transition state is like **5**, **6**, or **11**. The experimental entropies of activation for the inversion of **3** and **4** agree with these values within experimental error. For cyclohexane,[16] the experimental entropy of activation is also close to that calculated on the basis of symmetry considerations.

Experimental Section

Compounds **3** and **4** were obtained from Pierce Chemical Co., and used without further purification dissolved in dichlorodifluoromethane. Spectra were recorded on a Varian Associates A56/60A spectrometer at operating frequency 56.4 MHz, and were calibrated by the sideband technique using a Hewlett-Packard audiooscillator. The spectrometer was equipped with a V6040 temperature control unit and a probe capable of operating at $-150°$. Temperatures were measured immediately after recording spectra by stopping the spinning of the sample tube, inserting a calibrated thermocouple to the bottom of the tube, and measuring the potential relative to a second thermocouple in ice–water. Temperatures were reproducible to better than 0.5° but systematic errors[17] probably reduced the accuracy to ±1–2°.

The spectra calculated as a function of τ used a program devised by Gerig[7] based on the equations of Alexander.[18] Plots of these spectra were obtained from an IBM 7094 computer linked to a Calcomp plotter. The "line width in the absence of exchange" which must be provided for this program was taken to be the line width at room temperature for spectra above the coalescence temperature, and the line width at about $-150°$ for spectra below coalescence. There is certainly no contribution from kinetic broadening to these line-widths, but there must be contributions from small vicinal and long-range couplings, more or less obscured by field inhomogeneity. The assumed natural line width may therefore cause noticeable errors when the exchange contribution to line broadening is small, particularly near the upper temperature limit, so in these cases, the spectra with line widths less than about three times the natural line width were excluded. Nevertheless, measurements over a 40° temperature range (and more than two orders of magnitude in rate) were possible for both compounds. Within this range, which is the range of greatest change of the spectra, changes of 5% in the value of τ were quite noticeable, so that values quoted are considered to be accurate to at least this degree. Table II shows the values of τ so obtained at various temperatures.

The Arrhenius plots shown in Figure 3 were fitted by a least-squares computer program, which also provided the root-mean-square errors quoted for the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. The figures for $\Delta G^{\ddagger}$ were calculated by the Eyring equation from the experimental value of τ at that temperature. The value of the transmission coefficient was taken as 1, as explained above. The accuracy of values of $\Delta G^{\ddagger}$ based on the accuracy of measurement of the temperature and τ is thought to be ±0.1 kcal/mole.

(16) F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **89**, 760 (1967).
(17) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. Meinzer, *ibid.*, **88**, 3165 (1966).
(18) S. Alexander, *J. Chem. Phys.*, **37**, 974 (1962).

Photochemical Transformations of Small-Ring Carbonyl Compounds. XXII. Observations on the Scope of the Photoinduced Ring Expansion of Aroylazetidines[1,2]

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Abstract: The photoinduced ring expansion of selected arylaroylazetidines has been examined. Upon irradiation with ultraviolet light in ethanol solution, *cis*-N-*t*-butyl-2-phenyl-3-benzoylazetidine (**1**) rearranges smoothly and in high yield to N-*t*-butyl-2,4-diphenylpyrrole (**3**). The course of the over-all photoreaction is substantially altered for the *trans* isomer. Irradiation of *trans*-N-*t*-butyl-2-phenyl-3-benzoylazetidine (**2**) gave a mixture of 2,3- and 2,4-diphenyl-N-*t*-butylpyrroles. No photoepimerization of starting material or photoisomerization of product could be detected. Experiments with *p*-phenylbenzoylazetidines **6** and **8** and several differently deuterated azetidines helped elucidate the positions of the carbon atoms in the pyrrole ring after rearrangement occurred. Mechanistic discussion is given in the following paper.

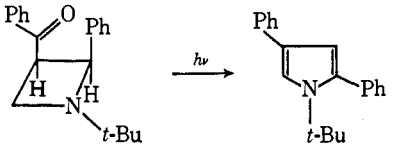
During the past several years, it has become increasingly apparent that the photochemistry of heterocyclic small-ring ketones has provided an intriguing new source of unusual molecular rearrangements. The general types of phototransformations which have been observed with aroylaziridines have been summarized in recent papers from this laboratory.[4,5] It is evident that the three-membered heterocyclic ring exhibits versatile and intriguing properties upon electron excitation and that its behavior is strongly influenced by its chemical environment and initial stereochemistry. As part of our continuing interest in the photochemistry of small-membered rings we have investigated the chemical response to ultraviolet radiation of the related four-membered nitrogen heterocycle. In preliminary reports[2,6] we have communicated that this system is exceptionally reactive, undergoing photochemical transformations that are seemingly dependent on the initial

(1) For part XXI, see A. Padwa and E. Alexander, *J. Amer. Chem. Soc.*, **90**, 6871 (1968).
(2) For a preliminary report of this work, see A. Padwa and R. Gruber, *ibid.*, **90**, 4456 (1968). This work was presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.
(3) Alfred P. Sloan Foundation Research Fellow, 1968–1970.
(4) A. Padwa and L. Hamilton, *J. Amer. Chem. Soc.*, **89**, 102 (1967).
(5) A. Padwa and W. Eisenhardt, *ibid.*, **90**, 2442 (1968).
(6) A. Padwa, R. Gruber, and L. Hamilton, *ibid.*, **89**, 3077 (1967).

stereochemistry about the azetidine ring. It is our intent in this work to investigate more fully the scope of these novel photoreactions so as to provide further insight into the mechanism of the reaction. This paper describes the products of photolysis of several *cis*- and *trans*-arylaroylazetidines, including detailed structure proofs for new compounds. Mechanistic discussion is given in the accompanying paper[7] which presents experimental evidence allowing characterization of the excited states responsible for these reactions and kinetic data which permit approximation of the rate constants for the primary processes.

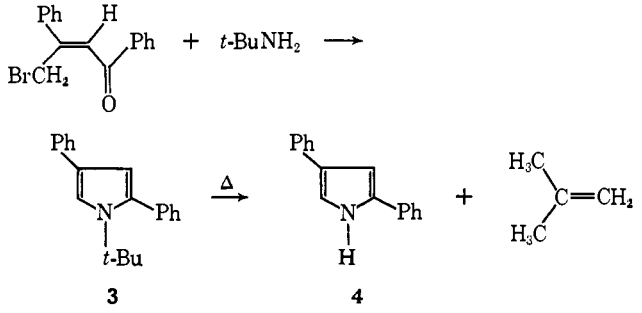
Results

cis- and *trans*-1-*t*-butyl-2-phenyl-3-benzoylazetidines (**1** and **2**) were conveniently prepared from *trans*-α-bromomethylchalcone and *t*-butylamine according to established procedures.[8] Irradiation of **1** in dilute alcohol solution using a 450-W Hanovia lamp with a Pyrex filter was followed by withdrawal of small aliquots at various time intervals and examination of these by infrared spectroscopy. In a typical case a solution of 0.5 g of **1** in 800 ml of 95% ethanol was irradiated for 3 hr. Conventional isolation procedures afforded 0.46 g of a solid (95%), mp 102–103°, whose structure is assigned as N-*t*-butyl-2,4-diphenylpyrrole (**3**) on the basis of its elemental analysis and spectral data. The



