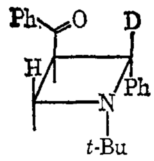
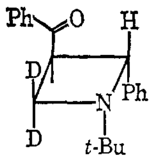


IX



X

readily rationalized if one assumes that the hydrogen transfer step is reversible.[15,16] The low quantum efficiency of the photoreaction coupled with the failure to quench the triplet[3] 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 deuterium for hydrogen retards the reverse transfer (*i.e.*, $k_{-2}^{D} < k_{-2}^{H}$), thereby enhancing ring closure. If indeed k_{-2}^{H}, $k_{-2}^{D} \gg k_4$ and $k_{-1}^{H} \gg k_3$, then the observed ratio of pyrroles obtained from I and X can be shown to be governed by eq 1 and 2. The resulting isotope effect is expressed by eq 3. The term k^{D}/k^{H} is a ratio of two equilibrium constants, and its value would be expected to be greater than unity since the zero-point energy for the stretching vibration of the OH bond is greater than for the CH bond.[17] This scheme would also predict an enhancement in the quantum efficiency of pyrrole formation as hydrogen is replaced by deuterium exactly as is observed.

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

Reactant	Pyrroles, ratio 2,3/2,4	Φ_{pyrrole}
I	2.0 ± 0.05	0.046 ± 0.004
IX	2.3 ± 0.06	0.065 ± 0.005
X	1.4 ± 0.04	0.087 ± 0.006

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

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

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

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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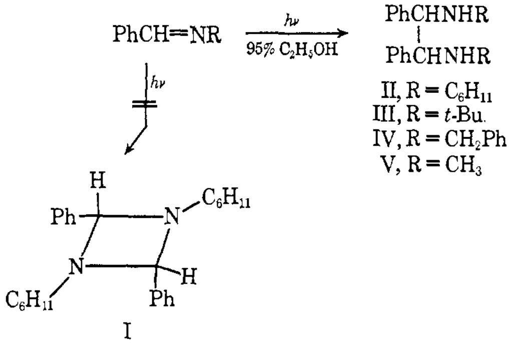
On the Photoreduction of Benzaldehyde N-Alkylimines

Sir:

Photoreduction of benzophenone and related ketones occurs readily *via* abstraction of hydrogen from alcohols and other hydrogen donors by the excited carbonyl compound.[1] Although the photoreductive dimerization of ketones has been extensively studied,[2,3] only scattered reports[4–6] 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.[7] 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.



I

Irradiation of benzaldehyde N-cyclohexylimine (VI) in 95% ethanol at 25° with >3100-Å light for 3 hr afforded II, mp 143–144°, in 95% yield.[8] The elemental analysis of the photoproduct (*Anal.* Calcd for $C_{26}H_{36}N_2$: C, 82.92; H, 9.64; N, 7.44; for $C_{26}H_{34}N_2$: 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.[9] 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 mμ.

[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.

azetidine I. The nmr peaks listed by Kan and Furey (τ 2.88, 6.29, and 7.92–9.40) are satisfactory for the dihydro dimer since the known benzyl analog IV shows a peak for the tertiary benzylic hydrogens as a singlet at τ 6.22.[10] Similarly, the infrared and ultraviolet spectra reported are entirely consistent with this revised structure. Structure II was further established by the identity of its infrared spectrum and undepressed mixture melting point with an authentic sample obtained by the quantitative reduction of VI with aluminum amalgam.[11] Irradiation of a series of related benzaldehyde N-alkylimines also afforded dihydro photodimers (III–V); the infrared, ultraviolet, nmr, and mass spectral properties are entirely analogous to those of II.[12]

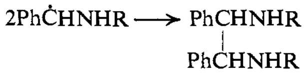
Although the reaction bears analogy to aryl ketone photoreduction, initial experiments indicate that mechanistically the reaction is quite different in that it appears not to involve the excited states of the imine as intermediates in the reduction. While direct irradiation of benzaldehyde N-benzylimine (VII) in 95% ethanol leads to very efficient photoreduction, the imine is *not* photoreduced in 2-propanol, a solvent which is very effective in photoreducing benzophenone.[13] Photoreduction proceeded readily, however, when 2-propanol was diluted with water and led to dihydro dimer IV and acetone. We attribute this behavior to partial hydrolysis of the imine in the aqueous solvent followed by sensitization by small amounts of benzaldehyde which can compete favorably with imine as a light-absorbing component.[14] The N-alkylimine is readily photoreduced when irradiated in 2-propanol in the presence of low concentrations of triplet photosensitizers such as benzaldehyde and benzophenone.

