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## Doctor's Dissertation

**Ketone Sensitized Photochemical Degradation  
of  
2-Methoxy-6-Methyltetrahydropyran**

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**January, 1980**

KETONE SENSITIZED PHOTOCHEMICAL DEGRADATION  
OF  
2-METHOXY-6-METHYLTETRAHYDROPYRAN

A thesis submitted by

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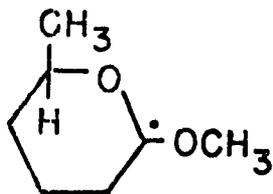
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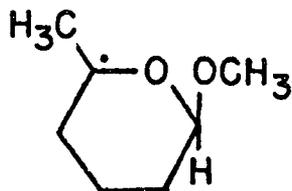
A study of the distribution of photoproducts as a function of time indicated that all of the isolated products were primary, and not the result of secondary degradations.

Optically active cis-I was synthesized and subjected to photolysis in the presence of acetophenone. The optical activity of isolated samples of trans-I, cis-I and lactone (III) showed that there had been no loss of optical activity for the latter two compounds. The observed rotation of trans-I, indicated it, however, must be formed by both isomerization of C-2 and C-6 of cis-I, with the latter process predominating.

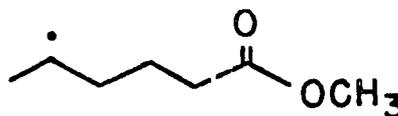
Product VI and some of trans-I must be formed from the C-2 radical VII, while V and most of trans-I are formed from the C-6 radical VIII. Products II and IV appear to derive from radical IX, which is produced from the opening of radical VII. Radical IX is apparently not capable of regenerating radical VII since lactone III and unconverted cis-I (both of which are presumably formed from radical VII) retain their optical purity. Lactone III is thought to arise by elimination of methyl radical from VII and/or reaction of VII with oxygen followed by elimination of methyl peroxide radical.



VII



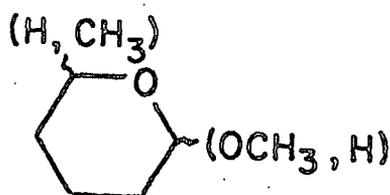
VIII



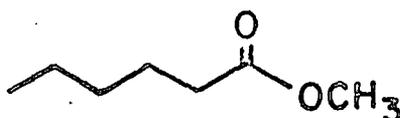
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SUMMARY

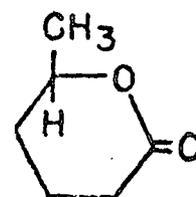
Photodegradation of 2-methoxy-6-methyltetrahydropyran(I) was studied as a model for the photodegradation of carbohydrates. The photolysis of cis-I for 20 hours in benzene with acetophenone as a sensitizer gave a mixture of products. The products were isolated by preparative gas chromatography and characterized by spectral means. The compounds isolated, along with approximate yields, were as follows: trans-I, 8.5%; methyl hexanoate(II), 12%; 6-methyltetrahydropyran-2-one(III), 1.9%; methyl 5-phenylhexanoate(IV), 6.7%; 1,7-dimethyl-7-phenyl-6,8-dioxobicyclo(3.2.1)octane(V), 1.4%; 2-methoxy-2-(1-phenyl-1-hydroxyethyl)-6-methyltetrahydropyran(VI), 7.2%.



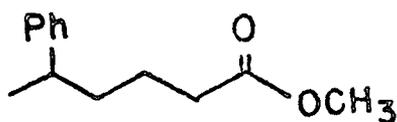
cis-I  
trans-I



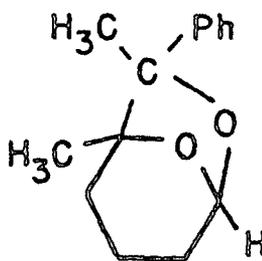
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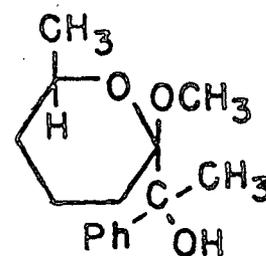
III



IV



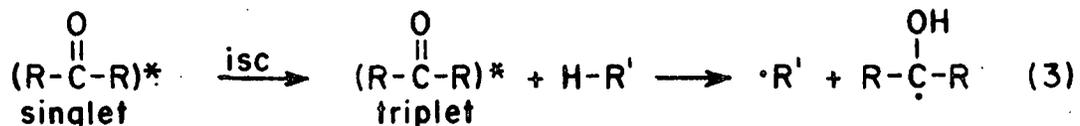
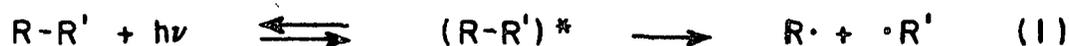
V



VI

The amount of lactone (III) produced was found to be highly dependent on the level of oxygen present during photolysis. Increased levels of oxygen led to increased amounts of lactone while reducing the overall yield. Thoroughly degassed solutions of cis-I gave small amounts of III upon photolysis.

is given below [Eq. (3)]. Ketones are excited to the  $S_1$  energy level by absorption of a photon in the near ultraviolet region. This singlet species quickly undergoes intersystem crossing, isc, to a more stable triplet state (1). It is this triplet state species which can then abstract a hydrogen atom forming two free radicals.



#### PHOTODEGRADATION OF CELLULOSE

Exposure of cotton cellulose to near ultraviolet light results in a loss in the degree of polymerization and an increase in the number of carbonyl and carboxyl groups (2). The increase in carboxyl groups correlates well with the number of chain cleavages. The predominant chemical change in the cellulose is the formation of carbonyl groups.

These results are in agreement with those for irradiation of cellulose at shorter wavelengths as well (3). Direct photolysis has been suggested to account

## INTRODUCTION

### GENERAL ASPECTS OF PHOTODEGRADATION

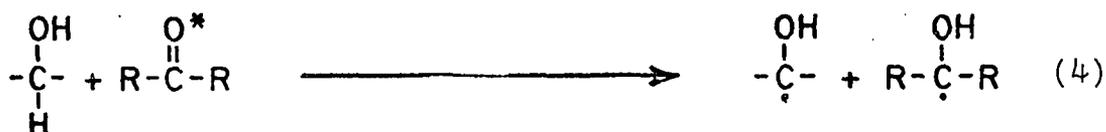
The energy available from a photon of light in the ultraviolet region is of the same order of magnitude as the energy of a covalent bond. The result of absorption of a photon by a molecule can be the dissociation of a bond. Bond breaking results in two unstable species which and recombine, fragment, and rearrange to form degradation products (1).

Even molecules which are incapable of absorbing light directly can be photodegraded by a process known as photosensitization. In the sensitized process the energy is absorbed by a sensitizer molecule. The energy promotes an electron in the sensitizer molecule, producing an excited state. This excited sensitizer molecule can then transfer its energy to, or react with, a second species in the system. Energy transfer produces an excited state (usually triplet) of the second molecule (acceptor). A typical intermolecular reaction of excited state (triplet) ketones is abstraction of a hydrogen atom (1).

Equation (1) depicts the process of direct photolysis. The molecule  $R-R'$  absorbs a photon of light and is promoted to the excited state. This excited state species can either reemit the energy as a photon (returning to the ground state), rearrange, or it may undergo cleavage into two free radicals. Equation (2) is an example of energy transfer. The sensitizer molecule,  $S$ , is promoted to the excited state by a photon of light. This excited state sensitizer,  $S^*$ , can then transfer its energy to the molecule  $R-R'$ . The excited species,  $(R-R')^*$ , can then undergo the same reactions discussed for Equation (1). An example of hydrogen abstraction by an excited state ketone

for the degradation seen at 254 nm (3). Pure carbohydrates do not absorb light in the near ultraviolet region, ca. 350 nm (4). For this reason it has been suggested that sensitized photolysis is important in the degradation of cellulose by sunlight (3). Natural impurities, such as lignin, or oxidized sites in cellulose could provide carbonyl sensitizers which would operate in the near ultraviolet region. Irradiation at shorter wavelengths could result in sensitized or direct photolysis reactions.

Carbonyl-sensitized photolysis of a secondary alcohol (e.g., a carbohydrate) is represented in Equation (4). A ketone, which has been excited by a near ultraviolet photon, could abstract a hydrogen atom from the carbohydrate. Substitution of oxygen on carbon atoms enhances the stability of radicals formed on that carbon atom via resonance. Disubstitution of oxygen (e.g., C-1 of a carbohydrate) should enhance this stability even further (5).



The selectivity of hydrogen abstraction is not known for cellulose and other complex carbohydrates. Information of this type would be important to the understanding of the pathways by which carbohydrates can photochemically degrade.

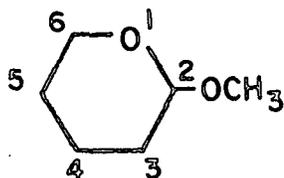
Understanding of the basic photochemical processes involved with carbohydrates is made difficult by the wide variety of conditions reported in the literature (6). Workers interested in textiles are concerned with the effects of dyes on the photochemistry of cellulose. Others have studied the effects

of inorganic additives on carbohydrate photochemistry (4). A very strong effect is reported for the presence of molecular oxygen (3). Oxygen was seen to increase the rate of photodegradation in some cases, including the formation of carbon dioxide (7). It has also been shown that primary photodegradation products often absorb ultraviolet light more strongly than the starting materials so that secondary reactions obscure primary processes (7).

Since actual carbohydrates are difficult to study with regard to the fundamental process of photodegradation, the logical approach is to study model compounds. The next sections deal with discussions of the photochemistry of carbohydrate models.

#### PHOTODEGRADATION OF 2-METHOXYTETRAHYDROPYRAN(X)

McKelvey (4) has studied the photochemical degradation reactions of X in the presence of benzophenone. He chose this compound as a model system for a glycoside. The six-membered pyran ring is an analog to the ring structure of the common monosaccharides. The methoxy group at the 2-position is analogous to the glycosidic linkage of polysaccharides.

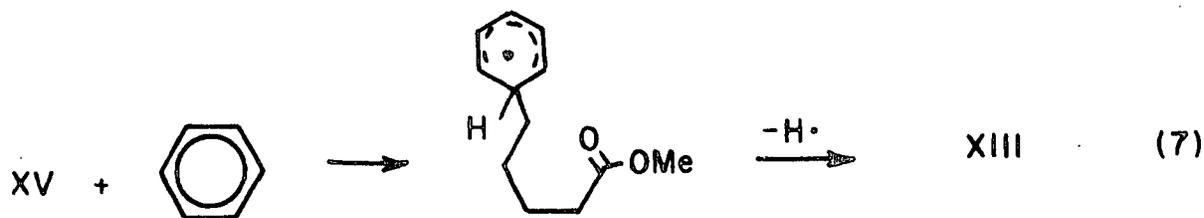
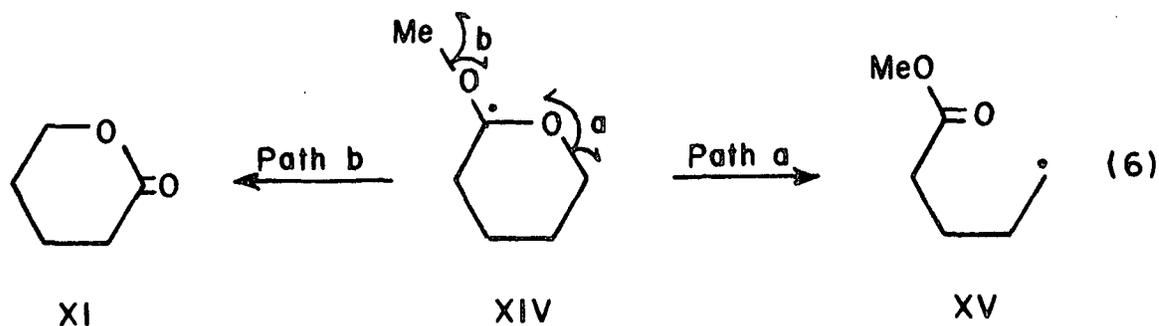
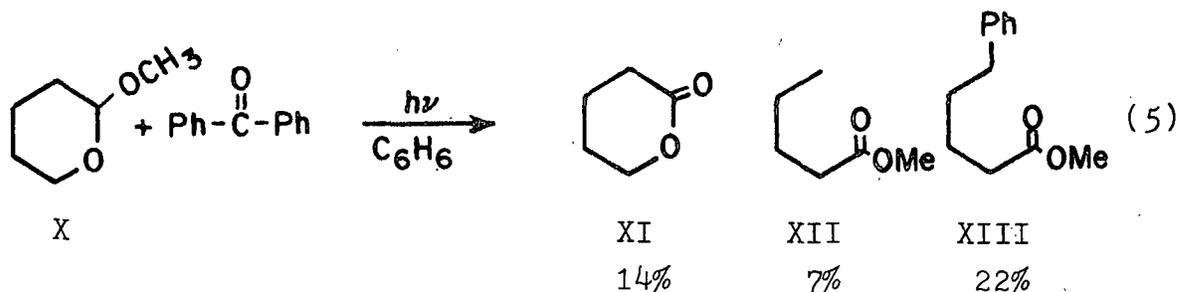


X

Omission of hydroxyl functions in this model was intentional. Because of the polyfunctionality of carbohydrates, hydrogen abstraction reactions can take place at many sites. Replacing the hydroxyl functions with hydrogens reduces the number of highly labile sites for abstraction. The most labile hydrogen in

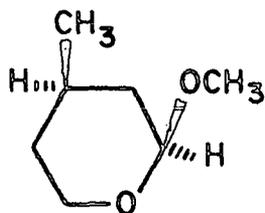
X should be the hydrogen at the 2-position. McKelvey reported that ketone-sensitized photodegradation of X was initiated by abstraction of the hydrogen from the 2-position (4).

Irradiation of X and benzophenone in benzene produced three volatile photo-products [Eq. (5)]. Two reaction pathways were suggested (4) to account for these products [Eq. (6)]. After the hydrogen abstraction step, the free radical XIV could decompose by elimination of a methyl radical (path b) or by a ring opening step to form a primary alkyl radical (path a). The primary alkyl radical (XV), formed as a consequence of path a, could then abstract hydrogen from a molecule of X (leading to a chain process) or from the solvent to form XII. The presence of XIII can be explained by the reaction of XV with the benzene solvent [Eq. (7)].

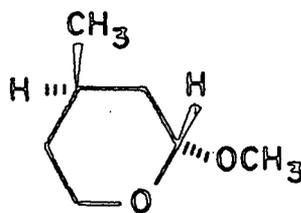


PHOTODEGRADATION OF 2-METHOXY-4-METHYLTETRAHYDROPYRAN (XVI)

Addition of a methyl group at the 4-position of the 2-methoxytetrahydropyran structure provides a model compound which has structural isomers, namely cis- and trans-XVI. McKelvey and Hayday studied the photochemical degradation of XVI in the presence of benzophenone (8).