1 **3**

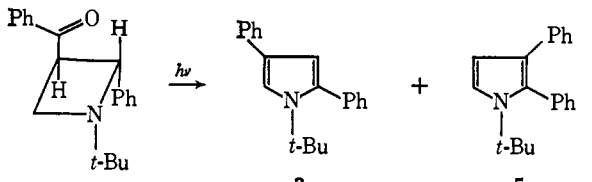
nmr spectrum exhibits a singlet at τ 8.60 attributable to the *t*-butyl protons, a pair of doublets at τ 3.80 and 2.96 (J = 1.9 Hz) that were assigned to the pyrrole hydrogens, and a multiplet centered at τ 2.62 due to the aromatic protons. The doublet pattern of the pyrrole protons is to be expected, as it has been shown that the cross-ring or *meta*-coupling constant ($J_{3,5}$) in the pyrrole system has a value of approximately 2.0 Hz.[9] Chemical confirmation of structure **3** was obtained by pyrolysis of the pyrrole at 225°. The product obtained in better than 97% yield was identical with an authentic sample of 2,4-diphenylpyrrole (**4**) synthesized by the method of Allen and Wilson.[10] Structure **3** was further



3 **4**

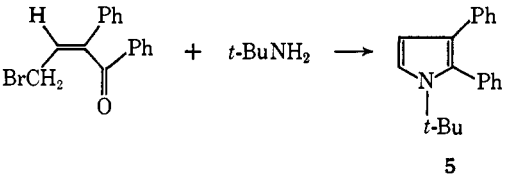
confirmed by its unequivocal synthesis from 1,3-diphenyl-4-bromo-2-buten-1-one and *t*-butylamine.[11,12]

The course of the over-all photoreaction was observed to be substantially altered with *trans*-azetidine **2**. Exposure of a dilute solution of **2** in 95% ethanol to a Hanovia 450-W lamp resulted in the formation of a mixture of two substances. The products were separated by column chromatography and identified as N-*t*-butyl-2,4-diphenylpyrrole (**3**) (33%) and N-*t*-butyl-2,3-diphenylpyrrole (**5**) (67%). The structure of **5** was



2 **3** **5**

elucidated from its elemental analysis, spectral data, and by an independent synthesis. Specifically, the nmr spectrum exhibits doublets at τ 3.74 and 3.14 (J = 3.2 Hz), with a typical *ortho*-coupling constant for the pyrrole ring,[9] together with a singlet at τ 8.62 (9 H) and a multiplet centered at τ 2.75 (10 H). Structure **5** was further established by the identity of its infrared spectrum and undepressed mixture melting point with an authentic sample obtained by the cyclization of 4-bromo-1,2-diphenyl-2-buten-1-one with *t*-butylamine.



5

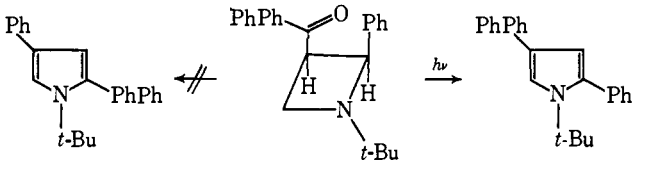
Spectral comparison of the minor component with an authentic sample of **3** served to confirm its structure.[13]

The formation of the pyrrole ring by reaction of an unsaturated bromo ketone with a primary amine may be explained by SN2 displacement of bromine by the amino group, followed by an intramolecular condensation involving amine attack on the carbonyl group and subsequent elimination of a molecule of water.

The photoreactions outlined above take place with major reorganization of the azetidine ring. Knowledge of the positions of the carbon atoms in the pyrrole ring after rearrangement would greatly aid the mechanistic interpretation. This may be accomplished either by substituent or deuterium labeling of the azetidine ring. In order to determine whether the phenyl substituent in the 2 position of the pyrrole ring originated from the benzoyl group of starting azetidine, the irradiation of *cis*- and *trans*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (**6** and **8**) was studied. The *p*-phenylbenzoyl group was chosen as the labeling substituent because of the synthetic availability of starting azetidine.[14,15]

(7) A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 107 (1970).
(8) J. L. Inbach, E. Doomes, R. P. Rebman, and N. H. Cromwell, *J. Org. Chem.*, **32**, 78 (1967).
(9) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).
(10) C. F. H. Allen and C. V. Wilson, "Organic Synthesis," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 348.
(11) A. Padwa, R. Gruber, and D. Pashayan, *J. Org. Chem.*, **33**, 454 (1968).
(12) R. Rodebaugh and N. Cromwell, *Tetrahedron Lett.*, **30**, 2859 (1967).
(13) Similar results were obtained from the irradiation of *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylazetidines. For this case, irradiation of the *cis* isomer gives exclusively the N-cyclohexyl-2,4-disubstituted pyrrole, whereas irradiation of the *trans* isomer results in a mixture of 2,3- and 2,4-disubstituted pyrroles; D. Pashayan, unpublished results.
(14) N. H. Cromwell and E. Doomes, *Tetrahedron Lett.*, 4037 (1966).
(15) This group was also chosen to provide further information on the nature of the excited state responsible for the photoreaction; see accompanying paper.

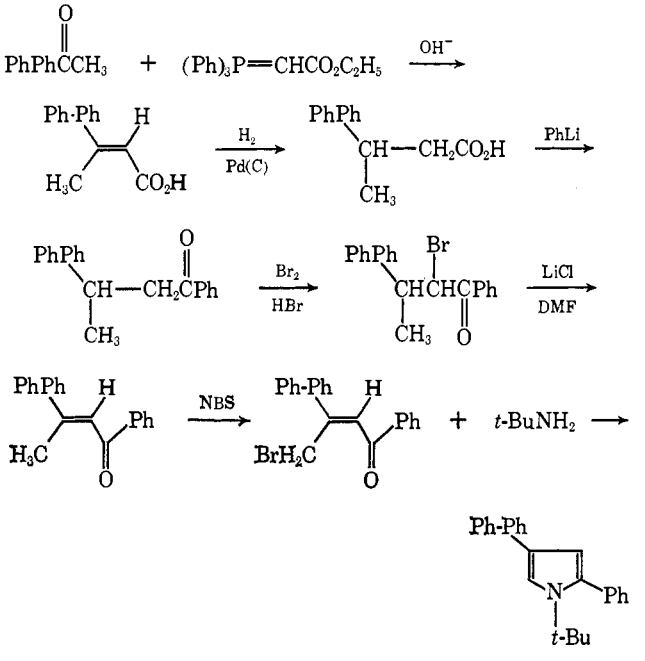
The isomeric aroylazetidines **6** and **8** were prepared according to literature methods.[14] Physical properties agreed with those reported in the literature. Irradiation of *cis*-azetidine **6** in 95% ethanol through Pyrex filters resulted in the formation in good yield of a single photoproduct **7**. The analytical and spectral data confirm the identity of the photoproduct as a N-substituted 2,4-diarylpyrrole. The nmr spectrum indicates the



