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ORGANIC PHOTOCHEMISTRY: A. PHOTOCYCLOADDITION
REACTIONS OF \( \alpha, \beta \)-UNSATURATED KETONES.
B. PHOTOCHEMICAL REACTIONS OF SOME NITROGEN-
CONTAINING HETEROCYCLIC COMPOUNDS.

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ORGANIC PHOTOCHEMISTRY

A. Photocycloaddition Reactions of $\alpha,\beta$-Unsaturated Ketones.

B. Photochemical Reactions of Some Nitrogen-containing Heterocyclic Compounds.

by

Walfred S. Haller

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Doctor of Philosophy

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ABSTRACT

ORGANIC PHOTOCHEMISTRY

A. Photocycloaddition Reactions of α,β-Unsaturated Ketones.

B. Photochemical Reactions of Some Nitrogen-containing Heterocyclic Compounds.

by

Walfred S. Haller

The photocycloaddition reactions of various enones are described. 3-Methylcyclohexenone forms derivatives of bicyclo[4.2.0]octan-2-ones when irradiated in the presence of olefins such as cyclopentene, acrylonitrile, 1,1-dimethoxyethylene, cis and trans-1,2-dichloroethylene and various other alkenes. The products as a whole are governed by electronic factors which involves the formation of a π complex of excited enone and ground-state olefin which subsequently collapses to an intermediate which is predominantly diradical in character. These cycloaddition reactions are believed to proceed via an n → π* excited state of the enone. Such excited states possess a relatively electron-rich β carbon atoms.

Also studied were the dimerization reactions of benzalacetone and furfurylideneacetone. These materials prefer to dimerize even in the presence of a large excess of olefin in marked contrast to 3-methylcyclohexenone which dimerizes fairly sluggishly.

Other materials studied involve photochemical reactions of various 1,2,5-heterodiazoles, 1,3,4-heterodiazoles, 2-acetylfuran, 2-acetylthiophene, acetyl and benzoyl substituted pyridines and various other heterocycles.
The compounds of the 1,2,5-heterodiazole series seem most prone to fragmentation. They give good yields of nitriles and related compounds in addition to fragments containing the heteroatom. In some cases the fragments may be trapped.

The 1,3,4-heterodiazoles give only complex mixtures of many products in low yield. The heterocyclic ketones, 2-acetylfuran and 2-acetylthiophene, are unreactive when irradiated in hydrogen donating solvents such as isopropanol whereas 2-acetylpyridine and 3-benzoylpyridine along with their various isomers form pinacols in good yield. It is believed that the 2-acetylfuran and 2-acetylthiophene have a lowest $\pi \rightarrow \pi^*$ excited state which is unreactive towards olefins and does not undergo hydrogen abstraction. The pyridine compounds most probably react via a lowest $n \rightarrow \pi^*$ triplet as do acetophenone and benzophenone.
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ACKNOWLEDGMENTS

I would like to express my sincere appreciation to Dr. T. S. Cantrell for his guidance and inspiration throughout the past few years without which this work would not have been possible. I would also like to express my thanks to Boyd Harrison for many helpful discussions and to Mr. and Mrs. L. E. Sharpe for their inspiring talks.
To my late father, mother, and sister and also, most respectfully, to Laurae and Mary
PART A. INTRODUCTION

The past decade has witnessed a tremendous increase in the importance of the field of organic photochemistry. Many different areas are presently under investigation and photochemistry has become an important tool to the modern organic chemist. A large amount of study has been performed on synthetic and mechanistic aspects of the photochemistry of ketones, dienones, non-conjugated ketones and α,β-unsaturated ketones.

The enormous amount of work that has been done on the photochemistry of simple carbonyl compounds is summarized by the statement that the excited states of saturated ketones undergo cleavage at the bond α to the carbonyl group (Norrish type I cleavage), producing alkyl and acyl radicals. These radicals undergo decarbonylation, disproportionation, and hydrogen abstraction.¹

\[
\begin{align*}
R-C- & \overset{\text{hv}}{\longrightarrow} R-C-R' + R' \cdot \\
R-C & \quad \quad + R' \cdot \quad \rightarrow + R-R + R'-H \\
& + R'-C \cdot \quad + R'-R' + \text{olefins} \\
& + R' \cdot \quad + \text{aldehydes}
\end{align*}
\]

This chemistry is similar to that of radical species produced by other means and has been given ample study by physical chemists.

In molecules containing a carbonyl group conjugated with one or more double bonds unusual and interesting rearrangements may occur. The laboratories of Zimmerman and Chapman have provided some of the best-studied examples of these reactions. Chapman found that 4,4-dialkyl-2-cyclohexenones undergo rearrangement in which the C₃ and C₄ carbon atoms actually exchange places, producing a bicyclo[3.1.0]hexan-2-one.²
This conversion was later postulated to involve a triplet excited state undergoing the initial rearrangement, followed by electron demotion to an ionic species which then rearranges to products.

Electron demotion to a zwitterion before \( \sim \) is reached regenerates the starting material but once past that point products are formed. \(^3\)

In the case where the \( C_4 \) carbon is substituted by two alkyl groups this "type A" rearrangement predominates. However, when the molecule is substituted at \( C_4 \) by two aryl groups one of these groups migrates to \( C_3 \)
and no further rearrangement occurs. The reason for this is that the electron on C₃ may be delocalized by the migrating aryl group, lowering the energy needed for the reaction, and also once migration has terminated the odd electron is now delocalized by the aryl group which did not migrate. Zimmerman has found that this process proceeds through a triplet state.⁴

From studies of the migratory aptitudes of para-methoxy and para-cyano aryl groups Zimmerman concluded that no appreciable charge developed on C₃ since both groups migrated to approximately the same extent and both were better than phenyl. He concluded that C₃ must have radical character during the actual migration⁵ (see next page).

The photochemical addition of α,β-unsaturated ketones to carbon-carbon double bonds has been the subject of much recent investigation.⁶
Cyclic enones are added to a variety of compounds including olefins, alkynes, alkenes and to themselves to give derivatives of cyclobutane.
The cycloaddition reaction can be applied to yield important synthetic intermediates for natural product research or interesting cage-like molecules as in the examples shown below.

\[ \text{ketone} + \text{cyclopentadiene} \xrightarrow{\text{hv}} \text{cycloaddition product} \xrightarrow{\text{CH}_3\text{Li}} \xrightarrow{\text{H}^+} \alpha\text{-caryophyllene alcohol} \]

\[ \text{ doubly brominated enone} \xrightarrow{\text{hv}} \text{cycloaddition product} \xrightarrow{\text{Cubane}} \]

A significant amount of evidence concerning the reaction mechanism has been obtained. Cycloaddition of enones occurs when a Pyrex filtered lamp (>2900 Å) is used, implying an initial \( n \rightarrow \pi^* \) excited singlet state must be formed. This initial excited state could give rise to either an \( n \rightarrow \pi^* \) triplet or a \( \pi \rightarrow \pi^* \) triplet. From experiments such as those by Eaton involving both sensitization and quenching as well as studies of emission spectra it is now generally believed that the reactive excited states in cycloadditions and dimerizations are \( n \rightarrow \pi^* \) 14-16 triplets. Corey and co-workers have provided further details of the mechanism of the cycloaddition process through a study of orientation and stereochemistry of the products resulting from the photolysis of cyclohexenone with various olefins. The significant finds were that trans-bicyclo[4.2.0]-octanones were usually obtained.
Both orientation and the relative rate of cycloaddition were dependent on the electronic properties of the substituent group attached to the olefin. The mechanism that they presented to explain these observed facts involved the formation of a $\pi$ complex between the excited state of the enone and the ground state of the olefin. The orientation is governed by the olefin in such a way that the electron rich carbon atom of the olefin is adjacent to the $\alpha$-carbon of the enone. This $\pi$ complex then collapses to yield a diradical intermediate which finally gives rise to the cyclobutane.
This hypothesis was supported by the observation that \textit{cis} and \textit{trans}-2-butene gave rise to identical product mixtures implying that a diradical intermediate which has lost steric identity was formed. The possibility of explaining the observed reactions through the formation of a zwitterionic intermediate is negated by the low orientational selectivity of cycloalkenones with weakly polarized olefins such as isobutylene\textsuperscript{9} and propene.\textsuperscript{17} Also the small differences in the relative rates of reaction of cycloalkenone with olefins bearing substituent groups of greatly different electron-donating properties is not enough to be consistent with an intermediate involving any large degree of charge separation. Many reports following Corey's original proposal have provided evidence consistent with his mechanism.\textsuperscript{18,19}

Reports of cycloadditions of enones bearing functional groups on the \pi-system are rather limited and are mostly concerned with enol acetates of cyclohexenone and cyclopentenone,\textsuperscript{20} chromone\textsuperscript{19} and bicyclic vinylogous imides.\textsuperscript{21} Many of the products obtained were of value as synthetic intermediates but the effects of the substituents on the mode of reaction were not dramatic. It is conceivable that enone photoaddition reactions which did not yield synthetically useful products may have gone unpublished.

In order to further elucidate details of substituted cyclohexenone reactions we undertook the study of the products resulting from the photolysis of 3-methylcyclohexenone with various olefins. We also examined various photochemical reactions on benzalacetone and furfurylideneacetone. Several goals were in mind as we tried various reactions; these were: (1) to elucidate the structures of the products obtained and thereby extend the synthetic usefulness of the cycloaddition reaction; (2) to use the knowledge gained of the orientation and stereochemistries of the
adducts to more clearly delineate the mechanism of the addition process and (3) to determine the relative rates of reaction of various substrates with 3-methylcyclohexenone in order to gain information of the eletrical and steric effects of the substituents and on the degree of charge separation in the excited states and intermediates involved.
PART A. DISCUSSION AND RESULTS

Cycloadditions involving α,β-unsaturated ketones have been studied by many groups. The 3-methylcyclohexenone system described below provides useful information as to the extension of the scope of the reaction. 3-Methylcyclohexenone is readily synthesized from acetoacetic ester and formaldehyde followed by treatment with acid.

\[
\begin{align*}
2 \text{EtO}2C\text{CH}2\text{CO}2\text{Et} + \text{HCHO} \rightarrow \overset{\text{B}^-}{\text{B}^-} \rightarrow \overset{\text{H}^+}{\text{H}^+} \\
\end{align*}
\]

Upon irradiation of 4 in ether with 1,1-dimethoxyethylene it was observed that the course of the reaction could be conveniently monitored by infrared by following the disappearance of the carbonyl band of 4 at 1675 cm\(^{-1}\) and the increase in the intensity of the newly forming band at 1702 cm\(^{-1}\). Analysis by gc showed two major products in 35 and 18% yield in addition to several smaller ones. The two materials were isolated by preparative gc. There was no vinyl hydrogen signal in the nmr and combustion analysis supported the formulation that these were the expected 1:1 cycloadducts shown.
That the methoxyls are at C-7 rather than C-8 was shown by hydrolyzing the materials with dilute acid and isolating the dione 3.

This is the γ-diketone shown and not the isomeric β-diketone since it is nonenolic as shown by nmr, ir and a negative ferric chloride test. Also the material is not hydrolyzed by base and shows normal cyclohexanone and cyclobutanone carbonyl bands in the infrared. Exposure of 2 to cold methanolic sodium methoxide effected its isomerization to 1. The compounds are therefore epimeric at C-1 and 2 must be the more strained trans-fused isomer.9,67

Further confirmation of the above structures was furnished by heating the purified materials with m-chloroperbenzoic acid in methylene chloride (Baeyer-Villiger reaction) for several days. This converts both 1 and 2 into lactones 1a and 2b.

The proton α to the lactone oxygen is now clearly removed from the methylene region of the nmr so as to reveal that it is coupled to the adjacent methylene group. This aids greatly in the establishment that
the methoxyls are at C-7 rather than C-8.

Irradiation of 4 with cyclopentene in ether gave three products 5, 6 and 7 in yields of 36, 25 and 4% respectively.

Compounds 5 and 6 were isolated and purified by preparative gc. Combustion analysis and spectral data supported the structures shown below.

The structures shown are further supported by evidence obtained from lactonizing 5 and 6 with m-chloroperbenzoic acid as described above. The corresponding lactone to 5 shows a doublet at τ 5.86 and that of 6 shows two doublets at τ 5.83. Compound 5 shows first-order coupling between the single proton α to the carbonyl and the one adjacent it on the cyclopentane ring. Compound 6 shows a further splitting of the proton α to the carbonyl by long range coupling to the single proton β to it on the cyclopentane ring.24

Compound 5 is converted to 7 by treatment with sodium methoxide in methanol suggesting that 5 is the less stable trans-isomer. Compounds 6 and 7 are inert to base treatment which supports the assignment of cis-stereochemistry. A definite assignment as to which isomer is syn or
anti could not be made on the basis of nmr coupling constants. Observations by workers$^{22,24}$ show that the coupling constants between cis and trans vicinal hydrogens of cyclobutane fused derivatives vary widely and are often of comparable magnitude. However, it seems probable that the major isomer 6 is the cis, anti, cis compound and 7 is the cis, syn, cis material by analogy to the addition of cyclopentene to cyclopentanone in which the anti isomer is formed exclusively.$^7$

Photocycloaddition of 4 to acrylonitrile proceeded very rapidly; work-up and analysis of the reaction mixture showed the presence of 8, 9 and 10 in yields of 29, 17 and 15%, respectively. Spectral data indicate that compounds 8 and 9 are the 8-cyanobicyclo[4.2.0]octan-2-ones.

