bands at 3.48, 4.52, 4.77, 5.98, 6.90, 7.35, 8.20, 9.93, 13.00, 13.43, and 14.40 μ. The nmr spectrum ($CDCl_3$) exhibited a singlet at τ 9.1 (9 H), doublets at τ 5.80 (1 H, J = 9.0 Hz) and 5.08 (1 H, J = 9.0 Hz), and a multiplet centered at τ 2.82 (10 H). The mass spectrum showed the parent ion at m/e 295, and major peaks appeared at m/e 57, 72, 77, 105, 119, 134, 146, 238, and 280.

Epimerization of 10 to *trans*-1-*t*-Butyl-2-phenyl-3-benzoylazetidine-4,4-d_2 (11). The dideuterated *trans*-azetidine **11** was prepared by epimerization of the *cis* isomer. To 50 ml of a 0.01 *M* sodium methoxide solution was added 1.50 g of **10** and the resulting solution was allowed to reflux for 5 hr. At the end of this time the mixture was diluted with water and extracted with benzene. The benzene solution was dried over sodium sulfate and the solvent was removed under reduced pressure. Recrystallization from heptane gave **11** as colorless needles, mp 59–60°. The infrared spectrum exhibits bands at 5.98, 8.10, 9.93, 10.20, 11.85, 12.92, 13.13, and 14.32 μ. The nmr spectrum ($CDCl_3$) showed a singlet at τ 9.08 (9 H), doublets at τ 6.25 (1 H, J = 7.0 Hz) and 4.35 (1 H, J = 7.0 Hz), and a multiplet centered at τ 2.53 (10 H). The mass spectrum showed the parent ion at m/e 295, and major peaks at m/e 57, 72, 77, 105, 119, 146, 238, and 280.

***cis*-N-*t*-Butyl-2-phenyl-3-benzoylazetidine-2-d_1 (12).** A mixture of 38 g (0.283 mol) of propiophenone and 30 g (0.283 mol) of benzaldehyde-1-d[28] was cooled to 0° and saturated with anhydrous hydrogen chloride gas. After standing for 35 hr at 10°, the mixture was diluted with 200 ml of benzene and the aqueous layer was discarded. The organic layer was concentrated and the residue heated to reflux for 1 hr in 500 ml of methanol containing 7 g of sodium methoxide. The solvent was removed and the semisolid residue was extracted with 50 ml of hot heptane. Distillation of the heptane residue afforded *trans*-α-methyl chalcone-β-d_1 as a light yellow oil, bp 150–155° at 0.1 mm. The infrared spectrum was similar to *trans*-α-methyl chalcone except for new bands at 7.55 and 7.70 μ. The nmr spectrum (CCl_4) showed a complex multiplet centered at τ 2.50 (10 H) and a singlet at τ 7.89 (3 H).

The desired *cis*-monodeuterated azetidine **12** was obtained from the unsaturated ketone by the same sequence of steps as was used in the preparation of **10**. The nmr spectrum of **12** ($CDCl_3$) showed multiplets centered at τ 2.52 (10 H), 5.71, 6.02, and 6.03 (3 H), and a singlet at τ 9.08 (9 H). The infrared spectrum exhibited bands at 3.41, 5.95, 6.95, 7.40, 8.18, 9.55, 10.56, 13.00, 13.35, and 14.35 μ. The deuterium content was determined as 98.2% by a deuterium falling drop analysis. This was further verified by a mass spectral analysis which showed the parent ion at m/e 294. The spectrum also contained major peaks at m/e 57, 77, 105, 119, 113, 147, 237, and 279.

Epimerization of 12 to *trans*-N-*t*-Butyl-2-phenyl-3-benzoylazetidene-2-d_1 (13). The *trans* isomer was obtained from **12** by the same procedure used for the epimerization of **10**. The infrared spectrum showed bands at 3.45, 7.01, 6.96, 7.43, 8.20, 10.75, 13.01, 13.70, and 14.31 μ. The nmr spectrum ($CDCl_3$) showed multiplets centered at τ 2.54 (10 H) and 6.42 (3 H) and a singlet at 9.08 (9 H). The mass spectrum showed the parent ion at m/e 294. The spectrum also contained major peaks at m/e 57, 70, 77, 105, 119, 147, 237, and 279.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-9385) and the Alfred P. Sloan Foundation.

---

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

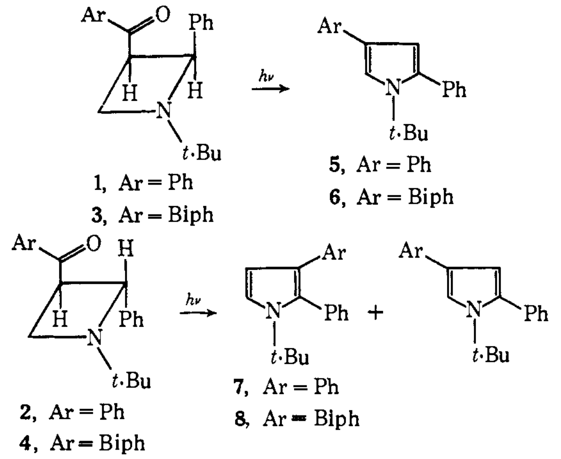
The Photoinduced Ring Expansion of Arylaroylazetidines. Mechanistic Studies and Characterization of the Excited State[1]

Albert Padwa[2] and Robert Gruber

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214.
Received June 6, 1969

Abstract: The photochemical rearrangement of arylaroylazetidines to diarylpyrroles was examined in mechanistic detail. The quantum efficiency of the photoreaction was low (Φ = 0.046) and increased slightly with deuterium substitution in the azetidine ring. Sensitization and emission studies indicate that the reaction is derived from the lowest 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 proton transfer and electron reorganization accounts for the observed rearrangement patterns. Reversal of hydrogen transfer rationalizes both the deuterium isotope effects and the low quantum efficiency of the reaction.

