Loss of Hydrogen Cyanide and Dihydrogen Cyanide Radical from Aromatic Nitrogen Heterocycles on Electron Impact

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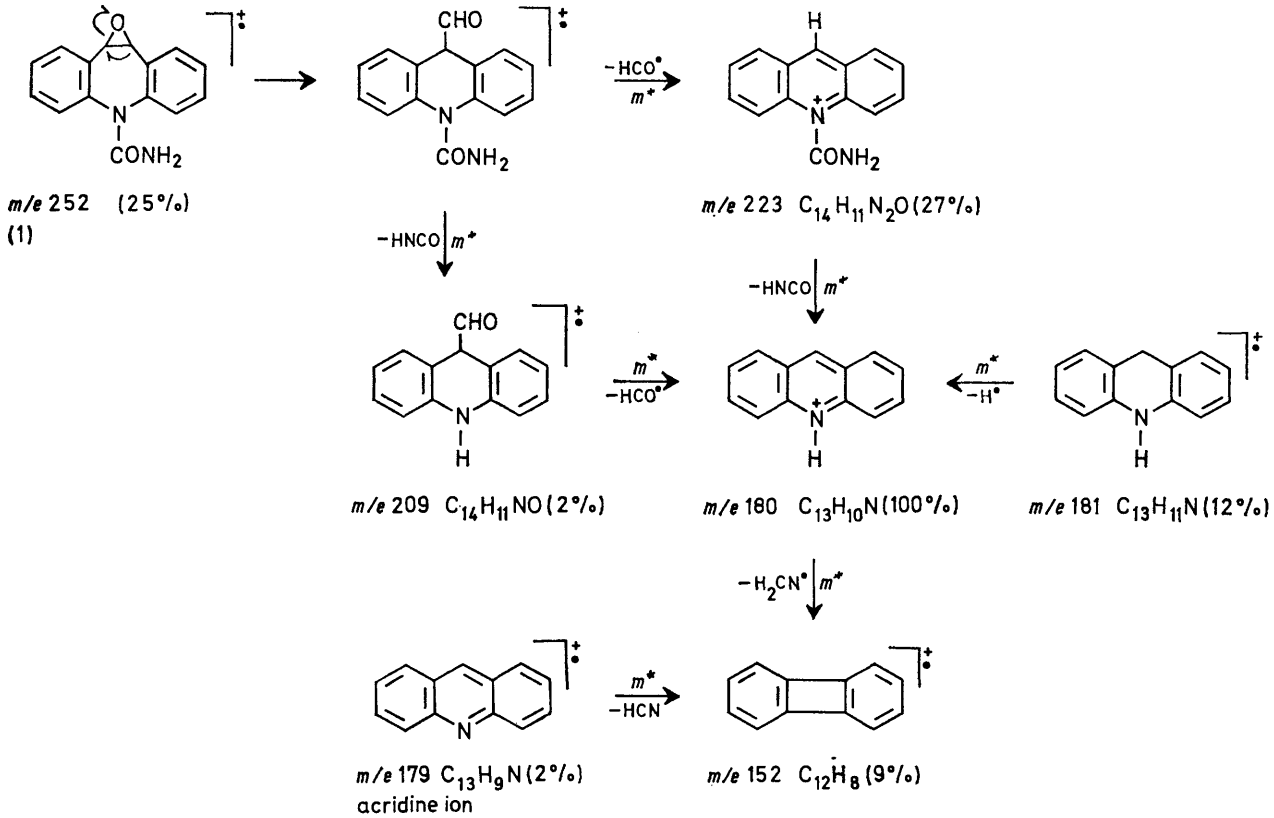
A mechanism for the concerted loss of the dihydrogen cyanide radical ($H_2CN^{\bullet}$) from heterocyclic species such as the ions of dibenz[*b,f*]azepine and its 5-carboxamide formed on electron impact is proposed. A mechanism is also proposed for the loss of hydrogen cyanide from the acridine ion.

Loss of hydrogen cyanide from six-membered nitrogen aromatic heterocycles on electron impact has been well described,[1-5] and much work on the mechanism of this process has been carried out. However the results for larger and more complex molecules have been mentioned only briefly.[6]

Work on the elimination of hydrogen cyanide from various substituted indoles [4,6] has shown which carbon loss of hydrogen cyanide on electron impact have been proposed for other aromatic systems.[1,7-9]

Of more interest is the apparent lack of data concerning the loss of the dihydrogen cyanide radical species ($H_2CN^{\bullet}$) as an entity from this type of molecule. In the work of Marx and Djerassi [3] the process $M - (H + HCN)$ described, does not refer to the loss of the H_2CN radical, but to two distinct separate processes.



