

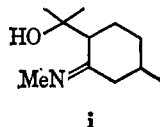
sensitizer to give the excited triplet of **1** followed by bond cleavage would result in the diradical **6**. Intramolecular hydrogen transfer *via* a seven-membered transition state leads directly to **5**. Because **6** is a *t*-alkoxy radical, competing fragmentation could occur. In support of this postulated mechanism, we have succeeded in trapping acetone (as the 2,4-DNP) by sweeping the reaction mixture with nitrogen. The newly generated diradical **7** would be expected to rearrange to an imine (**8**), and 3-methylcyclohexanone was characterized after work-up with aqueous acid.<sup>5</sup>

Production of **5** in the base-promoted rearrangements can take place *via*  $\beta$  elimination. Direct evidence for the occurrence of this pathway in the reaction of **1c** and *t*-butoxide has been obtained by isolation of imino alcohol **5c**. When the reaction mixture was quenched by pouring into water, the primary amino alcohol **4** (R = H) was obtained; however, if sufficient acid was present to neutralize the base, both **4** (R = H) and **5c** were detected. The isopropylideneimine **5c** was synthesized by condensation of **4** (R = H) with acetone. Presumably **5c** does not cyclize readily to a tetrahydro-1,3-oxazine because of steric hindrance.

Other polycyclic isoxazolidines have been subjected to these rearrangement conditions, and studies to define the limitations of such reactions are in progress

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(5) An alternate pathway to acetone and **8** is also possible: intramolecular hydrogen transfer involving a five-membered ring to give **i** which could undergo a retroaldol reaction.



**i**  
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### A Novel Photoinduced Ring Expansion of *1-t*-Butyl-2-phenyl-3-benzoylazetidines<sup>1</sup>

Sir:

As part of our broad interest in the ground-state and electronically excited-state behavior of small-membered rings,<sup>2</sup> we have investigated the photochemical behavior of *cis*-1-*t*-butyl-2-phenyl-3-benzoylazetidines<sup>3</sup> (**I**) and wish to describe an unusual photoinduced ring expansion of the four-membered azetidines. To our knowledge this represents the first example of a photochemical migration of an alkyl group from the  $\alpha$  position to the carbonyl carbon of an  $n-\pi^*$  excited state.

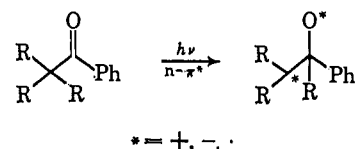
The initial experiments were carried out in a nitrogen atmosphere using an internal water-cooled mercury arc

(1) Photochemical Transformations of Small Ring Carbonyl Compounds, part XV. For part XIV, see A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Am. Chem. Soc.*, in press.

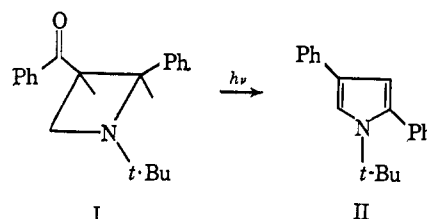
(2) A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 91.

(3) Before the completion of our investigation a report appeared describing the synthesis of azetidines I.<sup>4</sup> Our spectral data are in good agreement with those reported.

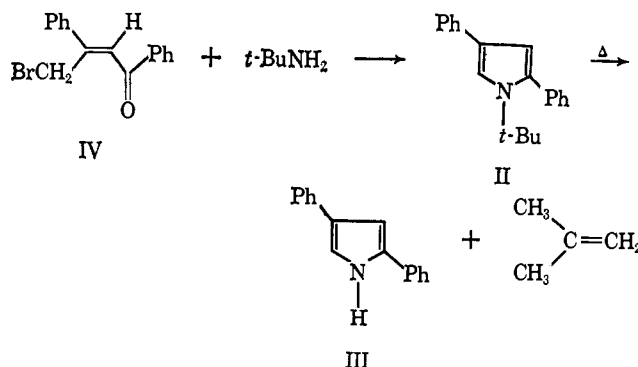
(4) J. L. Imbach, E. Doomes, R. P. Rebman, and N. H. Cromwell, *J. Org. Chem.*, **32**, 78 (1967).