Under the influence of ultraviolet light, arylaroylazetidines undergo deep-seated rearrangements to diarylpyrroles. The previous paper[3] described the products of photolysis of *cis*- and *trans*-N-*t*-butyl-2-phenyl-3-benzoylazetidine (**1** and **2**). One of the most intriguing aspects of the reaction is the specificity of the rearrangement, leading to one primary product from *cis* starting material and a mixture of two primary products from the *trans* isomer. Investigations on the scope of the rearrangement and attempts to correlate some of our findings with new results in the rapidly growing



1, Ar = Ph
3, Ar = Biph
5, Ar = Ph
6, Ar = Biph
2, Ar = Ph
4, Ar = Biph
7, Ar = Ph
8, Ar = Biph

---

[1] Part XXIII of a series on the photochemical transformations of small ring carbonyl compounds.

[2] Alfred P. Sloan Foundation Research Fellow, 1968–1970.

[3] Previous paper, part XXII: A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, 92, 100 (1970).

field of photolysis of small-ring heterocyclic compounds[4] have been made. The possible connection between this photorearrangement and the photochemistry of acyclic α-amino ketones was pointed out earlier,[5] and investigations on this reaction have been designed to shed some light on this hypothesis. The data which follow allow postulation of a complete mechanistic scheme for these unusual photorearrangements.

Results

Quantum Yield Determinations. The absorption spectra of benzoylazetidines **1** and **2** in hydrocarbon solvents showed the $n-\pi^*$ band at 320–350 mμ (78 kcal/mol estimated for 0–0). A decided blue shift in more polar hydroxylic solvents was observed. This and the relatively low extinction coefficients (*ca.* 130) clearly are consistent with the $n-\pi^*$ singlet transition assignment.[6] The $\pi-\pi^*$ transition is at 246 mμ (115 kcal/mol) and consequently the $n-\pi^*$ singlet is the lowest energy state of this multiplicity. Since there was no evidence in the ultraviolet, infrared, or nmr spectra of the benzoylazetidines for interaction between the amino and carbonyl functions,[7] we assume that the lowest triplet state is mostly $n-\pi^*$ in character as are those of other phenyl alkyl ketones.[8–12] This aspect will be considered later. Filters were used in all irradiations which effectively removed all light below 310 mμ and that above 360 mμ.

The quantum yields for the appearance of products in several solvents were determined by using benzophenone–benzhydrol actinometry.[13] Degassed and sealed Pyrex tubes containing solutions of the azetidines were irradiated along with actinometer tubes in the rotating photochemical assembly. The light from a 450-W Hanovia lamp was filtered through a nickel–cobaltous sulfate solution (transmission 300–340 mμ). Reactions were carried to low conversions to prevent appreciable light absorption by the products and yields of products were determined by glpc using internal standards (Table I). The quantum yields for formation of the biphenylpyrroles are also included in Table I. The results of these runs show the average quantum yield for pyrrole formation to be very low (0.046).

Table I. Quantum Yield Data for Product Formation at 3130 Å[a]

Reaction	Solvent	Conversion,[b] %	Φ
1 → **5**	Pentane	6	0.046
	95% ethanol	9	0.046
	Methanol	12	0.039
2 → **5** + **7**	Pentane	10	0.040
	95% ethanol	8	0.043
	Methanol	13	0.042
3 → **6**	95% ethanol	8	0.045
4 → **6** + **8**	95% ethanol	6	0.045

[a] Irradiation conditions, azetidine concentration 1.48 × 10^{-2} *M*, lamp intensity, 0.486 × 10^{17} quanta sec. [b] Analysis by glpc on $^1/_4$ in. × 6 ft 10% SE-30 on Diatoport-S. Benzalazine was used as the internal standard and was added after irradiation.

Table II. Irradiation of *cis*- and *trans*-N-*t*-Butyl-2-phenyl-3-benzoylazetidine (**1** and **2**). Sensitization and Quenching Studies[a]

Reactant[b]	Additive	Quantum yield[d]
cis		0.046
cis	Acetophenone (3.45 *M*)[c]	0.048
cis	Naphthalene (5 × 10^{-2} *M*)[e]	0.046
cis	1,3-Cyclohexadiene (2.0 *M*)	0.045
cis	1,3-Cyclohexadiene (10.5 *M*)	0.037
cis	Piperylene (neat)	0.050
cis	Biacetyl (0.05 *M*)	0.037
cis	Ferric dipivaloylmethide	0.046
trans		0.043
trans	Acetophenone (3.45 *M*)[c]	0.045
trans	Naphthalene (0.1 *M*)[e]	0.038
trans	Biacetyl (0.05 *M*)	0.038
trans	Piperylene (neat)	0.046

[a] All runs at 25°; irradiation conditions described in the Experimental Section. [b] Azetidine concentration was 1.5 × 10^{-2} *M* in 95% ethanol. [c] Absorbing over 98% of incident light. [d] Average of pyrrole formation for three runs. [e] Absorbing negligible light.

Sensitization and Quenching Studies. Quantum yields for acetophenone sensitized runs were determined in 95% ethanol. The concentrations were adjusted so that acetophenone absorbed more than 98% of the light. The concentration of azetidine was kept sufficiently low (1.5 × 10^{-2} *M*) to ensure unimolecular destruction of acetophenone excited singlet molecules prior to collision with ground state azetidine, yet sufficiently high to guarantee collision of acetophenone triplets with azetidine at a rate faster than acetophenone decay.[14] Under these conditions the photorearrangement of azetidines **1** and **2** proceeds with its usual quantum efficiency. The results of these runs are collected in Table II. Were the acetophenone, which is absorbing essentially all of the light in the sensitized runs, wasting this energy, then the quantum yields in these runs would be zero. This is not the case and we can conclude that an acetophenone excited state is transferring its energy to the azetidine. Furthermore, the intersystem crossing efficiency of acetophenone is known to be unity.[15] Since the quantum yield of photoproducts in the sensitization runs is the same as in the direct photolysis, we can conclude that the very low quantum efficiency of the azetidine rearrangement is not attributable to poor intersystem crossing in **1** and **2**. Whatever inefficient steps detract from the quantum yield, it must come after intersystem crossing.

The formation of the usual products starting with preformed triplet (*i.e.*, in the sensitized runs) shows that rearrangement by the triplet is possible. Most importantly, the product distribution of the pyrroles obtained from *trans*-azetidine **2** in the sensitized runs is the same

---

(4) For a review see A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 92.

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

(6) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 179–187.

(7) Such transannular interactions have been found in cyclic amino ketones; N. J. Leonard, D. F. Morrow, and M. T. Rogers, *J. Amer. Chem. Soc.*, **79**, 5476 (1957).

