

# Mass Spectrometry in Structural and Stereochemical Problems. CCXLII. Analysis of Mixtures Based on the Distribution of Fragment Ions Arising from Unimolecular Decomposition of Metastable Molecular Ions<sup>1,2</sup>

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**Abstract:** The technique of analysis of metastable ions which decompose in the second field free region of a double focusing mass spectrometer of reversed geometry is applied to mixtures of compounds. Examples drawn from the steroid field indicate the potential of this technique for component identification, differentiation of structural isomers, and determination of metastable ion spectra of monoisotopic species in instances of low isotopic purity.

The importance of metastable ions to studies in mass spectrometry needs no elaboration. Recent reviews have summarized investigations of metastable ions.<sup>3-6</sup> Several years ago, Barber and Elliott<sup>7</sup> demonstrated that metastable ion decompositions could be detected and analyzed without interference of ions from the conventional mass spectrum utilizing a double focusing mass spectrometer. This technique, termed "metastable defocusing,"<sup>8</sup> allows the study of metastable transitions occurring in the first field free region of an instrument of conventional design (electric sector preceding magnetic sector). This technique has several advantages and disadvantages which have been summarized.<sup>9</sup> A single accelerating voltage scan identifies all progenitors ("parents") of each fragment ion ("daughter") analyzed.

More recently, double focusing mass spectrometers of reversed geometry (magnetic sector followed by electric sector) have become available.<sup>10</sup> These instruments can be used to study metastable ions in both the first field free region preceding the magnetic sector and the second field free region between the magnetic and electric sector. The former region can be utilized exactly as in instruments of conventional design, subject to the same advantages and disadvantages.<sup>9</sup> Meta-

stable decompositions occurring in the second field free region of a reversed geometry instrument are studied by focusing a selected mass on the detector, followed by scanning the electric sector voltage. This technique allows identification of all daughter ions arising from the selected parent ion.<sup>11,12</sup> Advantages and disadvantages of this technique have been discussed.<sup>10-12</sup>

The way in which data obtained utilizing this technique complement those obtained from the first field free region of instruments of either geometry can be illustrated with the aid of the symbolic fragmentation map presented in Figure 1. Fragmentation begins at level zero with P, the molecular ion. Fragment ions (F's) at level one become parent ions for the fragment ions at level two, and so forth. This map (Figure 1) expands outward and downward and may be viewed as a tree structure; the top of the tree is the molecular ion. Fragment ions which do not fragment further are ends of branches, e.g., F<sub>3c</sub>, F<sub>3e</sub>. Data from MIKES/DADI indicate the progression of the fragmentation down from the top of the tree by specifying the daughter ions of each parent. The Barber-Elliott technique and its variations specify the progression of fragmentation in the reverse sense as the parents of each daughter ion are determined.

The particular approach taken in studies of metastable ions depends entirely on the application. If information about the origins of a particular fragment ion is required, the Barber-Elliott technique is clearly desirable. In this study, however, we wish to explore applications to mixtures of compounds. In general, under 70 eV electron impact ionization, there will be many more fragment ions than molecular ions. We assume that techniques exist to assist in determination of which ions are molecular ions, e.g., data from the techniques of field ionization or low-ionizing voltage. The technique of MIKES/DADI applied to the rela-

(1) For part CCXLI, see B. Grant and C. Djerassi, *J. Amer. Chem. Soc.*, **96**, 3477 (1974).

(2) Financial assistance from the National Institutes of Health (Grant No. AM 04257 and RR 00612-03) is gratefully acknowledged.

(3) D. H. Williams, *Advan. Mass Spectrom.*, **5**, 569 (1971).

(4) F. W. McLafferty, *Advan. Mass Spectrom.*, **5**, 589 (1971).

(5) K. R. Jennings in "Mass Spectrometry," G. W. A. Milne, Ed., Wiley, New York, N. Y., 1971, p 420.

(6) J. H. Beynon and R. M. Caprioli in "Biomedical Applications of Mass Spectrometry," G. R. Waller, Ed., Wiley-Interscience, New York, N. Y., 1972, p 157.

(7) M. Barber and R. M. Elliott, presented at the 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, 1964.

