Photochemical Transformations of Small-Ring Carbonyl Compounds. XXVIII. 1,5-Hydrogen Transfer in the Photochemistry of Aroylaziridines[1,2]

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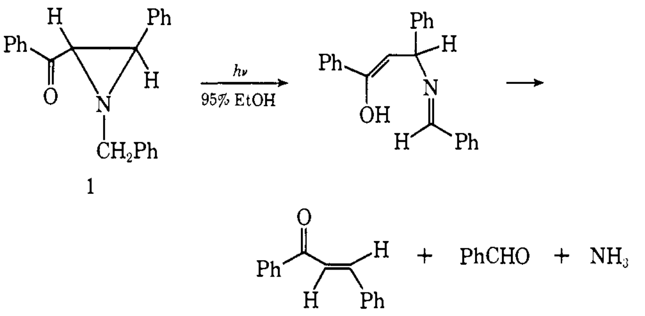
Abstract: The photolysis in pentane of *trans-N-tert*-butyl-2-phenyl-3-benzoylaziridine (**4**) has been found to afford four products. The structures have been assigned as 2,5-diphenyloxazole (**5**), (β-*tert*-butylamino)-*trans*-benzalacetophenone (**6**), *N-tert*-butylbenzalimine, and benzaldehyde. The course of the overall photoreaction is substantially altered for the *cis*-aziridine. Irradiation of *cis-N-tert*-butyl-2-phenyl-3-benzoylaziridine (**3**) gave diphenyloxazole and *N-tert*-butylbenzalimine with no detectable quantities of **6**. Sensitization and emission studies indicate that the reaction is derived from the n–π* triplet state. The failure to quench implies that the reaction of the ketone is too rapid for diffusion of the excited state to quencher molecule. A mechanism involving transfer of an electron from nitrogen to the excited triplet state followed by a 1,5-proton transfer accounts for the formation of **6**. The 1,5-hydrogen transfer route does not seem to be important in the photolysis of the related α,β-epoxy ketone system.

As part of our inquiries into the photochemical behavior of small ring nitrogen heterocycles, we have investigated the chemical response to ultraviolet radiation of a series of *N*-alkylphenylbenzoylaziridines. In our studies we have found that the nature and position of substituents about the aziridine ring produce markedly different chemical effects.[4] To account for the products obtained from the irradiation of *trans-N*-benzyl-2-phenyl-3-benzoylaziridine (**1**), we proposed that the reaction proceeds by intramolecular hydrogen transfer from carbon to the p_y orbital of oxygen of the n–π* excited state.[4] The course of the overall photoreaction was noted to be drastically altered for the cis isomer. Irradiation of *cis-N*-benzyl-2-phenyl-3-benzoylaziridine (**2**) gave acetophenone and *N*-benzylbenzalimine as the major photoproducts. We previously suggested that the excited state of the *cis*-aziridine undergoes hydrogen abstraction followed by homolytic ring cleavage to give a radical which can lead to the observed products by a succession of hydrogen abstraction and photoelimination reactions.[4]



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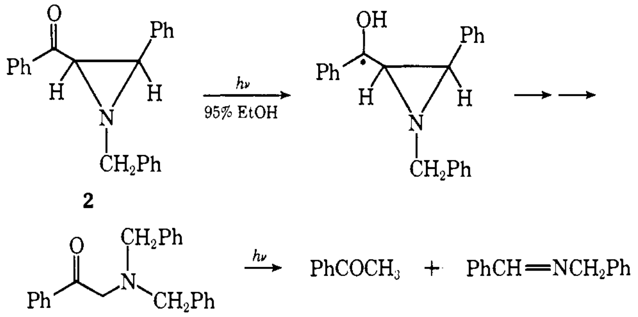
Because such strikingly different photobehavior was observed, a more thorough investigation of N-substituted 2-phenyl-3-benzoylaziridines seemed desirable.



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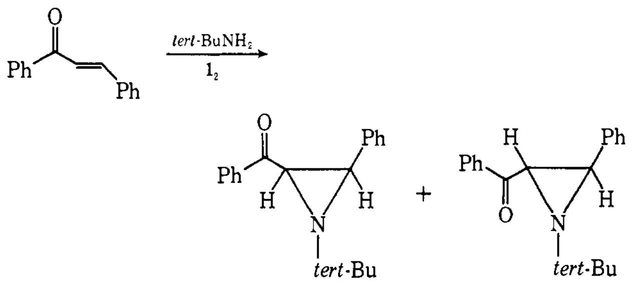
In particular, it was of interest to inspect the photochemistry of an aziridine system in which the group attached to the nitrogen atom was devoid of α-hydrogens. One approach which seemed worthwhile required the synthesis and photochemical study of the *N-tert*-butyl-2-phenyl-3-benzoylaziridine system.

The desired *cis*- and *trans-N-tert*-butyl-2-phenyl-3-benzoylaziridines **3** and **4** were prepared by treating a mixture of *trans*-benzalacetophenone and *tert*-butylamine with iodine in ether. Fractional crystallization gave **3**, mp 106–107°, and **4**, mp 69–70°. Assignment of the higher melting and less soluble isomer as the cis form (**3**) has strong analogy in the literature.[5,6] The stereochemical assignment is also based in part on ultraviolet spectroscopy. Evidence has been obtained



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(1) For part XXVII, see A. Padwa and J. Smolanoff, *J. Amer. Chem. Soc.*, **93**, 548 (1971).

(2) For a preliminary report of this work, see A. Padwa and W. Eisenhardt, *ibid.*, **90**, 2442 (1968).

(3) Alfred P. Sloan Foundation Research Fellow, 1968–1970.

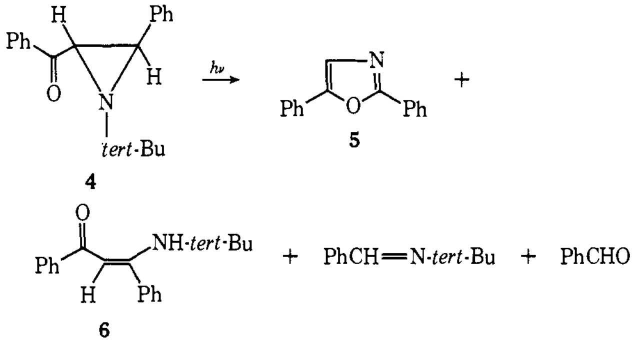
(4) A. Padwa and L. Hamilton, *J. Amer. Chem. Soc.*, **89**, 102 (1967); **87**, 1821 (1965).

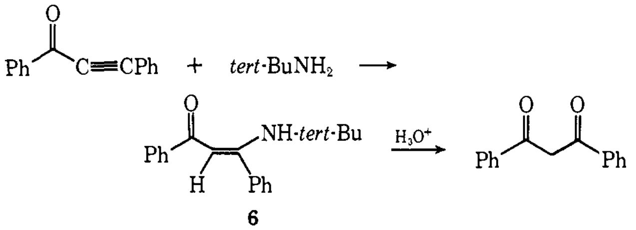
(5) N. H. Cromwell, *Rec. Chem. Progr.*, **19**, 215 (1958).

(6) N. H. Cromwell, N. Barker, R. Wankel, P. Vanderhost, F. Olson, and J. Anglin, *J. Amer. Chem. Soc.*, **73**, 1044 (1951).