(8) A. A. Lamola, *J. Chem. Phys.*, **47**, 4810 (1967).

(9) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

(10) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenberg, *ibid.*, **89**, 5466 (1967).

(11) R. D. Rauh and P. A. Leermakers, *ibid.*, **90**, 2246 (1968).

(12) J. N. Pitts, D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5902 (1968).

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

(14) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 3080 (1963).

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

within experimental error as in the direct photolysis. The literature contains reports which are very relevant to these observations. Zimmerman has noted that identical product distributions and similar quantum efficiencies under both triplet sensitization and direct irradiation conditions provides for a "fingerprint".[16] He has argued that the failure of the product distribution to change with sensitization can be taken to mean that only one species is involved in the direct and sensitized photolysis. This deduction was based on the assumption that the singlet product distribution should be appreciably different from that of the triplet state. We conclude from our observations that the triplet state of azetidines **1** and **2** is the state responsible for the rearrangement in the direct irradiation. This is certainly not unreasonable since it is known that phenyl ketones have very high intersystem crossing efficiencies.[17]

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. Irradiation of **1** in ethanol solution containing piperylene, or in neat piperylene as solvent, was studied (Table II). On the basis of the ultraviolet spectrum of piperylene, it can be shown that this diene was absorbing only a minimal portion of the incident light under the conditions employed. The results clearly indicate that the photolysis of **1** is not quenched by piperylene. It was also found that 0.05 and 0.1 *M* naphthalene produced no diminution of the quantum yield beyond experimental error. Similarly, the photolysis of **2** could not be quenched by piperylene, naphthalene, or high concentrations (2.0 *M*) of 1,3-cyclohexadiene.[18] The failure to quench implies that rearrangement of the triplet is too rapid for diffusion of the excited state to quencher molecule. A similar situation has been encountered in the diphenylcyclohexadienone system by Zimmerman and Swenton.[21]

To provide complementary evidence that the triplet states of the azetidines rearrange too rapidly to be quenched, we have attemped to utilize the azetidines as triplet sensitizers. Triplet counting by the technique of Lamola and Hammond[22] depends on the comparison of the rates of photoisomerization of a *cis*-olefin using benzophenone as sensitizer and the compound in question (*i.e.*, azetidine) as sensitizer. The technique used in these triplet counting experiments assumes that the triplets being "counted" exist long enough for near diffusion-controlled quenching by the olefin to be the major reactive pathway. This is the case with the standard, benzophenone, which has a lifetime on the order of 10^{-6} sec. Experimentally, a solution 0.5 *M* in azetidine (**1** or **2**) and 0.1 *M* in *cis*-stilbene was irradiated for 1 hr with 3130-Å light. The conditions were chosen such that over 98% of the incident light at 3130 Å was absorbed by the azetidine. Under these conditions an insignificant amount of isomerization occurred while photorearrangement 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 40% isomerization to the *trans* isomer. This result demonstrates that some other triplet consuming process, such as photorearrangement, is competitive with energy transfer.

Conservatively assuming that 20% quenching of azetidine **1** or **2** would have been observed with 2.0 *M* 1,3-cyclohexadiene and assuming diffusion-controlled quenching with a rate of diffusion in ethanol of 5×10^9 l. mole^{-1} sec^{-1},[23] we can estimate a lower limit for the rate of rearrangement of azetidine triplet by using eq 1.

$$\phi_q/\phi_0 = [kr + kd]/[kr + kd + kq[Q]] \qquad (1)$$

In this equation ϕ_0 represents the unquenched quantum yield, ϕ_q is the quantum yield with quencher present, [Q] is the concentration of quencher, kd is the unimolecular rate of triplet decay, and kr is the estimated rate of triplet reaction. Solution of eq 1 indicates a minimum value of 4.0×10^{10} sec^{-1} for $(kr + kd)$. Taking the triplet quantum yield of pyrrole as 0.046 and equating this to $kr/(kr + kd)$, we obtain $kd = 20Kr$ and a value of $kr > 1.8 \times 10^9$ sec^{-1}. Since this is a very conservative lower limit it is likely that the rate of azetidine to pyrrole rearrangement is 10^{10} sec^{-1} or greater. What is most surprising is that although the excited state rearranges at a particularly rapid rate, the quantum efficiency is so low. That a ketone with a triplet lifetime of only *ca.* 0.25×10^{-10} sec should react with only 4% quantum efficiency is rather remarkable, since there are no known physical mechanisms for such rapid radiationless decay of excited states. We suspect that the inefficiency of the reaction is due to the occurrence of trivial chemical processes. This aspect will be considered in some detail at a later point in the Discussion.

Phosphorescence Emission Studies. Although the lowest energy singlet state of benzoylazetidines **1** and **2** is n–π*, as evidenced by absorption data, this is not necessarily true for the corresponding triplets. In order to demonstrate conclusively that the *n*–π* state is the lowest triplet energy state, we have examined their phosphorescence emission in a rigid glass at 77°K. The emission data were determined in an EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) glass and are recorded in Table III. We note that the 0–0 bands of **1** and **2** correspond to a triplet energy of *ca.* 74 kcal/mol. The vibrational spacing between the 0–0 and 0–1 band is typical of emission from a n–π* triplet state.[24] The lifetime of the triplet of **1** (or **2**) was approximately 50 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.[25]

Deuterium substitution has proved a useful technique to slow down the nonradiative deactivation process,

---

[16] H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968); H. E. Zimmerman and R. L. Morse, *ibid.*, 90, 954 (1968); H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, 90, 4892 (1968).

[17] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

[18] The triplet energy of azetidines 1 and 2 is *ca.* 74 kcal/mol while that for 1,3-cyclohexadiene is 54 kcal/mol.[19] Triplet transfer that is exothermic by more than 4 kcal/mol is diffusion controlled.[20]

[19] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

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

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

[22] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[23] F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

[24] M. Kasha, *Radiation Res. Suppl.*, **2**, 265 (1960).

