Concerning the Mechanism of the Photodeamination of 2-Benzoylaziridines[1-3]

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Abstract: The photolysis in 95% ethanol of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine has been found to afford five products. The structures have been assigned as cis- and trans-benzalacetophenone, cyclohexylhydroxylamine, N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine, and cyclohexanone. The formation of the products in polar solvents proceeds via a dual sequence. One path involves the formation of benzalacetophenone and cyclohexylhydroxylamine as primary photoproducts. The competing sequence is reasonably formulated as proceeding via N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine followed by a rapid ground-state reaction to trans-benzalacetophenone and cyclohexanone. It is suggested that the reaction proceeds by intramolecular hydrogen transfer to yield an enol, followed by rearrangement of the latter to a carbonyl compound. The course of the over-all photoreaction is altered drastically for the cis isomer. Irradiation of cis-1-cyclohexyl-2-phenyl-3-benzoylaziridine gave acetophenone and N-cyclohexylbenzalimine. It is postulated that the excited state undergoes homolytic ring cleavage to give a radical which can lead to the observed products by a succession of hydrogen abstraction and photoelimination reactions. The phototransformations of both isomers were shown to proceed by way of a triplet n-π* excited state.

A common and fundamental reaction in the chemistry of three-membered ring heterocycles is the removal of the heteroatom and the formation of the corresponding olefin. Past investigations have established that under appropriate reaction conditions, olefins may be formed by the removal of oxygen from epoxides. Reagents which are known to be effective for this deoxygenation are triphenylphosphine,[6] triethyl phosphite,[7] hydrogen iodide,[8] 2,4-dinitrothiophenol,[9] thiourea,[10] potassium selenocyanate,[11] and chromous chloride.[12] The reaction of episulfides with organolithium compounds,[13] Grignard reagents,[14] and tervalent phosphorus compounds[15] has also been shown to result in the loss of sulfur and gives the corresponding olefin, presumably by nucleophilic attack of the reagent on sulfur.[16] An interesting analogy to both the desulfurization and deoxygenation reaction is the removal of nitrogen from aziridines by the action of nitrosating agents such as 3-nitro-N-

nitrosocarbazole,[17] nitrosyl chloride,[18] and methyl nitrite.[18]

As part of our continuing interest in small-membered rings and in connection with a study on the photochemical transformations of carbonyl compounds, we recently reported on the photoextrusion of sulfur and nitrogen from benzoyl episulfides and aziridines.[19,20] The photochemistry of the 2-benzoylaziridine system was of particular interest since it had been observed that the relative position of the substituents on the three-membered ring influenced the mode of reaction.[20] It was our intent in this work to investigate more fully the scope of this novel photodeamination and to examine some of the factors which lead to the diverse types of reactions. The present paper describes the photochemical properties of such systems in which structural modifications have been made to provide further insight into the mechanism of the photodeamination process.

Results

trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (I) was prepared by treating a mixture of trans-benzalacetophenone (II) and cyclohexylamine with iodine in methanol.[21] This isomer was initially prepared by Cromwell and co-workers from α,β-dibromobenzylacetophenone and cyclohexylamine.[22] The irradiation of I was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. The photolysis was followed by withdrawal of small samples at fixed intervals and examination of these by thin layer chromatography. Upon irradiation of

(1) Photochemical Transformations of Small Ring Carbonyl Compounds, part XII. For part XI, see A. Padwa and R. Hartman, J. Am. Chem. Soc., 88, 3759 (1966).

(2) Support of this research by a grant from the National Science Foundation (Grant GP-6511) is acknowledged with appreciation.

(3) For a preliminary report of this work, see A. Padwa and L. Hamilton, J. Am. Chem. Soc., 87, 1821 (1965). This work was presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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(5) National Institutes of Health Predoctoral Fellow, 1964-present.

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(11) C. C. J. Culvenor, W. Davies, and K. H. Pauscacker, ibid., 1050 (1946).

(12) W. Cole and P. L. Julian, J. Org. Chem., 19, 131 (1954).

(13) N. P. Neureiter and F. G. Bordwell, J. Am. Chem. Soc., 81, 578 (1959).

(14) F. G. Bordwell, H. M. Anderson, and B. M. Pitt, ibid., 76, 1082 (1954).

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(17) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, ibid., 83, 4417 (1961).

(18) R. D. Clark and G. K. Helmkamp, J. Org. Chem., 29, 1316 (1964).

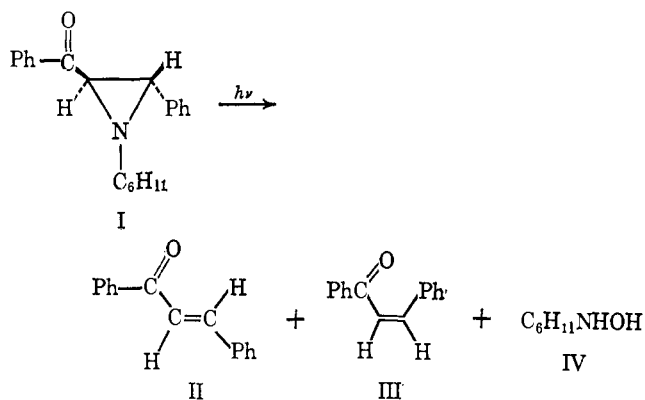(19) A. Padwa, D. Crumrine, and A. Shubber, J. Am. Chem. Soc., 88, 3064 (1966).

(20) A. Padwa and L. Hamilton, ibid., 87, 1821 (1965).

(21) P. L. Southwick and D. R. Christman, ibid., 74, 1886 (1952).

(22) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. G. Vanderhorst, F. W. Olson, and J. H. Anglin, ibid., 73, 1044 (1951).

750 mg of I in 95% ethanol for 3 hr, the spot on a thin-layer plate due to I had completely disappeared and several new spots had appeared in its place. Chromatography of the crude photolysis mixture on a Florisil column afforded *trans*- and *cis*-benzalacetophenone (II and III). Part of the nitrogen was accounted for in the form of N-cyclohexylhydroxylamine (IV), which was identified by its reaction with benzaldehyde to give the known N-cyclohexyl nitrone of benzaldehyde, mp 80–82°.[23] It is noteworthy that the yield of benzaceto-
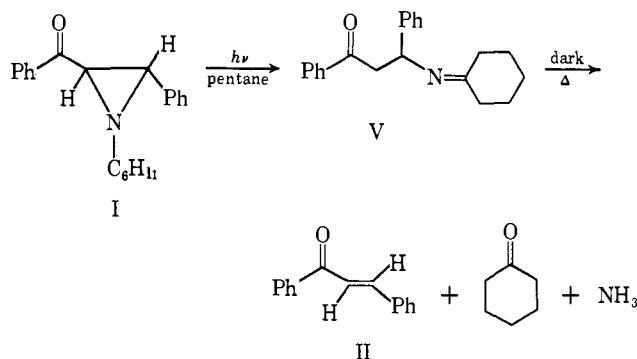

phenone was nearly quantitative but that of N-cyclohexylhydroxylamine was significantly lower (25%).