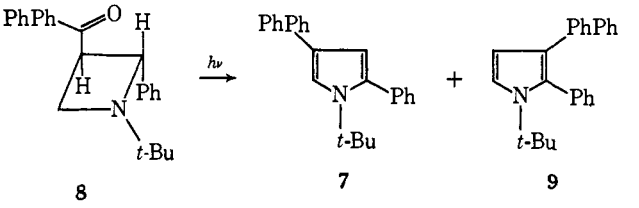
6 **7**

presence of two pyrrole hydrogens, whose coupling constant of 2.0 Hz is in agreement with couplings reported for other 2,4-disubstituted pyrroles.[9] The location of the biphenyl group on the 4 position of the pyrrole ring was determined by an independent synthesis of **7**. The preparation of N-*t*-butyl-2-phenyl-4-biphenylpyrrole (**7**) required 4-bromo-3-biphenyl-1-phenyl-2-butenone as a key intermediate. The synthesis of this ketone was achieved by treating 4-acetylbiphenyl with ethyltriphenyl phosphoramylidene acetate so as to give 2-biphenylcrotonic acid. The next step intended involved the conversion of the carboxyl group to a phenyl ketone by treating the acid with phenyllithium. However, all attempts to effect this transformation failed to yield the desired product. Similarly, conversion of the acid to the corresponding acyl chloride and treatment with diphenyl cadmium also failed to produce the expected product. In both cases a complex mixture of products was obtained. This difficulty was circumvented by hydrogenating the acid over 10% palladium on carbon. Subsequent treatment of the saturated acid with phenyllithium gave 1-phenyl-3-biphenylbutanone. The double bond was reintroduced by a bromination–dehydrobromination sequence utilizing lithium chloride. Treatment of the unsaturated ketone with N-bromosuccinimide afforded an allylic bromide which could be cleanly converted to **7** by refluxing with *t*-butylamine. The sample of **7** produced by this route showed no melting point depression on admixture with the photoproduct obtained from **6**. These syntheses are summarized in Chart I.

Chart I. Synthesis of N-*t*-Butyl-2-phenyl-4-biphenylpyrrole



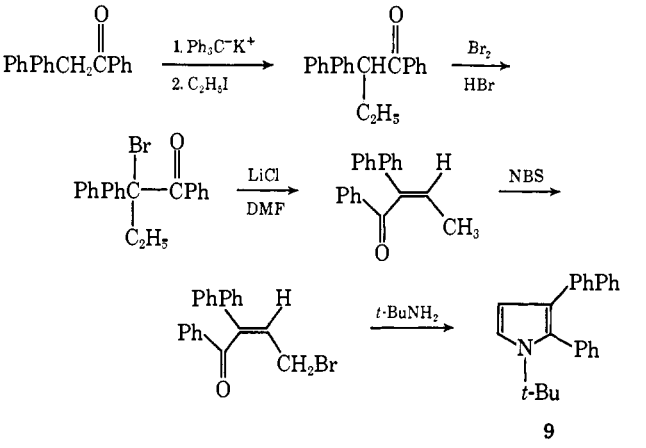
When *trans*-azetidine **8** was photolyzed in alcohol solution with a broad-spectrum lamp in Pyrex vessels, a mixture of pyrroles was produced. The minor component present in the photolysis mixture (35%) was identified as **7**; the major component was assigned as N-*t*-butyl-2-phenyl-3-biphenylpyrrole (**9**) (53%). The



8 **7** **9**

structure of pyrrole **9** was proved by an independent synthesis. Thus cyclization of 1-phenyl-2-biphenyl-4-bromo-2-buten-1-one with *t*-butylamine led to **9** as shown in Chart II. Pyrrole **9** was obtained in good

Chart II. Synthesis of N-*t*-Butyl-2-phenyl-3-biphenylpyrrole



9

yield and proved identical in all respects with the photochemically obtained material. This synthesis unambiguously defines the location of the aryl groups at C-2 and C-3 of the pyrrole ring.

Substituent labeling of the azetidine ring with deuterium was chosen as an alternate method for obtaining additional information on the reaction mechanism. Deuterium would not be expected to produce gross substituent effects in this type of reaction and should distort the nature of the rearrangement under investigation to a minimal extent. Location of the deuterium atom after reaction could be readily accomplished by nmr spectroscopy. The nmr of disubstituted pyrroles have been extensively investigated by Abraham and Bernstein who have shown that they give simple spectra with coupling constants characteristic of the mode of disubstitution.[9] The preparation of deuterated azetidines **10–13** was carried out as delineated in Charts III and IV. *trans*-N-*t*-Butyl-2-phenyl-3-benzoylazetidine-3-d_1 (**14**) was readily prepared by heating **1** in CH_3OD that contained a small amount of potassium carbonate. Mass spectrograph analysis indicated that all of the ketones were fully deuterated (>98%) at the specified position. The nmr of the diarylpyrroles obtained from

Chart III. Synthesis of *cis*- and *trans*-N-*t*-Butyl-2-phenyl-3-benzoylazetidine-4,4-d_2

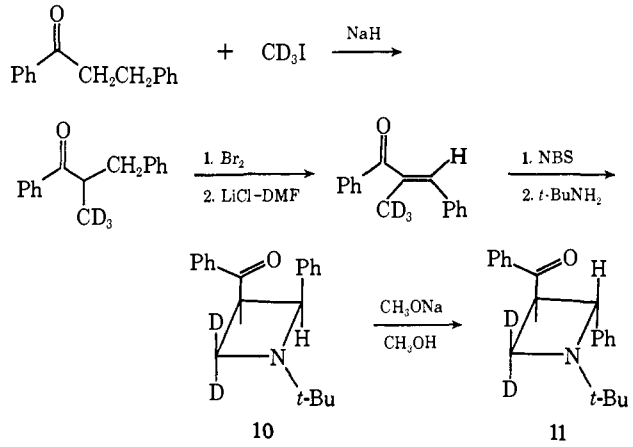
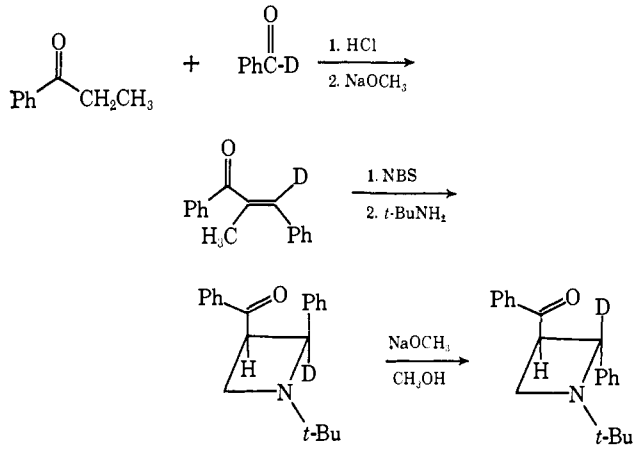
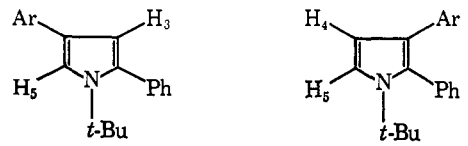


Chart IV. Synthesis of *cis*- and *trans*-N-*t*-Butyl-2-phenyl-3-benzoylazetidine-2-d_1



irradiation of the above azetidines showed an internally consistent chemical shift pattern. The pyrrole hydrogen adjacent to the nitrogen atom (H_5) is shifted downfield with respect to the remaining hydrogens (H_3 and H_4) as shown in Table I. An analysis of the AB spectra of the diarylpyrroles gave average values of J_{meta} = 2.0 Hz and J_{ortho} = 3.1 Hz indicating no unexpected effect of the aryl group on the coupling constants.[16] The results obtained are summarized in Chart V.