lamp (Hanovia Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 300  $m\mu$ . In a typical case a solution of 0.5 g of **I** in 150 ml of 95% ethanol was flushed with nitrogen and irradiated for 3 hr. Conventional isolation procedures afforded 0.46 g of a solid (95%), mp 102–103°, whose structure is assigned as 1-*t*-butyl-2,4-diphenylpyrrole (**II**) on the basis of the chemical and physical data cited. The infrared spec-



trum of **II** was characterized by a series of sharp bands at 6.24, 8.21, 12.47, 13.08, 14.25, and 14.40  $\mu$ . The ultraviolet spectrum ( $\lambda_{\max}$  (95% alcohol) 235  $m\mu$  ( $\epsilon$  15,800) and 276  $m\mu$  ( $\epsilon$  16,200)) of **II** shows an absorption curve very similar to 2,4-diphenylfuran, with peaks occurring at approximately the same wavelengths ( $\lambda_{\max}$  (95% alcohol) 242  $m\mu$  ( $\epsilon$  19,400) and 277  $m\mu$  ( $\epsilon$  20,000)).<sup>5</sup> The nmr spectrum in deuteriochloroform exhibits a singlet at  $\tau$  8.60, a pair of doublets at  $\tau$  3.80 and 2.96 ( $J = 1.9$  cps), and a multiplet centered at  $\tau$  2.62. The peak areas are in the ratio of 9:1:1:10. The doublet pattern of the 3- and 5-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 cps.<sup>6</sup> The elemental analysis of this component (*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) is also consistent with structure **II**. Chemical confirmation was obtained by pyrolysis of **II** at 225°. The product obtained in better than 97% yield was identical with an authentic sample of 2,4-diphenylpyrrole (**III**) synthesized by the method of Allen and Wilson.<sup>7</sup> Structure **II** was further confirmed by its unequivocal synthesis from 1,3-diphenyl-4-bromobuten-2-one-1 (**IV**) and *t*-butylamine.



(5) S. M. King, C. R. Bauer, and R. E. Lutz, *J. Am. Chem. Soc.*, **73**, 2253 (1951).

(6) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

(7) C. F. H. Allen and C. V. Wilson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 348.

The mechanism by which I undergoes rearrangement and the identification of the excited state(s) responsible for the reaction were deemed of considerable interest. That the  $n-\pi^*$  singlet configuration is first populated and is the lowest energy state of this multiplicity seems to be a valid assumption since the absorption spectrum of I showed the  $n-\pi^*$  band at  $320\text{ m}\mu$ , whereas the  $\pi-\pi^*$  transition is at  $246\text{ m}\mu$ .<sup>8,9</sup> The nature of the lowest lying triplet configuration remains somewhat questionable at this time, although in the present instance the benzoyl group is involved, and the lowest triplet configuration of such a moiety is  $n-\pi^*$ . The quantum yield for formation of II in 95% ethanol is 0.046 at  $3660\text{ \AA}$ .<sup>10</sup> In an attempt to determine the rate constant for the unimolecular rearrangement of the excited state, we have studied the variation of quantum yield *vs.* quencher concentration. Surprisingly, the photolysis of I could not be quenched by a moderate concentration (0.3 mole) of piperylene, 1,3-cyclohexadiene, naphthalene, or ferric dipivaloylmethide. The failure to quench could mean that the rearrangement of the  $n-\pi^*$  triplet is too rapid for diffusion of the excited state to quencher molecules or that most of the reaction proceeds from the singlet manifold.

With acetophenone present in a concentration so as to absorb 99% of the light a twofold increase in quantum yield resulted, despite the negligible direct excitation of azetidine I. The observation that the same product was obtained in the sensitized photolysis as in the direct irradiation provides proof that the azetidine triplet can rearrange to pyrrole II. Since the quantum yield of II increases by sensitization, we can conclude that either the intersystem crossing efficiency of the  $n-\pi^*$  singlet is low or the rate of crossing in this case may be much slower than in benzophenone or acetophenone, thereby allowing for a competing unimolecular rearrangement.<sup>11</sup> The increased quantum yield can also be equally well explained by reaction *via* singlets in the direct irradiation which is less efficient than reaction *via* triplets in the sensitized reaction, both configurations leading to the same product.

These results are consistent with a picture involving reaction of the  $n-\pi^*$  state as depicted in terms of the ensuing mechanism.

A possible explanation for the exclusive formation of the 2,4 isomer may be related to the preferred migratory aptitude of methyl *vs.* benzyl toward an electron-deficient center.<sup>14</sup> In view of the uncertainties in the electronic nature of the carbonyl carbon atom, we prefer to postpone further discussion of the reaction mechanism until a more thorough study can be undertaken.

(8) Pyrex filters were used in all irradiations to remove all light below  $300\text{ m}\mu$ .