The nmr spectra of 8 and 9 show the C-1 protons as sharp doublets due to coupling with the proton on the carbon bearing the cyano group. These doublets are shifted further down field on lactonization of 8 and 9 with m-chloroperbenzoic acid in methylene chloride supporting the above structures. The hydrogens on C-8, α to the cyano group, show eight-line multiplets due to coupling with the hydrogen α to the carbonyl and also to the two nonequivalent hydrogens (due to the asymmetry induced by the neighboring cyano group) on C-7.

Exposure of 8 to sodium methoxide in methanol converts it to 9. At first one may be tempted to say that this is a trans-cis type of interconversion. However, the chemical shifts of the C-1 protons of the two
isomers are virtually identical, unlike compounds 1 and 2, which possess a cis or trans ring fusion, respectively. Compounds 1 and 2 have their C-1 protons differing by 0.12 ppm in sharp contrast to 8 and 9. The chemical shifts of the C-8 protons of 8 and 9 however differ by 0.4 ppm suggesting that these materials differ by configuration at C-8. The relative stability of the compounds suggests that 8 is the more hindered endo-cyano isomer and 9 is the exo-cyano compound.

Compound 10 was impossible to separate from 9 though many gc columns were tried. Thus 10 was never obtained pure. Its infrared shows bands characteristic of a cyano group and a saturated carbonyl group suggesting it is a 2 + 2 cycloadduct. However, nothing could be discerned concerning its orientation or stereochemistry.

The photocycloaddition of 4 to ethoxyethylene proceeded quickly and cleanly to give two cycloadducts 11 and 12 in 22 and 65% yield (gc) respectively. They give the correct combustion analysis and show saturated carbonyl and C-O single bond in the infrared.

Treatment with sodium methoxide in methanol gives no change in the gc pattern of the mixture indicating they are cis-fused isomers. Also since no new product peaks appear in the gc it is probable that the ethoxyl group is on C-7 as shown. If the ethoxyl were on C-8 it might be
expected to undergo elimination of ethanol to some extent as shown below.

Further evidence to support the structures as the C-7 ethoxy compounds comes from the irradiation of \( \text{4} \) with benzyloxyethylene. The reaction proceeds rapidly to yield 39\% of the photocycloadduct mixture as a viscous oil (13 and 14).

Treatment of the mixture with sodium methoxide yields a product exhibiting no olefinic signals in the nmr indicating once again that the compounds are the C-7 benzyloxy substituted materials. However, the number of peaks in the \( \tau 5.5 \) to 5.9 range diminishes. This may be due to a trans-cis interconversion.

The epimerized material was hydrogenated at moderate pressure with 10\% Pd/C in ethyl acetate in order to cleave the benzyl group and produce the secondary alcohol shown.
The alcohol, a viscous oil, showed the usual –OH infrared stretch at 3400 cm\(^{-1}\) and a saturated ketone band at 1710 cm\(^{-1}\). This material was easily oxidized by Jones reagent to give an oil which was chromatographed. There was thus obtained the pure diketone \(\tilde{3}\) identical with the sample obtained previously from the hydrolysis of compounds \(\sim 1\) and \(2\). Thus the structures of \(\tilde{13}\) and \(\tilde{14}\) must have the \(\tilde{\text{\acetoxyloxy}}\) group at C-7 and it is plausible to assume that the ethoxy compounds are likewise.

Irradiation of \(\sim 4\) in the presence of \(\tilde{\text{cis}}\) or \(\tilde{\text{trans}}\)-1,2-dichloroethylene gave two major products (\(\sim 15\) and \(\sim 16\)) and three unidentified minor products. The yields of \(\sim 15\) and \(\sim 16\) from \(\sim \text{trans}\)-dichloroethylene were 37 and 24\%, and from \(\sim \text{cis}\)-dichloroethylene were 22 and 41\% (gc).

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl} \quad \text{Cl} \quad \text{hv} \quad \text{CH}_3 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

Compound \(\sim 15\) was rather unstable and lost hydrogen chloride even in the freezer to give \(\sim 17\) (see next page).

Upon treating mixtures of \(\sim 15\) and \(\sim 16\) with mild base followed by fractional distillation or by simply putting the mixture through the gc \(\sim 15\) was converted in high yield (ca. >70\%) to \(\sim 17\). The \(\tilde{\text{nmr}}\) of \(\sim 17\) shows an AB pattern with \(J = 13.2\) Hz indicating \(\tilde{\text{cis}}\) geometry. Woodward-Hoffman
rules state that the thermal ring opening of cyclobutenes is a conrotatory process as shown below.

If the compound $15\overset{\sim}{\sim}$ has the stereochemistry as shown above it may open to give $17\overset{\sim}{\sim}$. That it does so readily gives support for the structure of $15\overset{\sim}{\sim}$ with a methyl group trans to the C-7 chlorine atom. Also the ready thermal elimination of hydrogen chloride from $15\overset{\sim}{\sim}$ suggests strongly that the H-1 atom and the chlorine atom adjacent to it are cis since thermal eliminations of hydrogen halides is a cis process.\[^{25}\] The compound $15\overset{\sim}{\sim}$ is formed in greater yield from the trans-dichloroethylene suggesting that the chlorines are trans to one another. The compound $16\overset{\sim}{\sim}$ is formed in greater yield from cis-dichloroethylene indicating the chlorines are cis\[^{26}\] to each other. It is also stable at $110^\circ$ and not effected by mild base indicating the H-1 and C-8 chlorine atoms are trans and the ring juncture is cis.
Upon irradiation of 4 in 10% solution in ether a white crystalline solid was formed in very low yield (ca. 4%). The material gave a combustion analysis and infrared and nmr spectra consistent with its formulation as a photodimer. The sharpness of its melting point indicated it was a pure material. The stability of the compound to base and even when heated above its melting point of 146° suggested it was a cis-fused isomer rather than a trans-fused one.

There are four possible structures (I-IV) shown below.

![Structures I-IV](image)

The spectral data available could not distinguish between the four compounds. Recently studies by others have shown that the material is the anti-isomer IV. Also smaller quantities of III were isolated and identified by these workers.

The products of irradiation of 4 with isobutene were studied by Corey who reported the compounds 18, 19 and 20 in unstated yields. We repeated his experiment and found yields of 14, 50 and 27% respectively. This repeat experiment was also needed to aid in identification of components involved in the competition studies presented below.
Mixtures of the various olefins were irradiated with \( \tilde{A} \) and the relative rates of addition were determined by integrating the peaks on the gc which were previously assigned to the individual compounds from the single olefin reactions done previously. The results of the study are shown below.

**Table I**

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<th>Relative rate</th>
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<tr>
<td>Acrylonitrile</td>
<td>7.68</td>
</tr>
<tr>
<td>Ethoxyethylene</td>
<td>1.96</td>
</tr>
<tr>
<td>1,1-Dimethoxyethylene</td>
<td>1.27</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>1.00</td>
</tr>
<tr>
<td>Isobutene</td>
<td>0.59</td>
</tr>
<tr>
<td>trans-1,2-dichloroethylene</td>
<td>0.40</td>
</tr>
</tbody>
</table>

The reactivities of cyclopentene and dichloroethylene are divided by two since they contain two reactive centers that lead to the same product.

Sensitization reactions done by others in this laboratory\(^{27}\) show that although the reaction proceeded slightly less efficiently under sensitized conditions (\( \phi / \tilde{\phi} = 0.54 \)) the results indicate the process proceeded through an initial triplet excited state. This excited state is most probably of the \( n \to \pi^* \) type.
The results of the above study are, in general, consistent with the Corey hypothesis that an oriented $\pi$ complex of excited enone and ground state olefin is formed and subsequently collapses to an intermediate which is predominantly diradical in character.

The orientation of the enone and substrate in the complex, and subsequently in the adduct, is governed mainly by the electron distribution in the substrate with the more electron-rich carbon of the substrate being adjacent to the $\alpha$-carbon of the enone; these states possess relatively electron-rich $\beta$-carbons. In this study we have seen that the olefins 1,1-dimethoxyethylene, ethoxyethylene, and benzyloxyethylene give rise to the 7-substituted bicyclooctanones. However isobutene gives rise to the 8-substituted product. Since isobutene is less electron-rich than the substrates mentioned previously it may be less subject to electronic factors involving the enone's excited state in the formation of the $\pi$ complex. Perhaps steric hindrance is encountered when the two methyls of the isobutene group approach the methyl group of the enone and the
Electronic factors are outweighed by this steric effect. Eaton\(^6\) has recently reported evidence to support this hypothesis in that the photo-
cycloaddition of cyclopentenone to propene gives a nearly equal product orientation (1.2:1) in the manner predicted by equation 1 above.

Of interest is the rapid rate of cycloaddition of acrylonitrile to 4. Corey found acrylonitrile to be very slow in cycloaddition to cyclo-
hexenone. Slower, in fact, than any other substrate. The unusual speed of reaction may be due to sensitization of the enone by the acrylo-
nitrile. This olefin absorbs a major portion of the light at the wave-
length used and may be acting as a triplet or singlet sensitizer. Also it is possible that the excited acrylonitrile molecules attack the ground state enone molecules.

The formation of trans fused materials may be accounted for by two different mechanisms. One involves the cycloaddition of olefin to the trans-cyclohexenone ground state as shown below.

\[
\text{trans-adducts}
\]

\text{trans-2-Cycloheptenones have been observed to undergo a thermal 2 + 2 cycloaddition.}^{64} \text{ Although we did not detect trans-2-cyclohexenones it seems possible that they may be precursors to the trans-fused cycloadducts from some cyclohexenes.}

Another possible explanation involves the hypothesis that the trans
adducts arise from a different triplet state than the cis adducts. These triplet states may also be of different geometry. Our data cannot discern between these two possible mechanisms; it is hoped further studies by other workers will clarify this point.

Having met with a fair amount of success in our first study of unsaturated ketones we now turned to other similar materials to see if they would be as reactive and provide rewarding information.

The compounds chosen for study are shown below.

\[ \text{21} \]

\[ \text{22} \]

Benzalacetone 21 was the first of the new series of compounds to be studied. It is easily prepared by condensing benzaldehyde and acetone with base.

Upon irradiation in the presence of cyclopentene a slow reaction takes place over the course of several days to yield a product mixture which was found to be identical with that formed from irradiating the material itself in ether. Apparently dimerization takes place in preference to cycloaddition. Indeed, even in the presence of neat tetramethylethylene in large excess only dimers of benzalacetone are formed. No cycloadducts with the olefin could be detected by spectral means. This is in marked contrast to 4 above where dimers were formed only with the greatest of difficulty and in very low yield. The reaction proceeds in >60% yield. The structures of these dimers have recently been shown by other workers to be those shown below.
They are simply the head to head or head to tail dimers one may have expected. Having come to this point we decided to irradiate compound 22 in the hope that it would form cycloadducts with olefins.

Compound 22, furfurylideneacetone, is prepared in a manner exactly analogous to 21. The material gives upon irradiation in ether for 3 hours a quantitative conversion into a mixture of at least two dimers in about a 2:1 ratio. As in the case of compound 21, compound 22 gives no cycloadducts when irradiated in the presence of cyclopentene or neat tetramethylethylene; only the same mixture of dimers is formed. Analysis by preparative thin layer chromatography failed to separate the materials and it was suspected the compounds are not stable on the silica gel thin layer plates. Attempted gas chromatographic separation led to thermal decomposition at the column temperature required.

From the limited data available one can only guess as to the stereochemistry of the materials formed. The fact that the four ring protons of the minor isomer appear as a single peak at τ 6.42 suggests that it may be one of the two isomers shown, where the hydrogens α to acetyl would be deshielded by a nearly edge-on furan ring. The other material has a completely unknown stereochemistry and it cannot be told whether it
is a head to head or head to tail dimer. It may be the analogous product to one of the dimers of benzalacetone shown above but one cannot say for certain. Perhaps more important than its actual structure is the fact that 22 prefers to dimerize than cycloadd.

In conclusion we may say that compounds 21 and 22 undergo only very selective reactions with themselves.

The factors governing the behavior of the excited states of these enones are not known. It may be that excimers are involved in these dimerizations. Excimers are excited bimolecular species formed by collision of an electronically excited molecule with a similar one in the ground state.

