A three-dimensional Patterson synthesis was computed from the observed data.[27] The positions of the two independent bromine atoms were obtained from this synthesis. The remaining nonhydrogen atoms were found by successive structure factor calculations and electron density syntheses. The positions were refined by full matrix least-squares techniques with anisotropic thermal parameters for all atoms to a conventional discrepancy index [$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$] of 0.089 and a weighted R factor [$wR = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2}$] of 0.119.[28,29] The scattering factors were those of Hanson, *et al.*[30]

A final electron density difference map showed no peaks greater than 0.4 e/Å^3. No unusual trends in F_o and F_c values were found and the weighting scheme was judged to be a reasonable one.

In Tables VII and VIII we give the final values of the positional parameters and the anisotropic thermal parameters.

In Tables IX and X we give the final intramolecular bond distances and angles along with their standard deviations as derived from the inverse matrix.[31]

In Table XI[32] are given the values of $10F_o$ and $10F_c$, respectively. A drawing of the molecule including anisotropic thermal motion is presented in Figure 1.[33]

Acknowledgment. This research was supported by Grant G-6740 from the National Science Foundation.

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[27] J. Rodgers and R. A. Jacobson, "ALF: A General Fourier Program in PL1 for Triclinic, Monoclinic, and Orthorhombic Space Groups," U. S. Atomic Energy Commission Report IS-2155, Iowa State University, Ames, Iowa 50010.

[28] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, The Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[29] The W's calculated from $\sigma[F_o]$'s were calculated for each reflection by means of $\sigma F_o = \sqrt{F_o{}^2 + \sigma[I]/Lp} - |F_o|$: see D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

[30] H. P. Hanson, F. Merman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

[31] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Function and Error Program," ORNL-TM-306, The Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[32] Listings of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publication, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of aritcle, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

[33] C. K. Johnson, ORTEP, "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, The Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Photochemical Transformations of Small Ring Carbonyl Compounds. XXX. Electron Transfer in the Photochemistry of Azetidinyl Ketones[1]

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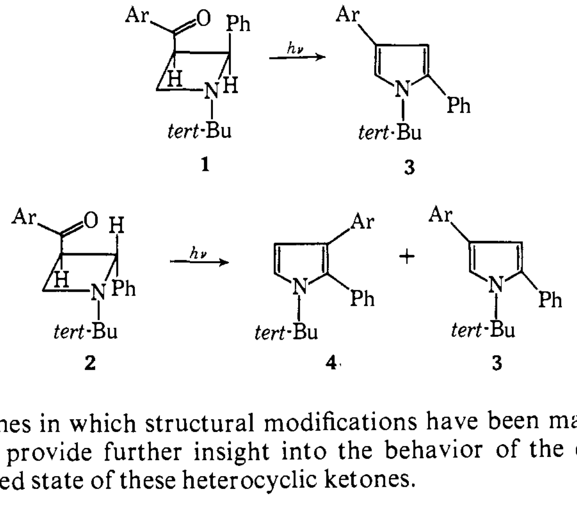
Received August 15, 1970

Abstract: The photoinduced ring expansion of several azetidinyl ketones has been examined. Upon irradiation with ultraviolet light in ethanolic solution, 3-aroylazetidines **5** and **6** rearrange smoothly and in high yield to arylpyrroles **9** and **10**. Irradiation of 3-*N*-*tert*-butylazetidinyl *n*-butyl ketone (**7**) gave two primary photoproducts. The ratio of the two products was found to vary with the nature of the solvent. A mechanism involving intramolecular electron transfer from nitrogen to the excited triplet state and subsequent formation of a charge transfer complex is proposed. While 3-aroylazetidines undergo smooth rearrangement to arylpyrroles, the isomeric 2-azetidinyl ketone system affords a complex mixture of photoproducts.

Recently, we described the photochemical rearrangement of 3-aroylarylazetidines to diarylpyrroles.[4] In our studies we showed that the photoreaction proceeds with low quantum efficiency and low sensitivity to diffusion-controlled quenchers. These properties led us to suggest initial rapid intramolecular electron transfer between the ketone triplet and the electron pair on nitrogen followed either by proton transfer or charge destruction and quenching.[4] Further studies on the excited state behavior of azetidinyl ketones seemed desirable for several reasons: (a) to determine whether the photorearrangement was a general phenomenon, (b) to explore the photobehavior of the isomeric 2-aroylazetidinyl ketone system, (c) to relate photobehavior to selected structural modifications, and (d) to assess the importance of electronic perturbations on the electron-transfer route. The present paper describes the photochemical properties of several azetidinyl ketones in which structural modifications have been made to provide further insight into the behavior of the excited state of these heterocyclic ketones.



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[1] For part XXIX, see A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).

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

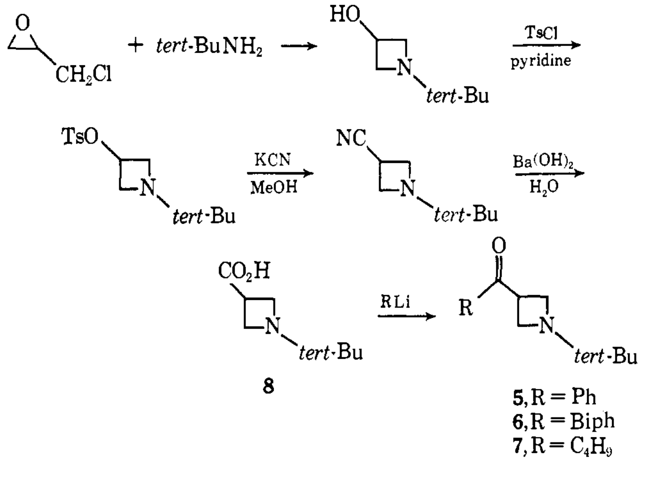
[3] NDEA Predoctoral Fellow, 1968–1970.

[4] A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 100, 107 (1970).

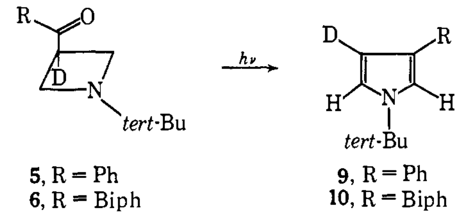
Results

The nature of the principal photoreaction in the 3-aroylarylazetidine system appears to be dependent on the stereochemistry of the substituents.[4] The rearrangement leads to a single pyrrole from cis starting material (**1**) and to a mixture of two pyrroles from the trans isomer (**2**). In an effort to determine the generality of the photorearrangement, we have investigated the photochemistry of monosubstituted azetidines **5**, **6**, and **7**. The azetidinyl ketones were prepared in good yield by treatment of the corresponding carboxylic acid (**8**) with the appropriate organolithium reagent. The four-step synthesis of *N*-*tert*-butylazetidine-3-carboxylic acid (**8**), illustrated in Scheme I, employs a modification of the sequence used by Chen and coworkers.[5] The spectral data (infrared, ultraviolet, nmr) and elemental analysis of the three ketones were consistent with their assignments and are summarized in the Experimental Section.

