration of nmr spectra of polymeric materials obtained during the course of this work was done by the "counting squares technique." Since the peaks in these spectra were broadened, it was difficult to obtain even base-lines, and the exact ratio of hydrogen atoms, especially in the methyl region, could not be realized for these polymeric products.

The irradiation of *p*-cyclopropylbenzyl acetate (43) at 2537 Å in a variety of solvent systems (dioxane-water was the major system studied and will be the one discussed here, although similar results were obtained with other solvent systems) at different concentrations and conditions afforded only polymeric photoproducts (Table 5; see end of Results section for Tables 5 through 8, p. 74 through 80).



high molecular weight polymer ( $R_f = 0.00$ , benzene)

+ low molecular weight polymer ( $R_f = 0.12$ , benzene)

These polymeric products were separated by preparative TLC into two fractions: low molecular weight polymer having a  $R_f = 0.12$  in benzene and a higher molecular weight polymer having a  $R_f = 0.00$  in benzene.

Spectral evidence (Table 2) indicated that both polymers had almost identical structural features. In both polymers the benzyl acetate moiety remained intact while the cyclopropyl ring was destroyed (as evidenced by lack of nmr absorption at  $9.5\tau$  characteristic of cyclopropane rings) and dioxane was incorporated into the polymeric chain. The low molecular weight polymer did not contain hydroxyl groups indicating absence of hydrolysis of the acetate function. The higher molecular weight polymer showed weak hydroxyl bands in the ir ( $3400\text{ cm}^{-1}$ ) and nmr,  $\tau 5.5$  (m, 3H,  $\phi\text{-CH}_2\text{-OH}$ ). This alcohol represents only 1-2% of the polymer product. The percent of alcohol in the polymer was determined by nmr area comparison of the benzyl acetate absorption at  $\tau 5.0$  with the benzyl alcohol absorption at  $\tau 5.5$ . This small

amount of alcohol could have come from work-up procedures in separation of photoproducts from prep TLC plates. A small amount of water soluble polymer was isolated from the photoreaction mixture and was identified as a polymeric benzylic alcohol with dioxane incorporated in the polymer chain: nmr ( $\text{CHCl}_3$ ,  $\text{CDCl}_3$ ),  $\tau$  8.8-9.0 (m, 2-3 H, methyl or methylene groups), 6.4 (s, 7H, dioxane), 5.5 (m, 3 H,  $\phi\text{-CH}_2\text{-OH}$ ), and 2.8 (m, 4 H, aromatic H).

Large amounts of polymer were deposited on the side of the phototube and ir analysis of this polymer film showed the presence of an acetate ( $1745$  and  $1240\text{ cm}^{-1}$ ) and phenyl ring ( $1600$ ,  $1580$ ,  $1500\text{ cm}^{-1}$ ).

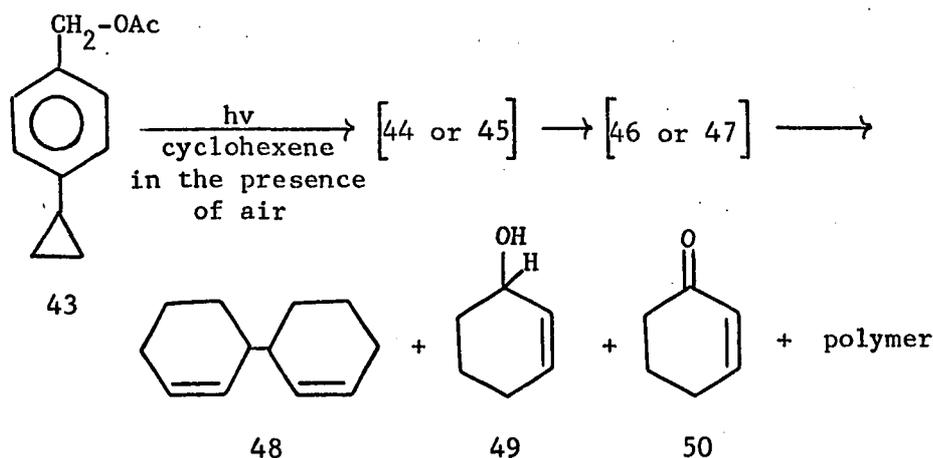
Prolonged irradiation of p-cyclopropylbenzyl acetate (43) resulted in 100% conversion of starting material to polymer and even short irradiation times failed to produce any other photoproducts or intermediates (46 or 47) other than recovered starting material (43) and polymer.

An ultraviolet difference spectra of p-cyclopropylbenzyl acetate (43) solutions during irradiation showed a maximum absorption at  $2800\text{-}2900\text{ \AA}$  (starting material 43  $\lambda_{\text{max}} 2600\text{ \AA}$ ), indicating possible increased conjugation with the phenyl ring. This bathochromic shift in  $\lambda_{\text{max}}$  could be caused by rearrangement of the cyclopropane ring into a styrene type intermediate (46 or 47) which would also explain the large amounts of polymer as the only detected photoproducts. All attempts to chemically trap intermediates 46 and 47 failed.

Control experiments showed that  $\beta$ -methylstyrene in dioxane-water could oligomerize under the conditions of the photolysis of

*p*-cyclopropylbenzyl acetate (43) (Table 7). The polymer from the photolysis of  $\beta$ -methylstyrene in dioxane-water showed similar nmr absorptions and splitting patterns in the methyl and dioxane regions of the spectrum (Table 4) compared to those same regions in the nmr spectrum of *p*-cyclopropylbenzyl acetate (43) polymeric photoproducts (Table 2).

Cyclopropane ring opening (44 or 45), rearrangement (46 or 47), and subsequent polymerization of *p*-cyclopropylbenzyl acetate (43) in cyclohexene resulted in free radical abstraction of the allylic hydrogens of cyclohexene and formation of 2,2'-bicyclohexenyl (48). Compound 2-cyclohexen-1-dioxane was the major product obtained from irradiation of the acetate in cyclohexene-dioxane (Table 5).



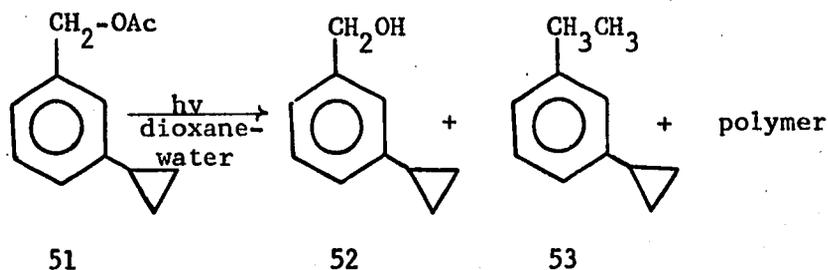
The photolysis reaction of *p*-cyclopropylbenzyl acetate (43) in the cyclohexene also showed incorporation of solvent in the polymer chain (Table 2).

The inability to detect norcarane and methylcyclohexene suggests that ejection of a carbene intermediate and formation of

p-vinylbenzyl acetate is not a primary photoprocess of p-cyclopropylbenzyl acetate under conditions employed in this investigation.

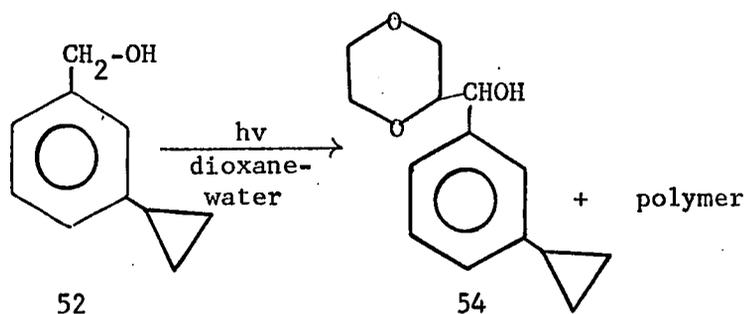
It was found that some type of oxidation of cyclohexene was taking place when the photolysis of p-cyclopropylbenzyl acetate (43) was carried out in cyclohexene in the presence of air as indicated by the formation of 2-cyclohexen-1-ol (49) and 2-cyclohexen-1-one (50) (Table 5). These same products (49 and 50) were also produced from the irradiation of cyclohexene in acetone in the presence of air (see p. 39 in the Experimental section, under 2,2'-bicyclohexenyl) and these oxidation products (49 or 50) were not produced by irradiation of cyclohexene in the presence of air without acetone or 43. Irradiation of degassed, oxygen-free solutions of acetone and cyclohexene have been studied by Bradshaw (1966) and these oxidation products (49 or 50) were not found. Evidence for photochemical oxidations is presented by Kan (1966, p. 211).

The deoxygenated nitrogen purged irradiation of m-cyclopropylbenzyl acetate (51) in dioxane-water afforded three primary photo-products: m-cyclopropylbenzyl alcohol (52), m-cyclopropylethylbenzene (53), and polymer (Table 6).



This photolysis resulted in complete conversion of starting material (51) to these products (52, 53, and polymer) and in this solvent system the alcohol (52) was the major component. Structural proof for these products (52, 53, and polymer) was confirmed by their characteristic spectra (Table 3).

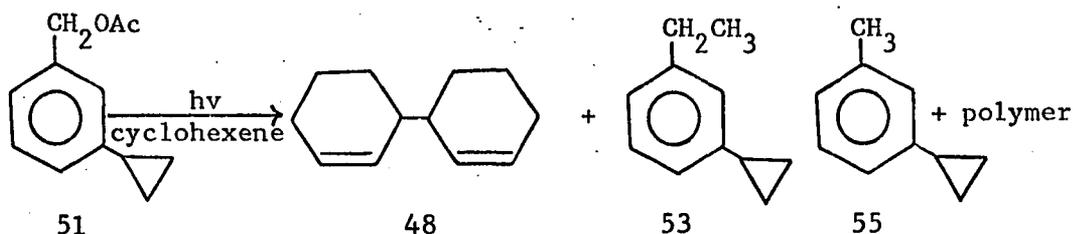
Irradiation of m-cyclopropylbenzyl alcohol (52) in dioxane-water, under conditions similar to those employed for the corresponding acetate (51), showed that this photoproduct was not stable to light and underwent secondary photolysis to give m-cyclopropyl- $\alpha$ -hydroxy- $\alpha$ -dioxanyltoluene (54) and polymer resulting from the opening of the cyclopropane ring (Tables 4, 7).



The polymer from the irradiation of m-cyclopropylbenzyl acetate (51) showed no evidence of starting material and was very similar to the polymer resulting from the control photolysis of the m-cyclopropylbenzyl alcohol (52). The polymer from the irradiation of m-cyclopropylbenzyl acetate (51) also showed a strong, broad triplet ( $J = 7-8$  Hz) absorption in its nmr spectrum which could arise from the copolymerization of m-cyclopropylbenzyl alcohol (52) with m-cyclopropylethylbenzene (53). Although m-cyclopropylethylbenzene (53) was not studied as a control, it was felt that this compound was not unlike cyclopropylbenzene which does polymerize under photolytic conditions

(Richardson et al. 1965) and ethylbenzene which also undergoes photo-induced polymerization (Hentz and Burton 1951).