The last enone studied was indenone, 51.

51

It may be prepared in small amounts by bromination of 1-indanone followed by dehydrobromination with \textit{sym}-collidine in ether. The material polymerizes rapidly at room temperature but is stable at 0° if a few crystals of \textit{sym}-trinitrobenzene are added.

After irradiation for 24 hours in ether in the presence of a large excess of cyclopentene (a very small amount of \textit{sym}-trinitrobenzene was also present) it was noted the infrared carbonyl band had disappeared. Work-up yielded only a yellow polymeric material from which no well-defined products could be isolated.

In summation the photochemistry of enones and other conjugated systems is a rewarding one. None of the above materials are totally
unreactive and only one, $5_1$, gave large amounts of polymer formation. It is hoped by the author that other compounds such as $4_{\sim}$ when studied will provide rewarding information as to the synthetic usefulness of photo-chemistry.
PART B. INTRODUCTION

The photochemistry of organic compounds has been the subject of much investigation during the last few years. Many new and interesting reactions have been observed which have no analog in ground state chemistry and only recently has insight been gained of the mechanisms through knowledge obtained of electronic excited states.

One of the most fruitful areas has been that of the photochemistry of aromatic compounds. Substituted Dewar benzene, prismane and benzvalene are all formed on photolysis of 1,2,4-tri-t-butylbenzene. Irradiation of benzene itself gave solutions containing a very small amount of benzvalene and fulvene but no Dewar benzene or prismane. Those cases of Dewar benzenes actually isolated by direct irradiation usually involve benzenes bearing t-buty1 groups or halogen atoms ortho to one another; the steric crowding of substituents in the parent benzenes is greatly reduced in the corresponding Dewar benzenes, thus favoring their formation.

Irradiation of benzene in the presence of olefins leads to adducts which are formally derived from the addition of the substrate to a double bond of Dewar benzene or benzvalene.

Heterocyclic compounds have received attention only very recently. At least one report exists of transformations of six-membered heterocyclic
rings which are similar to those occurring in benzenes. Alkylpyrazines are converted to mixtures of alkylpyrimidine isomers under conditions similar to those used in the photolysis of benzenes.\(^{40}\)

\[
\begin{align*}
\text{N} & \quad \text{N} \\
R & \quad \text{R} \\
\text{hv} & \quad \rightarrow & \quad \text{N} & \quad \text{N} \\
R & \quad \text{R} & \quad + & \quad \text{N} & \quad \text{N} \\
R & \quad \text{R}
\end{align*}
\]

The evidence available was consistent with the intermediary of strained valence tautomers analogous to benzvalene (azabenzvalenes) but not of aza Dewar benzenes.

When five membered ring heterocycles are photolyzed, scrambling of the ring atoms takes place, apparently through a ring opening and reclosure process.\(^{41}\) Thus the photolysis of 2-alkyl and 2-aryl thiophenes leads to the corresponding 3-substituted thiophenes.

\[
\begin{align*}
\text{R} & \quad \text{S} & \quad \text{R} \\
\text{hv} & \quad \rightarrow & \quad \text{R} & \quad \text{S} & \quad \text{R} \\
\text{R} & \quad \text{S} & \quad \text{S} & \quad \text{R} & \quad \text{R}
\end{align*}
\]

Isotope labeling experiments showed that C-2 and C-3 are interchanged with very little concomitant interchange of C-4 and C-5. It was advanced
that the intermediate in these reactions was the cyclopropene-3-thio-
aldehyde shown above.

Analogous processes have been postulated for the interconversions of
oxazoles and isoxazoles⁴² and of imidazole and pyrazole.⁴³ In this case,

\[
\begin{array}{c}
\phi \quad \phi \\
\phi \quad \phi \\
\end{array}
\quad \xrightleftharpoons{\text{hv}} \quad
\begin{array}{c}
\phi \\
R \\
\phi \\
\end{array}
\quad \xrightleftharpoons{\text{hv}} \quad
\begin{array}{c}
\phi \\
R \\
\phi \\
\end{array}
\]

Evidence to validate this general type of mechanism was found. The
expected intermediate, 2-phenyl-3-benzoylazirine, could be isolated and
was found to be converted to II on further irradiation.

Another example of this reaction is the conversion of furans to
cyclopropene-3-carboxyaldehydes and adducts thereof.⁴⁴,⁴⁵

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}
\quad \xrightarrow{\text{hv}} \quad
\left[ \begin{array}{c}
\text{O} \\
\text{H} \\
\text{CHO} \\
\end{array} \right] \quad \xrightarrow{\text{hv}} \quad
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{CHO} \\
\end{array}
\quad + \quad
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{CHO} \\
\end{array}
\quad + \quad \text{CO}
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\quad \xrightarrow{\text{hv}} \quad
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\quad \text{H}_3\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\quad \xrightarrow{\text{hv}} \quad
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\quad \text{H}_3\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\]
The irradiation of 4,5-diphenyl-1,2,3-thiadiazole leads to a mixture of tetraphenyldithiin and 2-benzhydrylidene-1,3-dithiole.\textsuperscript{46}

The initial step is the loss of nitrogen to give the primary fragment which may dimerize to give dithiin or undergo phenyl migration to yield a thioketene which can add to the primary fragment to give the dithiole.

Photolysis of 1,5-diphenyl tetrazole gives 2-phenylbenzimidazole as the sole product.\textsuperscript{47,48} This reaction was considered to proceed via a nitrene intermediate.

Intramolecular insertion of the nitrene into a C-H bond of benzene yields the product observed.

Irradiation of nucleic acids leads to loss of biological activity.\textsuperscript{49} Since the sugar and phosphate groups do not absorb the light used it must
be due to absorption by the purine and pyrimidine bases of the nucleic acids.

It has been shown that adjacent thymine residues in DNA undergo cycloaddition on irradiation of the DNA.\textsuperscript{50} The thymine dimer obtained on hydrolysis of the irradiated DNA is also obtained, along with other dimers, by irradiation of thymine itself in frozen aqueous solution.

\begin{center}
\begin{tikzpicture}
  \node[draw,align=left] (a) {\includegraphics[width=0.5\textwidth]{thymine_dimer.png}};
  \node[align=left, below=0.5cm of a] {R = sugar + phosphate \hspace{1cm} R = H};
\end{tikzpicture}
\end{center}

The structure of this compound has been firmly established as the \textit{syn}, head to head dimer.\textsuperscript{51} The photodimerization of $\alpha,\beta$-unsaturated lactones, esters and amides is well known\textsuperscript{52,53} and the thymine reaction is a typical example. This photoreaction may be reversed by simply using light of a shorter wavelength which cleaves the dimer units and restores the biological activity of the DNA.

The uracil moities of RNA undergo a reversible hydration on exposure to ultraviolet light.

\begin{center}
\begin{tikzpicture}
  \node[draw,align=left] (a) {\includegraphics[width=0.5\textwidth]{uracil_dimer.png}};
\end{tikzpicture}
\end{center}
The product, a substituted β-hydroxyamide, reverts to uracil in the dark under strongly acidic or basic conditions.\textsuperscript{54,55}

The above two reactions are believed to be responsible for a significant portion, if not the major portion, of the loss of biological activity in ultraviolet light-damaged RNA and DNA. In spite of much effort in the photochemistry of nucleic acids little is known of the photochemical changes which may occur in the purine bases adenine and guanine. Simple derivatives of adenine and guanine are irreversibly consumed on photolysis but no well defined products have been isolated. Prolonged irradiation of the parent purine bases leads to the destruction of the ring system with formation of urea and carbon dioxide.

It appears that the study of the photochemistry of simple purine derivatives, and of imidazoles, pyrimidines and certain other nitrogen heterocycles would be of value because of the possibility of finding new transformations of heterocyclic systems and perhaps relevance to nucleic acid photochemistry. Thus we undertook a study of various substituted heterocyclic systems involving sulfur and nitrogen in hopes of finding reactions of theoretical interest and possibly of analogs of reactions of biological importance.

In the past year several more heterocycle photochemical reactions have given products of interest. A few of these are shown below.\textsuperscript{56–9}

In Equation (1) is shown the preparation of Dewar pyridine which is trapped by reduction to the secondary amine. Equation (2) demonstrates the low degree of aromaticity of the heterocyclopentadiene system containing silicon or phosphorous in that dimers are formed whereas the thiophene analogs are not reactive.

Equations (3) and (4) show more rearrangement reactions involving
more familiar ring systems including the reverse of the reaction of Ullman.

It is clear from the above that possibilities of opening new avenues of chemistry involving photochemical reactions of heterocycles seem of wide scope and interest.
PART B. DISCUSSION AND RESULTS

The basic groundwork involving photochemical reactions of simple one heteroatom systems has been fairly well established and it was hoped systems containing two or more heteroatoms would further novel chemistry.

The first series of compounds studied was the 1,2,5-heterodiazoles shown below.

\[
\begin{array}{c}
\text{N} \\
\sim \\
\text{N} \\
\text{R} \\
\sim \\
\text{R}
\end{array}
\]

This series of compounds involving a hetero-hetero bond which may cleave under irradiation and might either result in net fragmentation or ring atom scrambling was thought to be of promise.

The 1,2,5-thiadiazole compounds of this series were prepared from the appropriate bis-oxime and sulfur monochloride as described by Weinstock. Irradiation of 27 in inert solvent led to the formation of both acetonitrile and sulfur in approximately 35% yield.

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\sim \\
\text{N} \\
\text{S} \\
\sim \\
\text{N} \\
\text{CH}_3
\end{array} \text{hv} \rightarrow \text{CH}_3\text{CN} + S
\]

Precipitation of the sulfur proceeds almost immediately and coats the vessel walls. Although a fair amount of tar was produced a reaction was observed which proceeded via cleavage of the hetero-hetero bond. The acetonitrile formed was identified by its gc retention time and by infrared. Careful concentration of the reaction mixture gave a
solution in which the acetonitrile present could be identified by infrared comparison with a synthetic solution of the same approximate composition.

Having met with this initial success we proceeded to photolyze the analogous diphenyl compound which had not been previously reported. The \( 3,4\)-diphenyl-1,2,5-thiadiazole \( \sim \) was prepared by the same procedure as the dimethyl compound.

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{H}_2\text{NOH} & \quad \text{HON} & \quad \text{NOH} & \quad \text{S}_2\text{Cl}_2 \\
\phi & \quad \phi & \quad \phi & \quad \phi & \quad \phi \\
\rightarrow & & \rightarrow & & \rightarrow \\
\text{N} & \quad \text{N} & \quad \phi & \quad \phi \\
\end{align*}
\]

28

Upon irradiation an immediate precipitate was formed which was later shown to be mostly tar containing a small amount of elemental sulfur. Benzonitrile was found by examination of the solution by gc and also by infrared using the methods analogous to those described above for acetonitrile. The yield of benzonitrile was only 11% by gc even taking into account that almost two-thirds of the starting material was recovered. The reaction was not as clean as with the dimethyl compound as evidenced by the brown sludge formed at the bottom of the vessel whereas in the dimethyl case the solid formed is sulfur in a good state of purity.

\[
\begin{align*}
\text{N} & \quad \text{N} & \quad \phi & \quad \phi \\
\rightarrow & & \rightarrow & & \rightarrow \\
\phi\text{CN} & \quad + & \quad \phi \\
\text{hv} & \quad \text{3 days} & \quad \text{S} \\
\end{align*}
\]

All attempts to trap the expected intermediate nitrile sulfide using cyclopentene as the trapping agent failed. However other workers have succeeded using dimethylacetylenedicarboxylate as the trapping agent in
a thermal reaction shown below.\textsuperscript{69}

![Chemical structure](image)

However, the same material when irradiated gave only benzonitrile and sulfur.\textsuperscript{69}

From the above examples we see that the substitution of the phenyl groups lowers the reactivity of the compound. A possible explanation for this is that the phenyl compounds, which absorb light at a much greater wavelength than do the methyl compounds (ca. 2900 Å), have their electronic excited states lying not far enough above their ground states (i.e., less energetic) for the fragmentation reaction to occur. The methyl compounds which absorb light only at much shorter wavelength (ca. 2500 Å) have excited states of sufficiently high energy for cleavage of the N-S bond to occur. With this in mind we began an investigation of the trimethyl- and triphenyltriazoles.

The triazoles were prepared by pyrolysis of the appropriate bishydrazone as shown.

![Chemical structure](image)
The trimethyl compound 30 is best prepared as above even though the bishydrazone is not very stable. All attempts to prepare the compound by the two step route shown below failed at the first step although work by others indicated the dimethyl compound could be prepared. The trimethyl compound had not been previously reported. Attempts to prepare the trimethyl compound by simply heating the bismethylhydrazone in a flask at 200° failed on two counts. First, the bismethylhydrazone is unstable in air and second, even when done under nitrogen no reaction takes place at this temperature. It was found after many trials that passing the melted bismethylhydrazone through a glass wool packed tube heated to 525-550° caused the desired reaction to proceed and gave the expected product in 40% yield.

