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THE FRAGMENTATION OF THE IONS OF NONAN-4-ONE: A STUDY BY TRIPLE--ETC(U)
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THE FRAGMENTATION OF THE IONS OF NONAN-4-ONE:
A STUDY BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The fragmentation of the ions of the compound nonan-4-one were studied in detail with low-energy collision-induced dissociation (CID) in a triple quadrupole mass spectrometer. Ions of the sample molecule created in an EI source are mass selected by a quadrupole mass filter, dissociated by low-energy collision with neutral molecules in a quadrupole collision chamber, and the dissociation products are mass-selected		

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by a second quadrupole mass analyzer. The normal EI mass spectrum of nonan-4-one shows 47 fragment ions. A fragmentation spectrum is obtained for each of the ions from the EI source. The result is the positive identification of over 400 parent-daughter pairs. This compares with a total of 47 observed pairs (37 confirmed) from all previous metastable ion studies. Normal alkanone fragmentations are observed: α -cleavage, loss of CO or C₂H₄ from α -cleavage ions, and McLafferty rearrangement in the long chain. The relative abundances of the short chain and long chain α -cleavage fragments are demonstrated to depend on the fragmentation energy available with the long chain fragment predominating at lower energies. *alpha*

The fragmentations observed are grouped for discussion. A number of parent-daughter structures and fragmentation mechanisms are confirmed and some new ones are proposed. New graphical representations of the fragmentation patterns have been devised to accommodate the large amount of information produced in this study. *alpha* ↑

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THE FRAGMENTATION OF THE IONS OF NONAN-4-ONE:
A STUDY BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

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The electron-impact induced fragmentation of aliphatic ketones has been widely investigated (1). The techniques which have been utilized to help in these studies include metastable decomposition studies (2-4), ion cyclotron resonance (ICR) (5), and the use of deuterium labelled compounds (4-7). The particular attention given to nonan-4-one includes a study of the metastable ions observed from this compound with an Ion Kinetic Energy (IKE) Spectrometer (7). This paper describes a detailed study of the fragmentation of this compound using low-energy collision-induced dissociation (CID) of selected ions in a triple quadrupole mass spectrometer.

Experimental

In selected ion fragmentation, several ion species are generated from a sample, ions of a particular mass are selected for fragmentation, and the resulting fragment ions are mass analyzed. As the present study illustrates, the use of two sequential stages of mass analysis with fragmentation occurring between them makes it possible to determine the routes of formation and fragmentation of ions in the mass spectrum.

We recently introduced the concept of performing selected ion fragmentation with a triple quadrupole mass spectrometer (8). The instrument used in this study has been described (9). It consists of, in series, a dual chemical ionization/electron impact (CI/EI) ionization source, a quadrupole mass filter, an RF-only quadrupole that can be pressurized for CID,

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a second quadrupole mass filter, and an electron multiplier. Mass resolution of one part in 1500 is possible over the entire mass range of 1-1000 amu. The high efficiency of each component in the system allows fragmentation processes of very low probability to be readily observed (9).

Results and Discussion

Figure 1 displays all the collisional fragmentations observed in this study (below the diagonal) and all the metastable transitions seen in the IKES study (above the diagonal) (7). The EI mass spectrum of nonan-4-one shows 47 fragment ions, and the metastable study indicates 37 confirmed and 7 unconfirmed metastable transitions. The triple quadrupole system shows over 400 CID peaks, which include the 44 fragmentations observed in the metastable data as well as a host of others. Not only does the triple quadrupole system with CID produce a significant increase in the number of fragmentations observed, it also provides direct mass analysis of both the parent and daughter ions at unit mass resolution.

A combination of complementary methods was used in the IKES study of metastable transitions (7). The kinetic energy loss upon metastable fragmentation results in broad peaks which make difficult the unambiguous mass assignment of the parent and fragment ions (e.g. $142^+ \rightarrow 99^+$ or $142^+ \rightarrow 98^+$) in IKES scans. (In these scans it is the ratio of parent ion mass/charge squared to daughter ion mass/charge that is actually measured, so that several pairs of parent/daughter ions (e.g. $142^+ \rightarrow 86^+$ and $71^+ \rightarrow 43^+$) may contribute to a single peak). Comparison of IKE spectra of isotopically labelled and unlabelled samples can help in the assignment of specific transitions for each peak. In the high voltage scanning technique that was also employed, mass losses of greater than 50% cannot be observed.

