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Final

ELECTRON IMPACT PROMOTED FRAGMENTATION OF ALKYL-N-(1-PHENYLETHYL)-CARBAMATES OF PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

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Abstract.- The mass spectra of twenty N-alkyl-(1-phenylethyl)-carbamates derived from primary, secondary and tertiary alcohols have been investigated using deuterium labeling and high resolution mass spectrometry. These derivatives are suitable for the determination of the isotopic purity of primary and secondary, but not of tertiary alcohols. Several of the primary and secondary alcohol derivatives yield an ion formally equivalent to the product ion of a McLafferty rearrangement. However, deuterium labeling established that the usual site specificity associated with the McLafferty rearrangement process was lacking in these carbamate derivatives. In addition a double hydrogen rearrangement process was observed in the mass spectra of several of the carbamates derived from tertiary alcohols.

During a study[1] concerned with the optical analysis of asymmetric secondary alcohols by gas chromatography, mass spectra were recorded for several alkyl-N-(1-phenylethyl)-carbamates. These initial spectra indicated several interesting hydrogen transfer processes which led to a mass spectrometric investigation of a wider selection of alkyl carbamates derived from primary, secondary and tertiary alcohols. By specifically labeling several compounds with deuterium it was possible to rationalize the fragmentation modes of these derivatives. Close similarities, interspersed with some significant differences, were observed in the mass spectra of the N-(1-phenylethyl)-carbamate derivatives of primary, secondary and tertiary alcohols.

The present investigation has been concerned with the mass spectra of twenty alkyl carbamates (I-XX). Since previous workers[2,3,4] who investigated mass spectra obtained from other carbamates, often found thermal processes superimposed upon electron impact phenomena, we used the direct inlet system and an ion source temperature of less than 160°. At source temperatures in excess of 200° extensive thermal fragmentation took place.

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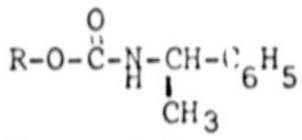
N-(1-Phenylethyl)-carbamates of Primary Alcohols.



I, R = n-C_3H_7-

II, R = n-C_4H_9-

III, R = n-C_5H_{11}-

IV, R = n-C_6H_{13}-

V, R = CH_2=CH-$(CH_2)_8$-

VI, R = neo-C_5H_{11}-

The mass spectra of the primary alcohol derivatives (I-VI) all display abundant molecular ions (Figs. 1-4). Thus the readily accessable N-(1-phenylethyl)-carbamate derivatives of primary alcohols[1] are suitable for the determination of the isotopic purity of labeled (deuterium or ^{18}O) primary alcohols.

The principle fragmentation modes of the primary alkyl carbamates can be interpreted as shown in Scheme 1 where the mass spectrum of the n-hexyl derivative (IV) is used as a typical example. The loss of a methyl radical from the molecular ion of IV can be envisaged in terms of the ion a, m/e 234. Elimination of hexene from this species would generate b, m/e 150 which by decarboxylation would yield c, m/e 106. At low voltage (15 eV) the intensity of c was markedly reduced (18% relative abundance) while b was reduced to 10% relative abundance in agreement with the postulated sequence of fragmentations.

The expulsion of hexanol from the molecular ion of IV (Fig. 2) would yield the isocyanate species d, m/e 147. The hydrogen atom transferred in this process was shown by deuterium labeling to be that attached to the nitrogen atom. Loss of a methyl radical (verified by the presence of a metastable ion in all the carbamate spectra studied) serves as genesis for the ion of mass 132 (e).

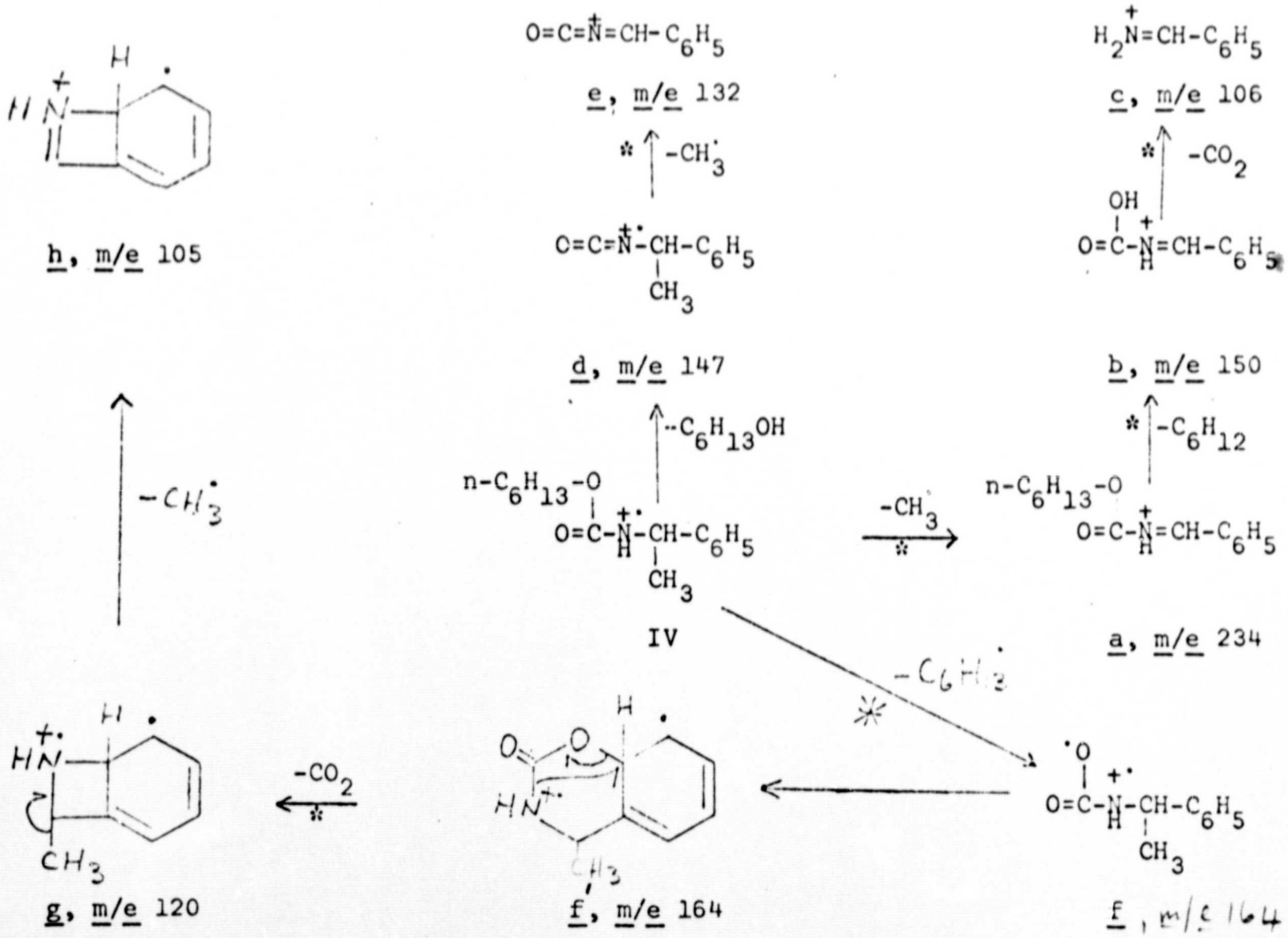
The formation of the peak at m/e 164 in the mass spectrum (Fig. 2) of the n-hexyl derivative IV can be explained by homolysis of the ether carbon-oxygen bond yielding the ionized product f, m/e 164 and a neutral hexyl radical. A more stable representation for f may be the bicyclic ion f'. The contention that the ion of mass 164 can be represented by f or f' received support from the mass spectrum of the n-butyl-2,2-d_2 analog where this ion remained at m/e 164. Decarboxylation of f' would yield g, m/e 120 and this process was verified by a metastable ion in the mass spectra of all the carbamates investigated. At low ionizing voltage (15 eV) (Fig. 2a) the species g was reduced to 7% relative abundance in accord with its proposed origin. Further fragmentation of g by the elimination of a methyl radical would afford h, m/e 105.