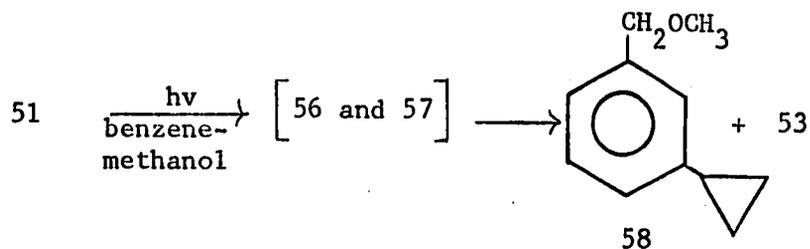
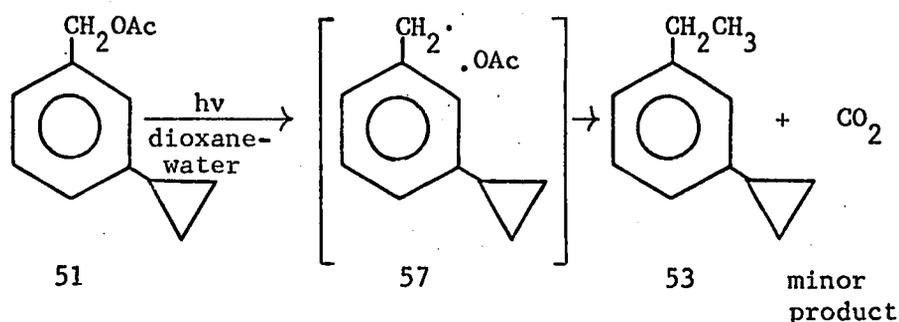
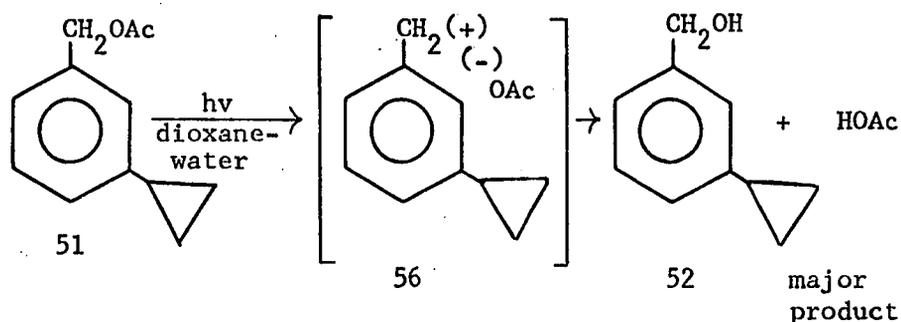
Irradiation of m-cyclopropylbenzyl acetate (51) in cyclohexene resulted in 2,2'-bicyclohexenyl (48), m-cyclopropylethylbenzene (53), and a very small amount of m-cyclopropylmethylbenzene (55). The m-cyclopropylmethylbenzene (55) could arise from hydrogen abstraction of a benzyl radical or a secondary photolysis reaction involving m-cyclopropylethylbenzene (53) (Tables 3, 6).



The inability to detect norcarane or methylcyclohexene also suggests that formation of a carbene intermediate (as is evident in the photolysis of cyclopropylbenzene in solution) (Richardson et al. 1965) is not a primary photoprocess of the cyclopropane ring in m-cyclopropylbenzyl acetate (51) photolysis under these conditions.

Variation of solvent polarity was found to have strong effects on the ratio of m-cyclopropylethylbenzene (53) to m-cyclopropylbenzyl alcohol (52). In more polar solvent systems (dioxane-water) an ionic intermediate (56) is favored and alcohol (52) is the major product. In the nonpolar solvent systems benzene, cyclohexene, and t-butyl alcohol, the free radical intermediate (57) is favored and in benzene-methanol both m-cyclopropylethylbenzene (53) and methyl

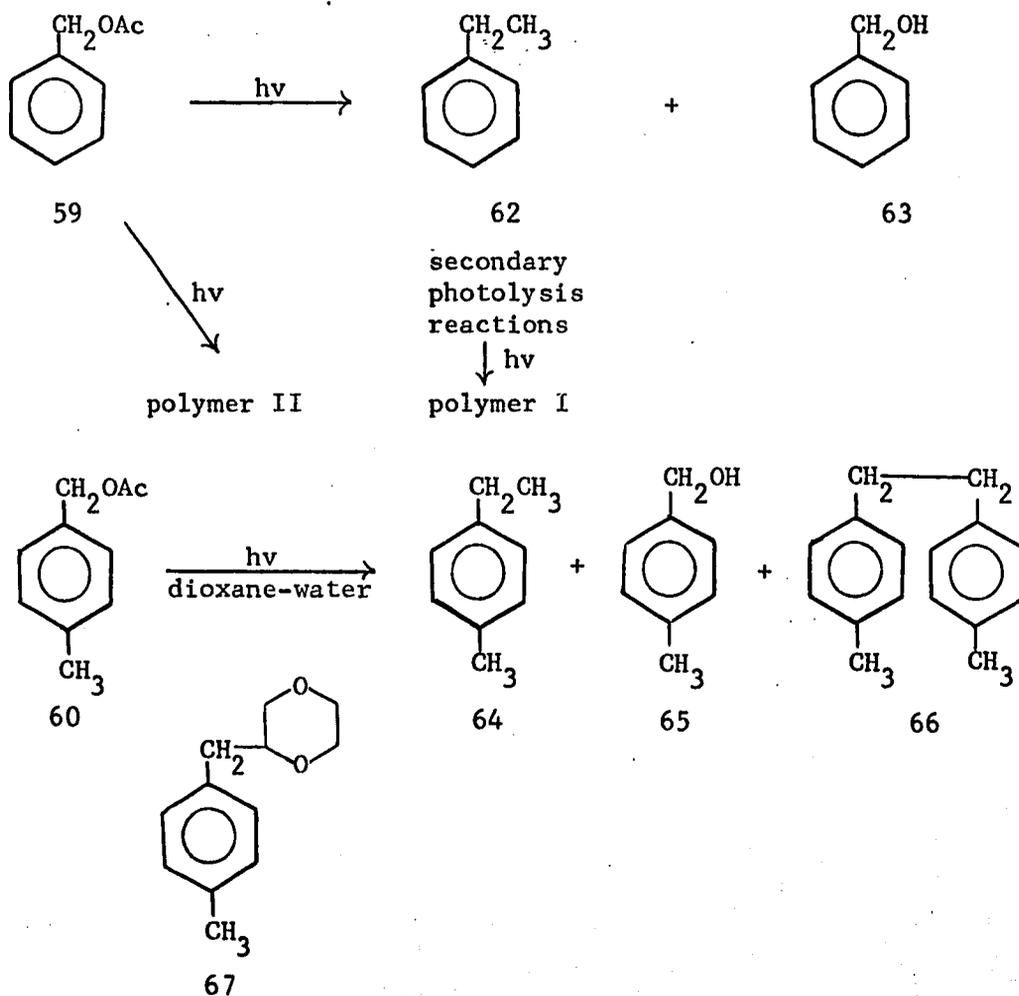
*m*-cyclopropylbenzyl ether (58), arising from 56 and 57, are equally favored (Table 6).

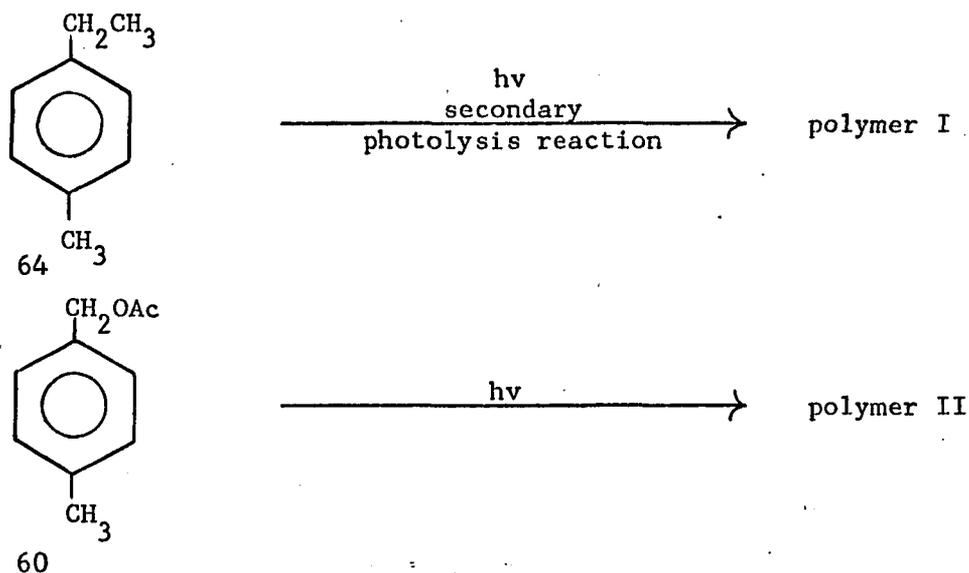


In an attempt to determine the scope of this photochemical solvolysis, other benzyl acetate systems were investigated. Those compounds found to undergo analogous reactions included benzyl acetate (59), *p*-methylbenzyl (60), and *m*-methylbenzyl (61) acetates (Table 7).

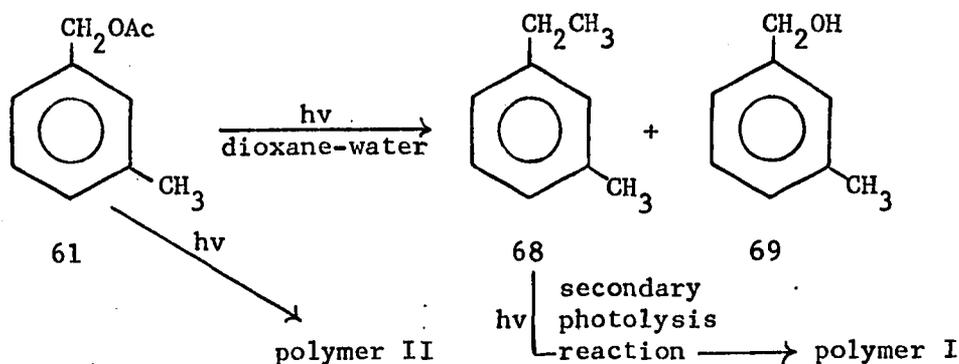
The products and their distribution from the irradiation of 59, 60, and 61 were similar to the results of the cyclopropyl substituted

benzyl acetates (43 and 51). The m-methyl isomer (61) produces large amounts of alcohol (69) relative to the ethylbenzene derivative (68) while the p-methyl isomer (60) and the unsubstituted benzyl acetate (59) form relatively small amounts of alcohol (63 and 65) and larger amounts of free radical products (62 and 64). Para-methylbenzyl acetate (60) forms p-methylbenzylidioxane (67) and 1,2-di-(4-methylphenyl)-methane (66) analogous to the work of Zimmerman and Sandel (1963) with para-methoxy-substituted benzyl acetates (32) (see Introduction).





Whether or not the alcohols (62 and 64) formed from the *p*-methylbenzyl acetate (59) and benzyl acetate (58) photolysis come from an electronically excited state or a vibrationally excited ground state is not known.



Polymer I (Table 4) from the photolysis reaction of 59, 60, and 61 in dioxane-water was found to be very similar to the polymer obtained from a control photolysis of ethylbenzene (62) under conditions identical to those used for the acetates (Table 4).

Polymer II (Table 4) from the photolysis of 59, 60, and 61 in dioxane-water was found to contain acetate groups and probably resulted from the polymerization of the starting material (Table 7). Photo-products were not obtained from irradiation of substituted benzyl acetates in Pyrex containers.

Solutions of those compounds found to undergo photolysis reactions were stable indefinitely in the dark at 30-50°. Irradiation of substituted benzyl acetates in Pyrex containers showed no reaction.

The product distributions obtained from irradiation of p-cyclopropylbenzyl (43), m-cyclopropylbenzyl (51), and various other substituted benzyl acetates are listed in Tables 5, 6, and 7, respectively. Spectral identification of these products are listed in Tables 2, 3, and 4 (see Experimental). The disappearance of these substituted benzyl acetates during photolysis was monitored by TLC and GLC analysis and found to be independent of concentration.