The major fragmentations observed in the CID studies are depicted in Figure 2. The stars indicate transitions that are also observed in the metastable studies (7). Redundant pathways are not shown (e.g., $142^+ \rightarrow 85^+$ is not shown since the transitions $142^+ \rightarrow 114^+$ and $114^+ \rightarrow 85^+$ do appear). Note that the CID data do not indicate any ions of m/z not seen in the EI mass spectrum; rather, they provide interconnections between these ions, specific fragmentation pathways for the production and further fragmentation of each ion.

The fragmentations normally attributed to alkanones are all observed: α -cleavage ($142^+ \rightarrow 99^+$ and $142^+ \rightarrow 71^+$), loss of CO or C_2H_4 from the α -cleavage ions ($99^+ \rightarrow 71^+$ and $71^+ \rightarrow 43^+$), McLafferty rearrangement in the long chain ($142^+ \rightarrow 86^+$), and the resultant double McLafferty rearrangement ($86^+ \rightarrow 58^+$). These transitions, also seen in the IKES study of metastables, account for the genesis of the five major fragment ions in the electron impact mass spectrum. These fragmentations also shed some light on the preferential α -cleavage of the short or long chain. At high collision gas pressures (1×10^{-4} torr Argon), the long chain is preferentially eliminated, as is the case in 70 eV EI spectra (1). At lower collision gas pressure (2×10^{-5} torr Argon), however, the short chain is preferentially lost, a feature that is also observed in 10 eV EI spectra (10) and metastable studies (2). It has been postulated (10) that further decomposition of the ion resulting from α -cleavage of the short chain is the cause of its reduced intensity in the 70 eV EI spectrum. Further fragmentations are minimized at 10 eV, and therefore the short chain α -cleavage ion remains the more intense. The CID data are in agreement with this rationalization, since multiple collisions and therefore further fragmentations are more likely at higher collision gas pressure. This rationale requires faster rates of decomposition and/or more pathways for the further decomposition of the ion which results from α -cleavage of the short chain compared to that from the long chain loss.

That reasoning can be checked by comparing the degree of fragmentation in the CID spectra of the two α -cleavage ions. The ion arising from α -cleavage of the short chain (99^+) shows 97% fragmentation (only 3% of the ion current is due to 99^+) at 1×10^{-4} torr compared to only 88% fragmentation for the ion 71^+ which arises from the α -cleavage of the long chain. This higher probability for further fragmentation of 99^+ compared to 71^+ explains why 71^+ predominates in cases where enough energy is available for further fragmentation (70eV EI or high pressure CID) and why 99^+ is larger when further fragmentation is unlikely (low energy EI or low pressure CID).

In addition to these fragmentations already observed, a number of new transitions not previously reported are observed, such as the McLafferty rearrangement in the short chain and its further fragmentation ($142^+ \rightarrow 114^+$, $114^+ \rightarrow 86^+$, $114^+ \rightarrow 70^+$, $114^+ \rightarrow 58^+$), eleven fragmentations of the methyl-loss ion (127^+) which confirm the methyl loss in the short chain, the formation and fragmentation of the hydrogen-loss ion ($142^+ \rightarrow 141^+$ and $141^+ \rightarrow 99^+$, $141^+ \rightarrow 86^+$), the loss of water from the α -cleavage ions ($99^+ \rightarrow 81^+$, $71^+ \rightarrow 53^+$, $57^+ \rightarrow 39^+$) and the fragmentation of the resultant hydrocarbon ions. Over 350 fragmentations not previously reported are shown in Figure 1. A number of these are discussed in the sections which follow, together with fragmentations which confirm or contrast with those reported by the IKES study. Discussion of the formation and fragmentation of specific ions appears in the following sections, arranged in order of decreasing m/z. All the transitions discussed can be seen in Figure 2.

Group A; 142^+ , 141^+

The CID spectrum of 142^+ is very similar in appearance to the EI spectrum of the molecule. The same fragments are observed, with the exception of the

isotopic peaks, which are eliminated by the selection of 142^+ . By controlling the collision gas pressure and ion kinetic energy, the relative intensity of the fragment peaks in the CID spectrum can be made to agree almost exactly with that in the normal EI spectrum. The $142^+ \rightarrow 141^+$ transition, not seen in the metastable study, is observed in the CID data.