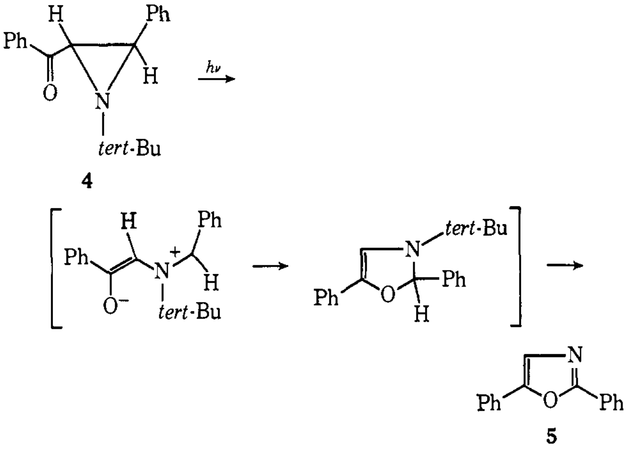
demonstrating that in a given pair of β-substituted ethylenimine ketone stereoisomers, the isomer possessing the trans structure exhibits an absorption maximum in the $\pi-\pi^*$ transition at longer wavelengths than does the cis isomer.[6] This difference was attributed to the nature of the electrical interaction between the three ring and the carbonyl group.[7] As expected, the uv spectrum of *cis*-aziridine **3** exhibited a maximum at 246 mμ (ϵ 13,000) while the maximum for the corresponding trans isomer (**4**) was shifted to slightly longer wavelength (248 mμ, ϵ 14,500) and had a slightly greater intensity. Structural assignments were further strengthened by nmr measurements. The ring protons of the cis isomer are known to absorb at higher field than those of the trans form.[8] The chemical shift of the aziridine ring protons of **3** appeared at τ 6.70 (singlet) while the corresponding trans isomer (**4**) exhibited an AB quartet centered at τ 6.48. Finally, isomerization of **4** to the thermodynamically more stable cis form (**3**) could be readily effected with methanolic sodium methoxide[9] providing additional support for the structural assignments.

With the stereochemistry of the isomeric *cis*- and *trans*-*N*-*tert*-butyl-2-phenyl-3-benzoylaziridines firmly established, a detailed study of their photochemistry was undertaken. Irradiation of the trans isomer **4** in moist pentane with a Pyrex filter gave, in addition to *tert*-butylammonium benzoate, a mixture of four components which could be separated by liquid–liquid partition chromatography. The two major products were identified as 2,5-diphenyloxazole (**5**) (38%) and (β-*tert*-butylamino)-*trans*-benzalacetophenone (**6**) (41%), mp 114–115°. The two minor components were shown to be *N*-*tert*-butylbenzalimine (6%) and benzaldehyde. The structure of enamine **6** is inferred from its composition, spectral data, and chemical behavior. The infrared spectrum of **6** was characterized by bands at 6.30, 7.51, 8.38, and 13.01 μ. The ultraviolet spectrum in 95% ethanol has maxima at 243 and 352 mμ (ϵ 10,200 and 23,900). The nmr spectrum in deuteriochloroform exhibits a singlet at τ −1.66, a multiplet centered at 2.42, a singlet at 4.46, and a singlet at 8.81. The peak areas are in the ratio of 1:10:1:9. The fact that the chemical shift associated with the proton attached to the nitrogen is markedly deshielded and is invariant with concentration strongly suggests that the *tert*-butylamino group of **6** is cis to the benzoyl group. Chemical confirmation was obtained by hydrolysis of **6** to dibenzoylmethane. Structure **6** was further verified by an independent synthesis from phenylbenzoylacetylene and *tert*-butylamine.





From the above results it is quite clear that the mode of reaction of the 2-benzoylaziridine system is markedly dependent on the nature of the substituent attached to nitrogen. With a *tert*-butyl group the intramolecular hydrogen transfer step is precluded on structural grounds and instead other, less efficient processes occur. The formation of diphenyloxazole from the irradiation of **4** may be rationalized by C–C scission followed by ring closure to a transient 2,3-dihydrooxazole which is subsequently oxidized to **5**. The ready oxidation of the 2,3-dihydrooxazole may be attributed both to the extremely low bond dissociation energy of the tertiary C–H bond and the stability of the heteroaromatic system formed. The formation of a stabilized 1,3-dipole intermediate[10–12] provides a reasonable explanation for the direction of ring opening.



The mechanism by which **4** undergoes rearrangement to **6** and the identification of the excited state responsible for the reaction are of considerable interest. Two fundamentally different mechanisms seemed possible and are presented in Scheme I. Path A involves C–N ring opening followed by a 1,2-H shift. This route bears a strong similarity to the photochemical interconversions of various substituted cyclopropanes and propenes in solution.[13–15] Path A is also closely related to the mechanism proposed for the photorearrangement of α,β-epoxy ketones to β-diketones.[16–19]

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(7) This interaction has been described as a type of hyperconjugation which results from orbital overlap of the bent bonds of the small ring with the π orbitals of the attached carbonyl group.[6]

(8) A. E. Pohland, R. C. Badger, and N. H. Cromwell, *Tetrahedron Lett.*, 4369 (1965).

(9) R. E. Lutz and A. B. Turner, *J. Org. Chem.*, **33**, 516 (1968).

(10) H. W. Hine, R. Peary, and A. J. Durbetaki, *ibid.*, **31**, 3924 (1966).

(11) A. Padwa and L. Hamilton, *J. Heterocycl. Chem.*, **4**, 118 (1967).

(12) A. M. Trozzolo, T. DoMinh, Abstracts of CIC–ACS Meeting, Toronto, 1970, p 60.

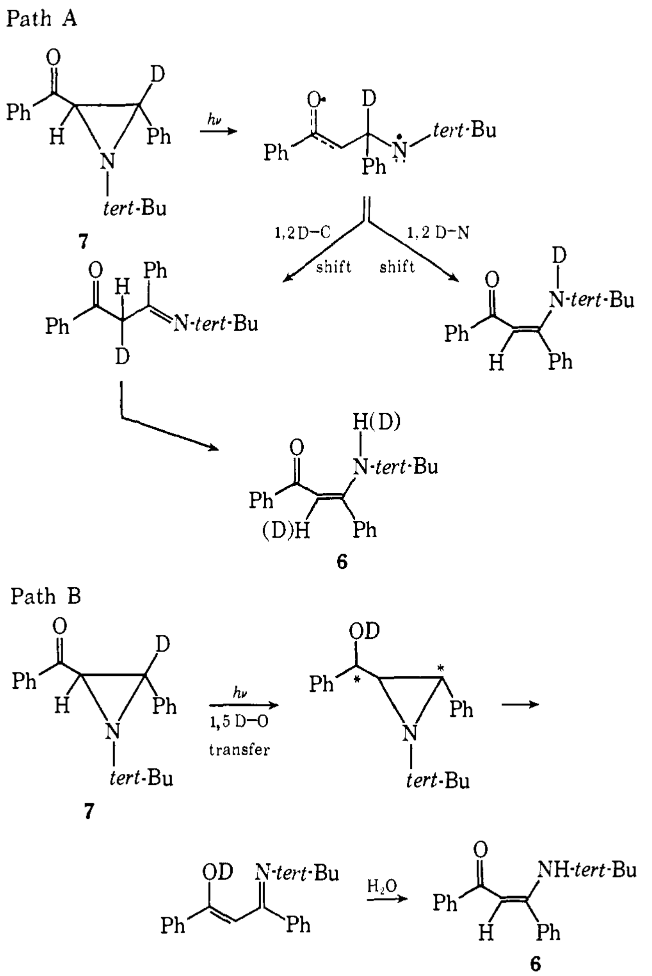
(13) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *J. Amer. Chem. Soc.*, **87**, 1410 (1965).

(14) H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 378 (1966).

(15) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(16) A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 92.