It is noteworthy that when a double bond is present at the terminal position of the alkyl chain, for instance V, peaks are observed (Fig. 3) at m/e 165 and 166 (corresponding to the transfer of one and two hydrogen atoms respectively) in addition to the base peak at m/e 164 (f or f'). Similarly the mass spectrum (Fig. 4) of the neo-pentyl derivative VI contains a peak at m/e 165 of 43% relative abundance in addition to the base peak at m/e 164. Tertiary alcohol carbamate derivatives frequently exhibit peaks in their mass spectra at m/e 164, 165 and 166 (Figs. 11 and 12) while carbamates derived from secondary alcohols display peaks in their mass spectra (Figs. 5-9) at m/e 164 and often 165. The rearrangement ions at m/e 165 and 166 are discussed in some detail below under the heading of secondary and tertiary alkyl-N-(1-phenylethyl)-carbamates where deuterated analogs were prepared in order to pin point the sources of the transferred hydrogen atoms.

Peaks of low abundance corresponding to M-59 are recorded in Fig. 3 and several of the spectra (Figs. 5, 6, 8 and 9) of the secondary alcohol carbamates. This process is perhaps best rationalized by the elimination of carbon dioxide from the M-15 ion and its genesis has been discussed[2] in detail for ethyl N-phenyl carbamate

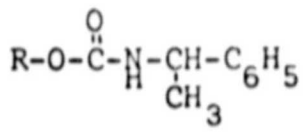
where this process was responsible for a peak in excess of 60% relative abundance. As this previous investigation[2] utilized a heated inlet system it seems probable, in view of the low intensity we have recorded for this process using direct sample insertion into the ion source, that the process may be thermal in origin.

The primary alcohol carbamates examined (I-VI) often contain peaks corresponding to ~~the O-alkyl fragment (OR$^+$)~~ the R^+ alkyl ion from O-R cleavage for instance m/e 85 in Fig. 2 and m/e 71 in Fig. 4.



Scheme 1. Principle Fragmentation Processes of n-Hexyl-N-(1-phenylethyl)-carbamate (IV).

N-(1-Phenylethyl)-carbamates of Secondary Alcohols.

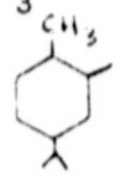


?

VII, R = C_6H_5-CH(CH$_3$)-CH$_3$

VIII, R = C_6H_5-CH(CH$_3$)-CH$_3$ $CH_2=CH-CH-n-C_5H_{11}$

IX, R = CH_3-CH=CH-CH(CH$_3$)-CH$_3$

X, R = 

XI, R = C_2H_5-CH(CH$_3$)-CH$_3$

XII, R = $(CH_3)_3$-C-CH(CH$_3$)-CH$_3$

XIII, R = CH_3-CH(CH$_3$)-n-C_5H_{11}

XIV, R = CH_3-CH(CH$_3$)-n-C_6H_{13}

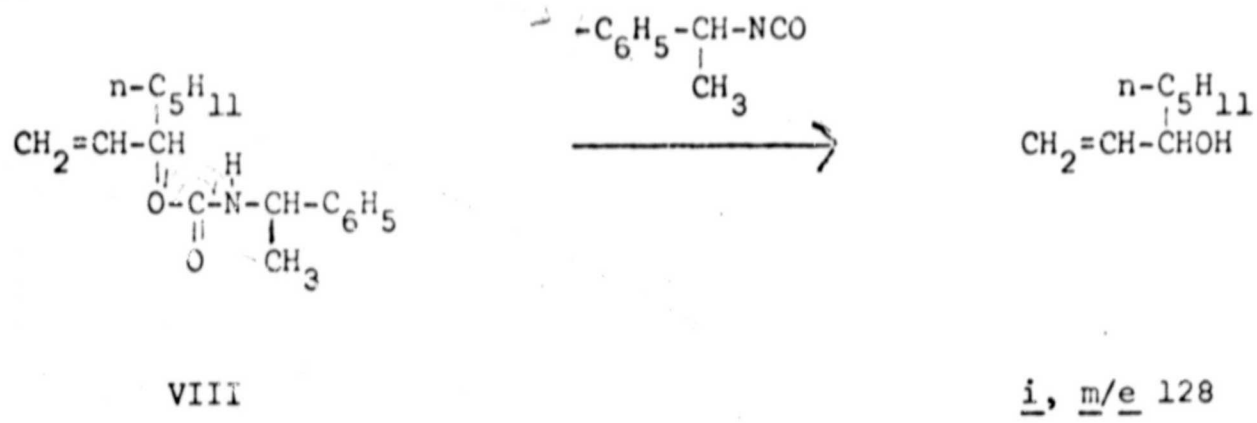
XV, R = C_2H_5-CH(CH$_3$)-n-C_5H_{11}

The mass spectra (Figs. 5-9) of nine secondary alcohol carbamates (XII-XV) were recorded and all display recognizable molecular ion peaks suitable for the calculation of isotopic purities of the labeled parent alcohols.

In many respects carbamate derivatives of secondary alcohols parallel the fragmentation behavior of the primary derivatives discussed above (Scheme 1). Consequently this discussion will concentrate only on the different fragmentation behavior of compounds VII-XV.

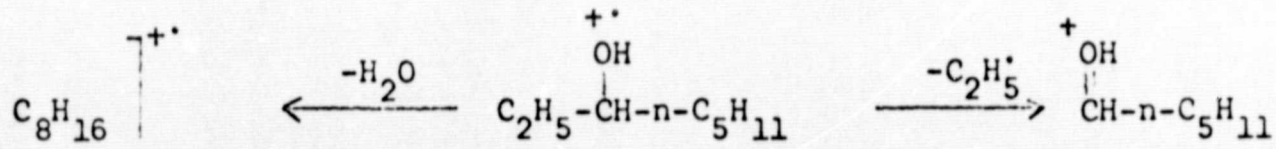
The benzylic (VII) and the two allylic derivatives (VIII and IX) studied display ions in their mass spectra (for example see m/e 122 and 128 in Figs. 5 and 6) corresponding to the parent alcohol. The source of the hydrogen atom transferred in this process was demonstrated by deuterium labeling of VII and VIII to be the hydrogen atom attached to nitrogen and this process can be rationalized by VIII → i, m/e 128. Thus the formation of either a benzylic or allylic alcohol is sufficient impetus for a

portion of the charge to remain with the alcohol fragment in the process depicted by IV → d, (m/e 147). This latter ion was also present in the spectra (Figs. 5-9) of the secondary alcohol N-carbamates.



