56.30; H, 5.25; N, 11.66.

Comparative TLC Analyses of Aryl-Substituted Vincadifformines. TLC analyses on Merck 60 F254 silica, developing with 2.5% methanol in dichloromethane and visualizing with ceric sulfate in phosphoric acid, gave the following results: vincadifformine (**1a**), R_f 0.37, staining blue fading to smoky gray then yellow; 15-chlorovincadifformine (**1b**), R_f 0.55, staining light pale blue and fading rapidly to yellow; 15-bromovincadifformine (**1c**), R_f 0.54, staining smoky blue and fading rapidly to a smoky purple and eventually to brown; 15-methoxyvincadifformine (**1d**), R_f 0.28, staining was dependent upon concentration (A heavy spot would show a flash of blue before changing over the course of ~10 min from green through yellow and brown to light reddish purple. A lighter spot showed no flash of blue, becoming green immediately and then proceeding through the above changes.); 16-methoxyvincadifformine (**1e**), R_f 0.31, staining blue, and in the case of a heavy spot a yellow center was present. (The spot faded to smoky blue, to olive green and eventually to yellow.)

5-Chloro-2-ethylpentanal (15). A solution of lithium diisopropylamide (65 mmol) was prepared by addition of 28.8 mL of 2.3 N *n*-butyllithium to 9.9 mL of diisopropylamine stirred in 60 mL of dry tetrahydrofuran and cooled to −78 °C. A solution of 10.0 g (65 mmol) of *N*-butylidenecyclohexylamine in 10 mL of tetrahydrofuran was then added dropwise, followed after 15 min by 11.3 g (71 mmol) of 1-bromo-3-chloropropane, which was added over 5 min. The solution was allowed to warm to 20 °C over 4 h, stirred at 20 °C for 2 h, and then poured into 100 mL of 3% HCl and stirred for 12 h. The organic material was extracted with ether and the extracts were washed with 3% HCl and brine. After drying ($MgSO_4$), the extracts were concentrated under vacuum and residual product was distilled to give 5.2 g (54% yield) of the chloro aldehyde **15**: bp 55 °C (0.3 mm); IR (neat) ν_{max} 2700, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (t, 3 H), 1.4–2.0 (m, 6 H), 2.2 (m, 1 H), 3.6 (t, 2 H), 9.8 (d, 1 H). A 2,4-dinitrophenylhydrazone derivative had mp 110–111 °C. Anal. Calcd for $C_{13}H_{17}N_4O_4Cl$: C, 47.49; H, 5.21; N, 17.04. Found: C, 47.63; H, 5.50; N, 16.76.

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Registry No.—(±)-**1a,** 18374-17-9; (±)-**1b,** 69069-54-1; (±)-**1c,** 69069-55-2; (±)-**1c** picrate, 69069-56-3; (±)-**1d,** 69069-57-4; (±)-**1d** picrate, 69089-21-0; **1e,** 25858-80-4; (±)-**1e,** 69126-63-2; (±)-**1e** picrate, 69126-64-3; **6b,** 69069-58-5; **6c,** 69069-59-6; **6d,** 69069-60-9; **6e,** 69069-61-0; **6f,** 69069-62-1; **7b,** 69069-63-2; **7b** hydrochloride, 69069-78-9; **9,** 3612-20-2; **10a,** 6208-43-1; **10b,** 19685-91-7; **10c,** 69069-64-3; **10d,** 69069-65-4; **10e,** 69069-66-5; **11a,** 69069-67-6; **11e,** 25858-80-4; **12,** 51048-46-5; **13b,** 69069-68-7; **13c,** 69069-70-1; **14a,** 69069-71-2; **14b,** 69069-72-3; **14c,** 69069-73-4; **14d,** 69069-74-5; **14e,** 69069-75-6; **15,** 62498-23-1; **15** 2,4-dinitrophenylhydrazone, 69069-76-7; *N*-benzyl-4-piperidone phenylhydrazone, 69069-77-8; thallium dimethyl malonate, 69120-36-1; *m*-methoxyphenylhydrazine hydrochloride, 39232-91-2; *p*-methoxyphenylhydrazine hydrochloride, 19501-58-7; 4-chlorophenylhydrazine, 1073-69-4; 4-bromophenylhydrazine hydrochloride, 622-88-8; 16-methoxytabersonine hydrochloride, 11021-77-5; *N*-butylidenecyclohexylamine, 1197-52-0; 1-bromo-3-chloropropane, 109-70-6.