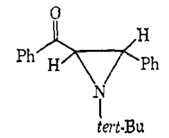
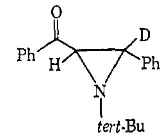
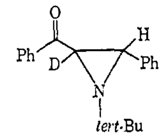
Scheme I



The alternative path (B) involves a prior 1,5-hydrogen transfer and subsequent ring opening. In order to help elucidate the correct pathway, the photoisomerization of *N-tert*-butyl-2-phenyl-3-benzoylaziridine-**2**-d_1 (**7**) was examined. Irradiation of **7** afforded product **6** (11%) that was shown to have lost better than 98% deuterium, as evidenced by nmr and mass spectral analysis. The isolation of nondeuterated **6** conclusively proves that a 1,2 H–C shift is not operative in path A since a normal deuterium isotope effect would be expected to give rise to a substantial amount of deuterium on the α-carbon atom. Control experiments demonstrated that no exchange of product **6** occurred under comparable photolytic conditions, thus negating a 1,2 H–N shift. In fact, no exchange of the N–H proton took place when **6** was treated with D_2O and only 60% exchange could be effected by treating **6** with sodium hydride and then quenching with D_2O. Furthermore, when **6** was irradiated in the presence of D_2O it did not incorporate any deuterium. These results imply that deuterium loss occurs before the formation of the final product and is perfectly consistent with route B.

Substitution of hydrogen with deuterium in organic compounds may exert a marked effect on certain properties of their excited states.[20–23] Theory predicts that deuterium should decrease the rate of $T^1 \rightarrow S^0$ and $S^1 \rightarrow S^0$ radiationless transitions.[24] In addition, the usual isotope effect involved in the breaking of a C–D bond may cause a modification in the photochemical behavior of an organic compound.[25,26] If a 1,5-hydrogen transfer mechanism (path B) is operative in the transformation of **4** to **6** then substitution of deuterium in the 2 position of the aziridine ring should have a marked effect on the observed quantum yield. On the other hand, substitution of deuterium in the 3 position should have little effect. The data in Table I show that replacement of hydrogen by deuterium in the 2 position causes a definite decrease in the quantum yield while no significant change is observed for deuterium substitution in the 3 position.

Table I. Representative Quantum Yields for Formation of Product **6** at 3130 A° [a]

Aziridine	Conversion, %	Φ
 **4**	7	0.018
 **7**	7	0.006
 **8**	9	0.018

[a] Irradiation conditions, aziridine concentration 7.16×10^{-3} *M*, lamp intensity, 3.56×10^{16} quanta sec^{-1}.

The diminished rate of formation of **6** from **7** is noteworthy and suggests that the hydrogen transfer step is not reversible as had been observed in the valerophenone[27] and benzoylazetidine[28] systems. This is reasonable in light of the driving force for ring opening of the initially formed diradical intermediate. If the reverse transfer step were important, then substitution of deuterium for hydrogen should retard the reverse transfer and result in an enhancement of the quantum yield.[28] This is not observed in the present case.

The deuterium isotope effect observed is difficult to rationalize on the basis of mechanism A unless the 1,2-H shift were the slow step. If this were the case, a sig-

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(17) C. K. Johnson, B. Dominy, and W. Reusch, *J. Amer. Chem. Soc.*, **85**, 3895 (1963).

(18) H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *ibid.*, **86**, 947 (1964).

(19) O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964).

(20) C. A. Hutchinson and W. M. Maugrum, *J. Chem. Phys.*, **32**, 1261 (1960).

(21) R. E. Kellogg and R. P. Schwenker, *ibid.*, **41**, 2860 (1964).

(22) S. G. Hudley, H. E. Rast, and R. A. Keller, *ibid.*, **39**, 705 (1963).

(23) M. R. Wright, R. P. Frosch, and G. W. Robinson, *ibid.*, **33**, 934 (1960).

(24) G. W. Robinson and R. Frosch, *ibid.*, **37**, 1962 (1962); **38**, 1187 (1963).

(25) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

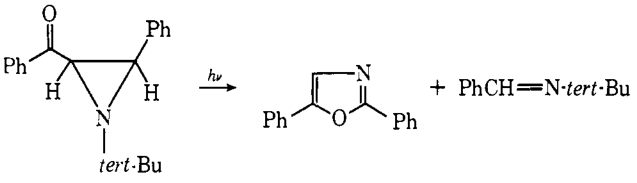
(26) A. Padwa and W. Bergmark, *Tetrahedron Lett.*, 5795 (1968).

(27) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

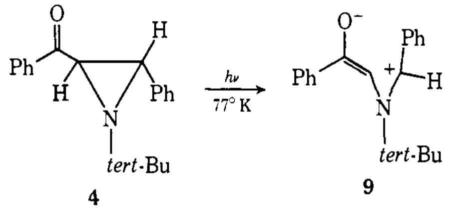
(28) A. Padwa and R. Gruber, *ibid.*, **92**, 107 (1970).

nificant amount of ring opening followed by rotation and closing should occur prior to hydrogen migration and thus allow for the formation of the thermodynamically more stable *cis*-aziridine (**3**). Experimentally, it was found that on short irradiation recovery of aziridine gave only the stereoisomer used as reactant. Deuterium substitution at the 2 position of the aziridine ring also reduced the rate of disappearance of starting material. Thus, irradiation of an equimolar mixture of **4** and **7** followed by recovery of the aroylaziridine demonstrated that **4** disappeared twice as fast as did **7**.

A most important observation that is only consistent with path B is that irradiation of *cis*-aziridine **3** produced oxazole **5** (51%), *tert*-butylammonium benzoate, and *tert*-butylbenzalimine with no detectable quantities of **6**. The deuterium labeling experiments and the total absence of **6** from the irradiation of **3** provide strong support for mechanism B. Other examples of intramolecular hydrogen transfer processes that proceed *via* a five-membered transition state are available in the literature.[28,29] Recent work by Padwa and Gruber on the photolysis of aroylazetidines bears similar characteristics to the above reaction (**4** → **6**).[28] In that case the photoreaction was shown to proceed *via* a 1,5-hydrogen transfer sequence.



The absorption spectra of **3** and **4** in hydrocarbon solvents showed the n–π* band at 320–370 mμ. The π–π* transition is at 246 mμ (115 kcal/mol) and consequently the n–π* singlet is the lowest energy state of this multiplicity. This is not necessarily true for the corresponding triplets. In order to demonstrate conclusively that the n–π* state of **4** is the lowest triplet energy state, we have examined its phosphorescence emission in a rigid glass at 77°K. The 0–0 band of **4** in an ethanol–methanol glass corresponds to a triplet energy of 74.1 kcal. The vibrational spacing between the 0–0 and 0–1 band (1730 cm^{-1}) is typical of emission from a n–π* triplet.[30] The lifetime of the triplet of **4** was approximately 10 msec. The preceding evidence, based on triplet excitation levels, vibrational structure, and lifetime of the emission, indicates the presence of the n–π* triplet at low temperature.[31] It was noted that if the phosphorescence emission spectrum was recorded after a short time interval, the intensity of the emission decreased and the vibrational fine structure disappeared. At this point the sample had developed an intense red color which disappeared on warming but could be regenerated by cooling and further irradiation. Analysis of the sample showed that no chemical reaction had occurred. It appears as though the colored species quenches the phosphorescence emission of ketone **4**. The photochromic behavior of aroylaziridines in the solid state or in a rigid matrix has previously been noted.[11,12] It has been suggested that the colored material formed is a 1,3-dipole which apparently can quench the emission of the n–π* triplet state of ketone **4**. To provide complementary evidence on the mode of emission quenching, we have measured the emission of a mixture of benzophenone and aziridine **4** under conditions where benzophenone absorbs greater than 90% of the light. At first, the spectrum obtained showed only emission of benzophenone. The intensity of the emission gradually decreased over a period of time. Once again a red coloration of the sample was observed. As the red color developed, emission of benzophenone diminished. The data implies that the 1,3-dipole produced on irradiation can quench the emission of n–π* triplet states, and in so doing, produce a 1,3-triplet biradical ($\mathbf{9}^{*3}$). To obtain additional evidence for the existence of such a triplet, a sample of **4** was irradiated at low temperatures in the cavity of an epr spectrometer. Triplet states are known to exhibit $\Delta m = 2$ epr transitions in addition to the $\Delta M = 1$ transition.[32] Experimentally, no signal for the $\Delta m = 2$ transition was obtained. This result implies that (1) the steady-state concentration of the triplet biradical is too low; (2) the $\Delta m = 2$ transition is too weak; or (3) the temperature is not low enough. At this time it is not possible to distinguish between these possibilities.



