The Mass Spectrum of 1,2,2a,3-Tetrahydrocyclobuta[*b*]quinoxaline (1)

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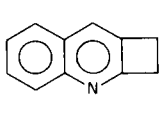
Previous papers in this series have established that fused strained rings adjacent to the heteroatom in aza-aromatic systems influence the physical properties of such compounds (3). During these studies it was observed that 1,2-dihydrocyclobuta[*b*]quinoline (**1**) fragmented under electron impact to generate 2,3-quinolyne (1). The mass spectrum of 1,2,2a,3-tetrahydrocyclobuta[*b*]quinoxaline (**2**) has been briefly noted (4); these data prompted the present study of its high resolution spectrum to assess similar structural effects.



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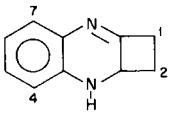
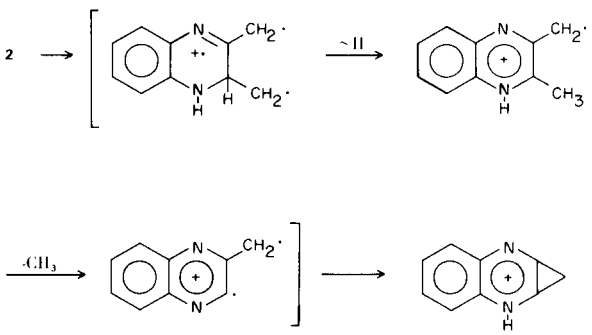


2

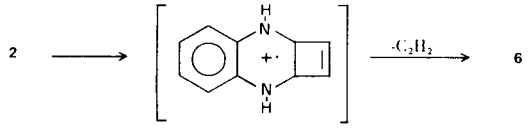
The low resolution spectrum of **2** is shown in Figure 1b. Only two metastable peaks were of sufficient relative abundance to be detected: $158^+ \rightarrow 157^+ + 1$ and $132^+ \rightarrow 131^+ + 1$. It was found, however, that the metastable transitions could be investigated in some detail by uniquely determining the precursor ions employing the ion accelerator decoupling technique (5). The results are summarized in Table I. In addition, accurate mass measurements determined the elemental composition of all principal fragments.

The metastable studies established that the molecular ion undergoes fragmentation by at least five pathways. Structures for the initial fragments are postulated in Scheme 1; some of these correspond to routes invoked for tetrahydroquinolines (6). Processes *a* and *b* are viewed as loss of hydrogen atoms with concomitant aromatization; species **3** and **4** correspond to the elusive 1,2-dihydrocyclobuta[*b*]quinoxaline system (4). Process *c* involves the direct loss of methyl, not the consecutive losses of hydrogen and methylene; a comparable fragmentation was not observed in the fully aromatic system **1**. The possibility of rearrangement of the molecular ion to the isomeric 2,3-dimethylquinoxaline (**8**) prior to decomposition was excluded by the observed spectrum of **8** (Figure 1a). Process *c*, therefore, is considered to involve scission of the C_1-C_2 bond, rearrangement of hydrogen, and subsequent loss of the methyl group. The fate of **5**



5

remains unknown. Ring expansion of **5** or its precursor to a diazatropylium ion is possible, but the failure to detect any metastable transition from the m/e 143 species (*e.g.*, loss of HCN) precludes further speculation. The loss of acetylene (process *d*) is also unusual. Derivation of a C_2H_2 fragment from the four-membered ring requires rearrangement of the hydrogens at C_1 and C_2 prior to decomposition. Alternatively, loss of 26 m.u. could occur from the benzene ring (either directly or *via* ring enlargement to an azatropylium ion). That the aromatic ring was not the source of C_2H_2 was established by suitable deuterium labeling. 1,2,2a,3-Tetrahydrocyclobuta[*b*]quinoxaline-4,5,6,7 d_4 (**9**) was prepared, and its spectrum is shown in Figure 1c. The peak at m/e 136 (with appropriate metastable peak for the $162^+ \rightarrow 136^+ + 26$ transition) confirmed that the aliphatic portion was the source of C_2H_2. Prior to fragmentation (or concurrent with it) tautomeric shifts must occur to produce a species such as **10**, which is considered the precursor of **6**. Finally,



10

process *e* is consistent with the generation of the benzimidazolium ion (**7**), which is a reasonable intermediate for subsequent loss of HNC and H_2CN.

