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2,3-DIAZABICYCLO[2.2.0]HEX-2-ENE

Eva A. Wildi and Barry K. Carpenter*,
Department of Chemistry, Cornell University,
Ithaca, N.Y. 14853.

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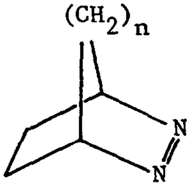
The diazabicyclo[2.2.n] alkenes (1; n = 1-4) have received considerable attention both for their spectral properties[1] and for their thermal nitrogen extrusion reactions.[2] We now report the synthesis of the lowest, and presumably most strained, member of this series, 2,3-diazabicyclo-[2.2.0]hex-2-ene (2).



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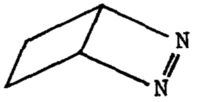

2

The reaction sequence employed in the preparation of 2 is outlined in Figure 1. Two feature of this synthesis warrant further discussion. Firstly, attempts to hydrolyze the bisurethane 3 under the usual conditions of potassium hydroxide in ethylene glycol at high temperature[3] were unsuccessful, resulting in complete destruction of the molecule. Acid catalyzed hydrolysis was similarly unproductive. By contrast, we found that the medium employed by Gassman for the hydrolysis of amides[4] effected clean hydrolytic cleavage of 3 at room temperature in three hours. Subsequent experiments have shown that the reagent is equally effective for the hydrolysis of other bisurethanes and may thus provide a convenient method for synthesizing acid-sensitive or thermally labile azo compounds.[5]

The second feature of interest is that formation of the insoluble red cuprous complex 4 could be induced only upon addition of sodium sulfite to the aqueous medium resulting from neutralization of the hydrolysis reaction. This appears to be a unique phenomenon associated with 4, and one which we frankly do not yet understand. Nevertheless, the combination of the potassium tert-butoxide/water hydrolysis reaction and the cupric chloride/sodium sulfite oxidation represent an exceptionally convenient one-pot conversion of 3 to 4.

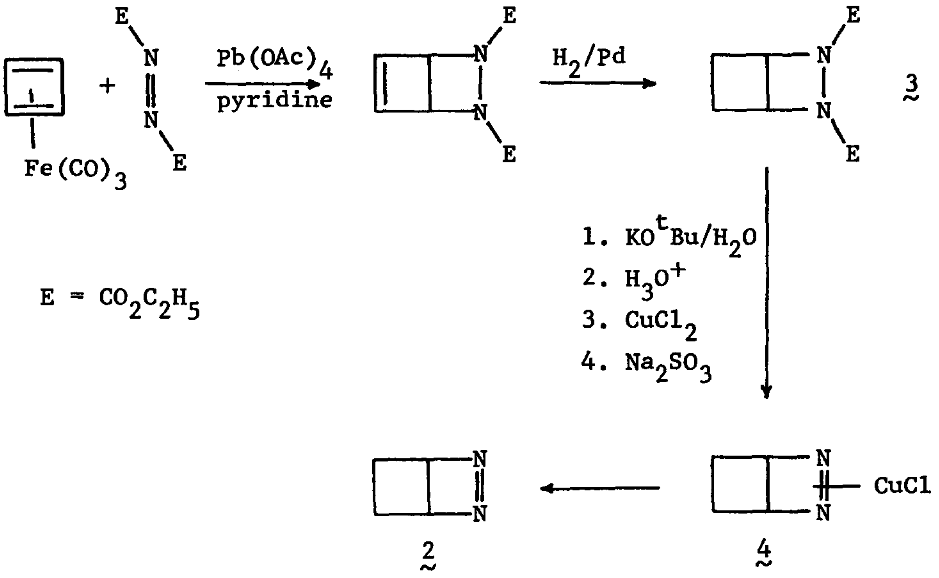

Figure 1

The azo compound **2** was purified by gas chromatography at 100°C on carbowax 20M, and found to be a colorless, strong-smelling liquid with the following spectral characteristics.