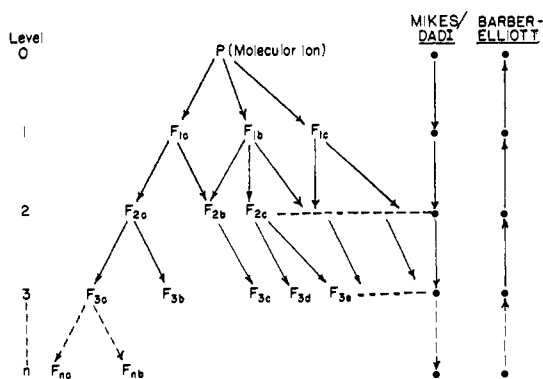
(8) The term metastable defocusing is, at best, misleading, as the mass spectrometer is defocused for ions giving rise to the conventional mass spectrum but focused for decomposition products of metastable ions. Like most jargon the term remains in use because it is recognized and used by many who are familiar with the technique.

(9) J. H. Beynon, *Anal. Chem.*, **42**, 97A (1970).

(10) (a) F. A. White, F. M. Rourke, and J. C. Sheffield, *Appl. Spectrosc.*, **12**, 46 (1958); (b) U. Löhle and Ch. Ottinger, *Int. J. Mass Spectrom. Ion Phys.*, **5**, 265 (1970); (c) K. H. Maurer, C. Brunee, G. Kappus, K. Habfast, U. Schroder, and P. Schulze, presented at the 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, 1971; (d) T. Wachs, P. F. Bente III, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 333 (1972); (e) J. M. Miller, J. Ross, J. Rustenberg, and G. L. Wilson, *Anal. Chem.*, **45**, 627 (1973).

(11) There is a conflict concerning descriptive names for this technique. It has been termed direct analysis of daughter ions, or DADI.<sup>10c</sup> The term which is used more frequently was coined by Beynon, the term being mass analyzed ion kinetic energy spectroscopy, or MIKES.<sup>12</sup> Some workers will be familiar with one term but not the other. We have, therefore, used both acronyms throughout the text.

(12) (a) J. H. Beynon, R. M. Caprioli, and T. Ast, *Org. Mass Spectrom.*, **5**, 229 (1971); (b) J. H. Beynon, *Res./Develop.*, **22**, 26 (1971); (c) J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Y. Ridley, *Anal. Chem.*, **45**, 1023A (1973).



**Figure 1.** A symbolic fragmentation map indicating the complementary information available on fragmentation pathways from two methods of recording decompositions of metastable ions.

tively small number of ions which are molecular ions seems a more straightforward experimental approach for mixtures than examination of many daughter ions. We seek to determine how much information about various types of mixtures can be obtained using this technique for molecular ions.

A report has appeared suggesting that decompositions of metastable ions (in a conventional double focusing instrument) may permit analysis of mixtures of isomeric compounds.<sup>13</sup> These ions have also been used in support of computer-aided analysis of mixtures of peptides.<sup>4,14</sup> In each case measurement of many transitions was necessary to establish, in the first case,<sup>13</sup> those few transitions which displayed significant differences in ion abundances and, in the second case,<sup>4,14</sup> those transitions which yielded new structural information. Ion kinetic energy spectroscopy (IKES) has been used to determine the relative amounts of toluene and deuterated toluene in a mixture of both, again utilizing an instrument of conventional geometry.<sup>15</sup> The utility of a reversed geometry instrument for a different application, the study of structures of gaseous ions, has recently been demonstrated.<sup>16</sup>

### Experimental Section

Metastable spectra (MIKES/DADI) were recorded on standard Varian-MAT 311 double focusing mass spectrometers at Varian-MAT, Bremen. Operating conditions were as follows: ionizing voltage, 70 eV; ionizing current, 1.0 mA; accelerating voltage, 3 kV. The energy resolution at this accelerating voltage was approximately one part in 130. Although this resolution is not as high as that described for special purpose instruments,<sup>12c</sup> it is sufficient to permit recording of dish-topped peaks arising from decompositions of metastable molecular ions accompanied by significant kinetic energy release, for example, the daughter ion of  $m/e$  244, Figure 2, and others observed during the course of these studies.