Scheme I



Photolysis of *N*-*tert*-butyl-3-benzoylazetidine (**5**) in 95% ethanol through Pyrex gave *N*-*tert*-butyl-3-phenylpyrrole (**9**) as the only photoproduct. Under similar conditions, irradiation of **6** gave **10**, mp 93–95°, in 98% yield. The structures of the photoproducts were elucidated from their elemental analyses and spectral data. The infrared, ultraviolet, and nmr[6] spectra were similar to those of pyrroles **3** and **4** obtained from azetidine **2** and are summarized in the Experimental Section.



Irradiation of azetidinyl ketone **7** in absolute ethanol with a Pyrex filter gave two primary photoproducts, **11** and **12**, in a ratio of 6:1. The nmr, ir, and uv spectra (see Experimental Section) indicate the major product to be *N*-*tert*-butyl-3-*n*-butylpyrrole (**11**). The structure of the minor product (**12**) was elucidated from its analysis, spectral data, and by an independent synthesis from **8** and methyllithium. The ratio of the photoproducts produced on irradiation of **7** was found to vary substantially with the nature of the solvent. The product distribution for the photoreaction is shown in Table I. In the very polar solvents, the yield of **12** is relatively high. As the solvent becomes less polar, the yield of **12** drops off rapidly until it becomes negligible. The effect of solvent is not simply a polarity effect. This is most clearly seen by comparison of the relative amounts of **11** and **12** in ethanol (ϵ 24.3) and trifluoroacetic acid (ϵ 8.5).[7] The capacity for hydrogen bonding by solvent seems to be of major importance. This is borne out by noting that irradiation of the hydrochloride salt of **7** in ethanol affords **12** with no detectable quantities of **11**. We also find that the corresponding hydrochloride salts of ketones **5** and **6** are photochemically inert. Thus the pathway leading to pyrrole is highly dependent on the availability of the electron pair on nitrogen. This aspect will be considered later.

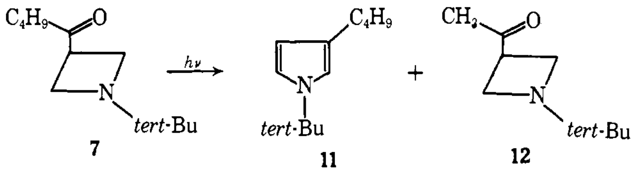


Table I. Variation of Product Distribution of 7 with Solvent

Solvent	% photoproducts 11	 12
Acetone	100	0
Hexane	98	2
2-Propanol	90	10
Ethanol	84	14
Trifluoroacetic acid	0	100
HCl-ethanol	0	100

Quantum Yield Determinations. Determination of the quantum yields for the appearance of product for azetidinyl ketones **5** and **6** were carried out in order to determine the facility of the photorearrangement. Degassed and sealed Pyrex tubes containing solutions of the azetidines were irradiated along with actinometer tubes in the rotating photochemical assembly.[4] 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. Sensitization experiments using acetophenone and quenching with piperylene were also investigated. The results are indicated in Table II.

Direct runs showed that the photoinduced ring expansion of the azetidinyl ketone system is one of modest efficiency with quantum yields ranging from 0.05 to 0.12. Sensitization experiments suggest that the triplet state is responsible for the rearrangement of ketones **5** and **6**. In experiments where the sensitizer absorbed more than 95% of the light and concentrations were adjusted to avoid singlet transfer, the photoreaction proceeds with its usual quantum efficiency. Were the acetophenone, which is absorbing all of the light in the sensitized runs, wasting this energy, then the

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(5) T. Chen, T. Sanjiki, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jap.*, 40, 2398, 2401 (1967).

(6) See R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, 37, 1056 (1959), for position and coupling constants of pyrrole hydrogens.

(7) F. E. Harris and C. T. O'Konski, *J. Amer. Chem. Soc.*, 76, 4317 (1954).

Table II. Quantum Yields for Pyrrole Formation in Direct, Sensitized, and Quenched Irradiations of Azetidinyl Ketones **5** and **6**[a]

Azetidinyl[b] ketone	Additive (concn, *M*)	Quantum yield[d]
5		0.12
5	Acetophenone (3.5)[c]	0.11
5	Piperylene (2.0)	0.09
6		0.05
6	Acetophenone (3.5)	0.046
6	Piperylene (2.0)	0.05

[a] All runs at 25° in 95% ethanol; irradiation conditions described in the Experimental Section. [b] Azetidine concentration was 0.03 *M*. [c] Absorbing over 95% of incident light. [d] Average of pyrrole formation for three runs.

Table III. Quantum Yield Data for Product Formation of Azetidinyl Ketone **7**[a]

Solvent[b]	Additive (concn, *M*)	Φ_{11}	Φ_{12}
Hexane		0.04	0.0004
Hexane	Piperylene (2.0)	0.043	0.0004
Acetone		0.043	
Trifluoroacetic acid			0.047
Trifluoroacetic acid	Naphthalene (0.7)		0.047

[a] Irradiation conditions described in Experimental Section. [b] Azetidine concentration was 0.2 *M*.

quantum yield would be expected to be zero. Since the quantum yield of the photoproduct in the sensitized runs is essentially the same as in the direct photolysis, we can conclude that the low quantum efficiency of the azetidine rearrangement is not attributable to poor intersystem crossing in **5** and **6**. This is quite reasonable in view of the very rapid rates of intersystem crossing of benzoyl-type ketones and the known unit crossing efficiency of benzophenone[8] and acetophenone.[9]

Further support for the triplet nature of the reactive states of ketones **5** and **6** was obtained from phosphorescence emission studies. The emission data were determined in a methanol–ethanol glass at 77°K. The 0–0 band of **5** corresponds to a triplet energy of *ca.* 75 kcal. The vibrational spacing between the 0–0 and 0–1 band (1490 cm^{-1}) and the lifetime of emission (5 msec) of **5** is typical of an $n-\pi^*$ triplet state.[10,11] On the other hand, the lowest lying triplet of **6** is a $\pi-\pi^*$ state. This was demonstrated by examination of its phosphorescence emission spectrum in a methanol–ethanol glass at 77°K. The 0–0 band of **6** corresponds to a triplet energy of 61.6 kcal and the radiative lifetime was 0.72 sec. It thus appears that both $n-\pi^*$ and $\pi-\pi^*$ triplet states undergo ring expansion with similar quantum efficiency.