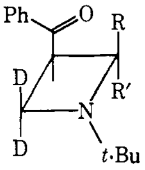
[25] H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

Table III. Triplet Emission of Aroylazetidines[a]

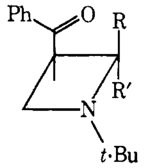
Compound	E_t, kcal	0–0 band, mμ	Spacings, cm^{-1}	Lifetime, msec	Transition
1	73.5	390	1600	40 ± 10	n-π^*
2	74.0	387	1450	60 ± 10	n-π^*
9	74.5	385	1680	35 ± 10	n-π^*
10	75.5	384	1500	50 ± 10	n-π^*
11	73.5	390	1500	50 ± 10	n-π^*
12	74.5	385	1600	60 ± 10	n-π^*
3	60.5	470	1700	750 ± 10	π-π^*
4	61.0	470	1480	750 ± 10	π-π^*
14	58.8	487	1430	2300 ± 20	π-π^*

[a] Excitation wavelength at 310 mμ; conditions described in the Experimental Section.

thus increasing the lifetime of an excited state.[17] Our experiments with deuterated azetidines **9–12** show that the lifetime of the triplet state is not significantly dependent on isotopic substitution. We cannot offer a simple explanation for this result but can note similar negative results in the literature.[26,27] It appears that these deuterated azetidines also possess the n–π* configuration as their low-lying triplet energy state.



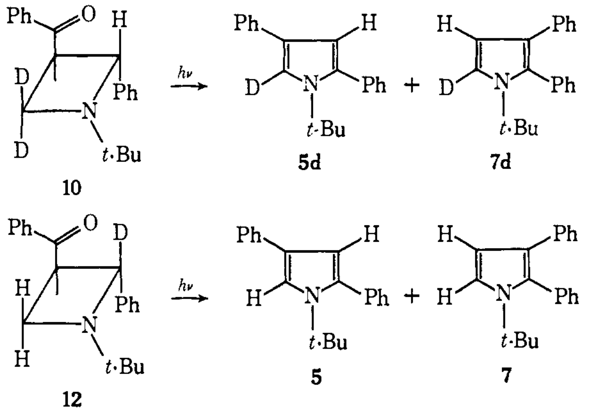
9, R = Ph, R' = H (*cis*)
10, R = H, R' = Ph (*trans*)



11, R = Ph, R' = D (*cis*)
12, R = D, R' = Ph (*trans*)

One experiment of interest was the irradiation of azetidine **1** (or **2**) in EPA at 77°K. A control run was also made in the same solvent at room temperature. Although diphenylpyrrole **5** 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.[21] 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.[28,29]

Deuterium Isotope Effects. Substitution of hydrogen with deuterium in organic compounds may exert a marked effect on certain properties of their excited states.[30–33] Theory predicts that deuterium should decrease the rate of T′ → S° and S′ → S° radiationless transitions.[34] 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.[35,36] Since information concerning radiationless decay paths of the benzoylazetidines under investigation is essential for a detailed understanding of the mechanism of these rearrangements, we were prompted to investigate the photochemical behavior of deuterated azetidines **9–12**. Of specific concern was what effect deuterium substitution had on the quantum efficiency and distribution of photoproducts of the *trans* isomers **10** and **12**.



The labeled azetidines **9–12** were synthesized *via* the method described in the preceding paper. The distribution of the diphenylpyrroles (**5** and **7**) and the quantum yields of formation of individual products were followed by quantitative gas chromatography. Irradiations were performed on degassed ethanol solutions at 3130 Å and quantum yields were determined by benzophenone–benzhydrol actinometry. The reproducibility was found to be better than ±0.006 on the quantum yield determinations. The 2,3- and 2,4-diphenyl-N-*t*-butylpyrroles were isolated by preparative vpc (or tlc) and analyzed for deuterium content by mass spectrometry. The results are shown in Table IV. The most striking observation noted is that *replacement of hydrogen by deuterium causes a definite change in both the product distribution and quantum yield.*

Table IV. Irradiation Runs of Deuterium Labeled Azetidines

Reactant	Pyrroles, ratio 2,3/2,4	Φ pyrrole
2	2.0 ± 0.05	0.046 ± 0.004
9		0.053 ± 0.003
10	1.4 ± 0.04	0.087 ± 0.006
11		0.051 ± 0.005
12	2.3 ± 0.06	0.065 ± 0.005

Discussion

Considerable information has now been accumulated about the photochemical behavior of a number of arylaroylazetidines. The results of these experiments allow the postulation of a mechanism which rationalizes the experimental observations. The more readily derived facts about the azetidine rearrangement are the following. (a) The rearrangement leads to a single pyrrole from *cis* starting material and to a mixture of two pyr-

---

(26) B. J. Cohen and L. Goodman, *J. Chem. Phys.*, **46**, 713 (1967).

(27) R. S. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 1492 (1969).

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

(29) Similar observations have been observed in a KBr matrix; J. N. Pitts, Jr., J. K. Wan, and E. A. Schuck, *ibid.*, **86**, 3606 (1964).

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

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

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

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

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

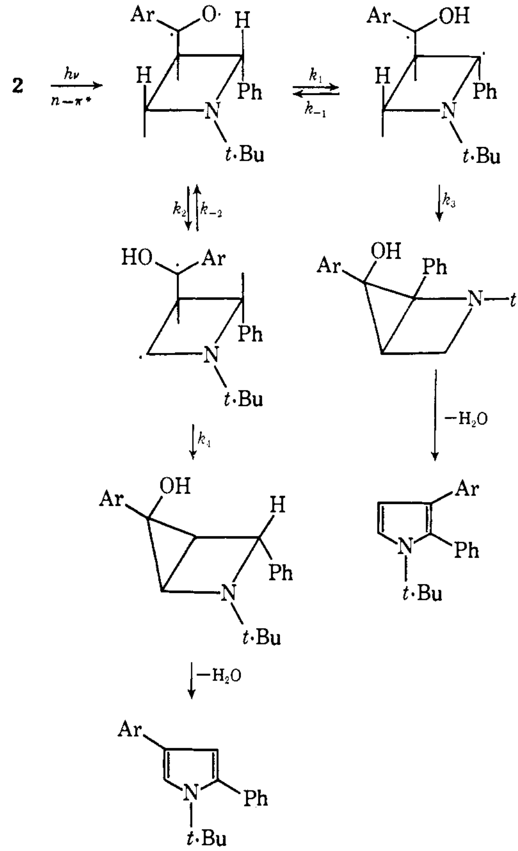
(35) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

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

roles from the *trans* isomer. The distribution of pyrroles appears to favor 2,3-diarylpyrroles over 2,4-diarylpyrroles. The ratio was observed to be *ca.* 2:1 for the case of *trans*-azetidine **2** and varied slightly with deuterium substitution on the azetidine ring. (b) The photorearrangement of several aroyl and deuterio azetidines occurs with a high degree of specificity and pinpoints the location of all the carbon atoms in the pyrrole ring after rearrangement. (c) The quantum efficiency of the rearrangement is low and increases slightly with deuterium substitution on the azetidine ring. (d) Sensitization and emission studies indicate that the reaction is derived from the lowest triplet state and that this state has an n–π* configuration for azetidines **1** and **2**. (e) The lack of quenching indicates that the n–π* state rearranges at a particularly rapid rate.