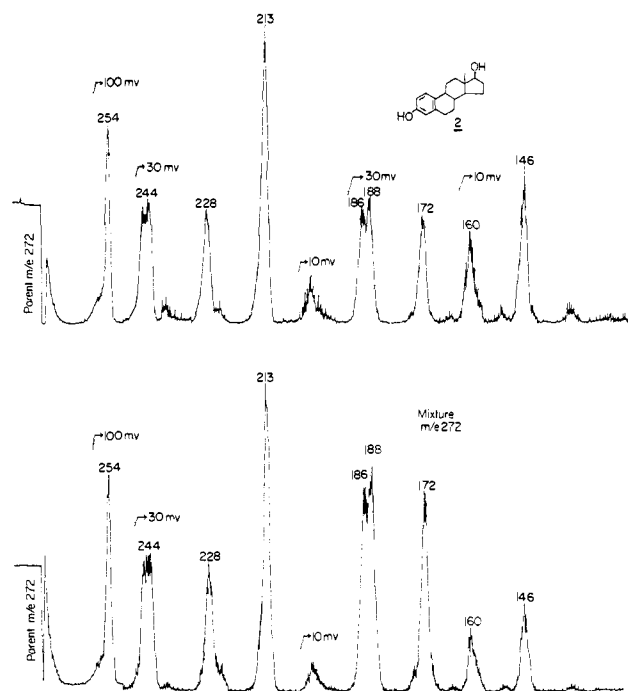
The electric sector voltages required to focus the parent ion and each daughter ion were recorded manually utilizing a digital voltmeter. Observed voltage ratios are directly proportional to observed mass ratios. Thus daughter masses can be determined directly. Scans of the electric sector voltage were recorded on strip chart paper from which metastable ion abundances were determined.

(13) F. W. McLafferty and T. A. Bryce, *Chem. Commun.*, 1215 (1967).

(14) H.-K. Wipf, P. Irving, M. McCamish, R. Venkataraghavan, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **95**, 3369 (1973).

(15) J. H. Beynon, J. E. Corn, W. E. Bahtinger, J. W. Amy, and R. A. Benkeser, *Org. Mass Spectrom.*, **3**, 191 (1970).

(16) F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente III, S.-C. Tsai, and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, **95**, 3886 (1973).



**Figure 2.** Top: spectrum of daughter ions recorded utilizing the molecular ion ( $m/e$  272) of estradiol (**2**) as the parent ion. Bottom: spectrum of daughter ions recorded utilizing the ion of mass 272 in the synthetic mixture of **1-3** as the parent ion. Full scale range changes and masses of daughter ions are as indicated.

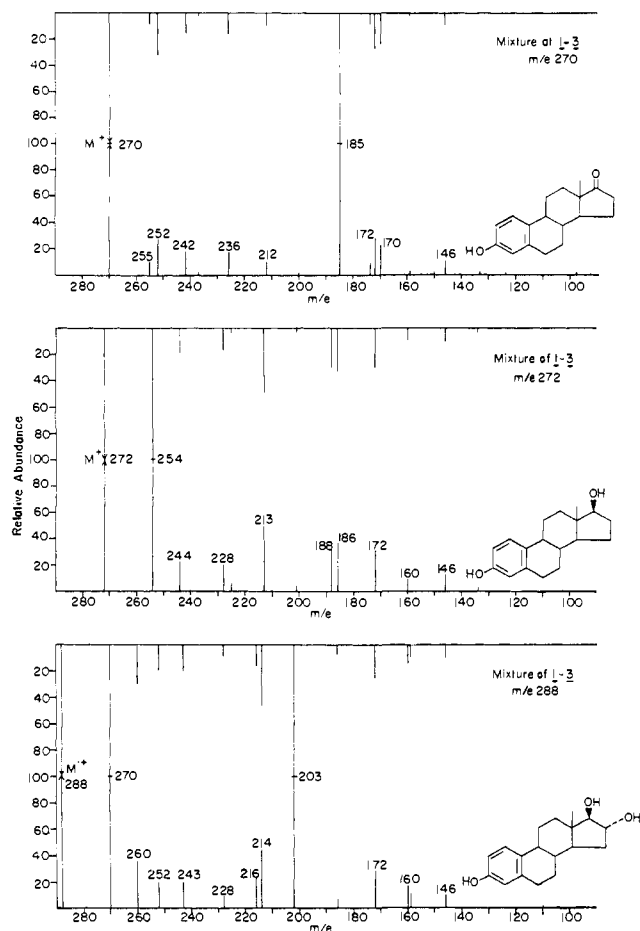
Samples of steroids were introduced *via* a direct insertion probe. Synthetic mixtures were made from approximately equimolar amounts of each component. Experiments on reproducibility utilized diphenyl ether introduced *via* a batch inlet system. The pressure observed in the ion source region for the largest sample flow rates used in these reproducibility experiments was  $2 \times 10^{-6}$  Torr. This relatively low pressure coupled with the fact that the ion source and mass analyzer regions are differentially pumped (and no increase in analyzer pressure was observed) precludes any significant influence of collision-induced<sup>16</sup> decomposition of metastable ions.