Quenching studies were also attempted using piperylene as the quencher (note Table II). However, only at *ca.* 2.0 *M* piperylene were the beginnings of quenching noted, and this quenching was minor. With the assumption that triplet quenching with piperylene occurs at a rate which approaches diffusion control, a rate of rearrangement of the triplet state of **5** (and **6**) can be estimated as $>10^9$ sec^{-1} taking 5×10^{-9} l. mol^{-1} sec^{-1} as the rate of diffusion in ethanol.[12]

Quantum yields for the photoreaction of **7** (affording **11** and **12**) were also determined using 2-hexanone actinometry[13] (Table III). Sensitization using acetone and quenching with piperylene were also investigated. As noted from the table, the formation of **11** proceeded with modest quantum efficiency whereas the quantum yield for methyl ketone (**12**) formation was found to be extremely low. Acetone sensitization gave only **11** with the same efficiency as in the direct irradiations. This indicates that the triplet state of **7** is responsible for the formation of pyrrole while the singlet state undergoes photoelimination to give **12**. The failure to quench both reactions with 2.0 *M* piperylene indicates that rearrangement of the triplet of **7** is too rapid for diffusion of excited state to quencher molecule. Similar situations have been encountered in the literature.[14,15] The quantum yield for pyrrole formation is reduced to zero when the irradiation is carried out in trifluoroacetic acid. Under these conditions, the photoefficiency of the Norrish type II path increases 100-fold. Interestingly, with trifluoroacetic acid as solvent, the formation of **12** cannot be quenched with 0.7 *M* naphthalene indicating again that the singlet state is responsible for its formation.

Discussion

Considerable information has now been accumulated about the photochemical behavior of a number of azetidinyl ketones. The more readily derived facts about the azetidine rearrangement are the low quantum yields and low sensitivity to diffusion controlled physical quenchers. These properties suggest that the above reactions proceed by a route similar to that previously proposed for the photoreduction of aromatic ketones by aliphatic amines.[16–19] The first step involves intramolecular electron transfer from the nonbonding electrons on nitrogen to the excited ketone and formation of a charge-transfer complex. The inability of piperylene to quench the reaction implies that this process proceeds at a rate exceeding diffusion control. Transfer of a proton from the adjacent carbon atom to the ketyl radical followed by electron reorganization, bond closure, and elimination of water accounts for the final product (eq 1). The charge-transfer complex can also revert to starting ketone by reverse electron (or hydrogen) transfer thereby accounting for the low quantum efficiency. It appears that electron transfer can occur with both $n-\pi^*$ and $\pi-\pi^*$ triplet states, as both **5** and **6** smoothly rearrange to arylpyrroles. This scheme (eq 1) would predict a decrease in quantum efficiency of pyrrole formation as the pair of electrons on nitrogen becomes less available. In accord with this expectation we find that the hydrochloride salts of **5** and **6** are photochemically inert.

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(8) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

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

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

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

(12) F. Wilkinson, *Advan. Photochem.*, 3, 241 (1964).

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

(14) H. E. Zimmerman and J. S. Swenton, *ibid.*, 89, 906 (1967).

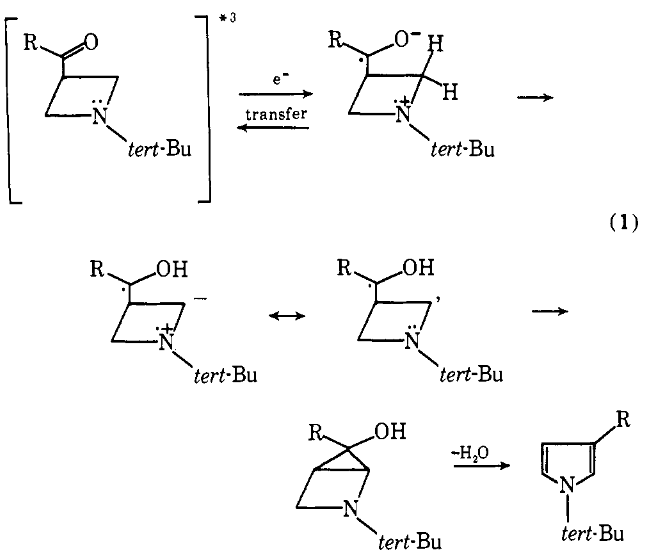
(15) A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *ibid.*, 91, 1857 (1969).

(16) S. G. Cohen and R. J. Baumgarten, *ibid.*, 89, 3471 (1967).

(17) S. G. Cohen and H. M. Chao, *ibid.*, 90, 165 (1968).

(18) S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, 90, 521 (1968).

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

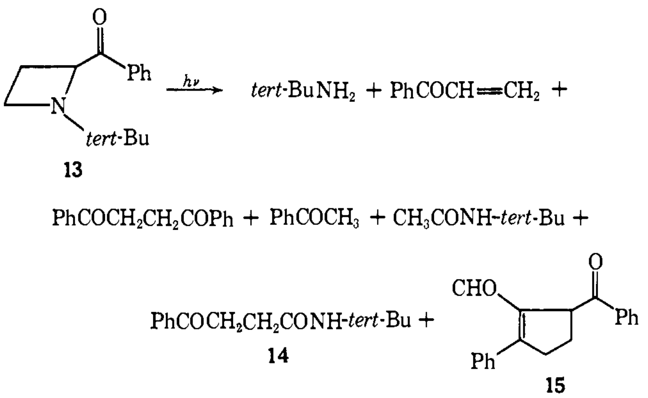


(1)

The photochemical behavior of *n*-butyl azetidinyl ketone **7** was of particular interest since this molecule should allow study of the electron transfer route in competition with Norrish type II elimination. From the data in Table II we note that the photobehavior of **7** is markedly dependent on the nature of the solvent. One might have anticipated that increasing the polarity of the medium would favor pyrrole **11** since a significant amount of charge develops in its formation. This was expected since it is known that ground-state reactions which proceed by electron transfer show large rate enhancements in acetonitrile relative to benzene.[19] The fact that hydroxylic solvents actually favor the Norrish type II route suggests that the hydrogen-bonding ability of the solvent is more important than its dielectric constant in influencing the outcome of the photoreaction. Hydrogen bonding by solvent with the nitrogen atom renders more difficult attack of the ketone triplet on the N electrons thereby allowing the photoelimination path to compete. A similar situation has been encountered by Cohen in the photoreduction of benzophenone with alkyl amines.[20]

Recent studies on the Norrish type II photoelimination have provided considerable insight into the nature of the carbonyl excited state.[21,22] The present evidence suggests that the abstraction of the γ-hydrogen is reversible and can occur from either the first excited singlet state or from the triplet state.[23,24] From quenching and sensitization studies with ketone **7** (see Table III) it appears that the Norrish type II product (**12**) is derived exclusively from the singlet state. Thus, when **7** is irradiated in acetone only pyrrole **11** is formed. In addition, the formation of **12** in ethanol could not be quenched with piperylene or naphthalene. This is somewhat unusual since it is known that the photoelimination of aliphatic ketones originates from both excited states.[21–24] This result implies that the triplet of **7** prefers the electron transfer rather than the photoelimination route. This is not at all unreasonable in view of the fact that the photoelimination of the triplet state of aliphatic ketones can be quenched while the electron transfer path cannot. It seems as though the singlet state of **7** can undergo photoelimination in competition with intersystem crossing and that this competition is solvent dependent. We cannot rule out, however, the possibility of electron transfer from the singlet state of **7**.