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Mass Spectrometric Location of Triple Bonds in Fatty Acids and Fragmentation Mechanisms of *N*-Acylpyrrolidines[1]

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Mass spectra of the pyrrolidide derivatives of isomeric octadecynoic acids are characterized by simple fragmentation patterns. Examination of the spectra indicates that if the triple bond in acetylenic fatty acids occurs between Δ5 and ω2, the unsaturation may be located by observing the most intense peak in each 14-amu cluster of fragments. *An interval of 10 amu (rather than the usual 14) between fragments corresponding to C_{n-2} and C_{n-1} of the acyl moiety indicates a triple bond at C_n. Confirmation of triple bond location is provided by intense peaks at C_{n-2} and C_{n+2}.* The rule has been found valid for all isomers within this series including Δ15, which produces a spectrum similar to but distinguishable from Δ17. Derivatization is accomplished by heating the fatty acyl moiety (methyl ester, triglyceride, phospholipid, etc.) with pyrrolidine. Because derivatization is performed on the carboxyl group, quantitation is assured regardless of the number and type of substituent groups present in the molecule. Electron impact of *N*-acylpyrrolidines produces fragments which arise from both amide-directed fragmentation (ADF) and substituent-directed fragmentation (SDF). ADF predominates in the acetylenic isomers which conform to the general rule for location of triple bonds. Simple spectra are obtained in which the position of the substituent group may be deduced directly without necessitating a library search.

Mass spectrometry (MS), although an extremely powerful aid in determination of structure, has been, until recently, unable to clearly distinguish isomeric unsaturated fatty acids. For example, the mass spectrum of methyl 9,12-octadecadienoate (linoleate) is quite similar to that of the isomeric methyl 9-octadecynoate (sterolate).[2a] The reason for this is twofold: (a) most of the carbon–carbon bonds in the molecules are equivalent in energy, thus yielding many ions of similar

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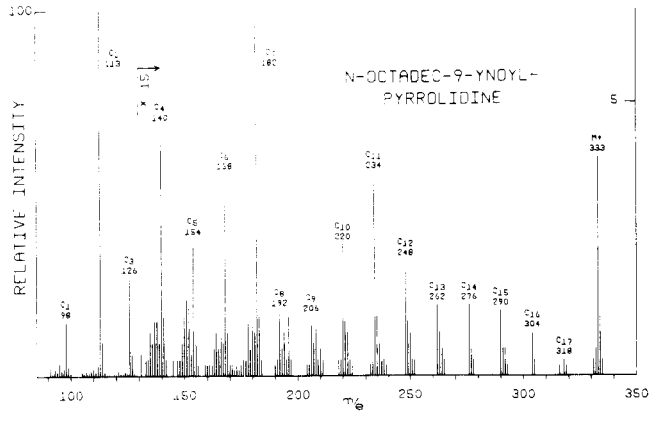


Figure 1. Mass spectrum of *N*-octadec-9-ynoylpyrrolidine (1).

stability, and (b) under electron impact, ions containing the carboxyl, acylium, or hydrocarbon moieties are all produced in significant amounts yielding a complicated spectrum.

Two distinct strategies are used to overcome these problems and both are concerned with the chemical alteration of the molecule prior to MS analysis. The most common approach is derivatization at the substituent group in order to facilitate cleavage of the molecule in its vicinity. This approach has been used to locate double bonds via MS of the *O*-isopropylidine derivative after OsO_4 treatment of monoenoic fatty acids,[3] methoxy derivatives,[4] trimethylsilyloxy derivatives,[5] oxymercuration products,[6] and other derivatives.[2] Derivatization of substituent groups has also been employed in the MS location of triple bonds using positional ethylene ketals[7] and more recently by oxymercuration followed by reduction and silylation.[8] Using these methods, stabilized fragmentation products are produced by the mass spectrometer which may be an aid in the identification of the unknown substance by a library search. Because most of these methods require two or more chemical reactions, the yield of derivatized material is rarely, if ever, quantitative. Although this approach produces several diagnostic fragments for monosubstituted fatty acids (normally four intense ions for a triple bond), di-, tri- and polysubstituted acids produce increasingly complex spectra, and the method requires additional chemical manipulation of the sample prior to analysis.[9] Moreover, the derivatization is normally specific for a single type of substituent group, and structural analysis must be normally performed on isolated (pure) samples.

A universal fatty acid derivative for mass spectrometry, analogous to the nearly universal methyl ester derivative for GLC, would be highly desirable. At the outset, the methyl ester of a fatty acid was widely used for MS analysis owing to its volatility, GLC applicability, and simplicity of preparation, and there are several papers reporting attempts to correlate mass spectra of acetylenic esters with structure.[10] The second approach toward simplification of mass spectra exploits their common feature, the carboxyl group. A variety of carboxyl derivatizations have been reported,[11] and of them, the amide derivative has been judged to possess the greatest potential for mass spectrometry.[12-15] The tertiary amides, in particular, produce mass spectra in which competing fragmentations are minimized due to the charge stabilizing effect of the alkyl substituents on the nitrogen. Encouraged by reports on the use of piperidides[16] and pyrrolidides[17] for MS, Andersson et al.[18] compared a number of amides of oleic acid and concluded that the pyrrolidide was the amide of choice for MS location of double bonds. This amide could be prepared in nearly quantitative (95–99%) yield, was of sufficient mass so that diagnostically useful fragments were located away from low mass secondary fragmentation products, and, although