N. M. R. (δ, $CDCl_3$, TMS): 2.0 (m, 2H), 2.19-2.71 (m, 2H), 5.13 (m, 2H).
I. R. (liquid film, cm^{-1}): 3100 (s), 2970 (s), 2868 (w), 1468 (w), 1434 (s),
1251 (s), 1237 (s), 1222 (s), 1077 (s), 917 (s),
829 (s).
U. V. (isooctane, λ_{max} nm (ε)): 350 (66), 341 (67), 334 (57).

The U. V. spectrum of **2** is particularly noteworthy in that the long wavelength $n \rightarrow \pi^*$ transition does not fit into the predicted[6] (and previously observed[1]) trend of decreasing λ_{max} with decreasing N=N-C bond angle. A similar anomalous result has recently been reported for a highly substituted monocyclic diazetine.[7] In the present case, extended Hückel calculations on **2** suggest that the unusually small HOMO-LUMO gap may be due, in part, to mixing of the nitrogen centered orbitals with the σ orbitals of the strained C-C bonds. The U. V. photoelectron spectrum of **2** is currently being obtained in order to further investigate this phenomenon.

One could anticipate that thermal nitrogen extrusion from 2 may be unique amongst the diazabicyclo[2.2.n] alkenes. Thus, for the higher homologues, concerted cleavage of the two C-N bonds could proceed to give a biradical or, alternatively, may involve a C-C bond in a $_{\sigma}2_s + _{\sigma}2_s + _{\sigma}2_s$ fragmentation,[8] resulting in a diene product (Figure 2). The former mechanism is found to prevail, except in cases where the C-C bond is severely strained.[2] For 2,3-diazabicyclo[2.2.0]hex-2-ene the three bond cleavage is still allowed but the concerted two bond cleavage is now a forbidden[8] $_{\sigma}2_s + _{\sigma}2_s$ process. (A formally allowed $_{\sigma}2_s + _{\sigma}2_a$ reaction is presumably precluded by the cyclobutane ring and the N=N double bond.) The orbital symmetry restriction should thus favor the $_{\sigma}2_s + _{\sigma}2_s + _{\sigma}2_s$ reaction. In addition, since this process leads to the thermodynamically more stable product, one could imagine that the greater exothermicity of the allowed reaction would result in a still lower activation energy.

Interestingly, despite these expectations, our preliminary results indicate that pyrolysis of 2 (gas phase, 125°C, 2.5 hrs, 1 atm initial pressure) affords predominantly cyclobutene. The product contained a small amount of butadiene (~5% by NMR) but at least some of this must have been derived from the cyclobutene. Hence the fragmentation of 2 is apparently a rare example of a reaction which gives the less stable product by the formally forbidden pathway. Further investigation of the mechanism of this fragmentation is now in progress.

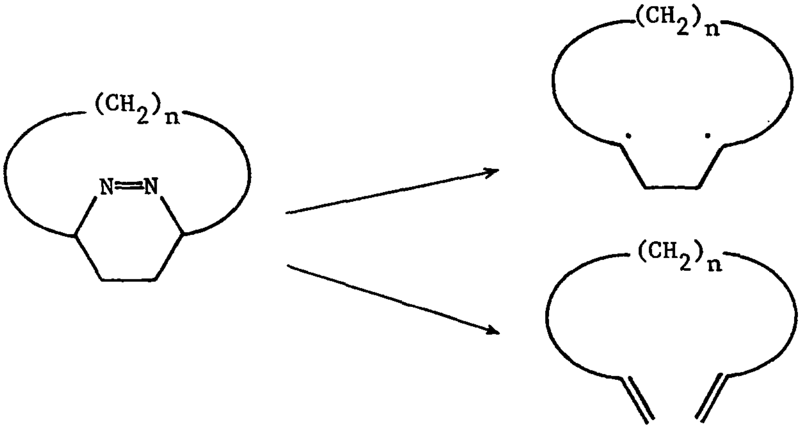

Figure 2

Acknowledgement. We gratefully acknowledge support of this work by the Research Corporation.

References and Notes.

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