

Figure 1. Two views of molecule I (not affected by structural disorder). Each view is obtained from the other by rotating the molecule around a horizontal axis. In the bottom view the planes of pseudo-symmetry of both rings are normal to the plane of the paper; their dihedral angle is shown. The Fe-C distances (top view) and the C-C bond lengths (bottom view) are also reported ( $\sigma_{\text{Fe-C}} \approx 0.02 \text{ \AA}$ ;  $\sigma_{\text{C-C}} = 0.03 \div 0.04 \text{ \AA}$ ).

atom. This atom is  $\pi$  bonded with six carbon atoms of one ring and four of the other (rings A and B, respectively, in Figures 1 and 2), so that the Kr electron configuration is attained. The main structural features of molecule I may be summarized from its comparatively accurate data as follows (see Figure 1).

(i) The conformation of the A ring and its coordination to the metal are similar to those found in the case of  $\text{C}_8\text{H}_8\text{Mo}(\text{CO})_3$ .<sup>7</sup> In fact, the values of the dihedral angles around C-C bonds and the Fe-C distances suggest an idealized mirror symmetry, in spite of some inconsistencies existing in the ring bond lengths and angles. Furthermore, the 2-3-4-5-6-7 group shows very much the same distortion from the planar arrangement as that reported for the Mo complex. Finally, in this case too, the distance between the two noncoordinated C atoms (8 and 1) seems to be close to the normal double bond length.

(ii) Also the over-all shape and coordination of the B ring resemble those found for  $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ .<sup>8</sup> A pseudo-mirror symmetry may be observed, and the two quasi-planar groups (14-15-16-9-10-11 and 11-12-13-14) form a dihedral angle of  $33^\circ$  (*cf.* with  $41^\circ$  for the  $\text{Fe}(\text{CO})_3$  complex).

(iii) The molecule as a whole has neither crystallographic nor idealized symmetry, since the planes of pseudo-symmetry for the separate rings are not coincident.

On the basis of the X-ray data presently available, we cannot decide whether the structural disorder of molecule II, representing one-third of the molecules in the crystal, is of a static type (*i.e.*, a random distribution of molecules having two alternative, fixed orienta-

(7) J. S. McKechnie and I. C. Paul, *J. Amer. Chem. Soc.*, **88**, 5927 (1966).

(8) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

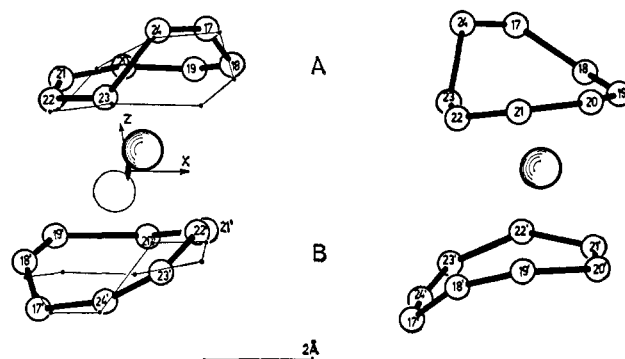


Figure 2. Two views of the disordered molecule II. On the left, it is seen along the crystallographic twofold axis ( $x = 1/2a$ ;  $z = 1/4c$ ); only the skeleton of one of the two symmetry related molecules is shown in heavy lines. On the right, a molecular projection similar to that in the top side of Figure 1 is reported.

tions) or of a dynamic type, involving a rapid interchange from the A to the B mode of coordination for each ring, and *vice versa* (internuclear tautomerism). The second hypothesis seems to be indirectly favored by nmr evidence, which shows that the internuclear tautomerism is certainly present in solution until  $-20^\circ$ .<sup>8</sup>

Crystallographic investigations on bis(cyclooctatetraene)iron at different temperatures are presently in progress in our laboratory.

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## Deuterium Isotope Effects in the Photochemistry of an Azetidine Ketone<sup>1</sup>

Sir:

Although the photochemistry of heterocyclic three-ring compounds has been extensively studied in recent years,<sup>2</sup> relatively little is known about the photochemistry of the homologous four-ring system. Recently, we reported on the photorearrangement of a *cis*-aroylazetidine, a photoreaction that involved expansion of the four-membered nitrogen ring.<sup>3</sup> The extensive structural reorganization observed prompted us to carry out a detailed investigation of the mechanism of this unprecedented photoreaction. At this time we wish to report the results of deuterium-labeling experiments which provide evidence for a 1,3-diradical intermediate.

