

97% loss in arginine, 18% loss in serine, and variable loss of methionine.<sup>8</sup> Losses of other susceptible amino acids (threonine, glycine, cystine, lysine, and histidine) were below 10%. Reactions of the neutral free amino acids appear to occur *via* the  $\alpha$ -amino groups. The reagent does not modify free tyrosine at neutral pH, although low recovery of tyrosine is found in hydrolysates of modified proteins. The loss occurs during the hydrolysis step and can be eliminated by including sacrificial phenol in the hydrolysis mixture.

Chromatographic analyses of samples of free arginine treated with stoichiometric amounts of reagent show two major, ninhydrin-positive, final products. Study of the products from this and related reactions is continuing in an effort to define the reaction mechanism.

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(8) Loss of methionine is apparently due to a noncovalent interaction with the reagent. The resulting complex is ninhydrin positive and appears just prior to aspartic acid.

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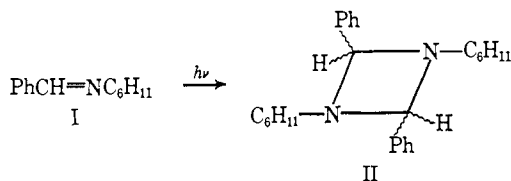
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### Photochemical Formation of 1,3-Diazetidines

Sir:

The multitude of reported photochemical dimerizations<sup>1</sup> is noteworthy for the absence among them of the formation of diazetidines from the combination of C=N containing monomers.<sup>2</sup> We now report the photochemical dimerization of benzaldehyde cyclohexylimine (I) to yield a stable dimer to which we have assigned the structure of N,N'-dicyclohexyl-2,4-diphenyl-1,3-diazetidene (II).



The benzophenone-sensitized irradiation of ethanolic or 2-propanolic solutions of I for 24 hr at 25° with artificial or solar ultraviolet light<sup>3</sup> yields 34% of II.

(1) For a review see R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

(2) The dimerization of 2-aminopyridines is a case in point: E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.*, **85**, 776 (1963).

(3) A Hanovia 450-W immersion lamp equipped with a Pyrex filter or a Rayonet photochemical reactor with 3500-Å lamps will suffice.

The structure of II was elucidated on the basis of its physical and chemical properties. N,N'-Dicyclohexyl-2,4-diphenyl-1,3-diazetidene is a solid, mp 143–144°. The elemental analysis<sup>4</sup> (*Anal.* Calcd for C<sub>26</sub>H<sub>34</sub>N<sub>2</sub>: C, 83.36; H, 9.15; N, 7.48; mol wt, 374. Found: C, 83.38; H, 9.24; N, 7.56; mol wt, 376) indicates that it is a dimer of I. The ultraviolet spectrum ( $\lambda_{\text{max}}$  (dioxane) 265 m $\mu$  ( $\epsilon$  480)) is indicative of two isolated benzene rings. The infrared spectrum (CHCl<sub>3</sub>) shows no other features than aliphatic and aromatic C–H and the presence of monosubstituted aromatic rings (3030 w, 2990 m, 2900 s, 2810 m, 1580 w, 1450 s, 720 m, and 700 s cm<sup>-1</sup>). The 60-Mc nmr spectrum shows the aromatic hydrogens as a singlet at  $\tau$  2.88 (10 H), the two ring hydrogens as a singlet at  $\tau$  6.29 (2 H), and cyclohexyl hydrogens at  $\tau$  7.92 (broad, 2 H) and 8.1–9.4 (broad, 20 H), the former being assigned to the carbon atoms attached to nitrogen.

Examination of the natural abundance <sup>13</sup>C–H satellite spectrum<sup>5</sup> of the ring hydrogens demonstrated the satellite to be a singlet, with a half-width of 3.5 cps. This fact, together with the pyrolysis studies cited below, allows the selection of a 1,3-diazetidene over a 1,2-diazetidene; the two equivalent ring hydrogens of the latter would have doublet satellites.

