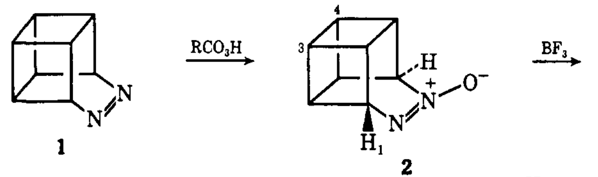
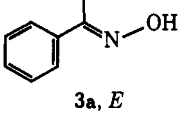
Reorganization of 7,8-Diazapentacyclo[4.2.2.0^{2,5}.0^{3,9}.0^{4,10}]dec-7-ene *N*-Oxide (Diazabasketene *N*-Oxide) in the Presence of Boron Trifluoride Etherate[1]

Sir:

A selected number of heterohomocubane derivatives are known.[2] They may be provoked to participate in several bond reorganization schemes[2a,3] in accord with current ideas derived from molecular orbital theory.[4] Our report concerns the preparation of the title compound **2** and its conversion to benzaldehyde oxime isomers **3** in the presence of a Lewis acid.



1 **2**

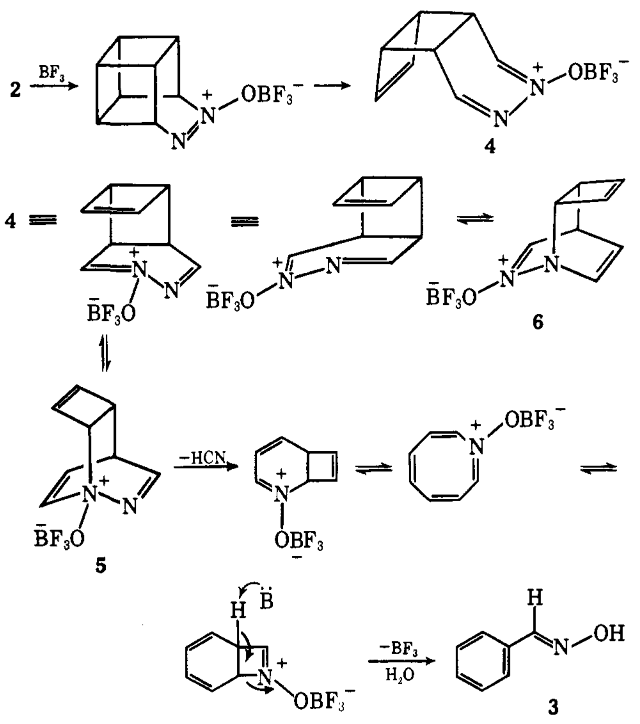


3a, *E*
b, *Z*

Diazabasketene **1**[2c,5] is oxidized to its *N*-oxy derivative **2** [70% yield; mp 141–143°; ir[1,8] ν (KBr) 1285 (s, NNO), 1492 cm^{-1} (s, NNO) (*Anal.* Calcd for $C_8H_8N_2O$: C, 64.85; H, 5.44, N, 18.91. Found: C, 64.19; H, 5.39; N, 18.86)] by the action of 85% *m*-chloroperbenzoic acid (in $CHCl_3$ at room temperature for 2 hr). Two broad singlets appear in the pmr spectrum ($CDCl_3$-TMS) at τ 4.78 (H_1,H_6) and 6.78 in the ratio of 1:3. Both bridgehead protons of compound **2** are thus shielded by 1.05 ppm relative to the corresponding protons of azo alkane **1** (τ 3.73[2c]). This result is diagnostic of the *cis*-azo-*cis*-azoxyalkane relationship.[1,9] Molecular asymmetry is nonetheless confirmed by natural abundance 100-MHz ^{13}C nmr. *N*-Oxide **2** affords five resonances at 126.0, 135.2, 152.4, 153.0, and 155.7 ppm upfield relative to $^{13}CS_2$. The nuclear response of the two carbons (C_3,C_4) most distant from the NNO moiety is most probably degenerate.[10]

Diazabasketene *N*-oxide **2** and an excess of boron trifluoride etherate[11] (in CH_2Cl_2 at reflux for 24 hr) deliver exclusively a mixture of the two isomers of benzaldehyde oxime (**3**). The major product is rotamer *E*[12] (**3a**) (70% yield), the minor *Z*[12] (**3a**) (5% yield).[13] Formation of these substances may be understood by reference to Scheme I.

Scheme I



Coordination of **2** with BF_3 followed sequentially by reverse Diels–Alder addition, Cope rearrangement to **5**, expulsion of HCN, valence isomerization,[15] and finally aromatization accounts for the observed products. A closely related [$_\pi 4_s + {}_\pi 2_s$] cycloreversion[17] in tandem with a [3,3]-sigmatropic shift best accounts for the formation of tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**5**, N,N$^+$-OBF_3^-=C) from basketene.[7] Furthermore, vacuum pyrolysis of diazabasketene **1** generates azacyclooctatetraene,[18] possibly by an identical pathway. The depicted aromatization is reminiscent of the behavior of cyclooctatetraene oxide under the influence

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[1] *cis*-Azoxyalkanes. II. Previous paper in this series: V. T. Bandurco and J. P. Snyder, *Tetrahedron Lett.*, 4643 (1969).