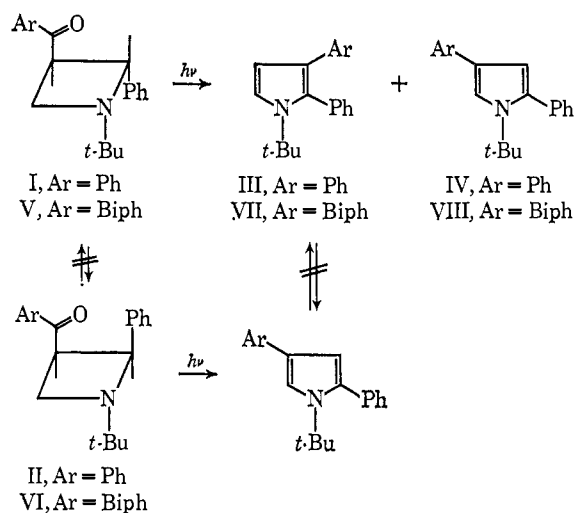
Exposure of a dilute solution of *trans*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (I) in 95% ethanol to a

(1) Photochemical Transformations of Small Ring Carbonyl Compounds. XVIII. For part XVII, see A. Padwa and W. Eisenhardt, *J. Am. Chem. Soc.*, **90**, 2442 (1968).

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

(3) A. Padwa, R. Gruber, and L. Hamilton, *J. Am. Chem. Soc.*, **89**, 3077 (1967).

Hanovia 450-W mercury arc lamp for 3 hr resulted in the complete disappearance of I and clean conversion to a mixture of two substances.<sup>4</sup> The products were separated by column chromatography and identified as N-*t*-butyl-2,3-diphenylpyrrole (III) (67%, mp 120–121°) and N-*t*-butyl-2,4-diphenylpyrrole (IV) (33%, mp 102–103°). The structure of III was assigned on the basis of physical and chemical data cited. *Anal.* Calcd for C<sub>20</sub>H<sub>21</sub>N: C, 87.22; H, 7.69; N, 5.09. Found: C, 86.88; H, 7.63; N, 4.85. Spectral peaks appeared at:  $\lambda_{\max}$  (KBr) 6.26, 8.20, 13.03, 13.63, and 14.43  $\mu$ ;  $\lambda_{\max}$  254 m $\mu$  ( $\epsilon$  10,600); 60-Mc nmr (deuteriochloroform): singlet at  $\tau$  8.62 (9 H), doublet at 3.74 ( $J = 3.2$  Hz, 1 H), doublet at 3.14 ( $J = 3.2$  Hz, 1 H), and multiplet centered at 2.75 (10 H). Structure III was further confirmed by an independent synthesis from 4-bromo-1,2-diphenyl-2-buten-1-one and *t*-butylamine.<sup>5</sup> Spectral comparison of the minor component with an authentic sample of IV served to confirm its structure.<sup>5</sup>



The possibility was considered that the formation of III might proceed through the intermediacy of IV. Recently, several examples of light-induced rearrangements of five-membered ring heterocycles have appeared in the literature,<sup>6–9</sup> 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 IV gave only 2,4-diphenylpyrrole and we are therefore led to conclude that III is not formed from the irradiation of IV. Similarly, the photolysis of III revealed that no detectable quantities of IV were formed. The further complication of a photocatalyzed epimerization of starting material ( $I \rightleftharpoons II$ ) was eliminated by the finding that irradiation of *cis*-azetidine II (or the *p*-phenylbenzoyl analog VI) did not afford I (or V).<sup>10</sup> Further, the only product observed from irradiation of *cis*-azetidine II or VI was the 2,4-disubstituted pyrrole,

(4) Pyrex filters were used in all irradiations to remove all light below 300 m $\mu$ .

(5) A. Padwa, R. Gruber, and D. Pashayan, *J. Org. Chem.*, **33**, 454 (1968).

(6) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **89**, 6911 (1967).

(7) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967).

