of acid[19] and azocine tautomers in the presence of base.[16c,20]

Transformation of postulated intermediate **4** as illustrated in Scheme I requires comment. Unlike its hydrocarbon analog,[7b,17] betaine **4** possesses nondegenerate sigmatropic rearrangement options represented by structures **5** and **6**. Since oxime products can be derived irreversibly from intermediate **5**, assemblage **6** may intervene as a short-lived species on the potential energy surface which is rapidly rerouted to the main decomposition sequence.

The interception of intermediates along the reaction pathway is under active investigation.

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James P. Snyder,* Ling Lee
Belfer Graduate School of Science, Yeshiva University
New York, New York 10033

Donald G. Farnum
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

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Azocine. The Flash Vacuum Pyrolysis of 7,8-Diazapentacyclo[4.2.2.$0^{2,5}$.$0^{3,9}$.$0^{4,10}$]dec-7-ene (Diazabasketene)[1]

Sir:

The attempt of Farnum and Snyder[2] to prepare cubane *via* 7,8-diazapentacyclo[4.2.2.$0^{2,5}$.$0^{3,9}$.$0^{4,10}$]dec-7-ene (**1**, diazabasketene) is an interesting example of an elegantly designed synthetic sequence which failed inexplicably at the last step. The pyrolyses of **1** at a variety of conditions generally led to intractable materials, although gas-phase pyrolysis in a flow system gave some evidence of a discrete highly reactive product.[2a] The photolysis of **1** was similarly complex with only cyclooctatetraene being obtained at low yields under a variety of reaction conditions.[2a,b]

We have investigated the pyrolysis of **1** at flask vacuum pyrolysis (FVP) conditions[3] and have found that **1** undergoes a novel fragmentation to azocine (**3**) (azacyclooctatetraene) and hydrocyanic acid instead of ring closure to cubane (**2**); azocine, itself, is a highly reactive, acid-sensitive molecule and is undoubtedly the source of the intractable materials previously obtained.

The pyrolysis of **1** was initially studied at low pressures (~1 μ) and short contact times (~1 msec) in an oven directly coupled to the ionization chamber of a mass spectrometer.[3] We observed that the primary thermal fragments had *m/e* 105 and 27 (AP (105) 8.4 eV; AP(27) 13.6 eV);[4a] (IP(HCN) 13.8 eV[4b]) (Figure 1).

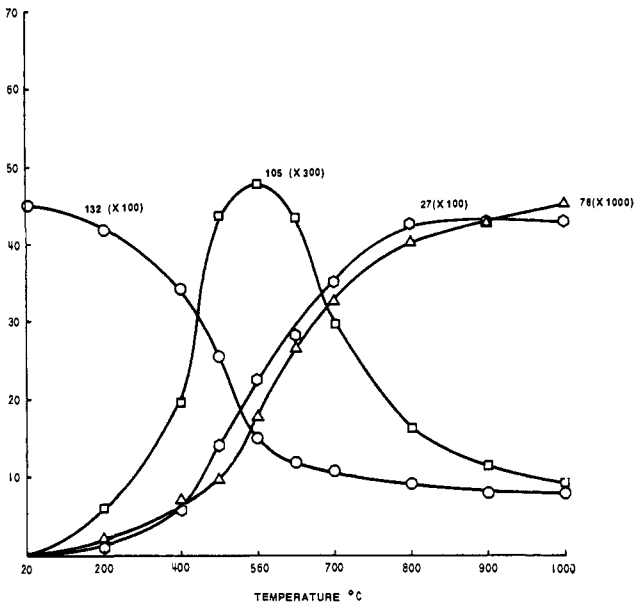
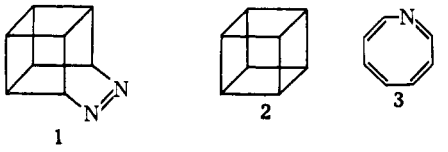


Figure 1. Diazabasketene pyrolysis: ○, diazabasketene; □, C_7H_7N; △, C_6H_6; ○, HCN. Intensity attenuations are indicated in parentheses. Electron-bombardment spectrum obtained using 11-eV electrons.



As the temperature was rasied above 560°, the signal at *m/e* 105 decreased and that at *m/e* 78, whose appearance potential corresponded to that of benzene, increased.

The isolation and characterization of the *m/e* 105 species was accomplished by carrying out the pyrolysis of **1** on a 0.5-g scale under conditions corresponding to that of the mass spectral experiments, and where the pyrolysate is rapidly quenched on the surface of a dewar at liquid nitrogen temperatures.[3] The products were isolated by vacuum distillation. Furthermore, it was necessary to use a potassium hydroxide coated quenching dewar and to transfer the reactive pyrolysate *via* traps containing potassium hydroxide pellets. The isolated pyrolysate was pale yellow and was obtained in about 60% yield. Upon warming *in vacuo* to temperatures $> -50°$, the color changed to red and then purple. Ultimately, a brown tar is obtained at room temperature.