The photoreduction of VII in 2-propanol proceeds in high quantum yield ($\Phi = 0.58$) when benzophenone is used as a sensitizer. It would appear, at first glance, that triplet energy is being transferred from benzophenone to the imine which then undergoes photoreduction. That the triplet state of the imine is not, nonetheless, the active hydrogen-abstracting species is shown by the fact that benzophenone phosphorescence is *not* quenched (EPA at 77°K) by the imine. Also noteworthy is the fact that the imine itself shows no detectable emission and does not quench the small amount of benzaldehyde emission. Although the phosphorescence of benzaldehyde and benzophenone is not quenched, the photoreduction of the latter in 2-propanol is completely inhibited by the imine. In the inhibited reaction, while the imine prevents conversion of benzophenone to benzpinacol, photoreduction of the imine does occur. Examination of the quantum efficiency of a number of triplet sensitizers in effecting imine photoreduction reveals a correlation with the ability of the sensitizer itself to photoreduce in the alcoholic medium. Thus benzophenone, benzaldehyde, acetophenone, and xanthone sensitize in that order of efficiency and are themselves not consumed. High-energy sensitizers, such as dibenzothiophene and triphenylamine, that do not themselves photoreduce in alcohol are ineffective as sensitizers. These observations when taken together suggest that the photoreduction does not involve an excited state of the imine but rather is brought about by one or more of the intermediates of the ketone photoreduction.[15] The photoreaction may be represented by the sequence of reactions 1–4, starting with abstraction of hydrogen from the carbinol carbon by the lowest excited triplet state of the sensitizer. It should be noted that this scheme

$$Ph_2CO^* + (CH_3)_2CHOH \longrightarrow (Ph)_2\dot{C}OH + (CH_3)_2\dot{C}OH \quad (1)$$

$$(Ph)_2\dot{C}OH + PhCH{=}NR \longrightarrow Ph_2CO + Ph\dot{C}HNHR \quad (2)$$

$$(CH_3)_2\dot{C}OH + PhCH{=}NR \longrightarrow CH_3COCH_3 + Ph\dot{C}HNHR \quad (3)$$



$$2Ph\dot{C}HNHR \longrightarrow \begin{array}{c} PhCHNHR \\ | \\ PhCHNHR \end{array} \quad (4)$$

involves radical intermediates similar to those proposed by Cohen in the photoreduction of aromatic ketones using amines as hydrogen sources.[16] For that case the reverse of reaction 2 has been suggested as an important step.

Further investigations to determine the generality of hydrogen atom transfer in imine photochemistry and a more systematic study of the relationship between structure, reaction product, and mechanism will be the subject of future reports.

Acknowledgment. We wish to thank the National Science Foundation (Grant GP-6511) for financial support and Professor Maurice Bursey for obtaining the mass spectra.

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[10] The formation of IV from the photolysis of N-benzylbenzalimine was first reported by A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **89**, 102 (1967).

[11] R. Jaunin, *Helv. Chim. Acta*, **39**, 111 (1956).

[12] Synthetic details and structure proofs will be reported in our full paper. All new compounds were properly characterized and acceptable chemical analyses were obtained.

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

[14] Excitation with 254-mμ light does not result in photoreduction, since most of the light is absorbed by the imine under these conditions.

[15] N. Filipescu and F. L. Minn, *J. Am. Chem. Soc.*, **90**, 1544 (1968).

[16] S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3471 (1967); S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968).

[17] Alfred P. Sloan Fellow, 1968–1970.

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Kinetic Studies in Mass Spectrometry. II. Wide-Range Electron Energy Kinetics. A Novel Transition-State Probe

Sir:

Recently the application of kinetic methods to the analysis of relatively simple mass spectral fragmentation pathways has been developed by McLafferty and Bursey.[1–4] Despite minor criticism,[5] this elegant technique promises to be of extreme value in the study of reactions of gaseous ions in the mass spectrometer, provided that one keeps in mind the approximations and limitations involved in its derivation[1–4] and application.[1–5] We report here a potentially useful ex-

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[1] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

[2] M. M. Bursey and F. W. McLafferty, *ibid.*, **89**, 1 (1967), and subsequent papers in this series.

[3] M. M. Bursey, *Org. Mass Spectrom.*, **1**, 31 (1968).

[4] F. W. McLafferty, *Chem. Commun.*, submitted for publication. We thank Professor McLafferty for helpful discussion and for kindly providing a preprint of his communication.

[5] I. Howe and D. H. Williams, *ibid.*, 220 (1968).