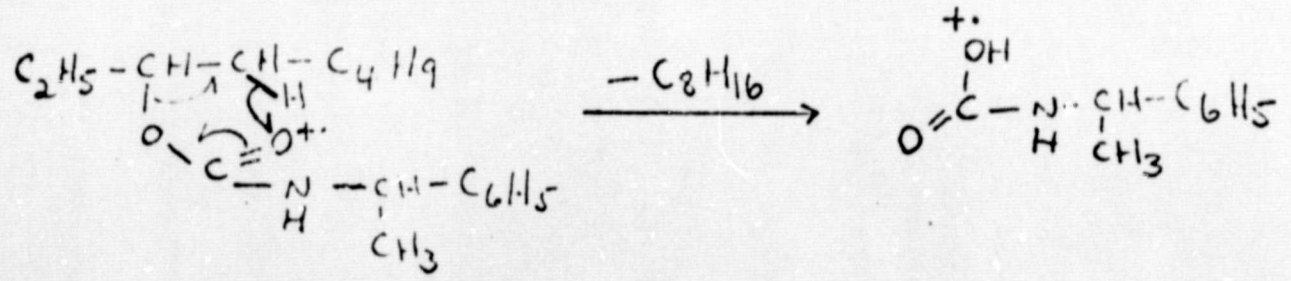
VIII i, m/e 128

The mass spectrum (Fig. 7) of the menthyl carbamate derivative (X) contains an ion of mass 138 corresponding by high resolution mass spectroscopy to $C_{10}H_{18}$, i.e. the product which would result from the elimination of water from menthol. Similar behavior was observed in the mass spectra of XII, XIII, XIV and XV although the peak corresponding to the alcohol molecular ion (unrecorded) minus water, j (m/e 112), was of more substantial abundance in the mass spectrum (Fig. 9) of XV. This latter spectrum also contains a prominent ion of mass 101 (k) which could be rationalized as the product resulting from the loss of an ethyl radical from the unrecorded molecular ion (i') of 3-octanol. This process would be equivalent to the well known propensity of alcohols to undergo α-cleavage.[5]



j, m/e 112 i' k, m/e 101

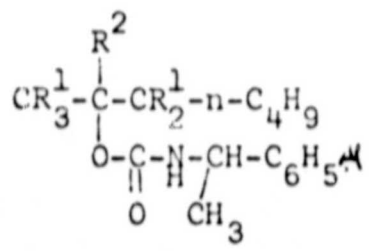
The mass spectra (Figs. 7-9) of the N-(1-phenylethyl)-carbamates (X-XV) contain an abundant ion of mass 165 which has the composition $C_9H_{11}NO_2$ and which must incorporate a hydrogen rearrangement. This ion became relatively more intense at low (15 eV) ionizing energy and it is interesting that it was virtually absent from the spectra of the benzylic (VII) and allylic (VIII and IX) derivatives. Clearly a McLafferty rearrangement process[6] (for instance XV → m, m/e 165) would account for the formation of this ion. However, deuterium labeling studies (XIIIa and XVa) indicated that the two γ-carbon atoms of the alkyl chain (relative to the carbonyl function) transferred a total of 67% and 60% respectively of one deuterium atom in this fragmentation process. The mono-labeled analogs XIIIb and XVb each exhibited only a 4% transfer of m/e 165 to 166 in their mass spectra. These percentage transfers remained at these levels when low energy (15 eV) electrons were used. This would suggest that hydrogen-deuterium randomization,[7] prior to fragmentation, is not prevalent in these compounds. In addition if this fragmentation was simply a McLafferty rearrangement (XV → m, m/e 165) then one could justifiably expect this process to be of some importance in the mass spectra (Figs. 1 and 2) of primary alcohol carbamates. In fact this process is absent from the spectra (Figs. 1 and 2) of these compounds. This nonspecific hydrogen transfer (in what a priori would have been considered a site specific process XV → m) is reminiscent of the behavior previously observed for aryl alkyl ethers.[8]



XV

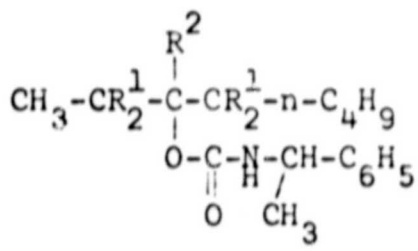
m, m/e 165

A characteristic fragmentation process of the species m is the expulsion of a methyl group (the appropriate metastable ion was recognized in the mass spectra of compounds X-XV) and the resultant ion can be formulated as n, m/e 150. This latter fragment is tautomeric with b which on decarboxylation would furnish the species c, m/e 106 as previously formulated in Scheme 1.



