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DISSERTATION

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by

Lewis Robert Hamilton, B.S.

****

The Ohio State University
1967

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INTRODUCTION

In view of the structural relationship that exists between ethylenimine, cyclopropyl, and α,β-epoxyketones, it became of interest to investigate the photolytic behavior of the 2-benzoylaziridine system. The only mention of photochemistry in the ethylenimine ketone system was a report by Cromwell who noted that when trans-1-benzyl-2-phenyl-3-p-toluylaziridine (II) was exposed to direct sunlight, it isomerized to the cis isomer.\(^1\) Solutions of the cis aziridine (I) were reported to be unaffected by direct irradiation.\(^1\) The experimental evidence used to support this interpretation was the observation of a general broadening of the ultraviolet absorption band of the trans aziridine. Since a freshly prepared mixture of the cis and trans aziridines showed a similar absorption spectrum, Cromwell concluded that photoisomerization had occurred.

Although photoisomerization of \textit{trans} aziridine (II) is reasonable in view of analogous findings in the cyclopropyl and \(\alpha,\beta\)-epoxyketone systems\(^2\), it seemed surprising that irradiation of the \textit{cis} isomer did not afford the related \textit{trans} aziridine. In view of this apparent difference in the aziridine system, it became of interest to study the photochemical behavior of the three-membered nitrogen heterocycle in greater detail.

\textit{cis}– and \textit{trans}-1-Alkyl-2-phenyl-3-aryloylaziridines were readily prepared by treating a substituted \(\alpha,\beta\)-dibromobenzylacetophenone with an appropriate primary amine\(^3\). The available photolytic pathways of the two isomeric aziridines were


investigated and it was found that, in contrast to what had been claimed, photoisomerization did not occur. Instead it was observed that the phototransformations of each isomer differed, indicating that the relative position of the substituents on the three-membered ring influenced the mode of reaction. The phototransformations of both isomers were shown to proceed by way of a triplet $n \rightarrow \pi^*$ excited state. A detailed reaction mechanism was invoked to explain the observed transformations and to account for the effect of stereochemistry on the reaction path.

Attempts to prepare a $N$-phenyl-benzoylaziridine by the action of diphenyliodonium iodide on trans-2-phenyl-3-benzoylaziridine gave an unexpected result. The major products obtained corresponded to benzalacetophenone and 2,5-diphenyl-oxazole. The generality of this reaction was extended to include related aziridines and a mechanism was advanced to account for these observations.

Exposure of cis- or trans-benzoylaziridines in the solid state or in a rigid matrix to light produced a pronounced coloration which faded upon standing in the dark. The photochromic behavior was studied and all attempts to trap the species responsible for the coloration by coirradiation with multiple bond substrates failed. However a reaction was found to occur upon heating various arylaroylaziridines with dimethylacetylene dicarboxylate in inert solvents.
As an extension of our interest in electronically excited states of small-membered rings, the photochemical behavior of cis-1-t-butyl-2-phenyl-3-benzoylazetidine was examined. This compound was found to undergo an unprecedented photoinduced ring expansion of the four-membered azetidine ring.
HISTORICAL BACKGROUND

The electronic absorption spectra of molecules containing a three-membered ring adjacent to a carbonyl group have provided an effective method of demonstrating the conjugative properties arising from the unsaturation character of these rings. The nature of the electrical interaction between the small ring and the carbonyl group has been described as a type of hyperconjugation which results from orbital overlap of the bent bonds of the small ring with the $\pi$-orbitals of the attached carbonyl group.\textsuperscript{4} In addition to these spectroscopic studies, increased emphasis has been given to the photochemistry of three-membered ring compounds which have a carbonyl attached to one of the ring carbons. In particular, recent investigations of a number of cyclopropyl ketones and $\alpha,\beta$-epoxyketones have demonstrated that these species are very reactive under the influence of ultraviolet light.\textsuperscript{5}

Simple aliphatic ketones are known to dissociate upon irradiation by a Norrish type I process in which alkyl and


aryl radicals are formed. However, the introduction of a three-membered ring as a substituent on the carbonyl carbon has a pronounced effect on the available primary photochemical processes. Pitts and Norman, for example, have reported that irradiation of methyl cyclopropylketone (III) in the vapor phase affords almost exclusively 2-penten-4-one (IV).\(^7\)

\[
\begin{align*}
\text{III} & \quad \text{h} \nu \quad \text{IV} \\
\end{align*}
\]

Initial homolysis of the cyclopropyl bond beta to the carbonyl group followed by 1,2 hydrogen migration was advanced to explain the formation of the α,β-unsaturated ketone.

In view of the related behavior of cyclopropyl rings and olefinic bonds, it is quite reasonable to expect that cyclopropylketones should undergo cis-trans isomerization upon ultraviolet irradiation. In accord with this expectation, Griffin and co-workers have recently reported that irradiation of trans-1,2-dibenzoylcyclopropane (V) affords


the isomeric cis-1,2-dibenzoylcyclopropane (VI). The photoisomerization of V to VI was shown to be reversible and the photostationary state could be attained by starting with either the cis or trans isomer.

\[
\begin{align*}
&\text{V} \\
\begin{array}{c}
\text{Ph} & \text{C} = \text{O} \\
\text{H} & \text{C} = \text{O} \\
\text{H} & \text{Ph}
\end{array}
\quad \xrightarrow{\text{hv}} \quad
\begin{array}{c}
\text{Ph} & \text{C} = \text{O} \\
\text{H} & \text{C} = \text{O} \\
\text{Ph}
\end{array} \\
&\text{VI}
\end{align*}
\]

A similar photoisomerization has been described for the related trans-1-benzoyl-2-phenylcyclopropane (VII).\(^9\)

\[
\begin{align*}
&\text{VII} \\
\begin{array}{c}
\text{Ph} & \text{C} = \text{O} \\
\text{Ph} & \text{C} = \text{O} \\
\text{H} & \text{Ph}
\end{array}
\quad \xrightarrow{\text{hv}} \quad
\begin{array}{c}
\text{Ph} & \text{C} = \text{O} \\
\text{Ph}
\end{array}
\quad \xrightarrow{\text{hv}} \quad
\begin{array}{c}
\text{Ph} & \text{C} = \text{O} \\
\text{Ph} & \text{Ph}
\end{array} \\
&\text{VIII}
\end{align*}
\]

The photolysis of VII in the presence of a photosensitizer and in a hydrogen donor solvent undergoes a


\(^9\)G. W. Griffin, unpublished results.
completely different reaction course. Under these conditions, the predominant path is reduction of VII to 1,3-dibenzoylpropane (IX). The reaction is complicated by the fact that IX is photochemically labile and upon further irradiation dissociates into acetophenone and benzylethane which polymerizes under the reaction conditions. It was suggested that the reaction involves energy transfer from the triplet state of the photosensitizer to form the triplet of VII, which subsequently abstracts hydrogen from the solvent. The overall reaction scheme was depicted as follows:

\[
\begin{align*}
\text{Ph} & \quad \overset{hv}{\longrightarrow} \quad \text{Ph}_2\text{C}=\text{O} \quad \overset{m}{\longrightarrow} \quad \text{Triplet} \\
\text{VII} & \\
\text{Ph} & \quad \overset{i-\text{PrOH}}{\longrightarrow} \quad \text{Ph} \quad \overset{h\nu}{\longrightarrow} \\
& \\
\text{Ph} & \quad \overset{i-\text{PrOH}}{\longrightarrow} \quad \text{Ph} \\
\text{Ph} & \quad \overset{h\nu}{\longrightarrow} \quad \text{Polymer}
\end{align*}
\]
The photochemistry of the related α,β-epoxyketone system has also been studied in some detail and it was found that a major reaction path involved an isomerization to a beta-diketone. As a typical example, irradiation of 3,4-epoxy-4-methyl-2-pentanone (X) gave 3-methyl-2,4-pentan dione (XI) as the major product in 2-12% yield. The low yield of XI was attributed to the photolability of XI which resulted in further photodecomposition to a number of secondary photoproducts.

An unusual order of migratory aptitudes has been observed in this photorearrangement. The preferential shift of alkyl rather than aryl groups appears to be a fundamental characteristic of the reaction. Thus irradiation of 3-phenyl-5,5-dimethyl-2,3-epoxycyclohexanone (XII) produced 2-benzoyl-

4,4-dimethylcyclopentanone (XIII) and afforded no detectable quantities of the isomeric cyclohexadione.\textsuperscript{12}

\begin{center}
\begin{tikzpicture}
  \node (XII) at (0,0) {\includegraphics[width=4cm]{xii.png}};
  \node (XIII) at (2,0) {\includegraphics[width=4cm]{xiii.png}};
  \node (XIV) at (-2,-3) {\includegraphics[width=4cm]{xiv.png}};
  \node (XV) at (0,-3) {\includegraphics[width=4cm]{xv.png}};
  \node (XVI) at (-2,-6) {\includegraphics[width=4cm]{xvi.png}};
  \node (XVII) at (0,-6) {\includegraphics[width=4cm]{xvii.png}};
  \draw[->,thick] (XII) to node[above]{$h\nu$} (XIII);
  \draw[->,thick] (XIV) to node[above]{$h\nu$} (XV);
  \draw[->,thick] (XVI) to node[above]{$h\nu$} (XVII);
\end{tikzpicture}
\end{center}

The absence of phenyl migration does not seem to be a consequence attributable to steric facts, but rather suggests that considerable bond breaking occurs in the transition state for the rearrangement. This same preferential order of migration has also been observed with open chain epoxyketones XIV\textsuperscript{12} and XVI.\textsuperscript{2}

\begin{flushright}
\end{flushright}
Movement of the hydrogen or alkyl group in preference to the phenyl group has been rationalized by assuming that the phototransformation involves migration of the group as a free radical.

![Diagram](attachment:image.png)

The migratory aptitudes observed in these studies are reminiscent of radical fragmentations that have been observed in the decomposition of cumyl peroxide\(^{13}\) and phenylidimethylcarbinylhypochlorite.\(^{14}\)

A striking dependence upon the nature of the particular carbonyl group involved in these transformations has also been noted. Thus in contrast to XIV, the structurally related trans-dypnone oxide (XVIII) underwent an entirely different photochemical reaction.\(^{12}\) Irradiation of XVIII in solution gave 1,3-diphenyl-3-buten-2-ol-1-one (XIX) as the major reaction product.


The mechanism of this transformation has been suggested to involve the abstraction of a gamma-hydrogen by the $n \rightarrow \pi^*$ excited state. Such intramolecular abstractions are well documented in the literature.\(^{15,16}\) Homolytic ring cleavage of the diradical followed by intramolecular disproportionation readily accommodates the observed product.


This sequence requires proximity of the methyl and benzoyl groups in order for effective intramolecular hydrogen transfer to occur. In agreement with this, Zimmerman has found that cis-dypnone oxide was inert under comparable photolytic conditions.\textsuperscript{12} The observed difference in the photochemistry of XIV and XVIII has been attributed to the greater electron delocalization that is possible with the benzoyl group, thereby diminishing the probability of ring scission. On the other hand, the excited acetyl group has an electron in the $\pi^*$ orbital localized on the carbon atom and consequently is more available for $\alpha$-elimination.

When the ultraviolet irradiation of XVIII was conducted in aqueous ethanol medium, an interesting series of photochemical transformations occurred.\textsuperscript{2} Under these conditions XVIII isomerized to the diastereoisomer cis-dypnone (XX) and decomposed to acetophenone and $\alpha$-hydroxyacetophenone. In this case, $\beta$-elimination of the carbon-oxygen bond resulted in the formation of a zwitterionic species. The heterolytic cleavage of the carbon-oxygen bond in aqueous ethanol is presumably related to the ability of the protic media to stabilize the dipolar ion by solvation. Once formed, the zwitterion can undergo rotation about the central carbon-carbon single bond, which after collapse results in the formation of the diastereoisomer, or can react with a molecule of water to form a glycol, which in turn undergoes photochemical dealdolization.
The mechanism advanced to explain the photochemical transformations of α,β-epoxyketones have avoided the problem of identifying the multiplicity of the excited states. There can be little doubt that for the systems described, the excited state initially formed by absorption of a light quantum is the n-π* singlet. Thus, these reactions are effected by irradiation with light absorbed in the long-wave length absorption bands of the substrates. The occurrence of homolytic or heterolytic C-O bond fission is strongly suggestive of an electron rich carbon, more in accord with an n-π* excited state than a π-π* state. However, the n-π* singlet initially formed may be transformed into the n-π* triplet. The intersystem crossing between the n-π* singlet and triplet is a common phenomenon and approaches unit
efficiency for some systems. Clearly, the identification of the multiplicity of the excited $n-\pi^*$ state is of fundamental importance. A knowledge of it could explain the chemical difference observed for many of the structurally related $\alpha,\beta$-epoxyketones. For example, it is conceivable that epoxyketone XIV rearranges to a beta-diketone via a singlet excited state, whereas XVIII rearranges by way of the triplet state. Since product analysis does not identify the multiplicity of the $n-\pi^*$ state, conclusive evidence regarding the nature of this state awaits further experimentation.

DISCUSSION

As a consequence of the structural relationship that exists between ethylenimine ketones and α,β-epoxyketones,\textsuperscript{18} it became of interest to determine the similarity of their photochemistry. With this objective in mind, trans-l-cyclohexyl-2-phenyl-3-benzoylaziridine (XXI) was synthesized according to the procedure outlined by Southwick and Christman.\textsuperscript{19,20} The irradiation of (XXI) was conducted with the use of an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) equipped with a Pyrex filter to eliminate wave lengths below 280 \textmu m. The photolysis was followed by withdrawal of small aliquots at fixed intervals and examination of these by thin layer chromatography. Upon irradiation of 750 mg. of XXI in 95% ethanol for 3 hours, the spot on a thin layer plate due to XXI had completely disappeared and several new spots had appeared in its place. Chromatography of the crude photolysis mixture on a florisil


column gave trans- and cis-benzalacetophenone (XXII, XXIII). Only part of the nitrogen was accounted for in the form of N-cyclohexylhydroxylamine (XXIV), which was identified by its reaction with benzaldehyde to give the known 1-cyclohexyl-2-phenylnitrone, m.p. 80-82°. It is noteworthy that the yield of benzalacetophenone was nearly quantitative but that of N-cyclohexylhydroxylamine was significantly lower (23%).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
C = O & \quad + \\
\text{H} & \quad \text{Ph} \\
\uparrow & \quad \downarrow \\
\text{N} & \quad \text{H} \\
\text{C}_6\text{H}_{11} & \quad \text{C}_6\text{H}_{11} - \text{NHOH}
\end{align*}
\]

\[
XXI \quad XXII \quad XXIII \quad XXIV
\]

Photolysis of XXI in anhydrous pentane with a Pyrex filter gave a mixture of products which were separated by scanning liquid-liquid partition chromatography. In addition to cis- and trans-benzalacetophenone (XXII, XXIII), two new compounds were obtained whose structures were


assigned as cyclohexanone and N-1-(2-benzoyl-1-phenylethyl)-cyclohexanimine (XXV). The structure of XXV was elucidated by elemental analysis, infrared, ultraviolet, n.m.r., and degradation. The elemental analysis of the clear oil indicated that it was an isomer of XXI.

The infrared spectrum shows a carbonyl band at 5.93 μ and a carbon-nitrogen double bond at 6.10 μ. The ultraviolet spectrum in 95% ethanol has a maximum at 245 μ (ε 18,200). The n.m.r. spectrum in deuteriochloroform is in excellent agreement with the proposed structure. The Schiff base XXV showed the expected magnetic nonequivalence of the methylene protons adjacent to the carbonyl group, there being the predicted eight-line multiplet (AB part of an ABX spectrum) centered at τ 6.17 and 6.67 with J_{AB} = 16.5 cps., J_{AX} = 8.3 cps., and J_{BX} = 4.5 cps. The X proton of the ABX system was centered at τ 4.98 and consisted of an unsymmetrical quartet. The remaining portion of the spectrum consisted of a multiplet at τ 2.45 (10 H) and a multiplet at 9.0 (10 H). Structure
XXV was further confirmed by hydrogenation over Adam's catalyst to give cyclohexylamine hydrochloride and benzylacetophenone.

\[
\text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{Ph} \quad \text{C} \quad \text{N} \quad \text{Ph} \\
\text{Ph} \quad \text{H}_2 \quad \text{HCl} \quad \text{Ph} \quad \text{HCl} \\
\text{Ph} + \text{C}_6\text{H}_5\text{NH}_2
\]

XXV

It was found that XXV could be converted rapidly and quantitatively to trans-benzalacetophenone and cyclohexanone by chromatography on florisil, but was partially recovered from liquid-liquid partition chromatography. Structure XXV was found to be readily converted to cyclohexanone and trans-benzalacetophenone by standing in the dark in a polar solvent. Trace amounts of acid or base greatly facilitated the cleavage. Thus, it appears as though the photodeamination of XXI in 95% ethanol proceeds via a dual sequence. One path involves the formation of benzalacetophenone and cyclohexylhydroxylamine as primary photoproducts. The low yield of cyclohexylhydroxylamine (23%) indicates that the competing sequence, which is reasonably formulated as proceeding via XXV followed by fragmentation to trans-benzalacetophenone and cyclohexanone, is the predominate path. This suggestion is supported by the isolation of small amounts
of XXV (8%) when the irradiation was carried out at low temperatures followed by liquid-liquid partition chromatography.