(9) Irradiation of alcohol solutions of I with 2537- $\text{\AA}$  light so as to populate the  $n-\pi^*$  manifold produced 2,4-diphenylpyrrole. The effect of different wavelengths of light on I and the photochemistry of the *trans* isomer will be the subject of a future publication.

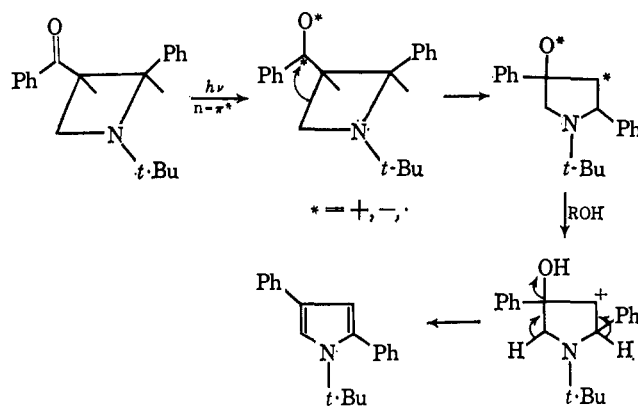
(10) Quantum yield measurements were carried out on a rotating photochemical assembly in sealed degassed Pyrex ampoules. Irradiation from a 450-w Hanovia lamp was filtered through Corning 7-51 filters. All the light is taken up by I under these conditions.

(11) A similar situation has been noted in the photochemistry of dibenzoyl ethylene, although in that case reaction proceeded predominantly by way of a  $n-\pi^*$  singlet.<sup>12,13</sup>

(12) G. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.*, **84**, 4148 (1962).

(13) H. E. Zimmerman, H. Durr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967).

(14) J. R. Owen and W. H. Saunders, Jr., *ibid.*, **88**, 5809 (1966).



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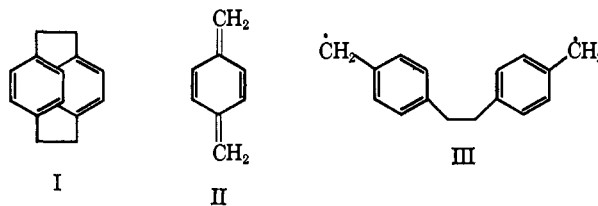
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### Racemization, Ring Opening, and Ring Expansion of the [2.2]Paracyclophane Nucleus through a Diradical Intermediate<sup>1</sup>

Sir:

The smallest of the  $[m.n]$ paracyclophanes in which  $m = n = 2$  (I) exhibits a strain energy of  $31.3\text{ kcal/mole}$ <sup>2a</sup> which is reflected in the highly deformed crystal structure of the molecule.<sup>2b</sup> The photochemical ring opening of [2.2]paracyclophane by both heterolytic and homolytic cleavage of the benzyl-benzyl bond results in release of this compression energy.<sup>3</sup> The thermal ring opening of the substance at  $400^\circ$  to give *p,p'*-dimethylbibenzyl and *p,p'*-dimethylstilbene<sup>4</sup> and at  $600^\circ$  to give *p*-xylylene<sup>5</sup> (II) also reflect the innate instability of the system. Octamethyl[2.2]paracyclophane is much more thermally unstable, a property attributed to diradical formation followed by polymerization.<sup>6</sup>

We wish to report the results of three types of experiments, all of which point to thermal cleavage of [2.2]paracyclophane to the *p,p'*-dimethylenebibenzyl diradical (III) whose fate depends on the medium.



When 40 mg of (-)-4-carbomethoxy[2.2]paracyclophane<sup>7</sup> (IV), mp  $174-175^\circ$ ,  $[\alpha]_{436}^{25} -583^\circ$  (c 1, chloro-

(1) The authors wish to thank the National Science Foundation for a grant used in support of this research.

(2) (a) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966); (b) P. K. Gantzel and K. N. Trueblood, *Acta Cryst.*, **18**, 958 (1965).

(3) R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966).

(4) J. R. Schaefgen, *J. Polymer Sci.*, **15**, 203 (1955).

(5) W. F. Gorham, *ibid.*, **4** (A-1), 3027 (1966).

(6) D. T. Longone and L. H. Simanyi, *J. Org. Chem.*, **29**, 3245 (1964).

(7) (a) Elemental analyses, nmr, and infrared spectra of all new compounds were in accord with the assigned structures. (b) Optically pure (-)-4-carboxy[2.2]paracyclophane [D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, **77**, 6289 (1955)] was previously reported.