Upon irradiation 30 gave acetonitrile in low yield (20%) and polymer. No other material could be identified. In hopes of trapping a possible fragment product the reaction was rerun in the presence of a large excess of cyclopentene. The pyrazoline 51 resulting from trapping the intermediate fragment was collected by preparative gc (see next page).

The pyrazoline 51 is unstable in air, being rapidly oxidized. Also storage in the cold under nitrogen was not effective in preventing decomposition over a period of a few days. The amount of pyrazoline formed is closely equal to that of acetonitrile (22%) as expected by the above mechanism.

It was found upon irradiation of 29 in ether that no reaction took
place under a variety of conditions.

For the second time it became clear that the phenylated compound is less reactive than its methyl analog.

An attempt was made to trap any fragments from the phenyl compound using cyclopentene but this failed to give results. Only unchanged starting material could be recovered with a very small amount of tar formation.

At this time we decided to prepare and irradiate compounds of the 1,3,4-heterodiazole series. The methyl compounds were chosen for reasons presented above and were readily prepared from diacetyldihydrazone as shown below.\textsuperscript{73,74}

[Chemical diagrams and equations are present in the image.]
Upon irradiation for several days of the above oxadiazole 31 in ether several products were formed in a rather small overall yield.

Hydrogen was being abstracted from the solvent as demonstrated by the isolation of compounds such as those shown below, from the dimerization of α-ethoxyethyl radicals.

\[
\begin{align*}
\text{CH}_3\text{CHO}\text{C}_2\text{H}_5 \\
\text{C}_2\text{H}_5\text{OCHCH}_3
\end{align*}
\]

It was hoped that the use of isopropyl alcohol as solvent might reduce the number of products formed and lead to the isolation of two or three major components. Unfortunately in isopropyl alcohol the result after irradiation was recovery of most of the starting material and a low (ca. <10%) conversion to many products as in the previous experiment. None of these were resolved sufficiently on analytical or preparative gc to permit collection. Perhaps the low yield and large number of products formed is really not unexpected. It was not supposed that the compound 31 would cleanly undergo loss of a molecule of acetamide as did some of the compounds previously studied. The carbon-oxygen bond, being considerably stronger than a nitrogen-oxygen bond, would not be expected to cleave as easily but still it was hoped some ring scrambled or ring opened products would be formed in fair yield. It is possible that some material did undergo a ring opening or scrambling reaction; several products were formed in very low yield (<1% each by gc) but the reaction is certainly not synthetically useful.

We proceeded to irradiate the thiadiazole 32 shown above in hopes that the carbon-sulfur bond which is more readily cleaved than the carbon-oxygen bond would give interesting products in good yield. Upon irradiation
in ether the starting material was completely consumed within a few hours as evidenced by the infrared spectrum. A large amount of an apparently polymeric brown, gummy material had formed on the vessel walls. The material was scraped off and analyzed in order to see if it contained any elemental sulfur. None could be detected and work-up of the solution gave only a small amount of unreacted starting material. As we had expected the sulfur-containing heterocycle was much more reactive than its oxygen analog but it failed to give well-defined products.

At this stage it was decided that the phenyl compounds analogous to the methyl compounds above would probably not give rewarding results and we turned our attention to the imidazole and isoimidazole compounds shown below.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} & \quad \text{N} & \quad \text{H} & \quad \text{H} \\
\phi & \quad \phi & \quad \phi & \quad \phi & \quad \phi
\end{align*}
\]

A sample of the triphenylimidazole \(33\) was available from our stock and the tetramethyl- and dimethyldiphenylimsoimidazoles \(34\) and \(35\) were readily prepared as shown below.\(^{75}\)

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R}
\end{align*}
\]

\[
\text{NH}_4\text{OAc} \quad \Delta 
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} & \quad \text{N} & \quad \text{H} & \quad \text{H} \\
\phi & \quad \phi & \quad \phi & \quad \phi & \quad \phi
\end{align*}
\]

\(R = \text{CH}_3, \phi\)

The triphenylimidazole \(33\) was very unreactive under all conditions of irradiation, giving only very small amounts of tar. Compound \(34\) gave only a complex mixture of products as did compound \(35\). The products were formed in very low yield (<2% each by gc). None of the products could be
purified or identified.

At this point we decided to irradiate compounds 23 and 24 shown below.

![Chemical structures](image)

The compound 23, 2-styrylfuran, is made via a Wittig reaction in excellent yields. The material was irradiated in pentane to check for dimer formation. After 24 hours of irradiation the mixture was worked up but showed no reaction by infrared analysis and thin layer chromatography. The material was not further studied and we decided to irradiate compound 24.

Compound 24, 2-(β-nitrovinyl)-furan is easily made from nitromethane, furfural and base. Upon irradiation in ether for a few hours a brown, gummy, apparently polymeric material is formed in moderate yield (ca. 50%). When the irradiation is done in the presence of cyclopentene the same reaction takes place. No photocycloducts could be found on work-up of the solution phase. When the crystals of pure 24 are placed in sunlight they become coated with the brown material. The polymer shows a saturated nitro group absorption in the infrared but was not further characterized.

Upon reaching this point in our experimentation we decided to leave the five-ring heteroatom system and move on to the purine system. Purine itself is a difficult compound to prepare and purify so it was decided to prepare a substituted purine, namely N-methylpurine, whose preparation and purification was more easily executed in our lab.

Upon irradiation in acetonitrile (N-methylpurine is insoluble in ether) over a period of several days no reaction was noted by infrared analysis.
or thin layer chromatography. The solvent was changed to absolute methanol and the reaction repeated. Only unchanged starting material and polymer were uncovered on work-up. This was not expected since it had been reported that purine itself would add alcohols at the 6 position to give o-hydroxyalkyl compounds as shown below.

Due to the above mentioned difficulty in preparing purine derivatives it was decided to investigate six-membered ring systems containing one or more heteroatoms. The compounds chosen for study are shown below.

The sym-trimethyltriazine 36 is conveniently prepared from aceto-nitrile.

$$\text{CH}_3\text{CN} + \text{EtOH} \xrightarrow{\text{HCl}} \text{CH}_3\text{C} - \text{OEt}$$

$$\text{NH} \cdot \text{HCl}$$

$$\text{base}$$

$$\text{H}^+$$

$$\text{CH}_3$$

$$\text{N}$$

$$\text{N}$$

$$\text{N}$$

$$\text{H}_3\text{C}$$

$$\text{N}$$

$$\text{N}$$

$$\text{CH}_3$$
The dimethylpyridazine $38$ can be prepared from acetonylacetone and hydrazine hydrate followed by dehydrogenation with 10% palladium on charcoal in the presence of cyclohexene. $78$

$$\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{O} & \quad \text{O} \\
\text{H}_2\text{NNH}_2 & \quad \text{(C}_6\text{H}_{10}\text{N}_2\text{)}_2 \\
\text{Pd/C} & \quad \text{CH}_3
\end{align*}$$

Finally the trimethylypyrimidine $37$ is prepared from acetamidone hydrochloride and acetylacetone by treatment with potassium carbonate at room temperature for four days. $79$

Irradiation of $36$ in ether for 24 hours gave quantitative conversion to a colorless sticky polymer coating the vessel walls. No acetonitrile could be found in the ether solution. The compound $36$ was then irradiated in isopropyl alcohol in hopes of obtaining a photoreduction product but none was obtained. Only the same polymer was formed. Irradiation in n-hexane resulted in no reaction.

Irradiation of $37$ in ether gave only small amounts of polymer and unchanged starting material. Once again dimers of $\alpha$-ethoxyethyl radicals were found. The irradiation was conducted in n-hexane but gave no products. Apparently a hydrogen donor is important for these compounds to undergo reaction.

Upon irradiation of $38$ in ether a product was formed in 14% yield. It was distilled and purified by preparative gc. Spectral data of the highly air sensitive compound indicate that it is the $\alpha$-ethoxyethyl adduct of the dimethylpyridazine $38$ as shown below.

This was the first time that we were able to obtain a product of
this kind. The NMR shows a slightly split quartet for the single proton α to oxygen due to the asymmetric center. This feature of the spectrum gives some assurance that we have assigned the product the correct structure. When the irradiation was carried out in pentane no reaction took place. The material 38 was then irradiated in methanol but gave no methoxy adduct. This was surprising in view of the above observations. A product was formed in small amount but was never identified. It was not a photoreduction product as evidenced by the failure of the material to show NMR signals for methylene or N-H hydrogens. It may be a ring rearrangement product but spectra are ambiguous and no definite conclusion may be formed.

Having met with rather limited success in the compounds described above we turned our attention to the study of one heteroatom five and six membered ring systems. All the systems studied involved molecules known to possess some degree of aromaticity. Almost all of the compounds are available in small quantities from chemical suppliers so that synthesis of the starting materials was not a factor.

We first photolyzed two well known aromatic compounds in isopropyl alcohol. These were acetophenone and benzophenone. Both reactions go quickly and in high yield (>70%) to the pinacol.

We were now ready to see if similar systems involving thiophene, furan and pyrrole rings would undergo the same reaction. The first two
compounds studied were 2-acetylfuran 39 and 2-acetylthiophene 40. Even after several days of irradiation at different wavelengths of light no reaction was noted.

It had been reported that acetophenone when irradiated in the presence of cyclohexene gave some oxetane. The compounds above were then irradiated in the presence of trimethylethylene to see if oxetane formation would occur. Once again no reaction was observed.
At this point we decided to study the benzophenone analogs, 2-benzoylthiophene, 41, and 2,2'-dithienylketone, 42. Unfortunately neither compound gave a pinacol when irradiated in isopropyl alcohol. The compound 41 gave some polymeric tars but the dithienylketone 42 was quantitatively recovered after four days of irradiation. The dithienylketone was checked for oxetane formation using trimethylethylene as the olefin. After four days the reaction mixture was worked up but gave only starting material and a small amount of tar.

\[
\text{41} \xrightarrow{hv} \text{some polymer} \quad \text{OH}
\]

\[
\text{42} \xrightarrow{hv} \text{no reaction} \quad \text{OH}
\]

It was now decided to try two compounds of the pyrrole series, N-acetyl-and 2-acetylpyrrole 43 and 44. They were conveniently prepared as shown. 80, 81

\[
\text{H} \xrightarrow{1. \text{K}} \text{O} \xrightarrow{2. \text{AcCl}} \text{43}
\]

\[
\text{H} \xrightarrow{1. \text{CH}_3\text{MgBr}} \text{N} \xrightarrow{2. \text{AcCl}} \text{44}
\]
Upon irradiation in isopropyl alcohol no reaction took place and the starting materials were recovered.

\[
\begin{align*}
\text{no reaction} & \\
\text{no reaction} & \\
\end{align*}
\]

Upon reaching this stage we decided to photolyze various substituted pyridines. These were the 2 and 4-acetylpyridines and 3 and 4-benzoylpyridines, 45, 46, 47 and 48.

Upon irradiation in isopropyl alcohol for 24 hours using 3500 Å light, as with the benzophenones and acetophenones, the materials gave pinacols in good yield (ca. 70%). The pinacols precipitate out of solution in a high state of purity.
Also 2-benzoylpyridine was irradiated but gave pinacol in only 10% yield. Compounds 45 and 47 were then irradiated in trimethylethylene in order to test for oxetane formation.

The 2-acetylpyridine gave after two days of irradiation a 17% yield (gc) of the oxetane 49 whose structure is shown below.

The compound was purified by preparative gc and is not stable in air. It was best kept under nitrogen in the cold. Likewise, 47 gave an oxetane mixture in 50% yield as indicated by the nmr of the crude reaction mixture. The most probable structure of the major product 50 is shown below.

This compound is also air-sensitive and was never obtained in pure form. However that the structure of both these oxetanes is as shown is
assured by the presence of a quartet at τ 5.5 for the proton α to oxygen and also its being slightly further split due to the presence of the asymmetric center.

Having this data in hand it is possible to speculate as to the mechanism of these reactions. Studies by other workers in this laboratory showed that 2,5-diphenyl-1,2,5-oxadiazole, when irradiated in the presence of sufficient xanthone to absorb 99% of the incident light, underwent photolysis at a rate of only 12% of that on direct irradiation. It appears from this that the 1,2,5-heterodiazoles may cleave through a singlet excited state. These double bond fragmentations are in marked contrast to the one bond cleavage observed in the photolysis of 3,5-diphenyl-1,2,4-oxadiazole and are reminiscent of the thermal splitting of 2,5-diphenyl-1,2,5-oxadiazole to give benzonitrile and phenylisocyanate.