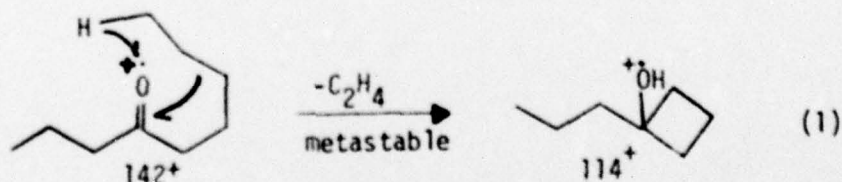
Group B; 127^+

The CID data confirm that the $142^+ \rightarrow 127^+$ transition is due to CH_3 loss from the short chain, as previously indicated by deuterium labelling in the metastable study. Major CID fragments of 127^+ are due to further loss in the short chain to produce 114^+ and 99^+ , indicating that the long chain in 127^+ is still intact. Another fragmentation is the loss of the elements of propanol to form 67^+ , C_5H_7^+ .

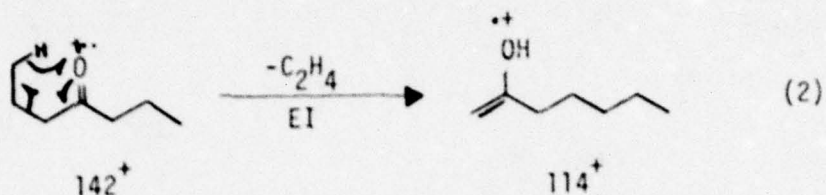
Group C; $113^+ - 115^+$

The fragmentation of 113^+ indicates that it is formed by loss of C_2H_5 , probably from the long chain of the molecular ion, since both 99^+ and 86^+ are missing. Note also the loss of $\text{C}_2\text{H}_4\text{O}$ to form C_5H_9^+ .

The authors of the metastable study assigned the weak $142^+ \rightarrow 114^+$ metastable to the fragmentation process in eqn. (1), based on deuterium labelling.

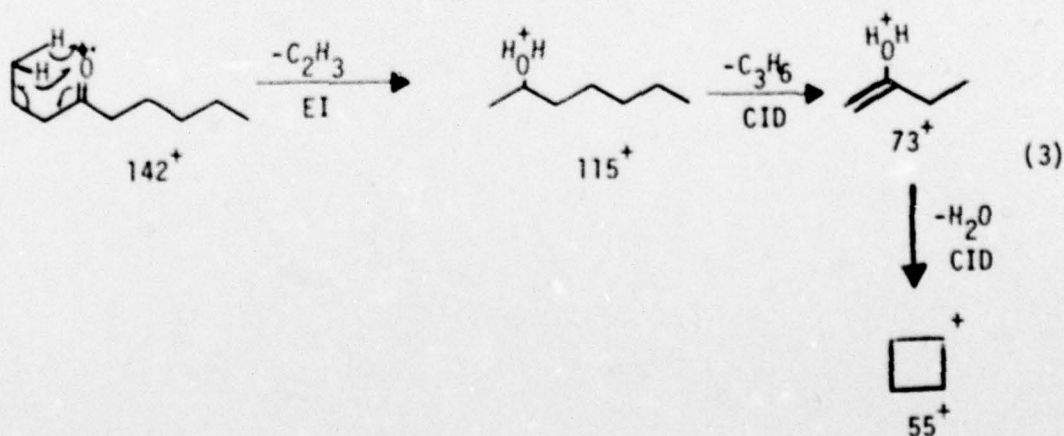


All fragmentations of the 114^+ ion, however, were attributed to the ion which arises from the McLafferty rearrangement in the short chain as shown in eqn. (2).