A striking feature of this photochemical reaction is the deamination to a mixture of cis- and trans-benzalacetophenone. Particular interest is attached to the mechanism of formation of the olefinic mixture. A conceivable pathway could involve rapid cis-trans photoisomerization of the 2-benzoyleziridine followed by deamination of the mixture to give comparable amounts of the isomeric olefins.
The cis-trans photoconversion of the three-membered nitrogen ring was considered a likely possibility, since similar photoisomerizations have been reported for related small-ring carbonyl compounds. However, this sequence was eliminated by the finding that the photolysis of cis-1-cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI) did not afford XXI. Instead, irradiation of XXVI in 95% ethanol gave N-cyclohexylbenzalimine (XXVII) and acetophenone as major products.

\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{O} \\
\text{Ph} & \quad \text{H} \\
\text{H} & \quad \text{N} \\
\text{C}_6\text{H}_{11} &
\end{align*}
\]

\[\xrightarrow{\text{hv}}\]

\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{O} \\
\text{Me} & \quad \text{H} \\
\text{Ph} & \quad \text{C} = \text{N} - \text{C}_6\text{H}_{11}
\end{align*}
\]

\[\text{XXVI} \quad \text{XXVII}\]

Careful examination of the photolysis mixture revealed that no detectable amounts of cis- or trans-benzalacetophenone (XXIII, XXII), phenacyl alcohol, phenacyl ethyl ether, phenylacetic acid, or ethyl phenylacetate were present.

Epimerization of cis and trans isomers of aziridines has seldom been observed.\(^{23}\) Cromwell, however, claimed that when trans-1-benzyl-2-phenyl-3-p-toluylaziridine (II) was exposed to direct sunlight, it isomerized to the cis

Solutions of the cis isomer (I) were reported to be unaffected by irradiation. The experimental evidence used to support this interpretation was the observation of a general broadening of the ultraviolet absorption band of II. Since a freshly prepared mixture of II and I showed a similar absorption curve, Cromwell concluded that photoisomerization occurred. In view of the apparent discrepancy between the two sets of results, the photochemistry of I and II was reinvestigated.

Photolysis of trans-1-benzyl-2-phenyl-3-p-toluyl-aziridine (II) in 95% ethanol with a Pyrex filter followed by florisil chromatography gave only trans- and cis-4'-methyl-benzalacetophenone (XXVIII and XXIX). No detectable amounts of cis-benzoylaziridine (I) could be found in this photolysis. All attempts to identify the nitrogen portion in the form of benzylhydroxylamine (or the N-benzyl nitrone of benzaldehyde) were unsuccessful. It was therefore concluded that trans-aziridine (II) did not photoisomerize to the cis isomer I and that the reaction sequence for II was partially different from that previously observed in the cyclohexyl case.

By using scanning liquid-liquid partition chromatography the crude photolysis mixture could be resolved into three major components. In addition to trans- and cis-4'-methyl-benzalacetophenone (XXVIII, XXIX), a new compound was obtained whose structure was assigned as N-1-(2-p-toluyl-1-phenylethyl)benzylidenimine (XXX) on the basis of chemical
and physical data cited. The elemental analysis of this component (Anal. Calcd. for C_{27}H_{21}NO: C, 84.37; H, 6.47; N, 4.28. Found: C, 83.55; H, 6.52; N, 4.18) indicates that it is an isomer of II. The infrared spectrum shows a carbonyl band at 5.93 μ and a carbon-nitrogen double bond at 6.13 μ. The ultraviolet spectrum in 95% ethanol has a maxima at 251 μ (ε, 27,400). The n.m.r. spectrum in deuteriochloroform is in excellent agreement with the proposed structure and consists of an ABX system of 12 lines, a singlet at τ 7.77 (3H), a multiplet at 2.61 (9H) and a singlet at 1.72 (1H). The X proton of ABX system was centered at τ 4.86 (1H) and consisted of an unsymmetrical quartet. The A and B protons of the ABX system were centered at τ 6.21 (1H) and 6.74 (1H). The coupling constants were \( J_{AX} = 8.3 \text{ cps,} \), \( J_{BX} = 4.5 \text{ cps,} \), and \( J_{AB} = 16.5 \text{ cps.} \) Structure XXX was further confirmed by hydrogenation over Adam's catalyst to benzylamine hydrochloride and 4'-methylbenzylacetophenone.
It was found that XXX could be converted to \textit{trans}-4'-methylbenzalacetophenone (XXVIII) and benzaldehyde by chromatography on florisil or by standing in 95% ethanol in the dark.

\begin{equation}
\begin{aligned}
&\text{CH}_3\text{-C}_6\text{H}_4\text{N}=\text{CHPh} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{C}=\text{O} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{H} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{Ph} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{C}=\text{O} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{N}=\text{CHPh} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{H} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{Ph} \\
&\text{CH}_3\text{C}_6\text{H}_4\text{C}=\text{O} \\
&\text{HCl}\end{aligned}
\end{equation}

The formation of a mixture of \textit{cis}- and \textit{trans}-4'-methylbenzalacetophenone (XXIX and XXVIII) upon irradiation of II in 95% ethanol is reasonably formulated as proceeding via XXX, which then fragments by a ground-state sequence to \textit{trans}-4'-methylbenzalacetophenone. Control experiments demonstrated that XXX did not degrade photochemically to XXVIII and benzaldehyde. The formation of the \textit{cis} isomer XXIX is due to \textit{in situ} photoisomerization of the \textit{trans} olefin XXVIII present in the reaction cell. This suggestion is supported by carrying out the photolysis of II in pentane as solvent.
With long irradiation time, XXX and trans-4'-methyl-benzalacetophenone (XXVIII) account for all the products produced. The small amount of trans olefin (XXVIII) formed is due to partial cleavage of XXX by chromatography on a liquid-liquid partition column. No cis isomer XXIX was detected, thereby indicating that XXVIII is not a primary photoprodut, since the photostationary state of XXVIII and XXIX under comparable photolytic conditions was shown to be 20% XXVIII and 80% XXIX.

In order to determine whether cis-benzoylaziridine (I) would undergo photochemical epimerization or whether it would behave analogously to cis-aziridine (XXVI), the photolysis of I was carried out. In this photolysis no II, XXX, XXVIII, or XXIX could be detected, and instead 4'-methylacetophenone, N-benzylbenzalimine (XXXI) and
N,N'-dibenzyl-1,2-diphenyl-1,2-diaminoethane (XXXII) were the only products formed.

\[
\begin{align*}
\text{XXXI} & : \\
\text{XXXII} & :
\end{align*}
\]

Suspicion that XXXII was a secondary photoproduct was confirmed by finding that the photolysis of N-benzylbenzalimine (XXXI) in ethanol gave the dimer in high yield.

\[
\begin{align*}
\text{XXXI} & : \\
\text{XXXII} & :
\end{align*}
\]

It was therefore concluded that the photoreaction of cis aziridines XXVI and I are mechanistically similar but drastically different from the trans isomers XXI and II.

The molecular changes involved in the photochemistry of the 2-benzoylaziridine system are quite dependent on the
initial stereochemistry. From the experimental results, it was apparent that the relative position of the substituents influences the mode of ring opening. The products obtained from trans isomer (II) can be readily accommodated by assuming that the reaction proceeds by intramolecular hydrogen transfer to yield an enol, followed by rearrangement of the enol to a carbonyl compound.

This process may be considered to be analogous to the Norrish Type II cleavage observed with the irradiations of aliphatic ketones containing gamma hydrogens.\textsuperscript{24}

Rapid inversion of the geometrical configuration of the groups bonded to nitrogen in ammonia and related molecules has been known for a long time. The data thus far

obtained indicate that substituted aziridines with molecular asymmetry due to trivalent nitrogen are likely only to be resolved into stable optical antipodes at temperatures below -50°. The temperature dependence of the n.m.r. spectra of a number of substituted aziridines has been previously investigated. At sufficiently low temperatures, the lifetime with respect to inversion of the two configurations of the groups bonded to the nitrogen atom is long enough that separate signals may be obtained from the ring protons cis and trans to the substituent on nitrogen. The configurations of the trans-aziridines under consideration in this study may be represented by XXXIII A, B and those of the cis compounds by XXIV A, B.

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26 A. T. Bottini and J. D. Roberts, ibid., 78, 5126 (1956).


In the two configurations of the trans isomer, the amount of steric crowding should be approximately equal and consequently the trans form should exist as a rapidly inverting mixture of both configurations. It seems probable, however, that steric crowding would cause the cis form to exist predominantly in one configuration, XXXIVA, especially since the group on nitrogen is large. In this configuration the group on nitrogen is on the same side of the ring as the two hydrogen atoms and the steric nonbonded interactions will be much less than in XXXIVB where all three bulky groups are on the same side of the ring.
Some evidence pertaining to the question of configuration population of the aziridines used in these studies is provided by examination of low temperature n.m.r. spectra. Since in both the cis and trans isomers the aziridine ring protons are nonequivalent, one would expect to obtain two signals of equal intensity which might be split further by spin-spin coupling with each other, thereby leading to a total of four peaks. However, for the compounds studied, the difference in chemical shift for the ring protons is small in comparison with the spin-spin coupling constant and consequently they appear either as a singlet or as an A-B quartet. The ring protons of either isomer may occupy two distinct positions—cis or trans to the substituent on nitrogen, each of which has its own particular associated chemical shift, $\delta_c$ or $\delta_t$, respectively. At ambient temperatures an average line position is observed, $\delta_{\text{obsd}}$. At temperatures where the inversion rate is comparable to or less than $2\pi (\delta_c - \delta_t)$, the lifetime with respect to inversion of the two configurations of the group bonded to the nitrogen is long enough that separate signals may be obtained from the ring protons cis and trans to the substituent on nitrogen. The spectrum of trans-aziridine II is in accord with this prediction. The signals of the ring protons of II at first broaden with decreasing temperature and ultimately split into a quartet. This behavior is illustrated in Figure I for trans-1-benzyl-2-phenyl-3-p-toluylaziridine (II).
Figure 1. Temperature dependence of n.m.r. spectrum of \textit{trans}-1-benzyl-2-phenyl-3-\textit{p}-toluylaziridine II.
Since the magnetic environment of each of the ring protons in the two configurations of the cis-aziridine are dissimilar, one would expect to obtain further splitting at sufficiently low temperatures. No additional multiplicity was observed, however, in any of the low temperature spectra of the cis isomer. These results may be rationalized if it is assumed that the concentration of XXXIVA or XXXIVB is very small. It seems likely on steric considerations that the equilibrium between XXXIVA and XXXIVB should favor XXXIVA.

### TABLE 1

N.m.r. Parameters for 1-Benzyl-2-phenyl-3-p-toluylaziridines\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ring Protons(^c) (c.p.s.)</th>
<th>JAB</th>
<th>Ring Protons (c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>6.42(^d)</td>
<td>--</td>
<td>6.33(^e)</td>
</tr>
<tr>
<td>I</td>
<td>6.75(^e)</td>
<td>7</td>
<td>6.60(^e)</td>
</tr>
</tbody>
</table>

\(^a\)All n.m.r. spectra were taken at 100 Mc.p.s. on a Varian A-100 spectrometer. Deuterochloroform was used as solvent with tetramethylsilane as an internal standard.

\(^b\)\(\pm 3^\circ\).

\(^c\)Chemical shifts downfield from T.M.S. are reported in tau values.

\(^d\)Broad singlet.

\(^e\)Center of quartet.
The small but significant shift at lower temperatures of the ring protons of the \textit{cis} isomer with respect to the signal of tetramethylsilane may be interpreted as meaning that a small amount of XXXIVB is present in equilibrium at room temperature. Heine and co-workers reached a similar conclusion in interpreting the temperature insensitivity of the spectrum of \textit{cis}-1-methyl-2,3-dibenzoylaziridine.\textsuperscript{29}

In one of the two configurations of the \textit{trans} isomer (XXXIIIB), the benzoyl group and the substituent on the nitrogen are the same side of the plane of the three-membered ring. In this configuration intramolecular hydrogen abstraction by the $n \rightarrow \pi^*$ excited state can proceed via a quasi six-membered transition state. It seems probable, however, that steric crowding would allow the \textit{cis} form to exist predominately in the one structure XXXIVA, especially since the group on nitrogen is large. In this case, the excited $n \rightarrow \pi^*$ state is incapable of intramolecular hydrogen abstraction and instead other, less efficient, processes occur.

To account for the products obtained from the \textit{cis} isomer, it can be suggested that fission of the carbon-carbon bond of the heterocyclic ring is occurring. Measurements of the bond distance and bond angles for ethylene oxide can probably be used without introducing any important error in this qualitative discussion of the aziridine ring. Cunningham has pointed out that carbon-oxygen bond distance
is about normal but the carbon-carbon bond distance is considerably shortened, and consequently most of the ring strain must be accounted for in the carbon-carbon bond.\(^3\)

It is suggested that the crowded cis-aziridine relieves its strain by cleavage of the carbon-carbon bond after hydrogen abstraction from solvent. The opening of the three-membered ring by carbon-carbon bond cleavage may also be rationalized by consideration of the stability of the incipient radical formed. Further removal of hydrogen from solvent produces a transient \(\alpha\)-amino ketone which then undergoes a facile photoelimination to yield the observed products.

A mechanism by which the excited state collapses to the Schiff base and a ketocarbene may be eliminated as it has been demonstrated that benzoylmethylene forms equimolar quantities of acetophenone and ethyl phenylacetate in 95% ethanol.\(^3\) Since all attempts to detect the ester have failed, we must conclude that such a process does not occur.


In initial agreement with this rationalization, it was observed that the preparative photoreaction of the cis isomers XXVI and I proceeded much more slowly than the photochemical transformation of the trans isomers XXI and II. More quantitative evidence was obtained from quantum yield studies (Table 2) of the two photoreactions. The photoefficiency of the trans-aziridine (II) conversion was 0.62 and that of the cis-aziridine (I) was 0.052. The inefficiency of the cis isomers may be due to the occurrence of trivial chemical processes.
<table>
<thead>
<tr>
<th>Run</th>
<th>Compound</th>
<th>Solvent</th>
<th>Quencher, Molarity</th>
<th>Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>XXI</td>
<td>C₂H₅OH</td>
<td>None</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>2</td>
<td>XXI</td>
<td>C₂H₅OH</td>
<td>Piperylene, 0.3M</td>
<td>0.37 ± 0.03</td>
</tr>
<tr>
<td>3</td>
<td>XXI</td>
<td>----</td>
<td>Piperylene, 6M</td>
<td>----</td>
</tr>
<tr>
<td>4</td>
<td>II</td>
<td>C₂H₅OH</td>
<td>None</td>
<td>0.58 ± 0.05</td>
</tr>
<tr>
<td>5</td>
<td>II</td>
<td>Pentane</td>
<td>None</td>
<td>0.62 ± 0.05</td>
</tr>
<tr>
<td>6</td>
<td>II</td>
<td>Pentane</td>
<td>Piperylene, 0.3M</td>
<td>0.60 ± 0.05</td>
</tr>
<tr>
<td>7</td>
<td>II</td>
<td>----</td>
<td>Piperylene, 6M</td>
<td>----</td>
</tr>
<tr>
<td>8</td>
<td>I</td>
<td>C₂H₅OH</td>
<td>None</td>
<td>0.05 ± 0.005</td>
</tr>
<tr>
<td>9</td>
<td>I</td>
<td>C₂H₅OH</td>
<td>Piperylene, 0.3M</td>
<td>----</td>
</tr>
</tbody>
</table>

*The filter combination used (see experimental) has a maximum transmission of 62.8% at 313 mµ and transmits less than 1% below 290 mµ and above 436 mµ.*

*Aziridine concentration ranged from 0.008 to 0.010M.*
Cleavage of the three-membered ring provides a mechanism for radiationless decay of the excited state of the cis isomer if it is assumed that the reaction produces the ground state of the original molecule. Vibrational relaxation of the intermediate diradical followed by ring closure prior to rotation readily rationalizes the return to ground state.

However there remains the possibility that the low quantum yield observed is caused by the inefficient removal of hydrogen from solvent by the benzylic radical, thereby allowing for the regeneration of starting material.
a possible sequence is the following:

![Chemical structure diagram]

A similar hydrogen transfer has been suggested by Neckers as a step in the reaction of aryl ketones with α-hydroxyalkyl radicals.\textsuperscript{32}

It is interesting to note that configuration XXXIIIA of the \textit{trans} isomer could in principal undergo a photoreaction comparable to that undergone by the \textit{cis} isomer. The failure to observe these products from the irradiation of \textit{trans}-aziridines XXI and II suggests that a low quantum efficiency may be attributed to the excited $n \rightarrow \pi^*$ state of this particular configuration. Alternatively, the result may indicate that the time allowed for reaction of excited states is long enough to allow for exploration of all possible inversion arrangements.

The most direct interpretation of our results for the photolysis of \textit{cis}-aziridines XXVI and I involves an α-amino-

ketone as a reaction intermediate. The failure to observe such species from the photolysis runs can be attributed to their further photoreaction under the photolytic conditions. For this argument to be valid, it must be assumed that the photoelimination of the transient α-aminoketone occurs more rapidly than does the cis-aziridine. Our studies are entirely consistent with this explanation. Irradiation of α-aminoketone XXXV in ethanol afforded \( p \)-methylacetophenone and N-benzylbenzalimine as the major products.

Furthermore, the photoefficiency of XXXV is substantially higher than that of I.