SCHEME 1

atoms are involved and the type of rearrangements which can take place. Ring expansions prior to the

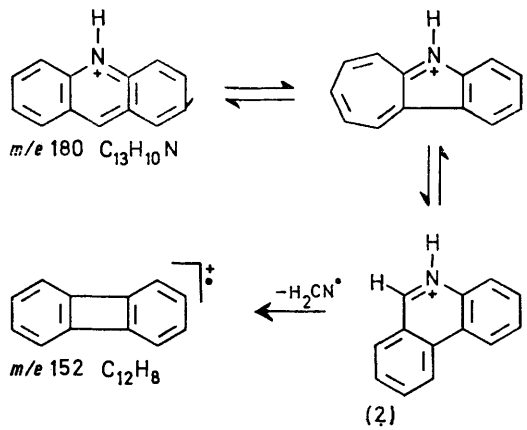
We report here that the base peak at *m/e* 180 in the mass spectrum [10] (Scheme 1) of 10,11-epoxy-5*H*-di-

[1] Q. N. Porter and J. Baldas, ' Mass Spectrometry of Heterocyclic Compounds,' Wiley-Interscience, New York, 1971, pp. 398, 400, 419.
[2] S. D. Sample, D. A. Lightner, O. Buchardt, and C. Djerassi, *J. Org. Chem.*, 1967, **32**, 997.
[3] M. Marx and C. Djerassi, *J. Amer. Chem. Soc.*, 1968, **90**, 678.
[4] S. Safe, W. D. Jamieson, and O. Hutzinger, *Org. Mass. Spec.*, 1972, **6**, 33.
[5] D. H. Williams and J. Ronayne, *Chem. Comm.*, 1967, 1129.
[6] C. E. Loader, T. F. Palmer, and C. J. Timmons, in ' Some Newer Physical Methods in Structural Chemistry,' eds. R. Bonnett and J. G. Davis, United Trade Press, London, 1967, p. 80.
[7] J. C. Powers, *J. Org. Chem.*, 1968, **33**, 2044.
[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, ' Mass Spectrometry of Organic Compounds,' Holden-Day Inc., San Francisco, 1967, p. 567.
[9] G. Spiteller, *Adv. Heterocyclic Chem.*, 1966, **3**, 301.
[10] A. Frigerio, R. Fanelli, P. Biandrate, G. Passerini, P. L. Morselli, and S. Garattini, *J. Pharm. Sci.*, 1972, **61**, 1144.

benz[*b*,*f*]azepine-5-carboxamide (carbamazepine 10,11-epoxide) (1) loses the H_2CN radical in a concerted process as shown by high-resolution measurements and metastable defocusing data. A possible mechanism involving a rearrangement of the protonated acridinium ion to the benzoquinoline species (2) is shown in Scheme 2. A similar process can be written for the loss of hydrogen cyanide from the molecular ion of acridine itself.

Preparation and study of the electron-impact-induced fragmentation of [*NN*-$^2H_2$]carbamazepine 10,11-epoxide showed the loss of the HDCN radical from *m/e* 181 (*N*-deuterioacridinium ion) consistent with the postulated mechanism.

A study of some compounds structurally related to carbamazepine 10,11-epoxide (1) provided us with similar examples of this type of rearrangement mechanism. Carbamazepine (3) loses HNCO on electron impact to give dibenz[*b*,*f*]azepine (4). The subsequent fragmentation of the ion (4), including the loss of the

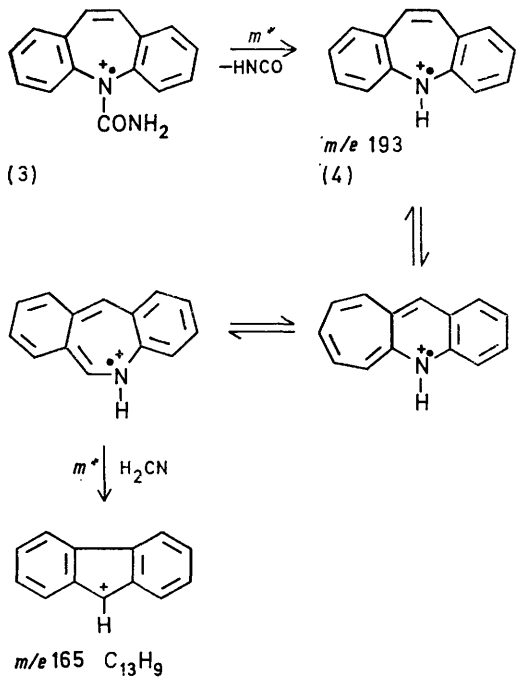


SCHEME 2

H_2CN radical (HDCN radical from the corresponding ion from [*NN*-$^2H_2$]carbamazepine) may proceed *via* a similar mechanism (Scheme 3), here incorporating a dibenz[*b*,*e*]azepiniumyl intermediate.

It should be pointed out that those ions which lose the H_2CN radical species also decompose *via* the transition (*M*, —H, —HCN).

These mechanisms resemble that proposed for quinoline in involving substituted cyclobutadienes as product ions. The extensive rearrangements proposed may explain why the loss of the H_2CN radical in carbamazepine 10,11-epoxide (1) and hydrogen cyanide from acridine is less ready (9% and 7% respectively) than the loss of hydrogen cyanide from quinoline (20%), although other factors affect the abundance of ions.



SCHEME 3

EXPERIMENTAL

The mass spectrometry was carried out on an LKB 9000 spectrometer using the direct injection technique, the metastable defocusing on an A.E.I. MS9 instrument, and the high resolution measurements on a Varian MAT 311 instrument. The deuterio-derivatives [*NN*-$^2H_2$]-carbamazepine and [*NN*-$^2H_2$]carbamazepine 10,11-epoxide were prepared by exchange with a large excess of deuteriomethanol.

Carbamazepine and carbamazepine 10,11-epoxide were generously supplied by Geigy, Milan and by Professor G. Pifferi, Italseber, Milan, respectively.

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