Photolysis of I in pentane with a Pyrex filter gave a mixture of products which were separated using scanning liquid–liquid partition chromatography.[24] In addition to *cis*- and *trans*-benzalacetophenone, two new compounds were obtained whose structures were assigned as cyclohexanone and N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine (V). The structure of V was elucidated by elemental analysis, infrared, ultraviolet, nmr, and degradation. The elemental analysis of the clear oil (*Anal.* Calcd for $C_{21}H_{23}NO$: C, 82.55; H, 7.59; N, 4.59. Found: C, 82.22; H, 7.75; N, 4.26) indicates that it is an isomer of I. 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 mμ (ϵ 18,200). The nmr spectrum in deuteriochloroform is in excellent agreement with the proposed structure. The Schiff base V 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 V was further confirmed by hydrogenation over Adam's catalyst to give cyclohexylamine hydrochloride and benzylacetophenone.
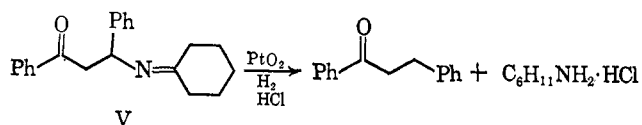

We found that V is converted rapidly and quantitatively to *trans*-benzalacetophenone and cyclohexanone by chromatography on Florisil but can be partially recovered from liquid–liquid partition chromatography. Further evidence for the mechanism of the photodeamination was provided by the observation that V was converted to cyclohexanone and *trans*-benzalacetophenone in 95% ethanol in the dark. Trace amounts of acid or base greatly facilitated the cleavage. Thus, it appears as though the photodeam-

ination of I in 95% ethanol proceeds *via* a dual sequence. One path involves the formation of benzalacetophenone and cyclohexylhydroxylamine as primary photoproducts. The low yield of the cyclohexylhydroxylamine (23%) indicates that the competing sequence, which is reasonably formulated as proceeding *via* V followed by fragmentation to *trans*-benzalacetophenone and cyclohexanone, is the predominant path. This suggestion is supported by the isolation of small amounts of V (8%) when the irradiation of I in ethanol was carried out at low temperatures.

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-benzoylaziridine followed by deamination of the mixture to give comparable amounts of the isomeric olefins. The *cis–trans* photoconversion of the three-ring nitrogen was considered a likely possibility since similar isomerizations have been reported for related small-ring carbonyl compounds.[25,26] This sequence, however, is eliminated by the finding that irradiation of *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridine (VI) does not afford I. *Further, the course of the over-all photoreaction is altered drastically for the cis isomer.* Irradiation of VI in aqueous ethanol gave N-cyclohexylbenzalimine (VII) and acetophenone as major products, together with a number of minor components. Careful examination of the photolysis
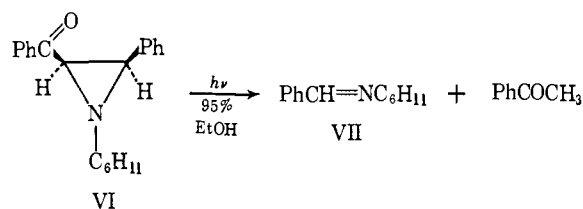
(23) H. Thesing and W. Sirrenberg, *Chem. Ber.*, **91**, 1978 (1958).
(24) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(25) G. W. Griffin, W. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963).
(26) H. E. Zimmerman, Abstracts, Seventeenth National Organic Symposium, Bloomington, Ind., June 1961, p 31.

mixture revealed that no detectable amounts of *cis*- or *trans*-benzalacetophenone, phenacyl alcohol, or phenacyl ethyl ether were present.

Epimerization of *cis* and *trans* isomers of aziridines has seldom been observed.[27] Cromwell, however, reported that when *trans*-1-benzyl-2-phenyl-3-*p*-toluyl-aziridine (VIII) was exposed to direct sunlight it isomerized to the *cis* isomer.[28] Solutions of the *cis* isomer IX were reported to be unaffected by irradiation.[28] The experimental evidence used to support this interpretation was the observation of a general broadening of the ultraviolet absorption band of VIII. Since a freshly prepared 50:50 mixture of VIII and IX showed a similar absorption curve, Cromwell concluded that photoisomerization occurred. In view of the apparent discrepancy between the two sets of results, we have reinvestigated the photochemistry of VIII and IX.

Photolysis of *trans*-1-benzyl-2-phenyl-3-*p*-toluyl-aziridine (VIII) in 95% ethanol with a Pyrex filter followed by chromatography over Florisil afforded *trans*- and *cis*-4′-methylbenzalacetophenone (X and XI). In this irradiation no *cis*-benzoylaziridine (IX) could be detected. All attempts to identify the nitrogen portion in the form of benzylhydroxylamine (or the N-benzyl nitrone of benzaldehyde) were unsuccessful. We may therefore conclude that *trans*-aziridine VIII does not photochemically epimerize to the *cis* isomer and that the reaction sequence for VIII is partially different from that previously observed in ethanol. 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′-methylbenzalacetophenone, a new compound was obtained whose structure was assigned as N-1-(2-*p*-toluyl-1-phenylethyl)benzylidenimine (XII) on the basis of chemical and physical data (see Experimental Section). We found that XII is converted to *trans*-
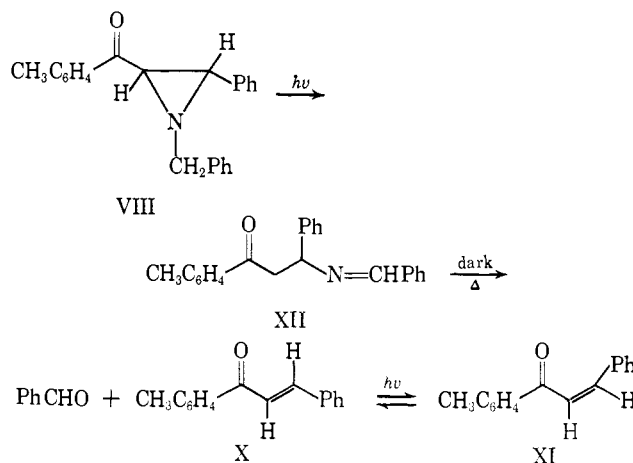

VIII

CH₃C₆H₄COCH=CHPh + (XII structure) $\quad$

X and XI $\qquad$ XII
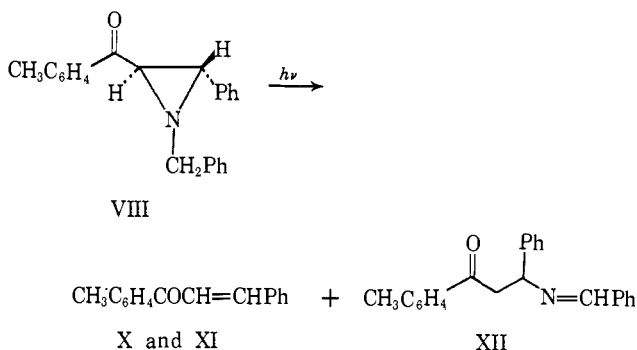
4′-methylbenzalacetophenone and benzaldehyde by chromatography on Florisil or by standing in 95% ethanol in the dark. The formation of a mixture of *cis*- and *trans*-4′-methylbenzalacetophenone upon irradiation of VIII in ethanol is reasonably formulated as proceeding *via* XII, which then fragments by a ground-state sequence to *trans*-4′-methylbenzalacetophenone.[29] The formation of the *cis* isomer XI is due to *in situ* photoisomerization of the olefin present in the reaction cell. This suggestion is supported by

(27) A. Turner, H. W. Heine, J. Irving, and J. B. Busch, *J. Am. Chem. Soc.*, 87, 1050 (1965).
(28) N. H. Cromwell and H. Hoeksema, *ibid.*, 71, 708 (1949).
(29) Control experiments demonstrated that XII did not degrade photochemically to X and benzaldehyde.