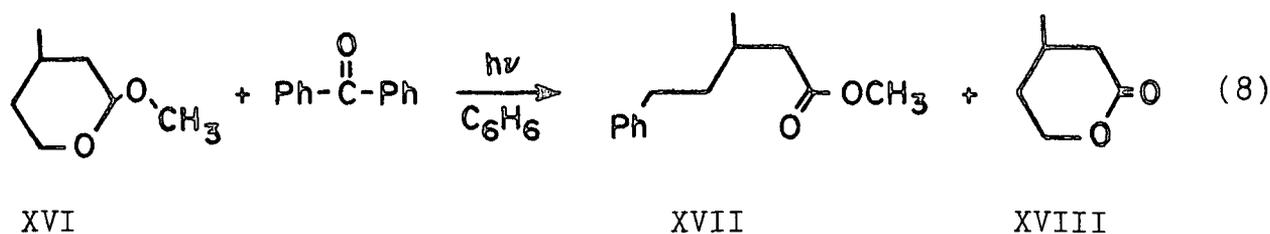


cis-XVI



trans-XVI

Irradiation of XVI and benzophenone in benzene produced a mixture of methyl 3-methyl-5-phenylvalerate (XVII) and 4-methyltetrahydropyran-2-one (XVIII). The yields of XVII and XVIII, based on consumed starting material, were 5 and 29%, respectively. Interestingly, no methyl 3-methylvalerate was produced (8) even though the analogous product was formed in the photodegradation of 2-methoxytetrahydropyran (4).



McKelvey and Hayday (8) observed that in direct competition the cis isomer was 8 times more reactive than the trans and explained their results on differences in conformation. It is known that cis- and trans-XVI exist as primarily single conformers (9), illustrated in Fig. 1. The transition state leading to the C-2 radical form of XVI involves abstraction of the hydrogen from the 2-position. They suggested that abstraction of an axial hydrogen (as would be the

case for cis-XVI) would be stabilized to a greater extent than abstraction of an equatorial hydrogen (trans-XVI). Overlap of the bond being broken with nonbonding orbitals on the ring oxygen was the reason given for this stabilization effect. Abstraction of an axial hydrogen allows overlap with two nonbonding orbitals, while equatorial abstraction is stabilized by only one such overlap. This proposed stereoelectronic effect is depicted in Fig. 2.

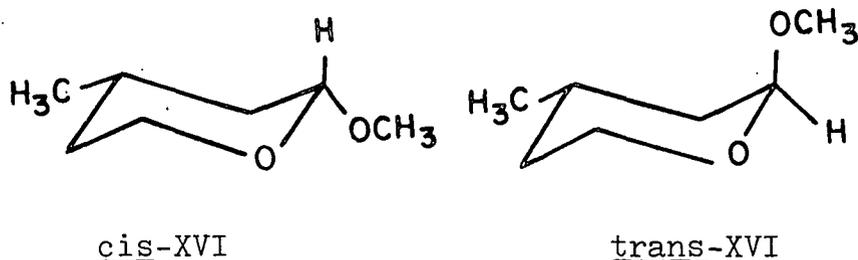


Figure 1. Preferred Conformations for cis- and trans-XVI (8)

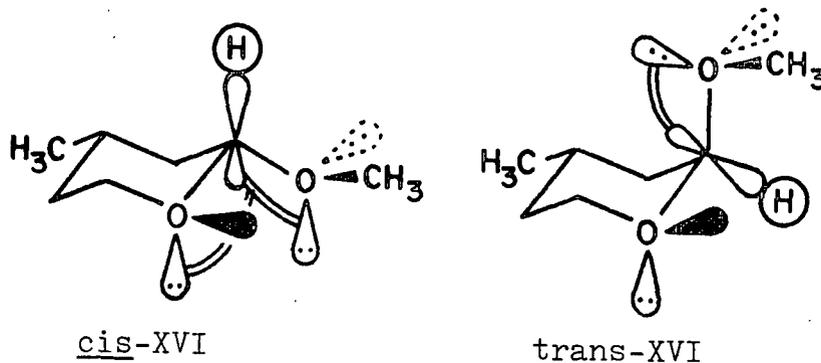
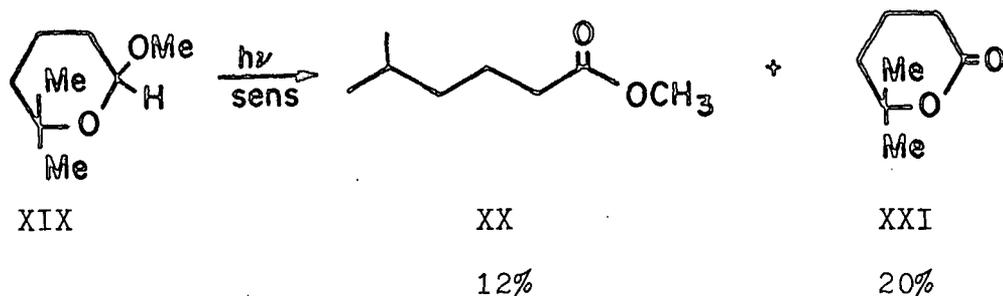


Figure 2. Enhancement of Axial Hydrogen Abstraction by the Stereoelectric Effect (8)

#### PHOTODEGRADATION OF 2-METHOXY-6,6-DIMETHYLTETRAHYDROPYRAN (XIX)

Bernesconi and Descotes (10) investigated the photodegradation of XIX with benzophenone in benzene solvent. The products were methyl 5-methylhexanoate (XX) and 6,6-dimethyltetrahydropyran-2-one (XXI). Products XX and XXI were explained by abstraction of the hydrogen from the 2-position of XIX, followed by ring opening or elimination of a methyl radical, respectively (10).



The yields of XX and XXI were 12 and 20%, respectively, based on consumed starting material. Since XIX exists as only one isomer (racemic pair) no comparison of axial versus equatorial hydrogen abstraction was possible. It is interesting to note that elimination of a methyl radical can compete with ring opening which would provide a much more stable tertiary radical. On the basis of radical stability one would have expected ring opening to be strongly favored in this system.

#### UNANSWERED QUESTIONS

Some unanswered questions remain from the earlier work. The formation of lactone, at the expense of the energetically more favorable pathway of ring opening, is not well understood. The possibility of a reversible ring opening step was proposed (8) but no evidence was available to answer this question. If ring opening is reversible this could increase the concentration of the C-2 radical; this could, in turn, allow an increased amount of lactone formation.

It has been suggested (11) that stereoelectronic effects could account for lactone formation at the expense of ring opening. It has been shown that 2-alkoxytetrahydropyran-2-yl radicals are not planar at the radical center (12). Because of the geometry of these radicals, it is possible for the O-CH<sub>3</sub> bond to nearly align itself with the semioccupied orbital at the radical center (Fig. 3). The transition state leading to loss of a methyl radical could thus be stabilized by overlap with the semioccupied orbital at the radical center (11).

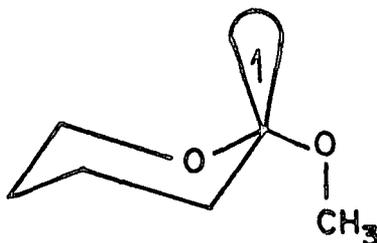


Figure 3. Stabilization of Transition State Leading to Loss of a Methyl Radical

Finally, the importance of molecular oxygen to lactone formation has not been explored. McKelvey (4,8) mentioned that his reaction samples were degassed prior to irradiation. Bernesconi and Descotes (10) did not disclose whether this precaution was taken in their work. It seems possible that coupling of the C-2 radical with molecular oxygen followed by elimination of methyl peroxy radical could account for some of the variability in lactone formation (Fig. 4).

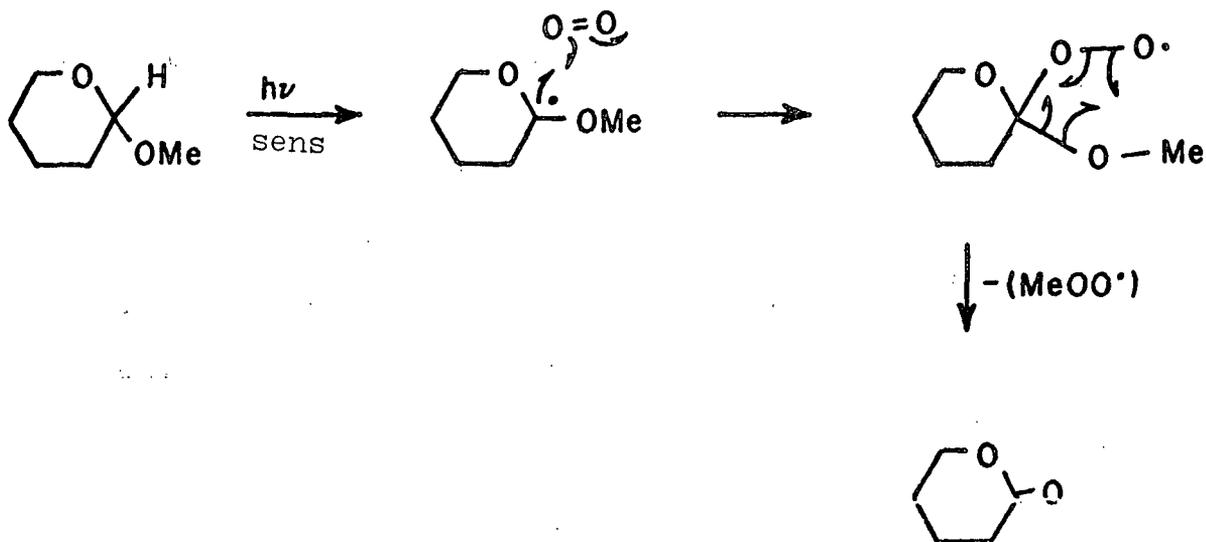


Figure 4. Possible Contribution of Molecular Oxygen to Lactone Formation

#### RESEARCH OBJECTIVES

Ketone-sensitized photodegradation of 2-methoxy-6-methyltetrahydropyran(I) was studied. This compound was selected for two primary reasons. The first reason was that I was more representative of common hexoses than models previously studied. Secondly, I could be made readily in an optically active form which

allowed a study of the reversibility of the ring opening step. Research objectives were designated as follows:

1. To synthesize racemic and optically active I and anticipated photo-products.
2. To identify the best set of reaction conditions for studying the photodegradation of I.
3. To identify the photoproducts of I.
4. To investigate the importance of molecular oxygen to lactone formation.
5. To study the reaction mixture composition as a function of time, for the purpose of determining primary versus secondary photoproducts.
6. To degrade optically active I and observe the specific rotation of any lactone produced.
7. To assimilate the observations into a general mechanism which should be applicable to carbohydrate photodegradation.

Figure 5 represents the reaction scheme envisioned for the photodegradation of I. This scheme was tested by the experimental program. The question marks designate specific research goals, namely, the detection of coupling products, the influence of molecular oxygen on lactone formation and the importance of interconversion of radical intermediates.