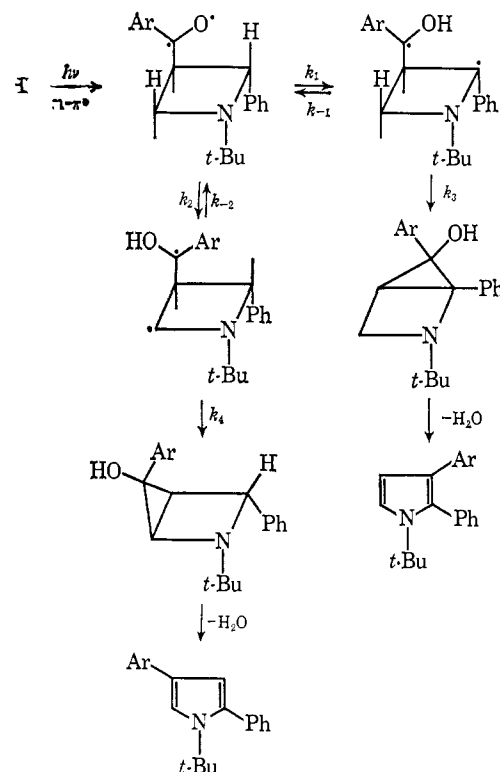
(8) H. Tiefenthaler, W. Dorscheln, H. Goth, and H. Schmid, *Tetrahedron Letters*, 2999 (1964).

(9) P. Beak, J. L. Miesel, and W. R. Messer, *ibid.*, 5315 (1967).

(10) All attempts to detect photoepimerization using *trans*-azetidines and V were unsuccessful.

whereas a mixture of two isomeric pyrroles was obtained from *trans*-azetidines I and V.<sup>11</sup>

Among the several mechanistic schemes that might be considered adequate to explain the formation of the photoproducts, we currently favor the one outlined below. It is based on the knowledge that hydrogen abstraction of aryl ketones proceeds by way of their  $n-\pi^*$  triplet state.<sup>12,13</sup> In this postulated mechanism,



intramolecular hydrogen transfer from carbon to the  $p_y$  orbital of oxygen of the  $n-\pi^*$  excited state produces a spin-unpaired 1,3-biradical intermediate.<sup>14</sup> Spin inversion followed by ring closure affords a transient azabicyclo[2.1.0]pentane that may readily lose water to give a disubstituted pyrrole. The fact that the 2,3-disubstituted pyrrole was formed in preference to the 2,4 isomer from the irradiation of I is in accord with known trends of relative reactivities of hydrogen atoms toward abstraction by alkoxy radicals. Also, the exclusive formation of IV from the irradiation of II is fully compatible with the above scheme. In this case the geometry of the ring only allows for abstraction of the methylene hydrogen.

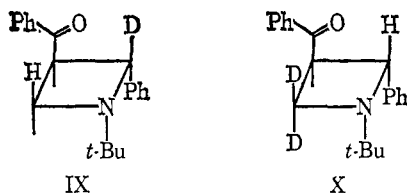
Additional evidence in support of this mechanism is obtained from experiments using deuterium-labeled *trans*-azetidines IX and X.<sup>11</sup> The results obtained from these systems are summarized in Table I. The first striking observation noted is that *replacement of hydrogen by deuterium enhances the amount of ring closure at that position*. This apparent inverse isotope effect is

(11) Synthetic details and structure proofs will be reported in our full paper. All new compounds were properly characterized, and acceptable chemical analyses were obtained.

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

(13) The phosphorescence emission spectra of I and II in EPA at 77°K is characteristic of  $n-\pi^*$  emission.

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



readily rationalized if one assumes that the hydrogen transfer step is reversible.<sup>15,16</sup> The low quantum efficiency of the photoreaction coupled with the failure to quench the triplet<sup>3</sup> suggests that the reverse transfer of hydrogen (or deuterium) back to carbon (rates governed by  $k_{-2}^H$  or  $k_{-2}^D$  for azetidine X) is faster than spin inversion and ring closure ( $k_4$ ). Substitution of deu-

Table I. Irradiation Runs of Deuterium-Labeled *trans*-Azetidines

Reactant	Pyrroles, ratio 2,3/2,4	$\Phi_{\text{pyrrole}}$
I	2.0 $\pm$ 0.05	0.046 $\pm$ 0.004
IX	2.3 $\pm$ 0.06	0.065 $\pm$ 0.005
X	1.4 $\pm$ 0.04	0.087 $\pm$ 0.006

terium for hydrogen retards the reverse transfer (*i.e.*,  $k_{-2}^D < k_{-2}^H$ ), thereby enhancing ring closure. If indeed  $k_{-2}^H, k_{-2}^D \gg k_4$  and  $k_{-1}^H \gg k_3$ , then the observed ratio of pyrroles obtained from I and X can be shown to be governed by eq 1 and 2. The resulting

$$\text{ratio } 2,3/2,4 \text{ (I)} = \frac{k_3 k_1 k_{-2}^H}{k_4 k_2^H k_{-1}} \quad (1)$$

$$\text{ratio } 2,3/2,4 \text{ (X)} = \frac{k_3 k_1 k_{-2}^D}{k_4 k_2^D k_{-1}} \quad (2)$$

isotope effect is expressed by eq 3. The term  $k^D/k^H$  is

$$\frac{\text{ratio } 2,3/2,4 \text{ (I)}}{\text{ratio } 2,3/2,4 \text{ (X)}} = \frac{k_{-2}^H k_2^D}{k_2^H k_{-2}^D} = \frac{K^D}{K^H} \quad (3)$$

a ratio of two equilibrium constants, and its value would be expected to be greater than unity since the zero-point energy for the stretching vibration of the OH bond is greater than for the CH bond.<sup>17</sup> This scheme would also predict an enhancement in the quantum efficiency of pyrrole formation as hydrogen is replaced by deuterium exactly as is observed.