The mass spectrum<sup>6</sup> of II is noteworthy for the ease of elimination of C<sub>6</sub>H<sub>11</sub>N from the molecular ion, resulting in a peak with *m/e* 277 (M<sup>+</sup> – C<sub>6</sub>H<sub>11</sub>N) as the highest *m/e* peak. The stability of this fragment is expected in view of the stabilization allowed through two benzylic systems. A similar result is obtained with the dimer of *p*-chlorobenzaldehyde cyclohexylimine, and only a change to direct inlet at 110° revealed the expected M<sup>+</sup> peaks. All other fragments are in complete agreement with the structure of II. Most prominent are those due to the loss, in addition to the C<sub>6</sub>H<sub>11</sub>N fragment mentioned above, of C<sub>6</sub>H<sub>11</sub>, C<sub>6</sub>H<sub>5</sub>C, C<sub>6</sub>H<sub>5</sub>CH, and a second C<sub>6</sub>H<sub>11</sub>N.

In view of the above-noted instability of the molecular ion, we investigated the pyrolysis of II and its more readily available *p*-chloro derivative (mp 183–184°), the infrared, ultraviolet, and mass spectral properties of which were entirely analogous to those of II. Heating of either dimer causes sublimation, but decomposition occurred only after heating in a sealed tube at 235° for 30 min. The only identifiable products from such mixtures were the dimer and the monomer, obtained in yields up to 30%, giving evidence of the wide variance in thermal stability between the molecular species and its ions.

The transient formation of a 1,2-diazetidene, proposed by Searles and Clasen<sup>7</sup> to account for the reported isolation of stilbenes and azobenzene derivatives from the photolysis of a substituted anil, prompted us to look for similar products in the pyrolysis mixtures; although such stilbenes would have survived the reaction conditions, they were never observed. These products would of course not be expected to form from a 1,3-diazetidene.

A surprising characteristic of II is its unusual chem-

(4) Spang Microanalytical Laboratory, Ann Arbor, Mich., and Galbraith Laboratories, Inc., Knoxville, Tenn.

(5) A Varian A-60 nmr spectrometer equipped with spin decoupler and computer of average transients was employed.

(6) Morgan Shaffer Corp., Quebec, Canada.

(7) S. Searles, Jr., and R. A. Clasen, *Tetrahedron Letters*, 1627 (1965).

ical stability, II (and its *p*-chloro derivative) being recovered unchanged after refluxing for many hours in reagents as diverse as concentrated NaOH,  $\text{LaAlH}_4$ -tetrahydrofuran, sodium in ethanol, concentrated HCl, and 20%  $\text{H}_2\text{SO}_4$ . There is no apparent steric interference with protonation on nitrogen, and the compounds are bases, readily dissolved in dilute acids and recovered by basification. This behavior is unexpected if one considers 1,3-diazetidines to be the nitrogen analogs of the acid-labile acetals, a comparison apparently not accurate, perhaps due to the unreactivity of the diprotonated species.<sup>8</sup>

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(8) As suggested by a referee.

(9) To whom correspondence and requests for reprints should be directed at the School of Medicine, Case Western Reserve University, Cleveland, Ohio.

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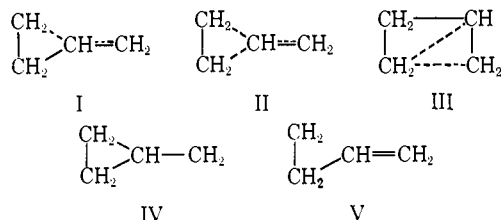
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### A Nonclassical Free Radical<sup>1</sup>

Sir:

Molecular orbital calculations have helped to explain rate and product data for carbonium ion reactions of cyclobutyl, cyclopropylcarbinyl, and allylcarbinyl compounds by implicating a common, nonclassical intermediate.<sup>2,3</sup> Such calculations for radical systems suggest that nonclassical free radicals should also be intermediates in some reactions. Howden and Roberts<sup>2</sup> calculated that nonclassical radical I should be more stable than bicyclobutyl radical III, cyclopropylcarbinyl radical IV, or allylcarbinyl radical V, although the stabilization is small relative to that in the corresponding cation.<sup>4</sup>



Compelling experimental evidence for nonclassical radicals appears to be lacking. Wilt and coworkers<sup>6,7</sup>

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (Grant 1396-A4).