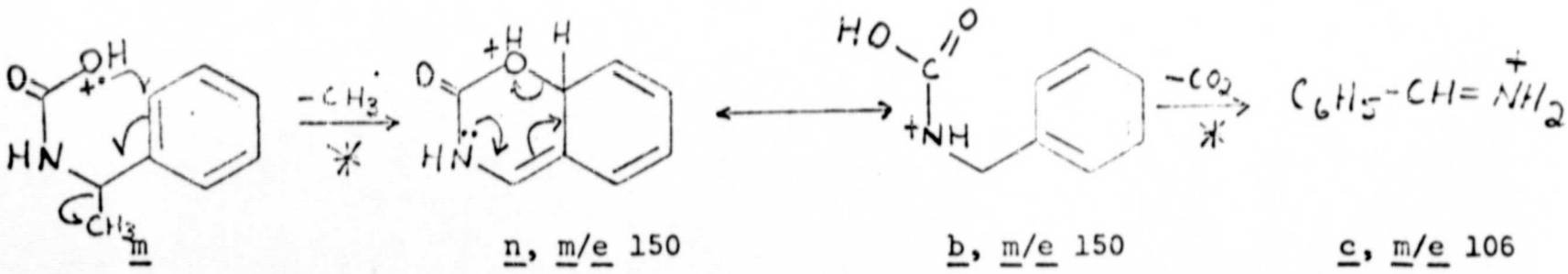
XIIIa; R^1 = D; R^2 = H

XIIIb; R^1 = H; R^2 = D



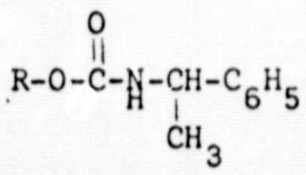
XVa; R^1 = D; R^2 = H

XVb; R^1 = H; R^2 = D



m n, m/e 150 b, m/e 150 c, m/e 106

N-(1-Phenylethyl)-carbamates of Tertiary Alcohols



XVI, R = t-C_4H_9

XVII, R = iso-C_3H_7-C-$(CH_3)_2$

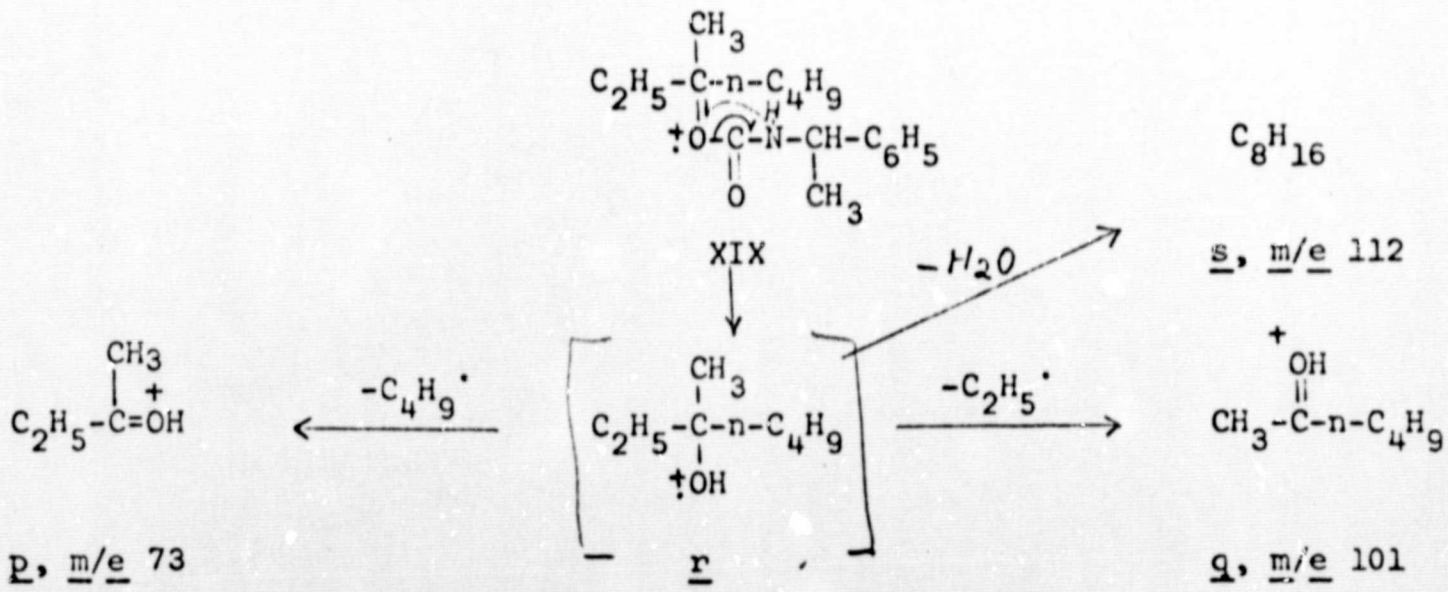
XVIII, R = n-C_3H_7-C(CH_3)-C_2H_5

XIX, R = n-C_4H_9-C(CH_3)-C_2H_5

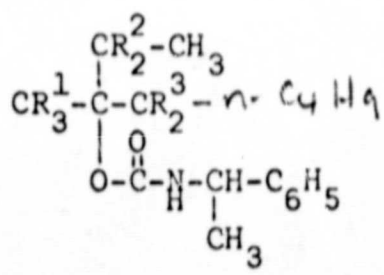
XX, R = n-C_5H_{11}-C(CH_3)-C_2H_5

The molecular ions of N-(1-phenylethyl)-carbamates of tertiary alcohols are of very low abundance or absent from their mass spectra and thus not suitable for the calculation of the isotopic purity of tertiary alcohols.

It is noteworthy that the mass spectra (Figs. 11 and 12) of the carbamates XIX and XX contain prominent hydrocarbon ions at m/e 112 (C_8H_{16}) and m/e 126 respectively. These ions could result from the molecular ion by loss of water from the parent ion of the preformed tertiary alcohol. No molecular ions were recorded for these tertiary alcohols (analogous to i') but the anticipated product ions resulting from elimination of a butyl radical (p, m/e 73, C_4H_9O) and at ethyl radical (q, m/e 101, $C_6H_{13}O$) from a 3-methyl 3-heptanol parent ion (r) were evident in the mass spectrum (Fig. 11) of XIX. This behavior is thus completely analogous to that observed for the carbamate derivatives of secondary alcohols and rationalized by the sequence i' → j and i' → k. In addition the mass spectrum of the N-d_1 derivative of XIX showed that the hydrogen atom transferred to yield r arose from the nitrogen atom of the carbamate while the species p and q each increased by one mass unit in accord with their postulated origin. Furthermore, the product ion (s) of dehydration of r remained at mass 112 in the spectrum of the N-d_1 analog of XIX.



The ions of mass 164, 165 and 166 are also of interest in the mass spectra (Figs. 11 and 12) of the tertiary alkyl carbamates (XVIII-XX). As already described the ion of mass 164 can be associated with the species f or f'. Portion of the ion yield (m) of mass 165 can be attributed to a process analogous to that (XV → m) used to rationalize the presence of this ion in the mass spectra of N-(1-phenylethyl)-carbamates of secondary alcohol carbamates. However, the site specificity for the formation of m in the deuterated analog XXb indicated a more random hydrogen transfer than encountered previously in compounds XIII and XV. Thus in the spectrum of XXb, 40% of m/e 165 was now located at m/e 166 while in that of penta-deuterated compound XXa, 30% of m/e 165 was transferred to m/e 166. These percentage transfers were not altered to any appreciable extent when low energy (15 eV) ionizing electrons were used.



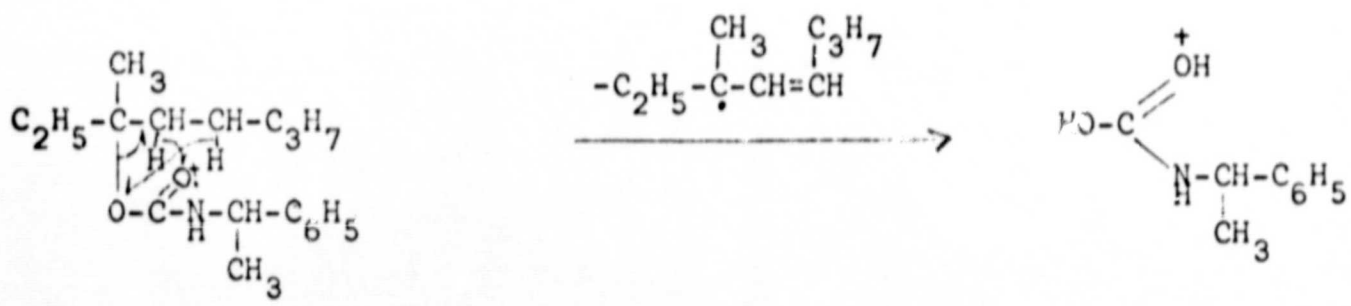
XXa; $R^1 = R^3 = D$; $R^2 = H$

XXb; $R^1 = R^2 = R^3 = D$

The peak at m/e 166 in the mass spectra (see for instance Figs. 11 and 12) of the carbamate derivative of tertiary alcohols (XVIII, XIX and XX) must result from a double hydrogen transfer process. It is noteworthy that the mass spectra (Fig. 10) of the t-butyl and that of the 2-(2,3-dimethylbutyl) N-(1-phenylethyl)-carbamates (XVI and XVII) exhibit virtually no ion current at m/e 166. This may be associated with the fact that in XVI only primary hydrogen atoms (relative to the carbonyl function) are available for transfer while in XVII only one γ-hydrogen is available and all other hydrogen atoms of the alkyl chain are primary and situated δ with respect to the

carbonyl group. It is known[6b] that transfer of primary, as compared to secondary hydrogen atoms, is less favored in the McLafferty rearrangement.