Secondary fragmentations, derived from species **3** - **7**, involve a multiplicity of pathways (*cf.* Table I). Many of

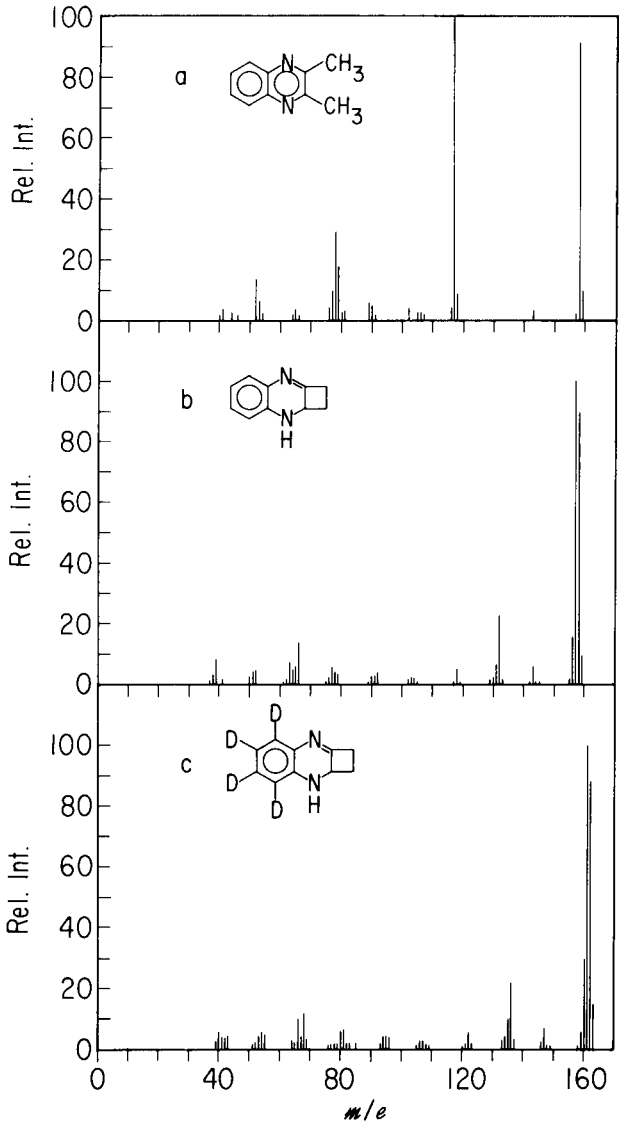
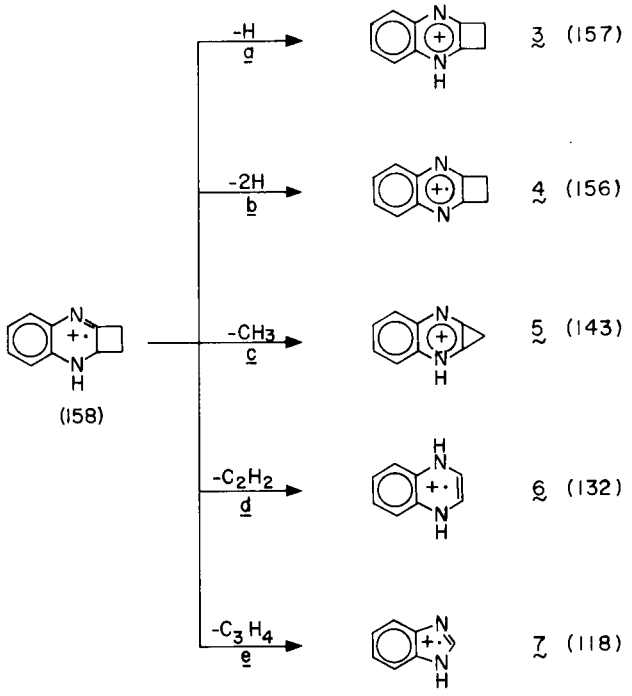
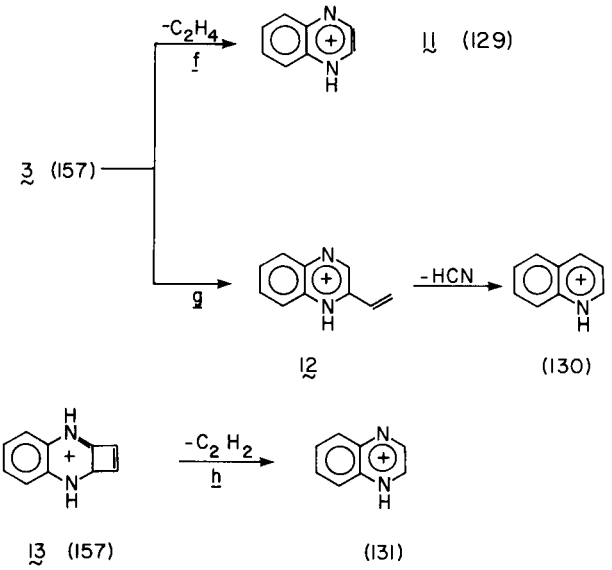