The simplest mechanism consistent with the observed rearrangement patterns of the substituted azetidines is the one outlined in Scheme I. It is based on the knowledge that hydrogen abstraction of aryl ketones proceeds by way of their *n*–π* triplet state.[37] In this postulated mechanism, intramolecular hydrogen transfer from carbon to the p_y orbital of oxygen of the *n*–π* excited state produces a spin unpaired 1,3-biradical intermediate.[38] Spin inversion followed by ring closure affords a transient azabicyclo[2.1.0]pentane that may readily lose water to give a disubstituted pyrrole.

Scheme I



The fact that the 2,3-disubstituted pyrrole was formed in preference to the 2,4 isomer from the irradiation of *trans*-azetidine **2** is in accord with known trends of relative reactivities of hydrogen atoms toward abstraction by alkoxy radicals. The reactivity of the triplet *n*–π* state is quantitatively similar to that of alkoxy radicals,[39,40] and is consistent with the preference of the reactive triplet of azetidine **2** to abstract the tertiary benzylic hydrogen. Also, the exclusive formation of the 2,4-diphenylpyrrole from the irradiation of the *cis* isomer is fully compatible with the above scheme. In this case the geometry of the ring only allows for abstraction of the methylene hydrogen. This mechanism also satisfactorily explains the rearrangement paths of the deuterio and aroyl-substituted arylazetidines.

Additional evidence in support of this mechanism was obtained from experiments using deuterium-labeled *trans*-azetidines **10** and **12**. The results obtained have been summarized in Table IV. The most significant result is that *replacement of hydrogen by deuterium enhances the amount of ring closure at that position.* This apparent inverse isotope effect is readily rationalized if one assumes that the hydrogen transfer step is predominantly reversible. This suggestion is not without analogy in the literature. The lines of evidence implicating reverse hydrogen transfer in the related Norrish Type II process are based on kinetic data[41,42] and are reinforced by stereochemical,[43,44] thermal,[45] and deuterium isotope effects.[35,36] In our system, the low quantum efficiency of the photoreaction coupled with the failure to quench the triplet suggests that the reverse transfer of hydrogen (or deuterium) back to carbon (rates governed by k_{-2}^{H} or k_{-2}^{D} for azetidine **10** in Scheme I) is faster than spin inversion and ring closure (k_4). Substitution of deuterium for hydrogen retards the reverse transfer (*i.e.*, $k_{-2}^{D} < k_{-2}^{H}$), thereby enhancing ring closure. If indeed k_{-2}^{H}, $k_{-2}^{D} \gg k_4$ and $k_{-1}^{H} \gg k_3$, then the observed ratio of pyrroles obtained from **2** and **10** can be shown to be governed by eq 2 and 3. The resulting

$$\text{ratio } 2,3/2,4\ (\textit{trans}\text{-azetidine } \mathbf{2}) = \frac{k_3 k_1 k_{-2}^{H}}{k_4 k_2^{H} k_{-1}} \qquad (2)$$

$$\text{ratio } 2,3/2,4\ (\textit{trans}\text{-azetidine } \mathbf{10}) = \frac{k_3 k_1 k_{-2}^{D}}{k_4 k_2^{D} k_{-1}} \qquad (3)$$

isotope effect is expressed by eq 4. The term $K^{D}:K^{H}$

$$\frac{\text{ratio } 2,3:2,4\ (\mathbf{2})}{\text{ratio } 2,3:2,4\ (\mathbf{10})} = \frac{k_{-2}^{H} k_2^{D}}{k_2^{H} k_{-2}^{D}} = \frac{k^{H}}{k^{D}}(\text{OH}) / \frac{k^{H}}{k^{D}}(\text{CH}) = \frac{K^{D}}{K^{H}} \qquad (4)$$

is a ratio of two equilibrium constants and its value would be expected to be greater than unity since the zero point energy for the stretching vibration of the OH

---

(37) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Amer. Chem. Soc.*, **83**, 2795 (1961).

(38) Examples of intramolecular hydrogen abstraction proceeding *via* a five-membered transition state are available in the literature; *i.e.*, P. A. Leermakers and G. F. Vesley, *ibid.*, **85**, 3776 (1963); A. Padwa and W. Eisenhardt, *ibid.*, **90**, 2442 (1968).

(39) C. Walling and M. J. Gibian, *ibid.*, **86**, 3902 (1964); **87**, 3361 (1965).

(40) A. Padwa, *Tetrahedron Lett.*, 3465 (1964).

(41) P. J. Wagner, *ibid.*, 1753 (1967); *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

(42) J. A. Barltrop and J. D. Coyle, *Tetrahedron Lett.*, 3235 (1968).

(43) K. H. Schulte-Elte and G. Ohloff, *ibid.*, 1143 (1964).

(44) J. Orban, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, **85**, 3033 (1963).