### Results and Discussion

**Reproducibility.** Observed patterns (masses and abundances) of metastable ions and their decomposition products must be reproducible if these data are to be used in comparison of different compounds. Short-term reproducibility of ion kinetic energy spectra of benzene has been reported.<sup>17</sup> We have investigated the reproducibility of the MIKES/DADI spectrum of the molecular ion of diphenyl ether under a variety of operating conditions of the mass spectrometer. The spectrum displays abundant ions resulting from two metastable decompositions corresponding to  $[M^+ - H]$  and  $[M^+ - CO]$ .<sup>18</sup> The results may be briefly summarized as follows. The abundances of the daughter ions relative to the parent (precursor) ion and relative to the most abundant daughter ion depend strongly on the ion source potentials, specifically the potentials of the repeller and draw-out plates. This is expected, as these potentials affect the residence times of ions within the ion source. The abundances of the two daughter ions relative to the parent ion increase

(17) E. M. Chait and W. B. Askew, *Org. Mass Spectrom.*, **5**, 147 (1971).

(18) For a discussion of the conventional mass spectrum of diphenyl ether, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 249.



**Figure 3.** Comparison of distributions of daughter ions recorded utilizing as parent ions the molecular ions of reference compounds estrone (1), estradiol (2), and estriol (3) (top, middle, and bottom normal graphs) with the corresponding MIKES/DADI spectra of  $m/e$  270, 272, and 288 in a mixture of 1-3 ("reflected" spectra).

with decreased residence time, as does the abundance of  $[M^+ - CO]$  relative to  $[M^+ - H]$ . However, the increased abundance of metastable ions relative to the parent ion does not make up for the decrease in absolute sensitivity under these conditions. Thus it seems advantageous to standardize operation of the mass spectrometer by maximizing the absolute sensitivity. Under constant conditions the short-term reproducibility seems limited only by ion statistics. The abundances of daughter ions in the range of 0.1% of the parent ion abundance (metastable ion current  $\approx 10^{-14}$  A) are reproducible to 1-2%. Metastable ion abundances in the 10 ppm range (of the same parent ion) typically are reproducible to 10-20%.

Abundances of the two daughter ions relative to the parent ion increased by a factor of 4 as sample flow through the ion source was increased by a factor of 15. However, the ratio of the abundances of  $[M^+ - H]$  and  $[M^+ - CO]$  remained constant over this range of sample flow. For this reason, all ion abundances reported below are expressed as percentages of the most abundant daughter ion.

Long-term reproducibility appears to be limited to about  $\pm 10\%$  variation in peak height ratios for abundant daughter ions ( $\sim 0.1\%$  of parent ion). This is presumably due to minor variations in the operating conditions of the mass spectrometer and cleanliness of

the ion source. This degree of variation was also noted for a mixture of estrogenic steroids (see subsequent section) analyzed on two "identical" mass spectrometers.<sup>19</sup>

**Mixture Types.** We have investigated several mixtures of compounds and reported results for three categories of mixtures: (1) mixtures of nonisomeric compounds; (2) mixtures of isomeric compounds, but not stereoisomers; (3) mixtures of isotopes resulting from incomplete isotopic labeling or from the presence of a polyisotopic element. Analysis of stereoisomeric pairs will be reported in a subsequent publication; none were analyzed as mixtures.