No attempt was made to isolate and identify gaseous products that might have been generated during photolysis.

Sensitized irradiations were conducted in an attempt to gain information regarding the nature and possible energy of the excited state species involved.

The photolysis of p-cyclopropylbenzyl acetate (43) was carried out in deoxygenated, nitrogen-purged benzene solutions, and the observed products were polymer and unreacted starting material (Table 5). Analysis of this polymer showed that the benzyl acetate moiety remained intact and the cyclopropane ring was destroyed (Table 2). Polymerization

occurred through the opening of the cyclopropane ring (44 or 45) followed by rearrangement to a styrene type of intermediate (46 or 47) which in turn led to the polymeric products.

Since benzene was the major component in the solution, it was assumed that most of the light would be absorbed by the solvent (in this case benzene) and that the triplet energy of benzene ( $E_T = 85$  kcal/mole) might be high enough to cause photosensitization of *p*-cyclopropylbenzyl acetate (43). If, however, the triplet energy of the benzyl acetate is not lower than the triplet energy of benzene, efficient transfer of energy would not be realized. Since *p*-cyclopropylbenzyl acetate (43) (acceptor) absorbs strongly in the same region as the donor (benzene), direct photoreaction of the acceptor may still occur.

Photolysis of *m*-cyclopropylbenzyl acetate (51) in deoxygenated, nitrogen-purged benzene solutions afforded three photoproducts, *m*-cyclopropylethylbenzene (53), unreacted starting material (51), and unidentified polymer (Table 6).

The same arguments of sensitized irradiation apply for the *meta*- as well as the *para*-isomer in that both compounds absorb in the same region as benzene and one cannot tell if direct or photosensitized reactions are taking place. In the irradiation of *m*-cyclopropylbenzyl acetate (51), one of the main photoproducts is *m*-cyclopropylethylbenzene (53) which should be very similar to benzene, and this substance could also promote photosensitization reactions.

When the solvent system was changed to a 50/50 mixture of benzene-methanol, irradiation of m-cyclopropylbenzyl acetate (51) showed competition between radical and ionic intermediates (56 and 57) in the formation of photoproducts. In this reaction almost equal amounts of m-cyclopropylethylbenzene (53) (benzyl radical intermediate 57) and methyl m-cyclopropylbenzyl ether (58) (carbonium ion intermediate 56) were produced. Again, both products as well as starting material absorb in the same region as benzene. Consequently, it is difficult to distinguish between direct and photosensitized reactions. Even if photosensitized reactions are occurring, it is difficult to determine what species is actually causing photosensitization (solvent or photoproducts) (Table 6).

Irradiation, in a Vycor container, of a degassed methanol solution 0.046 M in m-cyclopropylbenzyl acetate (51) and 0.46 M in piperylene afforded two photoproducts, m-cyclopropylethylbenzene (53) (59% of the photoproduct mixture), and methyl m-cyclopropylbenzyl ether (58) (41% of the mixture). An ultraviolet spectra of this solution before irradiation showed that the acetate (51) absorbed most of the light (2537 Å) at these concentrations, but piperylene also showed some absorption in this region. Dimerization products of piperylene were not detected from this photolysis reaction. Attempts to effect the dimerization of piperylene in Pyrex containers using m-cyclopropylbenzyl acetate (51) as the sensitizer failed.

Photosensitized dimerization of 2-norbornene was observed using m-cyclopropylbenzyl acetate (51) as the sensitizer. The results of

these studies are summarized in Table 8 and page 48 of the Experimental section.

A small amount of dimer (21%) was formed from the direct irradiation of 2-norbornene in tertiary butyl alcohol (control reaction) with the absence of a sensitizer, but irradiation of 2-norbornene in the presence of m-cyclopropylbenzyl acetate (51) as the sensitizer produced almost a twofold excess (41%) of the dimerization product, indicating that a definite photosensitized reaction had taken place.

Photosensitized dimerizations of 2-norbornene, using m-cyclopropylbenzyl acetate (51) as the sensitizer, are difficult to interpret. The acetate (51), under these conditions, reacts to give products (m-cyclopropylethylbenzene 53) which absorb in the same region as the acetate (51) and these products could also cause sensitized dimerization.

The fluorescence emission spectrum of p-cyclopropylbenzyl acetate (43) was investigated at room temperature, and a  $\lambda_{\max}$  at 318 m $\mu$  (corresponding to a singlet energy of 89.9 kcal/mole) upon excitation at 270 m $\mu$  was obtained. The m-cyclopropylbenzyl acetate (51) showed an emission spectra with  $\lambda_{\max}$  at 328 m $\mu$  (87 kcal/mole) upon excitation at 260 m $\mu$ .

Table 5. Results of the Irradiation of *p*-cyclopropylbenzyl acetate under varying conditions and in different solvent systems.<sup>a</sup>

| Irradiation conditions or solvents <sup>b</sup>                          | Concentration (moles/liter) | Irradiation time in hrs | Products % yield <sup>c</sup>                                                                                      |
|--------------------------------------------------------------------------|-----------------------------|-------------------------|--------------------------------------------------------------------------------------------------------------------|
| Dioxane-water (60/40 volume percent) in the presence of air <sup>d</sup> | $1.18 \times 10^{-2}$       | 96                      | 8 polymer (Rf=0.12, benzene)<br>91 polymer (Rf=0.00, benzene)                                                      |
| Dioxane-water (60/40) freeze-thaw degassed <sup>d</sup>                  | $7.00 \times 10^{-3}$       | 144                     | 12 polymer (Rf=0.12, benzene)<br>88 polymer (Rf=0.00, benzene)                                                     |
| Dioxane-water (60/40) deoxygenated nitrogen purged <sup>d</sup>          | $9.40 \times 10^{-2}$       | 100                     | 6.2 polymer (Rf=0.12, benzene)<br>37.5 polymer (Rf=0.00, benzene)<br>56.3 <i>p</i> -cyclopropylbenzyl acetate (43) |
| Acetonitrile-water (60/40) deoxygenated nitrogen purged <sup>d</sup>     | $1.63 \times 10^{-2}$       | 16                      | 20 ( polymer (Rf=0.14, benzene)<br>( polymer (Rf=0.00, benzene)<br>80 <i>p</i> -cyclopropylbenzyl acetate (43)     |
| Benzene deoxygenated nitrogen purged <sup>d</sup>                        | $5.80 \times 10^{-2}$       | 120                     | polymer (Rf=0.00, benzene)<br><i>p</i> -cyclopropylbenzyl acetate (43)                                             |

Table 5.--Continued.

| Irradiation conditions<br>or solvents <sup>b</sup>                          | Concentration<br>(moles/liter) | Irradiation<br>time in hrs | Products % yield <sup>c</sup>                                                                                                                    |
|-----------------------------------------------------------------------------|--------------------------------|----------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| Cyclohexene in the<br>presence of air <sup>e</sup>                          | 1.80 x 10 <sup>-1</sup>        | 144                        | 64 2-cyclohexen-1-ol ( <u>49</u> )<br>polymer (Rf = 0.00, benzene)<br>28 2-cyclohexen-1-one ( <u>50</u> )<br>8 2,2'-bicyclohexenyl ( <u>48</u> ) |
| Cyclohexene-dioxane<br>(50/50) deoxygenated<br>nitrogen purged <sup>e</sup> | 1.80 x 10 <sup>-1</sup>        | 96                         | 42 three unidentified photoproducts<br>58 2-cyclohexen-1-dioxane unidenti-<br>fied polymer                                                       |

- a. All irradiations were done with a Srinivasan-Griffin Photochemical Reactor using 2537 $\text{\AA}$  light, and Vycor containers at 30-40°.
- b. Solvent mixtures were based on volume percent.
- c. Yield % is the relative concentration of products to each other, not overall conversion from starting material.
- d. Percentages determined by prep TLC.
- e. Percentages determined by integrating each GLC peak by cutting and weighing each GLC cutout with an analytical balance.

Table 6. Results of the Irradiation of *m*-cyclopropylbenzyl acetate under varying conditions and in different solvent systems.<sup>a</sup>

| Irradiation conditions<br>or solvents <sup>b</sup>                                       | Concentration<br>(moles/liter) | Irradiation<br>time in hrs | Products % yield <sup>c</sup>                                                                                                                                                |
|------------------------------------------------------------------------------------------|--------------------------------|----------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dioxane-water (60/40<br>volume percent) deoxy-<br>genated nitrogen purged <sup>d,e</sup> | 4.3 x 10 <sup>-2</sup>         | 48                         | 49.4 <i>m</i> -cyclopropylbenzyl alcohol<br>( <u>52</u> )<br>12.0 <i>m</i> -cyclopropylethylbenzene ( <u>53</u> )<br>8.6 three unidentified liquid<br>products<br>30 polymer |
| Tertiary butyl alcohol<br>freeze-thaw degassed <sup>d,f</sup>                            | 2.6 x 10 <sup>-2</sup>         | 24                         | 33-35 <i>m</i> -cyclopropylethylbenzene ( <u>53</u> )<br>13-8 <i>m</i> -cyclopropylbenzyl acetate ( <u>51</u> )<br>50-56 unidentified polymer                                |
| Benzene deoxygenated<br>nitrogen purged <sup>e</sup>                                     | 2.6 x 10 <sup>-1</sup>         | 120                        | 62 <i>m</i> -cyclopropylethylbenzene ( <u>53</u> )<br>38 <i>m</i> -cyclopropylbenzyl acetate ( <u>51</u> )<br>unidentified polymer                                           |
| Benzene-methanol (50/50)<br>deoxygenated nitrogen<br>purged <sup>e</sup>                 | 1.85 x 10 <sup>-1</sup>        | 120                        | 52 <i>m</i> -cyclopropylethylbenzene ( <u>53</u> )<br>48 methyl <i>m</i> -cyclopropylbenzyl<br>ether ( <u>58</u> )<br>unidentified polymer                                   |

Table 6.--Continued.

| Irradiation conditions<br>or solvents <sup>b</sup> | Concentration<br>(moles/liter) | Irradiation<br>time in hrs | Products % yield <sup>c</sup>                                                                                                                                                                                                    |
|----------------------------------------------------|--------------------------------|----------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Cyclohexene deoxygenated<br>nitrogen purged        | $4.2 \times 10^{-2}$           | 48                         | 4 <u>m</u> -cyclopropylmethylbenzene ( <u>55</u> )<br>49 <u>m</u> -cyclopropylethylbenzene ( <u>53</u> )<br>13 <u>m</u> -cyclopropylbenzyl acetate ( <u>51</u> )<br>32 2,2'-bicyclohexenyl ( <u>48</u> )<br>unidentified polymer |

- a. All irradiations were done with a Srinivasan-Griffin Photochemical Reactor using 2537 Å light, and Vycor containers at 30-40°.
- b. Solvent mixtures were based on volume percent.
- c. Yield % is the relative concentration of products to each other, not overall conversion from starting material.
- d. Percentages determined by prep TLC.
- e. Percentages determined by GLC.
- f. Percentages determined by column chromatography.