The double hydrogen transfer process in XX (m/e 166 in Fig. 12) was shown to involve deuterium from XXb to the extent of 15% of two deuterium atoms (the peak in question was shifted to m/e 168) and 77% of one deuterium atom. The corresponding values for the penta-deuterated analog became 11 and 58% respectively and all transfers were little affected by using low energy (15 eV) electrons. This double hydrogen transfer process can be rationalized by XX → t, m/e 166 where the product ion is depicted as a protonated carbamic acid although no firm evidence is available for the precise site (s) of the second hydrogen atom transferred.



XX

t, m/e 166

EXPERIMENTAL

Low resolution mass spectra were recorded by Mr. R. C. Conover in the Chemistry Department of Stanford University using an Atlas CH-4 mass spectrometer. High resolution mass spectra were recorded by Mr. R. G. Ross using an MS-9 mass spectrometer on-line with the ACME computer system of the Stanford University Medical School. Samples were introduced by the direct inlet system and the ion source was maintained at 160° in each instrument. The ionizing energy was 70 eV and low voltage measurements refer to nominal values only.

General Preparation of Alkyl N-(1-phenylethyl)-carbamates.-

3-Methyl-3-hexyl-N-(1-phenylethyl)-carbamate (XVIII).- 3-Methyl-3-hexanol (232 mg., 2 mmole) and 1-phenylethylisocyanate[1] (294 mg., 2 mmole) were heated in a sealed ampoule at 120° for 10 hours. The crude product was purified on a silica gel column using hexane followed by hexane-methylene chloride mixtures (20:1, 10:1, 5:1, 1:1). The product was shown to be homogeneous by TLC on silica gel using benzene:ether (95:5), and distilled at 122-124°C (0.1mm Hg). Anal. calc. for $C_{16}H_{25}NO_2$: C, 73.0; H, 9.6; N, 5.3. Found: C, 73.1; H, 9.5; N, 5.2. The physical constants of the other alkyl-N-(1-phenylethyl)-carbamates studied are summarized in Table 1.

Alkyl N-D-(1-phenylethyl)-carbamates.- These compounds were prepared by dissolving the carbamate in methanol-O-D and removing the solvent *in vacuo*. Repetition of this procedure yielded carbamates of between 50 and 60% d_1 species, the remainder being d_0.

n-Butyl-2,2-d_2 N-(1-phenylethyl)-carbamate.- This compound was prepared from butanol-2,2-d_2[9] according to the general procedure described above.

2-Heptyl-1,1,1,3,3-d_5 N-(1-phenylethyl)-carbamate XIIIa.- 2-Heptanone-1,1,1,3,3-d_5 (95% d_5, 5% d_4) was prepared from the unlabeled ketone by basic exchange (twice) during 24 hours in a diglyme-deuterium oxide mixture containing sodium. Lithium aluminum hydride reduction yielded 2-heptanol-1,1,1,3,3-d_5 which was condensed with 1-phenylethyl

isocyanate[1] according to the general method described above to yield XIIIa.

2-Heptyl-2-d_1 N-(1-phenylethyl)-carbamate (XIIIb).- 2-Heptanol-2-d_1 (the product of lithium aluminum deuteride reduction of 2-heptanone) was condensed with 1-phenylethyl isocyanate[1] according to the described general method to yield XIIIb.

3-Octyl-2,2,4,4-d_4 N-(1-phenylethyl)-carbamate XVa.- This compound was prepared from 3-octanone-2,2,4,4-d_4 (95% d_4, 5% d_3) as detailed for the preparation of XIIIa.

3-Octyl-3-d_1 N-(1-phenylethyl)-carbamate (XVb).- This carbamate was synthesized from 3-octanone by a procedure similar to that described for XIIIb.

(3-Methyl-d_3) 3-octyl-4,4-d_2 N-(1-phenylethyl)-carbamate (XXa).- 2-Heptanone-1,1,1,3,3-d_5 was prepared by basic exchange of the unlabeled ketone in a diglyme-deuterium oxide mixture and reacted with the Grignard reagent prepared from ethyl bromide to yield 3-(methyl-d_3)-3-octanol-4,4-d_2. Condensation of this labeled alcohol with 1-phenylethyl isocyanate[1] yielded XXa.

3-(Methyl-d_3)-3-octyl-2,2,4,4-d_4 N-(1-phenylethyl)-carbamate (XXb).- 3-Octanone was equilibrated in refluxing diglyme-deuterium oxide solution containing sodium for two periods of 24 hours to yield 3-octanone-2,2,4,4-d_4 of 93% d_4 and 7% d_3 species. This labeled ketone was reacted with the Grignard reagent prepared from methyl-d_3 iodide to yield 3-(methyl-d_3)-3-octanol-2,2,4,4-d_4 which was then converted to XXb.

Acknowledgement.- Financial assistance from the National Aeronautics and Space Administration (Grant NGR-05-020-004) is gratefully acknowledged. We would like to thank the management of the ACME Computer Facility for free computer time.

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Legends to Figures

Fig. 1. Mass spectrum (70 eV) of n-propyl N-(1-phenylethyl)-carbamate (I).

Fig. 2. Mass spectrum (70 eV) of n-hexyl N-(1-phenylethyl)-carbamate (IV).

Fig. 2a. Mass spectrum (15 eV) of n-hexyl N-(1-phenylethyl)-carbamate (IV).

Fig. 3. Mass spectrum (70 eV) of dec-9-en-1-yl N-(1-phenylethyl)-carbamate (V).

Fig. 4. Mass spectrum (70 eV) of neopentyl N-(1-phenylethyl)-carbamate (VI).

Fig. 5. Mass spectrum (70 eV) of 1-phenylethyl N-(1-phenylethyl)-carbamate (VII).

Fig. 6. Mass spectrum (70 eV) of oct-1-ene-3-yl N-(1-phenylethyl)-carbamate (VIII).

Fig. 7. Mass spectrum (70 eV) of menthyl N-(1-phenylethyl)-carbamate (X).

Fig. 8. Mass spectrum (70 eV) of 2-heptanyl N-(1-phenylethyl)-carbamate (XIII).

Fig. 9. Mass spectrum (70 eV) of 3-octanyl N-(1-phenylethyl)-carbamate (XV).

