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The Chemistry of Dibenzo[d,f][1,3]diazepines

2.[1] Mass Spectrometric Studies of 6-Methyl- and 6-Ethyl-5,7-dihydroxy-6,7-dihydro-5*H*-dibenzo[d,f][1,3]diazepine

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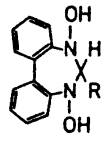
The mass spectra of 6-methyl- and 6-ethyl-5,7-dihydroxy-6,7-dihydro-5*H*-dibenzo[d,f][1,3]diazepine are given. The main fragmentation pathways are suggested from the use of deuterium labelling, high resolution mass measurements and the metastable defocusing technique. Characteristic features are the loss of an oxygen atom and a molecule of water from the molecular ion and the formation of several abundant odd-electron fragments which may be ascribed to various heterocyclic structures derived from 2,2′-substituted biphenyles.

Continuing the investigation[1] on 5,7-dihydroxy-6,7-dihydro-5*H*-dibenzo-[d,f][1,3]diazepines * we have examined the electron impact induced fragmentation of 6-methyl- and 6-ethyl-5,7-dihydroxy-6,7-dihydro-5*H*-dibenzo[d,f][1,3]diazepines (I and II).



I: R=CH_3
II: R=C_2H_5

Only little knowledge of the chemical behaviour of these compounds is available at present. I and II were found to decompose by melting and upon oxidation to give rise to a mixture of unstable radicals. Probably the oxidized form, *i.e.* the α-nitronyl nitroxide, is unstable because of the enforced planarity

* The syntheses, properties and spectroscopic data of a number of other dibenzo[d,f][1,3]-diazepines will be published.

of the non-aromatic 1,3-diazepine ring. Reduced 1,3-diazepines in general display the lability of diaminomethane derivatives, and the oxidized form of some dibenzo[d,f][1,3]diazepines are easily cleaved upon methylation or acetylation.[2]

The ring system of I and II can be regarded as a 2,2′-disubstituted biphenyl. Therefore, either ring rupture or ring contraction might give rise to stable heterocyclic products.[3] It cannot be excluded that such processes may also be reflected in the electron-impact induced fragmentation of these compounds.

DISCUSSION

On account of the thermal instability of these compounds it could be expected that thermal decomposition would take place prior to the ionization process. However, mass spectra recorded at ion source temperatures well below the melting points of the compounds were reproducible, and low energy spectra did not indicate any contribution of other molecular ions. Raising the temperature caused a drastic change in the appearance of the spectra. The fragmentation was increased considerably and especially the abundances of *m/e* 196, 167, 152, 140, and 139 (in the mass spectrum of I) were augmented.