$$\mathbf{4}_0 \xrightarrow{h\nu} \mathbf{4}^{*1} \rightsquigarrow \mathbf{4}^{*3}$$

$$\mathbf{4}^{*3} + \mathbf{9}_0 \longrightarrow \mathbf{4}_0 + \mathbf{9}^{*3}$$

One experiment of interest was the irradiation of aziridine **4** in EPA at 77°K. A control run was also made in the same solvent at room temperature. Although **6** was formed in the control run, no photoreaction was detected at 77°K. The inhibition of rearrangement at low temperature can be ascribed to either a matrix effect or to a small activation energy for the triplet rearrangement. A similar observation has been noted by Zimmerman and Swenton in the 4,4-diphenylcyclohexadienone system.[33] The literature also contains related reports where species that photoreact readily at ordinary temperatures are stable to light when placed in glasses at low temperatures.[34,35]

In order to elucidate further the nature of the excited state responsible for the conversion of **4** to **6**, sensitization experiments were undertaken. The sensitizer's (acetophenone) concentration was adjusted to absorb greater than 95% of the light and the concentration of *trans*-aziridine **4** was kept sufficiently low (7×10^{-3} *M*) to ensure unimolecular destruction of acetophenone excited singlet molecules prior to collision with ground-state aziridine, yet sufficiently high to guarantee col-

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(29) P. A. Leermakers and G. F. Vesley, *J. Amer. Chem. Soc.*, **85**, 3776 (1963).

(30) M. Kasha, *Radiat. Res., Suppl.*, **2**, 265 (1960).

(31) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

(32) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(33) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

(34) W. E. Lee, J. G. Calvert, and E. W. Malmberg, *ibid.*, **83**, 1928 (1961).

(35) J. N. Pitts, Jr., J. K. Wan, and E. A. Schuck, *ibid.*, **86**, 3604 (1964).

lision of acetophenone triplets with aziridine at a rate faster than acetophenone decay.[36] Under these conditions the photolysis of **4** gave the same product distribution as was observed in the direct irradiation. Moreover, the quantum yield for the sensitized irradiation was identical in value with that obtained in the unsensitized irradiation (see Table II). These results imply that acetophenone is effectively transferring its energy to the aziridine. It also may be concluded that the very low quantum efficiency of the aziridine isomerization is not due to a low intersystem crossing efficiency in **4**, but rather is attributable to other deactivating processes which occur after intersystem crossing. The fact that both the direct and sensitized irradiations of **4** gave similar quantum yields suggests that the triplet state of aziridine **4** is responsible for the observed rearrangement upon direct irradiation.

Table II. Irradiation of *trans-N-tert*-Butyl-2-phenyl-3-benzoylaziridine. Sensitization and Quenching Studies[a]

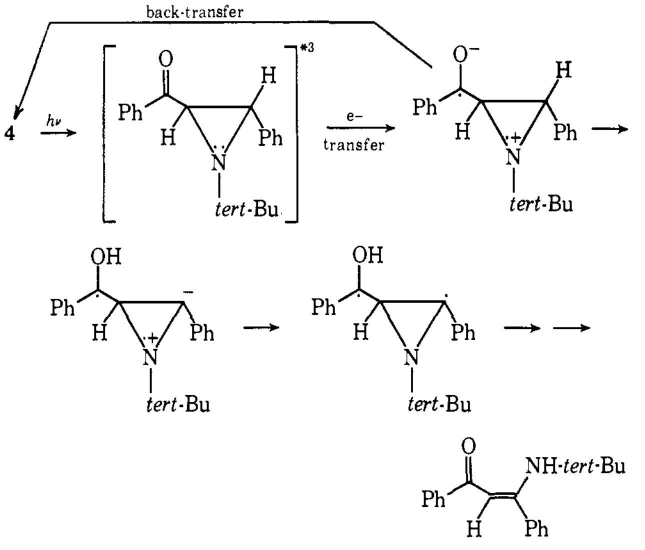
Reactant	Additive	Quantum yield[d]
4[b]		0.018
4	Piperylene (0.03 *M*)	0.019
4	Piperylene (neat)	0.02
4	1,3-Cyclohexadiene (1 *M*)	0.02
4	Naphthalene (5×10^{-3} *M*)[e]	0.02
4	Acetophenone (3.5 *M*)[c]	0.017
7		0.006
7	Piperylene	0.006
8		0.018
8	1,3-Cyclohexadiene	0.018

[a] All runs at 25°; irradiation conditions described in the Experimental Section. [b] Axiridine concentration was 7.16×10^{-3} *M*. [c] Absorbing over 95% incident light. [d] Average of enamine **6** formation for three runs. [e] Absorbing negligible light.

In an attempt to determine the rate constant for the unimolecular rearrangement of the triplet state, we have studied the variation of quantum yield *vs.* quencher concentration. Considering the low quantum efficiency of the photoreaction, we anticipated that the reaction would be readily quenched. Most surprisingly, the rearrangement of the various *trans*-aziridines (**4**, **7**, and **8**) in pentane solution containing piperylene, naphthalene, or 1,3-cyclohexadiene was not quenched (see Table II). The failure to quench the reaction implies that rearrangement of the triplet is too rapid for diffusion of the excited state to quencher molecule. Similar situations have been described in the literature.[28,33] An experiment designed to provide further evidence that the triplet state of **4** is too short lived to be quenched involved the use of **4** as a sensitizer for the cis–trans isomerization of an olefin. This experiment involves comparing the rate of photoisomerization of a cis olefin using benzophenone as sensitizer and the compound in question (*i.e.*, aziridine) as sensitizer.[37] *cis*- and *trans*-stilbenes undergo photoisomerization when irradiated in the presence of a triplet sensitizer with $E_t > 68$ kcal.[38] If the lifetime of the sensitizer's triplet state is less than 10^{-9} sec there will not be sufficient time for energy transfer to occur.[39] Experimentally, it was found that under conditions where greater than 98% of the light was absorbed by aziridine **4**, an insignificant amount of stilbene isomerization occurred. The photoreaction of aziridine **4**, however, proceeded with its usual efficiency. A control experiment using acetophenone as the sensitizer under similar conditions and for the same length of time resulted in 45% isomerization to the trans isomer. These results demonstrate that some other triplet deactivating process, such as photorearrangement, is competitive with energy transfer. Considering the short triplet lifetime of **4** it is somewhat surprising that the quantum efficiency of the reaction is so low, since most known physical mechanisms for radiationless decay of excited states occur in the order of 10^6 sec^{-1}.[27,40]

An attractive explanation which accounts for the low quantum efficiency and high triplet reactivity involves transfer of an electron from nitrogen to the excited state of ketone **4** to form an ion pair or charge transfer complex. Transfer of a proton from the adjacent carbon atom to the ketyl radical followed by electron reorganization will produce the same biradical intermediate as would be obtained by simple hydrogen abstraction (Scheme II). The failure to quench the reaction shown in Scheme II implies that this process proceeds at a rate exceeding diffusional control. Back-transfer of an electron in the complex would generate the starting ketone and account for the low quantum yield. The sequence of steps outlined is closely related to the scheme proposed by Cohen to account for the results obtained in the benzophenone and *p*-aminobenzophenone alkylamine system.[41,42] A related case has also been encountered by Padwa and coworkers with benzoylazetidines[28] and acyclic amino ketones.[43]

Scheme II



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Of the various routes considered for the photoisomerization of cyclopropyl[44] and α,β-epoxy ketones,[18,19] it is surprising that an internal 1,5-hydrogen transfer

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(37) A. A. Lamola and G. S. Hammond, *ibid.*, **43**, 2129 (1965).