**(1) Mixtures of Nonisomeric Compounds.** Several investigators<sup>6,13,17</sup> have reported the use of data from metastable defocusing experiments and related ion kinetic energy spectra to provide a "fingerprint" of molecular identity to supplement conventional mass spectra. This has obvious implications for mixture analysis as the mass spectrum of the mixture may represent the superposition of very similar individual mass spectra whereas it may be possible to detect metastable transitions which are characteristic of a particular component.<sup>13</sup> The technique of MIKES/DADI has been applied to the molecular ions of the estrogenic steroids estrone (1), estradiol (2), and estriol (3) (structures presented in Figure 3) and to each molecular ion in a synthetic mixture of 1-3. Strip chart traces of the MIKES/DADI spectra of the molecular ion of estradiol (2) ( $m/e$  272) and  $m/e$  272 from the mixture of 1-3 are reproduced in Figure 2 (note full-scale range changes). It is seen that the traces are identical in all respects. These spectra provide information on both relative abundances and peak shapes which can be used to characterize a compound. For example, the broad metastable peak centered at  $m/e$  244 represents a dish-topped metastable peak for loss of 28 mass units from the molecular ion (may be either loss of CO or  $C_2H_4$ ; both losses yield minor peaks in the conventional mass spectrum).

Relative abundance data from the MIKES/DADI spectra of the molecular ions of 1-3 are presented in Figure 3 with the corresponding spectra from the mixture presented as "reflections" of the reference spectra. The characteristic relative abundances in the spectrum of each reference compound are reproduced in the spectra recorded on the mixture. Peak shapes are also identical in all cases, although this information is lost in the bar graph presentation of Figure 3.

This approach requires only as many scans as there are mixture components (or fewer if some molecular weights are the same; see next section) to obtain a qualitative analysis of the mixture. Standard spectra of reference compounds are required for matching and identification purposes. The amount of information inherent in both relative abundances and peak shapes facilitates the matching task. The approach can be complicated if the fragmentation of a higher molecular component yields an ion of the same mass as the molecular ion of a lower molecular weight component. If this fragment ion yields abundant metastable ions for subsequent decompositions, these ions will be superimposed on the MIKES/DADI spectrum of the lower

(19) We are indebted to Dr. A. L. Burlingame, Space Sciences Laboratory, University of California, Berkeley, for allowing us to perform these measurements on a Varian-MAT 311 in his laboratory.

weight component. This problem did not arise in the few examples presented in this work, although opportunity existed. For example, estriol (**3**) displays a low abundance fragment ion (normal spectrum) of mass 270 [ $M^+ - H_2O$ ] which represents the most frequent metastable process in the MIKES/DADI spectrum (Figure 3). However, the MIKES/DADI spectrum of estrone (**1**),  $m/e$  270, recorded from the mixture of **1-3** showed no interference from subsequent decomposition of  $m/e$  270 from estriol (Figure 3).

Quantitation of this mixture was not attempted as the sample was vaporized as required from a direct insertion probe; gc analyses of derivatives are better suited for quantitation of estrogens. Quantitation of a mixture may be possible if the components can be introduced through a batch inlet system.

(2) **Mixtures of Isomeric Compounds.** We carried out an extension of the approach described in the previous section by analysis of MIKES/DADI spectra of the molecular ions of the isomeric reference compounds 16-ketoestradiol (**4**) and 16-hydroxyestrone (**5**) (Figure 4) and the single molecular ion  $m/e$  286 in a synthetic mixture of **4** and **5**. The results are presented in Figure 4. Although the resulting spectra of **4** and **5** have several ions in common, there are significant differences in relative abundances, peak shapes, and in the presence or absence of ions of lower abundance. For example, the MIKES/DADI spectrum (Figure 4) of 16-ketoestradiol (**4**) displays daughter ions of mass 250, 226, and 198 which are absent in the corresponding spectrum of 16-hydroxyestrone (**5**). Compound **5** displays daughter ions of mass 241, 230, and 201 which are absent in the MIKES/DADI spectrum of **4**. The MIKES/DADI spectrum of ions of mass 286 in the mixture of **4** and **5** represents a superposition of these features and, furthermore, allows an estimation that 50–60% 16-hydroxyestrone was vaporizing from the direct insertion probe at the time the spectrum was recorded.

The conventional mass spectra of **4** and **5** display significant differences; it is not surprising that their MIKES/DADI spectra are different. We have examined several pairs of epimeric compounds and note that MIKES/DADI spectra do not always display significant differences if the conventional mass spectra are identical, an observation made previously with data obtained from the Barber–Elliott technique.<sup>13,17</sup> This represents a potential limitation of the technique of MIKES/DADI for differentiation of epimeric compounds.