Figure 1. Mass spectra of (a) 2,3-dimethylquinoxaline (**8**), (b) 1,2,2a,3-tetrahydrocyclobuta[*b*]quinoxaline (**2**), and (c) 1,2,2a,3-tetrahydrocyclobuta[*b*]quinoxaline-4,5,6,7 d_4 (**9**).

these, which involve the loss of HCN or H, seem relatively uncomplicated. Of more interest are the M-1 species (m/e 157), which lose ethylene, hydrogen cyanide, and acetylene. As shown in Scheme 2, ion **3** can accommodate the loss of C_2H_4 (process *f*) to produce a 2,3-quinoxalyne species (**11**). This pathway parellels the thermolytic generation of 2,3-quinoxalyne (7) and the aforementioned fragmentation of **1** to 2,3-quinolyne. Ion **3**, however, is not an obvious precursor of the HCN and C_2H_2 fragments and additional structures for $C_{10}H_9N_2^+$ are necessary. Rearrangement of **3** (process *g*, initiated by scission of the C_2-C_{2a} bond) affords **12**, which is well suited for the



Scheme 1. Initial fragmentation of **2**.



Scheme 2. Fragmentation of M-1 species.

observed consecutive losses of 27 m.u. The loss of acetylene from m/e 157 corresponds to the same route in the molecular ion. Thus **13**, formed by loss of H from **10**, is a reasonable precursor of m/e 131 (process *h*). That the loss of 26 m.u. does not occur from the benzene ring is again substantiated by the spectrum of **9**.

TABLE I

Metastables of **2**

Transition					Intensity
158^+	→	157^+	+	1	strong
158^+	→	156^+	+	2	weak
158^+	→	143^+	+	15	weak
158^+	→	132^+	+	26	strong
158^{++}	→	132^{++}	+	26	medium
158^+	→	118^+	+	40	weak
157^+	→	131^+	+	26	weak
157^+	→	130^+	+	27	medium
157^+	→	129^+	+	28	medium
132^+	→	131^+	+	1	strong
132^+	→	92^+	+	40	very weak
131^+	→	104^+	+	27	medium
130^+	→	103^+	+	27	medium
129^+	→	102^+	+	27	weak
118^+	→	91^+	+	27	weak
118^+	→	90^+	+	28	very weak
104^+	→	77^+	+	27	weak
103^+	→	76^+	+	27	weak
102^+	→	75^+	+	27	weak
92^+	→	65^+	+	27	very weak
91^+	→	64^+	+	27	medium
90^+	→	63^+	+	27	weak
64^+	→	63^+	+	1	medium
63^+	→	62^+	+	1	weak