Table 7. Irradiation of various acetates and related compounds.<sup>a</sup>

| Compound                                        | Solvents, Conditions,<br>and concentrations<br>(mole/liter) <sup>b</sup>           | Irradiation<br>time in hrs | % Yield <sup>c,d,e</sup> |          |                                                                                                                                                                                                                                                               |
|-------------------------------------------------|------------------------------------------------------------------------------------|----------------------------|--------------------------|----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                 |                                                                                    |                            | GLC                      | Prep TLC | Products                                                                                                                                                                                                                                                      |
| Benzyl acetate<br>( <u>59</u> )                 | Dioxane-water (60/40),<br>deoxygenated nitrogen<br>purged, $6 \times 10^{-1}$ M    | 72                         | 72.3                     | 65       | benzyl acetate<br>ethylbenzene ( <u>62</u> )<br>benzyl alcohol ( <u>63</u> )<br>(polymer I<br>polymer II)                                                                                                                                                     |
|                                                 |                                                                                    |                            | 21.3                     | 13       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | 6.4                      | 7        |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | -                        | 20       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | -                        | -        |                                                                                                                                                                                                                                                               |
| <u>p</u> -Methylbenzyl<br>acetate ( <u>60</u> ) | Dioxane-water (60/40),<br>deoxygenated nitrogen<br>purged, $4.05 \times 10^{-1}$ M | 168                        | 45                       | 35       | <u>p</u> -methylbenzyl acetate<br><u>p</u> -methylethylbenzene ( <u>64</u> )<br><u>p</u> -methylbenzyl alcohol ( <u>65</u> )<br>(polymer I<br>polymer II)<br><u>p</u> -methylbenzyl dioxane ( <u>67</u> )<br>1,2-di-(4-methylphenyl)-<br>ethane ( <u>66</u> ) |
|                                                 |                                                                                    |                            | 14                       | -        |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | 20                       | 15       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | -                        | 27       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | 10                       | 11       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | 11                       | 12       |                                                                                                                                                                                                                                                               |
| <u>m</u> -Methylbenzyl<br>acetate ( <u>61</u> ) | Dioxane-water (60/40),<br>deoxygenated nitrogen<br>purged, $4.05 \times 10^{-1}$ M | 168                        | trace                    | -        | <u>m</u> -methylbenzyl acetate<br><u>m</u> -methylethylbenzene ( <u>68</u> )<br><u>m</u> -methylbenzyl alcohol ( <u>69</u> )<br>polymer I<br>polymer II<br>( <u>m</u> -methylbenzyl dioxane<br>1,2-di-(3-methylphenyl)-<br>ethane                             |
|                                                 |                                                                                    |                            | 37                       | -        |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | 63                       | 60       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | -                        | 30       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | -                        | 10       |                                                                                                                                                                                                                                                               |
|                                                 |                                                                                    |                            | less than<br>1           | -        |                                                                                                                                                                                                                                                               |

Table 7.--Continued.

| Compound                                         | Solvents, Conditions,<br>and concentrations<br>(mole/liter) <sup>b</sup>                       | Irradiation<br>time in hrs | % Yield <sup>c,d,e</sup> |          |                                                                                                                                 |
|--------------------------------------------------|------------------------------------------------------------------------------------------------|----------------------------|--------------------------|----------|---------------------------------------------------------------------------------------------------------------------------------|
|                                                  |                                                                                                |                            | GLC                      | Prep TLC | Products                                                                                                                        |
| Ethylbenzene<br>(62)                             | Dioxane-water (60/40),<br>deoxygenated nitrogen<br>purged, $1.55 \times 10^{-1}$ M             | 48                         | -                        |          | polymer                                                                                                                         |
| <u>m</u> -Cyclopropyl-<br>benzyl alcohol<br>(52) | Dioxane-water (60/40),<br>deoxygenated nitrogen<br>purged, $8.8 \times 10^{-1}$ M <sup>f</sup> | 96                         | 72<br>12<br>16           |          | <u>m</u> -cyclopropylbenzyl alcohol<br><u>m</u> -cyclopropyl- $\alpha$ -hydroxy- $\alpha$ -<br>dioxanyl toluene (54)<br>polymer |
| $\beta$ -Methylstyrene                           | Dioxane-water (60/40)<br>in the presence of air<br>$8.5 \times 10^{-1}$ M                      | 24                         | -                        |          | polymer                                                                                                                         |

- All irradiations were done using 2537 Å light and Vycor containers at 30-40°.
- Solvent mixtures were based on volume percent.
- Yield % is the relative concentration of products to each other, not overall conversion from starting material.
- Percentages determined by integrating each GLC peak by cutting and weighing each GLC cutout with an analytical balance.
- Percentages determined by prep TLC.
- Percentages determined by column chromatography.

Table 8. Irradiation of 2-norbornene.<sup>a</sup>

| Solvent                             | Sensitizer                          | Concentration                                                            | Time hr | Products % yield <sup>b</sup>                                                                                                  |
|-------------------------------------|-------------------------------------|--------------------------------------------------------------------------|---------|--------------------------------------------------------------------------------------------------------------------------------|
| (CH <sub>3</sub> ) <sub>3</sub> COH | xylene                              | 0.21 M                                                                   | 24      | 68 dimer<br>32 unidentified seven products                                                                                     |
| (CH <sub>3</sub> ) <sub>3</sub> COH | <u>m</u> -cyclopropylbenzyl acetate | 5.5 x 10 <sup>-3</sup> M<br>in acetate and<br>17.7 M in<br>2-norbornene  | 24      | 41 dimer<br>59 unidentified seven products                                                                                     |
| (CH <sub>3</sub> ) <sub>3</sub> COH | --                                  | 17.7 M in<br>2-norbornene                                                | 24      | 21 dimer<br>79 unidentified seven products                                                                                     |
| CH <sub>3</sub> OH                  | <u>m</u> -cyclopropylbenzyl acetate | 5.25 x 10 <sup>-1</sup> M<br>in acetate and<br>1.06 M in<br>2-norbornene | 24      | 10 dimer<br>49 methyl <u>m</u> -cyclopropylbenzyl<br>ether ( <u>58</u> )<br>41 <u>m</u> -cyclopropylethylbenzene ( <u>53</u> ) |
| CH <sub>3</sub> OH                  | --                                  | 1.06 M in<br>2-norbornene                                                | 24      | no products                                                                                                                    |

- a. All irradiations were done using 2537 Å light, Vycor containers at 30-40°, and solutions were purged with deoxygenated nitrogen.
- b. Yield % is the relative concentration of products to each other, not overall conversion from starting material, and percentages were determined by integrating each GLC peak.

## DISCUSSION

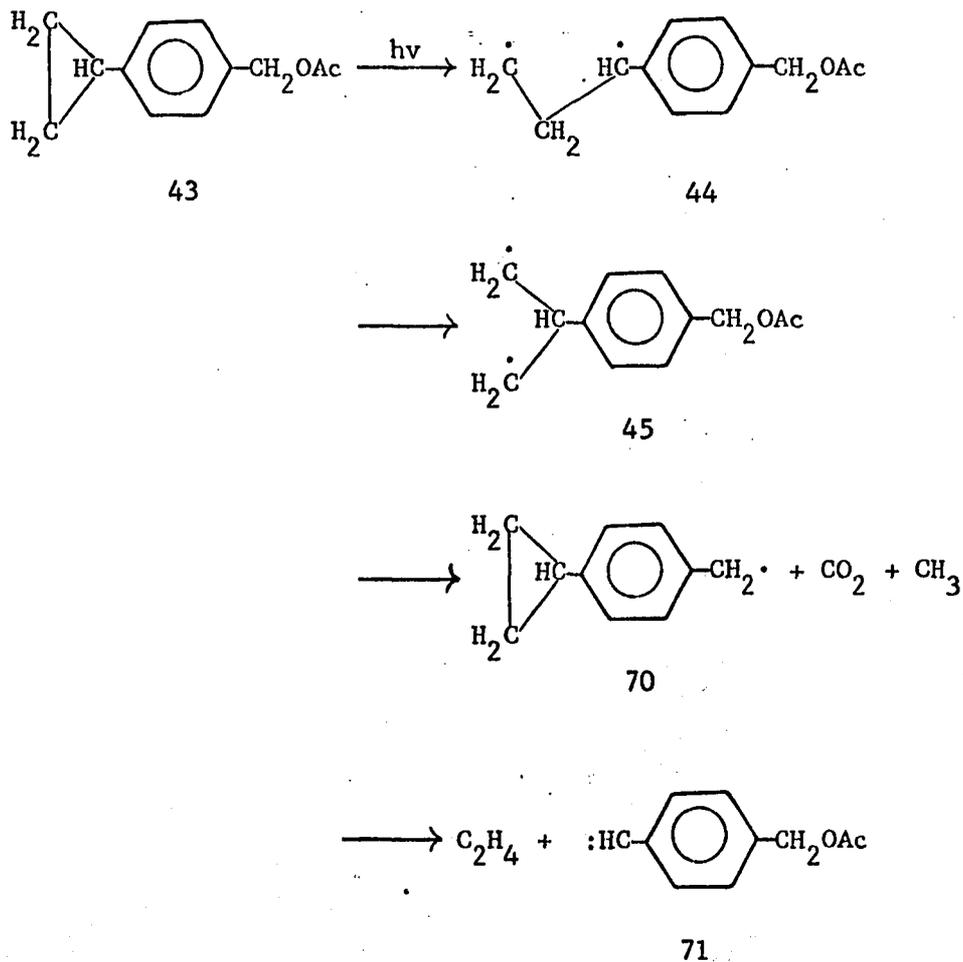
In the solution photolysis of *p*-cyclopropylbenzyl acetate at 2537 Å, the aromatic chromophore undergoes a  $\pi-\pi^*$  transition absorbing 112.5 kcal/mole of energy in the  $\pi$  electron system of the aromatic nucleus and results in population of the first excited singlet state of *p*-cyclopropylbenzyl acetate ( $S_1$ ). This energy may be emitted (fluorescence), or transmitted through the aromatic nucleus into the cyclopropane ring and utilized to achieve bond cleavage (formation of products). The excited *p*-cyclopropylbenzyl acetate ( $S_1$ ) could also undergo intersystem crossing to its triplet excited state ( $T_1$ ), and either react to give products or be deactivated through phosphorescence. Energy could also be lost by radiationless deactivation of either the singlet or triplet excited state.

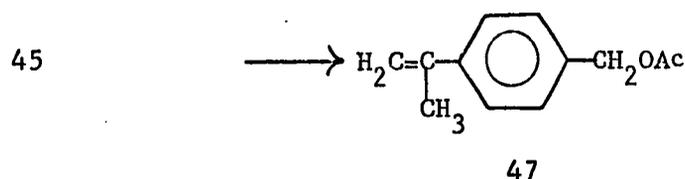
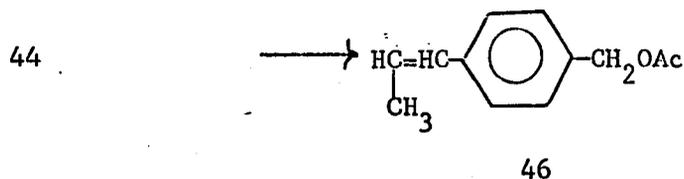
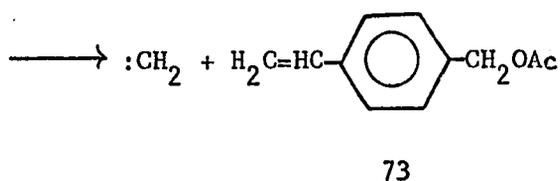
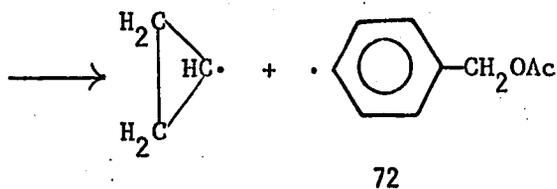
The acetate moiety, since it is not in conjugation with the aromatic ring, is assumed not to absorb light under these reaction conditions. The first absorption bands of acids, anhydrides, and esters generally lie below 2500 Å (Calvert and Pitts 1966, p. 427). There is, however, a possibility that some perturbation from the oxygen atoms in the acetate could cause mixing of singlet and triplet states and enhance intersystem crossing (Turro 1967, p. 27).