**Acknowledgment.** The authors are indebted to the National Science Foundation (Grant GP-6511) and the Air Force Office of Scientific Research (Grant No. AF-AFOSR-1213-67) for financial support of this research.

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

(16) P. Wagner, *ibid.*, **89**, 5898 (1967).

(17) Similar treatment of the data for azetidine IX would predict a value less than unity.

(18) Alfred P. Sloan Fellow, 1968-1970.

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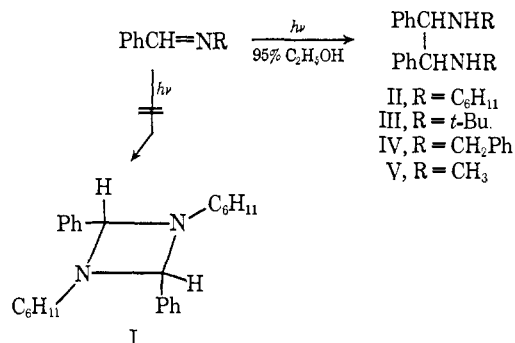
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## On the Photoreduction of Benzaldehyde N-Alkylimines

Sir:

Photoreduction of benzophenone and related ketones occurs readily *via* abstraction of hydrogen from alcohols and other hydrogen donors by the excited carbonyl compound.<sup>1</sup> Although the photoreductive dimerization of ketones has been extensively studied,<sup>2,3</sup> only scattered reports<sup>4-6</sup> have appeared concerning the photoreduction of the related imine system. We now wish to report on some aspects of the photoreductive dimerization of benzaldehyde N-alkylimines in alcoholic media.

Recently, Kan and Furey reported the synthesis of N,N'-dicyclohexyl-2,4-diphenyl-1,3-diazetidine (I) from the irradiation of benzaldehyde N-cyclohexylimine.<sup>7</sup> The authors considered two structures for the compound isolated and proposed that the 1,3-diazetidine structure best accounted for their data. We wish to point out that we have isolated from the photolysis in high yield a product consistent with that described by Kan and Furey to which we assign an alternate structure, *meso*-N,N'-dicyclohexyl-1,2-diphenyl-1,2-diaminoethane (II), based on the data and an independent synthesis.



Irradiation of benzaldehyde N-cyclohexylimine (VI) in 95% ethanol at 25° with  $>3100\text{-\AA}$  light for 3 hr afforded II, mp 143-144°, in 95% yield.<sup>8</sup> The elemental analysis of the photoproduct (*Anal.* Calcd for  $\text{C}_{28}\text{H}_{36}\text{N}_2$ : C, 82.92; H, 9.64; N, 7.44; for  $\text{C}_{28}\text{H}_{34}\text{N}_2$ : C, 83.36; H, 9.15; N, 7.48. Found: C, 82.99; H, 9.68; N, 7.43) is more in accord with structure II than with I. The mass spectrum of II shows an intense peak (base) at 188 ( $M/2$ ). This behavior is characteristic of diamines and generally provides for the most intense ion in the spectrum.<sup>9</sup> The presence of a metastable peak at  $m/e$  59.8 indicates the loss of cyclohexene from the base peak to yield a major peak at  $m/e$  106. This pattern would be expected for a dihydro dimer such as II which could fragment readily, but not for 1,3-di-

(1) For a review see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 6.

(2) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(3) G. Porter and P. Suppan, *Pure Appl. Chem.*, **9**, 499 (1964).

(4) H. Goth, P. Cerutti, and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965).

(5) F. R. Stermitz, R. P. Seiber, and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968).

(6) M. Fischer, *Tetrahedron Letters*, 5273 (1966).

(7) R. O. Kan and R. L. Furey, *J. Am. Chem. Soc.*, **90**, 1666 (1968).

(8) The initial photolysis was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L-450 W) with a Pyrex filter to eliminate wavelengths below 300 m $\mu$ .

(9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1964, p 63.