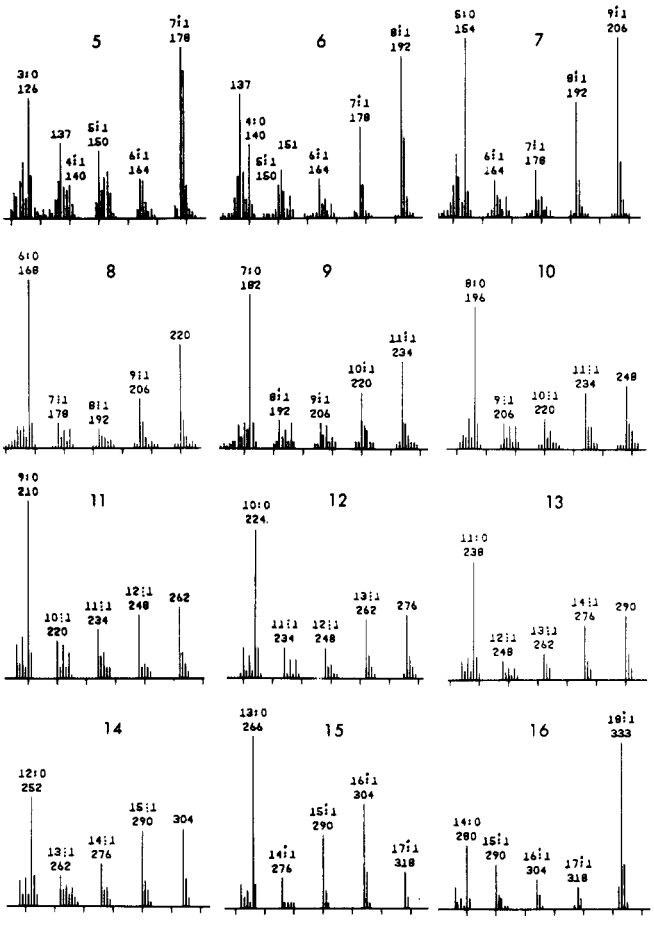


Figure 2. Diagnostic regions in the mass spectra of 5–16 octadecynoylpyrrolidines.

somewhat more polar than the corresponding methyl ester, was sufficiently volatile for GLC analysis.[18-21] Double bonds in monoenoic[22] and polyenoic[23] long chain fatty acids could be located via MS of their pyrrolidide derivatives by direct inspection of the spectra. Methyl branching[24] and deuterium atoms[25] could also be pinpointed by this method. Preliminary studies[11,26] indicate that the method may be applicable to the location of cyclopropane substitution in fatty acids. We now wish to report the MS analysis of a series of isomeric octadecynoic acids which extends the applicability of the pyrrolidide method to the location of yet another substituent group, and present evidence for a proposed mechanism of fragmentation.

Experimental Section

The octadecynoic acids used in the study were prepared by modifications[27] of published procedures.[28] Methyl octadecynoates were quantitatively converted to their pyrrolidide derivatives, as judged by TLC, by heating 1–10 mg of ester with 0.5–1.0 mL of pyrrolidine and 50–100 μL of glacial acetic acid as previously described.[22]

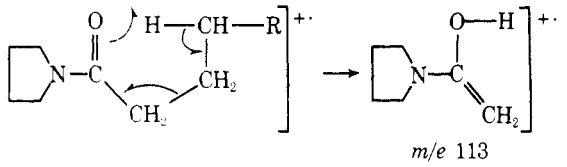
The mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6D single-focusing instrument operating at an ionization potential of 70 eV using an all-glass inlet system at 190 °C and source temperature of 230 °C.

Results and Discussion

The mass spectra of *N*-acylpyrrolidines are characterized by relatively intense fragments containing the polar end of the molecule.[14,15,18-26] The base peak in the spectrum of *N*-octadec-9-ynoylpyrrolidine (1) is *m/e* 113, produced by McLafferty rearrangement[14] (Figure 1). If one considers only the most intense peak in each successive 14-amu cluster, an interval of 14 amu occurs between these peaks in the diag-

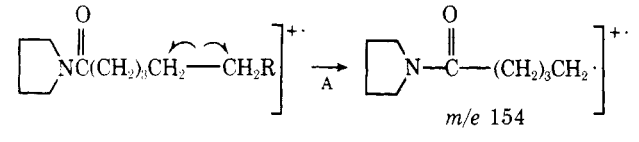
nostic region from *m/e* 126 to *m/e* 318, except for *m/e* 182 and *m/e* 192, fragments which include carbons 7 and 8 of the fatty acyl moiety, respectively. Examination of Figure 2 indicates that this behavior consistently occurs in octadecynoylpyrrolidines which possess the triple bond between Δ5 and Δ16. From these spectra, the following rule is proposed: *If a triple bond occurs at C_n, the mass spectrum will contain an interval of 10 amu between C_{n-2} and C_{n-1}* (rather than the usual 14 amu). This rule has been tested on a continuous series of C_{18} isomers and has been found valid from the Δ5–Δ16. As one observes from Figures 2 and 6, *N*-octadec-17-ynoylpyrrolidine (2) and the Δ15 isomer produce mass spectra containing the same diagnostic ions (most intense peak in each 14-amu cluster) in the region *m/e* 266–233. However, the Δ15 and Δ17 isomers are distinguishable (see Discussion). The mass spectrum of *N*-octadec-4-ynoylpyrrolidine (3) contains unique fragments which may be used to characterize this isomer.