(45) A. Padwa and E. Alexander, *ibid.*, 90, 6871 (1968).

bond is greater than for the CH bond.[46] The value of the pyrrole ratios ([2,3:2,4(**2**)/2,3:2,4(**10**)] = 1.43) is readily determined experimentally. The magnitude of $K^D:K^H$ can be estimated by considering the dissociation energies of the bonds X–H and X–D (X = O,C).

$$\frac{K^D}{K^H} = \frac{e^{\Delta E_0/RT(OH)}}{e^{\Delta E_0/RT(CH)}}$$

The difference between the two dissociation energies for a given X–H bond is

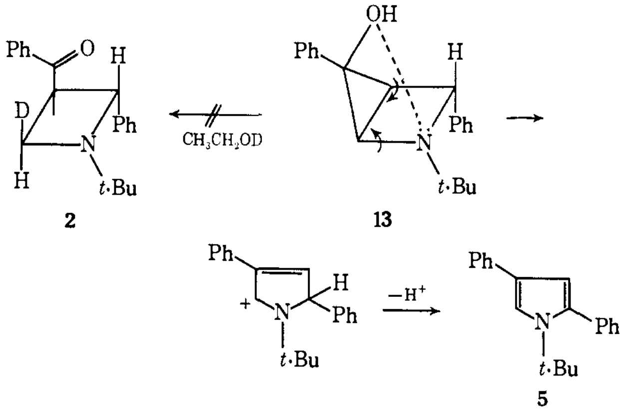
$$\Delta E_0 = E_0 - E_0' = {}^1\!/_2 h(\nu - \nu')$$

where ν and ν' refer, respectively, to the vibrational frequency of the bonds X–H and X–D. The frequencies can in turn be obtained from vibrational spectra.[47] The resulting isotope effect $K^D:K^H$ can now be expressed by eq 5. The theoretically calculated value of 1.54 is

$$\frac{K^D}{K^H} = \frac{e^{1.4/RT}}{e^{1.5/RT}} = \frac{10.6}{6.9} = 1.54 \qquad (5)$$

in excellent agreement with the observed value of 1.43 and is consistent with the mechanism outlined in Scheme I. This scheme would also predict an enhancement in the quantum efficiency of pyrrole formation as hydrogen is replaced by deuterium, exactly as is observed.

The mechanistic scheme outlined above is consistent with the deuterium isotope effects observed. The results indicate that the chemistry of the intermediates in the aroylazetidine rearrangement is complex. Apparently hydrogen transfer, ring closure, and return of an abstracted hydrogen atom to its original site are all competitive processes. Reversal of hydrogen transfer provides a mechanism for radiationless decay of the excited state and accounts for the low quantum efficiency of the reaction. A second way to rationalize the high decay rate is to attribute the inefficiency to reversible opening of the azabicyclo[2.1.0]pentanol.[48] In an elegant series of investigations, Depuy and coworkers have ably demonstrated the facile ring opening of substituted cyclopropanols under a variety of conditions.[49] Despite the fact that reversible ring opening of the transient azabicyclopentanol could occur, it appears as though this reactive species prefers to lose a molecule of water. This was demonstrated from experiments using ethanol-*d* as solvent. A solution of **1** or **2** in ethanol-*d* was irradiated with a 450-W Hanovia source to better than 90% conversion. The small amount of recovered starting material was examined by infrared and nmr; the spectra obtained gave no evidence for any incorporation of deuterium. The data are best explained by a mechanism involving simultaneous ring opening and ionization of the azabicyclopentanol with a transition state that shows appreciable relief of strain. The above reaction is closely related to the cyclopropyl to allyl cation rearrangement and hence is susceptible to treatment by the Woodward–Hoffmann rules.[50] Theoretical calculations predcit a disrotatory mode as the favored process for this type of transformation.[51] The calculations also predict,[51] and experiments show,[52–54] that substituents *cis* to the leaving group rotate inward while substituents *trans* to the leaving group rotate outward. To accommodate the lack of ring opening and the failure to spectroscopically detect the transient azabicyclopentanol, we suggest that only the *endo*-alcohol **13** is formed on irradiation. The *endo* isomer is the one that would be expected to proceed *via* a concerted disrotatory process and consequently react at a very rapid rate. We attribute the exclusive formation of the *endo*-alcohol to favorable hydrogen bonding between the hydroxyl and amino groups and to the severe steric interactions that exist in the *exo* isomer.



Although the mechanism outlined in Scheme I is consistent with most of the observed data, closer consideration of the experimental results suggest that this scheme is a gross simplification. It has been suggested that the tendency of an excited ketone to abstract hydrogen depends on the nature of the lowest triplet, with $^3(n-\pi^*)$ states being generally reactive and $^3(\pi-\pi^*)$ states nonreactive.[55,56] An illustration of this concept is that butyrophenone, with a low-lying $^3(n-\pi^*)$ state, undergoes the Norrish Type II reaction with ease, while *p*-phenylbutyrophenone, with a low-lying $^3(\pi-\pi^*)$ state, is unreactive.[60] Azetidine **3** (or **4**) is a substituted biphenyl ketone, a type of compound that would not be expected to abstract hydrogen since its lowest lying state should be $\pi-\pi^*$ in character. That the lowest lying triplet of **3** is indeed $\pi-\pi^*$, was demonstrated by examination of its phosphorescence emission spectrum in an EPA glass at 77 °K. The 0–0 band of **3** corresponds to a triplet energy of 61 kcal and the radiative lifetime was 0.75 sec. Similar results were obtained for **4** and for *trans*-N-*t*-butyl-2-phenyl-3-(2-naphthoyl)azetidine (**14**) (see Table III). The latter compound has a

---

(46) Similar treatment of the data for azetidine **12** would predict a value less than unity.

(47) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 184.

(48) Attempts to isolate or spectroscopically detect the hypothetical azabicyclo[2.1.0]pentanol by irradiation at low temperature (−80°) were unsuccessful.

(49) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(50) R. Hoffmann and R. B. Woodward, *ibid.*, **1**, 17 (1968).

(51) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(52) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).

(53) R. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(54) U. Schollkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967).

(55) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

(56) The generality of this correlation has recently been challenged.[57–59]

(57) N. C. Yang and R. Dusenberg, *J. Amer. Chem. Soc.*, **90**, 5899 (1963); ref 10.

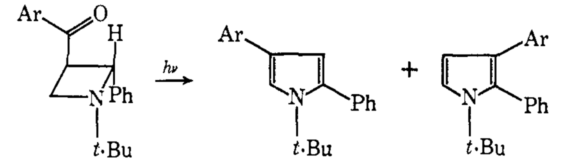
(58) J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5902 (1968).

(59) P. J. Wagner and A. E. Kamppainen, *ibid.*, **90**, 5898 (1968).