VIII

XII $\xrightarrow{\text{dark}\ \Delta}$

PhCHO + (X structure) $\rightleftarrows$ (XI structure)
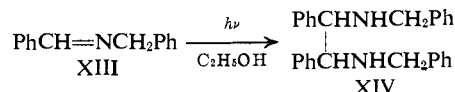
X $\qquad$ XI

carrying out the photolysis of VIII in pentane as solvent. With long exposure time, XII and *trans*-4′-methylbenzalacetophenone (X) account for all the products produced. The small amount of *trans* olefin X formed is due to partial cleavage of XII upon chromatography on a liquid–liquid partition column. No *cis* isomer XI was formed, thereby indicating that X is not a primary photoproduct since the photostationary state of X and XI under comparable photolytic conditions was shown to be 20% X and 80% XI.

In order to determine whether *cis*-benzoylaziridine IX would undergo photochemical epimerization or whether it would behave analogously to *cis*-aziridine VI, the irradiation of IX was performed. In this irradiation no VIII, X, XI, or XII could be detected, and instead 4′-methylacetophenone, N-benzylbenzalimine (XIII), and N,N′-dibenzyl-1,2-diphenyl-1,2-diaminoethane (XIV) were isolated. Suspicion that

IX

PhCH=NCH₂Ph + $\quad$ PhCHNHCH₂Ph
XIII $\qquad$ PhCHNHCH₂Ph
$\qquad$ XIV
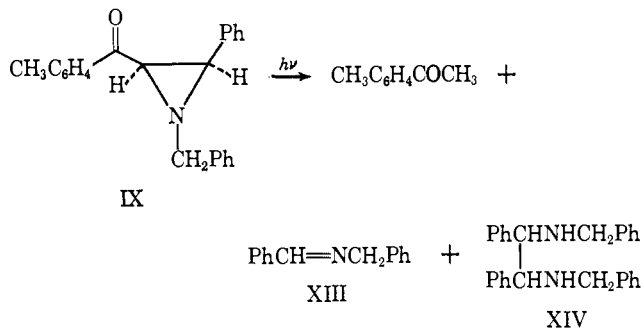
XIV was a secondary photoproduct was confirmed by the finding that the photolysis of N-benzylbenzalimine (XIII) in ethanol afforded the dimer in high yield.

PhCH=NCH₂Ph $\xrightarrow[\text{C}_2\text{H}_5\text{OH}]{hv}$ PhCHNHCH₂Ph
XIII $\qquad$ PhCHNHCH₂Ph
$\qquad$ XIV

We may therefore conclude that the photoreaction of VI and IX are mechanistically similar but drastically different from that of the *trans* isomers. It is quite clear that the mode of reaction of the 2-benzoylaziridine system is markedly dependent on the relative position of the substituents on the three-membered ring.

Discussion

The molecular changes involved in the photochemistry of the 2-benzoylaziridine system are markedly dependent on the initial stereochemistry. From the

results, we conclude that the relative position of the substituents influences the mode of ring opening. To account for the products obtained from the *trans* isomer, we suggest that the reaction proceeds by intra-molecular hydrogen transfer to yield an enol, followed by rearrangement of the latter to a carbonyl compound.

VIII

XII
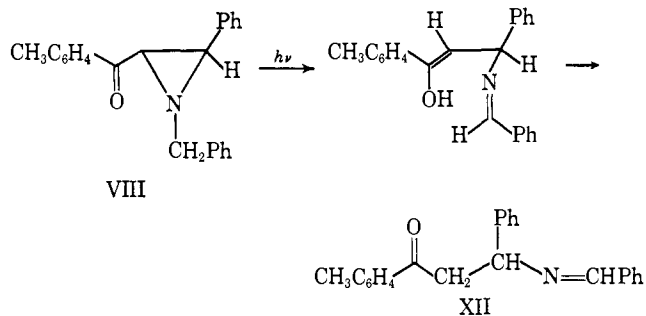
This process may be considered to be analogous to the Norrish type II cleavage observed with the irradiation of aliphatic ketones containing γ hydrogens.[30]

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 so far obtained indicate that substituted aziridines with molecular asymmetry due to trivalent nitrogen are likely only to be resolved into stable optical anti-podes at temperatures below $-50°$.[31] The temperature dependence of the nmr spectra of a number of substituted aziridines has been previously investigated.[32-35] 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.[35] The configurations of the *trans*-aziridines under consideration in this study may be represented by XVa,b and those of the *cis* compounds by XVIa,b. In

XVa   XVb

XVIa   XVIb
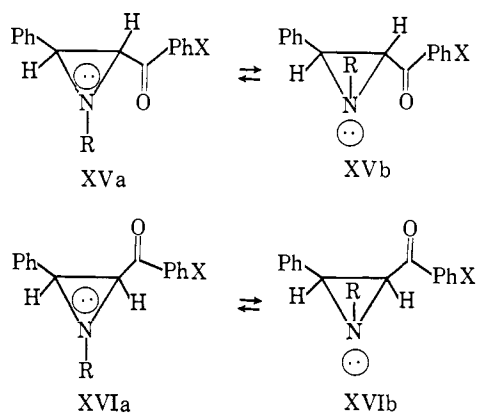
the two configurations of the *trans* compound the amount of steric crowding should be approximately equal and consequently the *trans* isomer should exist as a rapidly inverting mixture of both forms. It seems probable, however, that steric crowding would allow

(30) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).
(31) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, 80, 5203 (1958).
(32) A. T. Bottini and J. D. Roberts, *ibid.*, 78, 5126 (1956).
(33) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, 70, 786 (1958).
(34) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *J. Am. Chem. Soc.*, 82, 3599 (1960).
(35) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, *ibid.*, 87, 1050 (1965).

Figure 1. Temperature dependence of the nmr spectrum of *trans*-1-benzyl-2-phenyl-3-*p*-toluylaziridine (VIII).

the *cis* form to exist predominantly in the one structure, XVIa, especially since the group on nitrogen is large.

Some evidence pertaining to the question of configuration population of the aziridines used in these studies is provided by examination of the low-temperature nmr 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 J, and consequently they appear either as a singlet or as an AB 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, δ_c or δ_t, respectively. At normal temperatures an average line position is observed, δ_{obsd}. At temperatures at which the inversion rate is comparable to or less than 2π ($\delta_c - \delta_t$) the lifetime with respect to inversion of the two configurations of the group 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 result for *trans*-aziridine VIII is in accord with this prediction. The signals of the ring protons of VIII at first broaden with decreasing temperature and ultimately split into a quartet. This behavior is illustrated in Figure 1 for *trans*-1-benzyl-2-phenyl-3-*p*-toluylaziridine (VIII).[36a] 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 XVIa or b is very small. It seems likely on steric considerations that the equilibrium between XVIa and b should favor XVIa. The small but significant shift of the ring protons of the *cis* isomer with respect to the signal of the methyl hydrogens at lower temperatures may be interpreted as meaning that a small amount of XVIb is present in equilibrium at room temperature.[36b]

In one of the two configurations of the *trans* isomer XVa, the benzoyl group and the substituent on nitrogen are on the same side of the plane of the three-membered ring. In this configuration, hydrogen

(36) (a) J_{AB} = 1.4 cps for *trans*-1-benzyl-2-phenyl-3-*p*-toluylaziridine (VIII). (b) Heine and co-workers reached a similar conclusion in interpreting the temperature insensitivity of the spectrum of *cis*-1-methyl-2,3-dibenzoylaziridine.

abstraction by the n–π* excited state can proceed *via* a quasi-six-membered transition state.[37] It seems probable, however, that steric crowding would allow the *cis* form to exist predominantly in the one structure XVIa, especially since the group on nitrogen is large. In this case, the excited n–π* state is incapable of internal hydrogen abstraction and instead other, less efficient, processes occur.