(38) G. S. Hammond and J. Saltiel, *J. Amer. Chem. Soc.*, **84**, 4983 (1962).

(39) U. L. Ermolaev, *Opt. Spektrosk.*, **6**, 416 (1959).

(40) B. Singh and E. Ullman, *J. Amer. Chem. Soc.*, **89**, 6911 (1967).

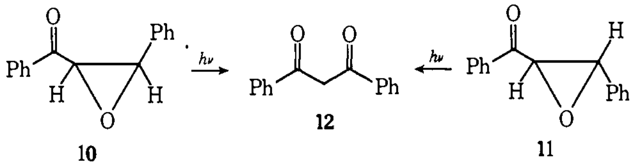
(41) S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, **90**, 521 (1968); S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3471 (1967).

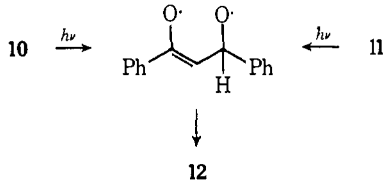
(42) S. G. Cohen and J. L. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

(43) A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 1857 (1969).

(44) J. N. Pitts and I. Norman *ibid.*, **76**, 4815 (1954).

sequence has not been entertained as a possible mechanism. In an attempt to determine the importance of the 1,5-hydrogen transfer route in other small-ring ketones, a photochemical study of the related α,β-epoxy ketone system was initiated. The system chosen for the preliminary study was *cis*- and *trans*-1,3-diphenyl-2,3-epoxy-1-propanone (**10** and **11**). This system seemed particularly suitable for study since there is no substituent on the heteroatom to complicate the photochemistry. In addition, both isomers are readily available.[45] Bodforss had described the photochemical rearrangement of **11** to **12** as early as 1918.[46] The mechanism of the isomerization has been suggested to involve cleavage of the C_α–O bond of the epoxide ring followed by a 1,2 shift of the β-hydrogen to the α position.[18,19] A mechanism of this type should be independent of the relative position of the substituents on the three-membered ring and would predict that both isomers (**10** and **11**) should display comparable photoefficiencies. On the other hand, if a 1,5-hydrogen transfer route was of major importance, then the isomerization should be highly dependent on the initial stereochemistry about the epoxide ring. Experimentally it was found that both **10** and **11** rearranged to dibenzoylmethane (**12**). The quantum yield for dibenzoylmethane formation from the *trans*-epoxide (Φ = 0.017) was four times that of the *cis*-epoxide (Φ = 0.004). The further complication of a photocatalyzed epimerization of starting material (**10** ⇌ **11**) was eliminated by the finding that irradiation of **11** did not afford **10**. Attempts to detect photoepimerization using *cis*-epoxide **10** were also unsuccessful.





The fact that *cis*-epoxide **10** undergoes photoisomerization to **12** implies that the 1,5-hydrogen transfer route is not as important in the epoxy ketone series as it is in the aziridine system. This may be a reflection of the facility with which electron transfer occurs when the heteroatom of the small ring has an electron pair of low ionization potential. The difference in quantum efficiency of the two epoxides is too small to attribute with confidence to the 1,5-hydrogen transfer path, although this certainly could be the case.

Since aroylaziridines and azetidines are the only small ring systems where the 1,5-hydrogen transfer route has been demonstrated, the applicability of this path to other small ring ketones must, of course, be considered speculative. Nevertheless, recognition of the existence of such a route now sets the stage for further studies with related heterocyclic systems.

Experimental Section[47]

Preparation of *cis*- and *trans*-1-*tert*-Butyl-2-phenyl-3-benzoylaziridine (3 and 4). To a mixture of 26.0 g (0.13 mol) of *trans*-benzalacetophenone and 32.0 g (0.13 mol) of iodine in 800 ml of anhydrous ether was added slowly and with stirring a solution of 67 ml of *tert*-butylamine in 100 ml of anhydrous ether. After the addition was complete the solution was allowed to stir until the color changed to light yellow. The precipitated *tert*-butylamine hydriodide was removed by filtration and the filtrate was washed with four portions of distilled water and dried over sodium sulfate. Evaporation of the solvent *in vacuo* afforded a viscous brown oil. The residue was taken up in pentane and cooled to afford a white crystalline solid, mp 106–107°. The structure of this material was assigned as *cis*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine (**3**) on the basis of the following observations.

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.87; H, 7.45; N, 5.22.

The infrared spectrum (potassium bromide pellet) of **3** was characterized by absorptions at 3.50, 5.96, 7.35, 8.15, 9.87, 13.12, 13.64, and 14.18 μ. The ultraviolet spectra (95% ethanol) exhibited maxima at 246 mμ (ε 13,230) and 327 mμ (ε 153). The nmr spectrum (CCl_4) showed a multiplet at τ 2.50 (10 H), a singlet at 6.70 (2 H), and a singlet at 8.88 (9 H). The mass spectrum exhibited a molecular ion at *m/e* 279.

Further cooling of the mother liquors afforded a white solid that was recrystallized from methanol–water to give white needles, mp 123° dec. The structure of this material is assigned as 2,3-di-*tert*-butylamino-1,4-diphenyl-1,4-butanedione on the basis of the following observations.

Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 76.00; H, 8.51; N, 7.55.

The infrared spectrum (potassium bromide pellet) was characterized by absorptions at 3.43, 6.00, 6.93, 7.90, 8.19, 8.52, 10.15, 12.12, 14.20, and 14.71 μ. The ultraviolet spectrum in 95% ethanol had a maximum at 256 mμ (ε 15,880). The nmr spectrum (CCl_4) showed a multiplet at τ 1.94 (4 H), a multiplet at 2.51 (6 H), a singlet at 5.67 (2 H), a broad singlet at 8.05 (2 H, N-*H*), and a singlet at 9.32 (18 H). Addition of D_2O to the nmr tube resulted in the disappearance of the broad singlet at 8.05. A molecular weight determination (ebullioscopic) gave a value of 391 (calcd 380) in good agreement with the proposed structure.

The above dione could also be prepared by treating phenacyl chloride with *tert*-butylamine. A mixture of 25 g of phenacyl chloride in 50 ml of dry ether and 150 ml of *tert*-butylamine was stirred together at room temperature for 10 hr. The precipitated hydrochloride salt was filtered, and the filtrate was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure afforded a white crystalline solid which was recrystallized from heptane–benzene to give white needles, mp 123° dec. This compound was identical in all respects with the compound obtained from the fractional crystallization outlined above. A mixture melting point was undepressed at 123°.

Further cooling of the mother liquors resulted in the precipitation of a white solid that was recrystallized from pentane to give colorless needles, mp 69.5–70.5°. The structure of this material is assigned as *trans*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine (**4**) on the basis of the following data.

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.44; H, 7.36; N, 5.24.

The infrared spectrum (potassium bromide pellet) was characterized by a series of bands at 3.45, 6.01, 8.18, 8.28, 9.91, 12.28, 14.27, and 14.52 μ. The ultraviolet spectrum (95% ethanol) showed maxima at 248 mμ (ε 14,350) and 330 mμ (ε 488). The nmr spectrum (CCl_4) was characterized by a multiplet at τ 2.60 (10 H), a doublet at 6.21 (1 H, *J* = 2.5 Hz, C*H*Ph), a doublet at 6.75 (1 H, *J* = 2.5 Hz, C*H*COPh), and a singlet at 8.83 (9 H). The mass spectrum exhibited a molecular ion at *m/e* 279.

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(45) H. H. Wasserman and N. E. Aubrey, *J. Amer. Chem. Soc.*, 77, 590 (1955).

(46) S. Bodforss, *Ber.*, 51, 214 (1918).

(47) 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-resolutions spectrometer. Tetramethylsilane was used as an internal standard.