In the photolysis of *p*-cyclopropylbenzyl acetate (43) liquid photoproducts were not observed and only polymeric materials could be isolated. These polymer products consisted of benzyl acetate units,

the cyclopropane ring was destroyed and solvent had been incorporated into the polymer network (determined by ir and nmr). Mass spectral analysis showed solvent as well as the acetate function in the polymer. The polymer was made up of at least one unit having a  $\bar{m}/\bar{e}$  of 190 ( $C_{12}H_{14}O_2$ ) and a cracking pattern similar to starting material 43.

The following equations, analogous to phenylcyclopropane (25) (Leermakers and Ross 1966) represent possible reaction pathways for the photochemical decomposition of p-cyclopropylbenzyl acetate (43):

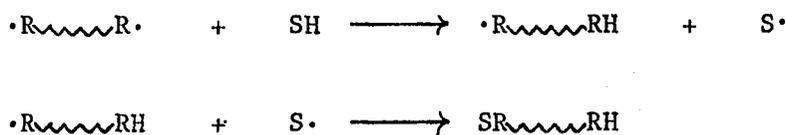




The fact that polymer is the only photoproduct isolated from the photochemical decomposition of 43 strongly suggests that the cyclopropane ring opens to give intermediates 44 and/or 45, which is then followed by hydrogen migration to produce  $\beta$ - and  $\alpha$ -methylstyrene derivatives 46 and 47. These methylstyrene derivatives (46 and 47) would certainly explain the polymeric photoproducts. A bathochromic shift in  $\lambda_{\text{max}}$  indicating increased conjugation with a phenyl ring (determined by ultraviolet difference spectra) and the benzyl acetate moiety remaining intact during the photolysis reaction are also consistent with

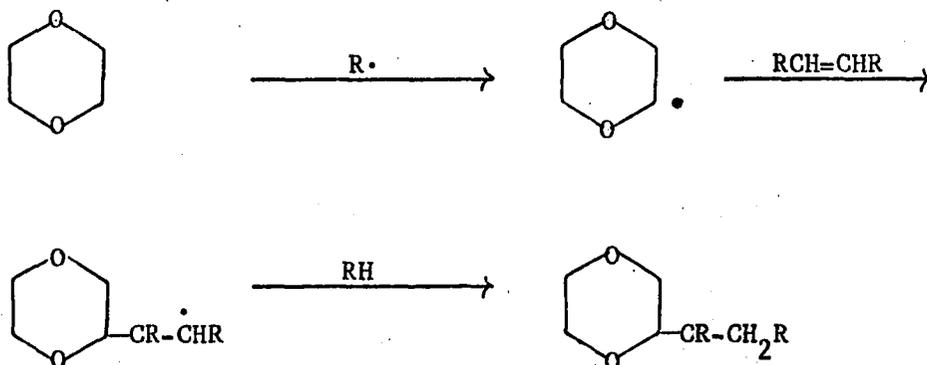
styrene derivatives 46 and 47. The mass spectrum of the polymer resulting from these methylstyrene derivatives (46 and 47) would have cracking patterns similar to starting material 43.

Recombination and hydrogen abstraction of polymer chain radicals with solvent (SH) and solvent radicals (S $\cdot$ ) would explain solvent incorporation in the polymer network.



The control photolysis of  $\beta$ -methylstyrene, under the same conditions as the irradiation of 43, also showed that solvent had been incorporated into the polymer network (Table 4).

There is also a possibility that, in dioxane-water solvent systems, a dioxanyl radical could undergo addition to an olefinic intermediate and thus become incorporated into a polymer network.

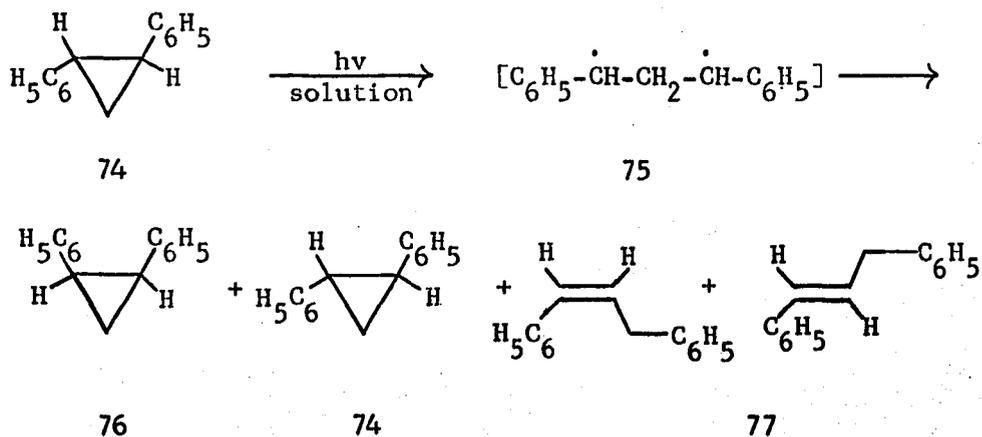


In this reaction, opening of the cyclopropane ring in p-cyclopropylbenzyl acetate (43) could produce as a radical source (R $\cdot$ ) and the

olefin might be some type of styrene intermediate (Elad and Youssefyeh 1964).

Photochemical rearrangement of phenylcyclopropane (gas phase photolysis) into methylstyrene type derivatives has been strongly substantiated by Foote (1966) and Leermakers and Ross (1966).

Solution photolysis of cyclopropane compounds can also promote isomerization to alkenyl derivatives, as demonstrated by the work of Dauben and Shaffer (1967), in which they carried out the irradiation of bicyclo[4.1.0]heptan-2-one in solution to produce 3-methyl-2-cyclohexenone as the major photoproduct. Kropp (1967) irradiated (+)-2-carne-ene-4  $\alpha$ -methanol in solution in the presence of photosensitizers having  $E_T \geq 74$  kcal/mole and observed selective isomerization involving the internal 1,6-cyclopropyl bond, to afford, as the only detectable photoproducts, a mixture of two bicyclo[3.2.0]hept-2-enes. Photoisomerization of cyclopropane derivatives in solution has also been observed by Griffin et al. (1965).



The diphenylpropenes 77 arise from a 1,2-hydrogen migration involving intermediate 75. Interconversion of trans-1,2-diphenylcyclopropane 74 into the cis isomer 76 through intermediate 75 can be obtained by triplet photosensitization, and this photoisomerization can be quenched efficiently by piperylene, suggesting that a triplet mechanism is operative (Hammond et al. 1964b, Griffin, O'Connell, and Hammond 1963).

The third reaction pathway of 43 indicates loss of the acetate to form acetoxy radicals, which further decompose into carbon dioxide and methyl radicals, and the p-cyclopropylbenzyl radical intermediate 70. One would expect some of the products arising from 70 to be p-cyclopropyltoluene or p-cyclopropylethylbenzene. These products would be analogous to m-cyclopropyltoluene (55) and m-cyclopropylethylbenzene (53) which were produced by the photochemical decomposition of m-cyclopropylbenzyl acetate (51) under similar conditions as the para isomer (43). Products arising from intermediate 70 could not be detected as separate entities even with short irradiation times, but there is a possibility that if these products were formed they could undergo secondary reactions and be incorporated into the polymer network (polymer was the only isolated product from the irradiation of 43). Spectral analysis of the polymeric products from the irradiation of 43 shows large acetate absorptions (determined by ir and nmr and very little absorption from toluene-like products (lack of nmr absorption at  $\tau$  7.5) indicating that formation of intermediate 70 did not occur to any great extent and is not a major pathway in the photochemical decomposition of p-cyclopropylbenzyl acetate (43).

The reaction pathway resulting in intermediate 71 and ethylene is a possibility, but all efforts to trap the aromatic carbene (71) failed and large amounts of gaseous products were not observed. No effort was made to trap small amounts of gaseous products. It is suggested that 71 is not a major intermediate in the photolysis of 43.

Products resulting from intermediate 72 were not observed (i.e., benzyl acetate and cyclopropane gas). Consequently, 72 is most likely not a major intermediate in the photochemical decomposition of 43.

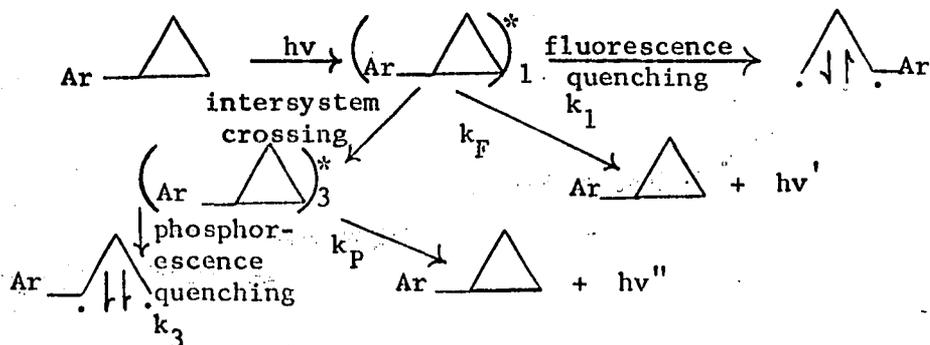
In the irradiation of *p*-cyclopropylbenzyl acetate (43) in cyclohexene (Table 5), *p*-vinylbenzyl acetate (73), norcarane, and other products, resulting from generation of methylene through photoelimination of the cyclopropane ring, were not detected. Thus generation of methylene and 73 is not considered a major reaction pathway in the photolysis of 43.

It is concluded that the major reaction pathway in the solution photolysis of *p*-cyclopropylbenzyl acetate 43 involves opening of the cyclopropane ring to give either intermediate 44 or 45 followed by hydrogen migration to produce  $\alpha$ - or  $\beta$ -methylstyrene derivatives (46 or 47). Unfortunately, it was not possible to distinguish between 1-methyl-2-(*p*-benzyl acetate)ethylene (46) or 1-methyl-1'-(*p*-benzyl acetate)ethylene (47), as these compounds could not be chemically trapped as separate entities and were only observed through ultraviolet spectroscopy. It is not possible to say whether one or both of these methylstyrene derivatives (46 or 47) give rise to the observed

polymeric products. At this time we also cannot completely exclude a photochemical chain mechanism, perhaps initiated by an adventitious radical species giving rise to the observed products. It has been shown by Foote (1966), however, that rearrangement of the cyclopropane ring in phenylcyclopropane (gas phase photolysis) to a propenylbenzene derivative was not caused by methyl radical attack, and thus a free radical chain mechanism for the observed photoisomerization can be tentatively ruled out.

The question now arises whether or not the opening of the cyclopropane ring to give intermediates 44 and 45 comes from the singlet or triplet excited states of p-cyclopropylbenzyl acetate (43).