To account for the products obtained from the *cis* isomer, we suggest 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 the carbon–oxygen distance is near normal but the carbon–carbon distance is considerably shortened, and consequently most of the ring strain must be accounted for in the carbon–carbon bond.[38] 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 α-amino ketone which then undergoes a facile photoelimination to yield the observed products.[39]
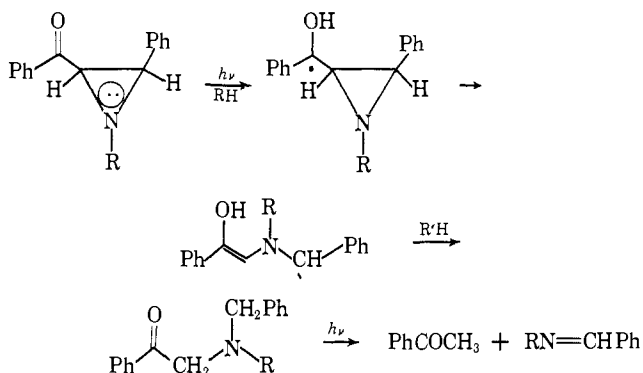
In initial agreement with this rationalization, it was observed that the preparative photoreaction of the *cis* isomers VI and IX proceeded much more slowly that the photochemical transformation of the *trans* isomers I and VIII. More quantitative evidence was obtained from quantum yield studies (Table I) of the two photoreactions. The photoefficiency of the *trans*-aziridine VIII conversion was 0.62 and that of the *cis*-aziridine IX was 0.052. The inefficiency of the *cis* isomers may be due to the occurrence of trivial chemical processes.[41]

(37) The low-energy n–π* bands in the spectra of the aziridine are undoubtedly the significant absorption bands, since light above 290 mμ was employed.

(38) G. L. Cunningham, A. W. Boyd, and W. D. Gwinn, *J. Chem. Phys.*, 17, 221, (1949).

(39) 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 phenyl acetate in 95% ethanol.[40] Since all attempts to detect the ester have failed, we must conclude that such a process does not occur.

(40) A. Padwa and R. Layton, *Tetrahedron Letters*, No. 26, 2167 (1965).

(41) 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.

Table I. Representative Quantum Yields[a]

| Run	Compound[b]	Solvent	Quencher, M	Quantum yield, %
1	I	C_2H_5OH	None	0.25 ± 0.03
2	I	C_2H_5OH	Piperylene, 0.3	0.27 ± 0.03
3	I	...	Piperylene, 6	...
4	VIII	C_2H_5OH	None	0.58 ± 0.05
5	VIII	Pentane	None	0.62 ± 0.05
6	VIII	Pentane	Piperylene, 0.3	0.60 ± 0.05
7	VIII	...	Piperylene, 6	...
8	IX	C_2H_5OH	None	0.05 ± 0.005
9	IX	C_2H_5OH	Piperylene, 0.3	...

[a] The filter combination used (see Experimental Section) has a maximum transmission of 62.8% at 313 mμ and transmits less than 1% below 290 mμ and above 436 mμ. [b] Aziridine concentration ranged from 0.008 to 0.010 M.

It is interesting to note that configuration XVb of the *trans* isomer could in principle undergo a photoreaction comparable to that undergone by the *cis* isomers. The failure to observe these products from the irradiation of *trans*-aziridines I and VIII suggests that a low quantum efficiency may be attributed to the excited n–π* state of this particular configuration.

Vibrational relaxation of the intermediate diradical followed by ring closure prior to rotation readily rationalizes the return to ground state.
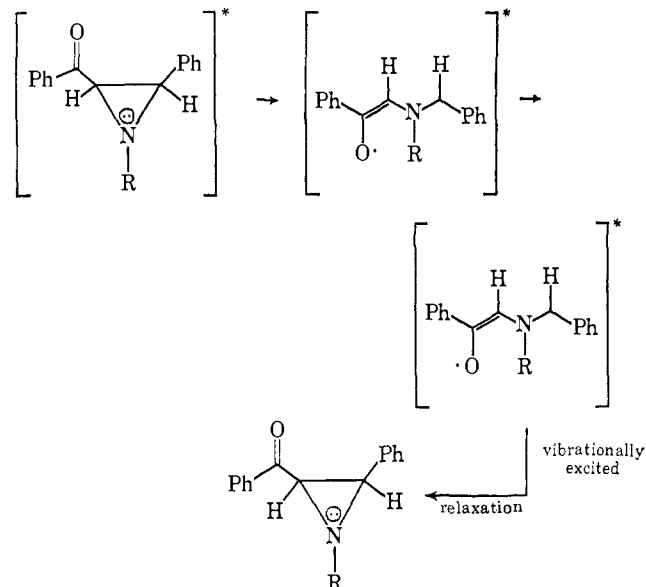
However, there remains the possibility that the low quantum yield observed is caused by the inefficient removal of hydrogen from solvent by the benzylic radical, thereby allowing for the regeneration of starting material. Here a possible sequence is the following.
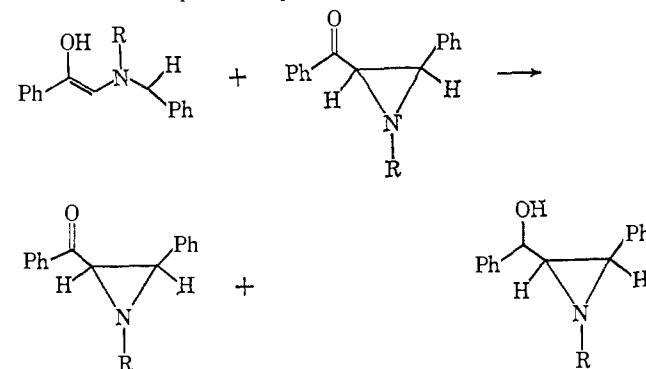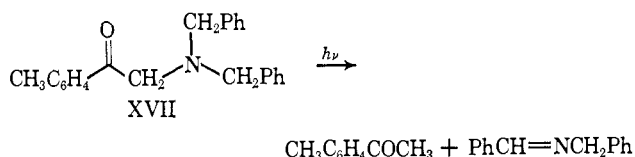
A similar hydrogen transfer has been suggested by Neckers as a step in the reaction of aryl ketones with α-hydroxyalkyl radicals.[42]

(42) D. C. Neckers, A. P. Schapp, and J. Hardy, *J. Am. Chem. Soc.*, 88, 1265 (1966).
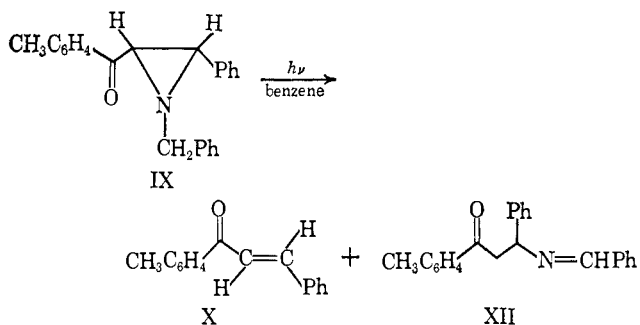
Alternatively, the result may indicate that the time allowed for reaction of excited states is long enough to allow for exploration of all possible inversion arrangements.