Further support for the structure of this material was obtained from the base-induced epimerization to *cis*-aziridine **3**. A solution of 2.64 g of **4** in 40 ml of a freshly prepared 0.43 *N* sodium methoxide solution was allowed to stir at room temperature for 4 hr. At the end of this time water was added which resulted in the precipitation of 2.4 g of a white solid. Recrystallization of this material from pentane gave colorless needles, mp 106–107°. This material was identical in all respects with the first solid obtained from the previous fractional crystallization. A mixture melting point of these two compounds was undepressed at 106°.

Both *cis*- and *trans*-aziridines (**3** and **4**) were thermally labile and were stored in the dark at −20° to minimize decomposition.

Irradiation of *trans*-1-*tert*-Butyl-2-phenyl-3-benzoylaziridine (4). A sample of 0.90 g of **4** in 1 l. of pentane was irradiated with a 450-W Hanovia mercury lamp using a Pyrex filter. Nitrogen was bubbled through the solution prior to and during the irradiation. Aliquots were periodically withdrawn and analyzed by tlc. After 2 hr of irradiation, the spot due to **4** had almost completely disappeared and several new spots appeared in its place. Evaporation of the solvent under reduced pressure left a viscous brown oil which was taken up in methylene chloride. A white precipitate slowly formed which was collected by filtration to give 0.20 g (32%) of a white crystalline material. This material was identified as the *tert*-butylammonium salt of benzoic acid by comparison with an authentic sample.

The crude residue remaining after the removal of the salt was subjected to liquid–liquid partition chromatography.[48] The optical density trace showed four well-resolved peaks. The first fraction was identified as *N*-*tert*-butylbenzalimine (0.03 g, 6%) by comparison of its infrared and nmr spectra with those of an authentic sample.

The second fraction afforded 0.374 g (42%) of a yellow solid. Recrystallization from heptane–benzene gave white prisms, mp 114.5–115.5°. The structure of this material is assigned as (β-*tert*-butylamino)-*trans*-benzalacetophenone (**6**) on the basis of the following observations.

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.94; H, 7.51; N, 5.06.

The infrared spectrum of **6** showed absorptions at 3.42, 6.30, 7.52, 7.67, 8.13, 8.38, 9.45, 9.76, 13.10, 14.24, and 14.50 μ. The ultraviolet spectrum (pentane) was characterized by maxima at 241 mμ (ε 15,000) and 344 mμ (ε 20,560) The nmr spectrum ($CDCl_3$) exhibited a broad singlet at τ −1.66 (1 H, N*H*), a multiplet centered at 2.42 (10 H), a singlet at 4.46 (1 H, PhCOC*H*), and a singlet at 8.81 (9 H).

Addition of deuterium oxide to the nmr tube did not reduce the intensity of the signal at −1.66. A partial exchange of the NH proton could be effected by treating the product with sodium hydride followed by the addition of D_2O.[49] To 0.3 g of **6** in 20 ml of benzene was added 0.04 g of sodium hydride (60% in mineral oil) under a nitrogen atmosphere. The mixture was allowed to stir for 3 hr at 50° and then 3 ml of deuterium oxide was slowly added. The organic layer was decanted, dried, and evaporated under reduced pressure to afford a crystalline solid whose nmr spectrum indicated that the signal at −1.66 had undergone significant exchange (60%).[50]

The mass spectrum of **6** showed a parent ion at *m/e* 279 and major peaks at 57, 77, 105, 146, 222, 236, and 264. Chemical confirmation of the structure of **6** was obtained by hydrolysis to dibenzoylmethane. To a mixture of 0.4 g of **6** in 15 ml of dioxane was added 5 ml of a 10% hydrochloric acid solution and the resulting mixture was allowed to reflux for 8 hr. At the end of this time water was added to the mixture and then it was extracted with benzene. The extracts were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure to afford a yellow oil which crystallized on standing. Recrystallization from methanol–water gave dibenzoylmethane as a light yellow crystalline solid, mp 76–77°.

Structure **6** was further confirmed by an independent synthesis starting with benzoylphenylacetylene and *tert*-butylamine. A mixture of 1.0 g of benzoylphenylacetylene and 50 ml of *tert*-butylamine was allowed to stir at 45° for 8 hr. Evaporation of the *tert*-butylamine *in vacuo* afforded a brown solid which was recrystallized from heptane–benzene to give white prisms, mp 114.5–115.5°. This material was identical in all respects with the material obtained from the irradiation of *trans*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine (**4**). The third fraction from the liquid–liquid partition chromatogram amounted to 0.27 g (38%) of 2,5-diphenyloxazole (**5**). The structure of the oxazole was established by comparison with an authentic sample. The last fraction isolated was identified as benzaldehyde (4%) by comparison with an authentic sample.

Irradiation of *cis*-1-*tert*-Butyl-2-phenyl-3-benzoylaziridine (3). A solution of 1.0 g of **3** in 1 l. of pentane (or methanol) was irradiated with a 450-W Hanovia mercury lamp using a Pyrex filter. A stream of nitrogen was passed through the solution during the irradiation. Aliquots were periodically removed and analyzed by infrared spectroscopy. After 6 hr, the band at 5.96 μ had almost disappeared and several new bands appeared. The solvent was evaporated under reduced pressure and the residual oil was taken up in 3 ml of methylene chloride. A white precipitate slowly formed and was collected by filtration to give 0.20 g (32%) of white needles, mp 221–223°. The structure of this material was assigned as the *tert*-butylammonium salt of benzoic acid on the basis of the following observations. The infrared spectrum (potassium bromide pellet) was characterized by strong absorptions at *ca.* 3.1–4.1, 6.14, 6.59, 7.23, 8.16, 9.45, 9.72, 11.90, and 13.78 μ. The nmr spectrum (D_2O) exhibited a multiplet centered at τ 2.26 (5 H) and a singlet at 8.68 (9 H). Chemical confirmation of the ammonium salt was obtained by the generation of benzoic acid from the salt. A 0.05-g sample of the salt was dissolved in 10 ml of a 10% sodium carbonate solution. The solution was extracted with benzene and the extracts were dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* afforded benzoic acid, mp 120–22°. The ammonium salt was prepared independently by treating a solution of 1.3 g of benzoic acid in 20 ml of ether with 1.0 g of *tert*-butylamine. The white precipitate that formed, mp 221–23°, was identical in all respects with a sample obtained from the photolysis of **3**. A mixture melting point was undepressed at 221°.

The remaining oil was subjected to liquid–liquid partition chromatography.[48] The optical density trace showed four peaks. The first and second peaks were combined and after the usual processing were distilled to afford 0.028 g (5%) of a clear yellow oil. The structure of this oil was assigned as *N*-*tert*-butylbenzalimine on the basis of the following observations. The infrared spectrum (CCl_4) showed bands at 3.44, 6.09, 6.92, 7.33, 7.38, 8.16, 10.34, 10.97, and 11.68 μ. The nmr spectrum (CCl_4) exhibited a singlet at τ 1.83 (1 H), a multiplet at 2.71 (5 H), and a singlet at 8.75 (9 H). This structure was further confirmed by an independent synthesis from benzaldehyde and *tert*-butylamine using the procedure of Campbell.[51] To 73 g (1.0 mol) of *tert*-butylamine at 0° was added, with stirring, 106 g (1.0 mol) of benzaldehyde over a period of 2 hr. Crushed potassium hydroxide pellets were added to the mixture which was then allowed to stand until two layers separated (*ca.* 30 min). The upper layer was removed and distilled over potassium hydroxide pellets under reduced pressure to give *N*-*tert*-butylbenzalimine as a colorless oil, bp 47–8° (0.6 mm). This material was identical in all respects with the sample obtained from the irradiation of **3**. The third and largest peak from the liquid–liquid partition chromatogram afforded 0.45 g (51%) of a white solid. Recrystallization from methanol–water gave 2,5-diphenyloxazole (**5**) as white needles, mp 71.5–72°. The structure of this component was demonstrated by comparison with an authentic sample. The last fraction from the chromatography was identified as benzaldehyde (3%) by comparison with an authentic sample.