The effect of neighboring cyclopropyl groups on the luminescence of some aromatic compounds has been investigated by O'Connell, Martin, and Lis (1970). It was observed that introduction of a cyclopropyl group near a chromophore which absorbs in the near-u.v. region can result in both fluorescence- and phosphorescence-quenching, and the degree of quenching depends on temperature and on the energy and lifetime of the emitting state. In this study the fluorescence and phosphorescence yields ( $\phi_F$  and  $\phi_P$ ) of phenylcyclopropane were compared to those of *n*-propylbenzene within the framework of the following scheme:



The phosphorescence yield ( $\phi_p$ ) for phenylcyclopropane in an isopentane glass at 77° K was shown to be 50 times less than  $\phi_p$  for n-propylbenzene and no large differences in their respective fluorescence yields ( $\phi_F$ ) were observed under these conditions. This suggests that the rate constant for ring opening in the triplet state of phenylcyclopropane ( $k_3$ ) is large compared to  $k_p$  while ( $k_1$ ) is insignificant relative to  $k_F$  [ca.  $10^7 \text{ sec}^{-1}$  (Berlman 1965, p. 42-58)]. A slight decrease in  $\phi_F$  for phenylcyclopropane relative to n-propylbenzene was observed at room temperature in isopentane solutions. From these studies it appears that ring opening from the triplet excited state of phenylcyclopropane (in a glass) is favored as a major reaction pathway over other modes of deactivation.

In the gas phase photolysis of phenylcyclopropane (Foote 1966) the observed fluorescence and styrene arose through reactions from the  $S_1$  state (singlet) of phenylcyclopropane with an efficiency of fluorescence  $\phi_F = 0.23$ . The propenylbenzenes and isomerization products came from longer-lived species and were a result of the triplet excited state  $T_1$ . The intersystem crossing efficiency between the first excited singlet and the first triplet state of phenylcyclopropane was  $\phi = 0.65$ .

In the solution photolysis of vinylcyclopropanecarboxylates, Jorgenson (1969) observed fragmentation of the cyclopropane ring, through loss of ethylene, and formation of a carbene intermediate (followed by collapse into allenes, furans, and cyclopropenes). The origin of fragmentation products were assigned to the  $\pi-\pi^*$  singlet

excited state of the cyclopropylacrylic ester analogous to the results of Richardson et al. (1965) in which the methylene generated from photofragmentation of arylcyclopropanes is extruded as a singlet, and hence from a singlet excited state of the cyclopropane precursor. Jorgenson (1969) observed that sensitized photolysis did not lead to fragmentation products but did result in cyclopentene products indicating a 1,3-diradical intermediate stemming from a triplet excited state. Photosensitization of a vinylcyclopropane rearrangement was also reported by Kropp (1967) in the case of (+)-2-carene-4 $\alpha$ -methanol.

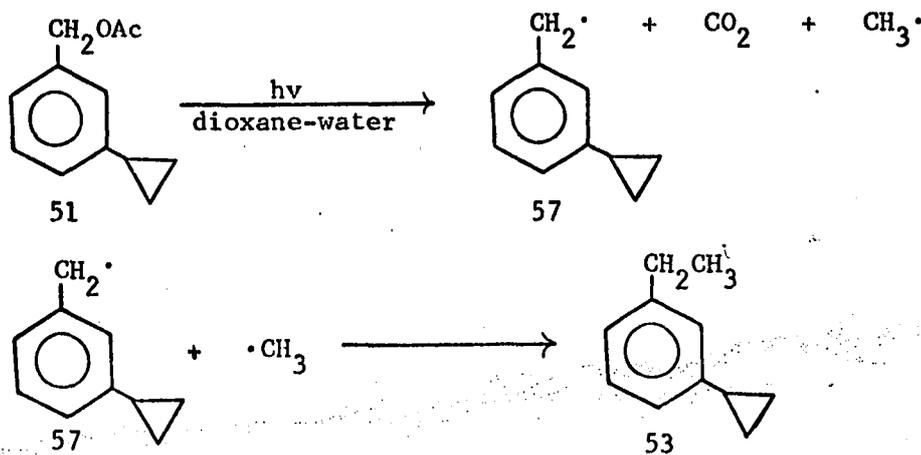
From the above discussion it appears that cyclopropane rings can undergo facile photoisomerizations from triplet excited states to yield alkenyl products.

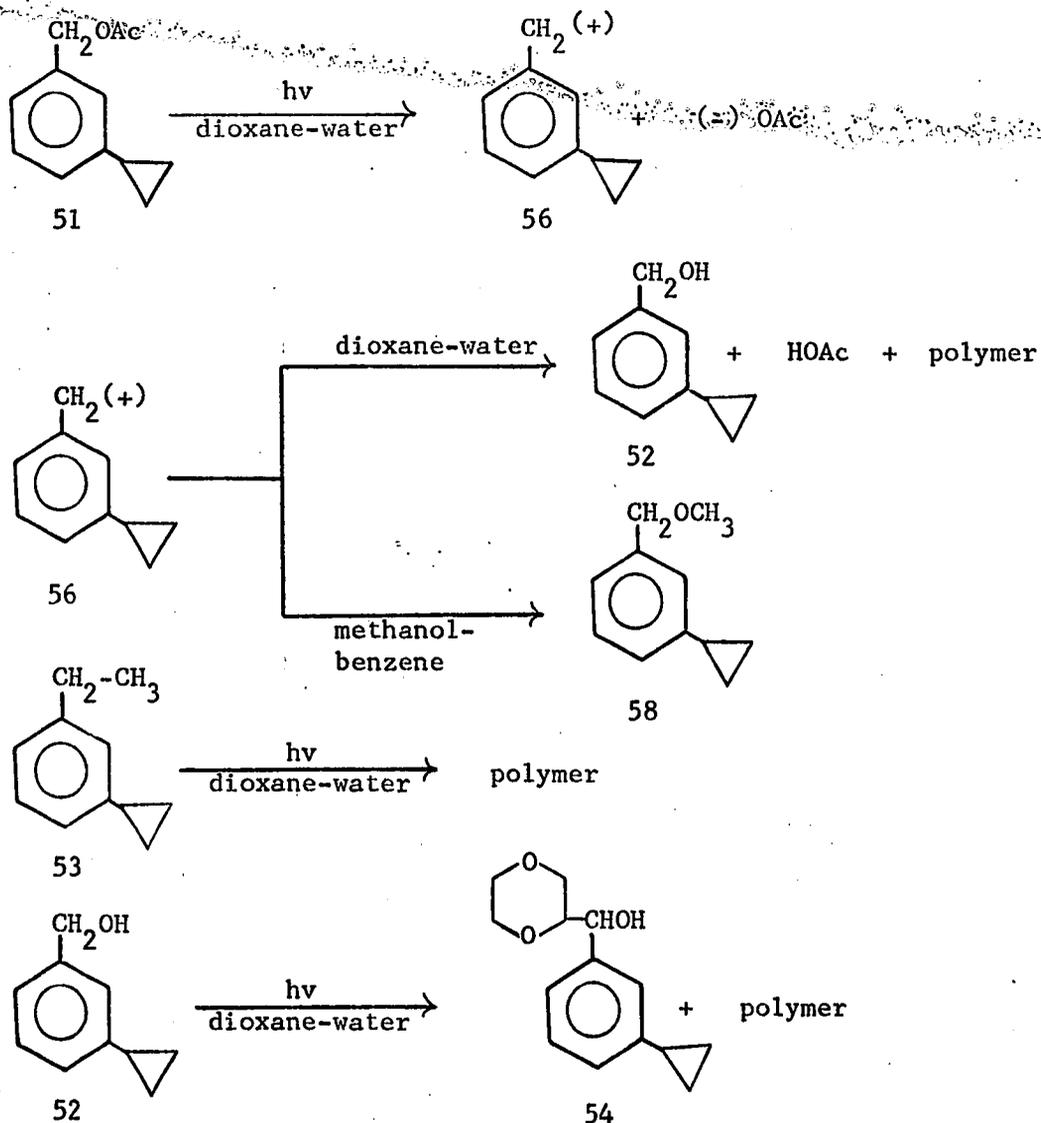
In the photolysis of *p*-cyclopropylbenzyl acetate (43), it is possible that intermediates 44 and 45 could arise from triplet excited states of 43 (analogous with the gas phase photolysis of phenylcyclopropane). Lack of the carbene intermediate 71, methylene, and 73 strongly suggests that reactions involving singlet excited states of 43 are not major reaction pathways. It must be pointed out that, although photoproducts and intermediates 44 and 45 are consistent with reactions from triplet excited states of 43, those products and intermediates arising from singlet excited states cannot be completely excluded. The photochemical reaction of cyclohexene and 43 in air yields 2-cyclohexen-1-ol (49) and 2-cyclohexen-1-one (50) (Table 5). The significance of the photochemical oxidation of cyclohexene is not clear, but it does appear that *p*-cyclopropylbenzyl acetate 43 acts as a

radical source (probably in its triplet excited state) and can abstract an allylic hydrogen atom from the cyclohexene followed by addition of oxygen to the newly created allyl radical (Kan 1966, p. 211). Similar results were obtained using acetone (triplet sensitizer) as the radical source in the presence of air, and no reaction products were detected from irradiation of cyclohexene in air in the absence of acetone or 43.

Attempts to effect triplet sensitized reactions of 43 by irradiation of 43 in benzene, using benzene as the sensitizer, were inconclusive. The products obtained from this reaction were polymeric (Table 5), but it is impossible to say whether these products arise from direct or sensitized excitation of 43 as both benzene and 43 absorb in the same region.

In the solution photolysis of *m*-cyclopropylbenzyl acetate (51) liquid products were detected, as well as small amounts of cyclopropane ring-opening products (polymer). The results can be rationalized by the following equations:





In the first reaction pathway, *m*-cyclopropylbenzyl acetate (51) undergoes initial homolytic fission into *m*-cyclopropylbenzyl radical (56) and acetoxy radicals. This is completely analogous to the benzyl radical intermediate 34 obtained from the irradiation of 3- or 4-methoxybenzyl acetate (32) or (37) (Zimmerman and Sandel 1963; see Introduction). The 3- or 4-methoxybenzyl radical intermediate (34) then

underwent dimerization to produce 4,4'- or 3,3'-dimethoxybibenzyl (35) and 3- or 4-methoxybenzylidioxane (36) by combination of dioxanyl and 3- or 4-methoxybenzyl radicals (34).

In reactions involving m-cyclopropylbenzyl radical intermediate (57) hydrogen abstraction, dimerization and combination with solvent radicals were not important processes. Meta-cyclopropylmethylbenzene (55) was detected only in small amounts and could arise from secondary photolysis reactions. Compounds m,m'-dicyclopropylbibenzyl and m-cyclopropylbenzylidioxane could not be detected as products in these reactions. The only product observed, directly involving the m-cyclopropylbenzyl radical intermediate (57), was m-cyclopropylethylbenzene (53). It seems that the acetoxy and m-cyclopropylbenzyl radicals (57) were held in close proximity to each other by some sort of solvent cage followed by decomposition of the acetoxy radical into CO<sub>2</sub> and recombination of the methyl and benzyl radicals to produce m-cyclopropylethylbenzene (53) (Pryor 1966, p. 87).

In the second reaction pathway, m-cyclopropylbenzyl acetate (51) undergoes ionization from an electronically excited state giving rise to m-cyclopropylbenzyl cation (56) and acetate anion. This cation 56 then can react with water to produce m-cyclopropylbenzyl alcohol (52) or react with methanol to produce methyl m-cyclopropylbenzyl ether (58).

The formation of alcohol 52 and ether 58 from a free radical process can be ruled out for several reasons. Combination of hydroxyl and m-cyclopropylbenzyl radicals (57) is unlikely since the hydroxyl radical is very unstable, highly reactive, and difficult to generate in

solutions. If the hydroxyl radical were formed, it would be in low concentrations, and in the presence of highly abstractable hydrogen atoms of solvents such as dioxane, it is doubtful that combination between benzyl and hydroxyl radicals would occur. Acyl-oxygen fission is also ruled out since the alcohol product 52 was not produced in solvents such as benzene and cyclohexene. Also, had acyl-oxygen fission occurred, only the alcohol 52 and no methyl ether 58 would be observed. If acyl-oxygen fission occurred, followed by loss of carbon monoxide and combination with a methyl radical to give the methyl ether product 58, one would expect this reaction to occur in other solvent systems as well as in methanol. Product 58 is only observed in solvent systems containing methanol. It is unlikely that the methyl ether product 58 would result from homolytic fission of 51 into acetoxy and m-cyclopropylbenzyl radicals 57 followed by combination with a methoxy radical. Hydrogen abstraction from the  $\alpha$ -carbon of alcohols is much more facile than from oxygen, and it is doubtful that methoxyl radicals would be formed (Zimmerman and Sandel 1963).