Fragmentation Mechanism of Acylpyrrolidines. Before examining the spectra of octadecynoylpyrrolidines, some discussion concerning the modes of fragmentation characteristic for acylpyrrolidines is appropriate. Fragmentation of these compounds gives a base peak in the spectrum of *N*-octadecanoylpyrrolidine (4), *m/e* 113, by the McLafferty re-

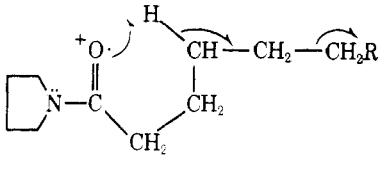


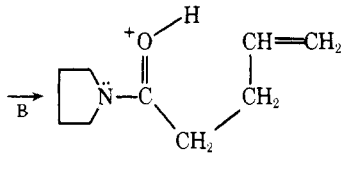
m/e 113

arrangement (Figure 3). The other mode of fragmentation produces a series of even-massed fragments beginning at *m/e* 126 incrementing by 14 amu and ending with one carbon less than the molecular ion. These fragments may arise from either homolytic cleavage of carbon–carbon bonds (A) or by hydro-



m/e 154





m/e 154

gen abstraction with cleavage (B).[29] This latter process, an amide-directed fragmentation (ADF), may well be the most favorable reaction pathway because when a heteroatom is present, electron impact yields more stable products by the formation of a new bond to the heteroatom,[30] and because an ion possessing a double bond is of lower energy than a diradical ion.

The concept of fragmentation directed by the amide is supported by the observation that tertiary amides produce spectra in which most of the significant ions contain the polar end of the molecule, and this phenomenon is much less pronounced in the mass spectra of secondary and primary amides.[12-14,18] The ease of formation of these amide-containing fragments may parallel the order of positive charge delocalization by resonance effects in which tertiary > secondary >

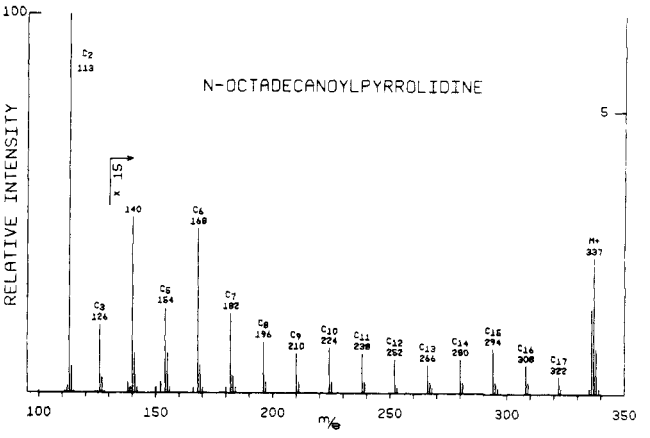


Figure 3. Mass spectrum of *N*-octadecanoylpyrrolidine (4).

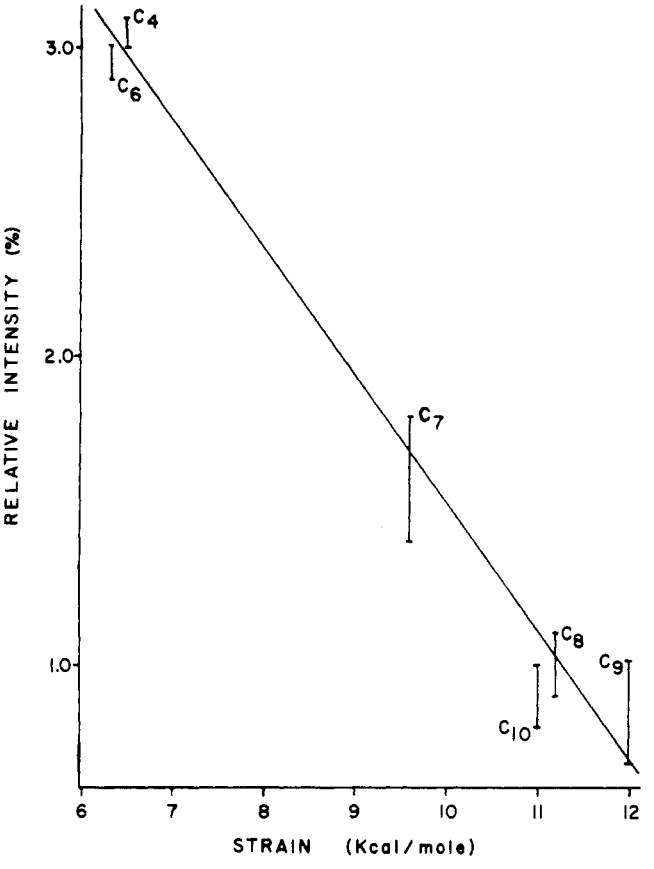


Figure 4. Relationship between the ring strain of fragmentation transition states and the relative intensities of the fragments produced in the mass spectra of *N*-octadecanoylpyrrolidine (4), e.g., C_6 is produced by a seven-membered ring transition state, C_7 from an α-membered ring, etc. The lengths of the lines represent the normal variation in ion intensities.

primary or the driving force in these reactions may be the result of the electronic participation of the nitrogen *during* the hydrogen abstraction (ADF).