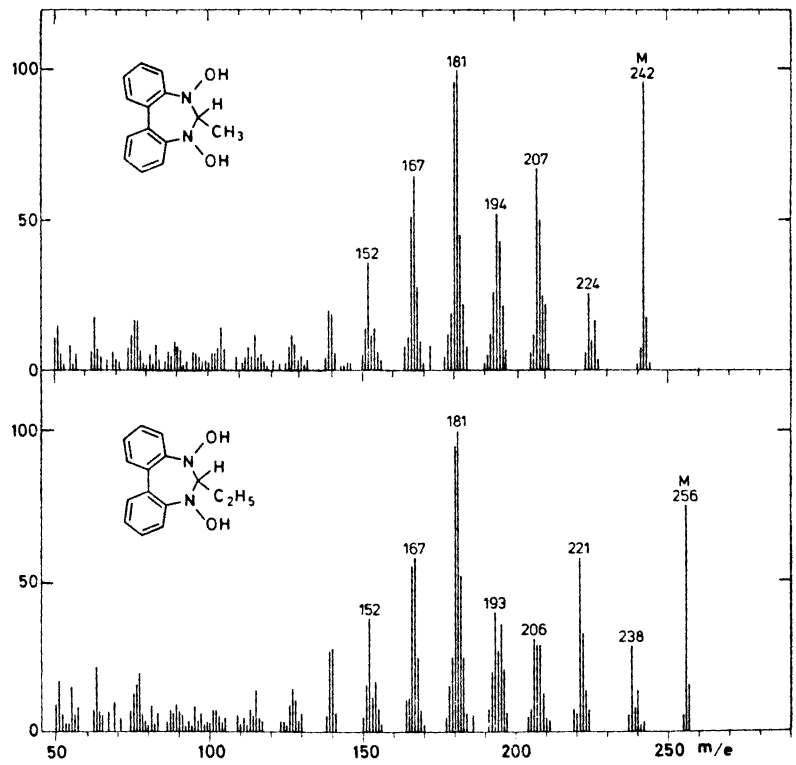
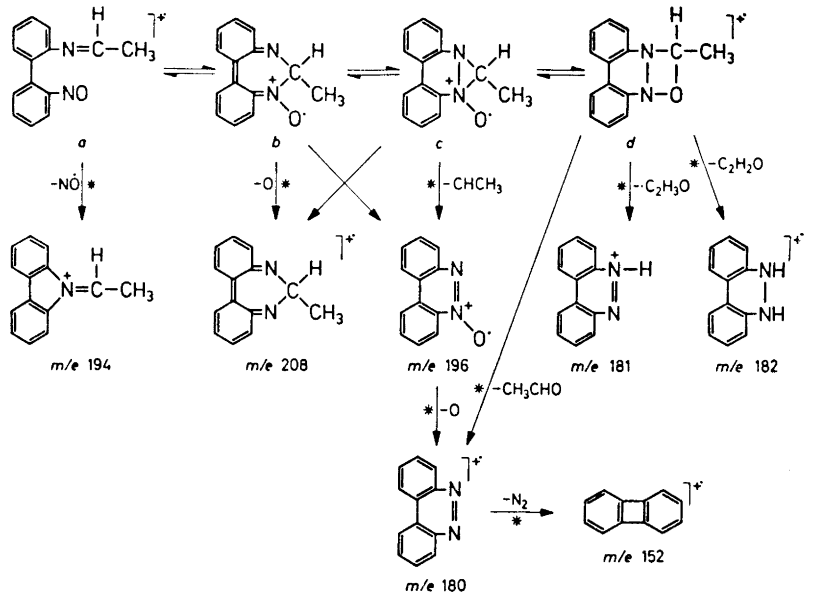


Fig. 1. The mass spectra of I and II.

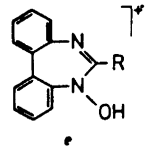
The mass spectra are shown in Fig. 1, where particular attention should be drawn to the abundant molecular ion peaks and to the considerable number of intense peaks in the higher mass range corresponding to even as well as odd-electron ions. The lower mass range exhibits peaks of low intensities at nearly every mass number.

A noteworthy feature in the mass spectra of I and II is the loss of an oxygen atom from the molecular ions. Such M-16 peaks are also important in the mass spectra of alicyclic and aromatic ketoximes [4] in which cases strong M − OH peaks are exhibited. The mass spectra of cyclic hydroxamic acids show direct loss of O or ·OH from the molecular ion.[5] The elimination of an OH-radical from the molecular ions of I and II is also observed but the loss of H_2O seems to be much more favoured. The odd-electron $M-H_2O$ ion is a progenitor of several abundant fragments (shown in Scheme 1 for I) and is twice as abundant as the even-electron M − OH ion. The mass spectrum of 5,7-dideuteriooxy-6-methyl-6,7-dihydro-5*H*-dibenzo[d,f][1,3]diazepine showed that both hydrogen atoms involved in the H_2O loss preferentially originated from the OH-groups. Inspection of Dreiding models has indicated, that in one of the conformations the two OH-groups could easily approach each other closely. The rather complex decomposition pattern observed for the $M-H_2O$ ion involves the elimination of the following neutral species: O, NO·, $CHCH_3$, CH_3CHO, $\cdot C_2H_3O$, and C_2H_2O, and may suggest the fragmentation to proceed through a number of intermediates (*a-d*) as visualized in Scheme 1.



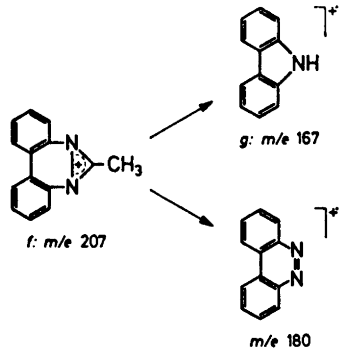
Scheme 1.