Photochemistry of the 2-Aroylazetidine System. With the above results in hand, we considered it relevant to explore the photochemistry of the isomeric 2-aroylazetidine system. *N-tert*-Butyl-2-benzoylazetidine (**13**) was synthesized by modification (see Experimental Section) of the procedure of Rodebaugh and Cromwell.[25] Exposure of dilute solutions of **13** in benzene to a Hanovia 450-W mercury arc lamp for short periods of time resulted in the complete disappearance of **13** and conversion to a variety of products. Preparative vpc and thick layer chromatography of photolysis mixtures permitted the purification and isolation of seven components. The products were identified as *tert*-butylamine (17%), phenyl vinyl ketone (28%), dibenzoylethane (4%), acetophenone (9%), *tert*-butylacetamide (4%), *N-tert*-butyl-3-benzopropionamide (**14**, 10%), and 1-phenyl-2-formyl-3-benzoylcyclopentene (**15**, 12%). Spectral comparisons of the first six components with authentic samples served to confirm their structures. The seventh component (**15**) was shown to



13

$$\xrightarrow{h\nu} tert\text{-}BuNH_2 + PhCOCH{=}CH_2 +$$

$$PhCOCH_2CH_2COPh + PhCOCH_3 + CH_3CONH\text{-}tert\text{-}Bu +$$

$$PhCOCH_2CH_2CONH\text{-}tert\text{-}Bu +$$

14

15

have the molecular formula $C_{19}H_{16}O_2$, mp 91–92°. The solid exhibited pertinent infrared bands at 3.69 (aldehyde CH stretch), 5.86 (aldehyde C=O), and 5.95 μ (benzoyl C=O); its ultraviolet spectrum showed maxima at 242 and 278 mμ. Its nmr spectrum revealed several important points, specifically, the presence of an uncoupled aldehyde proton and five (extensively coupled) saturated hydrogens. These spectral features were uniquely congruent with the cyclopentene assignment.

The above results clearly establish that the photochemical behavior of azetidinyl ketones is highly dependent on the location of the carbonyl group. 3-Aroylazetidines undergo smooth rearrangement to arylpyrroles whereas the isomeric 2-aroylazetidine system affords a complex mixture of photoproducts. This widely differing reactivity may be the result of the structural features of **13** which preclude hydrogen transfer from the carbon adjacent to both the carbonyl group and the nitrogen atom. Several mechanisms may be advanced to explain the formation of the above photoproducts. The formation of phenyl vinyl ketone and

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(20) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837 (1970).

(21) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4009 (1965); **88**, 1245 (1966).

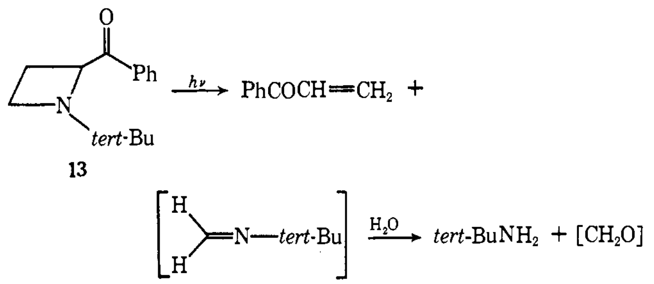
(22) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

(23) N. C. Yang and S. P. Elliot, *ibid.*, 91, 7550 (1969).

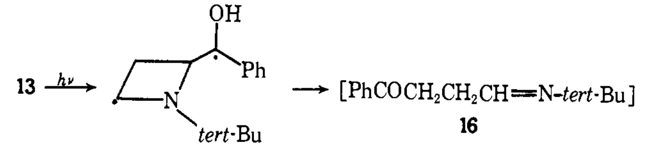
(24) N. C. Yang, S. P. Elliot, and B. Kim, *ibid.*, 91, 7551 (1969).

(25) R. M. Rodebaugh and N. H. Cromwell, *J. Heterocycl. Chem.*, **5**, 309 (1968).

tert-butylamine may be attributed to a photoinduced fragmentation of the four-membered ring followed by hydrolysis of the imine on work-up. The remaining

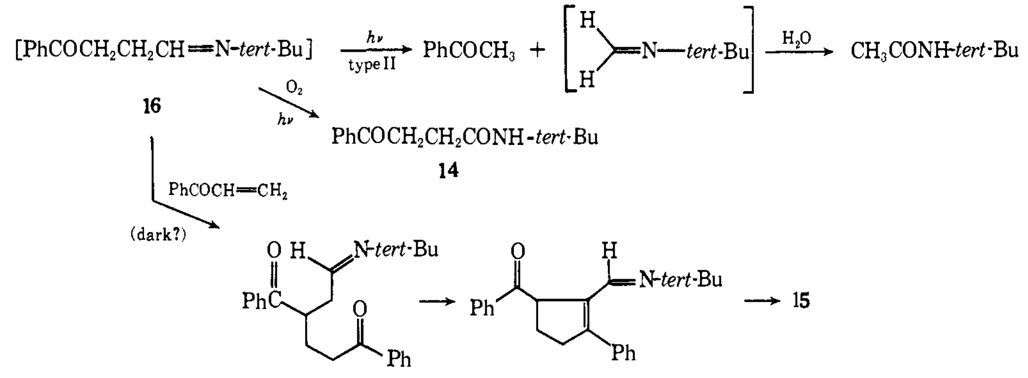


products can be ascribed to further secondary reactions of the *N*-*tert*-butylimine of 3-benzoylpropanal (**16**). Imine **16** could have arisen by a transannular hydrogen transfer similar to that previously encountered with cyclobutyl phenyl ketone.[26] The failure to observe

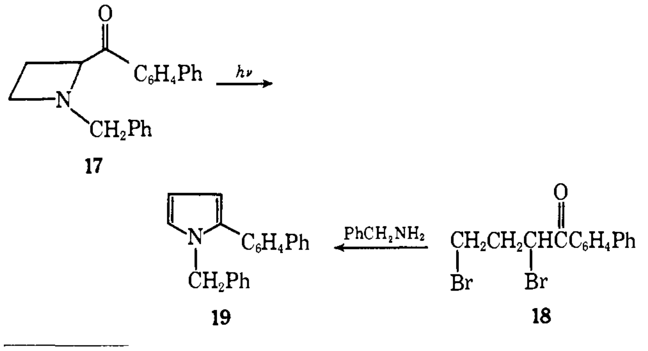


such a species from the photolysis runs can be ascribed to its further reactions under the photolytic conditions in the manner described in Scheme II.