The argument for ADF is strengthened by the observation that all amide-containing fragments produced by electron impact of *N*-acylpyrrolidines are derived directly from the molecular ion.[22] In addition, a proportionality exists between the approximate strain value associated with the cyclic transition state necessary to produce a C_n amide-containing fragment and the relative intensity of that fragment in the mass spectrum of 4. Approximate strain values of cyclic transition states were calculated from heats of combustion of cycloparaffins having different ring sizes.[31] The intensities

of the fragments in the spectrum of 4, corresponding to their different ring sizes, decrease linearly when plotted against the calculated strain values (Figure 4). Although the strain value of a six-membered ring is zero, the intensity of the C_5 fragment (*m/e* 154) produced from a six-membered ring transition state is lower than one would predict, because the competitive fragmentation via the McLafferty rearrangement is more favorable. Thus, for fragmentations derived from the postulated macrocyclic transition states producing amide fragments containing 4–10 carbon atoms, the ADF mechanism is substantiated.

The ultimate confirmation of a mass spectral fragmentation mechanism is often provided by selective deuteration of the substrate so that the proposed fragmentation mechanism gives rise to ions whose masses are altered. This method cannot be used to differentiate the two mechanisms in this study, because both homolytic cleavage and ADF would be expected to yield fragments having the same mass. However, the introduction of a deuterium atom causes a reinforcement of the carbon–carbon bonds in its vicinity, due to the isotope effect.[32] One can predict that a fragment produced by the cleavage of a C–D bond and a C–C(D) bond will have a lower relative intensity than the analogous fragment produced from a nonlabeled substrate. A comparison of the mass spectrum of 4 with that obtained from the labeled substrates[25] may thus elucidate the mechanistic problem.

A qualitative estimation of this effect is given by the ratio of the relative intensity of a fragment to the relative intensity of the analogous fragment from a deuterated fatty acyl pyrrolidine. If there is no difference in the ease of production of the fragments, this ratio should be unity. As is seen in Figure 5, an increase in the value of this ratio is observed when the fragments are formed by cleavage close to the deuterium substituent (secondary isotope effect). If these fragments are produced primarily by a mechanism of homolytic C–C bond cleavage, the curve should have a maximum at the fragment corresponding to C_9 in the acyl moiety of *N*-octadecanoylpyrrolidine-*9,10-d*$_2$ (**5**), because both substituted carbons bear a deuterium atom and hence the bond between them (c) has the greatest reinforcement relative to the nondeuterated compound. Figure 5 indicates that a maximum value is found at C_{10}, instead, with C_9 and C_{11} approximately equal in magnitude. This observation may be explained by the ADF mechanism which predicts the concerted cleavage of a C–H and a C–C bond to produce the observed amide fragment. In Figure 5, the production of the C_7 fragment involves the abstraction of the C_6 hydrogen (by the amide oxygen) and cleavage of bond a. No bond to deuterium is broken and no carbon bearing a deuterium atom has been involved and, therefore, the ratio of the relative intensity of the nondeuterated fragment to the relative intensity of the analogous fragment from the deuterated substrate (H/D) is unity. Even though no C–D cleavage is necessary for the production of the C_8 fragment, bond b (a CH–CD bond) must be broken, and H/D = 1.31. Generation of the C_9 fragment is accomplished by the rupture of the CD–CD bond c and the H/D ratio is high. However, the largest value of H/D is found for production of the C_{10} fragment, because this process requires the breaking of a C–D bond at C_9. If the C–D bond were not involved, one would predict that H/D for C_8 and C_{10} would have the same value, because the bonds b and d (both CH–CD bonds) would be approximately equal in energy and cleave with equal facility. The H/D value for C_{11} formation is less than that of C_{10}. The latter requires both C–D and CH–CD (bond d) cleavage, whereas C_{11} formation requires C–D cleavage (at C_{10}) and breaking of the nondeuterated C–C bond e. It appears that reinforcement of C–H bond energies from secondary isotope effects is felt at carbons 11–13, for H/D values for the production of C_{12}–C_{14} fragments are greater than unity.