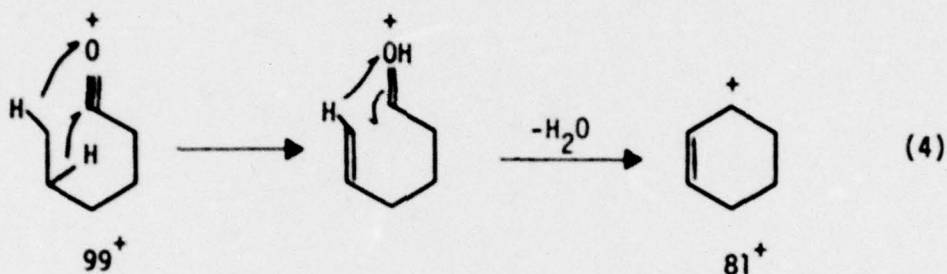
Based on the intense fragment ions of 114^+ observed at 57^+ and 58^+ in this study, the structure of the 114^+ ion produced by electron impact is that shown in eqn. (2). It is quite possible that the McLafferty rearrangement which is observed in EI also occurs by CID.

The ion at 115^+ is not an isotopic counterpart of 114^+ since its fragmentation bears little resemblance to that of 114^+ . The 55^+ fragment ion is approximately three times as intense as any other ion and could result from the following formation of 115^+ from a two-hydrogen rearrangement, loss of C_3H_6 to form 73^+ , and loss of H_2O to form 55^+ [eqn. (3)].



Group D; 98^+ - 100^+

In the study of metastable fragmentation, 99^+ was observed to be formed from 142^+ by α -cleavage of the short chain as well as from 114^+ . The CID data show formation of 99^+ from 141^+ and 127^+ as well. The fragmentation of 99^+ shows the expected losses, plus the unexpected loss of water to form 81^+ , as shown in eqn. (4).



The mechanism of H_2O loss in branched-chain ketones has been elucidated (17), but the very low intensity of the ion due to this loss in straight-chain ketones has precluded its study by deuterium labelling or from experiments involving metastables. Despite the low intensity of the water-loss ion, the CID data make it possible to observe not only the loss of water, but also the further fragmentation of the product ion (81^+). Analogous fragmentations which indicate the loss of water are seen for the other α -cleavage ion (71^+), as well as for 73^+ , 57^+ , 45^+ , 44^+ , and 31^+ .

The 98^+ ion is seen as a fragment of 142^+ in both the CID and metastable studies, with an intensity of approximately 5% of 99^+ . The CID spectrum shows a moderately intense $99^+ \rightarrow 98^+$ fragmentation, which suggests that the 98^+ may be formed by a two-step fragmentation from 142^+ through 99^+ .

Group E; 81^+ , 85^+ - 87^+

The 81^+ ion does not appear as part of any metastable transition with sufficient intensity to be observed in previous studies. In addition to its formation, as described in Group D above, its fragmentation is clearly observed. The ion series 53^+ , $41^+/39^+$, 29^+ , 14^+ from the even-electron ion suggests a 6-membered ring.

The formation of 85^+ from 142^+ and 114^+ was noted in metastable studies. We observe that it may also arise from the fragmentation of 100^+ , 99^+ and 86^+ . The 85^+ shows the ion series 57^+ , $43^+/41^+$, $29^+/27^+$, $15^+/14^+$; the absence of a 71^+ or 70^+ peak is in agreement with the cyclopentanone structure.

The ion at m/z 86^+ is formed as expected by the McLafferty rearrangement in the long chain of the molecular ion. Another route for its formation, however, is by loss of C_2H_4 from the other McLafferty rearrangement ion, 114^+ . The 87^+ ion is formed by the "McLafferty +1" rearrangement from the molecular ion. Its fragmentation is quite similar to that of 86^+ plus a hydrogen, with the exception of the very large $87^+ \rightarrow 45^+$ transition (loss of C_3H_6).

Group F; 67^+ - 73^+

The 67^+ ion has not been observed in earlier metastable studies. Its formation was discussed in Group B above. Its fragmentation pattern follows that expected for the even-electron $C_5H_7^+$ ion, and is analogous to the fragmentation of 81^+ and 53^+ . The 69^+ and 70^+ ions also show fragmentation patterns indicative of cyclic alkane ions. The CID spectrum of the even-electron 69^+ ion shows very good agreement with that of 69^+ from cyclohexane; the odd-electron 70^+ ion shows very similar fragmentation to the 70^+ ion of n-octane.