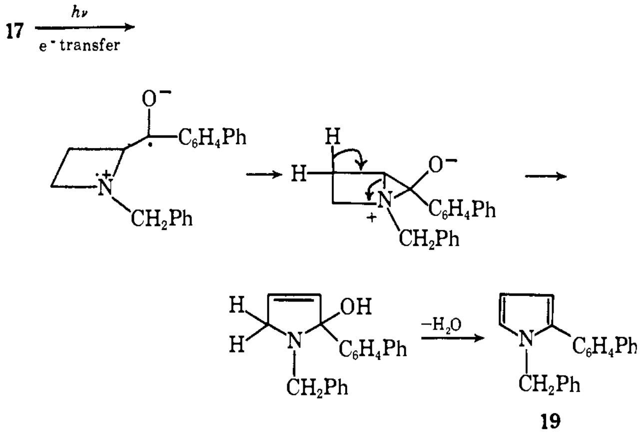
Scheme II



It is interesting, at this point, to compare the irradiation of **13** with that of *N*-benzyl-2-*p*-phenylbenzoylazetidine (**17**). Azetidine **17** was prepared from the reaction of α,γ-dibromo-*p*-phenylbutyrophenone (**18**) with benzylamine (see Experimental Section). Since **17** has available γ-hydrogens, we anticipated ready photoelimination by the Norrish type II electron transfer route.[15] Actually, irradiation of **17** gave **19** as the



only characterizable photoproduct. The bulk of the reaction mixture consisted of ill-defined tars. The structure of **19** was elucidated on the basis of its elemental analysis, spectral data (see Experimental Section), and by synthesis from **18** and benzylamine. It is premature to propose a precise mechanism to explain the formation of **19** from the irradiation of **17**. As a working hypothesis, however, we could envision a route involving electron transfer, bond closure, deprotonation with ring opening, and elimination of water.



The results obtained with the 2-aroylazetidine system, when compared with those for the 3-aroylazetidine series, serve to emphasize the difference in photobehavior of these two systems. At this time it is premature to invoke an electron transfer route in the 2-aroylazetidine series because of the limited number of examples studied. Experiments designed to investigate this point and further study of the scope and mechanism of the 2-aroylazetidine system are in progress and will be reported at a later date.

Experimental Section[27]

***N*-*tert*-Butyl-3-benzoylazetidine (5)** was prepared according to the procedure of Doomes and Cromwell.[28]

***N*-*tert*-Butyl-3-acetylazetidine (12).** To an ice-cooled suspension of 3.7 g of *N*-*tert*-butylazetidine-3-carboxylic acid[5] (**8**) in 100 ml of

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(26) A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, 91, 456 (1969).

(27) 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 Associate high-resolution spectrometer. Tetramethylsilane was used as an internal standard.

(28) E. Doomes and N. H. Cromwell, *J. Heterocycl. Chem.*, 6, 153 (1969).

anhydrous ether was added 25 ml of a 2.14 *M* methyllithium solution. The reaction mixture was warmed to room temperature and stirred for 2 hr. The excess methyllithium was destroyed by adding 0.5 ml of ethyl formate and the resulting solution was hydrolyzed with 20 ml of an aqueous ammonium chloride solution. The aqueous layer was extracted twice with ether and the combined extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure to yield a colorless oil. Distillation of the oil gave 3.1 g (85%) of *N-tert*-butyl-3-acetylazetidine (**8**), bp 87–89° (8.0 mm).

N-tert-Butyl-3-acetylazetidine was analyzed as its picrate, mp 141–143°.

Anal. Calcd for $C_{15}H_{20}N_4O_8$: C, 46.87; H, 5.25; N, 14.58. Found: C, 46.83; H, 5.40; N, 14.50.

The infrared spectrum (neat) was characterized by a series of strong bands at 3.40, 3.52, 5.83, 7.36, 8.05, 8.45, and 9.15 μ. The nmr spectrum (CCl_4) showed sharp singlets at τ 9.11 (9 H) and 7.93 (3 H) and a multiplet centered at 6.75 (5 H). The ultraviolet spectrum exhibited a maximum at 275 mμ (ϵ 30). The mass spectrum showed the parent peak at *m/e* 155 and had peaks at 141, 140 (base), 98, and 71.

Preparation of 3-*N-tert*-Butylazetidinyl *n*-Butyl Ketone (7). To an ice-cooled suspension of 7.4 g of *N-tert*-butylazetidine-3-carboxylic acid (**8**) in 100 ml of anhydrous ether was added 58.7 ml of a 1.6 *M n*-butyllithium solution. The mixture was warmed to room temperature and stirred for 1 additional hr. The excess butyllithium was destroyed with 0.5 ml of ethyl formate. The resulting mixture was hydrolyzed with 10 ml of a saturated ammonium chloride solution. The aqueous layer was extracted with ether and the ethereal extracts were dried over sodium sulfate. The solvent was removed under reduced pressure to give a yellow oil which was distilled to give 6.0 g (65%) of 3-*N-tert*-butylazetidinyl *n*-butyl ketone, bp 97–100° (5.0 mm).

3-*N-tert*-Butylazetidinyl *n*-butyl ketone was analyzed as its hydrochloride salt, mp 101–102°.

Anal. Calcd for $C_{12}H_{24}NOCl$: C, 61.66; H, 10.28; N, 5.99. Found: C, 61.73; H, 10.51; N, 5.74.

The infrared spectrum of **7** showed strong bands at 3.45, 3.55, 5.82, 6.35, 7.35, and 8.10 μ. The nmr spectrum (CCl_4) was characterized by a sharp singlet at τ 9.10 (9 H), a triplet at 7.64 (2 H, J = 7.5 Hz), a multiplet centered at 6.75 (5 H), and 8.65 (7 H). The ultraviolet spectrum exhibited a maximum at 272 mμ (ϵ 34). The mass spectrum showed the parent peak at *m/e* 197 and major peaks at 183, 182 (base), 140, 97, 84, 83, and 69.