The most direct interpretation of our results for the photolysis of cis-aziridines VI and IX involves an α-amino ketone as a reaction intermediate. The failure to observe such species from the photolysis runs can be ascribed to their further photoreaction under the photolytic conditions. For this argument to be valid, it must then be assumed that the photoelimination of the transient α-amino ketone occurs more rapidly than does that of the cis-aziridine. Our own studies are entirely consistent with this explanation. Irradiation of α-amino ketone XVII in ethanol afforded p-methylacetophenone and N-benzylbenzalimine as the major products. Furthermore, the photoefficiency of XVII

$$CH_3C_6H_4\overset{O}{\underset{}{\|}}C\,CH_2\overset{CH_2Ph}{\underset{}{N}}CH_2Ph \quad \xrightarrow{h\nu}$$

XVII

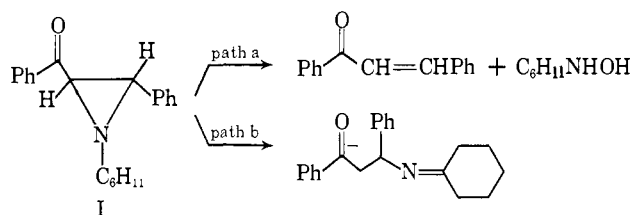$$CH_3C_6H_4COCH_3 + PhCH=NCH_2Ph$$

is substantially higher than that of IX.

The data accumulated do not constitute compelling evidence for the intermediacy of an α-amino ketone in the photodegradation of cis-aziridine IX, but they are 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 IX was carried out in benzene as solvent, trans-4'-methylbenzalacetophenone (X) and N-1-(2-p-toluyl-1-phenylethyl)benzylidenimine (XII) were the major products. It would appear, therefore, that the

$$CH_3C_6H_4\overset{H}{\underset{O}{\triangle}}\overset{H}{\underset{N}{}}Ph \quad \xrightarrow[benzene]{h\nu}$$

CH₂Ph

IX

$$CH_3C_6H_4\overset{O}{\underset{}{\|}}C=C\overset{H}{\underset{Ph}{}} \quad + \quad CH_3C_6H_4\overset{O}{\underset{}{\|}}C\overset{Ph}{\underset{}{}}N=CHPh$$

X   XII

observed difference between the two reaction paths of IX 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 IX to X and XII can be attributed to the existence of IX in a geometric arrangement which is favorable for subsequent reaction. Thus, the least stable configuration of IX would be expected to undergo internal hydrogen abstraction under conditions which suppress photoreduction of the more stable configuration. This interpretation is complicated by the possibility of a photocatalyzed epimerization of the cis isomer followed by subsequent reaction of the trans

isomer. However, all attempts to detect trans-aziridine VIII when the irradiation was carried out in benzene were unsuccessful. The absence of such a reaction supports our leanings toward considering the reactive configuration of the cis isomer to be XVIb when a poor hydrogen donor is employed as solvent.

Having demonstrated the dramatic difference in the photochemistry of cis- and trans-2-benzoylaziridines, we need to consider the mechanistic import of the formation of cyclohexylhydroxylamine in the photoreaction of I. It appears as though the photoreaction of I in polar solvents proceeds via a dual sequence. One path involves the formation of benzalacetophenone and cyclohexylhydroxylamine as primary photoproducts. The low yield of the cyclohexylhydroxylamine (23%) indicates that the competing sequence, which is reasonably formulated as proceeding via V followed by fragmentation to trans-benzalacetophenone and cyclohexanone, is the predominant path and is indeed analogous to the photochemistry of trans-aziridine VIII. In the case of I, the tertiary hydrogen of the

$$Ph\overset{O}{\underset{}{\|}}\overset{H}{\underset{H}{\triangle}}Ph \quad \overset{path\ a}{\underset{path\ b}{\nearrow}}\ Ph\overset{O}{\underset{}{\|}}CH=CHPh + C_6H_{11}NHOH$$

C₆H₁₁

I

$$Ph\overset{O\ Ph}{\underset{}{\|}}N=\bigcirc$$

cyclohexyl ring is presumably removed less rapidly than the benzylic hydrogen of VIII, thereby allowing another route to compete. Inspection of Table I shows that in the case of VIII there was an up to twofold increase in photoefficiency relative to I. This suggests that the lower quantum efficiency of I may be due to a conformational effect which retards internal hydrogen abstraction and allows for a competitive route (path a).

More than one mechanistic rationale may be envisaged for the mechanism of path a. The light adsorbed by I possesses sufficient energy to effect a bond cleavage. The energy corresponding to 316-mμ 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 rupture in I. Despite the fact that n–π* excitation would be expected to develop appreciable charge density on nitrogen as a result of a heterolytic cleavage of the aziridine carbon–nitrogen bond, the products obtained from the irradiation of I seem to be those characteristic of an electron-deficient nitrogen. A related situation has been noted for the n–π* photochemical transformations of cyclohexadienones.[24] An electron-demotion process was suggested for these cases in order to resolve the enigma of carbonium ion type reactions occurring from an n–π* 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–π* state has been considered to have dual potentiality; either an electron pair or an odd electron may be considered available on the carbonyl carbon.[43]
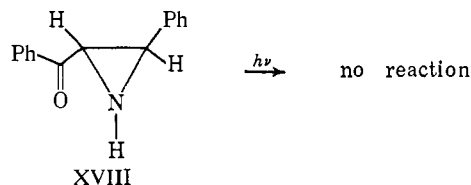
(43) H. E. Zimmerman, Advan. Photochem., 1, 183 (1963).

PhCH=CHCOPh + C_6H_{11}NHOH
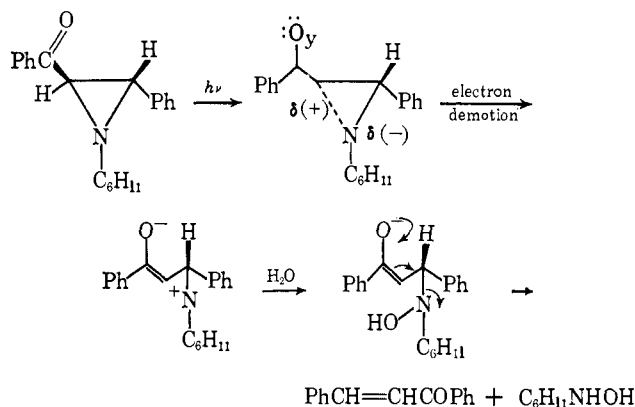
The heterolytic ring cleavage of the carbon–nitrogen bond may be related to the ability of the protic media to stabilize the zwitterion by solvation. The zwitterion can react with a molecule of water, as shown below, to form the observed products.

PhCH=CHCOPh + C_6H_{11}NHOH
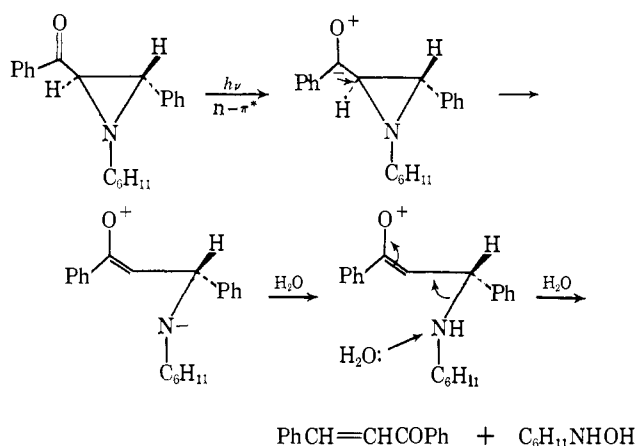
It is interesting, at this point, to compare the irradiation of I and VIII with that of *trans*-2-phenyl-3-benzoylaziridine (XVIII). Since XVIII cannot undergo an internal hydrogen transfer reaction, we would anticipate cleavage of the aziridine ring by a route comparable to that observed with I. Actually, irradiation of XVIII afforded only recovered starting material. Any attempt to account for this result should also consider the fact that *trans*-aziridine I affords some of the substituted hydroxylamine, whereas aziridine XVIII does not.