Preparation of *trans*-*N*-*tert*-Butyl-2-phenyl-3-benzoylaziridine-*2-d*$_1$ (7). The desired trans-deuterated aziridine **7** was prepared using the same sequence of reactions as was used for the preparation of aziridine **4**. To a solution of 11.6 g of sodium hydroxide in 104 ml of water and 65 ml of 95% ethanol was added 27.3 g (0.23 mol) of acetophenone and 24.0 g (0.23 mol) of benzaldehyde-*d*$_1$.[52] The mixture was maintained at *ca.* 25° for 5 hr, and then kept at 0° for 4 days. The yellow solid that formed was filtered, washed with water, and dried to give *trans*-benzalacetophenone-β-*d*$_1$ as a light

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(48) H. A. Zimmerman and D. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(49) When **6** was subjected to liquid–liquid partition chromatography using deuterium oxide in place of water in the phase formulations, no incorporation of deuterium into **6** could be detected by nmr analysis.

(50) When **6** was irradiated in pentane in the presence of deuterium oxide, an nmr analysis of the **6** isolated indicated no deuterium incorporation had occurred at any position.

(51) R. Campbell, *J. Amer. Chem. Soc.*, **66**, 82 (1944).

(52) D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).

yellow solid, mp 54–55°. The deuterium content at the *β* position was estimated to be at least 95% from the nmr integration and mass spectral analysis.

To a mixture of 26.25 g (0.13 mol) of *trans*-benzalacetophenone-*β*-d_1 and 32 g (0.13 mol) of iodine in 800 ml of anhydrous ether was added slowly 67 ml of *tert*-butylamine (0.65 mol) in 100 ml of anhydrous ether. After the addition the reaction mixture was stirred for an additional 2 hr at room temperature. The precipitated *tert*-butylamine hydriodide was removed by filtration and the filtrate was washed with four portions of distilled water and then dried over sodium sulfate. Evaporation of the solvent under reduced pressure afforded a viscous brown oil. Fractional crystallization of the oil from pentane afforded *cis*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine-*2*-d_1, mp 107–108°, as the first crop. The infrared spectrum (potassium bromide pellet) showed bands at 3.44, 5.95, 6.29, 6.94, 8.19, 9.53, 9.84, 10.11, 11.42, 13.24, 13.70, 13.97, 14.35, and 14.59 μ. The nmr spectrum (CDCl$_3$) exhibited a multiplet centered at τ 2.61 (10 H), a singlet at 6.72 (1 H), and a singlet at 8.88 (9 H). The mass spectrum showed a molecular ion at *m/e* 280.

Further cooling of the mother liquors afforded *trans*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine-*2*-d_1 (**7**), mp 69.5–70.5°. The infrared spectrum (potassium bromide pellet) was characterized by bands at 3.42, 6.01, 6.27, 6.93, 7.25, 7.35, 8.04, 8.28, 8.49, 9.71, 9.83, 11.36, 13.50, 14.03, 14.31, and 14.57 μ. The nmr spectrum (CDCl$_3$) showed a multiplet centered at τ 2.60 (10 H), a singlet at 6.78 (1 H, PhCOCH), and a singlet at 8.83 (9 H). The mass spectrum of **7** showed the molecular ion at *m/e* 280.

Preparation of *trans-N-tert*-Butyl-2-phenyl-3-benzoylaziridine-*3*-d_1 (8). To a mixture of 26.25 g (0.13 mol) of *trans*-benzalacetophenone-*α*-d_1[53] and 32 g (0.13 mol) of iodine in 800 ml of anhydrous ether was added slowly 67 ml of *tert*-butylamine-*N,N*-d_2 (0.65 mol). After the addition, the reaction mixture was allowed to stir for an additional 2 hr. The precipitated *tert*-butylamine hydroiodide was removed by filtration and the filtrate was washed with two portions of deuterium oxide and dried over sodium sulfate. Evaporation of the solvent *in vacuo* afforded a viscous brown oil which was subject to fractional crystallization in pentane. The first crop of material isolated was identified as *cis*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine-*3*-d_1, mp 107–108°. The infrared spectrum (potassium bromide, pellet) was characterized by bands at 3.41, 5.96, 6.89, 7.15, 7.33, 7.52 8.11, 8.46, 9.60, 9.77, 10.73, 13.14, 13.50, and 14.29 μ. The nmr spectrum (CDCl$_3$) exhibited a multiplet centered at τ 2.35 (10 H), a singlet at 6.56 (1 H), and a singlet at 8.85 (9 H). The mass spectrum showed the molecular ion at *m/e* 280.

The more soluble trans isomer (**8**), mp 69.5–70°, crystallized in the later fractions. The infrared spectrum (potassium bromide pellet) showed absorption at 3.42, 6.01, 6.92, 7.16, 7.36, 7.60, 7.83, 8.13, 8.49, 9.42, 9.75, 10.65, 10.78, 10.99, 13.12, 13.40, 14.09, 14.29, and 14.55 μ. The nmr spectrum (CDCl$_3$) was characterized by a multiplet centered at τ 2.34 (10 H), a singlet at 6.12 (1 H, C*H*Ph), and a singlet at 8.83 (9 H). The mass spectrum had a molecular ion at *m/e* 280 and prominent peaks at 77, 105, 118, 167, 207, 222, and 223.

Irradiation of *trans*-1-*tert*-Butyl-2-phenyl-3-benzoylaziridine-*2*-d_1 (7). A 0.9-g sample of **7** in 1 l. of pentane was irradiated with a 450-W Hanovia mercury lamp with a Pyrex filter for 5 hr. The solvent was removed under reduced pressure to give a viscous brown oil which was chromatographed on a liquid–liquid partition column. In addition to *tert*-butylammonium benzoate (3%) *N*-*tert*-butylbenzalimine (22%) was isolated from the first peak. The second peak in the chromatogram was identified as (*β*-*tert*-butyalmino)-*trans*-benzalacetophenone (**6**) (11%). Analysis of the nmr spectrum of **6** indicated that the molecule had lost essentially all the deuterium (>98%). The third fraction consisted of 2,5-diphenyloxazole (65%) while the fourth fraction was identified as benzaldehyde (8%).

Irradiation of *trans*-1-*tert*-Butyl-2-phenyl-3-benzoylaziridine-*3*-d_1 (8). A solution of 0.40 g of **8** in 1 l. of pentane was irradiated with a 450-W Hanovia mercury lamp and a Pyrex filter for 10 hr. The solvent was removed *in vacuo* to give a brown oil which was subjected to liquid–liquid partition chromatography. The first fraction of the liquid–liquid partition chromatogram consisted of *N*-*tert*-butylbenzalimine (6%). The second fraction afforded (*β*-*tert*-butylamino)-*trans*-benzalacetophenone (**6**) (43%). Analysis of the nmr spectrum of this material indicated that it contained less than 15% deuterium in the *α* position. The third fraction consisted of 2,5-diphenyloxazole (48%) whereas the last fraction contained benzaladehyde (4%). In addition, *tert*-butylammonium benzoate (30%) was isolated from the crude reaction mixture.

Irradiation of (*β*-*tert*-Butylamino-)-*trans*-benzalacetophenone-*α*,*N*-d_2 (6). A mixture of 2.0 g of benzoylphenylacetylene and 20 ml of *tert*-butylamine-*N,N*-d_2 was allowed to stir at 45° for 6 hr under a nitrogen atmosphere. Evaporation of the *tert*-butylamine under reduced pressure afforded a white solid which was recrystallized from heptane–benzene to give (*β*-*tert*-butylamino)-*trans*-benzalacetophenone-*α*,*N*-d_2 (**6**) as white prisms, mp 115–116°. The isotopic purity of the compound at the *α* and *N* positions was demonstrated to be >99% by nmr analysis. The mass spectrum showed a parent ion at *m/e* 281.