***N-tert*-Butyl-3-*p*-phenylbenzoylazetidine (6).** To a mixture of 1.94 g of metallic lithium in 100 ml of ether was added 16.3 g of 4-bromobiphenyl. The dark brown solution that formed was stirred for 2 hr and then it was added dropwise to an ice-cooled solution of 5.0 g of *N-tert*-butylazetidine-3-carboxylic acid. The resulting solution was allowed to warm to room temperature and was then hydrolyzed with 50 ml of a saturated ammonium chloride solution. The aqueous layer was extracted twice with ether and the combined ethereal extracts were dried over sodium sulfate. The solvent was removed under vacuum to give a yellow solid which was chromatographed on a Florisil column (100 cm × 3 cm). The column was eluted with 1.5 l. of benzene to give biphenyl. Further elution with ether gave a yellow solid which was sublimed at 80° (0.1 mm) to give *N-tert*-butyl-3-*p*-phenylbenzoylazetidine (78%), mp 86–87°, as a white crystalline solid.

N-tert-Butyl-3-*p*-phenylbenzoylazetidine was analyzed as its picrate, mp 201–202°.

Anal. Calcd for $C_{26}H_{26}N_4O_8$: C, 59.76; H, 5.02; N, 10.72. Found: C, 59.79; H, 5.08; N, 10.72.

The infrared spectrum (CCl_4) showed a series of strong bands at 3.42, 3.55, 5.95, 6.23, 7.37, 8.42, 9.55, 11.89, and 14.45 μ. The nmr spectrum (CCl_4) showed a sharp singlet at τ 9.06 (9 H) and complex multiplets centered at 6.32 (5 H) and 2.09 (9 H). The ultraviolet spectrum exhibited a maximum at 290 mμ (ϵ 24,300). The mass spectrum showed the parent peak at *m/e* 293 and major peaks at 279, 278 (base), 237, 226, 209, 181, 153, 138, and 127.

Irradiation of *N-tert*-Butyl-3-benzoylazetidine (5). A solution of 0.27 g of **5** in 500 ml of 95% ethanol was irradiated for 14 hr under a nitrogen atmosphere with a 550-W Hanovia mercury arc in an immersion well apparatus fitted with a Pyrex filter. The solvent was removed under reduced pressure and the resulting residue was subjected to preparative thick layer chromatography. The plate was developed with a 90% benzene–10% ethyl acetate solution. Extraction of the upper band with methylene chloride followed by evaporation of the solvent gave 0.1 g (42%) of a yellow oil. The oil was distilled in a Hickman distillation apparatus to give an analytically pure sample of *N-tert*-butyl-3-phenylpyrrole (**9**).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.45; H, 8.69; N, 6.91.

The infrared spectrum (CCl_4) was characterized by bands at 3.30, 6.24, 6.70, 7.30, 7.46, 8.70, 9.15, 10.71, and 14.50 μ. The nmr spectrum (CCl_4) showed a singlet at τ 8.55 (9 H), triplets at 3.69 (J = 2.0 Hz), 3.38 (J = 2.0 Hz), and 3.10 (J = 2.0 Hz), and a multiplet centered at 2.80 (5 H). The ultraviolet spectrum showed a maximum at 256 mμ (ϵ 9700). The mass spectrum showed the parent ion at *m/e* 199, and major peaks at 144, 143 (base), 116, 115, 57, and 41.

Irradiation of *N-tert*-Butyl-3-*p*-phenylbenzoylazetidine (6). A solution of 0.25 g of **6** in 500 ml of 95% ethanol was irradiated with a 450-W Hanovia mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ. After 12 hr, the carbonyl band of starting material had almost completely disappeared. The solvent was removed under reduced pressure and the resulting residue was recrystallized from ethanol to give 0.24 g (98%) of *N-tert*-butyl-3-biphenylpyrrole (**10**), mp 93–95°.

Anal. Calcd for $C_{20}H_{21}N$: C, 87.22; H, 7.69; N, 5.09. Found: C, 86.99; H, 7.66; N, 5.11.

The infrared spectrum of this compound was characterized by a series of bands at 3.35, 3.41, 6.29, 6.75, 7.31, 8.19, 8.69, 10.82, 11.90, and 14.40 μ. The nmr spectrum (CCl_4) consists of a sharp singlet at τ 8.62 (9 H), three triplets at 3.56 (J = 2.5 Hz), 3.25 (J = 2.5 Hz), and 2.92 (J = 2.5 Hz), and a multiplet centered at 2.55 (9 H). The ultraviolet spectrum showed a maximum at 298 mμ (ϵ 29,800). The mass spectrum showed the parent ion at *m/e* 275 and had peaks at 260, 220, 219 (base), 217, 190, and 165.

Irradiation of 3-*N-tert*-Butylazetidinyl *n*-Butyl Ketone (7). A solution of 0.5 g of **7** in 500 ml of 95% ethanol was irradiated for 4 hr with a Hanovia 450-W mercury lamp using a Corex filter. The photolysis was monitored by removing aliquots for glpc analysis. After 4 hr all of the starting material had disappeared and two new peaks had appeared. The solvent was removed under reduced pressure and the residue was subjected to preparative thick layer chromatography. The plate was developed with a 90% benzene–10% ethyl acetate solution. Extraction of the upper band with methylene chloride followed by evaporation of the solvent gave 0.4 g (78%) of a clear oil. This material was distilled in a Hickman distillation apparatus to give an analytically pure sample of *N-tert*-butyl-3-*n*-butylpyrrole (**11**).

Anal. Calcd for $C_{12}H_{21}N$: C, 80.38; H, 11.81; N, 7.81. Found: C, 80.51; H, 12.01; N, 7.94.

The infrared spectrum (CCl_4) of this material shows a series of bands at 3.38, 6.24, 6.70, 7.30, 8.01, 8.70, 9.48, 10.21, 10.81, and 14.50 μ. The ultraviolet spectrum has a maximum at 215 mμ (ϵ 4600). The nmr spectrum (CCl_4) consists of a singlet at τ 8.56 (9 H), a broad multiplet centered at 8.83 (7 H), a triplet at 7.61 (2 H, J = 7.5 Hz), a triplet at 4.22 (1 H, J = 2.5 Hz), a triplet at 3.55 (1 H, J = 2.5 Hz), and a triplet at 3.45 (1 H, J = 2.5 Hz). The mass spectrum showed the parent ion at *m/e* 179 and had major peaks at 164, 136, 94, 81, 80 (base), 57, and 53.

The second component in the reaction mixture was collected by preparative gas chromatography (6 ft × 10.25 in. 8% FS-1265 on Chromosorb W at 150°). The colorless oil obtained was identified as *N-tert*-butyl-3-acetylazetidine (**12**) (13%), by comparison with an authentic sample.

***N-tert*-Butyl-2-benzoylazetidine (13).** To an ice-cooled suspension of 8.4 g of *N-tert*-butylazetidine-2-carboxylic acid[25] in 100 ml of anhydrous ether was added 50 ml of a 1.92 *M* phenyllithium solution. The reaction mixture was warmed to room temperature and stirred for 2 hr. The excess phenyllithium was destroyed by adding 2 ml of ethyl formate and the resulting solution was hydrolyzed with 20 ml of an aqueous ammonium chloride solution. The aqueous layer was extracted twice with ether and the combined extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure to leave a yellow oil. Spinning band distillation of the oil gave 4.6 g (42%) of *N-tert*-butyl-2-benzoylazetidine (**13**), bp 86° (0.04 mm), which solidified upon standing to a waxy solid, mp 54–56° (picrate 189–190°).[29]

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.21; H, 9.07; N, 6.42.