(60) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966).

triplet energy of 59 kcal and a radiative lifetime of 2.3 sec. These observations verify that the low-lying triplet states of azetidines **3**, **4**, and **14** are $\pi-\pi^*$ in nature. In view of this fact one might expect that these ketones will not abstract hydrogen and consequently be photochemically inert. This is not the case. Although these ketones have low-lying $^3(\pi-\pi^*)$ states, they still exhibit photoreactivity comparable to that observed with azetidines **1** and **2** (see Table V). In analogy with the results obtained in the benzoyl azetidine system, we find that ketones **3**, **4**, and **14** could not be quenched by moderate concentrations (0.05 mol) of 1,3-cyclohexadiene or high concentrations of piperylene. Again the failure to quench implies that the reaction of the ketone is too rapid for diffusion of the excited state to quencher molecule.

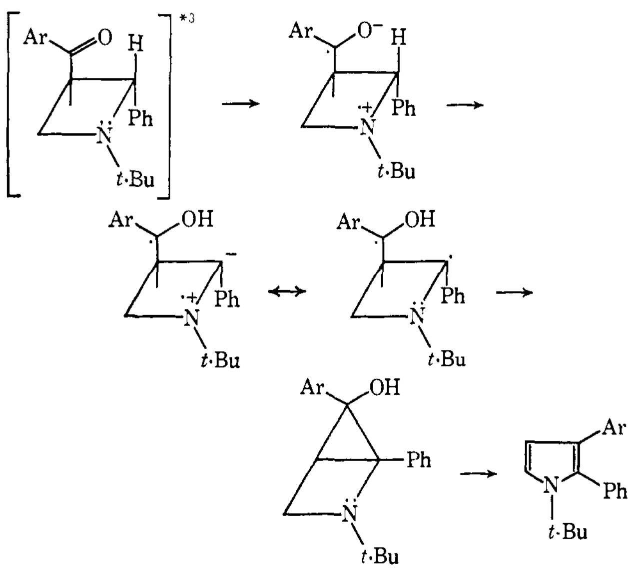
Table V. Representative Quantum Yields



Ar group	Φ pyrrole
Phenyl	0.046
Biphenyl	0.045
2-Naphthoyl	0.043

An alternate and attractive explanation of the hydrogen abstraction step involves the possibility of electron transfer from nitrogen to the excited state of the ketone. The interaction of an electron on nitrogen with the excited state will produce an ion pair or charge-transfer complex. The lack of quenching implies that this process proceeds at a rate exceeding diffusional control. 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 sequence of steps in Scheme II is not without analogy and is closely related to the scheme proposed by Cohen to account for the results obtained in the benzophenone and *p*-aminobenzophenone–alkylamine system.[61,62] A related case has also been reported by Padwa and coworkers with several acylic amino ketones.[5] Further analogy is provided by the work of Weller[63] and Ware[64] wherein aromatic amines are thought to quench $\pi-\pi^*$ singlets by charge-transfer interactions. It appears that attack at an electron of nitrogen occurs for $\pi-\pi^*$ triplet states and perhaps for $n-\pi^*$ triplet states as well, although rapid hydrogen abstraction by the $n-\pi^*$ state is not necessarily eliminated from the available data. Scheme II would predict a decrease in the quantum efficiency of photorearrangement as the pair of electrons on nitrogen becomes less available. In accord with this expectation, we find that the corresponding protonated azetidines are photochemically inert.

Further work both on the steric and electronic requirements for electron transfer as well as the scope and application to other systems is currently underway and will be the subject of future reports.

Experimental Section

Preparation of *trans*-N-1-*t*-Butyl-2-phenyl-3-(2-naphthoyl)azetidine (14). To an ice-cooled solution of naphthalene (78 g (0.608 mol)) and propionyl chloride (57 g (0.613 mol)) in 450 ml of nitrobenzene was added 135 g of aluminum chloride over a 40-min period. The mixture was poured onto crushed ice, the organic layer was separated, and the solvent was removed under reduced pressure. The residue was distilled under vacuum, bp 140–145°, 1.0 mm. The distillate solidified on standing and was subsequently recrystallized from 95% ethanol to give 60 g of propionaphthone, mp 58–59° (lit. mp 59°).[65] The infrared spectrum (KBr) showed strong bands at 5.97, 7.37, 8.41, 8.87, 6.67, 12.45, and 13.32 μ.

A solution of 53.8 g (0.292 mol) of propionaphthone and 31.0 g (0.292 mol) of benzaldehyde in 100 ml of benzene was saturated with gaseous hydrogen chloride and allowed to stand at 10° for 2 days. At the end of this time the solvent was evaporated and the residue was taken up in 600 ml of methyl alcohol containing 7.0 g of dissolved sodium metal. The solution was heated to reflux for 2 hr, cooled to 10°, and the precipitated salts were filtered. The residue obtained by removal of the solvent was dissolved in benzene, washed with water, and concentrated to a red oil. This oil was chromatographed on a silica gel column (26 × 1 in.). Elution with 550 ml of benzene afforded 26 g of a yellow solid, mp 62–67°. Recrystallization from methanol gave 22 g of *trans*-1-(β-naphthyl)-2-methyl-3-phenyl-2-propenone as a white crystalline solid, mp 70–71°.

The infrared spectrum (KBr) was characterized by bands at 6.05, 6.90, 7.80, 9.75 (split), 10.81, 11.00, 11.44, 11.93, 13.18, and 14.45 μ. The nmr spectrum (CCl_4) showed doublets at τ 7.75 (3 H, J = 1.2 Hz) and 2.85 (1 H, J = 1.2 Hz) and multiplets centered at τ 2.70 and 2.24 (12 H).

Allylic bromination of the unsaturated ketone was readily achieved by refluxing a mixture of 18.5 g (0.0682 mol) of *trans*-1-(β-naphthyl)-2-methyl-3-phenyl-2-propenone, 12.1 g of N-bromosuccinimide (0.0682 mol), and 0.3 g of benzoyl peroxide in 300 ml of carbon tetrachloride for 1 hr. The mixture was then cooled to 15° and the precipitated succinimide was removed by filtration. Evaporation of the carbon tetrachloride solution under reduced pressure left a yellow solid which was recrystallized from methanol to afford 17.1 g of *trans*-1-(β-naphthyl)-2-(bromomethyl)-3-phenyl-2-propenone, mp 98–99°.

---

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

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

(63) A. H. Weller and H. Leonhard, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

(64) W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).

(65) J. Sylvestre, *Ann. Chim.*, **7**, 129 (1952).

The infrared spectrum (KBr) showed strong bands at 6.01, 7.81, 8.18, 12.00, 13.15, and 14.43 μ. The nmr spectrum (CCl_4) showed singlets at τ 5.36 (2 H) and 2.75 (1 H), and multiplets centered at τ 2.45 and 2.11 (12 H).