Two ions are isobaric at 71^+ , $C_5H_{11}^+$ and $C_4H_7O^+$. By careful deuterium labelling in the metastable studies, the 71^+ ion from 142^+ , 141^+ , 113^+ and 86^+ has been shown to be $C_4H_7O^+$; the 71^+ peak from 99^+ has been found to correspond to both $C_5H_{11}^+$ and $C_4H_7O^+$. In this CID study, the formation of 71^+ from all of these ions is observed, as well as the production of 71^+ from 127^+ , 115^+ , 114^+ , 98^+ and 87^+ . By consideration of other fragmentations and the neutral losses involved, it is possible to assign the $C_4H_7O^+$ structure for the 71^+ fragment of 87^+ (by $87^+ \rightarrow 86^+ + 71^+$) and 98^+ (loss of 27). For the other three parent ions (127^+ , 115^+ , 114^+) it is not possible to confirm the structure of the 71^+ fragment based on the available data. Deuterium labelling would aid in these studies.

The fragmentation spectrum of 71^+ from the EI spectrum of nonan-4-one shows 43^+ as the most intense fragment, with other fragments at 27^+ , 29^+ , 31^+ (with intensities 0.40, 0.25 and 0.015 respectively, relative to 43^+), 15^+ , 39^+ , 41^+ , 53^+ , and 55^+ . For comparison, the CID spectra of $C_4H_7O^+$ from 2-pentanone and $C_5H_{11}^+$ from n-octane were measured under similar experimental conditions. The $C_4H_7O^+$ ion shows the most intense fragment at 43^+ , with other fragments at 27^+ , 29^+ , 31^+ (intensities 0.40, 0.08, and 0.075 relative to 43^+), 15^+ , 39^+ , 41^+ , 45^+ and 53^+ . The $C_5H_{11}^+$ ion produces a CID spectrum with 43^+ also the most intense fragment, and additional fragments at 27^+ and 29^+ (intensities 0.05 and 0.36 relative to 43^+), 15^+ , 39^+ , 41^+ , 55^+ , and 56^+ . The 71^+ ion from nonan-4-one shows fragments corresponding to both the possible ions, and is therefore undoubtedly composed of both $C_4H_7O^+$ and $C_5H_{11}^+$. Based on the relative intensities of the 27^+ and 29^+ peaks, the contributions to the 71^+ ion signal are estimated to be 30% $C_5H_{11}^+$ and 70% $C_4H_7O^+$.

The 72^+ ion yields the fragmentations expected for the addition of H^+ to 71^+ . The major pathways for formation of 72^+ are " γ -cleavage + 1" from 114^+ and 87^+ , and McLafferty rearrangement from 100^+ . The formation of 73^+ from 115^+ and its fragmentation by loss of H_2O to form 55^+ was discussed in Group C. Other major fragmentation pathways for 73^+ are loss of C_2H_4 and C_2H_6 to form 45^+ and 43^+ respectively.

Group G; 50^+ - 60^+

The ions at 50^+ , 51^+ , 52^+ , 53^+ , and 54^+ all show fragmentation spectra that are quite similar to those for the same m/z ions from hydrocarbons such as cyclohexane and n-octane. The 55^+ ion, however, shows a peak in the CID spectrum at 27^+ that is 1/3 greater in relative intensity than the 27^+ ion seen from 55^+ ($C_4H_7^+$) in reference alkane CID spectra. This may indicate that a small portion of the 55^+ peak is due to the $C_3H_3O^+$ ion. Although the CID spectrum of $C_3H_3O^+$ has not been measured for reference, the major fragmentation would likely be $55^+ \rightarrow 27^+$, with loss of CO. In the EI mass spectrum of cyclopentanone, the $C_3H_3O^+$ ion comprises 94% of the 55^+ base peak, and its formation has been carefully studied (11). It is improbable or impossible that 55^+ formed from 142^+ , 115^+ , 113^+ , 86^+ , 73^+ , 72^+ , 71^+ , ($C_5H_{11}^+$), 70^+ or 69^+ would be $C_3H_3O^+$, but it is possible that fragmentation of 127^+ , 99^+ , 98^+ , and 71^+ ($C_4H_7O^+$) could produce $C_3H_3O^+$ as well as $C_4H_7^+$.

