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A UTILIZATION OF THE NEW '<u>D</u>IRECT <u>A</u>NALYSIS OF <u>D</u>AUGHTER <u>I</u>ONS (<u>DADI</u>)' TECHNIQUE: EVIDENCE FOR RING CONTRACTION IN 2,3-DIHYDROBENZOXEPIN UPON ELECTRON-IMPACT.*

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The observation of metastable peaks has aided to a great extent in the interpretation of mass spectrometric fragmentation processes by relating daughter to precursor ions, thereby establishing distinct paths of ion decomposition. In addition, ion structures have been related to each other by comparing the decay of the respective species in terms of metastable characteristics such as mass, peak shapes and relative abundance.[1] Eliminating the main disadvantage of this approach, *i.e.* the necessity of having to match a multitude of mostly unrelated transitions overlapping in a conventional mass spectrum, a new technique recently introduced as '<u>D</u>irect <u>A</u>nalysis of <u>D</u>aughter <u>I</u>ons (DADI)' [2] holds promise of lending itself especially well to the structure identity problem. The method permits the singling out and observation of a whole generation of daughter ions characterized by descent from one common precursor.

This novel technique of selectively comparing limited and, more importantly, coherent sets of metastable decompositions is chosen for confirmation of a major rearrangement process in *2,3-dihydrobenzoxepin* (I) [3] with the aim of producing direct evidence for structural identity of the rearranged product ion with a species of the postulated structure, formed independently and in an unambiguous fashion from a suitable precursor. Rearrangement of I by ring contraction is strongly suggested by the prominence of an (M - CH_3) fragment (m/e 131, Fig. 1), previously shown to be formed in closely related systems, notably 2,3,4,5-tetrahydrobenzoxepin, [4] chroman,[4,5] and acylated cyclic amines of proper ring size,[5] by expulsion of α-methylene groups (C-2) together with hydrogen from the adjacent position (C-3).[4,6] This unusual positional origin of the expelled methyl radical is considered indicative of contraction of the saturated ring to the next lower cyclic homologue.

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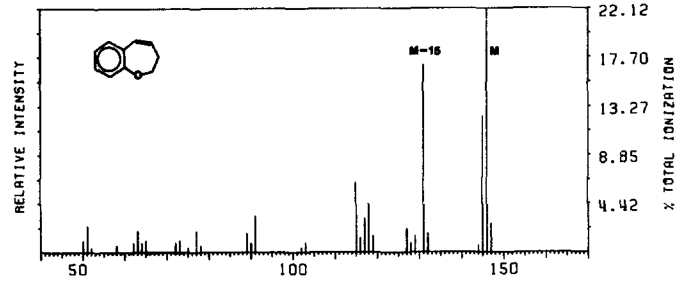
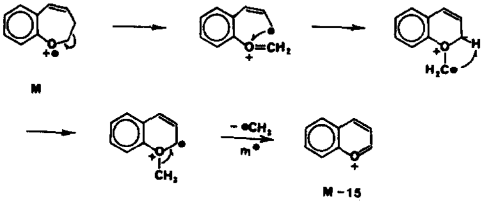


Fig. 1: Mass Spectrum of 2,3-Dihydrobenzoxepin (I).

The mechanism being proposed for this process follows analogous interpretations derived for the above systems, and is supported in all these cases by extensive isotope labelling:[4-6]



After ionization (M), rupture of the oxygen-containing ring should be greatly facilitated by the formation of an extensively conjugated radical center, favorably positioned for an attack at the π-system of the oxonium structure. Recyclization may regenerate M, yet for reasons of minimum strain a six-membered isomeric structure is likely to be preferred. The final formation of a highly stabilized benzopyrylium ion (M - CH_3) after allylic hydrogen abstraction should provide additional driving force to the overall process. An expected increase in the (M - CH_3) ion current in I relative to that of the tetrahydro-derivative as a result of the presence of an additional double bond in a favorable position is, in fact, observed (17% of total ionization as compared with only 11% in 2,3,4,5-tetrahydrobenzoxepin [4]).

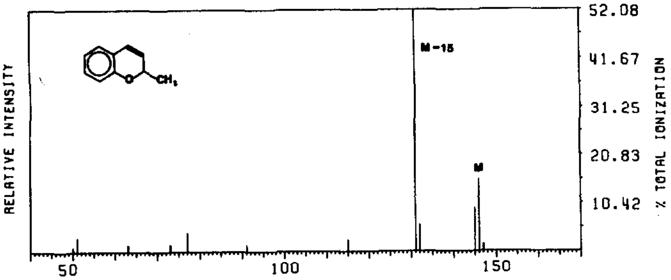
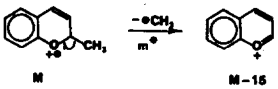


Fig. 2: Mass Spectrum of 2-Methylchromene (II).