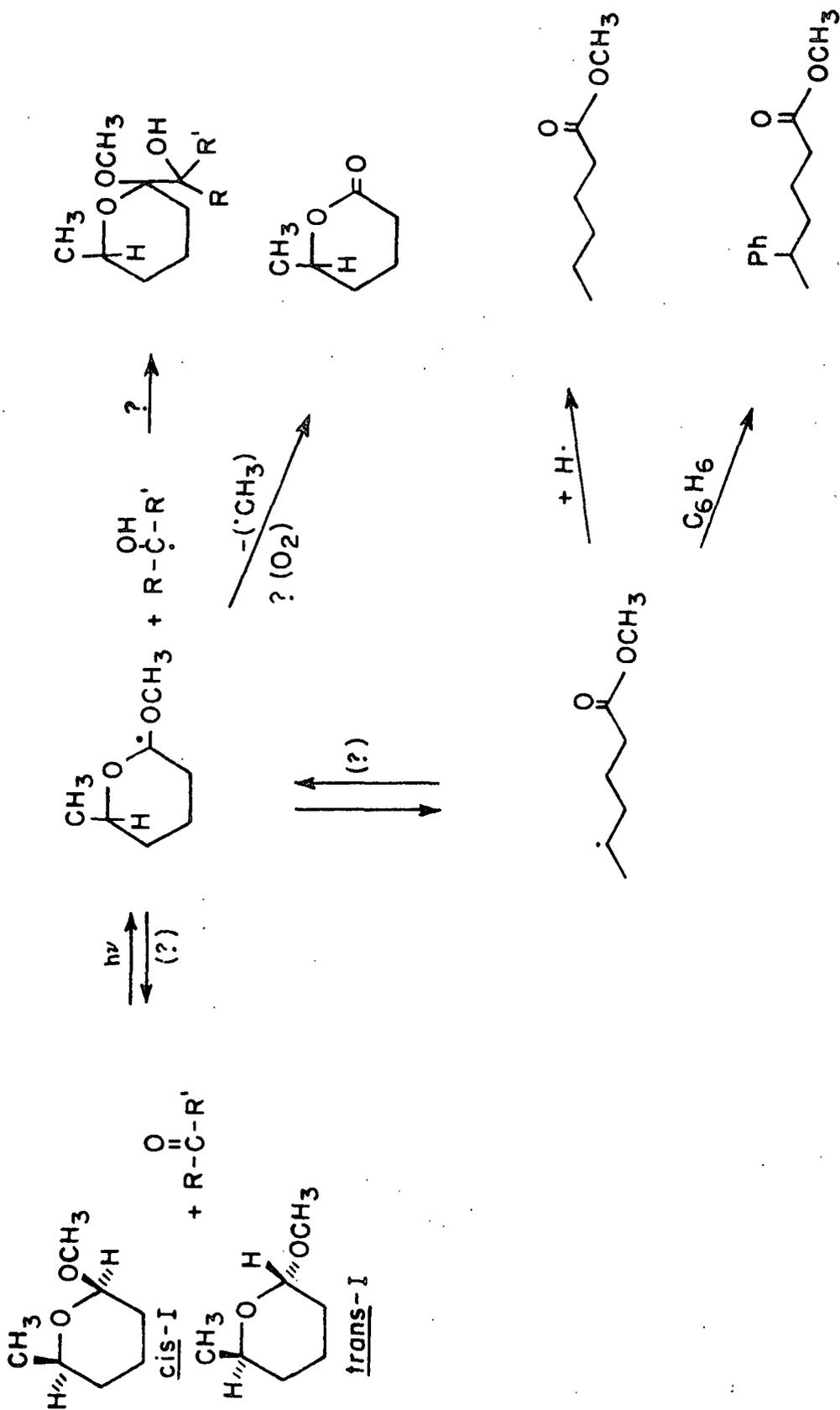


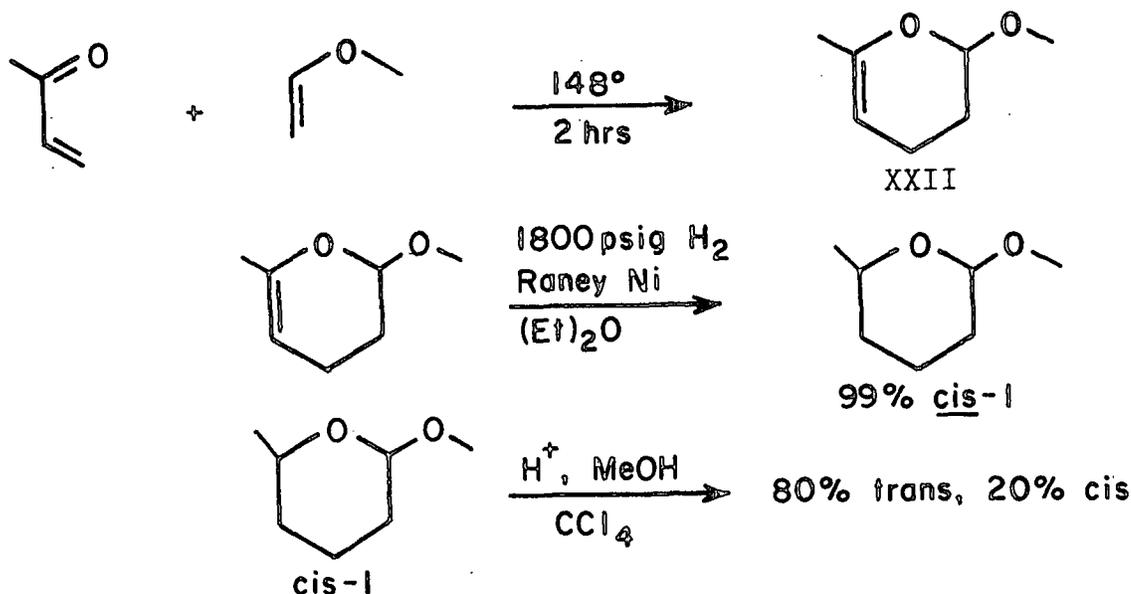
Figure 5. Anticipated Reaction Scheme

RESULTS AND DISCUSSION

SYNTHESIS OF MATERIALS

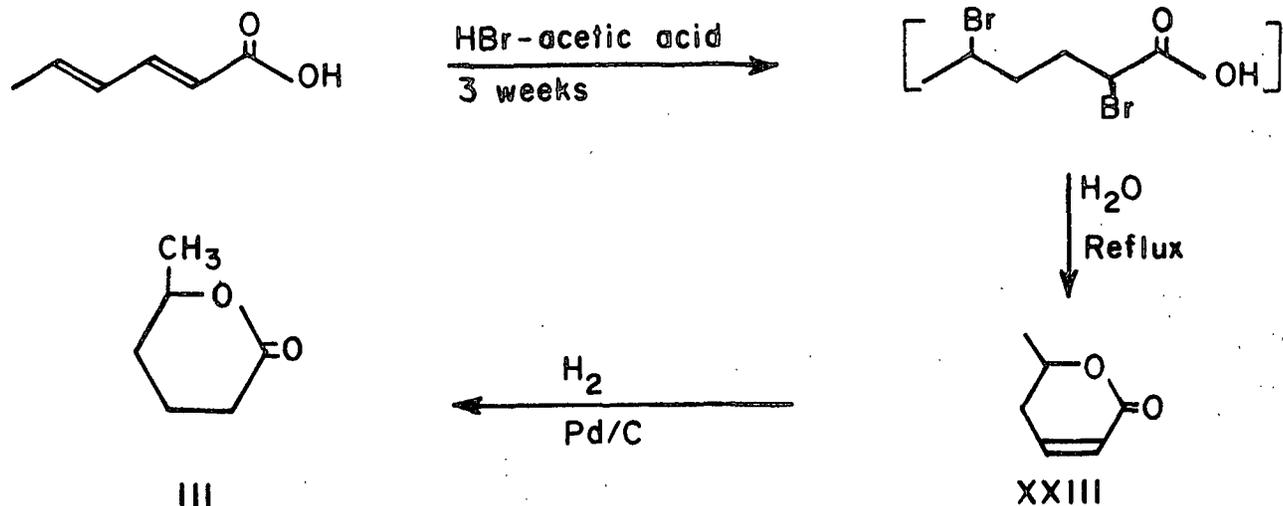
Racemic 2-methoxy-6-methyltetrahydropyran(I) was synthesized in three steps, as diagramed in Scheme I. Methyl vinyl ketone and methyl vinyl ether were combined in a Diels-Alder reaction (13) to provide 2-methoxy-6-methyl-2,3-dihydropyran(XXII). Hydrogenation of XXII with Raney nickel gave nearly pure *cis*-I. The *trans* isomer was obtained by equilibration of *cis*-I in acidic methanol-carbon tetrachloride, followed by spinning band distillation. Isomeric assignments were made by the method of Eliel and Giza (14) using the <sup>1</sup>H-NMR signal of the anomeric proton.

SCHEME I



Synthesis of 6-methyltetrahydropyran-2-one(III) was done to provide material for comparison to the anticipated lactone photoproduct and to develop a reaction pathway for making optically active I. Parasorbic acid(XXIII) was synthesized, using a published procedure (15), and hydrogenated over palladium on carbon catalyst to give pure, racemic, III (Scheme II).

## SCHEME II

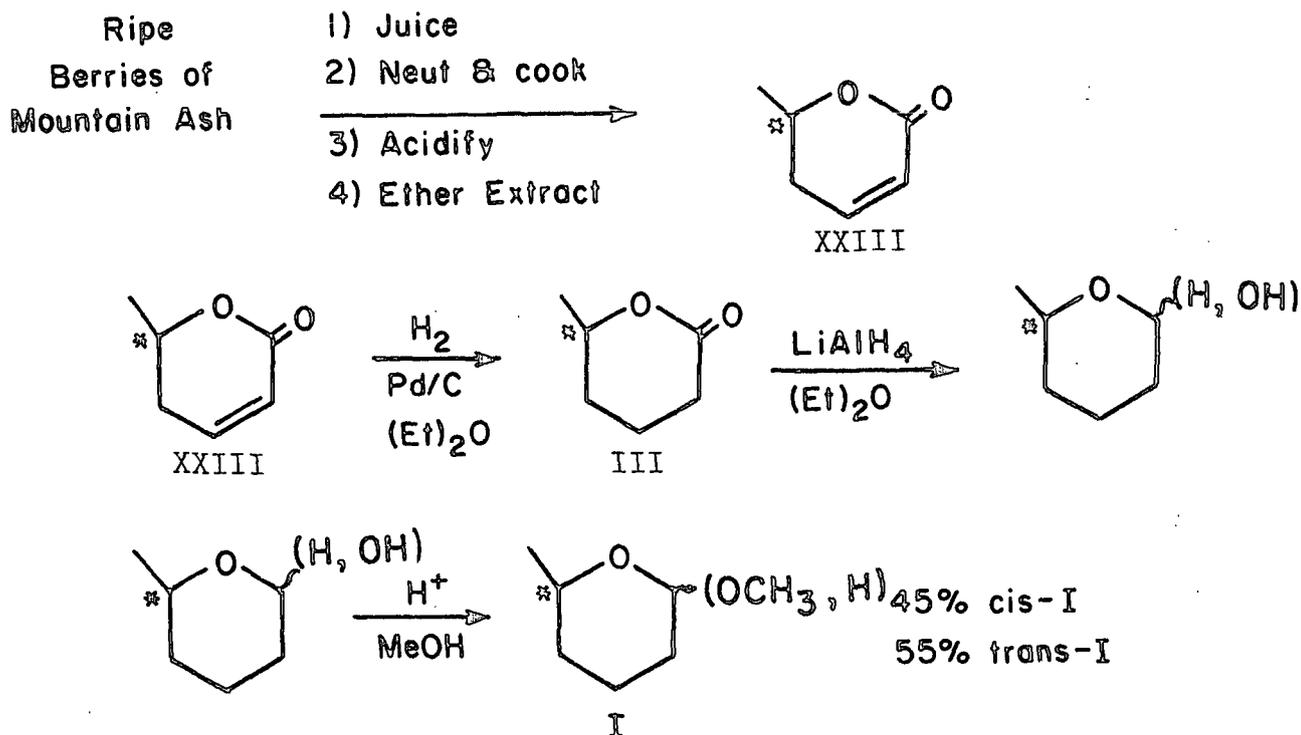


Optically active I was obtained from a four step synthesis which started with the ripe berries of the mountain ash, *Sorbus aucuparia*, according to the procedure of Kuhn and Jerchel (16). The berries were disintegrated in a Waring blender, filtered to remove the pulp, and adjusted to pH 7 by addition of calcium hydroxide. After cooking, reacidification, and ether extraction, an oil was obtained which was predominantly parasorbic acid(XXIII). Hydrogenation of this oil gave optically active (6S)-6-methyl-tetrahydropyran-2-one(III). The configuration of this natural product was determined by Kuhn and Kum (17). The asterisks in Scheme III denote the chiral centers in the various species seen in this reaction sequence. Reduction of III with lithium aluminum hydride, followed by treatment with acidic methanol, gave a mixture of cis- and trans-I with the 6S-configuration. Specific rotations were determined for III, cis-I and trans-I in absolute ethanol.

Methyl 5-phenylhexanoate(IV), an anticipated photoproduct, was not commercially available, and was therefore synthesized. The synthetic pathway is shown in Scheme IV. Methyl 5-oxohexanoate(XXIV) was produced by the method of Bently and Perkin (18) via an acetoacetic ester synthesis. Addition of phenyl magnesium bromide to XXIV followed by mild hydrolysis produced a mixture of the

lactone XXV and the straight chain ester, methyl 5-hydroxy-5-phenylhexanoate (XXVI). Hydrogenolysis of this mixture followed by esterification in acidic methanol produced IV as the major product. Distillation under reduced pressure was used to further purify IV.

SCHEME III

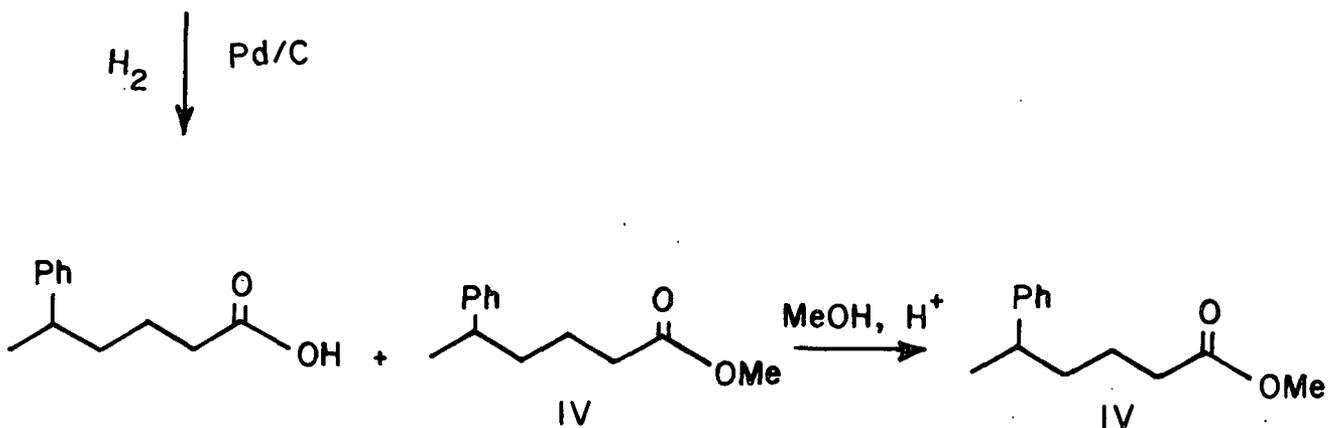
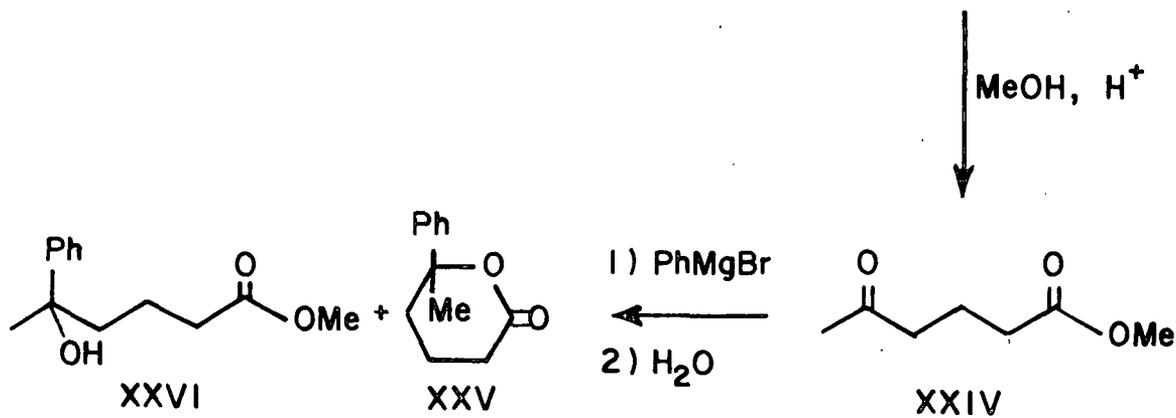
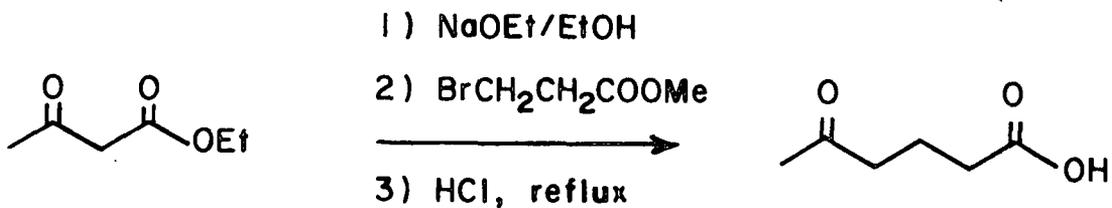


2,3-Diphenylbutane-2,3-diol (XXVII), an anticipated photoproduct of the acetophenone sensitizer, was synthesized using the technique of Wiezmann and co-workers (19). Scheme V depicts the synthesis of XXVII.

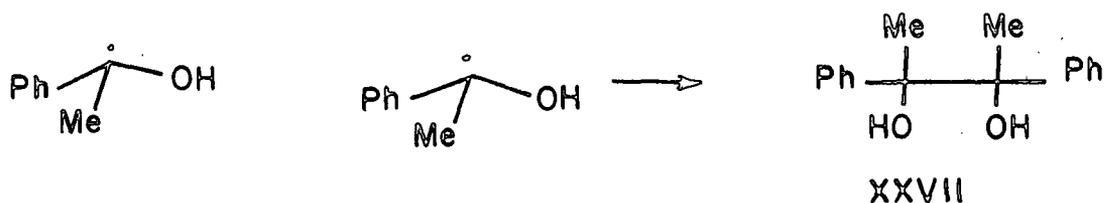
SELECTION OF REACTION CONDITIONS

Reaction conditions were sought which would provide the maximum yield of volatile photoproducts. Several variables were evaluated to reach this set of "best" conditions. Previous workers had reported the use of two solvents and three sensitizers in related studies (4,8,10). Other variables of interest were choice of isomer to be degraded and concentrations of starting materials.

SCHEME IV



SCHEME V



All reactions discussed in this section were done in a Rayonet reactor using sealed pyrex ampuls. Ampuls were degassed by repeated freeze-pump-thaw cycles. Analysis of reaction mixtures was done by gas chromatography.

Preliminary reactions were done using benzophenone sensitizer in t-butyl alcohol or benzene solvent. After many repeated trials, the best set of concentrations for starting materials was found to be 83mM for sensitizer and 77mM for the model compound. Using less model compound made gas chromatographic analysis of the reaction products difficult. Using a minimum concentration of model compound was desirable to reduce the likelihood of chain processes. The concentration ranges used agree with those reported for related systems (4,8,10).

Benzene was found to be more desirable than t-butyl alcohol as a reaction medium. The rates of degradation for the model compound were not significantly

different between the two solvents. The yield of photoproducts was greater in the benzene system mainly because of the appearance of an extra product. Use of t-butyl alcohol also presented some problems for gas chromatographic analysis. Tailing of the solvent peak made integration of the peaks corresponding to cis- and trans-I rather difficult.

Three sensitizers, namely acetone, acetophenone and benzophenone, were evaluated. Acetone was quite poor as a sensitizer due to a very slow reaction rate, and low yields (ca. 10%) of volatile photoproducts. Acetophenone and benzophenone were seen to be comparable in terms of their apparent reactivity towards the model compounds. However, acetophenone provided new products which increased the overall accountability of the photoreaction. These new products were desirable in as much as they provided additional insights into the routes of degradation.