The peak at m/z 56^+ can also correspond to two different ions, $C_4H_8^+$ and $C_3H_4O^+$. The fragmentation matches that of $C_4H_8^+$ with the exception of the 28^+ ion which is more intense than in the reference spectrum. The extra intensity at 28^+ is undoubtedly due to the $C_2H_4^+$ fragment of $C_3H_4O^+$. Both $C_4H_9^+$ and $C_3H_5O^+$ are possible structures for

the 57^+ ion. Only the 57^+ fragment from 85^+ has been assigned (as $C_3H_5O^+$) based on metastable results. The CID data show that the 86^+ ion also fragments to form $C_3H_5O^+$, but it is impossible to positively assign without further study either the $C_4H_9^+$ or $C_3H_3O^+$ structure to the other 11 fragmentations observed that lead to 57^+ . The CID spectrum of 57^+ from nonan-4-one shows a peak at 31^+ that is not observed in the otherwise similar spectrum of $C_4H_9^+$ from n-octane. The 31^+ ion probably corresponds to the loss of C_2H_2 from $C_3H_5O^+$.

The CID spectrum of the 58^+ ion shows two major fragments, 43^+ and 15^+ . The interpretation of the CID spectrum indicates the acetone ion $(CH_3)_2CO^+$; comparison with reference spectra shows it to be identical with those for $(CH_3)_2CO^+$ from acetone and 2-pentanone.

Group H; 38^+ - 45^+

The ions at 38^+ , 39^+ , 40^+ , and 41^+ all show very good agreement with alkane reference CID spectra. The ions at 42^+ , 43^+ , and 44^+ , however, are mixtures of alkane and ketone ions. The 42^+ ion shows an additional intense fragment at 14^+ undoubtedly due to the formation of CH_2^+ from CH_2CO^+ .

The reference CID spectra of the two possible 43^+ ions, CH_3CO^+ and $C_3H_7^+$, include all the same ions; the major difference is the ratio of the intensities of the 27^+ and 15^+ peaks: approximately 5:1 for $C_3H_7^+$, and 1:20 for CH_3CO^+ . The 43^+ peak from nonan-4-one shows fragments at 27^+ and 15^+ in the ratio 1:4. Based on these data, the 43^+ peak corresponds to 75% CH_3CO^+ , the remainder being $C_3H_7^+$. The 43^+ peak is quite common in the CID spectra; all but 3 ions above m/z 57^+ show a 43^+ peak.

The CID spectrum of 44^+ shows the fragmentations that would be expected for CH_3CO^+ with one C^{13} or an extra H. The 45^+ ion includes H_3O^+ (loss of acetylene) as one of the most intense fragment ions in its CID spectrum.

Group 1; 26⁺-31⁺

The ions at 26⁺, 27⁺, 28⁺, 29⁺ and 30⁺ all give CID spectra which agree well with the reference CID spectra for hydrocarbon ions. The 31⁺ ion, however, must contain O, and indeed fragment ions are observed at 18⁺ and (31-18)⁺.

CONCLUSIONS

The application of the triple quadrupole system to the collision-induced dissociation of the ions of nonan-4-one has identified over 400 fragmentation paths. This enormous increase in the amount of information available for the structure elucidation of the compound compared to that obtained by earlier IKES metastable studies is a result of several features of the triple quadrupole system: 1) The use of CID increases the number of fragmentations that occur, and their intensity. 2) The high sensitivity of the system makes it possible to study transitions of very low intensity. 3) The use of two stages of direct mass analysis eliminates any ambiguity in the identification of parent and daughter ion m/z . 4) There is no restriction on the neutral loss. 5) Unit mass resolution is achieved and is unaffected by the kinetic energy loss upon fragmentation.

Interpretation of the CID spectra has made it possible to assign specific structures to a number of the fragment ions of nonan-4-one. Confirmation of these structures can be achieved by comparison of the spectra with reference CID spectra of ions of known structure. In the case of fragment peaks which correspond to two isobaric ions, it is possible to estimate the contribution of each ion by comparison with the reference spectra, without resorting to the high resolution necessary to separate the isobaric ions. The ability

to measure the probability of further fragmentation for the fragment ions which arise from α -cleavage has made it possible to explain the apparent preference for α -cleavage in the long chain in 70eV EI spectra and for α -cleavage in the short chain at 10eV.