The data accumulated do not constitute compelling evidence for the intermediacy of an α-aminoketone in the photodegradation of cis-aziridine I, but it is at least highly compatible with this hypothesis. Additional evidence in support of this mechanism is obtained from experiments using benzene as solvent. The response of the photolytic pathway to the solvent change is remarkable. When the irradiation of cis-aziridine I was carried out in benzene as
solvent, \textit{trans}-4'-methylbenzalacetophenone (XXVIII) and \textit{N}-1-(2-\textit{p}-toluyl-1-phenylethyl)benzylidenimine (XXX) were the major products.

\begin{align*}
\text{CH}_3\text{C}_6\text{H}_4 & \quad \text{CH}_2\text{-Ph} \\
\text{CH}_3\text{C}_6\text{H}_4 & \quad \text{CH}_2\text{-Ph}
\end{align*}

It would appear, therefore, that the observed difference between the two reaction paths of I can be attributed to the ability of the solvent to serve as a hydrogen donor. In the case of benzene, hydrogen abstraction from solvent does not occur to an appreciable extent, presumably because the high activation energy required for hydrogen atom abstraction prohibits photoreduction. The relatively slow conversion of I to XXVIII and XXX can be attributed to the existence of I in a geometric arrangement which is favorable for subsequent reaction. Thus, the least stable configuration of I would be expected to undergo intramolecular hydrogen abstraction under conditions which suppress photoreduction of the more stable configuration. This interpretation is complicated by the possibility of a photoisomerization of the \textit{cis} isomer I
to the trans isomer II followed by subsequent photoreaction of the trans isomer. However, all attempts to detect trans-aziridine II when the irradiation was carried out in benzene were unsuccessful. The absence of such a photoepimerization reaction supports the interpretation that the reactive configuration of the cis isomer is XXXIVB when a poor hydrogen donor is employed as solvent.

Having demonstrated the dramatic difference in the photochemistry of cis- and trans-2-benzoylaziridines, it is now necessary to consider the mechanistic import of the formation of cyclohexylhydroxylamine in the photoreaction of XXI. It appears as though the photoreaction of XXI in polar solvents proceeds via a dual sequence. One path involves the formation of benzalacetophenone (XXI and XXIII) and cyclohexylhydroxylamine (XXIV) as primary photoproducts. The low yield of XXIV (23%) indicates that the competing sequence, which is reasonably formulated as proceeding via XXV followed by fragmentation to trans-benzalacetophenone (XXII) and cyclohexanone, is the predominate path and is indeed analogous to the photochemistry of trans-aziridine II.
In the case of XXI, the tertiary hydrogen of the cyclohexyl ring is presumably removed less efficiently than the benzylic hydrogen of II, thereby allowing another route to compete. Inspection of Table 2 shows that in the case of II there was more than a two-fold increase in photoefficiency relative to XXI. This suggests that the lower quantum efficiency of XXI may be due to a conformational effect which retards intramolecular hydrogen abstraction and allows for a competitive intermolecular route (Path A).

More than one mechanistic rationale may be envisaged for the mechanism of Path A. The light absorbed by XXI possesses sufficient energy to effect a bond cleavage. The energy corresponding to 316 m\(\mu\)-radiation (90.8 kcal/mole) is substantially greater than the maximum energy required for bond dissociation in aziridine itself, which in turn is higher than that required for bond breakage in XXI. Despite the fact that \(n \rightarrow \pi^*\) excitation would be expected to develop appreciable charge density of nitrogen as a result of a
heterolytic cleavage of the aziridine carbon-nitrogen bond, the products obtained from the irradiation of XXI seem to be those characteristic of an electron-deficient nitrogen. A related situation has been noted for the $n \rightarrow \pi^*$ photochemical transformations of cyclohexadienones. An electron-demotion process was suggested for these cases in order to resolve the enigma of carbonium ion type reactions occurring from an $n \rightarrow \pi^*$ state. It is tempting to hypothesize that the aziridine system is behaving analogously and that a related electron demotion from the already weakened C-N bond occurs. Alternatively, it may be argued that in the excited state an electron-rich nitrogen atom of the three-membered ring removes a proton from the solvent. The $n \rightarrow \pi^*$ state has been considered to have dual potentiality; either an electron pair or an odd electron may be considered available on the carbonyl carbon.\(^{33}\)

The heterolytic ring cleavage of the carbon-nitrogen bond may be related to the ability of the protic media to stabilize the zwitterion by solvation. The zwitterion can react with a molecule of water, as shown below, to form the observed products.
Both mechanism allow for free rotation of the zwitterion about the central carbon-carbon single bond and consequently are in accord with the formation of a mixture of cis- and trans-benzalacetophenone. The partial stereospecificity observed (80%) can be attributed to a slow rate of rotation about the carbon-carbon single bond as compared to collapse of the zwitterion to trans olefin and hydroxylamine.

It is interesting, at this point, to compare the irradiation of XXI and II with that of trans-2-phenyl-3-benzoylaziridine (XXXVI). Since XXXVI cannot undergo an intramolecular hydrogen transfer reaction, the expected photochemical path would be cleavage of the aziridine ring by a route comparable to that observed with XXI. Actually, irradiation of XXVI afforded only recovered starting material. Any attempt to account for this result should also consider the fact that trans-aziridine XXI affords some of the substituted hydroxylamine, whereas aziridine II does not.

A comparison of the ultraviolet absorption spectra of aziridines XXI, II, and XXVI is most informative.\(^{34}\) In the

irradiated portion of these spectra, XXI and II exhibit enhanced absorption which can be attributed to the $n \rightarrow \pi^*$ carbonyl excitation. The ultraviolet absorption of aziridine XXXVI, however, does not resemble those of the other two aziridines. The disappearance of the usual $n \rightarrow \pi^*$ band seems to indicate that this band has shifted to shorter wave length and coalesced with the benzoyl $\pi \rightarrow \pi^*$ band. It may be argued that the anomalous ultraviolet spectrum of XXXVI is a result of intramolecular hydrogen bonding between the lone pair of electrons on the carbonyl oxygen with the hydrogen attached to the nitrogen atom of the three-membered ring. The formation of this hydrogen bond lowers the energy of the $n$ orbital by an amount approximately equal to the energy of the hydrogen bond. Hence, this hydrogen bond must be broken in the process of promotion, thereby accounting for the anomalous blue shift in this case. The failure of XXXVI to undergo reaction may be attributed to the possible difference in the nature of its low-lying excited state. The dependence of the photochemical reaction on the nature of excited states has been demonstrated amply in the literature. The results are entirely consistent with this

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explanation and imply that the intramolecular hydrogen bonding in XXVI has a very marked effect on the level of the $n \rightarrow \pi^*$ state. In this case, the excited state of XXXVI may actually possess a low lying $\pi \rightarrow \pi^*$ configuration.

So far, the discussion has avoided the problem of identifying the excited state of the aziridine involved in the photoreaction, although this is a matter of fundamental importance. There can be little doubt that the excited state initially formed is the $n \rightarrow \pi^*$ singlet. The $n \rightarrow \pi^*$ band for the aziridines studied possesses a highly structured absorption band which exhibits a maximum near 325 m$\mu$. The oscillator strength ( ) of the transition was estimated as 0.0048. This is about eight times that of typical benzoyl ketones, but still well within the range of "symmetry-forbidden" $n \rightarrow \pi^*$ transitions. Hydrogen abstraction reactions encountered in photoreduction reactions of ketones are commonly associated with excited triplets. However, Hammond and Wagner have recently demonstrated that intramolecular hydrogen abstraction can occur with both excited singlets and triplets.\(^{38}\) It seems more probable, however, that the reactions observed for the aziridines proceed via the $n \rightarrow \pi^*$ triplet state in analogy with related aryl ketones.

The intersystem crossing between $n \rightarrow \pi^*$ singlet and triplet states of aryl ketones usually occurs with near unit

efficiency.\textsuperscript{39,40} Since intersystem crossing to the triplet has been found to be over 10\textsuperscript{-4}sec.\textsuperscript{-1} for related benzoyl ketones, the destruction of the singlet $n \rightarrow \pi^*$ state is probably proceeding too fast for reaction to occur from the singlet state.\textsuperscript{41} The predominance of the $n \rightarrow \pi^*$ triplet in these reactions may be attributed to the relatively long lifetime of these states. Unfortunately, it has not been possible to detect phosphorescence from the $n \rightarrow \pi^*$ excited aziridines (in rigid glasses) and consequently there is no direct spectroscopic evidence for the production of $n \rightarrow \pi^*$ triplets.\textsuperscript{42}

Evidence that the reacting $n \rightarrow \pi^*$ state is a triplet rather than a singlet is provided, however, by examination of the variation of quantum yields using piperylene as a triplet quencher. Energy transfer from the triplet state of the carbonyl compound to piperylene is sufficiently exothermic to insure diffusion control of triplet destruction.\textsuperscript{43} The quantum yields for photoreaction of the aziridines studied

\begin{itemize}
\item \textsuperscript{40}C. A. Parker and C. G. Hatchard, Analyst, \textbf{87}, 644 (1962).
\item \textsuperscript{42}Grateful acknowledgment to Dr. Edwin Ullman and Professor Angelo Lamola for obtaining this information.
\end{itemize}
are summarized in Table 2. Inspection of Table 2 shows that in Run 9 the quantum yield of cis-aziridine I is completely suppressed by the addition of 0.3 moles of piperylene. In contrast, trans-aziridine II is unquenched by such piperylene concentration (Run 6). It appears as though the rate of diffusion of piperylene quencher is too slow to compete with the intramolecular rearrangement of the aziridine while such diffusion is rapid enough to destroy triplets in the cis-aziridine case. However, the only reaction observed with XXI and II in samples containing piperylent as solvent (Run 3 and 7) was photodimerization of piperylene. Thus, a triplet state with $E_T = 60-70$ kcal/mole is implicated as a reactive intermediate in the photochemistry of the aziridines studies.

During the course of investigating the photolytic behavior of arylaroylaziridines, it became of interest to study the photochemistry of trans-1-phenyl-2-benzoyl-3-phenylaziridine (XXXVII). In this particular case, the

usual intramolecular hydrogen transfer step would not be feasible since there are no available gamma-hydrogens. Instead the predominate path may involve cleavage to benzalacetophenone and phenylhydroxylamine when aqueous ethanol is employed as a solvent. A very promising approach to the preparation of this compound appeared to be through the use of diphenyliodonium salts, since it had been reported that under relatively mild conditions organic amines and other nucleophiles effect nucleophilic displacement on the 1-carbon atom of diphenyliodonium ions.\textsuperscript{48,49}

Treatment of trans-2-benzoyl-3-phenylaziridine (XXXVI) with one equivalent of diphenyliodonium iodide (XXXVIII) in refluxing toluene for 12 hours resulted in complete disappearance of XXVI and the formation of a mixture of products as evidenced by thin layer chromatography. By using scanning liquid-liquid partition chromatography, the crude reaction mixture was resolved into three major components. The first two components were shown to be iodobenzene (60%) and trans-benzalacetophenone (XXII) (53%) by comparison with authentic samples. Iodobenzene was shown to be the major product formed in 65% yield in the thermolysis of XXVII in toluene for comparable reaction times. The remaining component in


in the reaction mixture was shown to be 2,5-diphenyloxazole (XXXIX) (41%) by comparison with an authentic sample.

![Chemical structure](image)

The novel diphenyliodonium iodide catalyzed rearrangement was found to be a general phenomenon for suitably substituted 2-benzoylaziridines. Table 3 summarizes data on the products obtained with a number of substituted cis- and trans-arylaroylaziridines. At this time the exact role played by the diphenyliodonium in the formation of substituted trans-benzalacetophenone is not known. Almost all of XXXVIII is accounted for in the form of iodobenzene. The reaction is very complex when diphenyliodonium iodide was absent.

![Chemical structure](image)
Table 3

Reaction of Arylaroylaziridines with Diphenyliodonium Iodide

<table>
<thead>
<tr>
<th>Arylaroylaziridine</th>
<th>% Yield of Oxazole</th>
<th>% Yield of trans Olefin</th>
<th>% Yield of Ketone</th>
<th>% Yield of R-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXXVI X=H, R=H (trans)</td>
<td>41%</td>
<td>53%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I X=CH₃, R=CH₂-C₆H₅ (cis)</td>
<td>41%</td>
<td>54%</td>
<td>43%</td>
<td>40%</td>
</tr>
<tr>
<td>II X=CH₃, R=CH₂-C₆H₅ (trans)</td>
<td>42%</td>
<td>53%</td>
<td>42%</td>
<td>40%</td>
</tr>
<tr>
<td>XXVI X=H, R=C₆H₁₁ (cis)</td>
<td>-</td>
<td>72%</td>
<td>69%</td>
<td>-</td>
</tr>
<tr>
<td>XXI X=H, R=C₆H₁₁ (trans)</td>
<td>-</td>
<td>76%</td>
<td>68%</td>
<td>-</td>
</tr>
<tr>
<td>XL X=H, R=CH₂-C₆H₅ (cis)</td>
<td>8%</td>
<td>75%</td>
<td>69%</td>
<td>8%</td>
</tr>
<tr>
<td>XLIX X=H, R=CH₂-C₆H₅ (cis)</td>
<td>7%</td>
<td>73%</td>
<td>70%</td>
<td>7%</td>
</tr>
<tr>
<td>XLII X=CH₃, R=C₆H₁₁ (cis)</td>
<td>-</td>
<td>65%</td>
<td>59%</td>
<td>-</td>
</tr>
<tr>
<td>XLIII X=CH₃, R=C₆H₁₁ (trans)</td>
<td>-</td>
<td>67%</td>
<td>60%</td>
<td>-</td>
</tr>
</tbody>
</table>

*All runs in tetrahydrofuran for 72 hours.*
The isolation of $\alpha,\beta$ unsaturated ketones from the reaction mixtures strongly suggests that the reaction occurs by a pyrolytic rearrangement involving an intramolecular transfer of a proton from the alkyl group attached to the nitrogen to the carbonyl oxygen as formulated below.

Support for the above contention was found in the observation that cis- or trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI and XXI) gave trans-benzalacetophenone and cyclohexanone in comparable yields. Similarly, 1-benzyl-2-p-tolyl-3-phenylaziridine (I and II) afforded benzaldehyde and ammonia.

Further confirming evidence for the above mechanism was obtained by the finding that an authentic sample of N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine (XXVI) was converted rapidly and quantitatively to trans-benzalacetophenone and cyclohexanone when subjected to the reaction conditions.
The above formulation is not without analogy. The related pyrolysis of N-acylaziridines having the necessary side chain proton has been demonstrated to involve a stereo-specific, concerted \textit{cis} elimination.\textsuperscript{50,51}

However, by assuming that an intramolecular hydrogen transfer mechanism occurs, it becomes difficult to rationalize why


for leading references
the reaction does not proceed in the absence of diphenylidonium iodide. Another possibility that accounts for this is that the hydrogen transfer is not intramolecular but rather is catalyzed by diphenylidonium iodide which acts as a very weak Lewis acid. However, all attempts to use other Lewis acids were unsuccessful.

With the limited amount of data, it is premature to propose a precise mechanism to encompass the diphenylidonium iodide catalyzed transformations of arylaroylaziridines to diaryloxazoles. As a working hypothesis, however, one could envision diphenylidonium iodide coordinating with the carbonyl group, thereby promoting carbon-carbon cleavage of the strained aziridine ring. Subsequent ring closure to a 2,3-dihydrooxazole followed by oxidation readily accounts for the observed product.
The possibility that the 2,3-dihydrooxazole was formed by an iodide ion catalyzed isomerization was discounted by the fact that reaction of arylaroylaziridines with sodium iodide in acetone did not afford the same products. It is also noteworthy that in the reaction of aziridines I, II, XL, and XLI toluene is formed as a byproduct. The fact that N-cyclohexylaziridines XXVI, XXI, XLII, and SLII afford only α,β-unsaturated ketones suggests that the initial 2,3-dihydrooxazole may either undergo further oxidation or revert back to starting material. In this case, the N-cyclohexyl substituted aziridine would be expected to be resistant toward further oxidation.
A similar reversal has been reported in the related oxazoline system.\textsuperscript{52} Interestingly, the yield of diaryloxazole is much higher with aziridines I and II than with XL and XLI. A reasonable interpretation of this is that a considerable amount of positive character appears on the carbonyl oxygen in the transition state for the rearrangement. This is compatible with the above mechanism if it is assumed that diphenyliodonium iodide behaves as a weak Lewis acid and by coordinating with the carbonyl oxygen promotes ring cleavage. Alternatively, it may be argued that an ion pair mechanism may be in operation, with carbon-oxygen bond formation preceding carbon-carbon bond breakage.