Table I. Position and Coupling Constant of the Pyrrole Hydrogen in the Nmr as a Guide to Structural Assignments[a]



Starting azetidine	Product pyrrole	Chemical shift, τ (J, Hz) H_3	H_4	H_5
1	3	3.80 (1.9)		2.96 (1.9)
2	5		3.79 (3.0)	3.18 (3.0)
6	7	3.72 (2.0)		2.89 (2.0)
8	9		3.74 (3.2)	3.14 (3.2)
10	15	3.78 (S)[c]		
11[b]	16		3.79 (S)[c]	
12	3	3.80 (1.9)		2.96 (1.9)
13[b]	5		3.79 (3.0)	3.18 (3.0)
14	17			2.90 (S)
14[b]	18			3.20 (S)

[a] Carbon tetrachloride employed as solvent. [b] *trans*-Azetidines **11**, **13**, and **14** gave a mixture of disubstituted pyrroles. The 2,4-disubstituted pyrrole isolated has the deuterium in the same position as does the pyrrole obtained from the related *cis* isomer. [c] Singlet.

The evidence obtained thus far shows that *trans*-aroylazetidines yield a mixture of 2,3- and 2,4-diarylpyrroles whereas irradiation of *cis*-aroylazetidines gives rise to a single pyrrole. However, before the importance of this could be assessed, it was necessary to determine the stability of these products on further irradiation. That the formation of the 2,3-diarylpyrrole might proceed through the intermediacy of the 2,4-isomer was considered a likely possibility. Recently, several examples of light-induced rearrangements of five-membered ring heterocycles have appeared in the literature,[17-21] providing reasonable chemical precedent for the above suggestion. As a preliminary step toward verifying this postulation, a search for the possible photoisomerization was made. Irradiation of **3** gave only 2,4-diphenylpyrrole[22] and we are therefore led to conclude that **5** is not formed from the irradiation of **3**. Similarly, the photolysis of **5** revealed that no detectable quantities of **3** were formed. The further complication of a photocatalyzed epimerization of starting material (**1** ⇄ **2**) was eliminated by the finding that irradiation of *cis*-azetidine **1** (or the *p*-phenylbenzoyl analog **6**) did not afford **2** (or **8**). Attempts to detect photoepimerization using *trans*-azetidines **2** and **8** were also unsuccessful. This result is important, since the distribution of pyrroles could have been attributed to rapid interconversion of the reactant followed by stereoselective rearrangement of each azetidine.

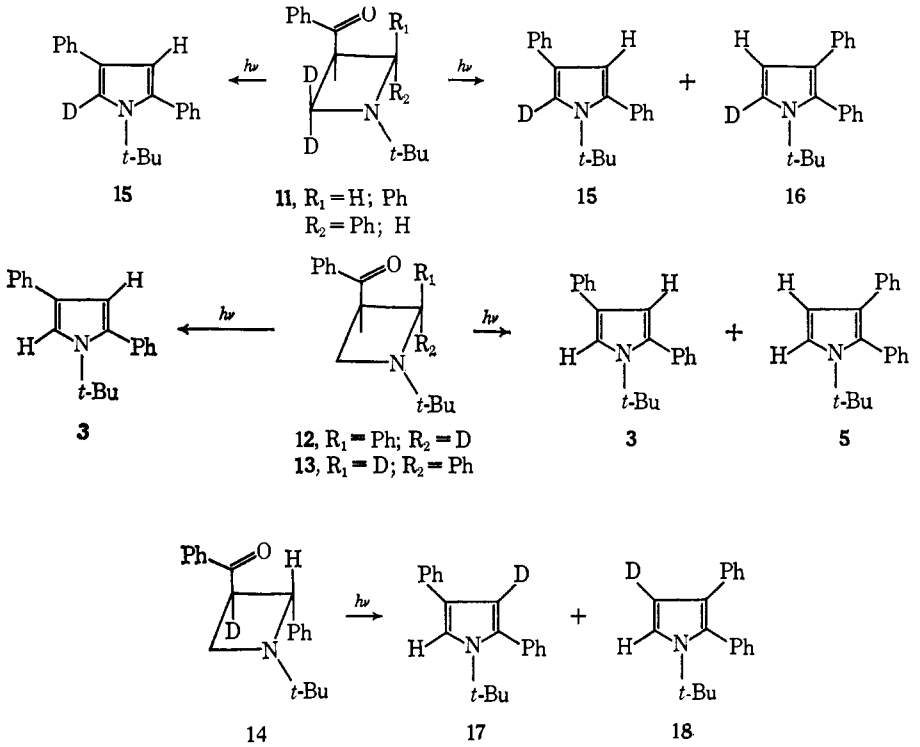
Discussion

The photoinduced ring expansion of aroylazetidines occurs with a number of different aroyl substituents. The most remarkable result obtained is perhaps the specificity of rearrangement, leading to one primary product from *cis* starting material and a mixture of two primary products 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**. Essentially the same distribution resulted with the *p*-phenylbenzoyl system. The rearrangement of several deuterated azetidines occurs with a high degree of specificity and pinpoints the location of all the carbon atoms in the pyrrole ring after rearrangement. The minor rearrangement product from the *trans*-azetidine has the same substitution pattern as the product obtained from the *cis* isomer. This suggests that the formation of 2,4-diarylpyrroles from both *cis*- and *trans*-aroylazetidines proceeds *via* a common photoroute. Discussion of the reaction mechanism and the nature of the excited state

(16) Values of J_{meta} = 1.5–2.1 Hz and J_{ortho} = 2.0–2.6 Hz have been reported.[9]

(17) E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967).
(18) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967).
(19) H. Tiefenthaler, W. Dorsheln, H. Goth, and H. Schmid, *Tetrahedron Lett.*, 2999 (1964).
(20) P. Beak, J. L. Miesel, and W. R. Messer, *ibid.*, 5315 (1967).
(21) E. E. van Tamalen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3894 (1968).
(22) A. Padwa, R. Gruber, D. Pashayan, M. Bursey, and L. Dusold, *Tetrahedron Lett.*, 3659 (1968).