$\xrightarrow{h\nu}$ no reaction

XVIII

A comparison of the ultraviolet absorption spectra of aziridines I, VIII, and XVIII is most informative.[44] In the irradiated portion of these spectra I and VIII exhibit enhanced absorption which can be attributed to the n–π* carbonyl excitation. The ultraviolet absorption of aziridine XVIII, however, does not resemble those of the other two aziridines. The disappearance of the usual n–π* band seems to indicate that this band has shifted to shorter wavelength and coalesced with the benzoyl π–π* band. It may be

argued that the anomalous ultraviolet spectrum of XVIII is a result of intramolecular hydrogen bonding of 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 XVIII to undergo reaction may be attributed to the possible difference in the nature of its low-lying excited state. The dependence of photochemical reaction on the nature of excited states has been demonstrated amply in the literature.[45-47] Our results are entirely consistent with this explanation and imply that the intramolecular hydrogen bonding in XVIII has a very marked effect on the level of the n–π* state. In this case, the excited state of XVIII may actually possess a low-lying π–π* 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–π* singlet. The n–π* band for the aziridines studied possesses a highly structured absorption band which exhibits a maximum near 325 mμ. The oscillator strength (f) 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–π* 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.[48] It seems to us likely, however, that the reactions observed proceed *via* the n–π* triplet state in analogy with related aryl ketones.

The intersystem crossing between n–π* singlet and triplet states of aryl ketones occurs with near unit efficiency.[49,50] Since intersystem crossing to the triplet has been found to be over 10^{11} sec^{-1} for related benzoyl ketones, the destruction of the singlet n–π* state is probably proceeding too fast for reaction to occur.[51] The predominance of the n–π* triplet in these reactions may be attributed to the relatively long lifetime of these states. Unfortunately, we have not been able to detect phosphorescence from n–π* excited aziridines (in rigid glasses) and consequently there is no direct spectroscopic evidence for the production of n–π* triplets.[52,53] We provide evidence that the reacting n–π* state is a triplet rather than a singlet, however, by examination of the variation of quantum yields using piperylene as a triplet

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(45) J. R. Platt, *Ann. Rev. Phys. Chem.*, **10**, 365 (1959).

(46) N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, No. 19, 1203 (1964).

(47) G. Porter and P. Suppan, *Pure Appl. Chem.*, **9**, 499 (1964).

(48) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).

(49) F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

(50) C. A. Parker and C. G. Hatchard, *Analyst*, **87**, 644 (1962).

(51) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(52) We wish to thank Dr. E. Ullman and Professor A. Lamola for obtaining this information for us.

(53) On irradiation in a rigid glass or in the solid state, the aziridines studied undergo pronounced color changes. The photochromic behavior of these materials will be the subject of a future publication.

quencher. Energy transfer from the triplet state of the carbonyl compound to piperylene is sufficiently exothermic to ensure diffusion control of triplet destruction.[54] The quantum yields for photoreaction of the aziridines studied are summarized in Table I. Inspection of Table I shows that in run 9 the quantum yield of cis-aziridine IX is completely suppressed by the addition of 0.3 mole of piperylene.[55] In contrast, trans-aziridine VIII is unquenched by such piperylene addition (run 6). It appears as though the rate of diffusion of piperylene quencher is too slow to compete with the unimolecular rearrangement of the trans-aziridine while such diffusion is rapid enough to destroy triplets in the cis-aziridine case.[56] However, the only reaction observed with I and VIII in samples containing piperylene as solvent (runs 3 and 7) was photodimerization of the quencher. Thus, a triplet state with $E_T = 60-70$ kcal/mole[60] is implicated as a reactive intermediate in the photochemistry of the aziridines studied.

Experimental Section[61]

Irradiation of trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine in Ethanol. trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine was prepared according to the procedure of Cromwell and Hoeksema.[28] A solution of 1.50 g of I in 1 l. of 95% ethanol was irradiated with an internal cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. Aliquots were removed and analyzed by tlc. After 3 hr, the spot on a thin-layer plate due to I had almost disappeared and several new spots has 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 × 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 equilibrate for at least 30 min before use. The liquid–liquid apparatus used in these experiments and the processing of the fractions have been described in detail elsewhere. 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 concentrated in vacuo.

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 × 90 cm alumina column (neutral grade, activity III). Elution of the chro-

matographic column with 1% ethyl ether–hexane gave 290 mg of a compound which upon crystallization from ethanol–water gave light yellow rosettes, mp 43–44°. The product obtained was identical with an authentic sample of cis-benzalacetophenone synthesized by the method of Lutz and Jordan.[62] 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, mp 55–56°. This material was identified as trans-benzalacetophenone by comparison of its infrared spectrum with that of an authentic sample.

N-1-(2-Benzoyl-1-phenylethyl)cyclohexanimine (V). The second fraction obtained from the liquid–liquid partition chromatogram contained 90 mg of a light yellow oil which resisted all attempts to induced 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-phenylethylcyclohexanimine (V) on the basis of the following observations.

Anal. Calcd for $C_{21}H_{23}NO$: C, 82.55; H, 7.59; N, 4.59. Found: C, 82.22; H, 7.75; N, 4.26.

The infrared spectrum in carbon tetrachloride shows strong absorption at 5.93, 6.10, 6.92, 6.94, 9.28, and 9.78 μ. The ultraviolet spectrum in 95% ethanol has a maximum at 245 mμ (ϵ 18,200). The nmr spectrum (deuteriochloroform) is in excellent agreement with the proposed structure and consisted of a multiplet at τ 2.45 (10 H) and a multiplet at 9.0 (10 H); the remaining part of the spectrum consisted on an ABX system of 12 lines. The X proton of the ABX system was centered at τ 4.98 (1 H) and consisted of an unsymmetrical quartet. The A and B protons of the ABX system were centered at τ 6.17 (1 H) and 6.67 (1 H) and each consisted of an unsymmetrical quartet. The coupling constants for the ABX system were $J_{AX} = 8.3$ cps, $J_{BX} = 4.5$ cps, and $J_{AB} = 16.5$ cps. Further proof of structure was shown by the following degradation sequence.

In a 5-cc, round-bottomed flask fitted with a reflux condenser, a mixture of 50 mg of V, 3 cc of 95% ethanol, and two drops of concentrated hydrochloric acid was refluxed for 5 hr. The resulting mixture was analyzed by vpc. 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°. Comparison of retention times and infrared spectra with those of known samples of cyclohexanone and trans-benzalacetophenone established the identity of the products.

To a sample of V (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 min under a pressure of 45 psi 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 8 hr. 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 min under a pressure of 45 psi of hydrogen. The catalyst was filtered, and the solvent was evaporated under reduced pressure. Addition of dry ether afforded crude dimethylcyclohexylamine hydriodide. Evaporation of the solvent gave 0.140 mg (83% yield) of benzylacetophenone, identified by comparison with an authentic sample.

Treatment of the Crude Photolysis Mixture of I with Benzaldehyde. A solution of 1.0 g of trans-aziridine I in 1 l. of 7% ethanol was purged with purified nitrogen for 45 min before irradiation commenced, and a positive nitrogen pressure 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 hr. After concentration in vacuo, the crude residue was chromatographed on a 2.5 × 90 cm Florisil column. Elution with 1% ethyl acetate–benzene gave 0.570 g (82%) of cis- and trans-benzalacetophenone. Further elution with 10% ethyl acetate–benzene gave 0.195 g (23%) of a compound with an infrared spectrum which was identical in every detail with that of an authentic sample of 1-cyclohexyl-2-phenyl nitrone.[63]

Irradiation of trans-1-Cyclohexyl-2-phenylbenzoylaziridine in Pentane. A solution of 1.5 g of trans-aziridine I in 1 l. of anhydrous pentane was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. Purified nitrogen was passed through the solution for at least 45 min before irradiation was commenced,

(54) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961).