During the course of studying the photochemical transformations of 2-benzoylaziridines, it was observed that these compounds developed a slight pink tinge on standing in the solid form at ambient temperature. This photoinduced reversible color change in the arylaroylaziridine system was first noted by Cromwell and co-workers,\textsuperscript{1,53} who reported that exposure of 1-benzyl and 1-cyclohexyl-2-phenyl-3-benzoylaziridine to diffuse daylight resulted in the rapid formation of a deep pink color, and that this coloration faded on standing in the dark. Reinvestigation of the properties of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine


(XXI) confirmed these observations. The red species formed on heating or on ultraviolet irradiation of the solid compound proved to be very sensitive to numerous solvents. Addition of a few drops of solvent immediately discharged the red coloration. All attempts to generate this colored species by carrying out the irradiation in a frozen glass at 77° K with filtered (310-390 mμ) light from a high pressure mercury arc. The color intensity attained by irradiation proved to be very dependent on both the stereochemistry of the aziridine and on the wave length of light used. On irradiation in a hydrocarbon glass (1:1 methylcyclohexane-3-methylpentane) at 77°K with 310-390 mμ light, the trans aziridine (XXI) turned pink, and on continued irradiation, it became orange. With light of wave length greater than 345 mμ, it turned orange initially. Although the colors faded completely on warming, the orange species seemed to fade slightly slower than the red, and became nearly yellow before fading completely. No fading due to visible light (> 390 mμ) was observed. cis-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI) also became colored, but at least ten times slower than the trans isomer. In a 1:1 ethanol-ether glass at 77°K, the trans-aziridine turned yellow on irradiation with 310-390 mμ light and at a greater rate than in the hydrocarbon glass. On warming, fading again occurred. The cis-isomer also turned yellow in this glass but again at a slower rate. No phosphorescence of either the cis- or trans-isomer was observed.
The photostationary state concentration of the colored species formed appears to be dependent on the intensity of the incident radiation, the reaction medium, the wave length of the light used, and on the relationship of the substituents on the three-membered ring. Although the physical property of primary concern in this system is the marked color change, other physical properties of the system may also be altered. In order to identify the colored species produced, attempts were made to follow its formation by spectroscopic methods.

Recently, Pitts has demonstrated the feasibility of qualitative and quantitative studies of solid-state chemical reactions in pressed alkali halide disks of the type customarily used for infrared analysis.\textsuperscript{54,55} Since the photochromic activity of the arylaroylaziridine appeared to be important only in the solid state or in a frozen glass, it seemed that the "pellet" technique would be a simple and convenient method for qualitative study of the structure of the colored species produced on irradiation. When a typical KBr pellet containing 0.18 mole \% of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (XXI) was exposed to light at 3650\textsuperscript{A°}, the pellet turned deep pink. The pink coloration


\textsuperscript{55} J. K. S. Wan, R. N. McCormick, E. J. Baum, and J. N. Pitts, Jr., ibid., \textbf{87}, 4409 (1965).
faded on standing in the dark for several hours. The infrared spectrum of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine was insignificantly affected by irradiation, a result which suggests that the photostationary state concentration of the colored species is too small to be detected by infrared spectroscopy. Similarly, no detectable changes in the infrared spectrum of the cis isomer (XXVI) were observed on irradiation in a KBr pellet, even though a marked coloration of the pellet occurred.

Since infrared spectroscopy was not sensitive enough to detect the extremely low steady state concentration of the colored material, an attempt was made to record the transient absorption spectrum of this species in the visible region. Brief irradiation (3-5 minutes) of the trans isomer XXI in a frozen glass at 77°K produced the colored species which displayed a single absorption maximum in the visible spectrum at 475 m\(\mu\). Since the preparation of solutions of known concentrations of the colored species was not feasible, it was necessary to determine its concentration by indirect means. The extinction coefficient of the colored material was estimated by irradiation of the arylaroylaziridine in the glass, rapidly scanning the spectrum in both the ultraviolet and visible region and noting the decrease in the optical density of the arylaroylaziridine in the ultraviolet range.\(^{56}\) On the assumption that the decrease in concentration

\(^{56}\) We are indebted to Dr. Angelo Lamola for these measurements.
of the arylaroylaziridine was equal to the increase in concentration of the colored form, it was possible to estimate its extinction coefficient. The resulting absorption maxima and extinction coefficients for a number of different arylaroylaziridines are summarized in Table 4.

**TABLE 4**

Visible Absorption Spectral Maxima for Colored Species Produced upon Irradiation of Arylaroylaziridines at 77°K<sup>a,b</sup>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Glass</th>
<th>( \lambda_{\text{max}}, \mu\text{m} )</th>
<th>( \epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI)</td>
<td>EA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>475</td>
<td>( 1 \times 10^3 )</td>
</tr>
<tr>
<td></td>
<td>3MP&lt;sup&gt;d&lt;/sup&gt;</td>
<td>463</td>
<td>( 1 \times 10^3 )</td>
</tr>
<tr>
<td>trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (XXI)</td>
<td>EA</td>
<td>493</td>
<td>( 1.4 \times 10^4 )</td>
</tr>
<tr>
<td></td>
<td>3MP</td>
<td>498</td>
<td>( 1.4 \times 10^4 )</td>
</tr>
<tr>
<td>cis-1-benzyl-2-phenyl-3-benzoylaziridine (XL)</td>
<td>EA</td>
<td>475</td>
<td>( 1 \times 10^3 )</td>
</tr>
<tr>
<td>trans-1-benzyl-2-phenyl-3-benzoylaziridine (XLI)</td>
<td>EA</td>
<td>485</td>
<td>( 1 \times 10^4 )</td>
</tr>
<tr>
<td>cis-1-benzyl-2-phenyl-3-p-toluylaziridine (I)</td>
<td>EA</td>
<td>475</td>
<td>( 1 \times 10^3 )</td>
</tr>
<tr>
<td>trans-1-benzyl-2-phenyl-3-p-toluylaziridine (II)</td>
<td>EA</td>
<td>486</td>
<td>( 1.4 \times 10^4 )</td>
</tr>
</tbody>
</table>

<sup>a</sup>Irradiation of the rigid matrix at 77°K was carried out with filtered light (3130 Å) from a high pressure mercury arc.

<sup>b</sup>Aziridine concentration was approximately \( 10^{-3} \)M.

<sup>c</sup>1:1 Ethanol-ether glass

<sup>d</sup>3-Methylpentane glass
It is obvious from the absorption spectra that the cis-compounds give different colored species than do the trans-compounds. The colored material formed from irradiation of the cis-isomers absorb at a somewhat lower wave length and with less intensity than do the trans-compounds. There is only a small solvent effect on the spectra of the colored species compared to what might be expected if the transitions had very large moments (e.g., charge transfer transitions). On changing to the more polar glass, the absorption band in the cis series moved to longer wave lengths while that in the trans series moved to shorter wave lengths. The rates of formation and disappearance of the colored species in both series were different. Also, the rate of formation of the colored form for both isomers was unchanged in a glass containing 40% isoprene. This indicates that either the triplet state of the arylaroylaziridine is not involved or that it rearranges within about $10^{-11}$ seconds.47

From these results it was concluded that the magnitude of the molar absorptivity and the position of the absorption maximum of the colored species is dependent on the initial disposition of the carbonyl group and the three-membered ring. The position of the absorption maximum in the visible region suggests that there is an extensive electrical interaction between the bent bonds of the aziridine ring and the pi orbitals of the benzoyl and phenyl groups. It is
difficult, however, to describe clearly by structural formulas the nature of this electronic interaction which ultimately leads to the formation of the colored species. The modified Lewis structures shown below are used to describe pictorially the resonance representations of such electronic interactions.

The above representations (XLIV and XLV) differ in their spatial arrangement which in turn affects the degree of orbital overlap of the bent bonds of the small ring with the π orbitals of the attached groups. The differences in the spectra observed may be rationalized in a matter similar to that suggested by Cromwell and Padwa to account for the ultraviolet absorption spectra of the two stereoisomers in the arylaroylaziridine system. The variation in color and absorption maximum is probably associated with the electrical vibrations and resonance in a slightly ionized state of the entire small ring system which has increasing difficulty in approaching coplanarity with the cis-isomer.
The trans arrangement provides for a more extensive polycentric molecular orbital than is possible with the more sterically hindered cis isomer and accounts for the larger molar absorptivity of the colored species in this series.

On the assumption that XLIV and XLV represent the correct structures for the colored material, attempts were made to trap them. Since these structures are closely related to 1,3-dipolar intermediates, it seemed reasonable to trap them with an unsaturated system. The preparation of five-membered ring heterocycles by 1,3-dipolar additions to unsaturated systems is a general reaction for a large number of 1,3-dipolarophiles, and it was felt that such trapping would provide additional evidence for the transient existence of XLIV and XLV. However, all experiments designed to trap the colored component at low temperatures in the presence of dimethylacetylene dicarboxylate, 2,5-diphenyl-3,4-iobenzofuran, cyclohexene, or with substituted butadienes were unsuccessful. Failure to detect a reaction under these conditions, however, does not necessarily reject XLIV or XLV as the structure of the colored components. The lack of reaction may be due to partial 1,3-bonding which markedly retards the reactions at the low temperatures employed.

Detailed clarification of the structures of the colored species produced upon irradiation of arylaroylaziridines has proved to be difficult because of the low steady state concentration and apparent unreactivity at the low temperatures used. With these difficulties in mind, it was considered desirable to carry out the trapping experiments at higher temperatures. At the beginning of this study there were no reports in the literature which described the thermal reactions of aziridines with alkenes and alkynes. Since beginning this study, other aziridines were subsequently reported to form adducts with various multiple bonds by carbon-carbon cleavage of the aziridine ring.

The reaction initially examined was the treatment of cis-2,3-diphenylaziridine with dimethylacetylene dicarboxylate in refluxing benzene. Initially it was hoped that the reaction would serve as a suitable model for comparison with the arylaroylaziridines to be used. Refluxing equimolar ratios of cis-2,3-diphenylaziridine and dimethylacetylene dicarboxylate in benzene for 12 hours resulted in the formation of an adduct XLV in 85% yield. The structure of XLVI


was assigned as dimethyl-2-[1-(2,3-diphenylaziridyl)]-maleate on the basis of the following data. The pure adduct, XLVI, was a solid, white needles from methanol, m.p. 94-95°C. The elemental analysis of this compound (Anal., Calcd. for C₂₀H₁₉NO₄: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.11; H, 5.85; N, 4.32) indicates that it is a 1:1 adduct. The infrared spectrum shows strong carbonyl bands at 5.70 and 5.80 μ. The ultraviolet spectrum (λ_max, 95% ethanol) 262 mμ (ε, 21,800) is essentially identical to dimethyl-2-[1-aziridyl]maleate. cis-2,3-Diphenylaziridine also forms an analogous adduct, XLVII, with diethylacetylene dicarboxylate.

\[ \text{Ph} \text{N} \text{H} \text{Ph} + \text{RO₂C} \equiv \text{C} \equiv \text{C} \text{CO₂R} \rightarrow \text{N} \text{CO₂R} \text{Ph} \text{H} \text{Ph} \text{H} \text{H} \text{Ph} \text{H} \text{H} \text{Ph} \text{H} \text{H} \text{Ph} \text{H} \text{H} \text{Ph} \]

\[ \text{R = Me \quad XLVI} \]
\[ \text{R = Et \quad XLVII} \]

The stereochemistry of the reaction product obtained has been assigned as the cis-diester by analogy with Dolfini's results. In the presence of a non-protic solvent, the

initially formed zwitterion would be expected to undergo stereospecific collapse via intramolecular protonation, leading to the cis-disposition of the ester functions.

The reaction course followed by refluxing trans-2-phenyl-3-benzoylaziridine (XXXVI) with dimethylacetylene dicarboxylate in xylene for 18 hours proved to be dramatically different. The reaction product obtained in this case (80%) was identified as 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (XLVIII). The structure of XLVIII was elucidated by elemental analysis, infrared, ultraviolet, n.m.r., and independent synthesis. Recrystallization from benzene-hexane gave a material melting at 159-160°. The elemental analysis of this compound indicates that it is a 1:1 adduct (see Experimental section). Spectral peaks appeared as follows: (ultraviolet spectrum) \( \lambda_{\text{max}} \) (95% ethanol) 246 \( \mu \) (\( \epsilon \), 17,000) and 312 \( \mu \) (\( \epsilon \), 11,700); (infrared spectrum) \( \lambda_{\text{max}} \) (KBr) 3.03, 5.81, 6.14, 7.92, 14.36 \( \mu \); (60-\( \mu \) n.m.r.) (deuterochloroform) multiplet at \( \tau \) 2.98. An authentic sample of 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (XLVIII), prepared by heating 2-phenyl-4-benzyl-5-oxazolone (XLIX)\(^{63}\) with dimethylacetylene dicarboxylate followed by selenium dioxide oxidation, was identical to XLVIII with respect to the infrared spectrum and melting point. A mixed melting point of the two samples was not depressed.

In order to further elucidate the mechanistic nature of the transformation, the reaction of dimethylacetylene dicarboxylate with cis- or trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI or XXI) was examined. In this case, dimethylacetylene dicarboxylate was found to react with either cis or trans aziridine to form two products in high yield. These adducts are assigned structures LI and LII. The assignments are supported by elemental analysis, n.m.r. data, and analogy with other aziridine reactions, and they are consonant with the observed ultraviolet data.
Data supporting LII as 1-cyclohexyl-2-phenyl-3,4-dicarboxymethoxy-5-benzoyl-2-pyrroline comes from consideration of the infrared, ultraviolet, and nuclear magnetic resonance spectra. The infrared has bands at 5.78, 5.96 and 6.37 μ. The ultraviolet spectrum of LII in 95% ethanol has maxima at 255 μ (ε, 15,600) and 303 μ (ε, 16,350). The n.m.r. spectrum (CCl₄) shows the aromatic hydrogens as a multiplet centered at τ 2.55, the methyl protons as singlets at 6.18 and 6.63, the methine protons as a pair of doublets at 5.15 and 6.42 (J = 4 c.p.s.) and the cyclohexyl protons as a complex multiplet centered at 8.67. The peak areas are in the ratio of 10:3:3:1:1:11. The stereochemistry of LII was
determined from the n.m.r. spectrum. The coupling constants are consistent with the Karplus correlation\(^ {64} \) and the observed values are in good agreement with those calculated by applying the Karplus equation to the dihedral angles measured on Dreiding models. A similar coupling constant observed in the n.m.r. spectrum of \( \text{trans} \)-3-methylproline (\( J = 4.6 \) c.p.s.) provides a reasonable spectroscopic analogy.\(^ {65} \) The n.m.r. of a substituted 3-pyrroline would not have had as large a coupling constant as that observed.\(^ {66} \) The formation of the 2-pyrroline in high yield is of interest since in the related reaction of triaryiaziridines with dimethylacetylene dicarboxylate only 3-pyrroles were isolated.\(^ {60} \)

Interestingly, adduct LII is markedly resistant to further oxidation. Heating LII with iodine in toluene or with palladium-on-charcoal in \( \pi \)-cymene resulted in recovered starting material. Only when LII was heated with selenium dioxide at 200° in a sealed tube was oxidation achieved. The stability of this adduct and the n.m.r. data are the major reasons for our current preference for the postulation of a \( \text{trans} \) relation of the hydrogens as opposed to a \( \text{cis} \) relationship. It is easier to account for the fact that the oxidation


of a **trans** species is more formidable than that of the **cis**, as the geometry of the **cis** isomer would appear to be more conducive for elimination of molecule hydrogen. The data therefore suggest that LI is not derived from LII, but rather results from the initially formed 3-pyrroline. Under the reaction conditions, the initial adduct may either rearrange to LII or lose hydrogen to give the substituted pyrrole.

The formation of the transient 3-pyrroline can be rationalized by the assumption that the initial step in the reaction involves cleavage of the carbon-carbon bond of the aziridine ring and the formation of a 1,3-dipolar intermediate (LIII) which subsequently adds to the unsaturated substrate.

This is consistent with the finding that **cis**-2,3-diphenylaziridine undergoes Michael addition as opposed to carbon-carbon cleavage. In this case the formation of a 1,3-dipolar intermediate would be expected to be difficult as the developing carbanion is not stabilized to the same degree as is possible in the arylaroylaziridine case.
On the basis of our studied it seems reasonable to conclude that 1,3-dipolar intermediates are involved in the addition of arylaroylaziridines to dimethylacetylene dicarboxylate. However, we cannot rule out a 1,3-diradical intermediate.

Since it seems necessary to invoke a similar species to explain the photochromic activity of these small rings, one can assume that more than one kind of 1,3-dipolararophile is involved. The main difference between dipolarophile LIII and dipolarophile XLIV (or XLV) is a matter of the degree of overlap of the carbon atoms of the three-membered ring. Dipolarophile XLIV is stabilized by overlap of the developing carbanion adjacent to the benzoyl group with the similarly developing carbonium ion adjacent to the phenyl ring. This interaction allows for an extensive polycentric molecular orbital that exhibits a pronounced coloration, but which is relatively unreactive in the matrix. Dipolarophile LIII, on the other hand, is essentially devoid of this overlap and is expected to have a lower 1,3-bond order, thereby accounting for its enhanced reactivity. Alternatively, it may be argued that at the higher temperatures the ionized state of the entire small-ring system is capable of addition to the multiple bond, whereas this is not possible in the matrix at low temperatures and instead, an increase in the steady state concentration of the dipolarophile is observed.
As an extension of our studies in the behavior of electronically excited states of small-membered rings, the photochemical transformation of cis-1-t-butyl-2-phenyl-3-benzoylazetidine$^{67}$ (LIV) was examined. Our initial interest in the electronically excited state behavior of the cis isomer was invoked because of the possibility of an intramolecular hydrogen transfer via a quasi eight-membered transition state. From examination of Dreiding models it seemed that when the conformation of the four-membered ring achieved planarity, the benzoyl oxygen was in a favorable position to abstract one of the hydrogens on the t-butyl group.