(2) M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963).

(3) R. J. Piccolini and S. Winstein, *ibid.*, **2**, 423 (1963).

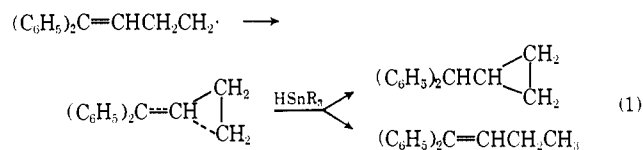
(4) The best description of the cation appears to be bishomoallyl structure II.<sup>5</sup>

(5) See, e.g., (a) H. G. Richey, Jr., and J. M. Richey, *J. Am. Chem. Soc.*, **88**, 4971 (1966); (b) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (c) references cited in ref 5a,b.

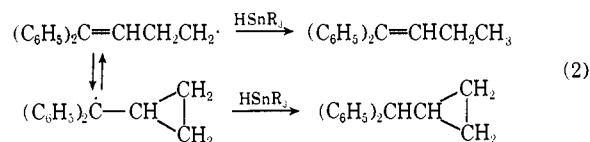
(6) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

(7) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967).

have suggested that the 7-norbornenyl radical and the 2,3-dibenzo-7-norbornenyl radical may be nonclassical, but the suggestion is based on qualitative and incomplete rate comparisons. Howden<sup>5</sup> found that the ratio of products from the ( $\gamma,\gamma$ -diphenylallyl)carbinyl radical is nearly constant over the range 110–150°, a result consistent with a nonclassical radical intermediate (eq 1). Equilibrating classical radicals (eq 2) were thought less



likely because the equilibrium constant should be



strongly temperature dependent while the ratio of rate constants for hydrogen abstraction might well be insensitive to temperature. Direct formation of the nonclassical radical (eq 1) from the substrate (the peracetate) was thought unlikely in view of the small effect of structure on rate.<sup>8</sup>

Recent studies of homoallylic radical systems indicate, however, that there is no general need to postulate nonclassical structures for such species.<sup>9,10</sup> In fact, there is some indication that the 3-methylcyclopropylcarbinyl radical is a classical species.<sup>10</sup>

We wish to report evidence that 7-norbornenyl is a nonclassical radical. A convenient method for generating a free radical is reduction of an organic halide with an organotin hydride.<sup>11–13</sup> Reduction of either *syn*- or *anti*-7-bromonorbornene with tri-*n*-butyltin deuteride in hexane leads to the *same* 7-deuterionorbornene. The yield is about 80%, and there are no other volatile products. That the same product is obtained and that it is a norbornene is evident from the nmr spectra (Figure 1) and from identity of its glpc retention time with that of norbornene. That 7-deuterium in the product is *anti* is based on a recent reassignment<sup>14</sup> of the signal at  $\tau$  8.93 to the *anti*-7-hydrogen of norbornene (Figure 1).

This stereochemical result cannot be accounted for readily in terms of either a single classical radical or equilibrating classical radicals. For VI to accommodate this result requires either a highly stereospecific reaction of the unhindered, classical C<sub>7</sub> radical or re-

(8) M. E. H. Howden, Ph.D. Thesis, California Institute of Technology, 1962.

(9) L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Am. Chem. Soc.*, **89**, 923 (1967).

(10) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 934 (1967).

(11) (a) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3584 (1962); (b) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963); (c) H. G. Kuivila in "Progress in Organometallic Chemistry," F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964, p 64.

(12) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875 (1967).

(13) L. Kaplan, *J. Am. Chem. Soc.*, **88**, 4531 (1966).

(14) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966).