The infrared spectrum was characterized by bands at 3.40, 3.52, 5.90, 5.99, 8.10, 8.20, 9.90, 10.40, and 11.40 μ. The mass spectrum

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(29) R. M. Rodebaugh and N. H. Cromwell, *J. Heterocycl. Chem.*, **6**, 439 (1969), have also prepared **13** by a different synthetic procedure.

had peaks at *m/e* 202, 195, 167, 152, 112, 105, 77, and 56. The nmr spectrum (CCl_4) consists of a singlet at τ 9.09 (9 H), a multiplet centered at 7.80 (2 H), a multiplet at 6.85 (2 H), a triplet at 5.40 (1 H, J = 8.5 Hz), a multiplet at 2.65 (3 H), and a multiplet at 1.90 (2 H).

Preparation of *N*-Benzyl-2-*p*-phenylbenzoylazetidine (17). A stirred suspension of 50 g of biphenyl and 44 g of aluminum chloride in 150 ml of carbon disulfide at 0° was treated in a dropwise manner over a period of 3 hr with 100 g of α,γ-dibromobutyryl bromide.[30] After stirring for 1 additional hr the reaction mixture was hydrolyzed by pouring it over cracked ice. The organic layer was separated, washed with water, and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure followed by trituration of the yellow residue gave α,γ-dibromo-*p*-phenylbutyrophenone as a yellow solid, 80 g (64%), mp 73–75°. This ketone had a strong carbonyl absorption in the infrared at 5.95 μ. The nmr spectrum ($CDCl_3$) consists of a quartet at τ 7.35 (2 H, J = 6.0 Hz), a triplet at 6.33 (2 H, J = 6.0 Hz), a triplet at 4.50 (1 H, J = 6.0 Hz), and a multiplet centered at 7.80 (9 H).

A solution of 3.8 g of the above dibromo ketone, 1.4 ml of benzylamine, and 10 ml of triethylamine in 50 ml of acetonitrile was stirred at room temperature for 24 hr. The solvent was evaporated under reduced pressure and anhydrous ethyl ether was added to the residue. Benzylamine hydrobromide was filtered from the ethereal solution and the mixture was allowed to stand in the freezer overnight. Recrystallization of the solid from hexane–benzene gave 1.8 g of *N*-benzyl-2-p-phenylbenzoylazetidine (**17**) as a white crystalline solid, mp 106–108°.

Anal. Calcd for $C_{23}H_{21}NO$: C, 83.47; H, 6.47; N, 4.28. Found: C, 83.47; H, 6.37; N, 4.22.

The infrared spectrum (KBr) was characterized by a series of bands at 5.95, 6.24, 7.10, 8.13, 10.40, 12.90, 13.30, 13.50, and 14.30 μ. The ultraviolet spectrum exhibited a maximum at 290 mμ (ϵ (18,700). The nmr spectrum ($CDCl_3$) consists of multiplets centered at τ 7.50 (2 H) and 6.86 (2 H), an AB quartet centered at 6.20 (2 H, J = 13.0 Hz), a triplet at 5.45 (1 H, J = 8.0 Hz), and a multiplet centered at 2.25 (9 H). The mass spectrum showed the parent ion at *m/e* 327, and had major peaks at 309, 221, 192, 181, 152, 146, 91 (base), and 69.

Irradiation of *N*-Benzyl-2-*p*-phenylbenzoylazetidine (17). A solution of 1.0 g of **17** in 1 l. of benzene was irradiated for 1 hr under a nitrogen atmosphere with a 450-W Hanovia mercury arc lamp in an immersion well apparatus fitted with a Pyrex filter. The solvent was removed under reduced pressure and the resulting residue was placed on a Florisil column using benzene as the eluent. The first 200 ml contained 0.03 g of a white solid (3%), mp 128–129°, that was subsequently identified as *N*-benzyl-2-biphenylpyrrole (**19**).[31] Further elution of the column afforded only ill-defined tars.

Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.34; H, 6.29; N, 4.46.

The infrared spectrum (KBr) was characterized by a series of bands at 6.20, 6.70, 6.87, 7.70, 9.31, 11.78, 13.05, 13.96, and 14.15 μ. The nmr spectrum ($CDCl_3$) consists of a singlet at τ 4.85 (2 H), a broad singlet at 3.68 (2 H), a multiplet centered at 3.25 (1 H), and a multiplet centered at 2.65 (14 H). The mass spectrum showed the parent ion at *m/e* 309 and had major peaks at 218 and 91.

The structure of the photoproduct was confirmed by an independent synthesis from α,γ-dibromo-*p*-phenylbutyrophenone and benzylamine. A solution of 1.9 g of the dibromo ketone, 0.7 g of benzylamine, and 5 ml of triethylamine in 25 ml of acetonitrile was stirred at room temperature for 20 hr. The solvent was removed under reduced pressure and the crude residue was taken up in anhydrous ether and separated from the hydrobromide salts. The solvent was removed under reduced pressure and the residue was chromatographed on a Florisil column using benzene as the eluent. The first 100 ml of solution contained 200 mg of a white solid. Recrystallization from hexane–benzene gave *N*-benzyl-2-biphenylpyrrole, mp 128–129°. The infrared and nmr spectra of this material were identical in every detail with those of the pyrrole obtained from irradiation of **17**. Further elution of the chromatography column gave *N*-benzyl-2-*p*-phenylbenzoylazetidine (**17**), mp 106–108°.

Irradiation of *N*-*tert*-Butyl-2-benzoylazetidine (13). A solution of 1.0 g of **13** in 1 l. of benzene was irradiated for 3 hr under a nitrogen atmosphere with a 450-W Hanovia mercury arc fitted with a Pyrex filter sleeve. Concentration of the solution left an oil which was triturated with ether to give the *tert*-butylammonium salt of benzoic acid (7%). Gas chromatographic and nmr analysis of the ethereal residue indicated the presence of phenyl vinyl ketone (28%), *tert*-butylamine (17%), dibenzoylethane (4%), acetophenone (9%), and *tert*-butylacetamide (4%). Phenyl vinyl ketone was identified by comparison with an authentic sample.[32]

Preparative thick layer chromatography of the residue resulted in the separation of five distinct bands which were taken up in chloroform. A yellow solid was isolated from the lowest band, which, after recrystallization from benzene–hexane, afforded a white crystalline solid, mp 115–116°. This material was assigned as *N*-*tert*-butyl-3-benzoylpropionamide (**14**) (10%) on the basis of the following data.