It is known that the first excited singlet state of benzophenone undergoes efficient intersystem crossing to the first excited triplet state, which reacts with alcohol solvents to abstract hydrogen atoms, resulting in pinacol formation. It seems most likely that the substituted pyridine compounds studied react via similar mechanisms. The 2-acetylthiophene, 2-acetylfuran and the two acetylpyrroles may have a lowest excited state involving a $\pi \rightarrow \pi^*$ transition and are hence unreactive. One may envision these systems as α, β, γ, δ unsaturated ketones. Studies by others of such a
system show from calculations that the lowest excited state could be
\( \pi^+ \pi^* \). This explanation seems plausible to carry over to the furan
case due to its low degree of aromaticity. The pyrrole case may be likewise
since pyrrole and furan are closely analogous. Thiophene however is much
more aromatic than either pyrrole or furan. It is hard to explain its
very low reactivity in the cases we have studied if one does not assume a
\( \pi^+ \pi^* \) lowest excited state. A study of the emission spectra of the above
compounds would be useful in resolving these problems. At this time such
a study has not been done but it is hoped in the near future that this
important work will be accomplished. As for the various other unreactive
compounds mentioned above it is probable that these materials have first
excited states which are not sufficiently high energy enough to undergo
cleavage or addition reactions. These include the pyrazine, isoimidazole,
imidazole and pyridine ring systems.

We may sum up our studies by saying that ring systems involving two
or more different heteroatoms seem to show the most promise of yielding
new photochemical transformations. Also rings bearing alkyl substituents
in preference to phenyl groups give the most satisfactory reactions. Our
studies have involved a wide range of different chromophores and it should
give further insight to experimental work planned by others in the future.
EXPERIMENTAL

**General Procedure for Irradiations.** Two types of apparatus were used. Type A consisted of a cylindrical Pyrex irradiation vessel which surrounded a quartz immersion well and was fitted by means of side arms with a cold finger condenser and a small serum bottle cap. Chilled water at 5°-8° was passed through an external bath in which the entire apparatus was immersed. For those reactions in which low boiling substrates such as isobutylene were employed an ethylene glycol-water mixture cooled to -20° was passed through the well and through a cooling coil in an external glycol-water bath. Solutions of the compounds in dry solvents were placed in the vessel and were deoxygenated by flushing with purified nitrogen for 1.5 hr. A slight positive pressure of nitrogen was maintained throughout the irradiations. Solutions irradiated in procedure A were irradiated with a Hanovia Type L medium pressure 450-W mercury arc. A Corex filter sleeve was employed unless otherwise stated. This filter is opaque to light of wavelength shorter than 250 nm.

The type B apparatus consisted of a Rayonet Srinivasan-Griffin photochemical reactor employing 350 nm lamps. A Pyrex test tube containing the solutions to be irradiated was suspended in this reactor and was flushed with purified nitrogen for 1.5 hr. For solvents of high volatility such as ether a condenser was used but otherwise none was needed. A slight positive pressure of nitrogen was maintained throughout the course of these irradiations.

The progress of the reactions using the type A apparatus was monitored by removing aliquots with a syringe and examination by gas chromatography or infrared spectral means.
The progress of type B reactions involved work-up of entire reaction mixture after an appropriate time had passed, usually 24 hr, and examination of the material by infrared spectral means.

Analytical gas chromatography was performed on the following columns: (1) 5 ft x 0.25 in. 5% SE-30 silicone rubber on Chromosorb P (column A), (2) 5 ft x 0.25 in. 5% Carbowax 20-M on Chromosorb P (column B) and (3) 12 ft x 0.25 in. 10% QF-1 fluorosilicone rubber on Chromosorb W (column C). Preparative gas chromatographic separations were accomplished using either a 10 ft x 3/8 in. 20% Carbowax on Chromosorb P (column D) or a 12 ft x 3/8 in. 10% QF-1 on Chromosorb P (column E). Gas chromatographic work was done on a Varian Aerograph Model 202-1B Gas Chromatograph utilizing a thermal conductivity detector. Infrared spectra were taken on a Beckman IR-8 infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian A56-60A instrument operating at 38°. Ultraviolet spectra were obtained on a Cary-14 spectrophotometer.

Preparation of 3-Methylcyclohexenone \( \Delta \). In a 500 ml Erlenmeyer flask was placed 260 g acetoacetic ester and 30 g of paraformaldehyde. To this mixture is added 25 g of piperidine and the flask swirled vigorously by hand. The flask is cooled in ice as necessary over a 15 minute period and then let stand 15 minutes more. After this time has elapsed the flask is warmed on a steam bath for 40 minutes and then let cool. A yellow oil, ca. 160 g, forms and is decanted off the lower aqueous layer. The decanted material is placed in a 1 L one-necked flask in which a solution of 300 ml glacial acetic acid in 200 ml of water to which 30 ml of concentrated sulfuric acid has been added. The mixture is refluxed for 5 hours. The acid is neutralized by addition of a solution containing 254 g of reagent grade sodium hydroxide in 700 ml of water. The resulting solution is
extracted with four 100 ml portions of ether and evaporated on a rotary evaporator with a water bath heated to 50° and operating at 1 atm. pressure. The residual oil was vacuumed distilled at 23 mm of Hg pressure and yielded ca. 25 g of 3-methylcyclohexenone; bp 92° (23 mm).

Photoaddition of 3-Methylcyclohexenone to Cyclopentene. A solution of 3-methylcyclohexenone (6.0 g, 0.054 mol) and cyclopentene (48 g, 0.70 mol) in ether (150 ml) was irradiated 2 hr in the type A apparatus. The solvent was evaporated and the residue distilled to give the adduct mixture as a faintly yellow oil, 6.9 g (.039 mol, 72%), bp 86°-98° (0.15 mm). Analytical gc on column C showed three major peaks amounting to 91% of the total area. These are in order of retention times at 160°, 7 (7.1 min, 6% of area, 4.0% yield), 6 (8.4 min, 25% yield) and 5 (9.2 min, 36% yield). The isomers were isolated by preparative gc on column E at 170°. Compound 7 was available only in very small amount, and was not obtained analytically pure; ir (film), 1705 (C=O) cm⁻¹; nmr (CCl₄), τ 7.4-8.6 (15 H, complex multiplet) τ 8.77 (3 H, s, CCH₃). Isomer 6 was obtained as a colorless oil: ir (film), 1694 (C=O) cm⁻¹; nmr (CCl₄), τ 7.78 (1 H, d, J = 7.0 Hz, CHCHCO) τ 7.5-8.5 (14 H, complex multiplet) and 8.65 (3H, s, CCH₃); no nmr signals below τ 6.5. Compound 5 is thus considered to be one of the stereoisomers of 7-methyltricyclo[6.3.0.0²,7]undecan-3-one. Anal. Calcd for C₁₂H₁₈O: C, 80.91; H, 10.11. Found: C, 80.67; H, 10.04.

Compound 5 was obtained as white prisms from ether-pentane; mp 34°-35°; ir (film), 1698 (C=O) cm⁻¹; nmr (CCl₄), τ 8.00 (1 H, d, J = ~6 Hz) (CHCHCO), τ 7.8-8.6 (14 H, complex multiplet) and τ 9.02 (3 H, s, CCH₃); no signals below τ 7.0. A 2,4-dinitrophenylhydrazone of 5 was prepared in the standard fashion and had mp 162-163°. Anal. Found: C, 81.13; H, 10.27.
Epimerization of 5. A solution of the mixture of 5, 6, and 7 (0.10 g, 0.62 mmol) obtained directly by distillation was stirred with sodium methoxide (20 mg) in methanol (3 ml) for 5 hr. Neutralization of the reaction mixture and work-up afforded a colorless oil which analysis on column C showed to contain only 7 and 6 in a ratio of 52:48. The nmr spectrum of the product showed no CH₃ singlet at τ 9.02, whereas the signal due to 7 at τ 8.77 was greatly increased in size. Evidently 5 is converted 7 by base.

Lactonization of 5 and 6. Samples of 5 and 6 were treated with m-chloroperbenzoic acid in 20% excess, in methylene chloride solution; for 4 days to effect Baeyer-Villiger oxidation. Work-up as described below for 1 and 2 gave the ɛ-lactones derived from 5 and 6 as oils. The 6 lactone showed the following spectral properties: ir (film), 1739 (C=O) cm⁻¹; nmr, τ 5.83 (1 H, 2 doublets J = 7.8 Hz, J' = 2.0 Hz, >CHOCO), τ 8.78 (3 H, s, CCH₃) and τ 7.0-8.6 (14 H, complex multiplet). The 5 lactone data are ir (film), 1740 (lactone C=O) cm⁻¹; nmr (CCl₄), τ 5.86 (1 H, doublet, J = 5.2 Hz, >CHOCO), τ 7.0-8.8 (14 H, complex multiplet) and τ 9.00 (3 H, s, CCH₃).

Photoaddition of 3-Methylcyclohexenone to 1,1-Dimethoxyethylene. A solution of 3-methylcyclohexenone (5.47 g, 0.050 mol) and 1,1-dimethoxyethylene (45 g, 0.52 mol) in dry ether (170 ml) was irradiated in the type A apparatus for 2.5 hr. Evaporation of the solvent and distillation of the residue gave two fractions: (1) bp 59-74° (0.15 mm), 1.3 g; analysis on column A showed >95% of starting enone (4) present; (2) 4.2 g bp 84-105° (0.15 mm), analysis on column A showed two major peaks comprising 86% of the total area and five minor peaks comprising the remaining 14% of the area. The two major components were isolated by preparative gc on
column E. The faster moving major component had a retention time of 17.4 min at 180° and was identified as 6-methyl-7,7-dimethoxy-cis-bicyclo[4.2.0]-octan-2-one (1, 35% based on unrecovered), ir (film) 1702 (C=O) cm⁻¹; nmr (CCl₄), τ 6.86 and 6.90 (s, 3 H each, OCH₃), τ 7.5–8.5 (9 H, complex multiplet) and τ 8.76 (3 H, s, CCH₃). Anal. Calcd for C₁₁H₁₈O₃: C, 66.65; H, 9.14. Found: C, 66.37; H, 9.05.

The second major peak, of retention time 19.5 min at 180°, was found to be 6-methyl-7,7-dimethoxy-trans-bicyclo[4.2.0]octan-2-one, (2, 18% based on recovered 4): ir (film), 1718 (C=O) cm⁻¹; nmr (CCl₄), τ 6.76 and 6.90 (s, 3 H each, OCH₃), τ 7.2–8.7 (9 H, complex multiplet) and τ 9.03 (3 H, s, CCH₃). Anal. Found: C, 67.00; H, 9.21.

Epimerization of 2 to 1. A solution of 0.10 g of the trans isomer 2 (0.50 mmol) and sodium (ca. 0.01 g) in methanol (2 ml) was stirred under nitrogen at room temperature for 2 hr. The solution was poured into water and extracted twice with pentane. The combined pentane extracts were washed with water, dried, and evaporated. The faintly yellow oil remaining showed one gc peak on column A with the same retention time as 1; the ir spectrum was identical with that of authentic 1.

Hydrolysis of 1 and 2 to the Diketone. A solution of 0.20 g (1.01 mmol) of a mixture of 1 and 2 was treated with sodium methoxide as described above. The material was added to a mixture of tetrahydrofuran (3 ml) and water (2 ml) containing 3 drops of concentrated hydrochloric acid and stirred at room temperature for 4 hr. Neutralization and work-up gave a yellow oil (0.18 g) which was distilled in a short-path apparatus to give colorless 6-methylbicyclo[4.2.0]octane-2,7-dione 3: bp 50–60° (bath temperature 0.4 mm); ir (film), 1779 and 1700 (cyclohexanone and cyclo-
butanone C=O) cm⁻¹; a ferric chloride test was negative. Anal. Calcd
for C₉H₁₂O₂:  C, 71.05; H, 7.89.  Found:  C, 70.81; H, 7.97.

**Baeyer-Villiger Oxidation of 1 and 2.** A solution of 2 (0.10 g, 0.50 mmol) and m-chloroperbenzoic acid (0.12 g, 0.65 mmol) in methylene chloride (5 ml) was allowed to stand at room temperature for 3 days. Filtration of the m-chloroperbenzoic acid and evaporation of the solvent gave a semisolid residue containing unreacted peracid. This was extracted three times with pentane and the pentane extracts were evaporated to give the ε-lactone 2b as a viscous oil:  ir (film), 1738 (lactone C=O) cm⁻¹; nmr (CCl₄), τ 5.86 (1 H, 2 doublets, J = 9.2 Hz, J' = 8.4 Hz, >CHOCO), τ 6.61 and 6.70 (3 H each, singlets, OCH₃), τ 7.3-8.8 (8 H, complex multiplet) and τ 8.89 (3 H, s, CH₃).