A 0.5-g sample of **6** in 1 l. of dry pentane was irradiated with a 550-W Hanovia mercury arc lamp using a Pyrex filter. The solution was flushed with nitrogen prior to irradiation and a positive pressure maintained throughout the irradiation. After 7 hr an aliquot was withdrawn and analyzed by nmr spectroscopy. The nmr spectrum was identical with that of starting material except for the appearance of two signals at τ -1.66 (N-*H*, *ca.* 0.6 H) and 4.46 (PhCOC*H*, *ca.* 0.6 H). If the irradiation was allowed to proceed for 10 hr both signals increased to approximately 1 H. A control experiment demonstrated that when 0.5 g of pure **6** in 1 l. of dry pentane was stirred in the dark for 20 hr essentially all the deuterium (>85%) was retained in the *α* position (by nmr analysis).

Coirradiation of *trans*-Aziridines 4 and 7. A mixture of 0.125 g of *trans*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine (**4**) and 0.125 g of *trans*-1-*tert*-butyl-2-phenyl-3-benzoylaziridine-*2*-d_1 (**7**) in 1 l. of pentane was irradiated with a 450-W mercury arc lamp using a Pyrex filter. After 19 min the solvent was removed under reduced pressure and the resulting oil was analyzed by nmr spectroscopy using nitromethane as the internal standard. The ratio of the peaks at τ 6.73 (C*H*COPh) and 6.21 (C*H*Ph) was determined to be 3:1. This result indicated that aziridine **4** is disappearing twice as fast as deuterated aziridine **7**. Irradiations were taken to 75% completion.

Irradiation of *cis*- and *trans*-1,3-Diphenyl-2,3-epoxy-1-propanone (10 and 11). The isomeric *cis*- and *trans*-1,3-diphenyl-2,3-epoxy-1-propanones (**10** and **11**) used in this study were prepared according to the general procedure of Wasserman and Aubrey.[45] The ultraviolet spectra (cyclohexane) of the cis isomer had a maximum at 322 mμ (ϵ 90) whereas the trans isomer had a maximum at 326 mμ (ϵ 197). To be sure that each epoxide absorbed >99% of the light the epoxide concentrations were set at 0.033 *M* in benzene. A 50-ml sample of each solution was placed in a 1.5 × 30 cm quartz tube. The tube was flushed with a stream of nitrogen and sealed under a nitrogen atmosphere. Irradiations were carried out using the "merry-go-ground" assembly equipped with a central 550-W Hanovia mercury arc lamp inside a water-cooled quartz immersion well fitted with a Pyrex filter sleeve. Light intensities were monitored by benzophenone–benzhydrol actinometry. After 13.3 hr of irradiation the solvent was evaporated under reduced pressure and the residue was analyzed by nmr spectroscopy using 2,5-dimethyl-2,4-hexadiene as an internal standard. The results indicate that the trans isomer (**11**) gave dibenzoylmethane ($\Phi = 0.017$) at a faster rate than the cis isomer (**10**) ($\Phi = 0.004$).

Quantum Yield Determinations. Quantum yield measurements were carried out on a rotating "merry-go-round" assembly using a Hanovia Type L-450-W mercury arc lamp as the central light source. Samples sealed in ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a cooled solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate/100 ml of water[54] through the cooling jacket of the quartz immersion well. This solution permitted light of the following wavelength distribution to pass through: 5% 2537 Å, 20% 3025 Å, and 10% 3340 Å. Studies were made at room temperature unless otherwise indicated. Samples placed in 13 × 150 mm Pyrex or quartz culture tubes were degassed to a pressure of 1 μ or less in three freeze-outgas-thaw cycles, and then sealed under vacuum. Benzophenone–benzhydrol actinometry was used to determine the lamp intensity. An actinometer quantum yield of 0.69 was chosen when the concentration of benzophenone and benzhydrol in benzene was 0.1 *M*.[55] Reliably reproducible output rates of 3.56×10^{16} quanta

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(53) D. S. Noyce, G. L. Woo, and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **83**, 1162 (1961).

(54) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(55) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

sec^{-1} were recorded. After the irradiation the degree of reaction was determined either by quantitative ultraviolet spectroscopy, nmr spectroscopy, or vapor phase chromatography (6 ft × 0.25 in. 10% SE-30 methylsilicone gum rubber on Diatoports at 243°). The conversions in the aziridine series were run to 15% or less. The mass balance in these runs was generally better than 95%.

Phosphorescence Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using EPA (ethyl ether–isopentane–ethanol 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All compounds having relatively long radiative lifetimes were recorded on a X–Y plotter. Samples having short radiative lifetimes (<100 msec) were measured by photographing the decay curve on an oscillograph. The chopper was rotated manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted *vs.* time and the slope of the line at a logarithmic value of 2.303 gave the mean lifetime (T_0).

Electron Paramagnetic Resonance Spectra. Electron paramagnetic resonance spectra were measured using a Varian X-band (Model *V*-4502) spectrometer having a modulation frequency of 100 KHz. Spectra were recorded with the rf magnetic field perpendicular to the static field. The sample solutions were sealed in 4-mm o.d. quartz tubes after degassing on a vacuum line. The sample was irradiated in a slotted face Varian *V*-4531 cavity. Light from a 450-W (Hanovia, type L) mercury arc lamp was focused through a quartz optical system. The sample was cooled by a flow of cold nitrogen gas which was passed through a heat-exchange coil submerged in liquid nitrogen.

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Reactions of the Hydrogen Atom in Solution. III. The Photolysis of Thiols. Studies of Tritium-Labeled Thiols[1-3]

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Abstract: Propanethiol, tritiated at the S–H bond, has been photolyzed in the presence of various organic hydrogen donors (QH). Tritium becomes incorporated both into the thiol side chain and into QH. A relation is derived between the rate of formation of labeled QH (*i.e.*, d(QT)/d*t*) and the rate constant k_H for the reaction $H\cdot + QH \rightarrow H_2 + Q\cdot$. In order to avoid errors produced by changes in light flux from run to run, the rate of formation of QT is measured relative to the rate of formation of side-chain labeled thiol. This method gives correct values of k_H for alkanes where the Q–H bond being broken is much stronger than the RS–H bond. Compounds such as toluene which contain weak C–H bonds give spuriously high values of k_H. For these compounds the thiyl radical, and possibly also the carbon radical resulting from hydrogen abstraction from the side chain of the thiol, are able to convert QH to $Q\cdot$. The isotope effect k_T/k_H for the reaction of $Q\cdot$ with RSH or RST must be known before values of k_H can be calculated; this isotope effect can be evaluated directly in independent measurements and data are presented for several $Q\cdot$ radicals.

The nature and reactivity of the hydrogen atom is inherently of great interest. Relative rate constants for the reaction of hydrogen atoms with a range of water soluble substances have been obtained from the radiolysis of aqueous solutions, and these relative rate constants can be put on an absolute basis using pulse radiolysis techniques.[4] The hydrogen atom has also been studied in the gas phase.[5] It is desirable to obtain rate constants for the reaction of hydrogen atoms with organic hydrogen donors in organic solutions. In other papers in this series, we have reported methods for obtaining these data.[2] In this paper, we report our earliest attempt[3] to discover a kinetic system which would lead to values of k_H, the rate constant for reaction I. The method we report here is the photolysis of

$$H\cdot + QH \xrightarrow{k_H} H_2 + Q\cdot \qquad (I)$$

mixtures of an aliphatic thiol which is tritiated at the S–H bond and an organic hydrogen donor QH. Tritium becomes incorporated into the donor, and the rate of formation of QT can be related to the rate constant for reaction I. As we have shown elsewhere,[2a-c] this method gives reliable values of k_H for cases where the Q–H bond is much stronger than the RS–H bond, as, for example, is true in the alkanes. This system gives spurious results, however, for QH compounds with weak bonds; in these cases the thiyl radical $RS\cdot$ also is

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