(55) The quenching may be due to chemical reaction with, as well as triplet energy transfer to, piperylene.

(56) It has been noted already by several workers[57-59] that the absence of quenching by triplet acceptors is inconclusive evidence against a triplet mechanism, as photoreaction of T_1 may be more rapid than energy transfer to quencher.

(57) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

(58) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(59) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Am. Chem. Soc.*, **87**, 2613 (1965).

(60) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. C. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

(61) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associates high-resolution spectrophotometer. Tetramethylsilane was used as an internal standard.

(62) R. Lutz and R. H. Jordan, *J. Am. Chem. Soc.*, **72**, 5090 (1950).

(63) L. Horner and E. Jurgens, *Ber.*, **90**, 2184 (1957).

and a positive pressure of nitrogen was maintained throughout. The solution was irradiated for 3 hr, 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 volumes of 1500 ml (75 fractions), 1700 ml (85 fractions), 1940 ml (97 fractions), and 2016 ml (108 fractions). The first peak (0.775 g) was identified as recovered starting material. The third peak (1.79 g) was shown to be the N-1-(2-benzoyl-1-phenyl-ethyl)cyclohexanimine. The final band contained 0.355 g of pure *trans*-benzalacetophenone. The second peak (0.200 g) contained a dark oil which resisted all attempts at crystallization. Finally, after repeated chromatography, small amounts of a white solid were obtained, mp 60°. The structure of this material has not yet been assigned.

Irradiation of *cis*-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (VI). *cis*-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (VI) was prepared according to the procedure of Cromwell and Hoeksema.[28] A solution of 0.500 g of the *cis*-aziridine in 1 l. of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate light below 280 mμ. Purified nitrogen was passed through the solution for at least 45 min before irradiation commenced, and a positive pressure of nitrogen was maintained throughout. The solution was irradiated for 6 hr, and the solvent was removed *in vacuo* to give a yellow oil. The crude reaction mixture was dissolved in 2 ml of upper phase and chromatographed on a liquid–liquid partition column. The eluate was scanned at 257 mμ 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), and 1960 ml (98 fractions). The first fraction, 0.17 g (16% based on recovered starting materials), was a colorless liquid. Comparison of its infrared spectrum and vpc retention time on a Dow 710 silicone oil (5% on Chromosorb W) with an authentic sample of N-cyclohexylbenzalimine established its identity.[64] The second fraction (0.13 g) was identified as acetophenone by comparison with an authentic sample. The last peak, 0.0145 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-p-toluylaziridine (VIII) in 95% Ethanol. *trans*-1-Benzyl-2-phenyl-3-p-toluylaziridine was prepared according to the procedure of Cromwell and Wankel.[65] A solution of 0.904 g of *trans*-aziridine VIII in 1 l. of 95% ethanol was purged with purified nitrogen for 45 min before irradiation, and a positive pressure of nitrogen was maintained throughout. The solution was irradiated for 3 hr with an internal cooled mercury arc lamp (Hanovia, Type L, 450 w) equipped with a Pyrex filter to eliminate wavelengths below 280 mμ. 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 volumes of 1560 ml (78 fractions), 1740 ml (87 fractions), and 1860 ml (93 fractions) of upper phase. The first fraction (0.175 g) upon recrystallization from 95% 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'-methylbenzalaceto-phenone by comparison with an authentic sample prepared according to the procedure of Weygand.[66]

N-1-(2-p-Toluyl-1-phenylethyl)benzylidenimine (XII). The second peak, 0.386 g (46% yield based on recovered starting material), was a light yellow oil which resisted all attempts to induce crystallization. The structure of this compound as assigned as N-1-(2-p-toluyl-1-phenylethyl)benzylidenimine on the basis of the following observations.

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.

The infrared spectrum in carbon tetrachloride showed strong absorption at 5.93, 6.13, 6.24, 8.50, and 9.74 μ. The ultraviolet spectrum in 95% ethanol has a maximum at 251 mμ (ε 27,400).

The nmr spectrum in deuteriochloroform is in excellent agreement with the proposed structure and consisted of a multiplet at τ 2.61 (9 H), a singlet at 1.72 (1 H), a singlet at 7.77 (3 H); 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 (1 H) and consisted of an unsymmetrical quartet. The A and B portions of the ABX system were centered at τ 6.21 (1 H) and 6.74 (1 H). Each consisted of an unsymmetrical quartet. The coupling constants for the ABX system were $J_{AX} = 8.3$ cps, $J_{BX} = 4.5$ cps, and $J_{AB} = 16.5$ cps. Further proof of structure was shown by the following degradation reactions.

A solution of 0.377 g of XII in 50 ml of 95% ethanol containing 0.1 ml of hydrochloric acid was refluxed for 9 hr. 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.

A 1.17-g sample of N-1-(2-p-toluyl-1-phenylethyl)benzylidenimine was chromatographed on a 1.5 × 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 with *trans*-4'-methylbenzalacetophenone as judged by infrared and mixture melting point comparison.

To a 0.5-g sample of XII in 100 ml of absolute alcohol was added 0.1 g of Adam's catalyst. The mixture was placed in a Parr shaker for 3 hr under a pressure of 45 psi 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, mp 68–69°, which had an infrared spectrum identical in every detail with that of pure 4'-methylbenzyl-acetophenone. The mixture melting point of these two materials was undepressed at 68–69°.

Irradiation of VIII in Anhydrous Pentane. A solution of 1.0 g of VIII in 1 l. of anhydrous pentane was photolyzed with an internal water-cooled mercury arc lamp (450 w) with a soft-glass filter to eliminate wavelengths below 300 mμ. Purified nitrogen was passed through the solution for at least 45 min before irradiation commenced, and a positive pressure was maintained throughout. The nitrogen atmosphere was purified by the vanadous ion method of Meites.[67] Concentration of the solution left an oil. The crude residue was chromatographed on a liquid–liquid partition column using a 4.5 × 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 infrared and mixture melting point. 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. The third peak (retention volume of 1860 ml) consisted of 220 mg (35%) of *trans*-4'-methylbenzalaceto-phenone. There was no indication of any *cis*-4'-methylbenzalace-tophenone in the chromatogram. Control experiments demonstrated the photostability of XII to the above irradiation conditions.

Photoisomerization of *trans*-4'-Methylbenzalacetophenone (X). The photoisomerization of X 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 0.220 g of *trans*-4'-methylbenzalaceto-phenone in 1 l. of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. Aliquots of 1 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

(64) T. F. West, *Chem. Ind.* (London), 61 (1942).
(65) N. H. Cromwell and R. A. Wankel, *J. Am. Chem. Soc.*, 71, 708 (1949).
(66) H. Weygand, *Ber.*, 35, 1068 (1902).

(67) L. Meites and T. Meites, *Anal. Chem.*, 20, 984 (1948).

Table II. Photoisomerization of
trans-4'-Methylbenzalacetophone (X)

Time, hr	% cis	% trans
0	0	100
1	10	90
3	25	75
4	45	55
5	60	40
10	80	20
180	80	20

Irradiation of trans-2-Phenyl-3-benzoylaziridine. trans-2-Phenyl-3-benzoylaziridine (XVIII) was prepared according to the procedure of Cromwell.[70] A solution of 1.0 g of the trans-aziridine in 1 l. of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. Purified nitrogen was passed through the solution for at least 45 min 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 tlc. Even after 28 hr of irradiation, infrared analysis and the tlc showed only unchanged starting material. Upon work-up, pure crystalline starting material was the only compound present.