![Chemical Structure](image)

\[CH_3\text{CH}_2\text{CH}_2\text{Ph}\]\[\text{hv}\]\[\text{CH}_3\text{CH}(\text{Ph})\text{N}\text{CH}_2\text{Ph}\] \[\text{LIV}\rightarrow\text{PRODUCTS}\]

The irradiation of LIV was conducted in a nitrogen atmosphere using an internal water-cooled mercury arc lamp (Hanovia Type L, 450 watts) with a Pyrex filter to eliminate

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wave lengths below 300 μ. The photolysis was followed by withdrawal of small aliquots at fixed intervals and examination of these samples by infrared spectroscopy. After irradiation of 0.5 g. of LV in 150 ml. of benzene for 3 hours, the carbonyl absorption band of LIV had completely disappeared. Removal of the solvent and recrystallization from 95% ethanol afforded 0.46 g. of a solid (95%), m.p. 102-103°, whose structure was assigned as 1-t-butyl-2,4-diphenylpyrrole (LV) on the basis of chemical and physical data cited. The infrared spectrum of LV was characterized by a series of sharp bands at 6.24, 8.21, 12.47, 13.08, 13.50, 14.25 and 14.40 μ. The ultraviolet spectrum (λ_max, 95% ethanol) 235 μ (ε, 15,800) and 276 μ (ε, 16,200) of LV shows an absorption curve very similar to 2,4-diphenylfuran, with peaks occurring at approximately the same wave lengths (λ_max, 95% ethanol) 242 μ (ε, 19,400) and 277 μ (ε, 20,000). The n.m.r. spectrum in deuterochloroform exhibits a singlet at τ 8.60, a pair of doublets at 3.64 and 2.81 (J = 1.9 c.p.s.) and a multiplet centered at τ 2.62. The peak areas are in the ratio of 9:1:1:10. The doublet pattern of the 3 and 5 proton is to be expected, as it has been shown that the cross ring or meta coupling constant (J 3,5) in the pyrrole system has a value of approximately 2

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The elemental analysis of this compound (Anal., Calcd. for C_{20}H_{21}N: C, 87.22; H, 7.69; N, 5.09. Found: C, 87.20; H, 7.85; N, 5.09) is also consistent with structure LV. Chemical confirmation was obtained by pyrolysis of LV at 325°. The product obtained in better than 97% yield was identical with an authentic sample of 2,4-diphenylpyrrole (LV I) synthesized by the method of Allen and Wilson.70

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An authentic sample of 1-t-butyl-2,4-diphenylpyrrole, LV, prepared by heating \textit{trans}-1,3-diphenyl-4-bromobutene-2-one-1 (LVII) with tertiary butyl amine, was identical with LV as evidenced by comparison of the infrared spectrum and melting point.\textsuperscript{71} A mixed melting point of the two samples was undepressed. Similarly, the only product detectable by n.m.r., U.V., and vapor phase chromatography, either initially or after 90\% photoconversion of azetidine LIV was pyrrole LV. To our knowledge, this represents the first example of a photochemical migration of an alkyl group from the alpha position to the carbonyl carbon of an n $\rightarrow$ $\pi$ excited state.

\[
\begin{align*}
\text{O} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qua
and light above 300 m\(\mu\) were employed. The quantum yield for the formation of LV in 95% ethanol was found to be 0.046 at 3600 Å. In an attempt to determine the rate constant for the unimolecular rearrangement of the excited state, the variation of quantum yield versus quencher concentration was studied. Surprisingly, the photolysis of LIV could not be quenched by moderate concentration of 1,3-pentadiene, 1,3-cyclohexadiene, naphthalene, or ferric dipivaloylmethide (see Table 5).

\[
\text{TABLE 5}
\]
Quantum Yields for cis-1-t-Butyl-2-phenyl-3-benzoylazetidine

<table>
<thead>
<tr>
<th>Run</th>
<th>Compound(^a,b)</th>
<th>Quencher, M</th>
<th>Quantum Yield (\Phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LIV</td>
<td>None</td>
<td>(0.046 \pm 0.001)</td>
</tr>
<tr>
<td>2</td>
<td>LIV</td>
<td>Piperylene, 2</td>
<td>(0.045 \pm 0.001)</td>
</tr>
<tr>
<td>3</td>
<td>LIV</td>
<td>Piperylene, 5</td>
<td>(0.046 \pm 0.001)</td>
</tr>
<tr>
<td>4</td>
<td>LIV</td>
<td>Piperylene, 10</td>
<td>(0.036 \pm 0.001)</td>
</tr>
<tr>
<td>5</td>
<td>LIV</td>
<td>1,3-Cyclohexadiene, 2</td>
<td>(0.045 \pm 0.001)</td>
</tr>
<tr>
<td>6</td>
<td>LIV</td>
<td>1,3-Cyclohexadiene, 10.5</td>
<td>(0.037 \pm 0.001)</td>
</tr>
<tr>
<td>7</td>
<td>LIV</td>
<td>Naphthalene, (10^{-3})</td>
<td>(0.045 \pm 0.001)</td>
</tr>
<tr>
<td>8</td>
<td>LIV</td>
<td>Naphthalene, (5 \times 10^{-3})</td>
<td>(0.046 \pm 0.001)</td>
</tr>
<tr>
<td>9</td>
<td>LIV</td>
<td>Ferric Dipivaloylmethide, (10^{-5})</td>
<td>(0.045 \pm 0.001)</td>
</tr>
<tr>
<td>10</td>
<td>LIV</td>
<td>---(^c)</td>
<td>(0.093 \pm 0.001)</td>
</tr>
</tbody>
</table>

\(^a\)Azetidine concentration was \(1.48 \times 10^{-2}\) m/\(L\)

\(^b\)95% Ethanol was used as solvent.

\(^c\)Acetophenone (3.45M) was used as a photosensitizer.
However, in the samples containing piperylene as solvent, the quantum yield for formation of LV decreased to 0.036. Since piperylene is a very efficient acceptor for high-energy ketone triplets, but does not quench their excited singlet states, it appears as though the photoreaction proceeds from both an excited n → π* triplet state and an unquenchable n-π* singlet state. Assuming complete destruction of the triplet state when piperylene was used as solvent, the quantum yield for the singlet would be 0.036 and the triplet quantum yield would be 0.010. The lack of quenching at moderate quencher concentration suggests that the rate of unimolecular rearrangement of the n-π* triplet is close to diffusion control.

With acetophenone present in concentration to absorb 99% of the light, a twofold increase in quantum yield resulted despite the negligible direct excitation of the azetidine LV, providing strong evidence for photosensitization by acetophenone. Since the same product resulted as in ordinary irradiation, it is reasonably assumed that the acetidine triplet is also an intermediate in the unsensitized reaction. Since the quantum yield of LV increases by sensitization, we can conclude that either the intersystem crossing efficiency of the n-π* singlet is low or that rate of crossing in this case may be much slower than

in benzophenone or acetophenone thereby allowing for a competing unimolecular rearrangement. A similar situation has been noted in the photochemistry of dibenzoylethylene, although in that case reaction proceeded exclusively by way of a n-π* singlet.\textsuperscript{73}

Aromatic aldehydes and ketones, such as benzophenone and benzaldehyde do not exhibit a fluorescence spectrum; indicating that the intersystem-crossing efficiency is near unity. In these systems the triplet π → π* state of the carbonyl group lies between the n-π* singlet and triplet state (Figure 2b). The location of the π → π* triplet between the n-π* singlet and the n-π* triplet level is known to lead to the enhancement of the intersystem-crossing process.\textsuperscript{74} However, location of the π-π* manifold and consequently increases the probability of reaction from the n-π* singlet state.


Figure 2. - Effect of the order and type of excited states on the rate of intersystem crossing.
It can be concluded, therefore, that the relative position of the $\pi-\pi^*$ triplet level has a pronounced effect on the efficiency of intersystem crossing of the n-$\pi^*$ state. A similar argument may be used to account for the low intersystem crossing efficiency of the n-$\pi^*$ singlet of LIV, i.e., the position of the energy levels is related to Figure 2a, rather than to Figure 2b. At any rate, these results are entirely consistent with reactions being described from the n-$\pi^*$ state as depicted in terms of the following mechanism.
One possible explanation for the exclusive formation of the 2,4-isomer, LV, may be related to the preferred migratory aptitude of methyl vs. benzyl groups toward an electron deficient center.\textsuperscript{75}

Alternatively, it may be argued that the exclusive formation LV is a result of severe steric interactions of the three bulky groups in the transition state for l-t-butyl-2,3-diphenylpyrrole (LVIII). Such steric interactions are not as pronounced in the formation of LV.

EXPERIMENTAL

Melting points

Melting points were determined with a Thomas Hoover capillary melting point apparatus. All melting points and boiling points are uncorrected.

Analyses

Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hogenweg, Germany.

Infrared spectra

Infrared absorption spectra were determined on a Perkin-Elmer Model 137 sodium chloride spectrophotometer, or a Perkin-Elmer Infracord spectrophotometer in potassium bromide pellets unless otherwise stated.

Ultraviolet spectra

Ultraviolet absorption spectra were measured with a Carey Recording Spectrophotometer, Model 14, using 1 cm. matched quartz absorption cells. All spectra were determined in 95% ethanol unless otherwise specified.
Nuclear magnetic resonance spectra

The nuclear magnetic resonance spectra were determined at 60 Mc with a Varian Associates high resolution spectro-photometer using deuterochloroform as solvent. Tetramethylsilane was used as an internal standard.

Irradiation apparatus

All irradiations (except quantum yield measurements) employed an internal water-cooled, medium pressure mercury arc lamp (Hanovia, Type L-450 watts) with appropriate filter sleeves to remove low wave length light unless otherwise stated.

Vapor phase chromatography

All analyses were performed on either an Aerograph HiFi, hydrogen flame ionization detector, model 600-D, using nitrogen as the carrier gas on 1/8" columns of length, packing material and temperature specified, or on an Aerograph Dual Column Temperature Programmer, Model A-350-B, with thermal conductivity detectors using helium as a carrier gas on 1/4" columns of length, packing and temperature specified.

Irradiation of trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (XXI) in Ethanol.

1-Cyclohexyl-2-phenyl-3-benzoylaziridine was prepared according to the procedure of Cromwell and Hoeksema. A
solution of 1.50 g. of XXI in one liter of 95% ethanol was
irradiated with an internal cooled mercury arc lamp (Hanovia,
Type L-450 watts) with a Pyrex filter to eliminate wave
lengths below 280 m\(\mu\). Aliquots were removed and analyzed by
thin layer chromatography. After three hours, the spot on a
thin layer plate due to XXI had almost disappeared and
several new spots had appeared in its place.

Concentration of the solution left an oil which was
subjected to liquid-liquid partition chromatography. The
separation was carried out in a water jacketed column
(150 x 3.5 cm.) which was kept at a constant temperature of
29.0 ± 0.05°. The two-phase system (prepared from 1000 ml.
of cyclohexane, 400 ml. of dimethylformamide, 250 ml. of
ethyl acetate and 30 ml. of water) was allowed to equili­
brate for at least 30 minutes before use. The liquid-liquid
apparatus used in these experiments and the processing of
the fractions have been described in detail elsewhere.\(^{22}\)
The optical density trace showed four imperfectly defined
peaks with retention volume of 1500 ml. (75 fractions), 1860
ml. (93 fractions), 1960 ml. (98 fractions), and 2004 ml.
(102 fractions). The fractions were washed three times with
an equal volume of water, dried over sodium sulfate and con­
centrated in vacuo.
Figure 3. Diagram for liquid-liquid partition chromatography.
The first peak (500 mg.) was identified as recovered starting material. Since the resolution of the third and fourth peak was poor, they were combined and chromatographed on a 1.5 x 90 cm. alumina column (neutral grade, activity III). Elution of the chromatographic column with 1% ethyl ether-hexane gave 290 mg. of a compound which upon crystallization from ethanol-water gave light yellow rosettes, m.p. 43-44°. The product obtained was identical to an authentic sample of cis-benzalacetophenone (XXIII) synthesized by the method of Lutz and Jordan. Further elution of the column with 2% ether-hexane gave 320 mg. of a light yellow oil. Recrystallization of this material from 95% ethanol gave a pale yellow solid, m.p. 55-56°. This material was identified as trans-benzalacetophenone (XXII) by comparison of its infrared spectrum with that of an authentic sample.

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The second fraction obtained from the liquid-liquid partition chromatogram contained 90 mg. of a light yellow oil which resisted all attempts to induce crystallization. This same compound was isolated in much higher yields when the photolysis was carried out in anhydrous pentane. The structure of this material was assigned as N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine (XXV) on the basis of the following observations.

**Analysis:**
Calcd. for C$_{21}$H$_{23}$NO: C, 82.55; H, 7.59; N, 4.59.
Found: C, 82.22; H, 6.75; N, 4.26.

The infrared spectrum in carbon tetrachloride shows strong absorption at 5.93, 6.10, 6.92, 6.94, 9.28, 9.78 $\mu$.
The ultraviolet spectrum in 95% ethanol has a maximum at 245 $\mu$ $\lambda$ ($\epsilon$, 18,200). The n.m.r. spectrum (deuterochloroform) is in excellent agreement with the proposed structure and consisted of a multiplet at $\tau$ 2.45 (10H) and a multiplet at 9.0 (10H); the remaining part of the spectrum consisted of an ABX system of 12 lines. The X proton of the ABX system was centered at $\tau$ 4.98 (1H) and consisted of an unsymmetrical quartet.
The A and B protons of the ABX system were centered at $\tau$ 6.17 (1H) and 6.67 (1H) and each consisted of an unsymmetrical quartet. The coupling constants for the ABX system were $J_{AX} = 8.3$ c.p.s., $J_{BX} = 4.5$ c.p.s., and $J_{AB} = 16.5$ c.p.s.

Further proof of structure was shown by the following degradation sequence.
In a 5 cc. round bottom flask fitted with a reflux condenser, a mixture of 50 mg. of XXV, 3 cc. of 95% ethanol and two drops of concentrated hydrochloric acid was refluxed for five hours. The resulting mixture was analyzed by vapor phase chromatography. The analytical gas chromatography was performed on an Aerograph 350-B instrument with helium as the carrier gas on a column of Carbowax (20% on Chromosorb W) at 120°C. Comparison of retention times and infrared spectra with those of known samples of cyclohexanone and trans-benzalacetophenone (XXII) established the identity of the products.

To a sample of XXV (250 mg.) dissolved in 20 ml. of methanol was added 100 mg. of Adam's catalyst. The mixture was placed in a Parr shaker for 10 minutes under a pressure of 45 p.s.i. of hydrogen. The catalyst was filtered through a porous funnel, a large excess of methyl iodide was added, and the resulting mixture was refluxed for eight hours. The solvent was removed in vacuo and the residual oil was dissolved in 100 ml. of 95% ethanol. To the alcoholic solution was added 0.1 g. of platinum dioxide and the mixture was again placed in a Parr shaker for 30 minutes under a pressure of 45 p.s.i. of hydrogen. The catalyst was filtered and the solvent evaporated under reduced pressure. Addition of dry ether afforded crude dimethylcyclohexylamine hydroiodide. Evaporation of the solvent gave .140 mg. (83% yield) of benzylacetophenone, identified by comparison with an authentic sample.
Treatment of the Crude Photolysis Mixture of XXI with Benzaldehyde.

A solution of 1.0 g. of trans-aziridine (XXI) in one liter of 70% ethanol was purged with purified nitrogen for 45 minutes before irradiation commenced and a positive pressure of nitrogen was maintained throughout the photolysis. The solvent was removed in vacuo and the crude photolysis residue was treated with 290 mg. of benzaldehyde in refluxing benzene for 12 hours. After concentration in vacuo, the crude residue was chromatographed on a 2.5 x 90 cm. florisil column. Elution with 1% ethylacetate-benzene gave .570 g. (82%) of cis- and trans-benzalacetophenone (XXIII and XXII). Further elution with 10% ethylacetate-benzene gave .195 g. (23%) of a compound whose infrared spectrum was identical in every detail with that of an authentic sample of 1-cyclohexyl-2-phenylnitrone.21
Product Distribution vs. Time in the Photolysis of XXI

The yields of cis- and trans-benzalacetophenone (XIII and XXIII) obtained from the irradiation of XXI are strongly affected by the length of the irradiation, as shown in Table 6. Consideration of the product distribution as a function of time in a number of photolyses showed that as XXII decreased, XXIII appeared. The photostationary state of cis- and trans-benzalacetophenone was shown by Lutz and Jordan\(^7\) to be 78% cis and 22% trans. By comparison of the ultraviolet spectrum of the cis and trans mixture of benzalacetophenone isolated from the irradiation with that of a known mixture, it was possible to calculate the ratio of cis- and trans-benzalacetophenone produced.

In a typical run, a solution of 1.0 g. of the trans-aziridine in one liter of 95% ethanol was photolyzed in the usual manner for a given length of time. The solvent was removed in vacuo and the crude residue was chromatographed on the previously described liquid-liquid partition chromatography column. The fractions which corresponded to a mixture of cis- and trans-benzalacetophenone were worked up in the usual manner and after complete removal of all traces of solvents, an ultraviolet spectrum was recorded in 95% ethanol. The spectrum was compared with known standards and the percentage of cis and trans isomers was calculated. The results are summarized in Table 6.
### TABLE 6.

Photolysis of trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (XXI)\(^a,b,c\)

<table>
<thead>
<tr>
<th>Run</th>
<th>Time of Photolysis, minutes</th>
<th>(%) cis XXIII</th>
<th>(%) trans XXII</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5(^d)</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>10.0</td>
<td>49</td>
<td>54</td>
</tr>
<tr>
<td>5</td>
<td>15.0</td>
<td>73</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>20.0</td>
<td>78</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>180.0</td>
<td>78</td>
<td>22</td>
</tr>
</tbody>
</table>

\(^a\)Material separated from trans-aziridine (XXI) by liquid-liquid partition chromatography.