In a direct competition, cis-I was seen to be ca. 10 times more reactive than trans-I. This is comparable to the reactivity differences observed for cis- and trans-2-methoxy-4-methyltetrahydropyran (8). Photosensitized degradation of pure cis-I, as compared to trans-I or a mixture, provided the best yield of products. Since products accumulated more quickly from the cis isomer, irradiation times were shorter and thus secondary photolysis was of less importance, resulting in enhanced yields of primary products.

The reaction conditions selected for further use in this study were the photolysis of cis-I with acetophenone in benzene. This system provided seven major reaction products which accounted for ca. 45% of the model compound degraded.

## IDENTIFICATION OF REACTION PRODUCTS

A mixture containing benzene, acetophenone, and cis-I was degassed and photolyzed until 30% of the model compound remained. The reaction mixture was concentrated and subjected to preparative gas chromatography. Five of the seven samples collected were analyzed via  $^1\text{H-NMR}$  spectroscopy and identified by comparison of gas chromatographic retention times and NMR spectra to those for authentic materials. The other two products did not correspond to available authentic materials and were, thus, identified by spectral means alone.

The products identified and their yields (calculated on a molar basis) were: trans-2-methoxy-6-methyltetrahydropyran (trans-I, 8.5%); methyl hexanoate (II, 11.6%); 6-methyltetrahydropyran-2-one (III, 1.9%); methyl 5-phenylhexanoate (IV, 6.7%); 1,7-dimethyl-7-phenyl-6,8-dioxobicyclo(3.2.1)-octane (V, 1.4%); 2-methoxy-2-(1-phenyl-1-hydroxyethyl)-6-methyltetrahydropyran (VI, 7.2%); 2,3-diphenylbutane-2,3-diol (XXVII, 70%, based on acetophenone consumed). Compounds V and VI were the two for which authentic samples were not available for comparison (see Fig. 6).

Roughly 20 other minor reaction products were seen which could account for ca. 20% of the starting material consumed. The remaining 40% of unaccounted material may be the result of condensation products deriving from radical intermediates expected in this system. It should be pointed out that the yields reported here are an improvement over the yields reported in earlier studies (4,8,10).

## EFFECTS OF MOLECULAR OXYGEN ON LACTONE FORMATION

Lactone formation has been widely variable in the previous studies on related systems (4,8,10). This variability may depend on several factors. One

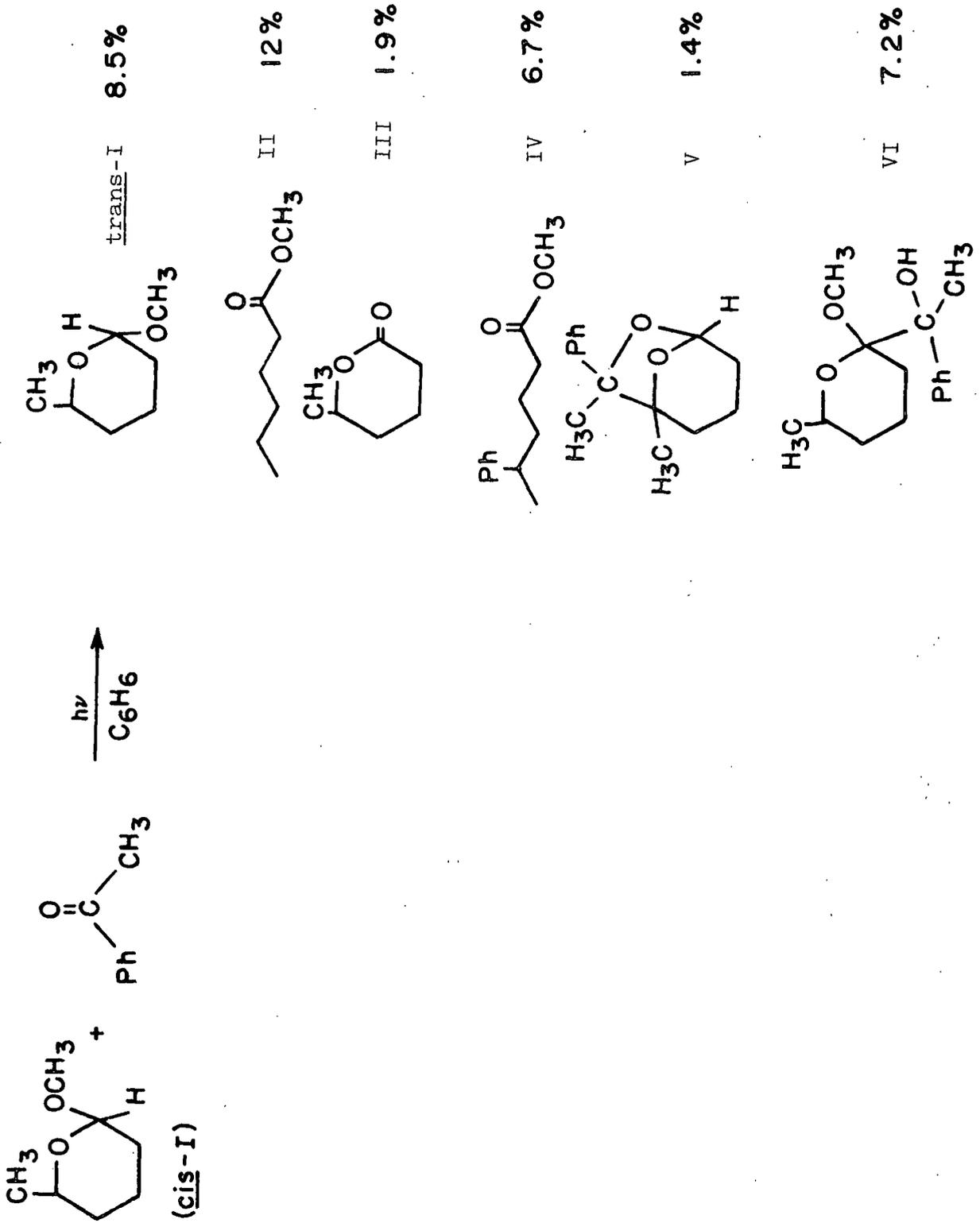
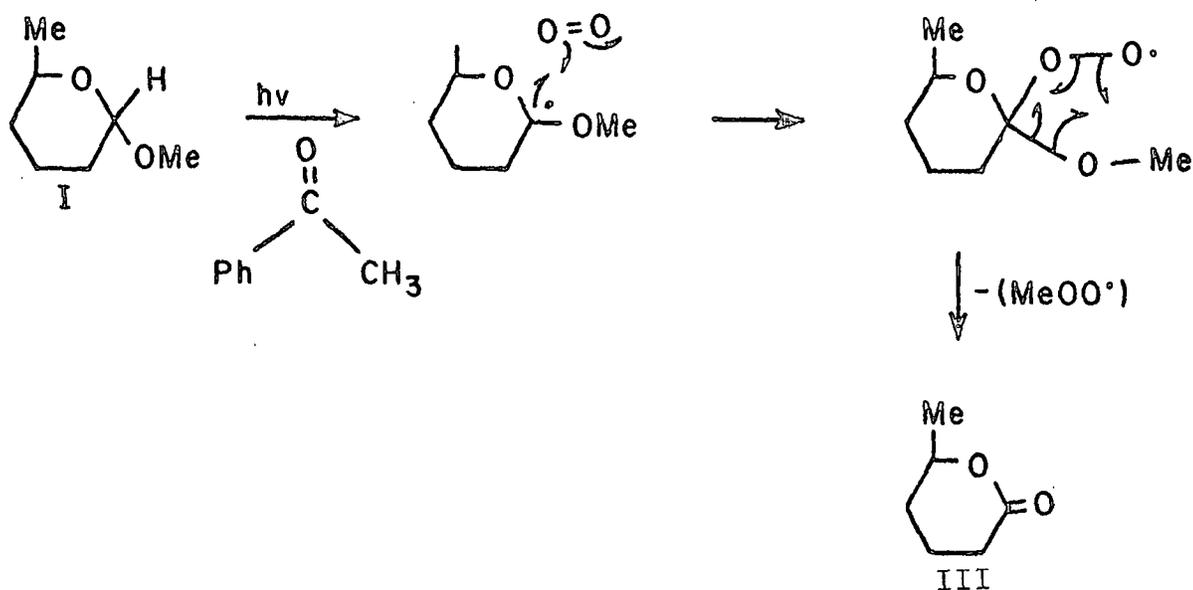


Figure 6. Identified Photoproducts of *cis*-I

such factor, proposed by McKelvey (8), was that the ring opening step may be reversible. This proposal is discussed in a later section of this dissertation. Another possible cause for this observed variability could be the presence of molecular oxygen in the reaction system. McKelvey (4,8) mentioned degassing of reaction samples by repeated freeze-pump-thaw cycles but Bernesconi *et al.* (10) did not describe any degassing steps. Because of the relatively low yield of lactone obtained from *cis*-I, the possible involvement of oxygen was investigated. Scheme VI depicts a possible way in which oxygen can participate in lactone formation.

SCHEME VI



Two reactions were run with different concentrations of molecular oxygen. One reaction mixture was purged, during irradiation, with a stream of air. The second reaction mixture was degassed via four freeze-pump-thaw cycles and sealed under vacuum in a pyrex ampul. This technique should result in a very low concentration of molecular oxygen in the reaction mixture. The results (Table I) indicate that as the amount of available molecular oxygen increased, the yield

of lactone also increased. At the same time the overall yield of volatile photoproducts decreased. A reduction in the rate of reaction was also seen as the amount of molecular oxygen increased.

TABLE I  
EFFECT OF OXYGEN ON LACTONE FORMATION

Reaction	Consumption of <u>cis-I</u>	Yields	
		Total	Lactone
Air Purge	62%	20%	10%
Degassed	78%	40%	3%

The 16% less reaction in the presence of molecular oxygen can be accounted for by oxygen deactivating the triplet excited state of acetophenone. Molecular oxygen is known to be an effective triplet quencher (1). When the reaction mixture was purged with pure oxygen, instead of air, cis-I appeared to be stable toward photolysis. Most importantly, the increase in the yield of lactone indicates that molecular oxygen is important to this reaction. This observation suggests that previous variability in lactone formation could be partially due to residual amounts of molecular oxygen. Degassing is obviously quite important and close attention should be given to this problem for studies of this type. The fact that lactone is produced under conditions of rigorous degassing suggests that elimination of a methyl radical is still a viable pathway for formation of lactone from the initial radical form of I.

#### KINETIC STUDY

A kinetic study was done to obtain data on the rate of disappearance of starting material and accumulation of photoproducts. The reason for this experiment was to determine if the reaction products were primary in nature

or if secondary degradation reactions were of importance. Primary photoproducts (curve B, Fig. 7) should accumulate from the beginning of the reaction and secondary products (curve D) should exhibit an apparent induction period before their accumulation became of importance. If any of the reaction products were unstable their concentration should be seen to go through a maximum during the course of the reaction (curve C). The disappearance of starting material is represented by curve A.

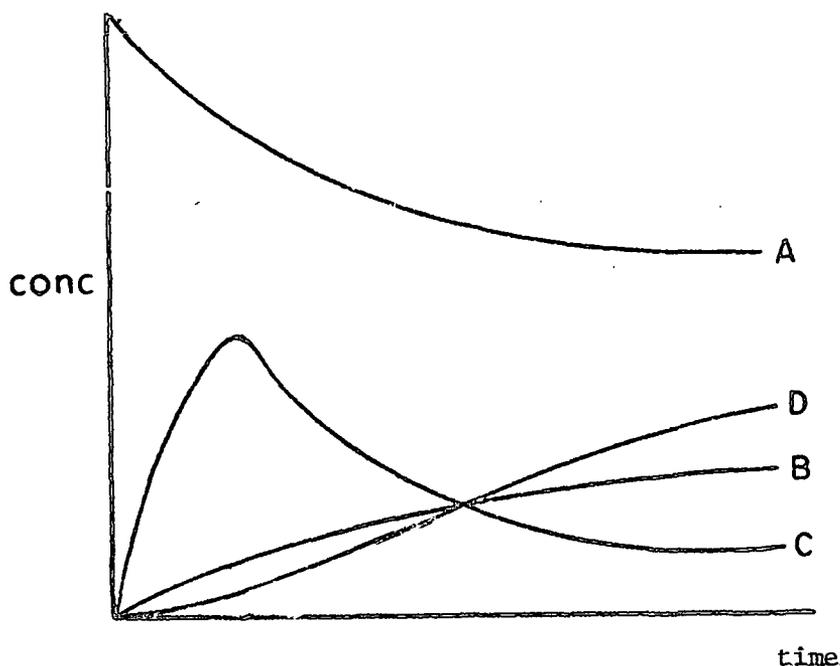


Figure 7. Idealized Accumulation of Degradation Products

A kinetic study was done on the photodegradation of cis-I. The reaction consisted of eight identical samples which were placed in pyrex ampuls, degassed via four freeze-pump-thaw cycles, and irradiated. One ampul was stored in the dark to provide an experimental control. The remainder of the ampuls were removed periodically and analyzed to provide the data which is reported in Fig. 8 and 9.