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.87; H, 8.25; N, 6.17.

The infrared spectrum (KBr) is characterized by a series of bands at 3.02, 3.40, 5.94, 6.07, 6.45, 8.13, 8.24, 9.91, 12.95, and 14.50 μ. The nmr spectrum ($CDCl_3$) consists of a singlet at τ 8.67 (9 H), a triplet at 7.45 (1 H, J = 7.0 Hz), a triplet at 6.70 (1 H, J = 7.0 Hz), and two multiplets centered at 2.60 (3 H) and 2.05 (2 H). The mass spectrum showed the parent ion at *m/e* 233.

The structure of this material was further verified by comparison with an independently synthesized sample. In 10 ml of anhydrous ether was dissolved 2.7 g of 3-benzoylpropionic acid and 1.4 ml of thionyl chloride. To the mixture was added 1 drop of pyridine and the solution was allowed to stir for 1 hr. The solvent was removed under reduced pressure to give a yellow oil which was recrystallized from methylcyclohexane to give 4-hydroxy-4-phenyl-3-butenoic acid γ-lactone, mp 92–93° (lit.[33] mp 93–94°).

To the above lactone (1.0 g) dissolved in 25 ml of acetonitrile was added 2 ml of *tert*-butylamine. The solution was heated to reflux for 12 hr. At the end of this time the solution was cooled and the solvent was removed under reduced pressure. Recrystallization of the solid from hexane–benzene gave *N*-*tert*-butyl-3-benzoylpropionamide, mp 114–116°. The infrared and nmr spectra of this material were identical in every detail with those of the material obtained from the irradiation of **13**.

Removal of the solvent from the second lowest band of the thick layer plate gave 0.13 g (12%) of a white crystalline solid, mp 91–92°. The material obtained was identified as 1-phenyl-2-formyl-3-benzoylcyclopentene (**15**) on the basis of its elemental analysis and spectral data.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.48. Found: C, 82.39; H, 6.09.

The infrared spectrum (CCl_4) is characterized by a series of bands at 5.86, 5.95, 6.23, 6.90, 7.31, 7.83, 8.28, 10.15, 10.42, 11.53, 13.20, 13.41, and 14.50. The nmr spectrum (CCl_4) consists of multiplets centered at τ 7.83 (2 H), 6.85 (3 H), 2.50, and 2.05 (10 H), and a singlet at 0.08 (1 H). The ultraviolet spectrum exhibits maxima at 242 and 278 mμ. The mass spectrum showed the parent ion at *m/e* 276 and had major peaks at 171, 146, 128, 120, 115, 105 (base), and 91.

The material in the next three bands of the thick layer plate were identified as dibenzoylethane, *tert*-butylacetamide, and phenyl vinyl ketone by comparison with authentic samples.

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 solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate/100 ml of water through the inner jacket.[21] 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 with the benzoylazetidines. Reliably reproducible output rates of 4.86×10^{16} quanta sec^{-1} were recorded. For the aliphatic azetidinyl ketone, a 2-hexanone solution was used as the chemical actinometer. An actinometer quantum yield of 0.33 was used[13] which gave a reproducible lamp output of 2.01×10^{16} quanta sec^{-1}. After the irradiation the degree of

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(30) B. Wladislaw, *J. Org. Chem.*, 26, 711 (1961).

(31) Pyrrole 19 is readily separated from azetidine 17 by thin layer chromatography. It could be easily shown that azetidine 17, used as the photochemical precursor for pyrrole 19, was pure and devoid of any pyrrole (19).

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reaction was determined by quantitative vapor phase chromatography. The conversions in the azetidines series were run to 15% or less. The mass balance in these runs was generally better than 90%.

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 sec) 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).

Acknowledgment. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Crystal and Molecular Structure of 4-Azoniaspiro[3.5]nonane Perchlorate

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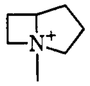
Abstract: The crystal and molecular structure of the title compound was determined by single-crystal X-ray diffraction techniques. The compound crystallizes in space group $P2_1/c$, with four molecules in a unit cell of dimensions $a = 6.6998 \pm 0.0007$ Å, $b = 13.244 \pm 0.001$ Å, $c = 12.743 \pm 0.001$ Å, $\beta = 97.75 \pm 0.01°$. The structure was solved by the heavy-atom method and refined by block-diagonal matrix least squares to a final value of $R = 0.066$ for 683 observed reflections. The azetidinium ring is very nearly planar with a dihedral angle of 176.5°, and average C–C and C–N distances of 1.50 ± 0.01 Å and 1.52 ± 0.02 Å, respectively. The piperidinium moiety is in the chair conformation with all ring distances being equivalent; the average of the C–C distances is 1.491 ± 0.02 Å and the average of the C–N distances is 1.498 ± 0.01 Å.

The study of 4-azoniaspiro[3.5]nonane perchlorate, $(C_9H_{16}N)^+ ClO_4^-$ (I), was undertaken as part of a more general study of simply substituted azetidine derivatives in various bonding situations. The interest in these compounds is due to their structural similarity to the biologically active β-lactam moiety found in the penicillins and cephalosporins, and the unusual molecular parameters generally found in the small strained rings. Several X-ray studies of simply substituted azetidine derivatives have been made since 1968.[1-5] Until the recent X-ray study of II,[6] no structural studies had been made of bicyclic derivatives of azetidine except as penicillins or cephalosporins. The present study is the first investigation of a spiro-fused azetidine derivative.

I



II

Crystal Data. A crystalline sample of the title compound was kindly furnished to us[7] by Professor Nelson J. Leonard of the University of Illinois. Single crystals suitable for X-ray study were obtained by recrystallization from a saturated solution of ethyl acetate and melted sharply at 169°. The crystal chosen for this study had approximate dimensions of 0.1 mm × 0.1 mm × 0.1 mm.

Systematic absences for the (*h0l*) reflections when *l* is odd, and for the (*0k0*) reflections when *k* is odd, led unambiguously to the assignment of the space group as $P2_1/c$. Lattice constants were determined by least-squares refinement[8] of 29 reflections whose 2θ values in the range from 55 to 59° were measured under fine conditions (1° take-off angle and 0.05° receiving slit) on a G.E. XRD-5 diffractometer using Cu Kα radiation. The constants obtained from the refinement, with their estimated standard deviations (ESD's), were: $a = 6.6998 \pm 0.0007$ Å, $b = 13.244 \pm 0.001$ Å, $c = 12.743 \pm 0.001$ Å, $\beta = 97.75 \pm 0.01°$. The calculated density of 1.338 g/cc for four molecules per unit cell was in agreement with the experimentally measured density of 1.35 g/cc using flotation techniques.

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