\(^b\)Internal water-cooled Mercury arc lamp (Hanovia Type L-450 watts) with a Pyrex filter was used.

\(^c\)One gram of trans-aziridine (XXI) was used in all irradiations.

\(^d\)Irradiation of XXI for a period less than 3.5 minutes was not attempted since there was not enough benzalacetophenone produced to detect by partition chromatography.
Photoisomerization of trans-Benzalacetophenone (XXII)

A solution of .220 g. of trans-benzalacetophenone in one liter of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, type L-450 watts) with a Pyrex filter to eliminate wave lengths below 280 mμ. Aliquots of one ml. were removed at different intervals and quantitatively diluted to 100 ml. The ultraviolet spectrum was recorded and the percent of cis- and trans-benzalacetophenone was calculated by comparison with known mixtures. The results are summarized in Table 7.

TABLE 7.

Photoisomerization of trans-Benzalacetophenone (XXII) in Ethanol\textsuperscript{a, b}

<table>
<thead>
<tr>
<th>Time of Photolysis in minutes</th>
<th>% cis XXIII</th>
<th>% trans XXII</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>1.5</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>3.5</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>5.0</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>7.5</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td>15</td>
<td>78</td>
<td>22</td>
</tr>
<tr>
<td>240</td>
<td>78</td>
<td>22</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Identical results were obtained with pentane as solvent.

\textsuperscript{b}220 mg. of trans-benzalacetophenone was used.
Irradiation of trans-1-Cyclohexyl-2-phenyl-3-benzoyl-aziridine (XXI) in Pentane.

A solution of 1.5 g. of trans-aziridine XXI in one liter of anhydrous pentane was irradiated with an internal water-cooled mercury arc lamp (Hanovia, type L-450 watts) with a Pyrex filter to eliminate wave lengths below 280 m\(\mu\). Purified nitrogen was passed through the solution for at least 45 minutes before irradiation was commenced and a positive pressure of nitrogen was maintained throughout. The solution was irradiated for three hours and the solvent was removed in vacuo. The crude photolysis residue was chromatographed on a liquid-liquid partition column in the usual manner.

The chromatogram showed four well-resolved peaks with retention volume of 1500 ml. (75 fractions), 1700 ml. (85 fractions), 1940 ml. (97 fractions), 2016 ml. (108 fractions). The first peak (.775 g.) was identified as recovered starting material. The third peak (.179 g.) was shown to be the N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine (XXVI). The final band contained .355 g. of pure trans-benzalacetophenone (XXI). The second peak (.200 g.) contained a dark oil which resisted all attempts at crystallization. Finally, after repeated chromatography, small amounts of a white solid were obtained, m.p. 69°. The structure of this material has not yet been assigned.
Irradiation of cis-1-Cyclohexyl-2-phenyl-3-benzoyl-aziridine (XXVI).  

\textbf{cis-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI)} was prepared according to the procedure of Cromwell and Hoeksema.\footnote{1} A solution of 0.500 g. of the \textit{cis}-aziridine in one liter of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, type L-450 watts) with a Pyrex filter to eliminate light below 280 \textmu m. Purified nitrogen was passed through the solution for at least 45 minutes before irradiation commenced and a positive pressure of nitrogen was maintained throughout. The solution was irradiated for six hours and the solvent was removed \textit{in vacuo} to give a yellow oil. The crude reaction mixture was dissolved in two ml. of upper phase and chromatographed on a liquid-liquid partition column. The eluate was scanned at 257 \textmu m and collected in 20 ml. fractions. The optical density trace showed four imperfectly defined peaks with retention volumes of 1600 ml. (80 fractions), 1700 ml. (85 fractions), 1800 ml. (90 fractions), 1960 ml. (98 fractions). The first fraction, (0.017 g.), (16\% based on recovered starting material) was shown to be benzaldehyde by comparison with an authentic sample. The second fraction, (0.150 g.), (80\% based on recovered starting material) was a colorless liquid. Comparison of its infrared spectrum and v.p.c. retention time on a Dow 710 silicone oil (5\% on Chromosorb W) with an authentic sample of N-cyclohexyl-
 benzalimine established its identity. The last peak, .0145 g., was shown to be recovered starting material. There was no indication of any other component in the chromatogram.

Irradiation of trans-1-benzyl-2-phenyl-3-para-toluyl-aziridine (II) in 95% Ethanol.

_trans-1-Benzyl-2-phenyl-3-para-toluylaziridine_ was prepared according to the procedure of Cromwell and Wankel. A solution of .940 g. of trans-aziridine (II) in one liter of 95% ethanol was purged with purified nitrogen for 45 minutes before irradiation and a positive pressure of nitrogen was maintained throughout. The solution was irradiated for three hours with an internal cooled mercury arc lamp (Hanovia, Type L-450 watts) equipped with a Pyrex filter to eliminate wave lengths below 280 m\(\mu\). The solvent was removed _in vacuo_ to give a yellow oil which was subjected to liquid-liquid partition chromatography. The chromatogram consisted of three imperfectly defined peaks with retention volume of 1560 ml. (78 fractions), 1740 ml. (87 fractions), 1860 ml. (93 fractions) of upper phase. The first fraction (.175 g.) upon recrystallization from 95%

77 T. F. West, Chem. and Ind., 61 (1942).

ethanol gave 100 mg. of pure starting material. The crude filtrate consisted mostly of benzaldehyde. The relative amounts of material in the second and third peaks were shown to be a function of the manner in which the solvent was removed from the photolysis cell. It appeared as though the material isolated from the second peak of the chromatogram decomposed on heating to the material to be found in the third set of fractions. This was later confirmed in a separate experiment. The material in the third peak was shown to be pure trans-4'-methylbenzalacetophenone (XXVIII) by comparison with an authentic sample prepared according to the procedure of Weygand. 79

N-1(2-p-Tolyl-1-phenylethyl)benzylidenimine (XXX).

The second peak, .386 g. (46% yield based on recovered starting materials) was a light yellow oil which resisted all attempts to induce crystallization. The structure of this compound was assigned as N-1-(2-para-tolyl-1-phenylethyl)benzylidenimine on the basis of the following observations.

Analysis:

Calcd. for C_{27}H_{21}NO: C, 84.37; H, 6.47; N, 4.28.
Found: C, 83.55; H, 6.52; N, 4.18.

The infrared spectrum in carbon tetrachloride showed

79 R. Weygand, Ber., 35, 1068 (1902).
strong absorption at 5.93, 6.13, 6.24, 6.94, 8.50, 9.74 μ. The ultraviolet spectrum in 95% ethanol has a maximum at 251 μ (ε, 27,400). The n.m.r. spectrum in deuterochloroform is in excellent agreement with the proposed structure and consisted of a multiplet at τ 2.61 (9H), a singlet at 1.72 (1H), a singlet at 7.77 (3H); the remaining part of the spectrum consisted of an ABX system of 12 lines. The X proton of the ABX system was centered at τ 4.86 (1H) and consisted of an unsymmetrical quartet. The A and B protons of the ABX system were centered at τ 6.21 (1H) and 6.74 (1H). Each consisted of an unsymmetrical quartet. The coupling constants for the ABX system were $J_{AX} = 8.3$ c.p.s., $J_{BX} = 4.5$ c.p.s., and $J_{AB} = 16.5$ c.p.s. Further proof of structure was shown by the following degradation reactions.

A solution of 0.337 g. of XXX in 50 ml. of 95% ethanol containing 0.1 ml. of hydrochloric acid was refluxed for nine hours. The solvent was evaporated under reduced pressure, leaving 0.308 g. of a brown, oily residue. The residue was taken up in ether and the ethereal solution was washed with a 10% solution of sodium bicarbonate. Upon acidification of the aqueous solution and extraction with ether, followed by drying and evaporation of the ether, 90 mg. (72%) of benzoic acid was obtained. The ethereal solution was dried over sodium sulfate and concentrated in vacuo leaving 280 mg. of a yellow oil. This was chromatographed using liquid-liquid partition chromatography. The
chromatogram consisted of only one peak with retention volume of 1840 ml. of mobile phase. The dried extracts afforded 200 mg. (89%) of a pale yellow oil which solidified on standing. Recrystallization from 95% ethanol gave pure trans-4'-methylbenzalacetophenone (XXVIII).

A 1.17 g. sample of N-1-(2-p-toluyl-1-phenylethyl)benzylidenimine (XXX) was chromatographed on a 1.5 x 30 cm. florisil column slurry packed in 1% ethyl acetate-pentane. The column was eluted with 100 ml. of 1% ethyl acetate-pentane and 750 ml. of 3% ethyl acetate-pentane. The clear oil obtained by elution with 1% ethyl acetate-pentane amounted to 310 mg. of benzaldehyde. The crystalline solid (800 mg., 97%) from elution with 3% ethyl acetate-pentane was identical to trans-4'-methylbenzalacetophenone (XXVII) as judged by IR and mixed m.p. comparison.

To a 0.5 g. sample of XXX in 100 ml. of absolute alcohol was added 0.1 g. of Adam's catalyst. The mixture was placed in a Parr shaker for three hours under a pressure of 45 p.s.i. of hydrogen. The mixture was filtered and concentrated under reduced pressure to afford 493 mg. of a yellow oil. Addition of anhydrous ether and gaseous hydrogen chloride gave 180 mg. of crude benzylamine hydrochloride. Evaporation of the ethereal solution gave 260 mg. (76%) of a colorless crystalline compound, m.p. 68-69°, whose infrared spectrum was identical in every detail with that of pure 4'-methylbenzylacetophenone. The mixed melting point of these two materials was undepressed at 68-69°.
Irradiation of II in Anhydrous Pentane

A solution of 1.0 g. of II in one liter of anhydrous pentane was photolyzed with an internal water-cooled mercury arc lamp (450 watts) with a soft glass filter to eliminate wave lengths below 300 mµ. Purified nitrogen was passed through the solution for at least 45 minutes before irradiation commenced and a positive pressure was maintained throughout. The nitrogen atmosphere was purified by the vanadous ion method of Meites. Concentration of the solution left an oil. The crude residue was chromatographed on a liquid-liquid partition column using a 4.5 x 150 cm. thermostated column. There were three major peaks in the chromatogram. The first peak (retention volume of 1520 ml.) was identified as starting material by IR and by mixed m.p. comparison. The second peak (retention volume of 1720 ml.) afforded 605 mg. (69% based on recovered starting material) of a colorless oil which was identified as N-1-(2-p-toluyl-1-phenylethyl)benzylidenimine (XXX). The third peak (retention volume of 1860 ml.) consisted of 220 mg. (35%) of trans-4'-methylbenzalacetophenone (XXVIII). There was no indication of any cis-4'-methylbenzalacetophenone (XXIX) in the chromatogram. Control experiments demonstrated the photostability of XXX to the above irradiation conditions.

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Treatment of the Crude Photolysis Mixture of II with Benzaldehyde.

A solution of 1.0 g. of the trans-aziridine in one liter of 70% ethanol was purged with purified nitrogen for 45 minutes before irradiation commenced and a positive pressure of nitrogen was maintained during the four-hour photolysis. Concentration in vacuo at 50° left a yellow oil. The crude photolysis residue was treated with 276 mg. of benzaldehyde in refluxing benzene for 12 hours. After concentration in vacuo, the crude residue was chromatographed on a 2.5 x 90 cm. florisil chromatography column. Elution with 1% ethyl acetate-pentane gave recovered benzaldehyde. Further elution with 2% ethyl acetate-pentane gave .640 g. (94%) of trans-4'-methylbenzalacetophenone (XXVIII). A further increase of solvent polarity (10% methanol) afforded no other products. Even when 20% aqueous dioxane was used as the irradiation solvent, there was no trace of the nitrone of benzylhydroxylamine. The nitrone itself was stable to florisil chromatography and could be eluted with 10% ethyl acetate-pentane.
The photoisomerization of XXVIII was studied in both 95% ethanol and anhydrous pentane as solvent. The rate of the photoisomerization in either solvent was found to be within experimental error of being identical. A solution of .220 g. of trans-4'-methylbenzalacetophenone (XXVIII) in one liter of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a Pyrex filter to eliminate wave lengths below 280 m\textmu. Aliquots of one ml. were removed at different time intervals, and quantitatively diluted to 100 ml. in a volumetric flask. The ultraviolet spectrum was recorded and the percentage of the cis- and trans-isomers was calculated by comparison with known mixtures. The results are recorded in Table 8.
TABLE 8.

Photoisomerization of trans-4'-Methylbenzalacetophone (XXVIII)

<table>
<thead>
<tr>
<th>Time</th>
<th>% cis XXIX</th>
<th>% trans XXVIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>180</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

Photolysis of cis-1-Benzyl-2-phenyl-3-p-toluylaziridine (I).

 cis-1-Benzyl-2-phenyl-3-p-toluylaziridine (I) was prepared according to the procedure of Cromwell and Wankel. A solution of 2.0 g. of cis-aziridine (I) in one liter of 95% ethanol was photolyzed for nine hours and the solvent was removed under reduced pressure. The concentrated solution gave 1.987 g. which was chromatographed on a liquid-liquid partition chromatography column. The optical density trace showed four peaks with retention volume of 1400 ml. (70 fractions), 1540 ml. (77 fractions), 1680 ml. (84 fractions), 2000 ml. (100 fractions). The fractions were worked up in the manner previously described. The last
peak in the chromatogram, .900 g., was shown to be recovered starting material. The first peak, .090 g. (26% based on recovered starting material) was shown to be benzaldehyde by comparison with an authentic sample. The second fraction consisted of a mixture of a colorless liquid, 0.5 g. (78% based on recovered starting material) and a white solid, 0.05 g. The colorless liquid was shown to be identical in all respects with an authentic sample of N-benzylbenzalimine (XXXI) prepared by the method of Juday and Adkins. The solid, m.p. 151-151.5°, was demonstrated to be N,N'-di-benzyl-1,2-diphenyl-1,2-diaminoethane (XXXII) by comparison with an authentic sample prepared by the procedure of Japp and Moir. Suspicion that this dimeric product was a secondary photoproduct was confirmed by the finding that the photolysis of N-benzylbenzalimine in ethanol afforded the dimer in high yield.

The third peak in the chromatogram, 0.320 g. (71% based on recovered starting material) was a colorless liquid whose infrared, ultraviolet, and nuclear magnetic resonance spectra were identical in all respects to an authentic sample of 4-methylacetophenone.

The photolysis of I was repeated using one liter of benzene as solvent. After the irradiation was completed,

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the solution was evaporated to dryness and the residue was chromatographed using liquid-liquid partition chromatography. The chromatogram showed four peaks. The infrared spectrum of the third band was identical in every detail with that of XXX. The fourth peak was identified as trans-4'-methylbenzalacetophenone (XXVIII) by mixture melting point. The first peak in the chromatogram was shown to be N-benzylbenzalimine (XXXI) by comparison with an authentic sample. Recovered starting material was the major component in the third peak.

Irradiation of trans-2-Phenyl-3-benzoylaziridine (XXXVI).

trans-2-Phenyl-3-benzoylaziridine (XXXVI) was prepared according to the procedure of Cromwell. A solution of 1.0 g. of the trans-aziridine in one liter of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a Pyrex filter to eliminate wave lengths below 280 m\(\mu\). Purified nitrogen was passed through the solution for at least 45 minutes before irradiation commenced and a positive pressure of nitrogen was maintained throughout. Aliquots were removed without interrupting the photolysis and analyzed by infrared spectroscopy and thin layer chromatography. Even after 28 hours of irradiation, infrared analysis and thin layer chromatography showed only unchanged starting material. Upon workup, pure crystalline starting material was the only compound present.
Quantum Yield Determinations.

The quantum yield apparatus described by Trecker and Henry was used in these experiments. It consisted of five borosilicate glass cylinders of 100 mm., 80 mm., 39 mm., and 28 mm. joined together by appropriate ring seals and standard taper joints. The two interior tubes with cell spaces of 3 mm. and 8 mm., respectively, contained 10 g. of hexahydrated nickel sulfate per 30 ml. of aqueous solution and 12.5 g. of heptahydrated cobalt sulfate per 30 ml. of aqueous solution. The filter combination had a maximum transmission of 62.8% at 313 μμ and transmitted less than 1% below 290 μμ and above 436 μμ. Circulation and external cooling of the cobalt sulfate solution provided effective cooling for both the lamp and the two exterior cells. An inlet tube equipped with a tapered capillary leading to the bottom of the reaction cell provided a continuous flush of nitrogen through the solution and maintained adequate mixing. The temperature in the reaction jacket (cell 3) was maintained at 38 ± 2°C.

Light intensities were monitored just before and just after sample irradiation. Quantum output rates for the 200 watt mercury arc lamp used were determined in the following manner. Each determination consisted of a first and third run with actinometer solution in cells 3 and 4 and a second

run with reactant in cell 3 and actinometer in cell 2. Potassium ferrioxalate actinometry was used in these experiments.\textsuperscript{84} The filter solution transmission properties were checked immediately after use. Reliably reproducible output rates of $0.75 \times 10^{18}$ quanta per sec. were recorded. After the irradiation, the degree of reaction was determined by quantitative column chromatography using a liquid-liquid partition column. The conversions in the 2-benzoylziridin system were run to 15\% or less. The mass balance in the ethanol runs was generally better than 98\%. Details of the measurements are given in Table 9.

TABLE 9.