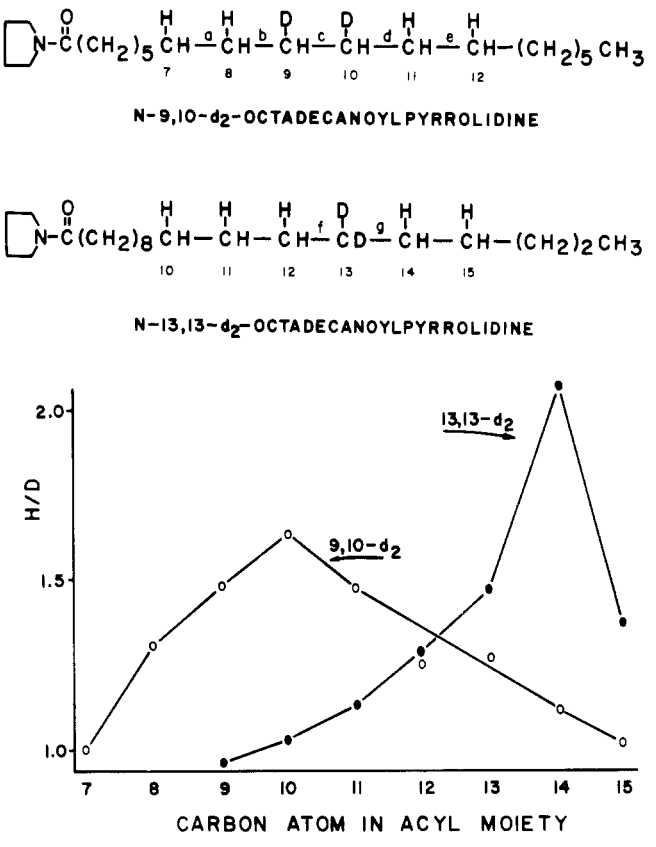
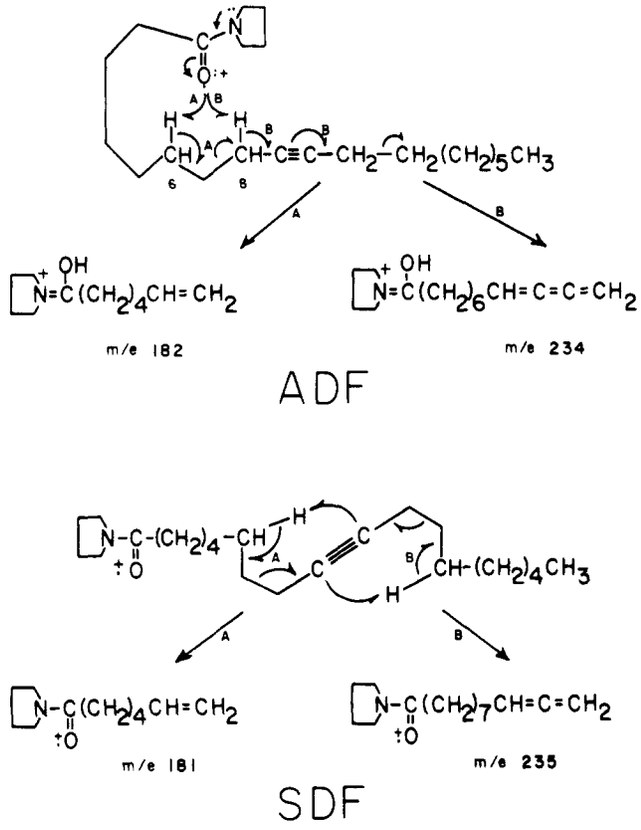


Figure 5. The structures of the deuterated *N*-octadecanoylpyrrolidines 5 and 6 and the effect of deuterium substitution on the relative intensities of fragments in the mass spectrum of *N*-octadecanoylpyrrolidine 4 as compared with those in the spectra of 5 and 6.

One must bear in mind, however, that fragmentation of **5** is not the ideal example for the substantiation of the ADF mechanism, because the amide linkage has a choice of abstracting either the H or D atom to induce fragmentation, and almost certainly more C–H bonds than C–D bonds are cleaved. A more definitive example is provided by comparison of the nondeuterated material with *N*-octadecanoylpyrrolidine-*13,13-d*$_2$ (**6**), in which *both* hydrogen atoms on carbon 13 have been replaced by deuterium. In this case, if ADF is operating, the amide linkage has no choice in abstraction–it must abstract a deuterium atom to produce the C_{14} fragment. Even though this substrate is only 60% deuterium content,[25] as compared with 85% deuterium for **5**, the effect is even more pronounced. Conversely, homolytic C–C cleavage would be expected to yield H/D values for the production of C_{12} and C_{13} fragments which should be equal and maximum for this compound, because in each case (f or g) cleavage of a C–C bond involves a bond to a carbon bearing two deuterium atoms. Homolytic cleavage is not substantiated by Figure 5.

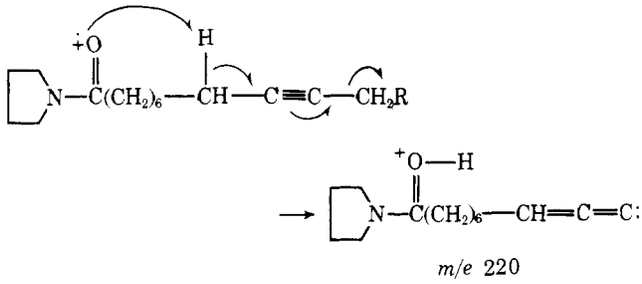
ADF predicts that the C_{14} fragment should display the highest H/D values, because its generation is totally dependent upon abstraction of a deuterium atom. In addition, the H/D for this fragment is nearly twice that of the maximum in **5**, most likely because both isotopic atoms are located on the same carbon. The effect of deuterium substitution is felt strongly at the carbons α to the deuterium atoms (C_{12} and C_{14}). Abstraction of hydrogens at these positions produces the C_{13} and C_{15} fragments with nearly equal H/D values. The slightly higher H/D value for the C_{13} fragment may be attributed to the breaking of a CD_2–CH_2 bond (g) in this case, but clearly the most significant influence in the fragmentation of fatty acyl pyrrolidines is due to C–H (C–D) cleavage induced by ADF[33] and not by homolytic cleavage of C–C bonds.