Lactonization of 1 in the same manner gave a colorless oil which appeared to be the expected ε-lactone 1g:  ir (film), 1731 (C=O) cm⁻¹; nmr (CCl₄), τ 5.99 (1 H, apparent triplet, J = 4.8 Hz, CH₂CHOCO), τ 6.82 and 6.94 (3 H each, s, OCH₃), τ 7.3-8.8 (8 H, complex multiplet) and τ 8.75 (3 H, s, CH₃).

**Photoaddition of 3-Methylcyclohexenone to Ethoxyethylene.** A solution of 3-methylcyclohexenone (5.0 g, 0.046 mol) and ethoxyethylene (50 g, 0.70 mol) in ether (150 ml) was irradiated in apparatus type A for 5 hr. Evaporation of the solvent and distillation of the residue gave the adduct mixture (5.8 g) as an oil bp 83-110° (0.2 mm). Analysis on column B showed two major peaks (11 and 12) representing 22 and 65% of the total peak area. Treatment of the mixture with sodium methoxide (0.2 g) in methanol (5 ml) caused no change in composition as shown by gc and nmr. A sample of the mixture was redistilled for analysis, bp 60-70° (bath) (0.15 mm). Anal. Calcd for C₁₁H₁₈O₂:  C, 72.53; H, 9.90.  Found:  C, 72.16; H, 9.64.
Photoaddition of 3-Methylcyclohexenone to Benzyloxyethylene. A solution of 3-methylcyclohexenone (5 g, 0.046 mol) and benzyloxyethylene (67 g, 0.50 mol) in ether (150 ml) was irradiated in the type A apparatus for 4.5 hr. Distillation of the residue gave, after 53 g of benzyloxyethylene recovered, the adduct mixture as a viscous oil, bp 173-210° (0.1 mm), 4.1 g (39%). The crude mixture of 13 and 14 showed ir maximum (film) at 1703 (C=O) cm⁻¹ and in the nmr (CCl₄) three broad singlets in the region τ 5.5-5.9 (methylene of benzyloxy). No olefinic hydrogen signals appeared in the nmr spectrum after base treatment with sodium methoxide in methanol indicating that the benzyloxy groups were in the 7 position. However the number of peaks in the τ 5.5-5.9 region was reduced, probably because a trans-fused isomer was being epimerized to a cis-fused one.

A sample of the crude mixture of isomers was degraded to the dione 3 by the following procedure. A solution of 13 and 14 (2.0 g, 8.0 mmol) and sodium methoxide (0.5 g) in methanol (50 ml) was stirred for 3 hr. The solution was neutralized and evaporated to dryness. The residue was extracted three times with 4:1 pentane-ether; the combined extracts were evaporated and the viscous oily residue was dissolved in ethyl acetate (70 ml) and hydrogenated over 10% palladium-charcoal under 15 psig hydrogen pressure. After the catalyst was removed by filtration the product was recovered by evaporation of the solvent. The infrared spectrum of the oil thus obtained showed a broad strong band at ~3400 cm⁻¹ and a ketonic band at 1710 cm⁻¹, in agreement with expectation for 6-methyl-7-hydroxybicyclo[4.2.0]octan-2-one.

The material was dissolved in acetone (40 ml) and oxidized with Jones reagent (8 N chromic acid) at 20°. Evaporation of most of the
acetone, addition of sodium chloride solution, and extraction with ether gave, after washing the extracts with sodium bicarbonate solution, drying, and removal of the solvent, a yellow oil which was distilled to afford 0.34 g of the diketone (bp 50-60° at 0.15 mm). This material was chromatographed on a 20 x 120 mm silica gel column and eluted with chloroform-hexane mixtures. Evaporation of the 1:2 chloroform-hexane fractions gave diketone 3 as a colorless oil (0.28 g) identical (ir and gc) with a sample previously obtained as described above.

Photoaddition of 3-Methylcyclohexenone to Acrylonitrile. A solution of 3-methylcyclohexenone (5.0 g, 0.046 mol) and acrylonitrile (41 g, 0.75 mol) in ether (160 ml) was irradiated in the type A apparatus for 2.5 hr. After filtration to remove some acrylonitrile polymer and evaporation of the solvent, the residue was distilled to give the adduct mixture as a viscous oil, bp 104-115° (0.15 mm), 4.9 g (66%). A viscous orange liquid (1.6 g) remained in the distilling flask. Analysis on column C showed three major peaks (~8, 9 and 10). Compounds 8 and 9 were isolated by preparative gc on column E at 195°; we were unable to obtain 10 free of 9 since none of the columns tried gave a clean separation. Compound 8 (retention time 13.0 min at 195° on column C; 17% by gc peak areas) was obtained as a colorless oil: ir (CCl₄), 2236 (C≡N) cm⁻¹ and 1696 (C=O) cm⁻¹; nmr (CCl₄), δ 6.58 (1 H, eight-line pattern which is the A portion of an ABXY multiplet; Jₐb = 10.4 Hz, Jₐₓ = 8.5 Hz, Jₐᵧ = 7.5 Hz, >CHCHCNCH₂), δ 7.28 (1 H, doublet, B portion of ABXY pattern where Jₐb = 10.4 Hz, Jₐₓ = 0 Hz, COCHCN), δ 8.73 (3 H, s, CCH₃) and δ 7.5-8.5 (8 H, complex multiplet). Anal. Calcd for C₁₀H₁₃NO: C, 73.61; H, 7.98. Found: C, 73.42; H, 8.24.

Compound 9 (retention time 11.0 min at 195° on column C; 29% yield
by gc) was collected from column E as a colorless oil, contaminated with ca. 30% of \( \sim 10 \); ir (film) 2240 (C≡N) cm\(^{-1}\) and 1707 (C=O) cm\(^{-1}\); nmr (CCl\(_4\)), \( \sim \tau 6.83\) (1 H, eight lines which are the A portion of an ABXY multiplet, \( J_{AB} = 6.6\) Hz, \( J_{AX} \sim 8\) Hz, \( J_{AY} \sim 6\) Hz, CHCN), \( \sim \tau 7.24\) (1 H, doublet, B half of AB pattern, \( J = 6.6\) Hz, COCHCH(CN)\(^-\)), \( \sim \tau 8.53\) (3 H, s, CCH\(_3\)) and \( \sim \tau 7.5-8.4\) (8 H, complex multiplet). Anal. Found: C, 73.18; H, 7.69.

Isomer \( \sim 10\) (retention time 10.4 min at 195\(^\circ\) on column C; ca. 15% by gc) was isolated only as mixtures with \( \sim 10\). It showed the following spectral properties: ir (film), 2240 (C≡N) cm\(^{-1}\) and 1701 (C=O) cm\(^{-1}\).

Epimerization of adduct \( \sim 8\). A solution of mixture as obtained directly from distillation (0.10 g) and sodium methoxide (0.025 g), and methanol (3 ml) was stirred at room temperature for 6 hr. Neutralization with Dry Ice and work-up gave a yellow oil (0.083 g) which showed peaks for \( \sim 10\), \( \sim 9\) and \( \sim 8\) in the ratio of 23:70:7; the ratio before the base treatment was 25:45:30. The nmr spectrum of the product mixture showed no signal for the methyl of \( \sim 8\) at \( \sim \tau 8.73\), whereas the methyl signal at \( \sim \tau 8.58\) was of increased intensity.

Baeyer-Villiger Oxidation of \( \sim 8\) and \( \sim 9\). Samples of \( \sim 8\) and \( \sim 9\) (0.10 g each) and m-chloroperbenzoic acid (0.14 g for each ketone) were refluxed in methylene chloride for 3 days. The reaction mixtures were filtered and examined by nmr directly. In the spectrum of the lactone derived from \( \sim 9\) the doublet at \( \sim \tau 7.24\) had almost vanished and was replaced by a new doublet at \( \sim \tau 5.90\) (J = 7.6 Hz, CHOCO); the multiplet at \( \sim \tau 7.24\), due to H-8, did not change position. In the spectrum of the lactone \( \sim 8\), the doublet at \( \sim \tau 7.28\) was missing and replaced by a broadened doublet at \( \sim \tau 5.87\). The multiplet for H-8 appeared at \( \sim \tau 6.62\).

Photoaddition of 3-Methylcyclohexenone to cis- and trans-1,2-Dichloroethylene. A solution of 3-methylcyclohexenone (5.00 g, 0.046 mol)
and trans-1,2-dichloroethylene (60 g, 0.62 mol) in dry ether (150 ml) was
irradiated in the type A apparatus for 7 hr. Evaporation of the solvent
and excess dichloroethylene gave the adduct mixture as a golden yellow
oil (7.0 g), bp 100-110° (0.2 mm), which underwent partial decomposition
on attempted distillation. Analysis on column C showed two major components,
15 and 16 in 37 and 24% yield by gc and a number of minor components
(17% of gc total peak area). Preparative gc on column E caused elimination
of hydrogen chloride from 15 and to the isolation of the monochloro ketone
17. Short path distillation gave 17 as a colorless oil, bp 100° (bath)
(0.2 mm), ir (film), 1688 (conjugated C=O) cm⁻¹; nmr (CCl₄), 0.38 and 3.62
(2 H, AB quartet, J = 13 Hz, cis CH=CH), 8.00 (3 H, s, CCH₃), and 7.4-7.9
(6 H, complex multiplet); uv (CH₃OH), 267 nm (ε 7300). Accurate
analytical data could not be obtained on 17 as the compound decomposed on
storage even at 0°.

Compound 16 was isolated either by preparative gc on column E or,
in larger amount, by stirring the crude adduct mixture at 5° with tri-
ethylamine and fractional distillation of the product. After 17 bp 65-80°
(0.2 mm) there was obtained 16 as a yellow oil, bp 116-121° (0.2 mm) which
solidified in the receiver. Recrystallization from pentane-ether gave
pure 16 as white prisms: mp 53-55°; ir (CCl₄), 1710 (C=O) cm⁻¹; nmr
(CCl₄), 5.82 and 5.98 (2 H, five-line multiplet, AB portion of ABX
pattern in which J_A = 0 Hz, J_AB = 8.0 Hz, J_BX = 8 Hz, CHClCHCl), 7.49
(1 H, doublet, J = 8 Hz, COCH₃), 8.66 (3 H, s, CCH₃), and 7.5-8.4
Found: C, 52.74; H, 5.57.

In the analogous manner a solution of 3-methylcyclohexenone (5.00 g,
0.046 mol) and cis-1,2-dichloroethylene (60 g, 0.62 mol) was irradiated,
worked-up and analyzed. The yield of compounds 15 and 16 was 20 and 48%, respectively.

Photodimerization of 3-Methylcyclohexenone. A solution of 3-methylcyclohexenone (15.0 g, 0.14 mol) in ether (150 ml) was irradiated in the type A apparatus for 6 days. The solution was filtered to remove a small amount of precipitated product (0.3 g) and the filtrate evaporated. The oily yellow residue was chromatographed on a 2 ft x 1 in. silica gel column using 100 ml portions of 50-50 mixtures of hexane-methylene chloride. Evaporation of the first three fractions yielded 0.3 g more of the product. The material was combined with the filtered material and recrystallized from 95% ethanol to give 0.55 g (4% yield) of white prisms: mp 145-46°; ir (CCl₄), 1695 (C=O) cm⁻¹; nmr (CCl₄) τ 8.90 (6 H, s, CCH₃), τ 7.58 (2 H, s, >CHCO) and τ 7.7-8.4 (12 H, complex multiplet). Anal. Calcd for C₁₄H₂₀O₂: C, 76.36; H, 9.09. Found: C, 76.10; H, 9.17.

Competition studies. Competition studies were performed by irradiating an enone in the presence of an equimolar amount of each of two olefins, usually a tenfold excess of each employed. The reactions were monitored by gc to ensure that the ratios of the two sets of products did not change appreciably during the course of the reactions. The area of the peaks corresponding to the sets of products from the two substrates were measured and the ratios were considered to represent the relative reactivities. Each value is the average of at least two determinations.

Preparation of 2,4,5-Triphenyl-2H-1,2,3-Triazole 29. In a 500 ml Erlenmeyer flask containing a hot solution of 20 ml of H₂O in 250 ml of glacial acetic acid was placed 43 g (0.20 mol) of benzil. After the benzil dissolved 3 ml of concentrated hydrochloric acid were added and then 45 g (0.41 mol) of phenylhydrazine. The solution was heated for
half an hour on a steam bath and then thoroughly chilled. The bisphenyl-
hydrazone was collected and washed with 95% ethanol and allowed to dry.
The crude bisphenylhydrazone, ca. 50 g, was put into a 250 ml round bottomed
flask and heated for 6 hr at 205° under nitrogen. The solution was cooled
and a yellow solid (proved later not to be the desired substance) separated
leaving a yellow oily solution. The yellow oil was decanted off and
extracted three times with 1:1 100 ml portions of hexane-methylene chloride.
These were evaporated to give a yellow solid. The solid was recrystallized
from methylene chloride by addition of small amounts of ethanol and through
chilling. The yield was 11 g (22%) of yellow prisms: mp 118-119°; lit.
119-120°.