A mixture of 14.1 g (0.0404 mol) of the above unsaturated bromo ketone and 5.9 g of *t*-butylamine (0.0808 mol) in 150 ml of benzene was added to 1500 ml of pentane. The resulting mixture was stirred overnight and the solution was then separated from the precipitated salts. The solvent was removed under reduced pressure to give 8.2 g of a white solid. Recrystallization from heptane gave 7.4 g of 2-[α-(N-*t*-butylamino)-benzyl]-3-naphthyl-1-propen-3-one, mp 98–99°, as white needles.

The infrared spectrum (KBr) showed strong bands at 6.07, 8.18, 9.02, 10.08, 10.56, 12.00, 12.57, and 14.38 μ. The nmr spectrum (CCl_4) showed a sharp singlet at τ 8.90 (9 H), three broad singlets at τ 3.72, 4.24, and 4.79 for a total of two protons, and multiplets centered at τ 2.60 and 2.20 (12 H).

The desired *trans*-azetidine **14** was obtained by dissolving 6.8 g of the above ketone in 1500 ml of chloroform that had been previously saturated with gaseous hydrogen bromide. After 6 hr the reaction mixture was cooled to 0°, neutralized with *t*-butylamine, and filtered. Removal of the solvent left a solid which exhibited a broad melting point range (90–98°) even after repeated recrystallizations from heptane. Chromatography of this material on a (33 × 1 in.) florisil column with 1300 ml of a 2% ethyl acetate-hexane mixture afforded 5.4 g of a white solid. Recrystallization from heptane gave 5.2 g of *trans*-N-*t*-butyl-2-phenyl-3(2-naphthoyl)-azetidine **14**, mp 109–110°.

Anal. Calcd for $C_{24}H_{25}NO$: C, 83.92; H, 7.34; N, 4.08. Found: C, 83.86; H, 7.39; N, 4.06.

The infrared spectrum (KBr) showed strong bands at 5.98, 7.37 (split), 7.81, 7.95, 8.06, 8.17, 8.35, 11.39, 12.02, 13.17, 13.79, and 14.30 μ. The nmr spectrum ($CDCl_3$) showed a singlet at τ 9.05 (9 H), multiplets at τ 4.27 (3 H) and 2.43 (12 H), and a doublet at τ 5.35 (1 H, J = 7.0 Hz). The nmr spectrum of the crude solid initially obtained (mp 90–98°) indicated the existence of both *cis*- and *trans*-azetidines. Specifically, the nmr showed a doublet (benzylic proton) at τ 5.03 (J = 9.0 Hz) for the *cis* isomer. It seems likely that a mixture of *cis*- and *trans*-azetidines was produced during the neutralization step. This is reasonable in view of the fact that the solution was basic and under these conditions isomerization could occur.

Irradiation of *trans*-N-*t*-Butyl-2-phenyl-3-(2-naphthoyl)azetidine (14). In 900 ml of 95% ethanol was dissolved 0.50 g of *trans*-N-*t*-butyl-2-phenyl-3-(2-naphthoyl) azetidine. The solution was then irradiated for 3 hr using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent under reduced pressure left a brown semisolid which was recrystallized from methanol to give 0.2 g of a light tan crystalline solid, mp 165–166°. This material was identified as 1-*t*-butyl-2-phenyl-3-naphthylpyrrole from the analytical and spectroscopic data.

Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.44; H, 7.26; N, 4.25.

The infrared spectrum (KBr) showed strong bands at 8.20, 11.60, 12.12, 12.91 (split), 13.36, 14.17, and 14.48 μ. The nmr ($CDCl_3$) showed a singlet at τ 8.56 (9 H), doublets at τ 3.48 (1 H, J = 3.2 Hz) and τ 2.98 (1 H, J = 3.2 Hz), and a multiplet centered at τ 2.60 (12 H).

When the irradiation was carried to *ca.* 20% conversion and then examined by nmr spectroscopy it became clear that the solution contained both the 2,3- and 2,4-disubstituted pyrroles in the ratio of 1.8:1. The nmr spectrum ($CDCl_3$) of the mixture showed (in addition to the bands described above) a singlet at τ 8.53 (9 H), doublets at τ 3.51 (1 H, J = 2.5 Hz) and 2.78 (1 H, J = 2.5 Hz), and a multiplet centered at τ 2.62 (12 H).

Low-Temperature Photolysis of *cis*-1-*t*-Butyl-2-phenyl-3-benzoylazetidine. Irradiation of 0.5 g of *cis*-1-*t*-butyl-2-phenyl-3-benzoylazetidine in 900 ml of pentane was carried out at −35° for 2 hr using a 550-W Hanovia lamp equipped with a Pyrex filter. Evaporation of the solvent at −10° left 0.45 g of a white solid, mp 99–102°. The infrared spectrum of this material was identical in all respects with an authentic sample of N-*t*-butyl-2,4-diphenylpyrrole. No other component was detected by infrared and nmr spectroscopy at −10°. Irradiation of the *cis*-azetidine was also carried out in a degassed and sealed 13 × 150-mm Pyrex test tube which was suspended inside a liquid nitrogen filled quartz dewar. The quartz dewar was centered inside a Rayonet chamber reactor which utilized 16 3500-Å lamps. After 3 hr of irradiation time, only starting material was recovered. A similar run carried out at 25° resulted in an 80% conversion of starting azetidine to N-*t*-butyl-2,4-diphenylpyrrole.

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450-W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate per 100 ml of water[66] through the inner jacket. This solution permitted the following wavelength distribution to pass through: 6% 2967 Å, 20% 3025 Å, 62% 3130 Å, 10% 3340 Å. All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer quantum yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 *M*.[13] Reliably reproducible output rates of 4.86×10^{16} quanta sec were recorded. After the irradiation the degree of reaction was determined by quantitative ultraviolet spectroscopy and vapor phase chromatography (6 ft × 0.25 in. 10% SE-30 methylsilicone gum rubber on Diatoport S at 243°). The conversions in the azetidine series were run to 15% or less. The mass balance in these runs was generally better than 96%.

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 *xy* 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 (τ_0). Table III summarizes the emission characteristics of the various substituted azetidines examined.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-9385).

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