A potentially powerful system for structure elucidation of organic compounds should be realized by the combination of complete CID fragmentation data with computer programs which use heuristic or pattern recognition techniques for structure identification. The completeness of the CID fragmentation data and their ability to show relationships among the ions in the mass spectrum should make computer interpretation extremely powerful.

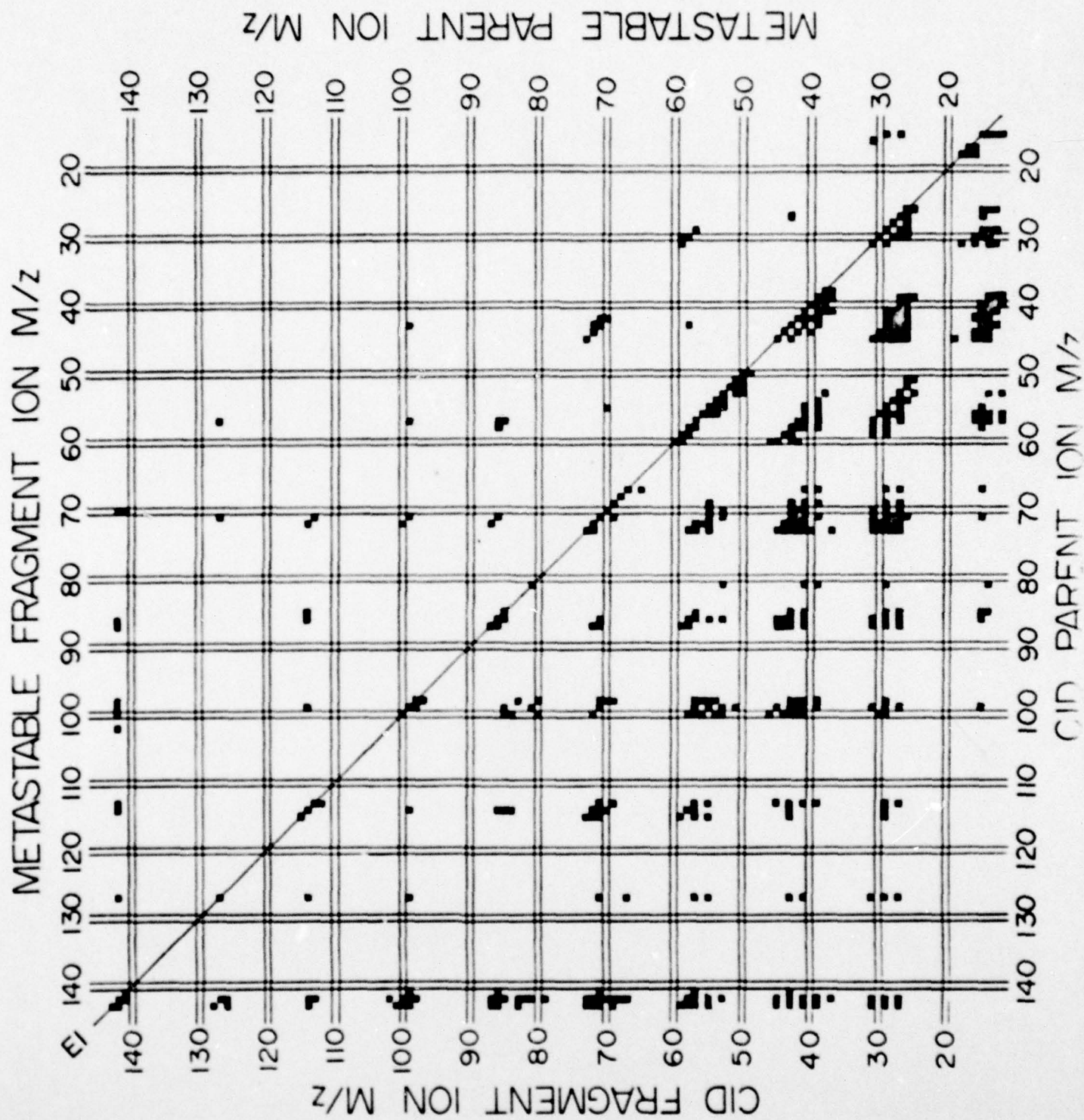
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FIGURE CAPTIONS

Figure 1. Collision-induced fragmentations of nonan-4-one from this study (below the diagonal), metastable fragmentations from previous IKES study (7) (above the diagonal), and EI mass spectrum (along the diagonal).