Fig. 9a. Mass spectrum (15 eV) of 3-octanyl N-(1-phenylethyl)-carbamate (XV).

Fig. 10. Mass spectrum (70 eV) of t-butyl N-(1-phenylethyl)-carbamate (XVI).

Fig. 11. Mass spectrum (70 eV) of 3-methyl-3-heptyl N-(1-phenylethyl)-carbamate (XIX)

Fig. 12. Mass spectrum (70 eV) of 3-methyl-octyl N-(1-phenylethyl)-carbamate (XX).

Fig. 12a. Mass spectrum (15 eV) of 3-methyl-octyl N-(1-phenylethyl)-carbamate (XX).

Table 1. Physical Constants of the Alkyl-N-(1-Phenylethyl)-carbamates Studied.*

Compound	b.p. (°C/mm Hg)	Found (%) C	Found (%) H	Found (%) N	Calc(%) C	Calc(%) H	Calc(%) N	Formula
n-propyl (I)	106-7°/0.1	69.3	8.3	6.5	69.5	8.3	6.8	$C_{12}H_{17}NO_2$
n-butyl (II)	114° /0.1	70.5	8.6	6.1	70.6	8.7	6.3	$C_{13}H_{19}NO_2$
n-pentyl (III)	132° /0.2	71.3	8.9	6.0	71.5	9.0	6.0	$C_{14}H_{21}NO_2$
n-hexyl (IV)	135-8°/0.1	72.0	9.2	5.5	72.3	9.3	5.6	$C_{15}H_{23}NO_2$
9-decen-1-yl (V)	165-6°/0.1	75.2	9.6	4.6	75.2	9.6	4.6	$C_{19}H_{29}NO_2$
neo-pentyl (VI)	112-4°/0.1	71.3	9.0	5.9	71.5	9.0	6.0	$C_{14}H_{21}NO_2$
pent-3-en-2-yl (IX)	118° /0.1	72.1	8.2	5.7	72.1	8.2	6.0	$C_{14}H_{19}NO_2$
3-octyl (XV)	160° /0.7	73.6	9.6	4.8	73.6	9.8	5.1	$C_{17}H_{27}NO_2$
t-butyl (XVI)		70.6	8.7	6.5	70.6	8.7	6.3	$C_{13}H_{19}NO_2$
3-methyl-3-hexyl (XVIII)	122-4°/0.1	73.1	9.5	5.2	73.0	9.6	5.3	$C_{16}H_{25}NO_2$
3-methyl-3-heptyl (XIX)	122-4°/0.1	73.7	9.9	5.2	73.6	9.8	5.1	$C_{17}H_{27}NO_2$
3-methyl-3-octyl (XX)		74.0	10.0	4.6	74.2	10.0	4.8	$C_{18}H_{29}NO_2$

* Those compounds studied but not included in this table have been described previously.[1]