(3) **Mixtures of Isotopes.** A previous study has indicated the utility of ion kinetic energy spectra in quantitative analysis of mixtures of deuterated toluenes.<sup>15</sup> We were not so much interested in quantitation as in determining the utility of MIKES/DADI spectra in examination of the decomposition of a particular molecular ion (or fragment ion) in the presence of other molecular ions differing only in isotopic composition. In the steroid field, for example, many deuterium labeling experiments yield relatively low incorporation. It would be a considerable advantage if metastable decompositions of the desired labeled material could be studied without significant interference from incompletely labeled contributors to the mixture.<sup>12c</sup> A MIKES/DADI spectrum of the appro-

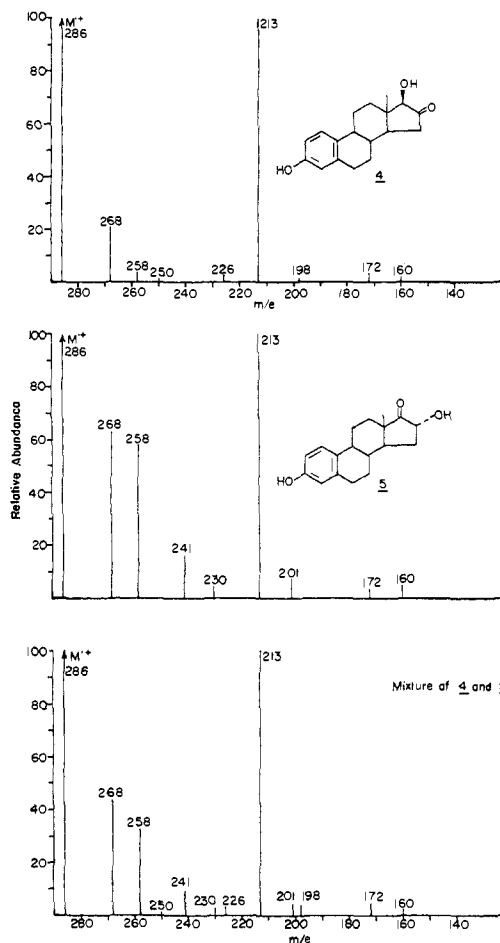


Figure 4. Top: spectrum of daughter ions recorded utilizing the molecular ion ( $m/e$  286) of 16-ketoestradiol (**4**) as the parent ion. Middle: spectrum of daughter ions recorded utilizing the molecular ion ( $m/e$  286) of 16-hydroxyestrone (**5**) as the parent ion. Bottom: spectrum of daughter ions recorded utilizing the ion of mass 286 in a synthetic mixture of **4** and **5** as the parent ion.

priate molecular ion seems an ideal way to investigate metastable decompositions in these cases. This molecular ion consists of material labeled 100% in the desired position(s). The resulting MIKES/DADI spectrum is that of completely labeled material. However, interferences can result from  $^{13}C$  contributions from ions of lower mass or fragment ions arising from loss of hydrogen or deuterium atom from ions of higher mass. (The occurrence of incomplete labeling may actually be beneficial if one can be sure of the location of the isotopic label in each component. In this case MIKES/DADI spectra of the unlabeled and each specifically labeled component can be determined from a single sample.)

As an example, consider the series of deuterated cholestan-6-ones summarized in Table I. The conventional mass spectra and fragmentation pathways of these compounds have been described previously.<sup>20</sup> MIKES/DADI spectra were recorded on the molecular ion(s) for each compound and the results for the major transitions are summarized in Table I.

None of the transitions summarized in Table I result in loss of any deuterium label; the peak shifts are essen-

(20) C. Djerassi, R. H. Shapiro, and M. Vandewalle, *J. Amer. Chem. Soc.*, **87**, 4892 (1965).