Chart V



responsible for the rearrangement is deferred to the following paper.

Experimental Section[23]

Irradiation of *cis*-1-*t*-Butyl-2-phenyl-3-benzoylazetidine (1). A solution of 0.5 g of **1**[8] in 800 ml of 95% ethanol was irradiated with a Hanovia 450-W mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ.[24] After 3 hr, the carbonyl band of starting material had almost completely disappeared and a new band at 6.24 μ developed. The solvent was removed under reduced pressure and the resulting residue was recrystallized from methanol to give 0.46 g (95%) of N-*t*-butyl-2,4-diphenylpyrrole (**3**), mp 102–103°.

Anal. Calcd for $C_{20}H_{21}N$: C, 87.22; H, 7.69; N, 5.09. Found: C, 87.20; H, 7.85; N, 5.09.

The infrared spectrum of this compound was characterized by a series of bands at 6.24, 8.21, 12.47, 13.08, 13.50, 14.25, and 14.40 μ. The ultraviolet spectrum showed maxima at 235 mμ (ε 15,800) and 276 mμ (ε 16,200). The nmr spectrum ($CDCl_3$) consists of a singlet at τ 8.60 (9 H), a pair of doublets at τ 3.80 (1 H) and 2.96 (1 H) (J = 1.9 Hz), and a multiplet centered at τ 2.62 (10 H). The mass spectrum exhibits the parent ion at m/e 293.

Chemical confirmation of this structure was obtained by pyrolysis of **3** to the known 2,4-diphenylpyrrole (**4**). A sealed tube containing 0.20 g of **3** was heated at 225° for 1 hr. Upon cooling the light brown oil solidified and was recrystallized from toluene to afford 0.185 g (93%) of a white crystalline solid, mp 178–179°. This compound was identical in all respects with an authentic sample of 2,4-diphenylpyrrole prepared according to the procedure of Allen and Wilson.[10] A mixture melting point was undepressed at 178–179°.

The structure of the photoproduct was confirmed by its unequivocal synthesis. A solution of 5.0 g of 4-bromo-1,3-diphenyl-2-buten-1-one[25] and 20 g of *t*-butylamine in 80 ml of benzene was refluxed for 4 hr. After being cooled the mixture was filtered from the amine hydrobromide and the benzene solution was evaporated to dryness. Recrystallization of the residue from hexane–benzene gave colorless prisms, mp 102–103°. The infrared and nmr spectra of this material were identical in every detail with those of N-*t*-butyl-2,4-diphenylpyrrole isolated from the photolysis of **1**.

Irradiation of *trans*-1-*t*-Butyl-2-phenyl-3-benzoylazetidine (2). Photolysis of 0.293 g of **2** in 950 ml of 95% ethanol was carried out for 3 hr with a Pyrex filter using a 450-W Hanovia medium pressure arc. The solvent was removed under reduced pressure and the resulting residue was placed on a florisil column. A 1% ethyl acetate–hexane solution was used to elute the column (25 × 300 mm). The first 300 ml contained 0.17 g (62%) of a white solid, mp 125–128°. Recrystallization from 95% ethanol gave 0.16 g of a crystalline white solid, mp 128–129°. This component was subsequently identified as N-*t*-butyl-2,3-diphenylpyrrole (**5**).

Anal. Calcd for $C_{20}H_{21}N$: C, 87.22; H, 7.69; N, 5.09. Found: C, 86.88; H, 7.63; N, 4.85.

The infrared spectrum was characterized by bands at 6.85, 7.31, 8.20, 13.15, 13.65, and 14.42 μ. The ultraviolet spectrum (95% ethanol) showed a maximum at 254 mμ (ε 10,600). The nmr spectrum ($CDCl_3$) showed a singlet at τ 8.62 (9 H), doublets at τ 3.79 (J = 3.0 Hz, 1 H) and 3.16 (J = 3.0 Hz, 1 H), and a multiplet centered at τ 2.65 (10 H). The mass spectrum showed the parent ion at m/e 293.

The next 400 ml of solvent afforded 0.07 g of a crude solid, which, after repeated recrystallization from methanol, gave 0.055 g (20%) of a white solid, mp 102–103°. This material was identified as N-*t*-butyl-2,4-diphenylpyrrole (**3**). Gas chromatographic analysis indicated only the presence of **3** (33%) and **5** (67%). The chromatographic analysis was carried out on a 6 ft × 0.25 in. 10% SE-30 methyl silicone gum rubber on Diatoport S at a column temperature of 235°.

N-*t*-Butyl-2,3-diphenylpyrrole (5). An authentic sample of **5** was prepared by the reaction of 4-bromo-1,2-diphenyl-2-buten-1-one with *t*-butylamine according to the following procedure. A solution of 8.0 g (0.041 mol) of 1-bromo-1-phenyl-1-propene in 50 ml of anhydrous ether was added to 1.06 g (0.045 mol) of magnesium metal in 80 ml of ether. To the above solution was added 4.3 g (0.041 mol) of benzaldehyde at 10°. The reaction mixture was stirred for 30 min at room temperature and then decomposed with a saturated ammonium chloride solution. The ethereal layer was removed, dried over magnesium sulfate, and then concentrated under reduced pressure to give a light yellow oil. The infrared

(23) 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.

(24) Similar results were obtained when benzene, pentane, 2-propanol, or methanol was used as the solvent.

(25) H. H. Wasserman, N. E. Aubrey, and H. E. Zimmerman, *J. Amer. Chem. Soc.*, 75, 96 (1953).

spectrum (neat) of the oil showed a series of bands at 2.95, 5.98, 6.71, 6.92, 9.70, 11.70, 13.21, and 14.34 μ. The nmr spectrum (CCl_4) showed a doublet at τ 8.32 (3 H, J = 6.8 Hz), broad singlets at τ 6.52 (1 H) and 5.70 (1 H), and multiplets centered at τ 4.22 (1 H) and 2.93 (10 H). The structure of this material was assigned as 1,2-diphenyl-1-hydroxy-2-butene.

To the above alcohol in 300 ml of pentane was added 16 g of activated manganese dioxide. The mixture was allowed to stir at room temperature for 22 hr. At the end of this time the mixture was filtered and the solvent was evaporated under reduced pressure to give a yellow oil. The oil was filtered through a florisil packed column (0.8 × 14 in.) with 1.2 l. of a 0.5% ethyl acetate–hexane mixture. Evaporation of the solvent left 6.8 g of a colorless oil which was distilled (pot temperature 150° at 0.05 mm) in a Hickman distillation apparatus to give an analytically pure sample of 1,2-diphenyl-2-butenone.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.15; H, 6.21.

The infrared spectrum (neat) of the unsaturated ketone exhibits bands at 6.00, 6.92, 8.20, 9.81, 11.45, 13.10, 13.82, and 14.35 μ. The nmr spectrum (CCl_4) showed a doublet at τ 8.30 (3 H), a quartet at τ 3.80 (1 H, J = 7.1 Hz), and multiplets centered at τ 2.72 (8 H) and 2.17 (2 H).