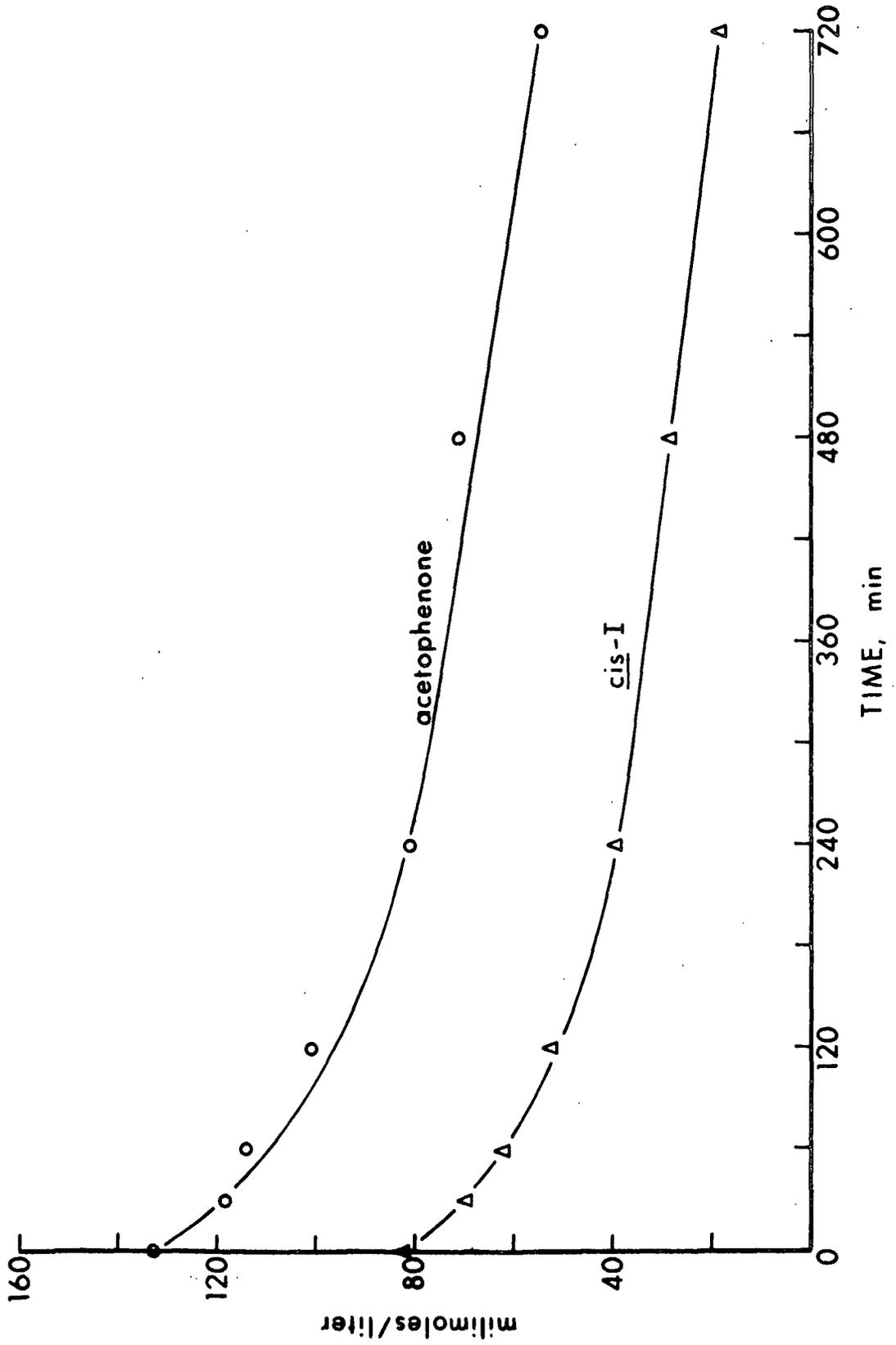


Figure 8. Loss of Starting Materials

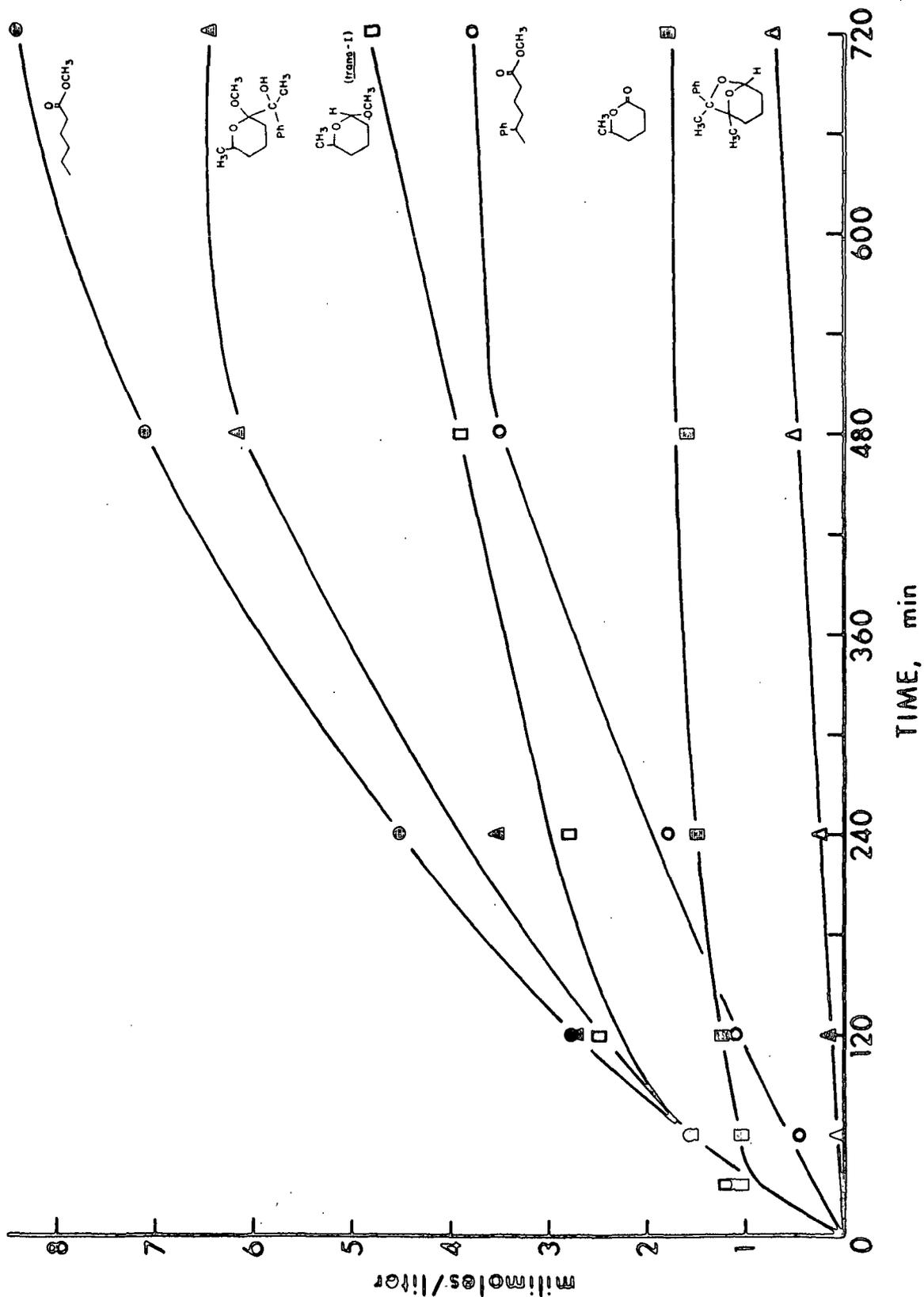


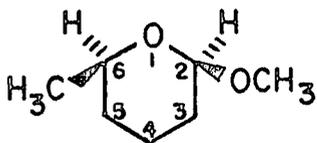
Figure 9. Photoproducts of cis-I as a Function of Time

It is interesting to note that all of the reaction products (Fig. 9) seem to accumulate from the start of the reaction. None of the curves seem to represent a secondary degradation product. Also, none of the curves suggest that secondary degradation of reaction products is important. On the basis of these observations it appears that the identified reaction products accumulate directly from starting material, without an intermediate. Lactone production has a peculiar shape; it appears to increase rapidly and level off. This behavior can be explained by (1) lactone formation reaching a steady state, where its rate of production matches its rate of degradation or (2) lactone formation is totally dependent on the presence of molecular oxygen and its initial production reflects the level of molecular oxygen still left in the system.

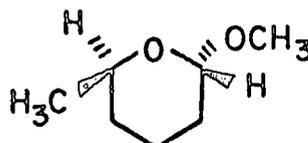
PHOTODEGRADATION OF OPTICALLY ACTIVE  
2-METHOXY-6-METHYLTETRAHYDROPIRAN

The occurrence of methyl hexanoate(II) and its 5-phenyl derivative IV suggests that the C-2 radical produced from I can undergo ring opening. The open chain radical could then close to regenerate the C-2 radical from of (I). This reversible ring opening step was proposed by Hayday and McKelvey (8) as an explanation for the occurrence of lactone. They suggested that if the ring opening process was reversible, an energetically (enthalpy) less favorable but irreversible process (such as loss of methyl radical to form lactone) could compete with ring opening. To study the reversibility of ring opening, optically active (+)cis-I was degraded.

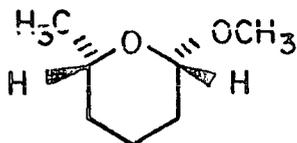
Four structural isomers of (I) can be drawn. These isomers are depicted below with their names. The abbreviated name [e.g., (+)cis-I] indicates the cis isomer which rotates polarized light to the right. The assignment of absolute configurations to these isomers was made possible by the work of Kuhn and Kum (17).



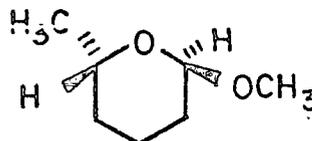
(2R,6R)-2-methoxy-6-methyl-tetrahydropyran (-)cis-I



(2S,6R)-2-methoxy-6-methyl-tetrahydropyran (+)trans-I



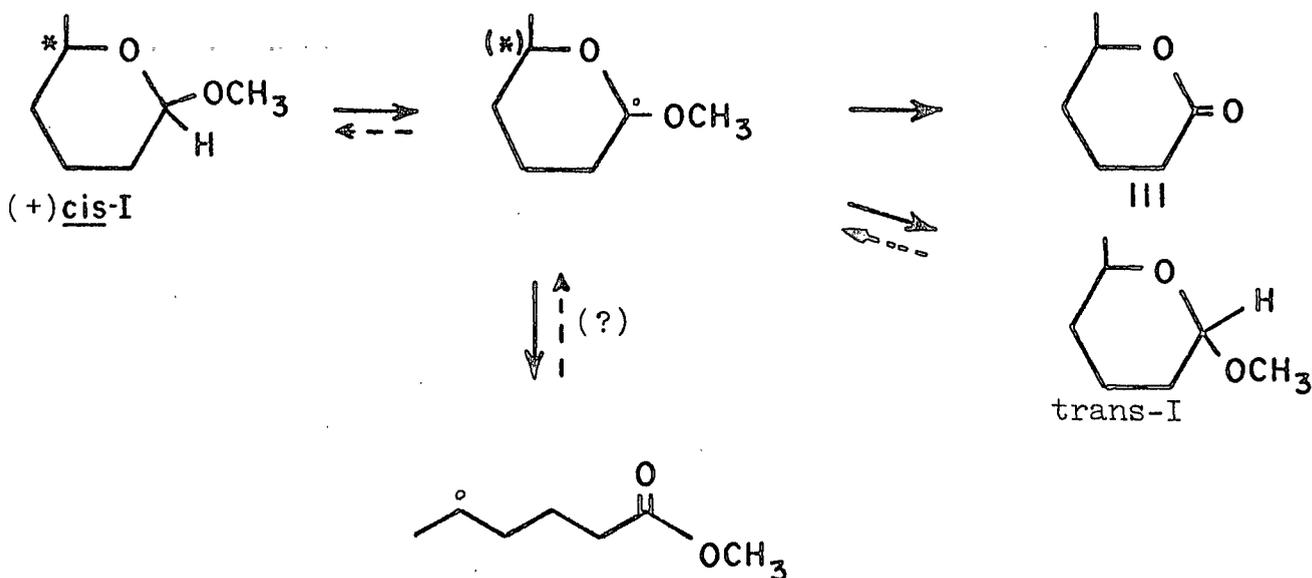
(2S,6S)-2-methoxy-6-methyl-tetrahydropyran (+)cis-I



(2R,6S)-2-methoxy-6-methyl-tetrahydropyran (-)trans-I

If the ring opening step is reversible, any lactone which accumulates should reflect a loss of optical activity. One would expect the same behavior for the trans-I which accumulates. If reversibility applies to the initial hydrogen abstraction step (as suggested by the accumulation of trans-I) dilution of the optical purity of residual cis-I might also be expected Scheme VII depicts the reaction pathways under consideration.

SCHEME VII



Duplicate reactions were run in which (+)cis-I was photodegraded. Samples of the cis and trans isomers, as well as the lactone (III), were isolated by preparative gas chromatography. A detailed description of this experiment is given in the Experimental Section under "Photoreaction of Optically Active (I)." Isolation of the (III) produced in this reaction provided evidence for irreversibility of the ring opening step. The specific rotation measured for the (III) isolated was  $-51^\circ$ . This value agrees very well with the literature value of  $-49^\circ$  (17) for optically pure (6S)-6-methyltetrahydropyran-2-one(III).

Further evidence for the irreversibility of ring opening was obtained from the residual cis-I. Isolation of the remaining cis-I, from both reaction mixtures, provided two samples whose specific rotations,  $+107^\circ$  and  $+104^\circ$  were in very good agreement with the value for (+)cis-I,  $+106^\circ$ .

Addition of a hydrogen atom to the C-2 radical [produced from (+)cis-I] to provide trans-I should result in the formation of (2R,6S)-2-methoxy-6-methyltetrahydropyran [e.g., (-)trans-I]. The specific rotation of (-)trans-I is  $-144^\circ$ . The trans-I isolated provided a rather unusual result, the two values observed for its specific rotation were  $+34^\circ$  and  $+32^\circ$ . There has been a considerable loss of optical purity which might at first glance support the idea of reversibility of ring opening. However, a reversible ring opening process involving the C-2 radical should lead to a zero rotation or a small negative rotation. The unusual aspect of this observation is that there is actually a net inversion of the symmetry at the 6-position of the starting material. This net inversion can be explained by the competition of two pathways leading to the production of trans-I. Figure 10 depicts these two routes. Of the two pathways, the one involving hydrogen abstraction at the 6-position must predominate over the pathway involving the C-2 radical. A calculation of the

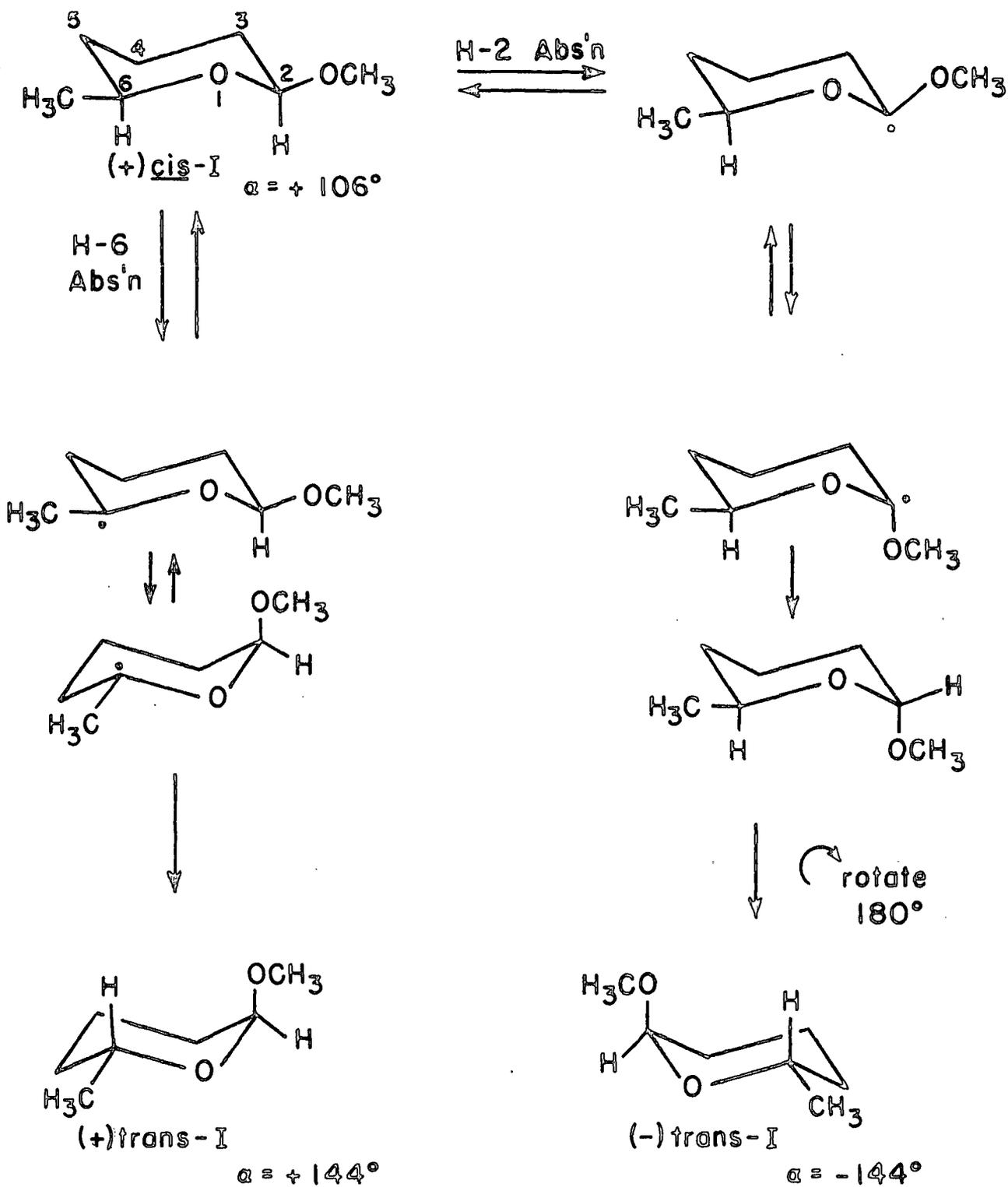


Figure 10. Two Routes of Formation for trans-I

ratio of these two pathways indicates that 62% of the trans-I which accumulated was produced via the C-6 radical pathway.