Fig. 1

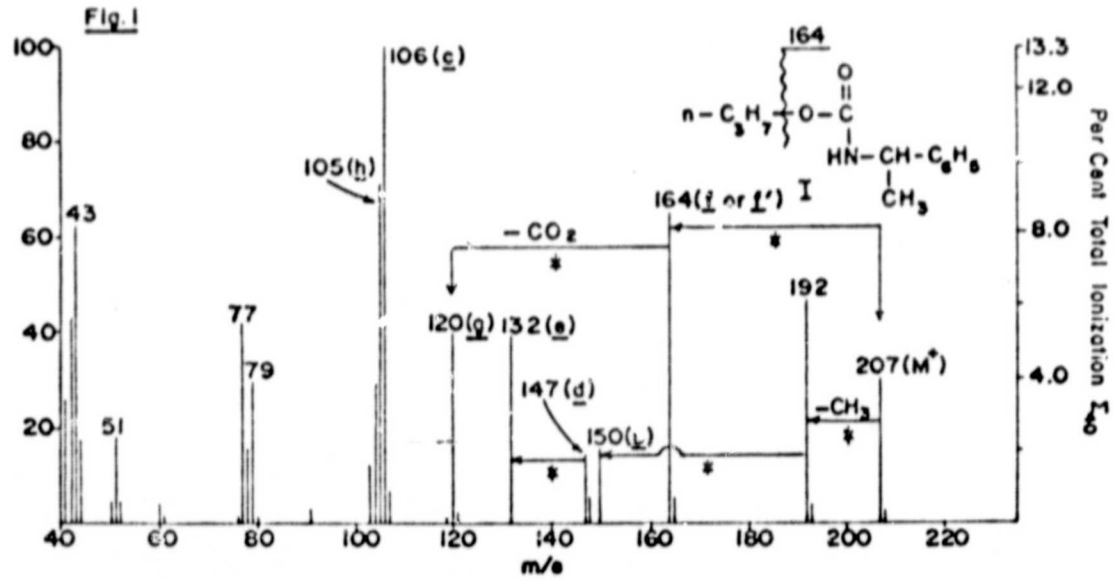


Fig. 2

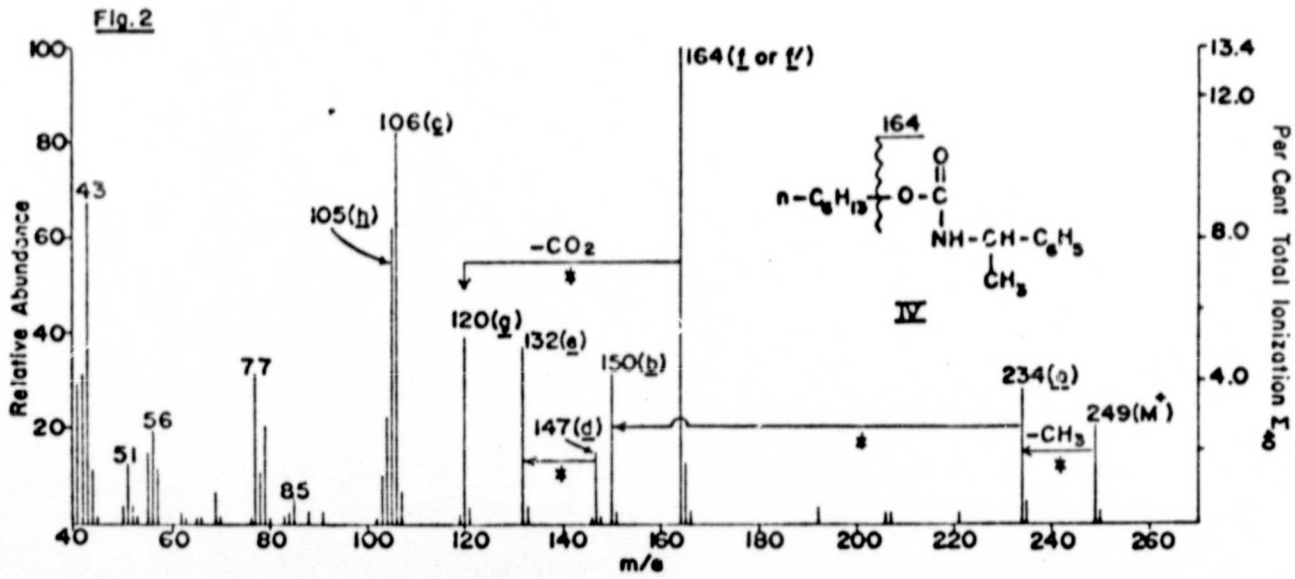
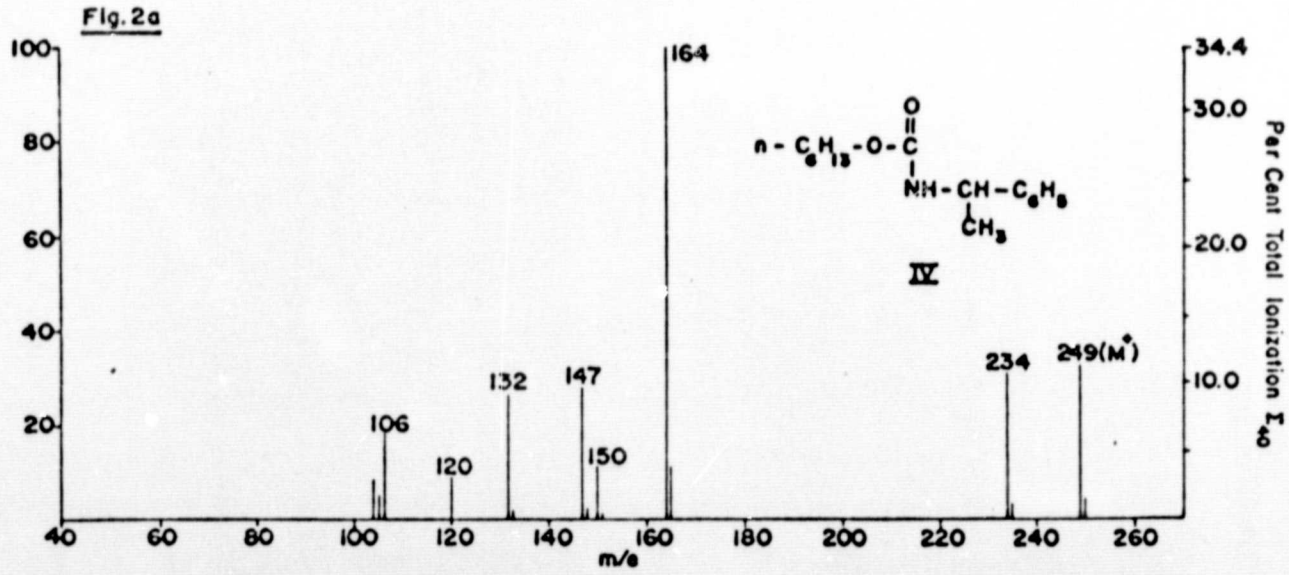


Fig. 2a



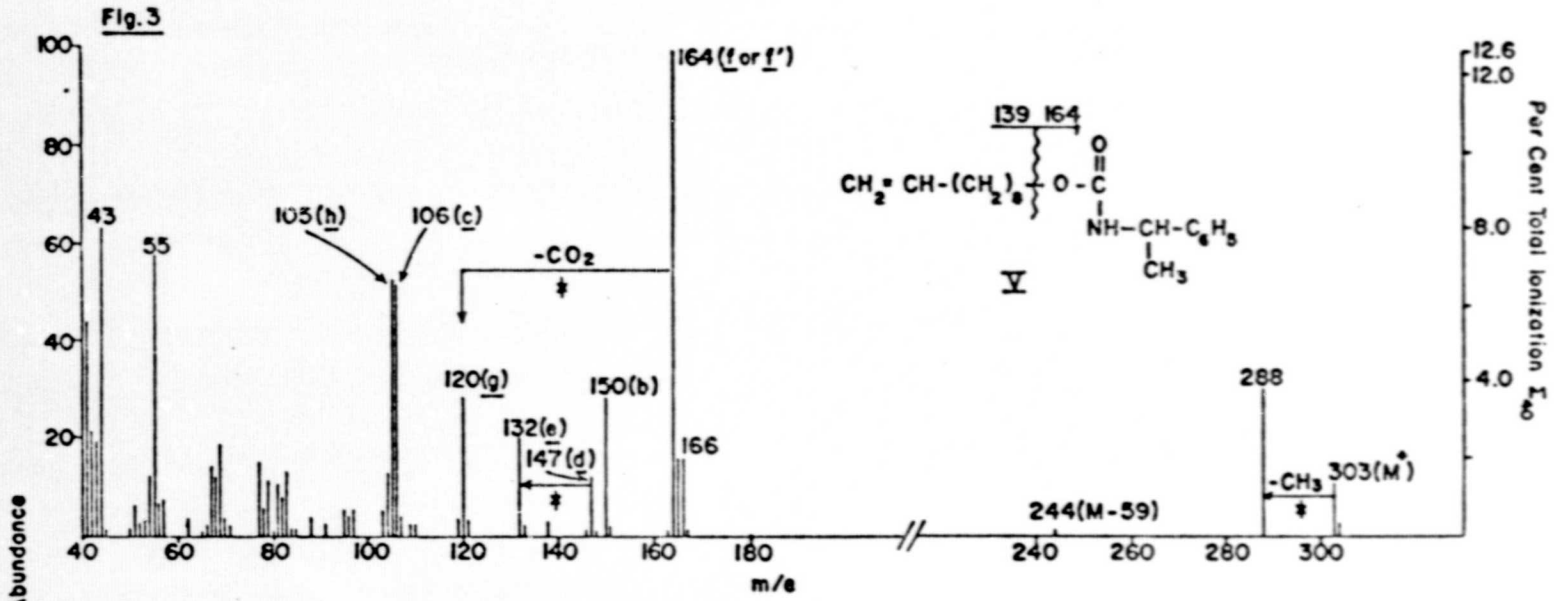


Fig. 3
Relative Abundance
Per Cent Total Ionization Σ_{40}
m/e
43
55
105(h)
106(c)
-CO2
120(g)
132(e)
147(d)
150(b)
164(f or f')
166
244(M-59)
288
-CH3
303(M+)
139 164
CH2 = CH-(CH2)8 - O - C
NH-CH-C6H5
CH3
V