A solution containing 3.10 g (0.0140 mol) of 1,2-diphenyl-2-butenone, 0.05 g of benzoylperoxide, and 2.6 g (0.0147 mol) of N-bromosuccinimide in 60 ml of carbon tetrachloride was refluxed for 7 hr. At the end of this time the insoluble succinimide was removed by filtration and the filtrate was evaporated under reduced pressure to give a colorless oil. The material obtained was identified as 4-bromo-1,2-diphenyl-2-butenone by its infrared and nmr spectra. The infrared spectrum (neat) showed a series of bands at 6.01, 6.92, 8.12, 13.01, and 14.32 μ.

A solution of the above bromide in 500 ml of benzene containing 20 g of *t*-butylamine was refluxed for 2 hr. The benzene solution was then washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure followed by crystallization of the residue from methanol gave 1.9 g of a crystalline solid **5**, mp 128–129°. The infrared and nmr spectra of this material were identical with the major product obtained from the irradiation of *trans*-azetidine **2**.

Irradiation of *cis*-1-*t*-Butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (6). A solution of 1.50 g of 6[14] in 900 ml of 95% ethanol was irradiated for 3 hr under a nitrogen atmosphere with a 450-W medium pressure Hanovia Type L mercury arc in an immersion well apparatus fitted with a Pyrex filter. The solvent was removed under reduced pressure at 50° to yield 1.4 g (98%) of slightly crude N-*t*-butyl-2-phenyl-4-biphenylpyrrole (7). Recrystallization from methanol gave 1.35 g of a crystalline solid, mp 136–137°.

Anal. Calcd for $C_{26}H_{25}N$: C, 88.84; H, 7.17; N, 3.99. Found: C, 88.52; H, 7.15; N, 3.89.

The infrared spectrum was characterized by bands at 6.80, 7.35, 8.20, 11.80, 12.30, 13.02, 13.41, and 14.31 μ. The nmr spectrum (CCl_4) showed a singlet at τ 8.55 (9 H), doublets at τ 3.72 (1 H) and 2.86 (1 H, J = 2.0 Hz), and a multiplet centered at τ 2.55 (10 H). The ultraviolet spectrum exhibited a maximum at 303 mμ (ϵ 29,250). The structure of this compound was verified by an independent synthesis as described below.

N-*t*-Butyl-2-phenyl-4-biphenylpyrrole (7). To a solution of 90 g (0.0459 mol) of 4-acetylbiphenyl dissolved in 300 ml of cumene was added 160 g of ethyl triphenylphosphoramylidene acetic acid. The solution was heated at reflux for 13 hr. At the end of this time the precipitated triphenylphosphine oxide was filtered and the cumene was removed under reduced pressure. A solution of 36 g of sodium hydroxide in 1 l. of 80% ethanol was added to the above residue and the mixture was heated to reflux for 1.5 hr. The mixture was cooled to room temperature and diluted with 2 l. of water. The white precipitate that formed was removed and discarded. Acidification of the clear filtrate with concentrated hydrochloric acid gave a solid which was subsequently filtered. Recrystallization from benzene gave colorless needles, (22 g (22%)) mp 203–204°, of 2-biphenyl crotonic acid.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.67; H, 6.10.

The infrared spectrum exhibited bands at 5.95, 8.01, 10.71, 11.50, 11.90, 12.95, and 14.45 μ. The neutralization equivalent was determined at 237 (calcd 238).

A solution of 20 g of the above acid in 150 ml of methanol was hydrogenated in a Parr shaker over 1 g of Raney nickel for 24 hr at 50 psig. The catalyst was removed by filtration and the filtrate was concentrated to give a white solid. Recrystallization from methanol afforded 18 g of 3-biphenyl butyric acid as colorless crystals, mp 122–123°.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.31; H, 6.82.

The infrared spectrum showed strong bands at 5.88, 7.18 (split), 11.89, 12.96, 13.60, and 14.25 μ. The nmr spectrum (CCl_4) showed doublets at τ 8.72 (3 H, J = 6.8 Hz) and 7.42 (2 H, J = 6.5 Hz) and multiplets centered at τ 6.81 (1 H) and 2.65 (9 H).

A solution of 17.2 g (0.072 mol) of the above acid in 150 ml of ether was added dropwise to a cooled (10°) solution of 6.6 g (0.0788 mol) of phenyllithium in 150 ml of ether. After the addition, the reaction mixture was decomposed with a saturated ammonium chloride solution. The organic layer was washed with water, dried over sodium sulfate, and the solvent was evaporated under reduced pressure. Recrystallization of the residue from heptane gave 15.3 g (71.5%) of a white crystalline solid, mp 98–99°, whose structure was assigned as 1-phenyl-3-biphenylbutanone.

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.94; H, 6.75.

The infrared spectrum showed strong bands at 5.93, 6.73, 8.13, 9.98, 11.98, 13.26, and 14.38 μ. The nmr spectrum ($CDCl_3$) showed a doublet at τ 8.62 (3 H, J = 7.5 Hz) and multiplets centered at τ 4.55 (3 H), 2.52 (12 H), and 2.11 (2 H).

To the above ketone (12.6 g, 0.042 mol), dissolved in 200 ml of acetic acid containing a catalytic amount of gaseous hydrogen bromide, was added 6.4 g (0.040 mol) of bromine. After the addition, the mixture was diluted with cold water and filtered to give a white solid. Recrystallization from methanol afforded 2-bromo-1-phenyl-3-biphenylbutanone as white crystals, mp 125–126°, yield 15 g (95%).

Anal. Calcd for $C_{22}H_{19}BrO$: C, 69.66; H, 5.06. Found: C, 69.94; H, 5.10.

The infrared spectrum showed sharp bands at 5.95, 11.76, 12.89, 13.58, and 14.40 μ. The nmr spectrum ($CDCl_3$) showed doublets at τ 3.66 (J = 6.5 Hz), 8.42 (J = 6.5 Hz), 3.61 (J = 6.5 Hz), and 3.74 (J = 6.5 Hz), and multiplets centered at τ 6.32 (1 H) and 2.61 (1 H).

The bromo ketone was dehydrobrominated by treatment with lithium chloride. A solution of 14.0 g (0.037 mol) of the above ketone and 15.0 g of lithium chloride in 100 ml of dimethylformamide was heated to reflux for 3 hr. The cooled reaction mixture was then diluted with cold water and extracted with carbon tetrachloride. Removal of the solvent and crystallization of the solid from heptane–benzene gave 1-phenyl-3-biphenyl-2-buten-1-one as a light yellow solid, mp 103–105°.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.55; H, 6.07. Found: C, 88.63; H, 6.07

The infrared spectrum was characterized by strong bands at 6.05, 6.31, 6.83, 6.92, 8.23, 9.45, 10.40, 11.83, 12.32, and 14.25 μ. The nmr spectrum ($CDCl_3$) showed doublets at τ 7.51 (3 H, J = 1.0 Hz) and τ 2.93 (1 H, J = 1.0 Hz) and multiplets centered at τ 2.70 (12 H) and 2.15 (2 H).