#### GENERAL REACTION SCHEME

The general reaction scheme for the photolysis of cis-I is depicted in Fig. 11 and discussed below. Several novel, unanticipated, results were obtained which enhanced our overall understanding of the photolysis of carbohydrate models.

Accumulation of trans-I as a reaction product of cis-I was taken as evidence for the reversibility of the initial hydrogen abstraction. The results of the photodegradation of optically active cis-I indicated that this product accumulated from two different pathways. Abstraction of a hydrogen from the 6-position followed by inversion and addition of H<sup>•</sup> has been advanced as a major (62%) contributor to the formation of trans-I. In Fig. 11 these two routes are depicted by the cyclic portion of the reaction scheme. The possibility of reversible hydrogen abstraction was considered in the initial phase of this study and was shown by the photoisomerization of cis-I to trans-I. The importance of C-6 hydrogen abstraction was not anticipated, since the C-6 radical was considered to be less stable than the C-2 radical.

The formation of a coupling product (VI) between the ketyl radical (from the sensitizer) and the C-2 radical [from (I)] was anticipated. McKelvey (4) had speculated that the analogous product should exist in another system but had not detected it by gas chromatography. The use of acetophenone sensitizer provided a coupling product (VI) which was volatile enough to be seen in the chromatograms. Identification of (VI) has provided additional direct evidence for hydrogen abstraction at C-2.

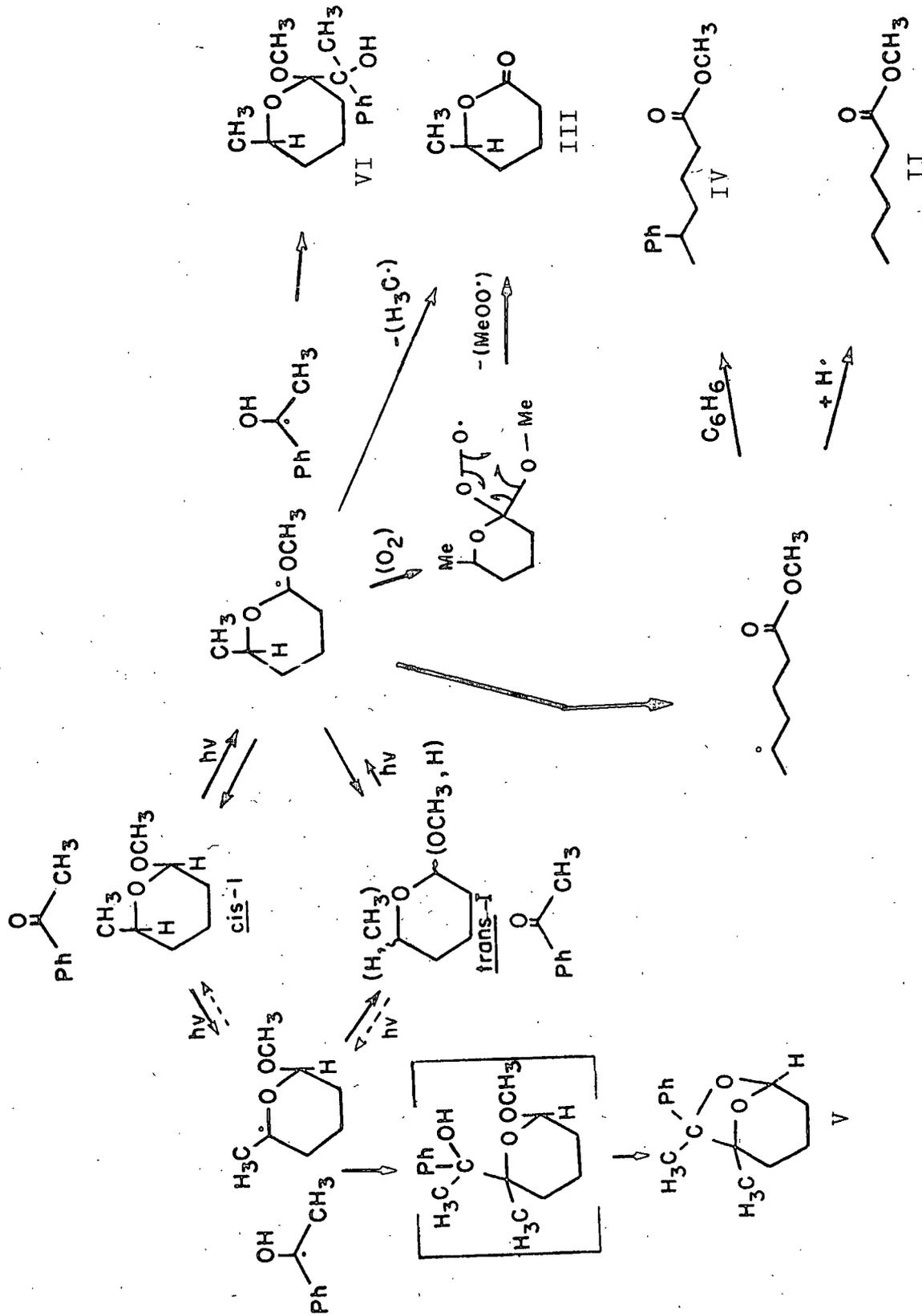


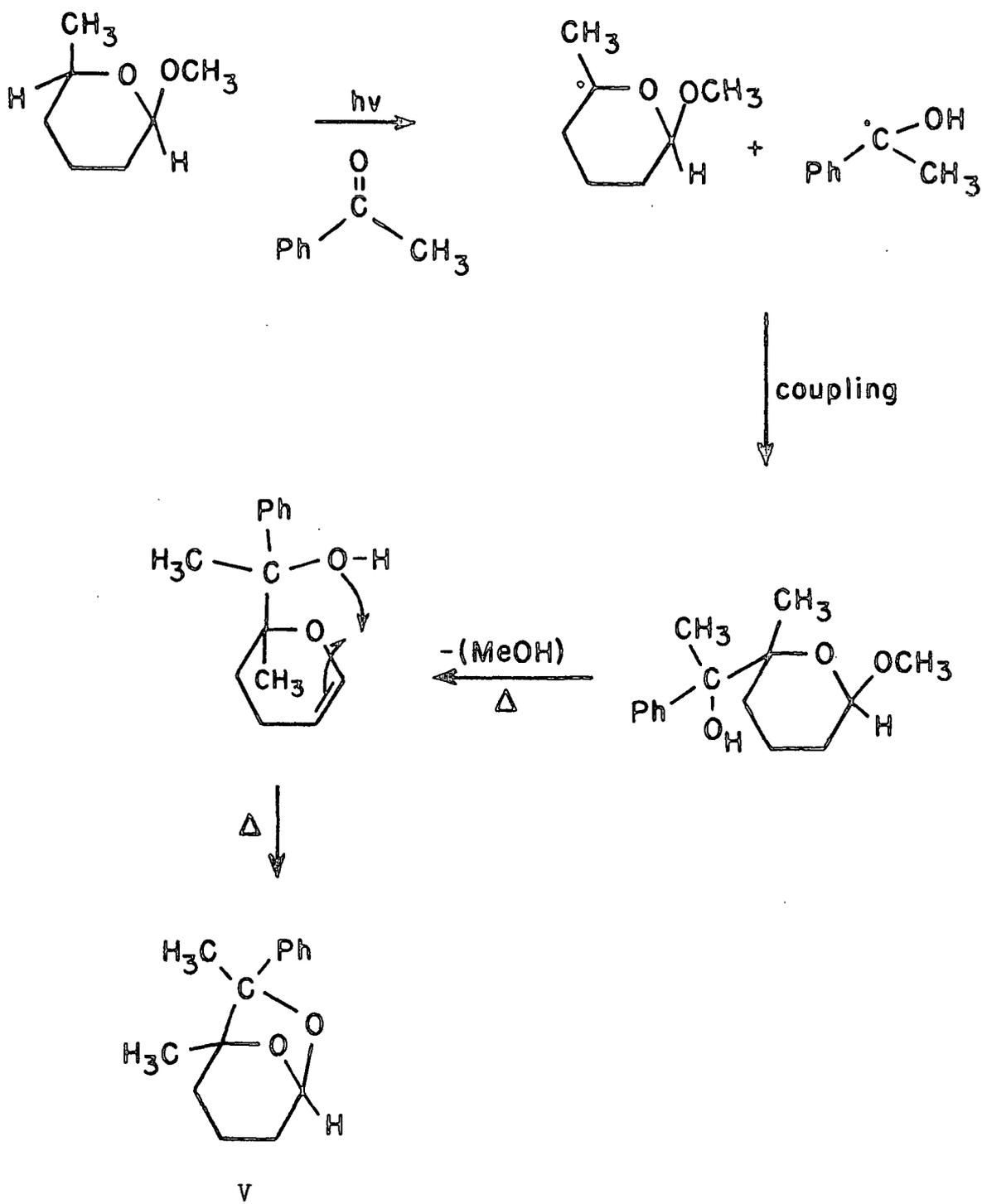
Figure 11. General Reaction Scheme

Lactone (III) may result from two different pathways; elimination of methyl radical from the C-2 radical, as proposed by previous workers (4,8,10), and oxidation of the C-2 radical by molecular oxygen. Lactone production increases markedly in the presence of air. The rapid initial accumulation of lactone, followed by a leveling off of its concentration as the reaction progresses, suggests that lactone formation may depend wholly on residual oxygen in the reaction mixture. These experiments were, however, conducted in such a way as to exclude oxygen as completely as possible. Since both pathways can be supported by the experimental results, both are included in the general reaction scheme.

Methyl hexanoate(II) and methyl 5-phenylhexanoate(IV) were anticipated photoproducts based on previous work (4,8,10). The identification of these two photoproducts was taken as evidence for ring opening of the C-2 radical. The secondary alkyl radical which is produced by ring opening can abstract a hydrogen atom from a molecule of (I) or possibly from the solvent to form (II). Product (IV) was only formed when benzene was used as solvent. This suggests that the open chain radical can add a phenyl group from the benzene solvent.

Identification of 1,7-dimethyl-7-phenyl-6,8-dioxobicyclo(3.2.1)octane(V) as a photoproduct of cis-I and acetophenone was not anticipated. Several reaction sequences were considered to account for (V). The problem with most of these routes is that more than one hydrogen abstraction is required. This would mean that (V) is a result of secondary degradation which is not supported by the results of the kinetic study. A reaction pathway has been advanced which could account for the observations, Scheme VIII. Hydrogen abstraction from the 6-position produces the C-6 radical which could then couple with the ketyl

SCHEME VIII



radical from acetophenone. The C-6 coupling product may be unstable under conditions of gas chromatography. Loss of methanol followed by addition of the hydroxyl functional group across the double bond could account for the formation of acetal (V).

A gas chromatographic experiment was done in which the injector temperature was varied to determine if the apparent size of the peak representing (V) varied. No such relationship could be established and the proposed mechanism for the formation of (V) is, therefore, largely speculative. The presence of (V) as a reaction product is, however, taken as evidence for additional C-6 hydrogen abstraction.

The total yield of reaction products derived from C-6 hydrogen abstraction of (+)cis-I was 6.1% [4.9% (+)trans-I and 1.2% adduct (V)]. The yield of reaction products from C-2 hydrogen abstraction was 42% [3% (-)trans-I, 21% (II), 6% (III), 5% (IV), and 6.6% (VI)].

#### IMPLICATIONS FOR CARBOHYDRATE PHOTOCHEMISTRY

Carbohydrates such as cellulose provide many sites for hydrogen abstraction leading to tertiary radicals on carbon. Hydrogen abstraction from the 1-position of glucose would provide a tertiary radical with di-oxygen substitution, C-2 through C-5 could provide a tertiary radical with mono-oxygen substitution. The results of this model study indicate that these mono-oxygen substituted sites may compete significantly with the di-oxygen substituted sites.

The isolation of coupling products between the model compound and acetophenone sensitizer provided evidence for the sites of hydrogen abstraction. Initial sites of hydrogen abstraction from actual carbohydrates could possibly be studied in the same way. Knowledge of the initial points of attack is fundamental to a complete understanding of such degradation reactions.

Molecular oxygen has major effects on the distribution of degradation products from cis-I. This observation suggests that further studies of carbohydrate photo-degradation must consider the role of oxygen in the reaction mechanism.

## CONCLUSIONS

Acetophenone-sensitized photodegradation of 2-methoxy-6-methyltetrahydro-pyran is initiated by hydrogen abstraction at C-2 and C-6. The identification of a C-2 coupling product with the ketyl radical of acetophenone and the implication of an analogous C-6 coupling product are direct evidence for the initial sites of hydrogen abstraction. Most of the remaining products may be derived from a C-2 radical or an acyclic radical produced from the C-2 radical. Based on observed products, the ratio of C-2 to C-6 hydrogen abstraction is approximately 7:1.

Lactone formation is still somewhat unclear, but reversibility of ring opening has been ruled out as an important contributor. Molecular oxygen has been shown to increase lactone formation and may be responsible for some of the variability seen in previous work (4,8,10). Since careful degassing did not eliminate lactone formation, loss of a methyl radical must be retained as a viable pathway.

## EXPERIMENTAL

### ROUTINE PROCEDURES

#### Analytical Gas Chromatography

Analytical gas chromatography was done on a Perkin-Elmer F-30 gas chromatograph. The column was 6 feet of 1/8 inch O.D. stainless steel tubing packed with 3% OV-17 on Supelcoport 80/100 mesh. Purified helium (Matheson Gas Company) was used as the carrier gas, with a flow rate of 60 mL/minute. The gas chromatograph was equipped with a flame ionization detector; the inlet pressure of hydrogen was 60 psig. Injector and detector temperatures were held constant at 250°. Standard conditions of analysis were as follows: injection volume was 1.0 microliter; oven temperature was 60° for 3 minutes, followed by a 5°/minute increase for 30 minutes, followed by 20 minutes at 210°; the range setting was 100 and the attenuator was varied from 1 to 64. Chromatograms were recorded on a Linear Instruments recorder with an electronic graphical integrator.

Peak integrals were determined by correcting the graphic integral. This was done by calculating a baseline integral value and subtracting this value from the total graphic integral. Appendix I describes the process of converting these integral values to concentrations.

#### Preparative Gas Chromatography

Preparative gas chromatography was done on a Varian Aerograph 712. The carrier gas flow was split between a flame ionization detector and a preparative collection port. The column was 20 feet of 1/4 inch O.D. nickel tubing packed with 3% OV-17 on Supelcoport 80/100 mesh. The carrier gas was purified nitrogen (Matheson Gas Company) with an inlet pressure of 130 psig and a column back

pressure of 40 psig. Injector and detector temperatures were constant at 250°. The oven temperature was varied from 75-245°; isothermal and temperature programming techniques were used.

Collection of samples was done by one of two methods. The method used to isolate pure samples was to trap them in a V-shaped glass tube. This tube was inserted into the preparative collection port when the peak of interest was passing out of the column. The second method of trapping was to bubble the carrier gas through a solvent such as absolute ethanol. This bubble trap method was used for the more volatile components. Deuterated solvents were used to trap volatile peaks for NMR analysis.