The low-temperature nmr of the pyrolysate provided our first evidence for the azocine structure. The assignments shown below were further strengthened by the close similarity of our spectrum with that obtained for the 2-alkoxyazocines recently prepared by Paquette and coworkers.[5] The nmr for **3** rapidly decayed as

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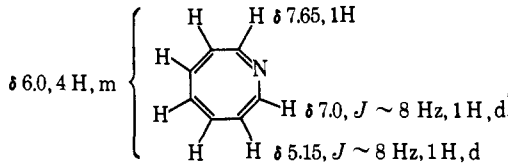
(3) (a) E. Hedaya, *Accounts Chem. Res.*, 2, 367 (1969); (b) P. Schissel, D. J. McAdoo, E. Hedaya, and D. W. McNeil, *J. Chem. Phys.*, 49, 506 (1968).

(4) (a) Appearance potential (AP), ionization potential (IP); (b) F. H. Field and J. T. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(5) (a) L. A. Paquette and T. Kakihana, *J. Amer. Chem. Soc.*, 90, 3897 (1968); (b) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Phillips, *ibid.*, 93, 152 (1971).

the temperature of the probe was increased. No other changes, however, were observed in the spectrum which could be ascribed to conformational, double-bond, or bicyclic isomers.

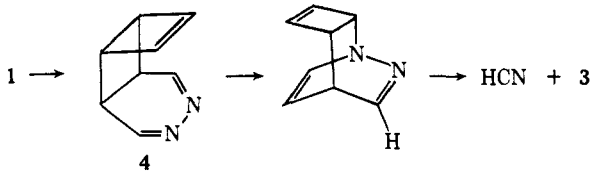


The mass spectrum (50 eV) of azocine consists of the following major ions (*m/e*, relative abundance): 105, 87; 104, 100; 78, 93; 52, 81; 51, 89; 50, 66; 39, 55. Its ionization potential (8.5 eV) and thermal behavior in our mass spectral reactor corresponded to that previously determined by pyrolysis of **1**.

Chemical evidence for **3** was obtained by its reduction to the dianion[6] using potassium in liquid ammonia. The white salt was hydrolyzed with aqueous ethanol and the resulting solution was reduced with hydrogen over platinum oxide. Heptamethylenimine was obtained, although in low yields, as evidenced by glpc–mass spectrometry.

We propose the following scheme for the thermal generation of azocine by analogy with the recently elucidated thermal rearrangement of basketene.[7] A similar scheme has been proposed for the boron trifluoride induced rearrangement of the *N*-oxide of **1** to benzaldehyde oxime.[8] It is probable that the explusion of hydrocyanic acid occurs in the oven. No evidence has been obtained so far regarding the possible initial formation of a bicyclic isomer of azocine.[9]

Obviously, one factor favoring the retro Diels–Alder reaction to give **4** rather than nitrogen extrusion must be strain release; however, a strain-releasing retro Diels–Alder reaction to give nitrogen and the syn dimer of cyclobutadiene is also possible for **1**, but does not occur. The totality of structural features governing the reaction course remains to be assessed.



4

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D. W. McNeil, M. E. Kent, E. Hedaya*
P. F. D'Angelo, P. O. Schissel
Union Carbide Research Institute
Tarrytown, New York 10591
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Conformations of Cyclic Dipeptides. Structure of *cyclo*-Glycyl-L-tyrosyl (L-3-(4-Hydroxybenzyl)-2,5-piperazinedione)[1]

Sir:

The current interest[2-10] in conformations of cyclic dipeptides (2,5-piperazinediones) makes timely the study of the interactions between α-carbon substituents and the dipeptide (diketopiperazine) ring. We report here the structural and conformational analysis of *cyclo*-glycyl-L-tyrosyl (*c*-Gly-L-Tyr) as determined by single-crystal X-ray diffraction.[11]

The structure was solved by direct methods with the symbolic addition procedure[12] and tangent formula refinement of phases.[13] The crystals are orthorhombic, space group $P2_12_12_1$ with $a = 7.775 \pm 0.003$, $b = 21.475 \pm 0.011$, $c = 6.170 \pm 0.001$ Å; $Z = 4$; $\rho_{calcd} = 1.418$ g/cm^3; and $\rho_{obsd} = 1.415$ g/cm^3. The 1045 independent integrated intensities with $2\theta < 135°$ were measured by the θ–2θ scan technique with Ni-filtered Cu Kα radiation on a Picker FACS-I diffractometer. Refinement of the structure by full-matrix least squares included anisotropic temperature factors for all but the hydrogen atoms. Positional parameters for all hydrogen atoms were derived from difference Fourier syntheses, but were kept fixed in the refinement. Comparison of calculated structure factors with the 1023 equally weighted observed structure factors gives a conventional *R* factor of 0.105.[14]

Bond distances and bond angles are shown in Figure 1. These values are generally not significantly different from those reported for other diketopiperazines;[4,9,10,15] our present estimated standard deviations range from 0.011 to 0.015 Å and from 0.8 to 1.0°. The internal angles at C$^\alpha$ follow the expected trend correlating increased substitution with lower angle. The corresponding angles in *c*-L-Ala-L-Ala are 112.0 and 110.5°,[4] whereas in unsubstituted diketopiperazine they are 115.1°.[15]

The overall shape of the molecule is best described in terms of the three possibilities shown in Figure 2. Without departing from amide planarity, the DKP ring can be planar (Figure 2A) or assume two possible

(1) This work was begun with Research Corporation assistance and completed under NSF Grant No. GB-7376 and NSF Instrumentation Grant No. GP-10343.
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(14) Tables giving the coordinates of bonded atoms and hydrogen bonds and principal contact distances in *cyclo*-glycyl-L-tyrosyl will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.
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