**Table I.** Major Metastable Transitions Determined in the MIKES/DADI Spectra of the Molecular Ions of Cholestan-6-one and Labeled Analogs

Compd	Isotopic purity	Molecular ion	Transition <sup>a</sup>			
			M - 15	M - 18	Side chain loss	Ring D loss
Cholestan-6-one		386	371 (100)	368 (14)	273 (22)	231 (36)
Cholestan-6-one-3 $\beta$ - <i>d</i> <sub>1</sub>	<i>d</i> <sub>1</sub> 98% <i>d</i> <sub>0</sub> 2%	387	372 (100)	369 (13)	274 (18)	232 (38)
Cholestan-6-one-3 $\alpha$ - <i>d</i> <sub>1</sub>	<i>d</i> <sub>1</sub> 96% <i>d</i> <sub>0</sub> 4%	387	372 (100)	369 (12)	274 (17)	232 (36)
Cholestan-6-one-2,2,4,4- <i>d</i> <sub>4</sub>	<i>d</i> <sub>4</sub> 8%					
	<i>d</i> <sub>3</sub> 23%	389	374 (100)	371 (11)	276 (16)	234 (35)
	<i>d</i> <sub>2</sub> 50%	388	373 (100)	370 (14)	275 (17)	233 (33)
	<i>d</i> <sub>1</sub> 16% <i>d</i> <sub>0</sub> 3%					

<sup>a</sup> Relative abundances (in parentheses) are uncorrected for <sup>13</sup>C contributions and are expressed in percentages.

tially quantitative. The results of the 3 $\alpha$ - and 3 $\beta$ -*d*<sub>1</sub> analogs are presented to indicate that the patterns of the DADI spectra shift in mass for these transitions, but not in relative abundance. The sample of cholestan-6-one-2,2,4,4-*d*<sub>4</sub> chosen for this investigation was of relatively low isotopic purity (Table I). Yet MIKES/DADI spectra of *m/e* 389 (*d*<sub>3</sub>) and *m/e* 388 (*d*<sub>2</sub>) display the same pattern of metastable ion abundances. Each component has, in effect, been analyzed independently of the other contributors.

Investigations of transitions involving loss of all or part of a deuterium label should be facilitated by employing the MIKES/DADI technique rather than the Barber-Elliott technique utilized previously.<sup>21</sup>

This technique should also be applicable to other mixtures of isotopes. Beynon, *et al.*, have described the MIKE spectra of ions containing one <sup>13</sup>C atom of natural abundance.<sup>12c</sup> Isolation of one molecular ion

(21) D. H. Smith, A. M. Duffield, and C. Djerassi, *Org. Mass Spectrom.*, **7**, 367 (1973).

of a compound containing a polyisotopic element (*e.g.*, chlorine, germanium) should assist in interpretation of the decomposition of this ion when the fragmentation pattern is complicated by losses of a hydrogen atom or molecule superimposed on the already complex isotopic distribution.

### Conclusion

The distributions of daughter ions arising from unimolecular decomposition of metastable molecular ions have been used in the analysis of several types of mixtures of compounds. The examples presented indicate that this technique may be widely applicable to mixtures and related problems involving studies of metastable ion decompositions. The ability in many cases to obtain metastable ion spectra of each component independent of other contributors to a mixture is a powerful asset of the technique whether applied to characterization of the mixture or to studies of metastable ion decompositions of selected components.

## Surface Crossings and Surface Touchings in Photochemistry

Lionel Salem

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**Abstract:** Eight major photochemical reactions [(1) hydrogen abstraction by ketones; (2) photoreduction of aza aromatics; (3) hydrogen abstraction by carbenes; (4) addition of ketones to electron-rich olefins; (5)  $\alpha$  cleavage of alkanones; (6)  $\alpha$  cleavage of dienones; (7) isomerization of furans to cyclopropenyl ketones; (8) ring opening of azirines] are interpreted in terms of surface crossings or surface touchings between ground singlet state and excited  $n, \pi^*$  singlet and triplet states. State correlation diagrams are drawn for each reaction and are confirmed by detailed *ab initio* calculations. In several cases these diagrams throw additional light on the reaction mechanism. Typical state correlation diagrams are given for the two coplanar reaction types described in the article:  $\sigma, \pi$  bitopic reactions and  $\sigma(\sigma, \pi)$  tritopic reactions. Finally, an attempt is made to relate the nature of diradical product and multiplicity of the photoreactive state: two general proposals are made.

Photochemistry, more than any other field, brings man in close touch with the realm of multidimensionality. The freedom enjoyed by an excited molecule is associated with the many directions along which

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it can explore the potential energy surface of the excited state. It has been widely assumed that at some point the molecule must leave this excited surface and decay, *via* a radiationless transition, possibly through a wide energy gap, to the ground surface. We show here that, for a large number of photochemical reactions, surface