Allylic bromination of the unsaturated ketone was achieved by reaction with N-bromosuccinimide. A solution of 6.0 g (0.020 mol) of the ketone, 3.6 g (0.021 mol) of N-bromosuccinimide, and 0.1 g of benzoyl peroxide in 300 ml of carbon tetrachloride was heated to reflux for 5 hr. The insoluble succinimide was removed by filtration and the filtrate was concentrated under reduced pressure. Crystallization of the oily residue from hexane gave 3.8 g (50%) of a light yellow crystalline solid, which was identified as 4-bromo-3-biphenyl-1-phenyl-2-buten-1-one, mp 112.5–113.5°.

Anal. Calcd for $C_{22}H_{17}BrO$: C, 70.03; H, 4.53. Found: C, 70.27; H, 4.54.

The infrared spectrum was characterized by strong bands at 6.08, 6.30 (split), 8.25, 11.94, 12.73, 13.10, and 14.35 μ. The nmr spectrum ($CDCl_3$) showed singlets at τ 5.01 (1 H) and 2.83 (1 H), and multiplets centered at τ 2.55 (12 H) and 2.02 (2 H).

A solution of 0.4 g of the bromo ketone and 10 g of *t*-butylamine in 50 ml of benzene was heated to reflux for 3 hr. The solution was subsequently washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 0.33 g of a white solid, mp 131–132°. Recrystallization from methanol afforded 0.28 g (75%) of colorless needles, mp 136–137°. This product was identical in all respects with the product obtained from the irradiation of *cis*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (6).

Irradiation of *trans*-1-*t*-Butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (8). A 1.0-g sample of **8** was dissolved in 1 l. of 95% ethanol and irradiated with a Pyrex filter for 3 hr. The infrared spectrum of an aliquot removed after 3 hr indicated complete disappearance of the carbonyl band at 5.95 μ. Removal of the solvent under reduced

pressure gave 0.93 g of a brown solid. The crude solid was chromatographed on a (0.75 × 36 in.) florisil packed column using a 0.5% ethyl acetate–hexane mixture as the eluent. The first 200 ml contained a light yellow solid which was recrystallized from methanol to give 0.50 g (53%) of a light tan crystalline solid, mp 120–121°. This component was subsequently identified as N-*t*-butyl-2 phenyl-3-biphenylpyrrole **9** on the basis of its physical and chemical data and by an independent synthesis.

Anal. Calcd for $C_{26}H_{25}N$: C, 88.84; H, 7.17; N, 3.99. Found: C, 88.75; H, 7.13; N, 3.76.

The infrared spectrum showed bands at 6.70, 8.10, 10.85, 11.95, 13.01, 13.55, and 14.30 μ. The nmr spectrum ($CDCl_3$) showed a singlet at τ 8.54 (9 H), doublets at τ 3.74 (1 H, J = 3.2 Hz) and 3.14 (1 H, J = 3.2 Hz), and a multiplet centered at τ 2.73 (1 H). The ultraviolet spectrum had a maximum at 296 mμ (ε 22,900).

The next 700 ml of solvent contained a crude solid which after three recrystallizations from methanol gave 0.08 g of 1-*t*-butyl-2-phenyl-4-biphenylpyrrole (7), mp 136–137°. The nmr spectrum ($CDCl_3$) of the crude photolysate indicated that the ratio of **9** to **6** was 1.5:1.0.

N-*t*-Butyl-2-phenyl-3-biphenylpyrrole (9). The structure of the major product isolated from the photolysis of *trans*-azetidine **8** was verified by an independent synthesis. During an 8-hr period a solution of 30 g (0.121 mol) of *p*-phenylbenzyl bromide in 200 ml of anhydrous ether was added to magnesium turnings.[26] The resulting Grignard solution was cooled to 10° and 13 g (0.122 mol) of benzaldehyde was added over a 30-min interval. The reaction mixture was then decomposed with a saturated ammonium chloride solution. The organic layer was removed and dried over magnesium sulfate. Concentration of the solution gave 30 g of a white solid, mp 107–110°. Recrystallization from benzene–heptane gave 27 g of α-(*p*-phenylbenzoyl)benzyl alcohol, mp 112–113°.

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.79; H, 6.63.

The infrared spectrum showed bands at 6.72, 9.70, 9.85, 13.25, and 14.32 μ. The nmr spectrum ($CDCl_3$) exhibited a broad singlet at τ 7.70 (1 H), a doublet at τ 7.03 (2 H, J = 6.5 Hz), and multiplets centered at τ 5.20 (1 H) and 2.65 (14 H).

To a solution of 30 g of the above alcohol in 500 ml of acetone was added a 3 *N* chromic acid solution (3:1 water–sulfuric acid) until the orange color persisted. The mixture was diluted with 1.5 l. of cold water and the yellow solid that formed was collected and recrystallized from benzene–heptane to give 25 g of *p*-phenylbenzyl phenyl ketone, mp 144–146°.

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.18; H, 5.92.

The nmr spectrum ($CDCl_3$) showed a singlet at τ 5.72 (2 H) and a multiplet centered at τ 2.53 (14 H). The infrared spectrum exhibited bands at 5.98, 7.12, 7.51, 10.00, 13.32, and 14.63 μ.

To the above ketone (7.0 g, 0.0257 mol) dissolved in 150 ml of dried glyme was added 1 equiv of triphenyl potassium at 20° under a nitrogen atmosphere. To the above solution was added 50 g of ethyl iodide in 100 ml of glyme. After 0.5 hr, the mixture was diluted with 500 ml of cold water and the organic layer was dried over magnesium sulfate. Evaporation of the solvent left a crude solid which was chromatographed on a 1.5 × 18 in. silica gel column. The column was eluted with 350 ml of benzene to give triphenylmethane. Further elution with 450 ml of benzene gave a white solid, mp 107–112°. Recrystallization from heptane afforded 1-phenyl-3-biphenylbutan-1-one, mp 118–119°, yield 6.0 g (78%).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.64; H, 6.73.

The infrared spectrum was characterized by bands at 5.95, 9.95, 12.25, 13.13, and 14.35 μ. The nmr spectrum (CCl_4) exhibited multiplets centered at τ 9.03 (5 H) and 2.72 (14 H) and a broad triplet at τ 7.90 (1 H).

1-Phenyl-3-biphenylbutan-1-one was brominated by adding 6.08 g (0.038 mol) of bromine to a solution of 5.7 g (0.019 mol) of the ketone in 350 ml of acetic acid at 20°. After the bromine color disappeared, the mixture was diluted with cold water and extracted with benzene to give 3.5 g of a yellow oil. The oil was then heated to reflux for 1.5 hr in 500 ml of dimethylformamide containing 10 g of lithium chloride. The mixture was poured into cold water and the solid that formed was collected. Recrystallization from benzene–heptane gave 2.1 g of 1-phenyl-2-biphenylbuten-1-one as a crystalline solid, mp 143–144°.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.55; H, 6.07. Found: C, 88.53; H, 6.09.