Photolysis of 2,4,5-Triphenyl-2H-1,2,3-Triazole 29. A solution of
4.5 g (0.016 mol) of 1,3,4-triphenyl-1,2,5-triazole in 210 ml of dry ether
was irradiated for 48 hours in the type A apparatus. The reaction was
monitored by thin layer chromatography on silica gel plates using carbon
tetrachloride as the solvent. After the above mentioned span of time had
passed no reaction had been noted and the starting material was recovered
by evaporation of the solvent. The infrared spectrum and melting point
of the recovered material were also identical to that of the starting
material. Repeating the above with methanol as the solvent gave the same
results.

Photolysis of 2,4,5-Triphenylimidazole 33. A solution of 2.0 g
(0.008 mol) of 2,4,5-triphenylimidazole in 190 ml of dry tetrahydrofuran
was irradiated for 24 hr in the type A apparatus using a pyrex filter.
No reaction had taken place as evidenced by thin layer chromatography and
a corex filter was then inserted and the solution irradiated for another
24 hr. The solvent was evaporated and the residue was proven to be
unreacted starting material from the infrared spectrum and melting point.

**Photolysis of 3,4-Dimethyl-1,2,5-Thiadiazole** 27. A solution of 3.0 g (0.026 mol) of 3,4-dimethyl-1,2,5-thiadiazole in 200 ml of dry ether was irradiated in the type A apparatus using a vycor filter for 3 days. A yellow solid formed evenly over the walls of the vessel. The solution was decanted off and the yellow solid collected and recrystallized from benzene. The material crystallized as yellow rhombohedrons, 0.25 g, mp 112-114°, and was proved by mixed melting point to be identical to rhombic sulfur. Examination by gas chromatography on column A at 50° of the decanted solution showed two peaks. One was ether and the other had a retention time identical to that of known acetonitrile. A mixed infrared of ether and acetonitrile was identical to the infrared of the partially concentrated decanted solution. The yield based on sulfur was 32% and on acetonitrile 35% (gc).

**Preparation of 3,4-Diphenyl-1,2,5-Thiadiazole** 28. Into a one liter three necked flask equipped with a stirring motor, condenser, dropping funnel and thermometer was placed a solution of 36.5 g (0.15 mol) of the bisoxime of benzil (prepared in the usual manner) in 100 ml of dry dimethylformamide. Slowly to this solution was added 48 ml (80 g) of sulfur monochloride so that the temperature did not rise above 75°. After addition was complete the reaction mixture was heated 3.5 hr and then allowed to cool to room temperature. Water was added slowly to the reaction mixture until gas evolution ceased. The solution was then extracted with four 100 ml portions of ether and evaporated to one-fourth volume. Hexane (20 ml) was added to precipitate most of the sulfur. The solution was then decanted to remove the sulfur precipitate and evaporated to yield a yellow oil which on cooling crystallized. The material was recrystallized
from the minimal volume of chloroform to yield 5 g (14%) of white prisms: mp 82-83°; ir (CCl₄), 692 (phenyl) cm⁻¹ and 731 (phenyl) cm⁻¹; λ max 293 μu, ε = 14,000; Anal. Calcd for C₁₄H₁₀N₂S: C, 70.60; H, 4.22. Found: C, 70.54; H, 4.41.

Photolysis of 3,4-Diphenyl-1,2,5-Thiadiazole 28. A solution of 1.5 g (0.006 mol) of 3,4-diphenyl-1,2,5-thiadiazole in 210 ml of dry ether was irradiated in the type A apparatus for 3 days. A yellow solid formed evenly over the walls of the vessel. The solution was decanted and the yellow solid (0.05 g) collected, recrystallized from benzene and identified as sulfur as described above. The decanted solution was partially evaporated and examined by gas chromatography on column A at 50°. Two peaks were seen. One was ether and the other had a retention time identical to that of benzonitrile. A solution consisting of ether, benzonitrile and starting material had an infrared identical to that of the reaction mixture. Evaporation of the remaining solvent led to recovery of 1.0 g of the starting material. The yield based on sulfur was 20% and based on benzonitrile was 11% (gc).

Preparation of 2,4,5-Trimethyl-2H-1,2,3-Triazole 30. In a 500 ml Erlenmeyer flask was placed a solution of 84 g (0.98 mol) of biacetyl in 200 ml of 95% ethanol. This mixture was thoroughly chilled in an ice bath and 100 g (2.18 mol) of methyl hydrazine was slowly added. After addition was complete the mixture was heated on a steam bath for 1 hr and allowed to cool. Thorough chilling yields the product which was washed with cold ethanol to give, ca. 40 g, of the bismethylhydrazone. The material decomposes rapidly in the air and therefore is stored under ethanol until used.

In a 10 ml round bottomed flask equipped with a nitrogen inlet tube was placed ca. 2 g of quickly filtered and ethanol washed bismethylhydrazone.
The flask is attached to a one foot long glass wool packed pyrolysis tube which was suspended horizontally in an oven heated to 525°. The outlet of the pyrolysis tube was connected to two round bottomed flasks connected in series and suspended in dry ice-acetone baths to act as traps. The bismethyldihydrazone was heated to melting by aid of an oil bath and the material slowly forced through the tube using nitrogen as the flush gas. The material collected in the traps melts on warming to room temperature and was poured out and vacuum distilled to yield a faintly yellow oil, 0.7 g (40%), bp 58-60° (4.5 mm): ir (film), 1630 (C=N) cm⁻¹; nmr (CCl₄), δ 7.90 (s, CCH₃, 6 H) and δ 6.09 (s, NCH₃, 3 H). Anal. Calcd for C₅H₉N₃: C, 54.1; H, 8.11. Found: C, 49.9; H, 7.92.

Photolysis of 2,4,5-Trimethyl-2H-1,2,3-Triazole 30. A solution of 2.3 g (0.02 mol) of 1,3,4-trimethyl-1,2,5-triazole in 200 ml of dry ether was irradiated in the type A apparatus using a vycor filter for 24 hr. Spinning band distillation of the resulting mixture yielded 2.5 g of a solution containing 22% acetonitrile (gc). The acetonitrile was identified as described above.

Under the same reaction conditions as described above 2.0 g of the triazole was photolyzed in the presence of 25 g (0.30 mol) of cyclopentene in 170 ml of dry ether. After 24 hr of irradiation the product mixture was worked up by first spinning band distillation to remove ether and cyclopentene and then vacuum distillation to yield a faintly yellow liquid, bp 40-42° (0.4 mm). Analysis on column C showed two peaks. One of these was starting material and the other was the pyrazoline, 51, in 25% yield (gc) based on recovered starting material: ir (film), 1597 (C=N) cm⁻¹; nmr (CCl₄), δ 6.56 (1 H, multiplet, H adjacent to nitrogen), δ 7.38 (3 H, s, N-CH₃), δ 7.79 (1 H, pair of doublets, J = 8.2 Hz, J' = 2.7 Hz, H on
C=N), τ 8.20 (3 H, s, CCH₃), τ 8.25-8.50 (6 H, multiplet). Accurate analytical data could not be obtained due to decomposition of sample on storage even in the cold.

**Photolysis of 2,5-Dimethyl-1,3,4-Oxadiazole 31.** A solution of 3.7 g (0.04 mol) of 2,5-dimethyl-1,3,4-oxadiazole in 200 ml of dry ether was irradiated through a vycor filter for six days in the type A apparatus. The resulting mixture was spinning band distilled to remove ether and the remaining material analyzed on column B. At least fifteen peaks were present in addition to some remaining starting material. None of the peaks were of sufficient amount or separated well enough from others to be collected. The reaction was rerun for three days in isopropyl alcohol in hopes of cutting down the number of products obtained. This was to no avail as again a large number of products were formed making analysis impossible. Irradiation in the presence of cyclopentene yielded no trapped fragments.

**Photolysis of 2,5-Dimethyl-1,3,4-Thiadiazole 32.** A solution of 0.7 g (0.006 mol) of 2,5-dimethyl-1,3,4-thiadiazole in 200 ml of dry ether was irradiated in the type A apparatus through a vycor filter for 7 hr. A large amount of tar was formed on the walls of the reaction vessel and analysis of the solution showed only unchanged starting material present. No sulfur or acetonitrile could be detected by analytical techniques.

**Preparation of N-Methylpurine.** The material was prepared as described in the literature ⁶⁰ from methylaminoacetonitrile and formamidine acetate in formamide. It was noted however that only two sublimations (perhaps only one) followed by recrystallization from absolute ethanol would give the product in high purity. Use of 95% ethanol leads to product resinification.
Irradiation of N-Methylpurine. A solution of 1.0 g (0.007 mol) of N-methylpurine in 200 ml of dry acetonitrile was irradiated through a pyrex filter for three days in the type A apparatus. Analysis of aliquots taken showed no reaction based on thin layer chromatography and melting point. A corax filter was inserted and the reaction run for 24 hr more. Again no reaction was noted upon analysis and a vycor filter was tried. Once again the results were negative. Finally the solvent was changed to methanol and the solution irradiated 48 hr through vycor. Analysis of the material resulting showed it to be mostly starting material with some amount of polymeric tar formed.

Photolysis of 2,4,6-Trimethyl-1,3,5-triazine 36. A solution of 3.3 g (0.027 mol) of 2,4,6-trimethyl-1,3,5-triazine in 200 ml of dry ether was irradiated in the type A apparatus for 20 hr. A transparent gummy material had formed over the walls of the vessel. Analysis of the ether solution showed the presence of neither acetonitrile nor starting material. The transparent material formed was scrapped from the walls of the vessel. It was found to be undistillable with a high boiling point, ca. >300° (0.2 mm). It could not be crystallized and was assumed to be a high polymer. The same result was obtained with a pyrex filter and the solvent changed to isopropyl alcohol.

Photolysis of 2,2-Dimethyl-4,5-Diphenylisomidazole 35. A solution of 2.0 g (0.008 mol) of 2,2-dimethyl-4,5-diphenylisomidazole in 200 ml of dry ether was irradiated in the type A apparatus through a pyrex filter for ten hours. The reaction was then worked up by distillation of the solvent followed by column chromatography on a 1 ft x 1/2 in. silica column using hexane followed by 1:1 hexane-methylene chloride as the eluent. A large amount of starting material was recovered from the hexane
fractions and a small amount of a viscous oily material was collected from the mixed eluent fractions. This material showed a very complex gc pattern on column A and was not further studied.

**Photolysis of 2,2,4,5-Tetramethylisoumidozole** 34. A solution of 1.2 g (0.01 mol) of 2,2,4,5-tetramethylisoumidozole in 200 ml of dry ether was irradiated in the type A apparatus through a pyrex filter for 24 hr and then through a corex filter for 24 hr more. Work-up and analysis by gc and infrared of the resulting material showed it to be a complicated mixture of products all of which were formed in low yield (<5% each).

**Photolysis of 2,4,6-Trimethylpyrimidine** 37. A solution of 3.0 g (0.025 mol) of 2,4,6-trimethylpyrimidine in 200 ml of dry ether was irradiated in the type A apparatus through a vycor filter (inert to pyrex) for 48 hr. Work-up and analysis showed the material had polymerized and products resulting from the dimerization of α-ethoxyethyl radicals had been formed (these were collected by gc) as shown by nmr spectra. The reaction was rerun using n-hexane as the solvent. Compound 37 did not react in this case.

**Photolysis of 3,6-Dimethylpyridazine** 38. A solution of 2.0 g (0.02 mol) of 3,6-dimethylpyridazine in 200 ml of ether was irradiated in the type B apparatus for 24 hr. The ether was distilled off and gc analysis on column A indicated the presence of a single product in addition to a large amount of starting material. The product was obtained by simple distillation of the material to yield 0.25 g (14.3% by gc) of a yellow oil which was the air sensitive ether adduct of the pyridazine, bp 110-112° (0.75 mm): ir (film), 1100 (C-O) cm⁻¹; nmr (CCl₄), τ 7.35 and 7.45 (3 H each, s, CCH₃), τ 2.77 (1 H, s, aromatic proton), τ 5.5 (1 H, slightly split quartet J = 6.2 Hz, CH-CH₃), τ 6.6 (2 H, quartet J = 7.0 Hz, CH₂),
τ 8.68 (3 H, triplet J = 7.0 Hz, CCH₃), and τ 8.80 (3 H, triplet J = 7.0 Hz, CCH₃). Accurate analysis of the product could not be obtained due to its rapid decomposition.

The reaction above was rerun in methanol but no product incorporating a methoxy group was obtained. Instead a dimer or polymer appears to be the product. The material was not further studied.

Irradiation of 2-Acetylfurane 39. A solution of 3.0 g (0.027 mol) of 2-acetyl furan in 90 ml of isopropyl alcohol was irradiated in the type B apparatus with 3500 Å lamps for 24 hr. Distillation yielded only the starting material and solvent. The reaction was rerun in the type A apparatus using a corex filter and adding a few drops of glacial acetic acid to the mixture. Once again work-up yielded only the starting material as verified by gc and infrared analysis.