[2] (a) T. J. Katz and E. W. Turnblom, *J. Amer. Chem. Soc.*, **92**, 6701 (1970); (b) C. M. Anderson, J. B. Bremner, I. W. McCay, and R. N. Warrener, *Tetrahedron Lett.*, 1255 (1968); (c) R. Askani, *Chem. Ber.*, **102**, 3304 (1969); J. P. Snyder, Ph.D. Dissertation, Cornell University, Ithaca, N. Y., 1965; *Diss. Abstr.*, **26**, 5738 (1966).

[3] R. Asakni, *Tetrahedron Lett.*, 3349 (1970); L. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970).

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 316–364.

[5] By analogy with the visual descriptors which have been used for the isoelectronic hydrocarbon, heterocycle **1** may be called diazabasketene[6] or 1,1′-diazabishomocubene.[7a]

[6] S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966).

[7] (a) W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966); W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *ibid.*, 787 (1970); (b) H. H. Westberg, E. N. Cain, and S. Masamune, *J. Amer. Chem. Soc.*, **91**, 7512 (1969).

[8] B. T. Gillis and K. F. S. Schimmel, *J. Org. Chem.*, **32**, 2866 (1967); **27**, 413 (1962).

[9] F. D. Greene and S. S. Hecht, *Tetrahedron Lett.*, 575 (1969).

[10] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 228–236.

[11] In the absence of boron trifluoride etherate, oxide **2** is inert to the reaction conditions.

[12] For rules concerning the use of the *E* and *Z* designations, see J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968); "IUPAC Tentative Rules for the Nomenclature of Organic Chemistry. Section E. Fundamental Stereochemistry," *J. Org. Chem.*, **35**, 2849 (1970).

[13] Compounds **3a** and **3b** (separated by preparative tlc, silica gel) are identical in all respects (tlc, nmr, ir, mass spectra) with samples prepared independently.[14] The ratio of isomers varied somewhat from run to run (a/b, 90/10–65/35; nmr integration) in accord with behavior in the presence of acid.[14] Directly prepared benzaloximes were similarly contaminated.

[14] O. L. Brady and F. P. Dunn, *J. Chem. Soc.*, **123**, 1783 (1923).

[15] Several azocine derivatives either exist[16a] or react[16b,c] as their bicyclo[4.2.0] tautomers with nitrogen in the 7 position.

[16] (a) L. A. Paquette, T. Kakihana, J. F. Kelly, and J. R. Malpas, *Tetrahedron Lett.*, 1455 (1969); (b) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **90**, 3898 (1968); (c) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *ibid.*, **93**, 152 (1971).

[17] E. LeGoff and S. Oka, *ibid.*, **91**, 5665 (1965).

[18] D. W. McNeil, M. E. Kent, E. Hedaya, P. F. D'Angelo, and P. O. Schissel, *ibid.*, **93**, 3817 (1971).

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.

Acknowledgments. We are grateful to the National Institutes of Health (GM15927-02) for support of the work and to Badische Anilin und Sodafabrik, A.G. for a supply of cyclooctatetraene. The ^{13}C nmr data were generously provided by Dr. Hans Koch and Professor Arthur Perlin (McGill University).

[19] W. Reppe, O. Schlictling, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948); *cf.* G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **84**, 3104 (1962).

[20] L. A. Paquette and T. Kakihana, *ibid.*, **90**, 3897 (1968).

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Received February 2, 1971

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).

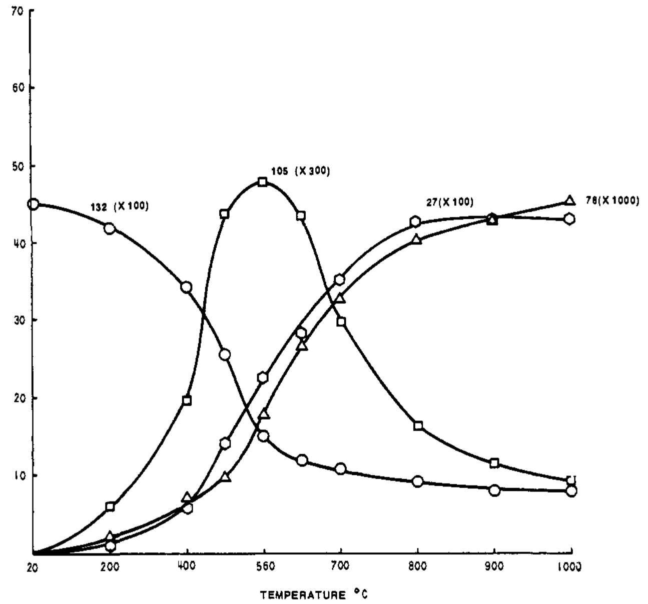
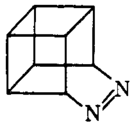


Figure 1. Diazabasketene pyrolysis: ○, diazabasketene; □, C_7H_7N; △, C_6H_6; ○, HCN. Intensity attenuations are indicated in parentheses. Electron-bombardment spectrum obtained using 11-eV electrons.



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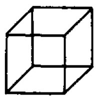

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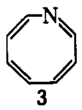

3

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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[1] Flash Vacuum Pyrolysis. X. Part IX: E. Hedaya and M. E. Kent, *J. Amer. Chem. Soc.*, in press.

[2] (a) J. P. Snyder, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1965; *Diss. Abstr.*, **26**, 5728 (1966); (b) private communication from Professor Farnum; (c) R. Askani, *Chem. Ber.*, **102**, 3304 (1969).

[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).