Figure 2. Major fragmentations of nonan-4-one observed in both this CID study. Starred transitions have also been observed in previous metastable studies (7).



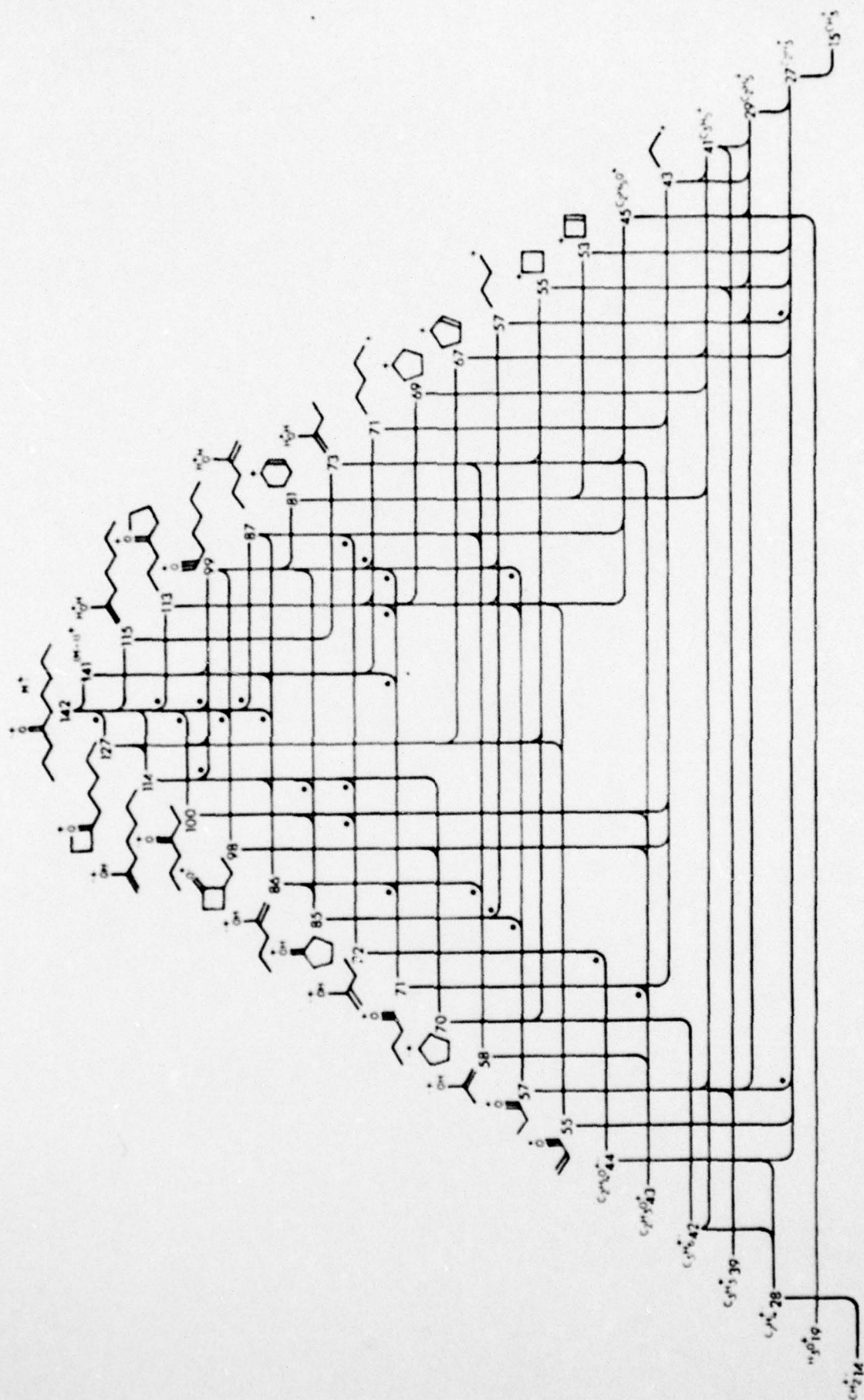


FIG. 2 - Yost, Enke

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