Irradiation of 2-Acetylthiophene 40. A solution of 3.5 g (0.021 mol) of 2-acetylthiophene in 200 ml of isopropyl alcohol was irradiated in the type A apparatus through a corex filter for 24 hr. Work-up and analysis by infrared and thin layer chromatography showed only unchanged starting material. The reaction was rerun in the type B apparatus in 60 ml ether containing 15 g of trimethylethylene. After 15 hr using the 2537 Å lamps the reaction mixture was worked up and analyzed by gc. Analysis indicated only unchanged starting material and a small amount of tar. No further work was done on this compound.

Irradiation of 2-Acetylurane in Trimethylethylene. A solution of 3.0 g (0.027 mol) of 2-acetylurane, 15 g of dry trimethylethylene and 60 ml of dry ether was placed in a vycor test tube and irradiated with 3500 Å lamps in the type B apparatus for 18 hr. Evaporation of the solvent and olefin yielded only unchanged 2-acetylurane. The reaction was rerun
using 2537 Å lamps but the results were the same as indicated by gc and infrared analysis. Also increasing reaction time to several days does not promote reaction.

Irradiation of 2,2'-Dithienylketone 42. In a pyrex test tube was placed a solution of 2,2'-dithienylketone (3.0 g, 0.015 mol), 4 ml of dry benzene and 60 ml of isopropyl alcohol. The solution was irradiated with 3500 Å lamps in the type B apparatus for 3 days. Evaporation of the solvent yielded only unreacted material. The reaction was repeated in the exactly analogous manner to the 2-acetylfuran reaction with trimethylene using 3500 Å lamps for 24 hr. Once again no reaction was noted and the starting material recovered.

Photoreduction of 2-Acetylpyridine 45. A solution of 3.0 g (0.025 mol) of 2-acetylpyridine in 65 ml of isopropyl alcohol was irradiated for 18 hr with 3500 Å lamps in the type B apparatus in a pyrex test tube. Colorless needles formed on the walls of the test tube and work-up and evaporation yielded 1.8 g, (60%), mp 141-2°C of the pinacol: ir (CCl₄), 3300 (OH) cm⁻¹, 1085 (C=O) cm⁻¹, 1145 (pyridine) cm⁻¹; nmr (CCl₄) τ 8.8 (s, CH₃, 6 H), τ 8.38 (s, O=H, 2 H), τ 1.2 (2 H, multiplet, protons α to pyridine nitrogen) and τ 2.0-3.0 (6 H, multiplet, remainder of pyridine ring protons). Anal. Calcd for C₁₄H₁₆N₂O₂: C, 68.9; H, 6.6. Found: C, 68.9; H, 6.5.

Irradiation of 2-Benzoylthiophene 41. A solution of 3.0 g (0.016 mol) of 2-benzoylthiophene in 70 ml of isopropyl alcohol was irradiated with 3500 Å lamps for 24 hr in the type B apparatus. Work-up yielded only starting material as indicated by infrared spectra and thin layer chromatography. No evidence of pinacol formation could be found.

Photoreduction of 4-Acetylpyridine 46. In the exactly analogous manner to the 2-acetylpyridine 45 reaction described above 3.0 g (0.025 mol)
of the 4-acetylpypyridine gave pinacol in 80% (2.4 g) yield: mp 228-30°,
ir (CCl₄), 3200 (OH) cm⁻¹, 1068 (C-O) cm⁻¹, 1140 (pyridine) cm⁻¹. Anal.
Found: C, 68.7; H, 6.8.

**Photoreduction of 3-Benzoylpyridine** 47. A solution of 3.0 g (0.018
mol) of 3-benzoylpyridine in 70 ml isopropyl alcohol was irradiated in
an analogous manner to 45 for 3 days. A white solid formed on the vessel
walls. The solution was evaporated and the solid collected and washed with
benzene and let dry to yield 2.2 g (70%) of the pinacol: mp 178-9°, ir
(KBr) 3200 (OH) cm⁻¹ and 1030 (C-O) cm⁻¹; Anal. Calcd for C₂₄H₂₀N₂O₂:
C, 78.1; H, 5.4. Found: C, 78.3; H, 5.6.

**Photoreduction of 4-Benzoylpyridine** 48. A solution of 3.0 g of
4-benzoylpyridine was irradiated in an analogous manner to 45 for 48 hr.
Evaporation of the solvent yielded a green residue which was recrystallized
from benzene to yield the pinacol as a gray powder, 1.9 g, (61%) mp 120-1°:
ir (CCl₄), 3180 (OH) cm⁻¹ and 1045 (C-O) cm⁻¹; Anal. Found: C, 77.8;
H, 5.7.

**Irradiation of 2-Acetylpypyridine in the presence of Trimethylethylene.**
A solution of 3.0 g (0.025 mol) of 2-acetylpypyridine, 15 g of trimethylethylene and 65 ml of dry ether was irradiated with 3500 Å lamps for 48
hr in the type B apparatus. The solvent was evaporated and the residue
distilled, bp 60-65° (0.5 mm), to yield 2.7 g of material. Analytical
gc showed two peaks on column B at 150°. One was starting material
composing 83% of the total peak area and the oxetane 49 composed the
remaining 17% (retention time 20 min). This second peak was collected on
column D at 180°. The material rapidly decolorizes in air and accurate
analytical data could not be obtained: ir (film), 1050 (C-O) cm⁻¹;
nmr (CCl₄), τ 2.0-3.9 (5 H, multiplet, pyridine), τ 5.3 (1 H, quartet,
\[ J = 6.5 \text{ Hz, O-C-H}, \tau 8.85 (3 \text{ H, doublet, } J = 6.5 \text{ Hz, C-CH}_3), \tau 9.45 (3 \text{ H, s, C-CH}_3), \tau 8.78 (3 \text{ H, s, CCH}_3) \text{ and } \tau 2.35 (3 \text{ H, s, CCH}_3). \]

**Irradiation of 3-Benzoylpyridine in the presence of Trimethylethylene.**

In a pyrex test tube was placed a solution of 3.0 g (0.018 mol) of 3-benzoylpyridine, 50 ml of dry ether and 20 ml of trimethylethylene. The solution was irradiated with 3500 Å lamps for 48 hr in the type B apparatus and worked up. Analysis by infrared showed considerable starting material to be present. The nmr of the crude material showed the presence of the oxetane \( \delta_0 \) in -57% yield. It was not purified: ir (CCl\(_4\)), 1072 (C-O) cm\(^{-1}\); nmr (CCl\(_4\)), \( \tau \) 2.1-3.1 (aryl hydrogen, multiplet), \( \tau \) 5.55 (1 H, slightly split quartet, \( J = 6.8 \text{ Hz} \)), \( \tau \) 9.05 (6 H, singlet, C-CH\(_3\)), \( \tau \) 8.85 (3 H, doublet, \( J = 6.8 \text{ Hz} \), C-CH\(_3\)).

**Irradiation of N-Acetylpyrrole 43.** A solution of 2.5 g (0.032 mol) of N-acetylpyrrole in 70 ml of isopropyl alcohol was irradiated for 48 hr in the type B apparatus with 3500 Å lamps. Evaporation of solvent and analysis of the residue by gc and infrared showed it to be starting material without any pinacol formation.

**Photoreduction of 2-Benzoylpyridine.** A solution of 3.0 g (0.018 mol) of 2-benzoylpyridine in 70 ml of isopropyl alcohol was irradiated in the type B apparatus with 3500 Å lamps for 15 hr. The pinacol had crystallized out of solution and evaporation and work-up gave 0.3 g (10% yield) of the material: mp 153-4° (needles from benzene); ir (KBr), 1058 (C-O) cm\(^{-1}\), 3150 (OH) cm\(^{-1}\), 705 and 760 (phenyl) cm\(^{-1}\); Anal. Found: C, 77.8; H, 5.6.

**Irradiation of 2-Styrylfuran 24.** A solution of 2.3 g (0.014 mol) of 2-styrylfuran in 200 ml pentane was irradiated in the type B apparatus for 48 hr with 3500 Å lamps. Evaporation of the solvent led only to the recovery of unreacted starting material as shown by infrared analysis and...
thin layer chromatography.

Photolysis of trans-Furfurylideneacetone 22. A solution of 3.0 g (0.022 mol) of trans-furfurylideneacetone and 30 g of cyclopentene and 170 ml of dry ether was irradiated in the type A apparatus through a pyrex filter for 5 hr. Evaporation of the solvent yields a viscous oil which could not be crystallized. The nmr of the material shows the possibility of quantitative formation of two dimers in a 2:1 ratio. Analytical and preparative thin layer chromatography was unsuccessful due to decomposition of the components on the adsorbents used. Analytical gc showed two partially resolved peaks. The reaction was also carried out in tetramethylethylene and in the absence of olefin. Both these reactions gave the same product mixture which was identical to that formed above. Compound 22 apparently prefers to dimerize rather than cycloadd to an unactivated olefin. Analytical data on the crude mixture include: ir (film), 1705 (C=O) cm⁻¹; nmr (CCl₄) τ 7.94 (s, 3 H, COCH₃), τ 6.42 (s, 4 H, cyclobutane ring protons), τ 7.85 (s, 3 H, COCH₃), τ 2.5-2.8 (3 H, multiplet, furan ring protons), τ 3.6-4.1 (3 H, multiplet, furan ring protons), τ 6.02 (4 H, AA'BB' system, cyclobutane ring protons).

Photolysis of Benzalacetone 21. A solution of 4.0 g (0.027 mol) of benzalacetone was irradiated analogously to the furfurylideneacetone in cyclopentene-ether solution for five days. The product mixture is the same if tetramethylethylene is substituted or if no olefin is used. Analysis shows the formation of dimers in preference to cycloaddition as with furfurylideneacetone. These photo-dimers have been described by other workers.62

Irradiation of 2-Acetylpurrole 44. The analogous reaction to N-acetylpurrole described above was tried with 2.5 g (0.032 mol) of
2-acetylpyrrole. The results were the same, no formation of pinacol or other products.

Irradiation of 2-(β-Nitrovinyl)-Furan 24. A solution of 3.0 g (0.021 mol) of 2-(β-nitrovinyl)-furan 24 in 200 ml of dry ether was irradiated in the type A apparatus through a pyrex filter for 24 hr. Infrared analysis indicated a saturated nitro band at 1550 cm⁻¹. Repeating the reaction in the solid state using sunlight as the source or in solution with cyclopentene-ether mixture gives the same product. A polymeric brown colored solid forms on the vessel walls and more may be obtained by evaporation of the ether solution. Crystallization of the residue from solvent evaporation yields only starting material and the viscous brown material which rapidly decomposes in air. The material could not be purified by thin layer chromatography and was too involatile to pass through the gc. This material showed a saturated nitro band in the infrared. The material is apparently a polymer of low stability.

Preparation of Indenone 52. Into a 500 ml round bottomed flask equipped with a condenser, stirring bar, and drying tube was placed 200 ml of carbon tetrachloride, 20 g (0.15 mol) of 1-indanone and 38 g (0.21 mol) of N-bromosuccinimide. The mixture was irradiated to reflux using a 500 watt unfrosted tungsten lamp for 4 hours. At the end of this time the reaction mixture was filtered and the filtrate collected and washed twice with water then 5% sodium bicarbonate and once again with water. The carbon tetrachloride was then evaporated and the residue vacuum distilled to yield 10 g (31%) of 3-bromodianone bp 115-120° (0.5 mm). The material may crystallize in the freezer, mp 55-56°.

One then takes 4 g of the bromo compound (larger scale gives very poor yields) and dissolves it in 50 ml of dry ether in a 100 ml one necked
flask equipped with stirring bar, condenser and drying tube. One then
adds 10 ml of *sym*-collidine and a few crystals of *sym*-trinitrobenzene and
lets the mixture stir 3.5 hours. The mixture is then heated to reflux for
one-half hour and then filtered, acidified with 6 N hydrochloric acid,
washed with 5% bicarbonate solution and washed twice with water. The
ether is then evaporated and the residue high vacuum distilled to give 1.5
g (61%) of indenone bp 61-63° (0.5 mm), ir (film) 1715 (C=O) cm⁻¹; lit.,
1715 cm⁻¹. The material is stable at 0° when a few crystals of *sym-
trinitrobenzene are added.

**Irradiation of Indenone.** A solution of 1.5 g of indenone and
20 g of cyclopentene in dry ether (170 ml) was irradiated in the type A
apparatus for 24 hr. Evaporation of solvent gave rise to a viscous
undistillable oil, apparently of a polymeric nature. It contained no
carbonyl band in the infrared spectrum but did show a significant C=O
stretch at 1100 cm⁻¹. The material was not further studied.
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