Due to some hydrogen/deuterium exchange taking place in the ion source when the mass spectrum of the deuterium labelled compound was recorded it cannot be excluded that *e* to some extent contributes to the $M-H_2O$ ion:



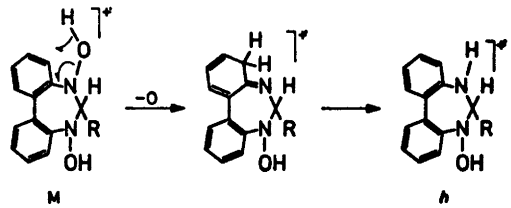
e

Ion *e* may readily eliminate ·OH and thus be a precursor for the abundant M-35 ion (*f*). Also *b* or *c* are possible progenitors for *f*, implying that a hydrogen rearrangement takes place. In addition *f* is formed directly from the molecular ion, probably by a concerted loss of H_2O and ·OH. Ion *f* is decomposed to form the *m/e* 180 ion and it is the main progenitor for the *m/e* 167 ion, *g*, by elimination of C_2H_2N·.



The molecular ion and the $M-H_2O$ ion are also found to be precursors for *g*.

It has recently been claimed [6] that the loss of an oxygen atom from the molecular ions of quinoline *N*-oxide and isoquinoline *N*-oxide is due to thermal, rather than electron-impact fragmentation. The M – O ions in the mass spectra of I and II may also be due to a thermal degradation prior to ionization as their abundances are increased when the ion source temperature is raised. However, application of the metastable defocusing technique revealed that the molecular ion is precursor for the M – O ion, thus clearly demonstrating the electron-impact induced origin of the M – O ion. This mechanistically interesting process may be depicted by the transformation M→*h*,



M *h*

Ion *h* is further decomposed by loss of ·OH to yield the M – 33 ion.

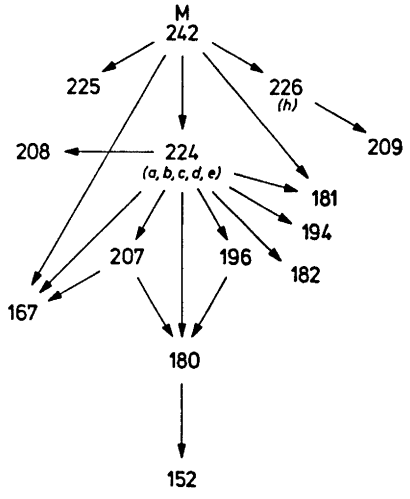
Loss of an oxygen atom is also found to take place both from the $M-H_2O$ ion and from the *m/e* 196 ion yielding *m/e* 208 and 180, respectively (mass spectrum of I). The *m/e* 180 ion is believed to possess the benzo[c]cinnoline structure, since N_2 is further expelled yielding the *m/e* 152 ion in parallel to the predominant electron-impact fragmentation of benzo[c]cinnoline.[7,8] Assuming the possibility of a fragment ion with an *N*-oxide structure to undergo further decomposition by elimination of the oxygen atom from the *N*-oxide function, the structure of the *m/e* 196 ion may correspond to that of benzo[c]cinnoline-*N*-oxide. The mass spectrum of this compound is reported [9] to exhibit an M – O ion. The precursor for the *m/e* 196 ion may also possess an *N*-oxide structure, as shown by *b* and *c* in Scheme 1. The oxygen loss observed to take place from the $M-H_2O$ ion may then similarly be interpreted as an elimination of the oxygen atom from the *N*-oxide function.

The *m/e* 180 ion is also generated directly from the $M-H_2O$ ion, by elimination of CH_3CHO (Scheme 1). This may suggest a formulation of the $M-H_2O$ ion as *d*. Also losses of C_2H_2O and $\cdot C_2H_3O$ from the $M-H_2O$ ion (*d*) are important processes yielding the abundant ions at m/*e* 182 and 181, respectively.