The polymeric products from the irradiation of m-cyclopropylbenzyl acetate (51) resulted from secondary photolysis reactions of m-cyclopropylbenzyl alcohol (52) and m-cyclopropylethylbenzene (53) (see Results). These polymeric products from secondary photolysis reactions were caused by cyclopropane ring opening and probably arose from a triplet excited state analogous to p-cyclopropylbenzyl acetate (43).

A control photolysis of m-cyclopropylethylbenzene (53) was not carried out, but polymer is the expected product (Richardson et al. 1965, Hentz and Burton 1951).

Opening of the cyclopropane ring in the control photolysis of m-cyclopropylbenzyl alcohol (52) resulted in  $\alpha$ -hydrogen abstraction of the benzyl alcohol 52 followed by combination of dioxanyl radicals with the newly created  $\alpha$ -hydroxybenzyl radical to produce  $\alpha$ -hydroxy- $\alpha$ -dioxanyltoluene (54). Dioxanyl free radicals seem likely to result from hydrogen abstraction of solvent dioxane upon cyclopropane ring opening.

Irradiation of m-cyclopropylbenzyl acetate (51) in cyclohexene produced m-cyclopropylethylbenzene (53), 2,2'-bicyclohexenyl (48), and other free radical abstraction products (polymer) resulting from opening of the cyclopropane ring. Since carbene intermediates were not detected (lack of norcarane, etc.), cyclopropane ring opening probably does not occur from singlet excited states of m-cyclopropylbenzyl acetate (51). The major reaction pathway involving ring opening appears to be through the triplet excited state of 51. No attempts were made to examine secondary photolysis reactions of 53 in cyclohexene.

In the solution photolysis of m-cyclopropylbenzyl acetate (51) it is difficult to determine which electronic state, singlet or triplet, gives rise to the observed intermediates 56 and 57.

At 2537 Å the aromatic chromophore undergoes a  $\pi-\pi^*$  transition absorbing 112.5 kcal/mole of energy in the  $\pi$  electron system of the aromatic nucleus and results in population of the first excited singlet

state of m-cyclopropylbenzyl acetate ( $S_1$ ). This energy may be emitted (fluorescence), transmitted through the aromatic nucleus into the benzyl carbon causing unimolecular homolytic cleavage of the acetate resulting in intermediate 57, or the excess energy could effect unimolecular heterolytic cleavage of the acetate bond resulting in intermediate 56. The m-cyclopropylbenzyl acetate (51) could also undergo intersystem crossing from the singlet excited state  $S_1$  to the triplet excited state  $T_1$ . It is possible that both intermediates 56 and 57 could arise from triplet excited states. Heterolytic cleavage and formation of intermediate 56 in the singlet excited state  $S_1$  could compete with intersystem crossing to give a triplet excited state  $T_1$  which results in homolytic cleavage and produces intermediate 57. Cyclopropane ring opening [bond-dissociation energy for cyclopropane is 54 kcal/mole (Benson and Amano 1962)] of m-cyclopropylbenzyl acetate (51) probably arises from the triplet excited state  $T_1$ . From the studies of O'Connell, Martin, and Lis (1970) it appears that fluorescence and phosphorescence are probably not the major pathways of deactivation for m-cyclopropylbenzyl acetate (51) in solution photolysis reactions.

The excess electronic energy of the system could also be lost by radiationless deactivation of either the singlet or triplet excited state.

Attempts to effect triplet sensitized reactions of 51 by irradiation of 51 in benzene or benzene and methanol, using benzene as the sensitizer, were inconclusive. The products obtained from these reactions were m-cyclopropylethylbenzene (53), derived from intermediate

57, and methyl m-cyclopropylbenzyl ether (58), derived from intermediate 56. It is impossible to say whether these products arise from direct or sensitized excitation of 51 as both benzene, 51, and the photoproducts absorb in the same regions. Quenching of photoproduct formation was not effected by irradiation of 51 in benzene.

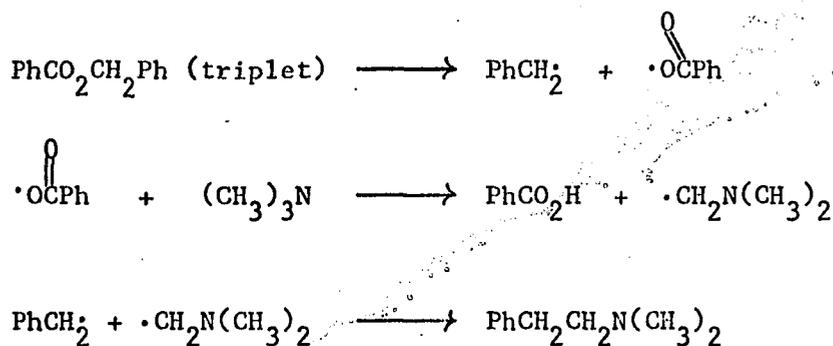
Irradiation of 51 in the presence of piperylene [a known triplet quencher (Turro 1967, p. 181)] was carried out to see if product formation would be inhibited. If the observed intermediates 56 and 57 come from triplet excited states, it should be possible to quench these states, using piperylene, and thus inhibit formation of photoproducts 53 and 58. However, a methanol solution of 0.046 M in 51 and 0.46 M in piperylene ( $E_T = 58$  kcal/mole) failed to quench photoproduct formation of 53 and 58 (see Results). This lack of quenching may be the result of a very rapid rate of unimolecular reaction from the triplet excited state  $T_1$  of 51. Since dimerization products of piperylene were not detected (efficient energy transfer to piperylene by  $T_1$  of 51 was not effected) it is possible that the concentration of piperylene was too low to involve a bimolecular quenching mechanism. The rate of quenching could be enhanced by increasing the concentration of piperylene but unfortunately piperylene has strong absorption bands in the 2537 Å regions. Consequently, its use as a quencher in this system is a poor one. Other quenchers have the same drawbacks as piperylene since they absorb light in the same regions as m-cyclopropylbenzyl acetate (51).

There is also a possibility that intermediates 56 and 57 arise from singlet excited states of 51 and therefore triplet energy

quenchers would have no effect on product formation of meta-cyclopropyl-ethylbenzene (53) and methyl meta-cyclopropylbenzyl ether (58).

It was of interest to see if m-cyclopropylbenzyl acetate (51) could act as a sensitizer and cause dimerization of 2-norbornene [a known dimerization effected through triplet energy sensitizers (Kropp 1969)]. Dimerization of 2-norbornene was observed (Table 8) but photo-products 53 and 58 were also produced at the same time as the dimer product. Since both 53 and 58 absorb light in same regions as 51, it is impossible to determine which species (53, 58, or 51) is actually causing the dimerization reaction.

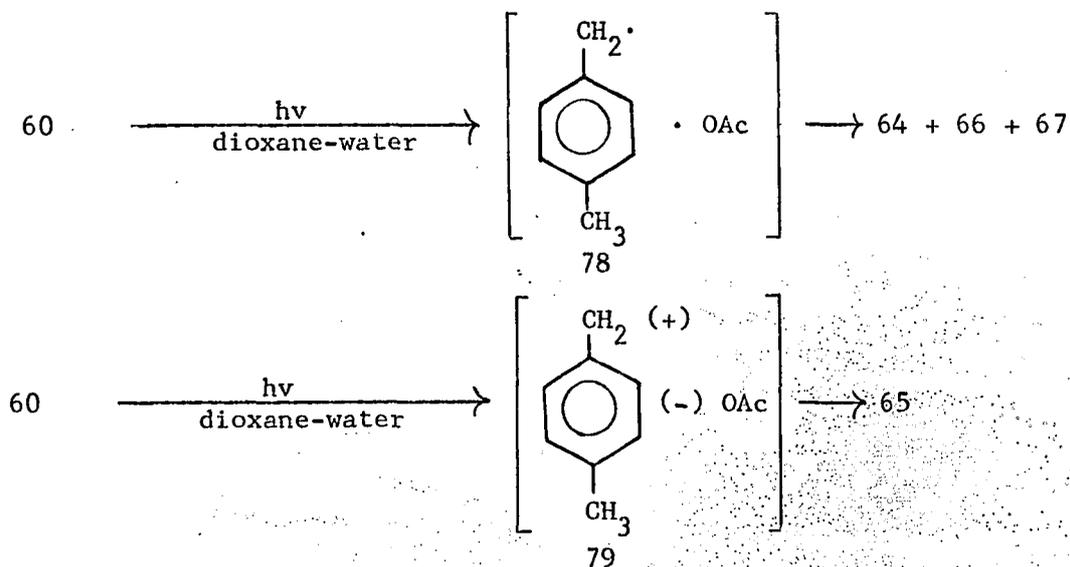
An example of a benzyl radical intermediate, similar to 57, arising from a triplet excited state has been observed by Cookson, Hudec, and Mirza (1967). Irradiation of benzyl benzoate in aliphatic alcohol or amine solvents results in benzylation possibly involving a triplet excited state giving rise to a benzyl radical intermediate similar to 57.



Other benzyl acetate systems were studied (para- and meta-methylbenzyl acetates 60 and 61, Table 7), and each gave results completely analogous with the studies of Zimmerman and Sandel (1963)

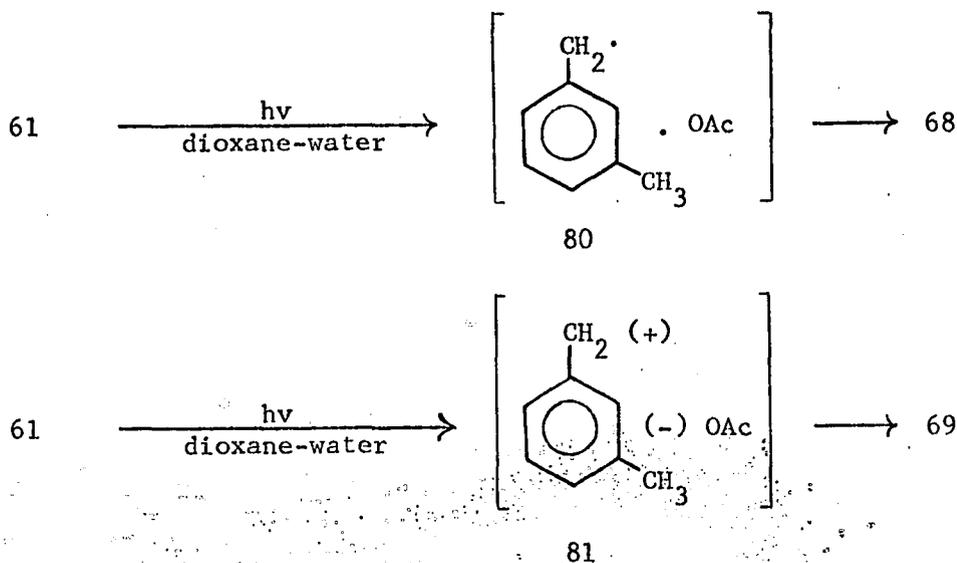
for para- and meta-methoxybenzyl acetates 32 and 37 (see Introduction section).