Scheme I

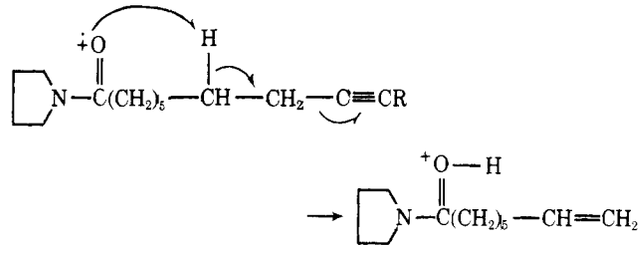


Octadecynoylpyrrolidines. The mass spectra of substituted fatty acyl pyrrolidines are characterized by fragments which are produced by substituent-directed fragmentation (SDF) and by ADF. When relatively "inert" substituents, such as methyl groups, deuterium atoms, or double bonds, are present, the principal peaks in the mass spectrum are derived almost entirely from ADF. If more polar substituents are present, such as hydroxy, keto, and epoxy groups, SDF may be the dominating influence in the diagnostic region of the mass spectrum.[35] Within the limits of the rule proposed in this study for the location of triple bonds, ADF is the more significant mechanism. As the acetylenic unsaturation approaches the carboxyl group, SDF becomes more evident, odd-mass ions are produced, and the general rule breaks down somewhat.

Scheme I illustrates the two competitive processes which may produce the large C_7 and C_{11} fragments in the mass spectrum of **1**. The large, even-mass peaks, *m/e* 182 and *m/e* 234, are only possible with the ADF mechanism; SDF derived peaks (*m/e* 181 and *m/e* 235) are of minor importance in the spectrum (see Figure 1). Because fragments corresponding to $n - 2$ and $n + 2$ carbons of the acyl moiety (where n = the Δ carbon) are easily produced, an additional diagnostic aid is realized: *a triple bond at C_n normally produces intense peaks at fragments C_{n-2} and C_{n+2}.* The fragment containing ten carbons of the acyl moiety, *m/e* 220, may arise by abstraction of the hydrogen atom at C-8 by ADF with expulsion of the hydrocarbon chain. However, the anticipated instability of this fragment does not agree with its relatively large abundance. Also, vinylic cleavage on the carboxyl side of the triple bond should also proceed by ADF with facility, because this type of fragmentation has recently been shown[36] to be a possible pathway of ion decomposition. However, it is *m/e* 192,



m/e 220



m/e 196

not *m/e* 196, which is the most intense peak in this cluster of fragments.

The C_{10} fragment, *m/e* 220, is of moderate intensity, the C_8 and C_9 clusters of fragments are low, and the masses of the most prominent peaks in these clusters indicate diunsaturation. These data would tend to indicate that migration of the triple bond had occurred prior to fragmentation. Migration of double bonds has been proposed[22,23] as the origin of analogous fragments in the mass spectra of mono-, di-, and polyunsaturated acylpyrrolidines. Although migration of triple bonds has been indicated[37] during electron impact of acetylenic hydrocarbons prior to fragmentation, this process is thought to be essentially complete upon formation of the intermediate allene.[36] Thus, even though further migration of the allene is presumably of minor importance in the spectra of hydrocarbons, this process seems to be more evident in the spectra of acetylenic acylpyrrolidines, due to their more complete fragmentation.

As the site of acetylenic unsaturation is located closer to the carboxyl end of the molecule, the spectrum becomes more complex, particulary in the C_4–C_7 region of the spectrum, due to increased competition from SDF and also to the nonregularity in the intensity of fragments produced by ADF in this region. For example, the $\Delta 7$ triple bond in *N*-octadec-7-ynoylpyrrolidine (**7**) is easily located by the general rule. An interval of 10 amu is observed between the most intense fragment at C_5 (*m/e* 154) and C_6 (*m/e* 164), locating the triple bond at C_7. In addition, the intense peaks at *m/e* 154 and *m/e* 206, corresponding to C_5 ($n - 2$) and C_9 ($n + 2$) of the acyl moiety, serve as confirmation of the $\Delta 7$ unsaturation. However, one anomalous peak is encountered in the spectrum. The most intense peak in the C_4 cluster is at *m/e* 137 (not at *m/e* 140, which is expected). This fragment is analogous to the *m/e* 139 fragment in $\Delta 3$- and $\Delta 4$-octadecenoylpyrrolidines[22] which is characteristic for these isomers. This *m/e* 139 fragment is thought to arise from SDF induced by the double bond in the case of the $\Delta 3$ isomer, and an isomerized ($\Delta 4 \rightarrow \Delta 3$) double bond in the case of the $\Delta 4$ isomer. The present study suggests that under electron impact, more extensive migration occurs for triple bonds than for double bonds under similar conditions. The diagnostic rule for double bond location involves carbons n and $n - 1$ and for triple bonds carbons $n - 1$ and $n - 2$.