Table III. Representative 3-Benzoylaziridine Quantum Yields

Run[a,b]	[I][c]	[VIII][c]	[IX][c]	Piperylene, moles	$10^{-18}I$, quantum sec^{-1}	$10^3 t$, sec	% conversion	Quantum yield, Ψ
1[a]	1.60	...	...	None	0.75	1.5	8.4	0.25 ± 0.03
2[a]	1.60	...	...	3	1.38	1.5	8.6	0.27 ± 0.03
3[d]	1.60	...	...	6	1.38	1.5	...	...
4[a]	...	1.60	...	...	0.75	1.5	11.5	0.58 ± 0.04
5[b]	...	1.60	...	...	0.75	1.5	15.2	0.62 ± 0.05
6[b]	...	1.60	...	3	1.38	1.5	15.0	0.60 ± 0.06
7[d]	...	1.60	...	6	1.38	1.5	...	...
8[a]	...	...	1.60	...	1.38	5.4	13.1	0.05 ± 0.005
9[a]	...	...	1.60	3	1.38	5.4	...	...

[a] All runs in 600 ml of 95% ethyl alcohol. [b] All runs in 600 ml of anhydrous pentane. [c] Concentration expressed in grams. [d] Pure piperylene (600 ml) as solvent.

calculated by comparison with known mixtures. The results are recorded in Table II.

Photolysis of cis-1-Benzyl-2-phenyl-3-p-toluylaziridine (IX). cis-1-Benzyl-2-phenyl-3-p-toluylaziridine (IX) was prepared according to the procedure of Cromwell and Wankel.[65] A solution of 2.0 g of cis-aziridine IX in 1 l. of 95% ethanol was photolyzed for 9 hr, 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), and 2000 ml (100 fractions). The fractions were worked up in the manner previously described. The last peak in the chromatogram, 0.900 g, was shown to be recovered starting material. The first peak, 0.090 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 prepared by the method of Juday and Adkins.[68] The solid, mp 151–151.5°, was demonstrated to be N,N'-dibenzyl-1,2-diphenyl-1,2-diaminoethane by comparison with an authentic sample prepared by the procedure of Japp and Moir.[69] 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 nmr spectra were identical in all respects with an authentic sample of 4-methylacetophenone.

The photolysis of IX was repeated using 1 l. of benzene as solvent. After the irradiation was completed, 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 XII. The fourth peak was identified as trans-4'-methylbenzalacetophenone by mixture melting point. The first peak in the chromatogram was shown to be N-benzylbenzalimine by comparison with an authentic sample.[68] Recovered starting material was the major component in the third peak.

(68) R. E. Juday and H. Adkins, J. Am. Chem. Soc., 77, 4459 (1955).
(69) F. Japp and M. Moir, J. Chem. Soc., 77, 624 (1900).

Quantum Yield Determinations. The quantum yield apparatus described by Trecker and Henry was used in these experiments.[71] It consisted of five borosilicate glass cylinders of 100, 80, 60, 39, and 28 mm joined together by appropriate ring seals and standard taper joints. The two interior tubes with cell spaces of 3 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 mμ and transmitted less than 1% below 290 mμ and above 436 mμ. Circulation and external cooling of the cobalt sulfate solution provided effective cooling for both the lamp and the 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°.

Light intensities were monitored just before and just after sample irradiation. Quantum output rates for the 200-w 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.[72] The filter solution transmission properties were checked immediately after use. Reliably reproducible output rates of 0.75 × 10^18 quanta/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-benzoylaziridine 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 III.

Photolysis of N,N-Dibenzyl-4-methylphenacylamine (XVII). A solution of 50 g of 4-methylphenacyl bromide and 100 g of dibenzylamine in 350 ml of 95% ethanol was refluxed for 20 hr. 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 (XVII), mp 77–80°. Recrystallization from ethanol gave crystals, mp 81–83°.

(70) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. G. Vanderhorst, F. W. Olson, and J. H. Anglin, J. Am. Chem. Soc., 73, 1044 (1951).
(71) D. J. Trecker and J. P. Henry, Anal. Chem., 35, 8182 (1963).
(72) C. C. Hatchard and C. A. Parker, Proc. Roy. Soc. (London), A235, 520 (1956).

Anal. Calcd for $C_{23}H_{23}NO$: 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 mμ (ϵ 19,400).

A solution of 0.5 g of XVII in 200 ml of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. The reaction was followed by glpc of aliquots withdrawn during the reaction, and product assignments were made by comparison of infrared spectra and glpc 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 1 and 6 min. Comparison of retention times and infrared spectra with those of authentic samples of 4-methylbenzalacetophenone and N-benzylbenzalimine established the identity of the two major products.

Photosensitized Isomerization of 1,3-Cyclooctadienes and Conversion to Bicyclo[4.2.0]oct-7-ene

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Abstract: The near-quantitative photosensitized cyclization reaction of *cis,cis*-1,3-cyclooctadiene to bicyclo-[4.2.0]oct-7-ene at 80° has been shown to involve first isomerization of the diene to its *cis,trans* isomer, which cyclizes under the reaction conditions. The highly strained *cis,trans* isomer has been isolated in good yield. Photostationary state compositions of the diene isomers were determined.

The generality of the photochemical conversion of conjugated dienes to cyclobutenes has been amply demonstrated by several research groups.[1] Evidence seems to indicate that this valence isomerization is not a triplet-state reaction since the reaction can neither be sensitized nor quenched.[1a,2] There are, however, two exceptional cases in the literature—1,3-cyclooctadiene and the recently reported 1,1'-bicyclohexenyl.[3] This report summarizes the results of our reexamination of the former case.

The conversion of *cis,cis*-1,3-cyclooctadiene (I, COD) to bicyclo[4.2.0]oct-7-ene (II) was reported independently by at least three research groups.[1a,b,4] A similar conversion under photosensitized conditions was indirectly reported by Schenck, *et al.*,[5] in a review article. The latter experiment, however, could not be reproduced successfully by others.[6] It appears to us that the recent observation by Fonken, *et al.*,[7] of the quantitative, facile thermal isomerization of *cis,trans*-COD to II at 80° offers an alternative mechanism for the sensitized reaction. The reaction may involve photo-sensitized isomerization to the *cis,trans* isomer, which cyclizes to II. Efficiency of the reaction would, therefore, depend upon the reaction temperature. Furthermore, since photosensitized isomerizations can conceivably provide a simple route to strained medium-size ring olefins, such as *cis,trans*-COD,[8] the system was reinvestigated in some detail.

Results

Irradiation of a solution of *cis,cis*-COD with acetophenone as sensitizer in *refluxing* benzene (or *n*-heptane at 80–90°) in a Pyrex immersion apparatus with a 550-w Hanovia medium-pressure mercury lamp for 12 hr led to complete disappearance of the diene with formation of one product. By fractional distillation, the photoproduct was isolated in 85% yield. Its infrared spectrum is identical with that reported for bicyclo[4.2.0]oct-7-ene (II).[10] Irradiation of a similar solution at 15° for the same period gave virtually no II. Instead, formation of a new product, III, was detected by vapor phase chromatography. The compound is apparently unstable under the analysis conditions since lowering the column temperature increased the size of the corresponding peak. At 50° or lower, thermal degradation of the labile photoproduct on the column apparently becomes negligible. Prolonged irradiation of this solution only results in the establishment of a photostationary state between I and III.

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(4) R. L. Cargill and W. G. Dauben, *J. Org. Chem.,* **27,** 1912 (1962); *Chem. Ind.* (London), **62,** 1198 (1962).

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(7) K. M. Shumate, P. N. Neuman, and G. J. Fonken, *J. Am. Chem. Soc.,* **87,** 3996 (1965).

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