Irradiation of p-methylbenzyl acetate (60) in dioxane-water gave rise to a benzyl radical intermediate 78, analogous to 34 and 57, and a carbonium ion intermediate 79, analogous to 39 and 56.



Products arising from intermediate 78 were p-methylethylbenzene (64), 1,2-di-(4-methylphenyl)ethane (66), and p-methylbenzyl dioxane (67). Both 66 and 67 are completely analogous to 35 and 36. The alcohol 65 from intermediate 79 was not a major product and may have come from a ground state reaction. In these photolysis reactions of 60, the benzyl radical intermediate 78 is of major importance in product formation (50% free radical products, 15% ionic products, Table 7).

Irradiation of m-methylbenzyl acetate (61) in dioxane-water gave rise to intermediates 80 and 81 in complete analogy with 34, 39, 78 and 79.



The product arising from intermediate 80 was m-methylethylbenzene (68), analogous with 53 and 64. The product arising from 81 was m-methylbenzyl alcohol (69), analogous to 40, 52, and 65. In these photolysis reactions of 61, the ionic intermediate 81 is of major importance in product formation (60% ionic products, 40% free radical products, Table 7).

### Summary

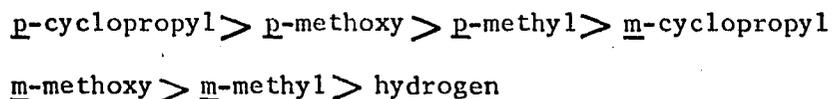
Cyclopropane ring opening followed by rearrangement and polymerization is the major reaction pathway in the photolysis of p-cyclopropylbenzyl acetate (43). This photoisomerization of the cyclopropane ring in 43 is more important than the ability of the cyclopropyl group to conjugate or effect orbital overlap with the aromatic nucleus. Thus the ability of the cyclopropane ring to transmit electron density toward an electron deficient center is lost upon excitation, and the cyclopropyl group cannot assist in the solvolysis of 43 in the excited state.

In the photolysis of m-cyclopropylbenzyl acetate (51) the cyclopropyl group remains intact during excitation and can effectively conjugate, through orbital overlap, with the aromatic nucleus. In the photolysis of 51 an ionic intermediate 56 is favored and the cyclopropyl group can transmit electron density toward an electron deficient center and assist in the solvolysis of 51 in the excited state.

In the photolysis of p-methylbenzyl acetate (60) and p-methoxybenzyl acetate (32) the methyl and methoxy groups could not transmit their electron density toward the benzylic carbon in order to assist solvolysis (ionization). Thus homolytic cleavage was observed as the major reaction pathway (see Introduction section).

In the photolysis of m-methylbenzyl acetate (61) and m-methoxybenzyl acetate (37) the methyl and methoxy groups can, in this case, transmit their electron density toward the benzylic carbon in order to assist solvolysis (ionization). Thus heterolytic cleavage was observed as the major reaction pathway (see Introduction).

A rough comparison of free radical products versus ionic products can be made from the photolysis of meta- and para-substituted benzyl acetate systems in dioxane-water. The effect of electron donating groups on the production of free radical products through photolysis of substituted benzyl acetates are in the following order:



Larger amounts of free radical products are produced from the photolysis of p-cyclopropylbenzyl acetate in dioxane-water than from p-methoxybenzyl acetate. The effect of electron donating groups on

the production of ionic products through photolysis of substituted benzyl acetate are in the following order:

m-methyl > m-cyclopropyl > m-methoxy > p-methyl > hydrogen

Larger amounts of ionic products (m-methylbenzyl alcohol, solvolysis product) are produced from the photolysis of m-methylbenzyl acetate in dioxane-water than from m-cyclopropylbenzyl acetate.

It is concluded that a cyclopropyl or methyl group can effect meta transmission of electron density toward an electron-deficient center in benzyl acetate systems and can result in photochemical solvolysis reactions.

#### LITERATURE CITED

- Benson, S. W., and Amano, A., J. Chem. Phys., 36, 3464 (1962).
- Berlman, I. B., "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, 1965.
- Bernett, W. A., J. Chem. Educ., 44, 17 (1967).
- Bradshaw, J. S., J. Org. Chem., 31, 237 (1966).
- Brown, H. C., and Cleveland, J. D., J. Amer. Chem. Soc., 88, 2051 (1966).
- Calvert, J. G., and Pitts, J. N., "Photochemistry," John Wiley and Sons, Inc., New York, 1966.
- Chapman, D., and Magnus, P. D., "Introduction to Practical High Resolution Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, 1966.
- Cheronis, N. D., and Entrikin, J. B., "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, 1961.
- Clark, R. A., and Fiato, R. A., J. Amer. Chem. Soc., 92, 4736 (1970).
- Cookson, R. C., Hudec, J., and Mirza, N. A., Chem. Comm., 824 (1967).
- Corbin, T. F., Hahn, R. C., and Shechter, H., "Organic Syntheses," Vol. 44, W. E. Parham, Ed., John Wiley and Sons, Inc., New York, 1964, p. 30.
- Dauben, W. G., and Berezin, G. H., J. Amer. Chem. Soc., 89, 3449 (1967).
- Dauben, W. G., and Shaffer, G. W., Tetrahedron Lett., 4415 (1967).
- Deno, N., Richey, H. G., Jr., Liu, J. S., Hodge, J. D. Houser, J. J., and Wisotsky, M. J., J. Amer. Chem. Soc., 84, 2016 (1962).
- Doering, W. von E., Buttery, R. G., Laughlin, R. G., and Chaudhuri, N., J. Amer. Chem. Soc., 78, 3224 (1956).
- Elad, D., and Youssefyeh, R. D., J. Org. Chem., 29, 2031 (1964).

- Ferguson, L. N., J. Chem. Educ., 46, 404 (1969).
- Fieser, L. F., J. Amer. Chem. Soc., 46, 2639 (1924).
- Fieser, L. F., "Organic Experiments," D. C. Heath and Company, Boston, Massachusetts, 1964.
- Fieser, L. F., and Fieser, M., "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, 1967.
- Foote, J. K., Ph. D. Dissertation, University of California, Riverside, 1966.
- Gilman, H., and Catlin, W. E., "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, 1967, p. 188.
- Goodman, A. L., and Eastman, R. H., J. Amer. Chem. Soc., 86, 908 (1964).
- Griffin, G. W., Covell, J., Petterson, R. C., Dodson, R. M., and Klose, G., J. Amer. Chem. Soc., 87, 1410 (1965).
- Griffin, G. W., O'Connell, E. J., and Hammond, H. A., J. Amer. Chem. Soc., 85, 1001 (1963).
- Hahn, R. C., Corbin, T. F., and Shechter, H., J. Amer. Chem. Soc., 90, 3404 (1968).
- Hahn, R. C., Howard, P. H., Kong, S. M., Lorenzo, G. A., and Miller, N. L., J. Amer. Chem. Soc., 91, 3558 (1969).
- Hammond, G. S., Saltiel, J., Lamola, A. A., Turro, J. N., Bradshaw, J. S., Cowan, D. O., Counsell, R. C., Vogt, V., and Dalton, C., J. Amer. Chem. Soc., 86, 3197 (1964a).
- Hammond, G. S., Wyatt, P., DeBoer, C. D., and Turro, N. J., J. Amer. Chem. Soc., 86, 2532 (1964b).
- Hauser, C. R., and Breslow, D. S., "Organic Synthesis," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, 1967, p. 408.
- Havinga, E., de Jongh, R. O., and Kronenberg, M. E., Helv. Chim. Acta, 50, 2550 (1967).
- Heathcock, C. H., and Poulter, S. R., J. Amer. Chem. Soc., 90, 3766 (1968).

- Hennion, G. F., and Sheehan, J. J., *J. Amer. Chem. Soc.*, 71, 1964 (1949).
- Hentz, R. R., and Burton, M., *J. Amer. Chem. Soc.*, 73, 532 (1951).
- Hess, L. D., Jacobson, J. L., Schaffner, K., and Pitts, J. N., Jr., *J. Amer. Chem. Soc.*, 89, 3684 (1967).
- Hess, L. D., and Pitts, J. N., Jr., *J. Amer. Chem. Soc.*, 89, 1973 (1967).
- Hoffman, R., *Tetrahedron Lett.*, 3819 (1965).
- Jones, L. B., and Jones, V. K., *Tetrahedron Lett.*, 1493 (1966).
- Jorgenson, M. J., *J. Amer. Chem. Soc.*, 91, 6432 (1969).
- Jorgenson, M. J., and Leung, T., *J. Amer. Chem. Soc.*, 90, 3769 (1968).
- Kan, R. O., "Organic Photochemistry," McGraw-Hill Book Company, New York, 1966.
- Kropp, P. J., *J. Amer. Chem. Soc.*, 89, 1126 (1967).
- Kropp, P. J., *J. Amer. Chem. Soc.*, 91, 5783 (1969).
- Leermakers, P. A., and Ross, M. E., *J. Org. Chem.*, 31, 301 (1966).
- Leermakers, P. A., and Vesley, G. F., *J. Org. Chem.*, 30, 593 (1965).
- LeGoff, E., *J. Org. Chem.*, 29, 2048 (1964).
- Levina, R. Ya., Gembitskii, P. A., Guseva, L. P., and Agasyan, P. K., *Zh. Obshch. Khim.*, 34, 146 (1964).
- Meisels, G. G., and Arnold, D. R., *J. Phys. Chem.*, 72, 3061 (1968).
- Mi'cović, V. M., and Mihailović, M. L. J., *J. Org. Chem.*, 18, 1190 (1953).
- Monti, S. A., *J. Org. Chem.*, 35, 380 (1970).
- Music, J. F., and Matsen, F. A., *J. Amer. Chem. Soc.*, 72, 5256 (1950).
- Nishida, S., Moritani, I., and Sato, T., *J. Amer. Chem. Soc.*, 89, 6885 (1967).
- O'Connell, E. J., Jr., Martin, G., and Lis, J. T., *Chem. Comm.*, 95 (1970).

- Pearson, D. E., Stamper, W. E., and Suthers, B. R., *J. Org. Chem.*, 28, 3147 (1963).
- Pews, R. G., and Ojha, N. D., *J. Amer. Chem. Soc.*, 91, 5769 (1969).
- Pittman, C. U., Jr., and Olah, G. A., *J. Amer. Chem. Soc.*, 87, 2998 (1965).
- Pitts, N. J., Jr., and Norman, I., *J. Amer. Chem. Soc.*, 76, 4815 (1954).
- Pryor, W. A., "Free Radicals," McGraw-Hill Book Company, New York, 1966.
- Randerath, K., "Thin-Layer Chromatography," Academic Press, New York, 1964.
- Rawson, R. J., and Harrison, I. T., *J. Org. Chem.*, 35, 2057 (1970).
- Richardson, D. B., Durrett, L. R., Martin, J. M., Jr., Putnam, W. E., Slaymaker, S. C., and Dvoretzky, I., *J. Amer. Chem. Soc.*, 87, 2763 (1965).
- Sadtler NMR, IR Vol. 19, Spectra Catalogue, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1966.
- Strait, L. A., Ketcham, R., Jambotkar, D., and Shah, V. P., *J. Amer. Chem. Soc.*, 86, 4628 (1964).
- Turro, N. J., "Molecular Photochemistry," W. A. Benjamin, Inc., New York, 1967.
- Vogel, A. I., "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, 1962.
- Weigert, F. J., and Roberts, J. D., *J. Amer. Chem. Soc.*, 89, 5962 (1967).
- Zimmerman, H. E., and Sandel, V. R., *J. Amer. Chem. Soc.*, 85, 915 (1963).