The infrared spectrum was characterized by bands at 6.00, 8.20, 13.05, 14.02, and 14.53 (split) μ. The nmr spectrum ($CDCl_3$) showed a doublet at τ 8.22 (3 H, J = 7.0 Hz), a quartet at τ 3.60 (1 H, J = 7.0 Hz), and a multiplet centered at τ 2.31 (14 H).

Allylic bromination of the unsaturated ketone was achieved by heating a solution of 0.45 g of the above ketone with 0.27 g of N-bromosuccinimide and 0.03 g of benzoylperoxide in 30 ml of carbon tetrachloride for 1.5 hr. The succinimide was removed at 10° by filtration and the solution was concentrated under reduced pressure to give a colorless oil. The resulting allylic bromide was dissolved in 25 ml of benzene containing 8 g of *t*-butylamine. After refluxing for 5 hr the benzene solutions was washed with cold water and dried over magnesium sulfate. Recrystallization of the residue from 95% ethanol gave 0.32 g of a crystalline white solid **9**, mp 120–121°. This material was identical in all respects with the major product obtained from the irradiation of *trans*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoylazetidine **8**. A mixture melting point of the two substances was undepressed at 120–121°.

***cis*-N-*t*-Butyl-2-phenyl-3-benzoylazetidine-4,4-d_2 (10).** Sodium hydride (1.56 g) was added to a solution of 13 g of 1,3-diphenyl-1-propanone in 100 ml of glyme. After heating to reflux for 10 min the mixture was cooled to 30° and 10 g of trideuteriomethyl iodide was slowly added. The solution was then heated to reflux for 10 min, cooled to 15°, and then poured onto crushed ice. Extraction with benzene followed by distillation gave 13 g (92.3%) of 1,3-diphenyl-2-methylpropanone-2,2,2-d_3 as a colorless oil, bp 160–162° at 1.5 mm. The infrared spectrum (neat) showed a series of bands at 4.50, 5.95, 6.91, 8.17, and 14.25 μ. The nmr spectrum (CCl_4) showed complex multiplets centered at τ 6.98 (3 H) and 2.80 (10 H).

To a solution of 12.8 g (0.0566 mol) of 1,3-diphenyl-2-methylpropanone-2,2,2-d_3 in 300 ml of acetic acid containing a catalytic amount of gaseous hydrogen chloride was added, over a 30-min period with stirring at 25°, 9.2 g (0.05 mol) of bromine. After stirring for an additional 1.5 hr, the solution was diluted with water and extracted with benzene. Evaporation of the solvent left a yellow oil which was added to 300 ml of dimethylformamide containing 15 g of lithium chloride. The resulting solution was heated to reflux for 2 hr. Distillation of the reaction mixture under reduced pressure gave 10.5 g of *trans*-α-methyl chalcone-α,α,α-d_3 as a yellow oil, bp 163–165° at 2.0 mm. The infrared spectrum (neat) was characterized by a series of bands at 3.35, 4.51, 6.07, 6.92, 7.90, 10.62, 10.91, 13.20, and 14.32 μ. The nmr spectrum (CCl_4) showed a singlet at τ 1.90 (1 H) and a complex multiplet centered at τ 2.42 (10 H).

A solution containing 10.0 g (0.046 mol) of *trans*-α-methyl chalcone-α,α,α-d_3, 0.2 g of benzoylperoxide, and 8.0 g of N-bromosuccinimide in 300 ml of carbon tetrachloride was refluxed for 4 hr. The mixture was cooled to 10° and the precipitated succinimide was removed by filtration. Removal of the carbon tetrachloride under reduced pressure left a white solid. Recrystallization from 95% ethanol yielded 5.2 g of *trans*-α(bromomethyl) chalcone-α,α,α-d_3, mp 78–79° (lit.[8] mp 79°). The nmr spectrum (CCl_4) exhibited a multiplet centered at 2.51 (10 H) and a singlet at τ 2.93 (1 H). The infrared spectrum (neat) showed a series of bands at 6.10, 6.24, 6.92, 7.98, 9.38, 10.47, 13.01, 13.70, and 14.35 μ.

A solution of 5.0 g (0.0165 mol) of the bromo ketone and 2.5 g (0.034 mol) of *t*-butylamine in 450 ml of pentane was stirred at room temperature for 26 hr. The pentane solution was separated from the precipitated salts and was concentrated under reduced pressure to give a white solid. Recrystallization from heptane gave 5.1 g of 2-[α-(N-*t*-butylamino)benzyl]-3-phenyl-1-propen-3-one-1,1-d_2 as colorless needless, mp 69–70°, (lit.[8] mp 69–70°). The nmr spectrum (CCl_4) exhibited a multiplet centered at τ 2.53 (10 H) and singlets at τ 4.85 (1 H) and 8.90 (10 H). The infrared spectrum was characterized by bands at 6.09, 6.92, 7.98, 10.73, 13.25, and 14.35 μ.

The desired dideuterated *cis*-azetidine **10** was prepared by a modification of a procedure described by Cromwell and Doomes.[8] To a saturated hydrogen bromide solution of chloroform was added 4.80 g of the above ketone and the resulting solution was allowed to stand for 12 hr at room temperature. The reaction mixture was cooled to 0°, neutralized with *t*-butylamine, and filtered. Removal of the solvent left a colorless oil that was recrystallized from 95% ethanol to give 3.0 g (62%) of **10** as white needles, mp 117–118°, (lit.[8] mp 116–118°). The infrareds pectrum was characterized by

(26) To avoid coupling during the preparation of the Grignard reagent, a "cyclic reactor" was employed.[27]

(27) D. C. Rowlands, K. W. Greenlee, and C. E. Boord, *Tech. Rept. Amer. Petrol. Inst.*, Research Project 45, **9**, 33 (1950).

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.

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(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]

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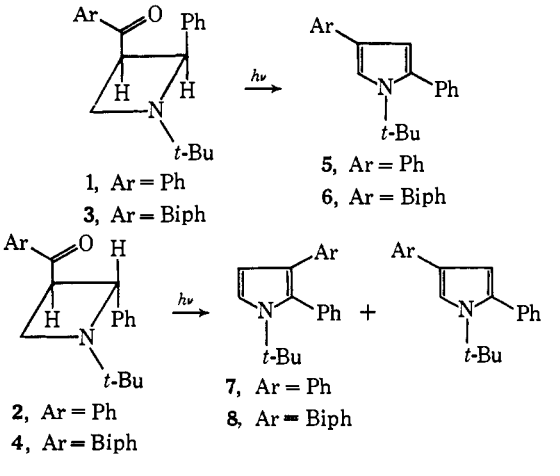
Abstract: The photochemical rearrangement of arylaroylazetidines to diarylpyrroles was examined in mechanistic detail. The quantum efficiency of the photoreaction was low (Φ = 0.046) and increased slightly with deuterium substitution in the azetidine ring. Sensitization and emission studies indicate 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) 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).