The fragmentation of **9** duplicates that of **2** and from this behavior an interesting observation follows. Studies of deuterated tetrahydroquinolines (6), alkylquinolines (8), quinolines (9), and alkylpyridines (9) have established that the isotopic label becomes randomized in the molecular ion prior to fragmentation. The complete scrambling across both rings observed with quinoline-5,6,8 d_3 is particularly pertinent (9). The arresting feature in the present case (**9**) is that the aromatic ring retains the four deuterium atoms throughout all the fragmentation processes. It is currently not clear to what structural features of **2** this difference can be ascribed; further studies are planned.

EXPERIMENTAL

Spectra were obtained with a CEC 21-110B mass spectrometer using the direct introduction probe and an ionizing voltage of 70 v; source temperature was 100-110°. Exact mass measurements were made with resolution of 10,000; perfluorokerosene was used to provide reference masses. Infrared spectra were determined on a Perkin-Elmer Model 237 spectrophotometer. Melting points are uncorrected.

Materials.

2-Bromocyclobutanone and 1,2,2a,3-tetrahydrocyclobuta[*b*]-quinoxaline (**2**) were prepared by the previously described methods (4). 2,3-Dimethylquinoxaline (**8**) was prepared by the condensation of *o*-phenylenediamine with biacetyl (10).

o-Phenylenediamine-3,4,5,6 d_4 was prepared by refluxing a solution of *o*-phenylenediamine dihydrochloride (3.6 g., 0.020 mole) in 10 ml. of deuterium oxide under an inert atmosphere for 10 hours, removing the water by distillation, and repeating the process with fresh deuterium oxide. The residual solid was dissolved in water, basified, and extracted with ether. Removal of the solvent from the dried extract afforded 0.69 g. of *o*-$C_6D_4(NH_2)_2$: m.p. 99°; molecular ion calcd. 112.0939, found 112.0937. This product (0.62 g., 5.5 mmoles) was condensed with 2-bromocyclobutanone (0.41 g., 2.7 mmoles) in 13 ml. of 80% aqueous methanol containing 1 ml. of acetic acid. The solution was refluxed 1.5 hours, concentrated on a rotary evaporator at reduced pressure, and basified. The solid material was collected, washed, dried, sublimed *in vacuo*, and chromatographed in chloroform on alumina to give 0.063 g. of **9**: m.p. 228-230°, infrared ν max (potassium bromide) 2282 cm^{-1} (C-D stretch); molecular ion calcd. 162.1095, found 162.1093.

Acknowledgment.

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REFERENCES

(1) Strained Heterocyclic Systems V. Part IV: J. H. Markgraf, R. J. Katt, W. L. Scott, and R. N. Shefrin, *J. Org. Chem.*, **34**, 4131 (1969).

(2) Visiting Professor (1968-1969); to whom inquiries should be addressed at Department of Chemistry, Williams College, Williamstown, Massachusetts 01267.

(3a) J. H. Markgraf and W. L. Scott, *Chem. Commun.*, 296 (1967); (b) J. H. Markgraf and R. J. Katt, *Tetrahedron Letters*, 6067 (1968).

(4) J. H. Markgraf, W. P. Homan, R. J. Katt, and W. L. Scott, *J. Heterocyclic Chem.*, **6**, 135 (1969).

(5) T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, 39, 1748 (1967).

(6) P. M. Draper and D. B. MacLean, *Can. J. Chem.*, **46**, 1499 (1968).

(7) M. P. Cava and L. Bravo, *Chem. Commun.*, 1538 (1968).

(8) P. M. Draper and D. B. MacLean, *Can. J. Chem.*, **46**, 1487 (1968).

(9) W. G. Cole, D. W. Williams, and A. N. H. Yeo, *J. Chem. Soc. B*, 1284 (1968).

(10) S. Gabriel and A. Sonn, *Ber.*, **40**, 4850 (1907).

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