Competition from SDF causes an even greater increase in the intensity of *m/e* 137 in the spectrum of *N*-octadec-6-ynoylpyrrolidine (**8**), as well as its homologue at *m/e* 151. Under these conditions, since these odd-mass peaks are not members of the ADF series of peaks, they may be ignored. The general rule then becomes valid for the $\Delta 6$ and $\Delta 5$ isomers.

The mass spectrum of **3** is not interpretable by the general rule under any circumstances because the C_{n-2} ion is the

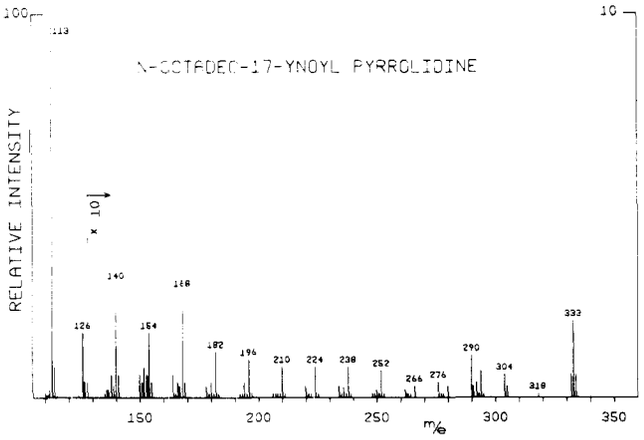
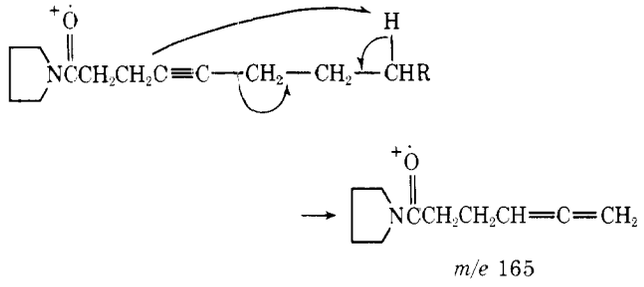


Figure 6. Mass spectrum of *N*-octadec-17-ynoylpyrrolidine (**2**).

McLafferty rearrangement ion. In addition, the proximity of the carboxyl group is such that the normal isomerization and fragmentation patterns are not seen. Instead, SDF produces an intense ion at *m/e* 165 (rather than the ADF-produced *m/e* 164). The SDF-derived hydrocarbon fragment, *m/e* 220, is also large for this isomer. Thus, at triple bond positions less than Δ5, SDF is more influential and the general rule cannot be used. For **3** the position of the triple bond may be deduced by the confirmatory rule. The intense peaks at C_2 and C_6 (*m/e* 113 and *m/e* 165) locate the triple bond at C_4.



m/e 165

The general rule, applied to **2**, indicates Δ15 unsaturation, because an interval of 10 amu is observed between *m/e* 266 (C_{13}) and *m/e* 276 (C_{14}) (see Figure 6). The diagnostic region of the spectrum is similar to that of the authentic *N*-octadec-15-ynoylpyrrolidine (**9**). The SDF derived fragment, *m/e* 293, is of insignificant intensity and indicates that the terminal triple bond is somewhat more labile than an internal triple bond under electron impact. Because the peaks in the diagnostic region C_{12}–C_{17} of **2** are of lower intensity than that in the mass spectrum of **9**, the confirmatory rule must be employed more rigorously in this case; the presence of intense peaks at *m/e* 266 ($n - 2$) and *m/e* 304 ($n + 1$) in the Δ15 isomer and the absence of these characteristic peaks in **2** diminish the similarity of the two spectra and aid in distinguishing these two isomers.

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Registry No.—**1**, 56630-92-3; **2**, 68950-87-8; **3**, 68950-88-9; **4**, 33707-76-5; **5**, 58746-25-1; **6**, 58746-23-9; **7**, 68950-89-0; **8**, 56600-12-5; methyl 9-octadecynoate, 1120-32-7; methyl 17-octadecynoate, 68950-90-3; methyl 4-octadecynoate, 61147-01-1; methyl octadecanoate, 112-61-8; methyl octadecanoate-*9,10-d*$_2$, 29800-73-5; methyl octadecanoate-*13,13-d*$_2$, 19905-67-0; methyl 7-octadecynoate, 18545-06-7; methyl 6-octadecynoate, 2777-64-2; pyrrolidine, 123-75-1; 9-octadecynoic acid, 506-24-1; 17-octadecynoic acid, 34450-18-5; 4-octadecynoic acid, 19307-18-7; octadecanoic acid, 57-11-4; octadecanoic-*9,10-d*$_2$ acid, 57396-97-1; octadecanoic-*13,13-d*$_2$ acid, 68950-91-4; 7-octadecynoic acid, 19220-35-0; 6-octadecynoic acid, 544-74-1.

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