In low voltage spectra the abundance of *m/e* 180 and 182 decrease more rapidly than that of *m/e* 181, and a metastable peak indicates that the process M→*m/e* 181 takes place. At 70 eV this decomposition also occurs, but it is to some extent overshadowed by the competing process now taking place.

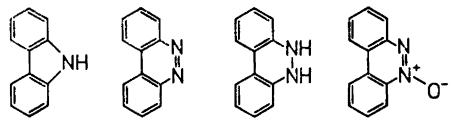
CONCLUSION

The electron impact induced fragmentations of the two diazepines give rise to similar, but rather complex mass spectra. A number of fragment ions are formed in several decomposition processes as shown in Scheme 2, where



Scheme 2. Main decomposition of I.

the main decomposition mode for I is given. The major degradation proceeds *via* the $M-H_2O$ ions, *a-e*, and is to a great extent conducted by the biphenyl function. A number of abundant odd-electron fragment ions are formed which are ascribed to ions corresponding to well known stable heterocyclic compounds such as:



MW 167 MW 180 MW 182 MW 196

The formation of these ions may be a natural consequence of the stability of the biphenyl system together with the easy interaction of the 2,2′-substituents.

EXPERIMENTAL

Mass spectra were obtained on an MS902 mass spectrometer using the direct sample insertion system (ion source temperature: 130°C). Unless otherwise stated, 70 eV electrons were used. All transitions given are verified by metastable defocusing, and the elemental compositions are substantiated by high resolution mass measurements (± 5 ppm). Peaks corresponding to double charged ions appearing at half masses and peaks of lower abundance than 2 % are omitted.

Microanalyses were carried out in the Microanalytical Department of the University of Copenhagen by Mr. Preben Hansen. Melting points (uncorrected) were determined on a Büchi melting point apparatus. Infrared spectra were recorded on a Perkin Elmer Model 137 infrared spectrophotometer. Compounds I and II were prepared as described previously.[1]

*5,7-Dideuteriooxy-6-methyl-6,7-dihydro-5*H*-dibenzo[d,f][1,3]diazepine.* 5,7-Dihydroxy-6-methyl-6,7-dihydro-5*H*-dibenzo[d,f][1,3]diazepine (40 mg) was dissolved in CD_3OD (1 ml) and D_2O (0.2 ml) was added. The precipitated crystals were collected, redissolved in CD_3OD (1 ml) and D_2O (0.5 ml) was added. The precipitated pale yellow crystals of 5,7-dideuteriooxy-6-methyl-6,7-dihydro-5*H*-dibenzo[d,f][1,3]diazepine (11 mg) had m.p. 158–160°d. (Found: C 68.80; H+D 5.74; N 11.46. Calc. for $C_{14}H_{12}D_2N_2O_2$: C 68.60; H+D 5.77; N 11.37.) IR: ν_{max}(nujol) 2400 cm^{-1}, (OD).

REFERENCES

1. Becher, J. *Acta Chem. Scand.* **26** (1972) 1659. (Part 1 in this series.)
2. Elderfield, R. C., Ed., *Heterocyclic Compounds*, Wiley, New York 1967, Vol. 9.
3. Buntrock, R. E. and Taylor, E. C. *Chem. Rev.* **68** (1968) 209.
4. Goldsmith, D., Becher, D., Sample, S. and Djerassi, C. *Tetrahedron, Suppl.* **7** (1966) 145.
5. Bapat, J. B., Black, D., St. C. and Brown, R. F. C. give a review of the mass spectra of cyclic hydroxamic acids in the chapter: Cyclic Hydroxamic Acids, *Advan. Heterocycl. Chem.* **10** (1969) 199.
6. Duffield, A. M. and Buchardt, O. *Acta Chem. Scand.* **26** (1972) 2423.
7. Eland, J. H. D. and Danly, C. J. *J. Chem. Soc.* **1965** 5935.
8. Bowie, J. H., Lewis, G. E. and Reiss, J. A. *Australian J. Chem.* **21** (1968) 1233.
9. Bowie, J. H., Cooks, R. G., Jamieson, N. C. and Lewis, G. E. *Australian J. Chem.* **20** (1967) 2545.

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