Representative 3-Benzoylaziridine Quantum Yields

<table>
<thead>
<tr>
<th>Run&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>(XXI)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>(II)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>(I)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Piperylene moles</th>
<th>$10^{-18}$ I, quantum sec&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>$10^3$ t sec</th>
<th>% Conversion</th>
<th>Quantum Yield $\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.60</td>
<td>--</td>
<td>--</td>
<td>None</td>
<td>0.75</td>
<td>1.5</td>
<td>8.4</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.60</td>
<td>--</td>
<td>--</td>
<td>3</td>
<td>1.38</td>
<td>1.5</td>
<td>8.6</td>
<td>0.27 ± 0.03</td>
</tr>
<tr>
<td>3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.60</td>
<td>--</td>
<td>--</td>
<td>6</td>
<td>1.38</td>
<td>1.5</td>
<td>--</td>
<td>-----</td>
</tr>
<tr>
<td>4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>--</td>
<td>1.60</td>
<td>--</td>
<td>3</td>
<td>0.75</td>
<td>1.5</td>
<td>11.5</td>
<td>0.58 ± 0.04</td>
</tr>
<tr>
<td>5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>--</td>
<td>1.60</td>
<td>--</td>
<td>6</td>
<td>0.75</td>
<td>1.5</td>
<td>15.2</td>
<td>0.62 ± 0.05</td>
</tr>
<tr>
<td>6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>--</td>
<td>1.60</td>
<td>--</td>
<td>3</td>
<td>1.38</td>
<td>1.5</td>
<td>15.0</td>
<td>0.60 ± 0.06</td>
</tr>
<tr>
<td>7&lt;sup&gt;d&lt;/sup&gt;</td>
<td>--</td>
<td>1.60</td>
<td>--</td>
<td>6</td>
<td>1.38</td>
<td>1.5</td>
<td>--</td>
<td>-----</td>
</tr>
<tr>
<td>8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>--</td>
<td>--</td>
<td>1.60</td>
<td>--</td>
<td>1.38</td>
<td>5.4</td>
<td>13.1</td>
<td>0.05 ± 0.005</td>
</tr>
<tr>
<td>9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>--</td>
<td>--</td>
<td>1.60</td>
<td>3</td>
<td>1.38</td>
<td>5.4</td>
<td>--</td>
<td>-----</td>
</tr>
</tbody>
</table>

<sup>a</sup>All runs in 600 ml. of 95% ethyl alcohol.

<sup>b</sup>All runs in 600 ml. of anhydrous pentane.

<sup>c</sup>Concentration expressed in grams.

<sup>d</sup>Pure piperylene (600 ml.) as solvent.
Figure 4. Schematic diagram of quantum yield apparatus.
Figure 5. Pumping and cooling system for photoreactor.
Photolysis of N,N-Dibenzyl-4-methylphenacyl amine (XXXV).

A solution of 50 g. of 4-methylphenacyl bromide and 100 g. of dibenzylamine in 350 ml. of 95% ethanol was refluxed for 20 hours. The mixture was allowed to cool and the solid which separated was filtered and dried to give 68 g. (83%) of N,N-dibenzyl-4-methylphenacylamine (XXXV), m.p. 77-80°. Recrystallization from ethanol gave crystals, m.p. 81-83°.

Analysis:
Calcd. for C\textsubscript{23}H\textsubscript{23}NO: C, 83.85; H, 7.04; N, 4.25.

Found: C, 83.69; H, 6.97; N, 4.42.

The infrared spectrum of this material in a potassium bromide pellet had bands at 5.95, 6.24, 8.42, 8.85, 10.45, 10.55, 12.39, 13.30 and 14.25 μ. The ultraviolet spectrum in 95% ethanol had a maximum at 253 mλ (ε, 19,400).

A solution of 0.5 g. of XV in 200 ml. of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a Pyrex filter to eliminate wave lengths below 280 mλ. The reaction was followed by gas-liquid chromatography of aliquots withdrawn during the reaction, and product assignments were made by comparison of infrared spectra and g.l.c. retention times with authentic samples. The analytical gas chromatography was performed on an Aerograph 350-B instrument with helium as the carrier gas on a column of SE-30 (0.1% on glass beads) at a flow rate of 66 cc/min and at a temperature of 160°. Analysis of the crude photolysis mixture showed two
major components with retention times of one and six minutes. Comparison of retention times and infrared spectra with those of authentic samples of 4-methylacetophenone and N-benzylbenzalimine established the identity of the two major products.

Reaction of trans-2-Benzoyl-3-phenylaziridine (XXXVI) with Diphenyliodonium Iodide in Toluene

A mixture of .446 g. of trans-aziridine (XXXVI) and .816 g. of diphenyliodonium iodide in 100 ml. of anhydrous toluene was heated to reflux for 12 hours. Concentration of the solution under reduced pressure left an oil which was subjected to liquid-liquid partition chromatography in the usual manner. The optical density trace showed three well-defined peaks with retention volume of 1800 ml., 2200 ml., and 2680 ml. The first fraction (0.490 g.) (60% yield) was shown to be iodobenzene by comparison with an authentic sample. The second fraction, .180 g. (41% yield), was a colorless oil which crystallized from 95% ethanol to give a colorless crystalline compound, m.p. 68-69°, whose infrared spectrum was identical in every detail with that of pure 2,5-diphenyloxazole (XXXIX). The mixed melting point of these two materials was undepressed at 68-69°. The last fraction, .220 g. (53% yield) was shown to be pure trans-benzalacetophenone (XXII). There was no indication of any other component in the chromatogram. Careful examination of
the crude reaction mixture by vapor phase chromatography showed that there were no detectable quantities of aniline, diphenylamine, or triphenyl amine.

Reaction of cis- or trans-1-Benzyl-2-para-toluyl-3-phenylaziridine (II or I) with Diphenyliodonium Iodide in Tetrahydrofuran.

A mixture of .494 g. of either cis- or trans-aziridine and .615 g. of diphenyliodonium iodide in 200 ml. of tetrahydrofuran was heated to reflux for 72 hours. Thin layer chromatography demonstrated the complete disappearance of starting material and the appearance of three major new spots. Removal of the solvent in vacuo left a red oil which was subjected to liquid-liquid column chromatography. The chromatogram showed three well-resolved peaks with retention volume of 1800 ml., 2400 ml., 2800 ml. The first fraction, .368 g. (60%) was shown to be pure iodobenzene by comparison with an authentic sample. The second peak in the chromatogram, .154 g. (44%) was a colorless oil which solidified upon standing. Recrystallization from 95% ethanol gave white crystals, m.p. 81-82°C. Comparison of the n.m.r., IR, and UV of this species with an authentic sample of 2-phenyl-5-para-tolyloxazole established its identity. The mixture melting point of these two materials was undepressed at 81-82°C. The last fraction in the chromatogram, .172 g. (52%) was shown to be pure trans-4-methylbenzalacetophenone
(XXVIII). Careful examination of the crude reaction mixture by vapor phase chromatography revealed the presence of two additional products. Analytical gas chromatography was performed on an Aerograph A-90 instrument with helium as the carrier gas on a Carbowax column (20% on Chromosorb W) at 90°C. The compounds had retention times of one and seven minutes. Collection and comparison of their IR and UV with authentic samples of toluene and benzaldehyde established their identity. By employing benzonitrile as a suitable internal standard, a 40% yield of benzaldehyde and a 43% yield of toluene was found.

Reaction of cis- or trans-1-Benzyl-2-benzoyl-3-phenyl-aziridine (XL or XLI) with Diphenyliodonium Iodide in Tetrahydrofuran.

A mixture of .525 g. of either the cis- or trans-aziridine and .815 g. of diphenyliodonium iodide was heated to reflux for 72 hours in 200 ml. of tetrahydrofuran. Thin layer chromatography showed complete disappearance of starting material and the appearance of three new spots. The solution was concentrated under reduced pressure to give a dark yellow oil which was subjected to liquid-liquid partition chromatography. The chromatogram consisted of three well-defined peaks with retention volume of 1800 ml., 2200 ml., and 2680 ml. The first peak, 0.51 g. (63%) was shown to be pure iodobenzene by comparison with an authentic
sample. The second peak of the chromatogram, 0.045 g. (8%), was shown to be pure 2,5-diphenyloxazole. The last peak, 0.307 g. (75%), was shown to be pure trans-benzalacetophenone (XXII). Careful examination of the crude reaction mixture by vapor phase chromatography showed two additional compounds. The analytical gas chromatography was performed on an Aerograph A-90 instrument with helium as the carrier gas on a Carbowax column (20% on Chromosorb W) at 90°C. The two compounds had retention times of one and seven minutes, respectively. Collection of these compounds and comparison with authentic samples of toluene and benzaldehyde established their identity.

Reaction of cis- or trans-1-Cyclohexyl-2-benzoyl-3-phenylaziridine (XXVI or XXI) with Diphenyliodonium Iodide in Tetrahydrofuran.

A mixture of .610 g. of either cis- or trans-aziridine and .815 g. of diphenyliodonium iodide in 200 ml. of tetrahydrofuran was refluxed for 72 hours. Complete reaction of the starting material was evident by thin layer chromatography. The solvent was removed in vacuo to give a dark yellow oil which was subjected to liquid-liquid partition chromatography. The chromatogram consisted of two well-resolved peaks with retention volume of 1800 ml. and 2700 ml. The first peak, 0.523 g. (64%), was shown to be pure iodobenzene. The other peak, .316 g. (76%), was identified
as trans-benzalacetophenone. There were no detectable quantities of 2,5-diphenyloxazole found in the reaction mixture. Careful examination of the crude reaction mixture by vapor phase chromatography showed the presence of cyclohexanone (69%). The analytical gas chromatography was performed on an Aerograph HiFi instrument employing a Carbowax column (20% on Chromosorb W) at 50°C.

Reaction of cis- or trans-1-Cyclohexyl-2-para-tolyl-3-phenylaziridine (XLII or XLIII) with Diphenyliodonium Iodide in Tetrahydrofuran.

trans- and cis-1-Cyclohexyl-2-para-tolyl-3-phenylaziridine was prepared according to the procedure of Cromwell and Hoeksema. A mixture of .638 g. of either the cis- or trans-aziridine and .816 g. of diphenyliodonium iodide in 200 ml. of tetrahydrofuran was refluxed for 72 hours. The reaction was complete as evidenced by the complete disappearance of starting material on a thin layer chromatography plate. The solution was concentrated under reduced pressure to give an oil which was chromatographed on a liquid-liquid partition chromatography column. The optical density trace showed two well-defined peaks with retention volume of 1800 ml. and 2800 ml. The first peak consisted of .496 g. (61%) of iodobenzene. The other peak consisted of .286 g. (67%) of pure trans-4-methylbenzalacetophenone. There was no detectable amount of 2-phenyl-5-para-tolyl oxazole found.
Analysis of the crude reaction mixture by gas chromatography confirmed the presence of cyclohexanone (59%). The analytical gas chromatography was performed on an Aerograph HiFi instrument on a SE-30 silicon column (20% on Chromosorb W) at 50°.

Attempts to detect the transient intermediate responsible for the photochromism of cis- and trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI and XXI).

Recently, Pitts has demonstrated the feasibility of qualitative and quantitative studies of solid-state chemical reactions in pressed alkali halide disks of the type customarily used for infrared analysis. Since the photochromic activity of the arylaroylaziridine appeared to be important only in the solid state or in the frozen glass, it seemed that the "pellet" technique would be a simple and convenient method for qualitative study of the structure of the colored species produced on irradiation. Typical potassium bromide pellets of cis- and trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (XXVI and XXI) were prepared in the dark and their respective infrared spectra were recorded on a Perkin-Elmer infracord spectrophotometer, model 137. The KBr pellets were then exposed to a utility sun lamp. The cis pellet immediately turned pink, but coloration was not as pronounced in the trans pellet. After five minutes of irradiation, infrared spectra were recorded for both pellets.
There was no discernible change in the infrared spectrum of either compound. Continued irradiation of the pellets caused a deepening of the pink coloration, but the infrared spectra were insignificantly altered. After ten hours, the pellets developed a yellow tinge and the infrared spectra showed broad absorption bands. This may be attributed to photochemical decomposition of the compounds. These results suggest that the photostationary state concentration of the colored species is too small to be detected by infrared spectroscopy.

**Attempted Trapping of the Colored Species Formed by Irradiation of an Arylaroylaziridine.**

Attempts to trap the hypothetical 1,3-dipolarophile by coirradiation of the arylaroylaziridine with acetylene, dienes, and olefins were unsuccessful. In a typical experiment, a clear Pyrex plate (4 x 8 x 1/16") was thoroughly sprayed with a methylene chloride solution containing the arylaroylaziridine and dimethylacetylene dicarboxylate. Evaporation of the solvent left a thin layer of both compounds on the plate. The resulting plate was exposed to a high pressure mercury arc (Hanovia, Type L-450 watts) for ten minutes. After irradiation, the initial colorless layer had turned deep pink. Chromatography of the mixture on a florisil column gave a 98% yield of recovered aziridine.
Dimethyl-2-[1-(2,3-diphenylaziridyl)]maleate (XLVI).

A solution of 0.15 g. of cis-diphenylaziridine\textsuperscript{85} and 0.08 g. of dimethylacetylene dicarboxylate in 10 ml. of benzene was refluxed for 12 hours. The solvent was removed in vacuo to give a yellow oil which was chromatographed on a 1.5 x 40 cm. alumina (Woelm, neutral, grade 3) column. The column was eluted with 500 ml. of 30\% benzene-hexane. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. Fractions 5-10 contained 117 mg. of a white solid, m.p. 90-95°. Recrystallization from methanol afforded pure dimethyl-2-[1-(2,3-diphenylaziridyl)]maleate (XLVI), m.p. 94-95°.

Analysis:
Calcd. for C\textsubscript{20}H\textsubscript{19}NO\textsubscript{4}: C, 7.12; H, 5.68; N, 4.15.
Found: C, 7.11; H, 5.85; N, 4.32.

The infrared spectrum shows two strong carbonyl bands at 5.70 and 5.80 μ and a series of sharp bands at 6.18, 6.86, 6.95, 7.06, 7.27, 7.37, 8.90, 9.56 and 11.62 μ. The ultraviolet spectrum in 95\% ethanol exhibited a maximum \( \lambda_{\text{max}} \) at 262 μ (ε, 21,800). The n.m.r. spectrum is in excellent agreement with the structure. There is a multiplet centered at τ 2.85, a singlet at 4.45, a singlet at 6.20, a singlet at 6.29, and a singlet at 6.33. The peak areas are in the ratio of 10:1:3:2:3.

Diethyl-2-[(1-(2,3-diphenylaziridyl)]maleate (XLVII)

_cis-_2,3-Diphenylaziridine (492 mg.) and diethylacetylene dicarboxylate (453 mg.) were dissolved in 25 ml. of benzene and the solution was refluxed for 12 hours. After cooling, the solution was evaporated to dryness to give an orange oil. The crude residue was chromatographed on a 1.5 x 50 cm. alumina (Woelm, neutral, grade 3) column. After elution of small amounts of material with 500 ml. of 10% benzene-hexane, 857 mg. (88%) of a colorless oil was eluted with 350 ml. of 90% benzene-hexane. The oil solidified on standing and recrystallization from methanol gave white, crystalline material, m.p. 71-72°.

**Analysis:**
Calcd. for C<sub>22</sub>H<sub>23</sub>N<sub>4</sub>O: C, 72.31; H, 6.34; N, 3.83.

Found: C, 72.22; H, 6.19; N, 4.01.

The infrared spectrum of this material showed intense absorption at 5.80, 6.18, 8.00, 8.35, 8.65, 9.00 and 9.60 μ. The ultraviolet spectrum (95% ethanol) has λ<sub>max</sub> 265 μ (ε, 19,700). The n.m.r. spectrum in carbon tetrachloride shows a multiplet at τ 2.86, a singlet at 4.47, a quartet centered at 5.79, a singlet at 6.29 and a triplet centered at 8.83. The peak areas are in the ratio of 10:1:4:2:6.
2-Benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (XIVIII).

A mixture of 223 mg. of trans-2-phenyl-3-benzoylaziridine (XXXVI)\(^1\) and 142 mg. of dimethylacetylene dicarboxylate in 25 ml. of xylene was heated to reflux for 18 hours. Evaporation of the solvent left 374 mg. of a yellow oil which was chromatographed on a column of florisil. The first fractions obtained with 3% ethyl acetate-benzene gave 290 mg. (80%) of a white solid, m.p. 153-160°. Recrystallization from hexane-benzene afforded a crystalline solid, m.p. 159-160°. The structure of this adduct was determined to be 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (XLVIII) on the basis of the following data.

**Analysis:**

Calcd. for C\(_{21}\)H\(_{17}\)NO\(_5\): C, 69.51; H, 4.72; N, 3.86.  
Found: C, 69.18; H, 4.82; N, 3.86.

The infrared spectrum had bands at 3.03, 5.81, 6.14, 7.93, 8.10, 12.69, 13.06, 13.57, 14.36 μ. The ultraviolet spectrum in 95% ethanol has maxima at 246 μ (ε, 17,000) and 312 μ (ε, 11.700).