#### Measurement of Optical Activity

Optical activity determinations were done on a Perkin-Elmer 141 polarimeter. All determinations were done at room temperature in a 1.0 dm quartz microcell. Absolute ethanol was the solvent and rotations were measured at a wavelength of 589 nm.

Calculation of the specific rotation was based on the observed rotation and the concentration was determined either gravimetrically or by analytical gas chromatography. When the gas chromatographic method was used, the sample from the polarimeter tube was combined with a known mass of internal standard (biphenyl) and injected into the gas chromatograph.

#### Nuclear Magnetic Resonance Spectroscopy

All NMR spectra were obtained on a Joel FX-100 spectrometer. The chemical shift values are in ppm and are referenced to the tetramethylsilane. Proton signal shapes or <sup>13</sup>C multiplicities are reported in parentheses with the assignments.

### Mass Spectroscopy

Mass spectra were obtained in a DuPont 21-491 mass spectrometer. The mass spectrometer was interfaced with a Varian Aerograph 1440-1 gas chromatograph via a jet separator. Gas chromatographic response was recorded on a Hewlett-Packard 7128A recorder; mass spectra were recorded on a Century GPO 460 oscillographic recorder. The internal standard was perfluorokerosene (low-mass). Gas chromatographic separation was done on OV-17. The injector and detector temperatures were 245°. Other operating conditions include:

GC block temp:	300°
GC to MS inlet tube temp:	300°
Source temp:	196-200°
Sensitivity:	4.0-5.0
Filament:	GC
Scan Rate:	100 seconds/decade
Pressure:	less than $3 \times 10^{-7}$ Torr
Chart Speed:	4 inches/second

### Photochemical Reactor

The reactor was a Rayonet RPR-100 manufactured by the Southern New England Ultraviolet Company. This reactor was provided with a MGR-100 merry-go-round for the simultaneous irradiation of up to 8 samples. The light source consisted of 16 RPR-3000A lamps. Irradiations done in sealed pyrex ampuls used the merry-go-round to provide equal exposure for all of the samples. Reactions done with a gas purge stream were done by suspending the ampul in the center of the reactor chamber.

### Degassing Techniques

Solutions to be irradiated were degassed by one of two techniques. The first technique used was to purge the reaction mixture with a stream of purified

nitrogen (Matheson Gas Company) prior to and during irradiation. The reaction mixture was placed in a pyrex ampul (17 x 140 mm) which was provided with a ground glass joint (14/35 female). A condenser was fitted to the open end of the ampul. A capillary tube was passed through the condenser and into the reaction mixture. Nitrogen was bubbled through the solution (10 mL/minute) and allowed to escape through a mineral oil bubble trap for 2-3 hours prior to irradiation. Before irradiation began, the capillary tube was adjusted so that the stream of gas blanketed the reaction mixture.

The second method used for degassing was a series of freeze-pump-thaw cycles. Pyrex ampuls (10 x 170 mm) were provided with ground glass joints (12/30 male) and tapered to facilitate sealing under vacuum. The solution to be irradiated was placed in the ampul and the ampul fitted to a stopcock on the vacuum system. The ampul was immersed in liquid nitrogen to freeze the contents. After freezing was complete, the stopcock was opened to evacuate the ampul. Pumping was continued until the pressure in the system fell below 0.01 mm Hg. At this time the stopcock was closed and the ampul was slowly warmed to room temperature. After thawing was complete the mixture was left to equilibrate for 5 minutes. At this time, the freeze-pump-thaw cycle was repeated. After 4 complete cycles the mixture was frozen and pumped down one more time. The ampul was then sealed under vacuum with a flame and removed from the system. The sample was then ready for irradiation.

#### SYNTHESIS REACTIONS AND REAGENTS

##### Acetophenone

Acetophenone was supplied by Matheson, Coleman & Bell. It was redistilled prior to use; bp 100°/24mm.

Benzene

All benzene used was the "Distilled in Glass" grade supplied by Burdick and Jackson Laboratories. The benzene was used as supplied and handled in a hood.

2-Methoxy-6-Methyl-2,3-Dihydropyran(XXII)

Compound XXII was synthesized by a published procedure (13). Methyl vinyl ketone (46.0 g) was placed in a weighing bottle (115 x 45 mm) with hydroquinone (1.0 g). The solution was cooled by immersion in an ice bath and methyl vinyl ether (37.0 g) was condensed in the bottle by bubbling through the cooled solution. The bottle was placed in a stirring autoclave. The autoclave was sealed and heated to 148° with stirring for 2 hours. The autoclave was quickly cooled to room temperature, the contents removed and distilled to yield 31 g (36% yield) of (XXII) bp 62-63°/44mm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 147.2 (s, OC=CH), 98.4 & 96.3 (d, HC=CO & OCO), 55.6 (q, OCH<sub>3</sub>), 26.1 & 16.6 (t, CH<sub>2</sub>'s), 19.9 (q, OCCH<sub>3</sub>). Literature: bp 81°/100 mm, 105°/160 mm (13).

Cis-2-Methoxy-6-Methyltetrahydropyran(cis-I)

Raney nickel [3.0 g of W-2 (20) prepared 3 months earlier] was placed in a weighing bottle. Anhydrous ethyl ether (50 mL) was added. Then (XXII)(30 g) was dissolved in the ether solution and the bottle placed in the stirring autoclave. The autoclave was purged with hydrogen and pressurized to 1800 psig. The pressure was maintained for 48 hours with stirring. At this time, a NMR spectrum of the crude reaction mixture indicated that no (XXII) remained. The mixture was filtered, concentrated and distilled on a spinning band column to yield 28 g (93% yield) of cis-I: bp 63°/46 mm & 36-37°/12 mm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 4.24 (m, 1H, HCOCH<sub>3</sub>), 3.78 (m, 1H, HCCH<sub>3</sub>), 3.46 (s, 3H, OCH<sub>3</sub>), 1.98-1.35 (m, 6H, CH<sub>2</sub>'s), 1.21 (d, 3H, J=6Hz, H<sub>3</sub>CCH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 103.0 (d, OCO), 71.8 (d, OCCH<sub>3</sub>), 55.6 (q, OCH<sub>3</sub>), 32.6,

30.8 & 22.2 (t, CH<sub>2</sub>'s), 21.6 (q, CCH<sub>3</sub>). Literature: bp 35-36°/12 mm; (14). The assignment of cis geometry is based on the C-2 proton's <sup>1</sup>H-NMR signal (14).

Trans-2-Methoxy-6-Methyltetrahydropyran(trans-I)

The trans isomer was produced by dissolving cis-I (11 g) in CCl<sub>4</sub> (75 mL) with acetyl chloride (1.0 mL) and methanol (2.0 mL). After 48 hours, analysis by gas chromatography indicated that an equilibrium mixture of trans-I and cis-I had been reached. The organic layer was separated and dried (Na<sub>2</sub>SO<sub>4</sub>). Distillation on the spinning band gave a major fraction containing 5 g (45% yield) of trans-I: bp 53°/43 mm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 4.96 (broad singlet, 1H, HCOCH<sub>3</sub>), 4.24 (m, 1H, HCCH<sub>3</sub>), 3.35 (s, 3H, OCH<sub>3</sub>), 1.98-1.35 (m, 6H, CH<sub>2</sub>'s), 1.14 (d, 3H, J=6Hz, HCCH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 98.1 (d, OCO), 63.8 (d, OCCH<sub>3</sub>), 53.2 (q, OCH<sub>3</sub>), 32.5, 31.8 & 18.0 (t, CH<sub>2</sub>'s), 20.8 (q, CCH<sub>3</sub>). Literature: bp 35-36°/12mm; (14). The assignment of trans geometry is based on the anomeric proton's <sup>1</sup>H-NMR signal (14). A second fraction was collected containing 50% cis-I and 50% trans-I (4 g, 36% yield, bp 60-63°/46 mm).

Racemic Parasorbic Acid(XXIII)

Compound (XXIII) was synthesized by a published procedure (15). Sorbic acid (180 g) was dissolved in saturated HBr-acetic acid (38% HBr by weight). The mixture was stored in a hood for 3 weeks with occasional shaking. The mixture was then concentrated on a rotary evaporator and the resulting oil refluxed in distilled water (1.5 L) for 4 hours. Upon cooling a large amount of unknown crystals were seen. The solution was extracted for 24 hours with ethyl ether, the ether dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to yield 50 g of crude product. Fractional distillation gave a major fraction containing 30 g (16% yield) of (XXIII): bp 105-112°/12 mm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.04-6.86 (m, 1H, HC CCO), 6.02-5.91 (m, 1H, C=CH-CO), 4.95-4.60 (m, 1H, HCCH<sub>3</sub>), 2.46-2.30 (m, 2H, CH<sub>2</sub>), 1.42 (d, 3H, J=6Hz, CH<sub>3</sub>);

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  164.1 (s, C=O), 145.5 (d, C=CCO), 120.4 (d, C=CCO), 74.3 (d,  $\text{HCCH}_3$ ), 30.8 (t,  $\text{CH}_2$ ), 20.6 (q,  $\text{CH}_3$ ). Literature: bp 104-105°/14 mm (16).

Optically Active Parasorbic Acid(XXIII)

Optically active (XXIII) was synthesized by a published procedure (16). Ripe berries from a mountain ash tree Sorbus aucuparia (2.0 kg) were placed in a Waring blender with distilled water (1.0 L) and disintegrated on medium speed for 60 seconds. The pulpy mass was filtered on a large Buchner funnel (34 cm). The filter cake was broken up and washed with enough water to bring the total volume of filtrate up to 4.0 L. The red filtrate was neutralized with calcium hydroxide powder, cooked in an autoclave at 120° for 45 minutes, and reacidified to pH 3 with sulfuric acid. The filtrate was then extracted for 24 hours with ethyl ether in a continuous liquid-liquid extractor. The ether fraction was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and evaporated to yield a dark brown oil. This procedure was repeated 11 times to yield 90 grams of crude product. The dark oil was distilled to yield 51 grams (0.2% yield) of (XXIII): bp 87°/5 mm;  $[\alpha]_D^{20} = 205^\circ$  (absolute ethanol). Literature: bp 104-105°/14 mm;  $[\alpha]_D^{20} = 210^\circ$  (absolute ethanol); (16).

(6S)-6-Methyltetrahydropyran-2-One(III)

Optically active (XXIII) (13.8 g) was dissolved in absolute ethyl ether (280 mL) and 10% Pd/C (1.0 g) was added. The mixture was subjected to hydrogenation until the uptake of hydrogen ceased (16). The catalyst was removed by filtration on Celite and the ether evaporated to yield a clear oil which crystallized upon refrigeration. Recrystallization from hexane provided 13 grams of (III): mp 31-32°;  $[\alpha]_D^{20} = -49^\circ$  (absolute ethanol);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.62-4.05 (m, 1H,  $\text{HCCH}_3$ ), 2.70-2.37 (m, 2H,  $\text{H}_2\text{CC=O}$ ), 2.25-1.52 (m, 4H,  $\text{CH}_2$ 's), 1.43-1.31 (d, 3H,  $J=6\text{Hz}$ ,  $\text{CH}_3$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  174.0 (s, C=O), 67.1 (d,  $\text{CCH}_3$ ), 38.4, 33.9 & 22.2 (t,  $\text{CH}_2$ 's), 23.3 (q,  $\text{CH}_3$ ). Literature: mp 31°;  $[\alpha]_D^{20} = -49^\circ$  (absolute ethanol); (16).

(2R,6S)- and (2S,6S)-2-Methoxy-6-Methyltetrahydropyran(I)

Compound (I) was produced by an adaptation of a published procedure (21). Optically active (III) (13 g) was placed in dry ethyl ether (50 mL), dried overnight ( $MgSO_4$ ), filtered and the ether solution placed in a round bottom flask. A 20% excess of reducing agent, 1.0M  $LiAlH_4$  in ethyl ether (35.0 mL), was added dropwise over a 1 hour period to the stirred solution, cooled at  $-10^\circ$  and under a blanket of nitrogen, The reaction mixture was allowed to warm slowly (2 hours) to room temperature and 2.0 mL of water, 2.0 mL of 15% NaOH and 5 mL of water added dropwise, in succession. Stirring was continued for 30 minutes. The gelatinous precipitate was removed by filtration over celite and the ether solution dried overnight ( $MgSO_4$ ), filtered, and evaporated to yield 10 g of 2-hydroxy-6-methyltetrahydropyran as a clear oil ( $^1H$ -NMR). This oil was dissolved in methanol (200 mL) and p-toluenesulfonic acid (0.25 g) was added. After 48 hours the mixture was shaken with sodium bicarbonate solution (50 mL) and extracted with ethyl ether (100 mL). The ether was dried ( $Na_2SO_4$ ), filtered and evaporated to give 14 g of an oil containing methanol (30%), cis-I (28%), and trans-I (39%). Preparative gas chromatography was used to isolate samples of pure (+)cis-I, (-)trans-I.  $^1H$ -NMR spectra were in agreement with those for racemic cis- and trans-I. Specific rotations were determined for both isomers: (+)cis-I,  $[\alpha]_D = +106^\circ$  (absolute ethanol); (-)trans-I  $[\alpha]_D = -144^\circ$  (absolute ethanol).

Methyl 5-Oxohexanoate(XXIV)

The free acid form of (XXIV) was synthesized by a published procedure (18). Sodium metal (3.4 g) was dissolved in absolute ethanol (45 mL) and then ethyl acetoacetate (19 g) was added to the cooled solution. Ethyl 3-bromopropionate (26 g) was added and the temperature of the solution rose quickly to  $50^\circ$ . After 30 minutes, the reaction mixture began to cool; it was then placed in a waterbath

and heated to 60° for 2 hours. Water (200 mL) was added and the oily product extracted 3 times with ethyl ether. The ether layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The resulting oil was dissolved in methanol (100 mL) and benzene (50 mL). Concentrated sulfuric acid (10 mL) was added and the mixture refluxed through a Dean-Stark trap until the water layer no longer increased. The mixture was cooled, water (50 mL) was added, and the mixture extracted with ethyl ether. The ether layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated and the resulting oil was distilled to give 11 g (58% yield) of (XXIV): bp 135°/60mm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 3.65 (s, 3H, OCH<sub>3</sub>), 2.61-2.27 (m, 4H, CH<sub>2</sub>'s α to carbonyls), 2.13 (s, 3H; H<sub>3</sub>CC=O), 2.00-1.78 (m, CH<sub>2</sub> β to carbonyls); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 207.0 (s, H<sub>3</sub>CC=O), 173.0 (s, COOCH<sub>3</sub>), 51.3 (q, OCH<sub>3</sub>), 42.3 & 32.9 (t, CH<sub>2</sub>'s α to carbonyls), 29.7 (q, H<sub>3</sub>CC=O), 19.0 (t, CH<sub>2</sub> β to carbonyls); elemental analysis, calculated 8.38% H, 58.3% C, found 8.42% H, 57.9% C.

#### Methyl 5-Phenylhexanoate(IV)

Phenyl magnesium bromide (22) (0.5M in 200 mL ethyl ether) was added dropwise to a vigorously stirred solution of (XXIV) (11 g) and absolute ethyl ether (100 mL). A white precipitate formed during the addition. After the addition was complete, the mixture was left at room temperature for 30 minutes. Water (150 mL) was added to decompose the precipitate. After shaking, an emulsion formed which was left to stand for 2 hours. Careful addition of dilute sulfuric acid dissolved the magnesium salts while not allowing the pH to drop below 7. The mixture was extracted with ethyl ether 5 times and the ether fractions dried (Na<sub>2</sub>SO<sub>4</sub>). The ether was evaporated to give 18.7 g of crude product. The oil was distilled to yield a 9 g fraction; bp 160-163°/3 mm; <sup>1</sup>H-NMR indicated that this fraction was methyl 5-phenyl-5-hydroxyhexanoate (15%) and 6-methyl-6 phenyltetrahydropyran-2-one (85%).