To confirm the proposed benzopyrylium structure of the rearranged product ion, an alternative direct formation from 2-methylchromene (II) [3] was attempted for comparison. In the mass spectrum of II (Fig. 2) the corresponding (M - 15) ion provides the base peak, and is very likely to arise *via* simple α-cleavage:



The conventional match of the entirety of metastable peaks contained in the 'normal' mass spectra of I and II reveals at once considerable similarity. The evidence obtained by this gross comparison is, however, of limited value, since plain resemblance may, in principle, also arise from ions having no relevance to the process in question. Direct Analysis of Daughter Ions applied to the (M - CH_3) precursors of unknown and known origin (I and II, respectively) appears in this case to be the method of choice. A sound basis for the inference of structural identity of the ions to be compared is provided in that the DADI-spectra [7] of m/e 131, in the one case generated by rearrangement from 2,3-dihydrobenzoxepin (I), and in the other case by direct cleavage from 2-methylchromene (II) both display a perfect match with respect to number, position and shape of metastable signals:[8] in each instance only one transition (m/e 131 → 103, loss of CO) is detected.

In order to increase the number of elements of comparison, the m/e 103 ions can, in turn, be regarded as precursors of a next generation of daughter ions, and consequently be subjected in the same way to a 'double match', thus considerably enhancing the evidence in favor of identity of the two ion structures. In this experiment, two identical transitions (Table I and Fig. 3) are recorded: m/e 103 → 102 and m/e 103 → 77.

Metastable Transition	2,3-Dihydrobenzoxepin (I) Relative Intensity (ppm)	2-Methylchromene (II) Relative Intensity (ppm)
m/e 131 → m/e 103	80	80
m/e 103 → m/e 102	870	1700
m/e 103 → m/e 77	400	740

Table I: Metastable Transitions Compared.

These two processes, effecting coincident ejection of hydrogen atoms and acetylene molecules from unknown positions, corroborate the precursor identity inferred, and thus leave little doubt as to the benzopyrylium structure of m/e 131.

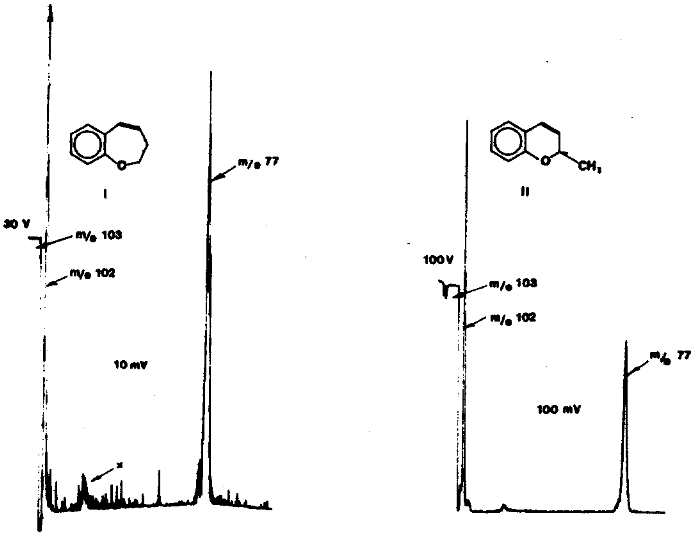


Fig. 3: DADI-Spectra of m/e 103 Ions produced from 2,3-Dihydrobenzoxepin (I) and 2-Methylchromene (II).

Thus, even in the absence of a detailed knowledge of the mechanisms of decomposition the repetitive application of this matching technique to coherent product ions can provide a convenient and flexible tool for assigning structures to gas phase ions with greater confidence than was previously possible.

References and Notes

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2. K. H. Maurer, C. Brunnèe, G. Kappus, K. Habfast, U. Schröder and P. Schulze, Nineteenth Annual Conference on Mass Spectrometry, ASTM Committee E-14, Atlanta, Ga., May 1971.
3. The authors are indebted to Prof. E. E. Schweizer of the University of Delaware for samples of this compound.
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7. DADI-spectra were obtained with a Varian MAT CH 5-DF double focusing mass spectrometer operated at 70 eV ionizing energy.
8. Differences in relative intensities of metastable peaks can in the case of identity reflect *e.g.* different energy distributions in the two precursor ions.