Structure XLVIII was further confirmed by its unequivocal synthesis from 2-phenyl-4-benzyl-5-oxazolone and dimethylacetylene dicarboxylate. 2-Phenyl-4-benzyl-5-oxazolone (XLIX) was prepared by the method of Mohr and Stroschein.\(^8^6\) A solution containing 13.8 g. of d,l-benzoyl

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\(^{8^6}\) M. Mohr and R. Stroschein, Ber., 42, 2521 (1909).
phenylalanine in 130 ml. of acetic anhydride was heated at 100° for one hour. Concentration of the solution left an oil which was crystallized from 100 ml. of hexane to give 11.5 g. (90%) of a crystalline solid, m.p. 69-70° (lit. m.p. 69-70°).

A mixture of the above 2-phenyl-4-benzyl-5-oxazolone (500 mg.) and dimethylacetylene dicarboxylate (284 mg.) was heated in a sealed tube at 160° for five hours. The impure material dissolved in benzene, was chromatographed on a 2.5 x 91 cm. column of florisil slurry packed in benzene. The column was eluted with one liter of 1% ethyl acetate-benzene, 500 ml. of 2% ethyl acetate-benzene, and 750 ml. of 3% ethyl acetate-benzene. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. The crystalline solid from elution with 3% ethyl acetate-benzene (0.71 g., 93%) was identified as 2-benzyl-3,4-dicarbomethoxy-5-phenylpyrrole (XLIX) on the basis of the following data. Recrystallization of the crude solid from ethanol afforded crystals, m.p. 132-133°.

Analysis:
Calcd. for C_{21}H_{19}NO_{4}: C, 72.19; H, 5.48; N, 4.01
Found: C, 72.11; H, 5.56; N, 4.15.

The infrared spectrum showed intense absorption bands at 3.10, 5.85, 8.15, 9.13, 12.80, 12.95 and 14.30 μ. The ultraviolet spectrum in 95% ethanol had a maximum at 278 μ (ε, 14,800).
A mixture of 150 mg. of the above pyrrole (XLIX) and 90 mg. of selenium dioxide was heated in a sealed tube at 200° for 20 minutes. The crude residue was recrystallized from hexane-benzene to give 140 mg. (90%) of 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (L), m.p. 159-160°. The infrared, ultraviolet, and n.m.r. spectra of this material were identical in every detail with those of 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole prepared from the thermal reaction of trans-2-phenyl-3-benzoylaziridine and dimethylacetylene dicarboxylate. The mixture melting point of these two materials was undepressed at 159-160°.

1-Benzyl-2-p-toluyl-3,4-dicarbomethoxy-5-phenylpyrrole

A solution containing 327 mg. of cis-1-benzyl-2-p-toluyl-3-phenylaziridine and 142 mg. of dimethylacetylene dicarboxylate in 25 ml. of benzene was refluxed for 17 hours. The solvent was removed in vacuo to give a yellow oil which was chromatographed on a 1.5 x 40 cm. florisil column. The column was eluted with 650 ml. of 2% ethyl acetate-benzene. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. Fractions 6-11 contained 400 mg. (84%) of a white solid, m.p. 126-130°. Recrystallization from methanol afforded pure 1-benzyl-2-p-toluyl-3,4-dicarbomethoxy-5-phenylpyrrole, m.p. 130-131°.
Analysis:
Calcd. for $C_{29}H_{25}NO_3$: C, 74.50; H, 5.39; N, 3.00.
Found: C, 74.54; H, 5.42; N, 3.08.

The infrared spectrum showed strong absorption at 5.78, 6.09, 8.25, 10.80, 12.10, 13.30, and 14.40 $\mu$m. The ultraviolet spectrum (95% ethanol) has maxima at 260 $\mu$m ($\epsilon$, 16,700) and at 305 $\mu$m ($\epsilon$, 11,300). The n.m.r. spectrum (CDCl$_3$) of the adduct shows a multiplet centered at $\tau$ 2.65, a singlet at 4.72, a singlet at 6.42, a singlet at 6.78, and a singlet at 7.67. The peak areas are in the ratio of 14:2:3:3:3.

Reaction of cis- and trans-1-Cyclohexyl-2-benzoyl-3-phenylaziridine with Dimethylacetylene Dicarboxylate.

trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine$^1$ (300 mg.) and dimethylacetylene dicarboxylate (142 mg.) were dissolved in 50 ml. of benzene and the solution was refluxed for 12 hours. After cooling, the solution was evaporated to dryness to give an orange oil. The crude residue was chromatographed on a 2.5 x 91 cm. florisil column. The column was eluted with one liter of 1% ethyl acetate-benzene, 500 ml. of 2% ethyl acetate-benzene, and 600 ml. of 3% ethyl acetate-benzene. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. The crystalline solid from elution with 2% ethyl acetate-benzene amounted to 320 mg., m.p. 134-140°. Recrystallization from
hexane-benzene afforded white, crystalline material, m.p. 140-141°.

**Analysis:**
Calcd. for $C_{27}H_{27}NO_5$:  C, 72.79;  H, 6.11;  N, 3.14.
Found:  C, 72.73;  H, 6.14;  N, 3.10.

The infrared spectrum (KBr) of this material showed strong absorption at 5.78, 6.05, 8.02, 8.25 and 8.62 μ. The ultraviolet spectrum (95% ethanol) has $\lambda_{max}$ at 252 μ (ε, 21.900) and $\lambda_{max}$ at 302 μ (ε, 5,500). The n.m.r. spectrum (CDCl$_3$) shows a multiplet at t 2.33, a singlet at 6.42, a singlet at 6.70, and a multiplet centered at 8.67. The peak areas are in the ratio of 10:3:3:11. The spectral evidence indicates that this compound is 1-cyclohexyl-2-phenyl-3,4-dicarbomethoxy-5-benzoylpyrrole (LI).

On further elution with 3% ethyl acetate-benzene, 120 mg. of a yellow crystalline solid, m.p. 155-156°, was obtained. This material was assigned structure (LII), 1-cyclohexyl-2-phenyl-3,4-dicarbomethoxy-5-benzoyl-2-pyrroline on the basis of physical and chemical data cited below.

**Analysis:**
Calcd. for $C_{27}H_{29}NO_5$:  C, 72.46;  H, 6.53;  N, 3.13.
Found:  C, 72.27;  H, 6.52;  N, 2.95.

The infrared spectrum shows two strong carbonyl bands at 5.78 and 6.05 μ and a series of sharp bands at 6.37, 7.91, 8.23, 8.45 and 8.57 μ. The ultraviolet spectrum (95%
ethanol) has maxima at 255 μ (ε, 15,600) and 303 μ (ε, 16,350). The n.m.r. spectrum (CCl₄) shows the aromatic hydrogens as a multiplet centered at τ 2.55, the methyl protons as singlets at 6.18 and 6.63, the methine protons as a pair of doublets at 5.15 and 6.42 (J = 4 c.p.s.) and the cyclohexyl protons as a complex multiplet centered at 8.67. The peak areas are in the ratio of 10:3:3:1:1:11.

A mixture of 200 mg. of the above 2-pyrroline (LII) and 100 mg. of selenium dioxide was heated in a sealed tube at 200° for 20 minutes. The crude residue was recrystallized from hexane-benzene to give 168 mg. (84%) of 1-cyclohexyl-2-phenyl-3,4-dicarbomethoxy-5-benzoylpyrrole (LI). The infrared spectrum of this material was identical in every detail with that of a sample of X. The mixture melting point of these two materials was undepressed at 139-140°.
cis-1-t-Butyl-2-phenyl-3-benzoylazetidine (LIV)

_Cis_-Azetidine (LIV) was prepared by a modification of a procedure described by Cromwell and Doomes. To a saturated hydrogen bromide solution of anhydrous chloroform was added 4.80 g. of \( \alpha \)-[\(-\text{N-t-butylamino}\)-benzyl]-acrylophenone and the resulting solution was allowed to stand for 12 hours at room temperature. The reaction mixture was cooled to 0° and neutralized with t-butyramine and filtered. Removal of the solvent left a colorless oil that was crystallized from 95% alcohol to give 2.88 g. (60%) of long white needles, m.p. 114-115°C.

**Analysis:**
Calcd. for \( \text{C}_{20}\text{H}_{23}\text{NO} \): C, 81.87; H, 7.90; N, 4.77.
Found: C, 81.72; H, 7.98; N, 4.72.

The infrared spectrum (KBr) shows a strong carbonyl band at 5.98 μ and a series of sharp bands at 6.90, 7.43, 8.25, 9.58, 10.55, 13.00, 13.29, 14.37, 15.58 μ. The ultraviolet spectrum in 95% ethanol exhibited a \( \lambda_{\text{max}} \) at 246 μ (ε, 10,500). The n.m.r. spectrum is in excellent agreement with the proposed _cis_ structure. There is a multiplet centered at \( \tau \) 2.85 (10H), and a doublet at 5.06 (1H) (J, 6.5 c.p.s.), a multiplet at 5.50-6.70 (eH) and a singlet at \( \tau \) 9.07 (9H).

trans-l-t-Butyl-2-phenyl-3-benzoylazetidine

The thermodynamically more stable trans azetidine was prepared by epimerization of the cis isomer (LIV) with sodium methoxide. To 100 ml. of a .01 M sodium methoxide solution was added 3.30 g. of LIV and the resulting solution was refluxed for six hours. The mixture was diluted with water and extracted with ether. The etherate solution was dried over sodium sulfate and the solvent was removed in vacuo to give 2.84 g. (86%) of trans-l-t-butyl-2-phenyl-3-benzoylacetidine, m.p. 53-60°C. Recrystallization from hexane gave tiny colorless needles, m.p. 59.9-60.6°C.

The infrared spectrum (KBr) shows a strong carbonyl band at 6.01 \( \mu \) and a series of sharp bands at 6.90, 7.38, 7.49, 8.23, 12.95, 13.71, 14.39, 15.40, 15.68 \( \mu \). The ultraviolet spectrum in 95% ethanol showed a \( \lambda_{\text{max}} \) at 246 m\( \mu \) (\( \epsilon \), 15,800). The n.m.r. spectrum is in excellent agreement with the proposed trans structure and showed a multiplet centered at \( \tau \) 2.61, a doublet at 5.45 (\( J \), 6.5 c.p.s.), a multiplet at 6.06-6.64, and a singlet at 9.06. The areas are in the ratio of 10:1:3:9.

Analysis:
Calcd. for \( \text{C}_{20}\text{H}_{23}\text{NO} \): C, 81.87; H, 7.90; N, 4.77.
Found: C, 82.16; H, 7.98; N, 4.78.
Irradiation of cis-1-\text{t}-Butyl-2-phenyl-3-benzoylazetidine (LIV) in Ethanol

A solution of 1.0 g. of the \textit{cis} azetidine in 250 ml. of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a Pyrex filter to eliminate wave lengths below 280 m\text{	extmu}. Purified nitrogen was passed through the solution for at least 45 minutes before irradiation, and a positive pressure of nitrogen was maintained throughout. Aliquots were removed without interrupting the photolysis and analyzed by infra-red spectroscopy. After 30 minutes, the infrared spectrum showed a decrease in the intensity of the carbonyl absorption band and a concurrent increase in the aromatic absorption band at 6.24 \text{	extmu}. After two hours of irradiation, the carbonyl absorption band had almost completely disappeared and the band at 6.24 \text{	extmu} had become the most intense absorption band in the spectrum. Concentration of the solution \textit{in vacuo} gave a light brown solid, m.p. 98-100°C. Recrystallization from 95% ethanol gave 900 mg. (95%) of pure white crystals, m.p. 102.4-103.4°C. There was no sign of any other product in the \textit{cis} azetidine system as evidenced by both liquid-liquid partition and vapor phase chromatography.

\textbf{Analysis:}

Calcd. for C_{20}H_{21}N: \text{C}, 87.22; \text{H}, 7.69; \text{N}, 5.09.

Found: \text{C}, 87.20; \text{H}, 7.85; \text{N}, 5.09.
The infrared spectrum (KBr) was characterized by a series of sharp bands at 6.24, 6.59, 7.30, 7.56, 8.21, 9.34, 9.70, 12.47, 13.08, 13.50, 14.10, 14.25, 14.45, 15.05 μm.

The ultraviolet spectrum in 95% ethanol exhibited maxima at 235 μm (ε 15,800) and 276 μm (ε, 16,200). The n.m.r. spectrum consisted of a multiplet centered at τ 2.62, a doublet at 3.64 (J = 2.0 c.p.s.), and a singlet at 8.60. The peak areas are in the ratio of 11:1:9. The structure of this compound was assigned 1-tert-butyl-2,4-diphenylpyrrole (LV). Chemical confirmation was obtained by pyrolysis to the known 2,4-diphenylpyrrole. In a sealed tube was placed .20 g. of LV and the solid was heated at 325°C. for one hour. The light brown oil solidified upon standing at room temperature. Recrystallization from toluene afforded 185 mg. (93%) of long white needles, m.p. 178-179°C. This compound was identical in all respects with an authentic sample of 2,4-diphenylpyrrole prepared according to the procedure of Allen and Wilson. A mixed melting point was undepressed at 178-179°C.
Attempted Acid Catalyzed Isomerization of cis-1-t-Butyl-2-phenyl-3-benzoylazetidine (LIV)

To 25 ml. of a cold saturated solution of hydrogen chloride in glacial acetic acid was added 430 mg. of LIV. The reaction mixture was allowed to stand for 24 hours at room temperature. The solution was then diluted with 200 ml. of water and extracted with ether. The etherate extracts were washed with a sodium bicarbonate solution and dried over sodium sulfate. Removal of the solvent left only 2 mg. of a crude yellow oil. The acidic aqueous solution was neutralized with dilute sodium hydroxide and then extracted with ether. The etherate solution was dried over sodium sulfate and concentrated in vacuo to give 380 mg. (89%) of a colorless oil which solidified upon standing. Recrystallization from 95% ethanol yielded white crystals, m.p. 85-86°. This solid was shown by infrared and n.m.r. spectroscopy to be a 50-50 mixture of cis- and trans-1-t-butyl-2-phenyl-3-benzoylacetidine (LIV and LV). The same result was obtained when boron trifluoride etherate or hydrogen chloride in ether was used as the Lewis acid.
Quantum Yield Determinations

All quantitative measurements were made on a rotating assembly known as the "Merry-go-Round" with a central light source. Samples in 12 mm. Pyrex ampoules were placed in holders on the assembly approximately 8 cm. from a 450 watt Hanovia lamp, No. 679A-36, maintained in a water jacketed immersion well. Corning No. 7-51 (2" x 2") filters were mounted in four filter holders flush against the well. The rest of the well was taped to eliminate stray light. All studies were made at room temperature. Samples in 12 mm. Pyrex test tubes were degassed to $2 \times 10^{-3}$ mm. in three freeze-thaw cycles and then sealed. Benzophenone-benzhydrol actinometry was used for quantum yield determinations. An actinometer quantum yield of 0.69 was used. Reliably reproducible output rates of $0.62 \times 10^{17}$ quanta/sec. were recorded. The conversions in the azetidine system were run to 8, 12, and 19%, and an average value for these conversions was reported. The amount of 1-t-butyl-2,4-diphenylpyrrole formed was determined by ultraviolet spectroscopy. The mass balance in the ethanol runs was generally better than 98%. Details of the measurements are given in Table 10.

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TABLE 10
Quantum Yields for *cis*-1-t-Butyl-2-phenyl-3-benzoylazetidine

<table>
<thead>
<tr>
<th>Run</th>
<th>Compound&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Quencher, M.</th>
<th>Quantum&lt;sup&gt;c&lt;/sup&gt; Yield φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>LIV</td>
<td>None</td>
<td>.046 ± .001</td>
</tr>
<tr>
<td>2</td>
<td>LIV</td>
<td>Piperylene, 2m/1</td>
<td>.045 ± .001</td>
</tr>
<tr>
<td>3</td>
<td>LIV</td>
<td>Piperylene, 5m/1</td>
<td>.045 ± .001</td>
</tr>
<tr>
<td>4</td>
<td>LIV</td>
<td>Piperylene, 10m/1</td>
<td>.036 ± .001</td>
</tr>
<tr>
<td>5</td>
<td>LIV</td>
<td>1,3-Cyclohexadiene, 2 m/1</td>
<td>.045 ± .001</td>
</tr>
<tr>
<td>6</td>
<td>LIV</td>
<td>1,3-Cyclohexadiene, 10.5m/1</td>
<td>.037 ± .001</td>
</tr>
<tr>
<td>7</td>
<td>LIV</td>
<td>Naphthalene, 10&lt;sup&gt;-3&lt;/sup&gt;m/1</td>
<td>.045 ± .001</td>
</tr>
<tr>
<td>8</td>
<td>LIV</td>
<td>Naphthalene, 5x10&lt;sup&gt;-3&lt;/sup&gt;m/1</td>
<td>.046 ± .001</td>
</tr>
<tr>
<td>9</td>
<td>LIV</td>
<td>Ferric Dipivaloylmethide, 10&lt;sup&gt;-5&lt;/sup&gt;m/1</td>
<td>.045 ± .001</td>
</tr>
<tr>
<td>10</td>
<td>LIV</td>
<td>---&lt;sup&gt;e&lt;/sup&gt;</td>
<td>.093 ± .001</td>
</tr>
</tbody>
</table>

<sup>a</sup>Azetidine concentration was 1.48 x 10<sup>-2</sup>m/1.

<sup>b</sup>95% Ethanol was used as solvent.

<sup>c</sup>Intensity of source was 0.62 x 10<sup>17</sup> quanta-sec.

<sup>d</sup>Average value of three runs (20%, 12%, 8% conversion).

<sup>e</sup>Acetophenone (3.45 M) was used as a photosensitizer.
Figure 6. "Merry-go-round" quantum yield apparatus.
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