This oil was dissolved in methanol (50 mL) and 10% Pd/C (0.2 g) was added. The mixture was subjected to hydrogenation until hydrogen uptake ceased, the catalyst filtered off and the methanol evaporated. At this time  $^1\text{H-NMR}$  indicated a mixture of 5-phenylhexanoic acid (80%) and methyl 5-phenyl-hexanoate (20%). This oil was esterified using methanol-benzene and a Dean-Stark trap. Distillation gave a fraction containing 3 g (14% yield) of (IV): bp 147-152°/12 mm;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.50-7.00 (m, 5H, phenyl), 3.56 (s, 3H,  $\text{OCH}_3$ ), 2.82-2.42 (m, 1H,  $\text{HCCH}_3$ ), 2.35-2.10 (t, 2H,  $J=6\text{Hz}$ ,  $\text{H}_2\text{CC}=\text{O}$ ), 1.65-1.30 (m, 4H,  $\text{CH}_2$ 's), 1.22 (d, 3H,  $J=7\text{Hz}$ ,  $\text{H}_3\text{CCH}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  173.3 (s,  $\text{C}=\text{O}$ ), 146.7 (s, substituted phenyl), 128.0 & 126.6 (d, ortho & meta phenyl), 125.6 (d, para phenyl), 51.1 (q,  $\text{OCH}_3$ ), 39.6 (d,  $\text{HCCH}_3$ ), 37.6, 33.8 & 23.0 (t,  $\text{CH}_2$ 's), 22.2 (q,  $\text{H}_3\text{CC}$ ); elemental analysis, calculated 8.80% H, 75.7% C, found 8.94% H, 75.4% C.

#### 2,3-Diphenylbutane-2,3-Diol (XXVII)

Compound (XXVII) was made via a published procedure (19). Acetophenone (25 g) was placed a pyrex flask (100 mL) with isopropyl alcohol (75mL). The flask was stoppered and irradiated for 73 hours in the Rayonet reactor. Gas chromatographic analysis indicated that 50% of the acetophenone had been converted to (XXIV). The solvent was evaporated and the remaining oil was dissolved in a minimum volume of warm hexane. When cooled overnight a crop of crystals formed which were recrystallized from fresh hexane. These crystals were dried in a vacuum oven to give 9.4 g (75% yield of converted acetophenone) of (XXVII): mp 121-122°;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.19-7.15 (m, 10H, phenyl), 2.76 & 2.44 (s, 2H, hydroxyls, mixture of isomers), 1.52 & 1.42 (s, 6H,  $\text{CH}_3$ 's, mixture of isomers). Literature: mp 122-123°; (19).

PHOTOCHEMICAL REACTIONS

Preparative Reaction

Acetophenone (0.168 g) and cis-I (0.120 g) were dissolved in benzene (12.0 mL) and placed in a pyrex ampul (17 x 140 mm) provided with a ground glass joint. The ampul was fitted with a condenser and degassed with a stream of nitrogen (see "Degassing Techniques"). The irradiation was done by suspending the ampul in the center of the Rayonet reactor and exposing it for 20 hours.

Analysis of the reaction mixture was done by gas chromatography (see Appendix II, Table III). Several components of the reaction mixture were collected by preparative gas chromatography. The properties of the 8 products collected are reported in the following way: compound; retention time and temperature on the analytical gas chromatograph; NMR spectra obtained; major mass spectral peaks where obtained; other pertinent data.

Trans-I; 1.25 minutes, 60°; retention time and <sup>1</sup>H-NMR compare with those for authentic material (see "Synthesis Section"). Methyl Hexanoate(II); 2.5 minutes, 60°; <sup>1</sup>H-NMR (acetone-d<sub>6</sub>) δ 3.59 (s, 3H, H<sub>3</sub>CO), 2.27 (t, 2H, J=7Hz, H<sub>2</sub>CC=O), 1.78-1.10 (m, 6H, CH<sub>2</sub>'s), 0.87 (t, 3H, J=6Hz, H<sub>3</sub>CC); retention time and <sup>1</sup>H-NMR compare with those for authentic material (Eastman Organic Chemicals). Acetophenone; 8.5 minutes, 88°; retention time and <sup>1</sup>H-NMR compare with those for authentic materials (see "Synthesis Reactions"). 6-Methyltetrahydropyran-2-One(III); 10.0 minutes, 95°; retention time and <sup>1</sup>H-NMR compare with those for authentic material (see "Synthesis Reactions"). Methyl 5-Phenylhexanoate(IV); 18.5 minutes, 139°; retention time and <sup>1</sup>H-NMR compare with those for authentic material (see "Synthesis reaction). 1,7-Dimethyl-7-phenyl-6,8-dioxobicyclo(3.2.1)octane(V); 21.0 minutes, 150°; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.27 (s, 5H, phenyl), 5.84 (s, 1H, HC(OR)<sub>2</sub>),

1.74 (s, 3H, H<sub>3</sub>CCPh), 2.05-1.05 (m, 6H, CH<sub>2</sub>'s), 0.87 (s, 3H, H<sub>3</sub>C); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 127.1 & 126.4 (d, phenyl), 101.4 (c, HC(OR)<sub>2</sub>), 32.4, 29.1 & 16.9 (t, CH<sub>2</sub>'s), 22.9 & 19.9 (q, CH<sub>2</sub>'s); mass spectrum (70 eV) m/e (relative intensity) 2.1 (23), 147 (20), 145 (13), 129 (18), 119 (15), 117 (12), 105 (26), 104 (17), 103 (13), 98 (100), 97 (10), 91 (19), 80 (11), 78 (12), 77 (30), 51 (10), 43 (54), 41 (12). 2-Methoxy-2-(1-phenyl-1-hydroxyethyl)-6-methyltetrahydropyran(VI); 26.75 minutes, 179°; <sup>1</sup>H-NMR (acetone-d<sub>6</sub>) δ 7.54-6.94 (m, 5H, phenyl), 3.72 (s, 1H, HO), 3.56, 3.53 & 3.49 (all singlets, 3H, OCH<sub>3</sub>, mixture of isomers), 2.13 (m, 1H, HCCH<sub>3</sub>), 1.88-1.16 (m, 6H, CH<sub>2</sub>'s), 1.46 (m, 3H, H<sub>3</sub>CCPh, mixture of isomers), 0.82 (m, 3H, H<sub>3</sub>CCH); mass spectrum (70 eV) m/e (relative intensity) 250 (0.4), 232 (5.7), 143 (12), 132 (14), 121 (100), 117 (16), 105 (20), 91 (20), 87 (13), 77 (15), 42 (27). 2,3-Diphenylbutane-2,3-diol(XXVII); 29.0 minutes, 190°; retention time and <sup>1</sup>H-NMR compare with those for authentic material (see "Synthesis Reactions").

#### Oxidative Photochemical Reaction

Acetophenone (0.108 g) and cis-I (0.062 g) were dissolved in benzene (10.0 mL). The mixture was placed in a pyrex ampul (17 x 140 mm) which was provided with a ground glass joint. The ampul was fitted with a condenser and a gas purge tube. The system was purged with air in the same manner as nitrogen was used to purge the preparative reaction. The mixture was irradiated for 20 hours and analyzed via gas chromatography (see Appendix II, Table IV).

#### Kinetic Photochemical Study

Acetophenone (0.160 g) and cis-I (0.106 g) were dissolved in benzene (10.0 mL). Portions of the reaction mixture (1.0 mL) were placed in each of 8 pyrex ampuls (10 x 170 mm). The ampuls were provided with a ground glass joint and tapered to facilitate sealing under vacuum. The ampuls and their contents were degassed via 4 freeze-pump-thaw cycles below 0.01 mm (see "Degassing Techniques").

After sealing, 7 of the ampuls were placed in the merry-go-round of the Rayonet reactor. One ampul was wrapped with aluminum foil and stored at 40° for 720 minutes. The 7 others were irradiated at 40° with periodic removal of an ampul at 30, 60, 120, 240, 480, and 720 minutes. At the end of the reaction, the ampuls were opened, a known amount of internal standard was added to each sample, and the samples were stored at 10° in the dark until gas chromatographic analysis (see Appendix II, Table V for the results of this analysis).

#### Photoreaction of Optically Active Cis-I

Acetophenone (0.317 g) and (+)cis-I (0.209 g) were dissolved in benzene (12 mL). This mixture was placed in 6 pyrex ampuls (10 x 170 mm) provided with ground glass joints and tapered to facilitate sealing under vacuum. The ampuls were degassed via 4 freeze-pump-thaw cycles below 0.01 mm. The ampuls were irradiated for 11 hours in the Rayonet reactor with the merry-go-round. The contents of the vials were combined and analyzed via gas chromatography (see Appendix II, Table VI for the results of this analysis).

Preparative gas chromatography was used to isolate trans-I, cis-I and (III), and optical activities determined. This reaction was done a second time. The amounts of each reaction component were: Acetophenone (0.505 g); (+)cis-I (0.259 g); and benzene (18.0 mL). The reaction was carried out exactly as above; see Appendix II, Table VI for the results of this second analysis.

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APPENDIX I

ANALYTICAL GAS CHROMATOGRAPHIC RESPONSE FACTORS

A response factor is defined below [Eq. (9)]. The definition of the terms used in Equation (9) are as follow:  $A_b$  is the area of the peak representing the internal standard (biphenyl);  $A_i$  is the area of the peak representing compound i;  $W_b$  is the weight of internal standard in the sample;  $W_i$  is the weight of compound i in the sample.

$$RF_i = \frac{A_i}{W_i} \times \frac{W_b}{A_b} \quad (9)$$

Once a response factor has been determined for a compound, in a known mixture, analysis of unknown solutions of that compound are possible. The technique used is to combine a known weight of internal standard with a measured amount of the unknown mixture and inject this mixture into the gas chromatograph. Peak areas are then determined and the values are substituted into Equation (10). The resulting value for the weight of compound i in the sample can then be converted to a concentration by dividing  $W_i$  by the weight of the sample.

$$W_i = \frac{A_i}{RF_i} \times \frac{W_b}{A_b} \quad (10)$$

Response factors were determined experimentally for (I), lactone (III), methyl 5-phenyl hexanoate (IV) and acetophenone. These values seemed to show a trend which followed the weight percentage of carbon in each compound. This observation is supported by the literature (23). An experimental relationship was established between C, H, O ratio and the response factor for each of the compounds investigated. Equation (11) expresses this theoretical relationship.

$$RF_i = C(R_c) + H(R_h) + O(R_o) \quad (11)$$

The known response factors for (III), (I), and acetophenone were used to set up 3 equations in 3 unknowns. The solution to this set of equations provided values for  $R_c$ ,  $R_h$ , and  $R_o$ . The matrix equation is given below [Eq. (12)].

$$\begin{bmatrix} 0.63136 & 0.08831 & 0.28033 \\ 0.64580 & 0.10839 & 0.24578 \\ 0.79973 & 0.06711 & 0.13316 \end{bmatrix} \times \begin{bmatrix} R_c \\ R_h \\ R_o \end{bmatrix} = \begin{bmatrix} 0.445 \\ 0.502 \\ 0.776 \end{bmatrix} \quad (12)$$

The 3 x 3 matrix contains the fractions of C, H, and O for each of the 3 compounds, one compound per row. The first row is for (III), the second for (I), and the third is for acetophenone. The column matrix on the right contains the experimental values found for the response factors for each of the three compounds. The solution to this matrix multiplication provides the following values for  $R_i$ 's:  $R_c = 1.115$ ;  $R_h = 0.2899$ ;  $R_o = -1.0152$ . These factors were used to calculate response factors for all reaction components. Table II lists the calculated values and the experimentally measured values.

The experimental values for response factors were used, when available, to calculate concentrations of reaction mixture components. For the compounds which are not determined experimentally the calculated values were used.

TABLE II  
EXPERIMENTAL AND CALCULATED RESPONSE FACTORS

Compound	RF calc.	RF exp.
I	0.502	*0.502 ± 0.006
acetophenone	0.776	*0.776 ± 0.007
III	0.445	*0.445 ± 0.005
biphenyl	1.061	1.000 ± 0.000
IV	0.712	0.679 ± 0.009
II	0.502	NA
VI	0.634	NA
V	0.734	NA
XXVII	0.772	NA

\* Values used for calculation of  $R_i$ 's.

APPENDIX II

RESULTS OF PHOTOCHEMICAL REACTIONS

TABLE III

RESULTS OF PREPARATIVE PHOTOREACTIONS

Component	Concentration, mM		*Yield
	Initial	Final	
<u>cis-I</u>	76.1	24.0	-
acetophenone	114.0	65.2	-
<u>trans-I</u>	0.0	4.46	8.5%
II	0.0	6.00	11.6%
III	0.0	1.05	1.9%
IV	0.0	3.59	6.7%
V	0.0	2.11	1.4%
VI	0.0	4.24	7.2%
XXVII	0.0	18.7	-

\*Yield calculated as amount of unrecovered cis-I accounted for.

TABLE IV

## RESULTS OF OXIDATIVE PHOTOREACTION

Component	Concentration, mM		*Yield
	Initial	Final	
<u>cis-I</u>	47.6	17.7	-
acetophenone	90.0	70.8	-
<u>trans-I</u>	0.0	0.61	2%
II	0.0	0.92	3%
III	0.0	2.98	10%
IV	0.0	1.21	4%
V	0.0	1.04	3.4%
VI	0.0	0.30	1%
XXVII	0.0	11.0	57%

\*Yield calculated as moles of cis-I accounted for except for XXVII which is based on acetophenone consumed.

TABLE V

## RESULTS OF KINETIC STUDY

Component	Concentration, mM						
	0 min.	30 min.	60 min.	120 min.	240 min.	480 min.	720 min.
<u>cis-I</u>	82.0	69.5	61.8	52.6	52.6	28.0	18.2
acetophenone	133.0	118.0	114.5	101.6	81.4	70.4	52.9
<u>trans-I</u>	0.0	1.21	1.62	2.50	2.80	3.90	4.80
II	0.0	0.92	1.53	2.76	4.53	5.10	8.40
III	0.0	1.05	1.05	1.23	1.50	1.66	1.84
IV	0.0	0.29	0.48	1.12	1.80	3.49	3.78
V	0.0	0.02	0.09	0.16	0.24	0.53	0.72
VI	0.0	0.96	1.56	2.72	3.52	6.16	6.40
XXVII	0.0	3.26	5.33	8.51	12.4	21.7	24.4

TABLE VI  
RESULTS OF OPTICALLY ACTIVE CIS-I PHOTOREACTION

Component	Concentrations, mM		Specific Rotations Reaction 1 / Reaction 2
	Reaction 1 Initial/Final	Reaction 2 Initial/Final	
<u>cis-I</u>	134.0 / 17.5	110.0 / 19.2	+107°      +104°
<u>trans-I</u>	0.0 / 9.23	0.0 / 8.15	+34°      +32°
III	0.0 / 6.40	0.0 / 4.56	*NA      -52°
acetophenone	224.0 / 123.0	236.0 / 134.0	-      -
II	0.0 / 24.8	0.0 / 15.9	-      -
IV	0.0 / 5.83	0.0 / 5.14	-      -
V	0.0 / 1.42	0.0 / 0.56	-      -
VI	0.0 / 7.68	0.0 / 7.32	-      -
XXVII	0.0 / 27.2	0.0 / 26.1	-      -

\* Data was not available due to loss of sample.