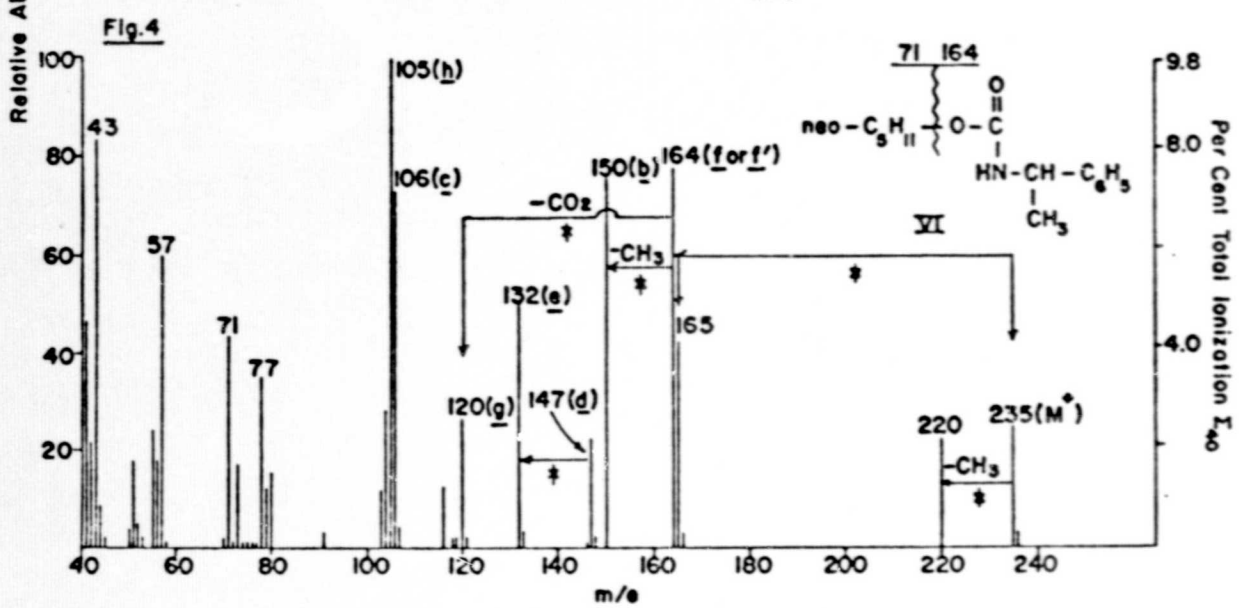


Fig. 4
Relative Abundance
Per Cent Total Ionization Σ_{40}
m/e
43
57
71
77
105(h)
106(c)
-CO2
150(b)
164(f or f')
-CH3
132(e)
165
120(g)
147(d)
220
235(M+)
71 164
neo-C5H11 - O - C
HN-CH-C6H5
CH3
VI

Fig.5

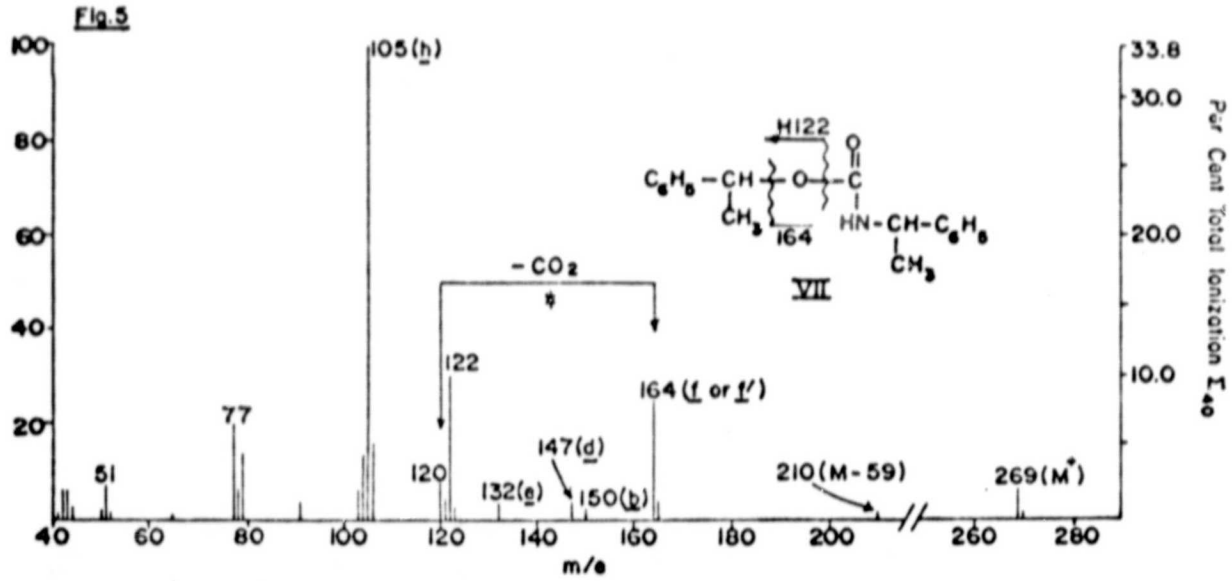


Fig.6

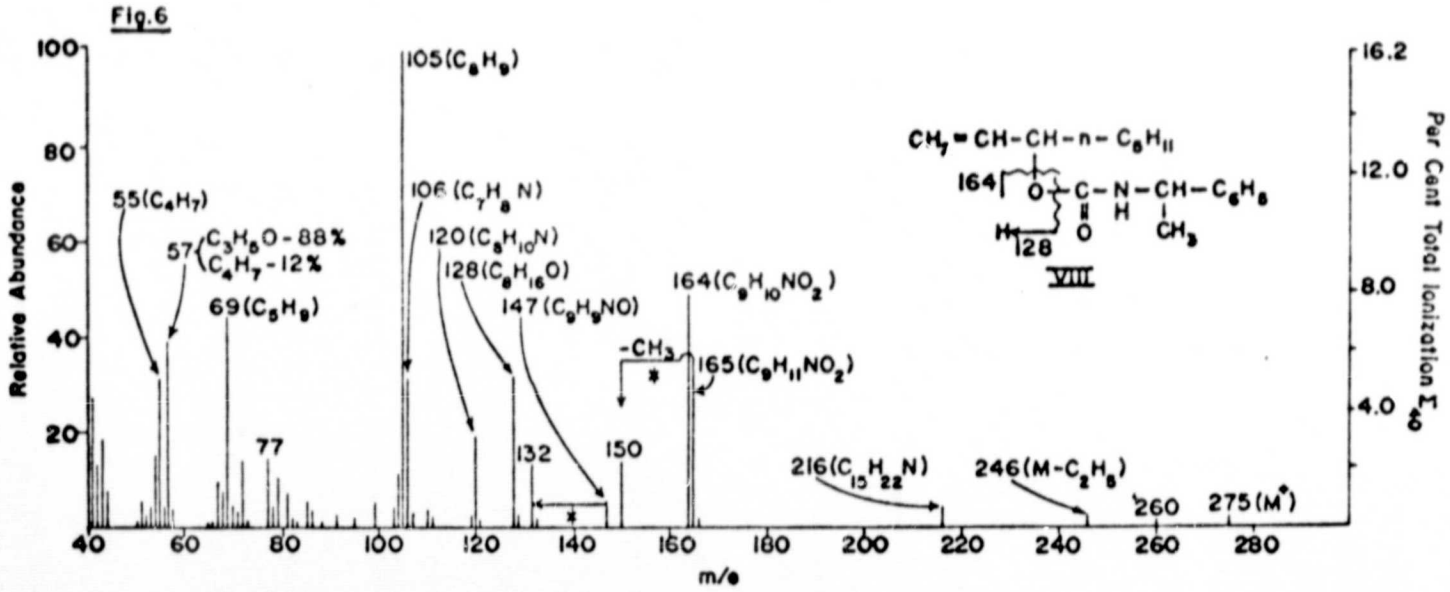


Fig.7

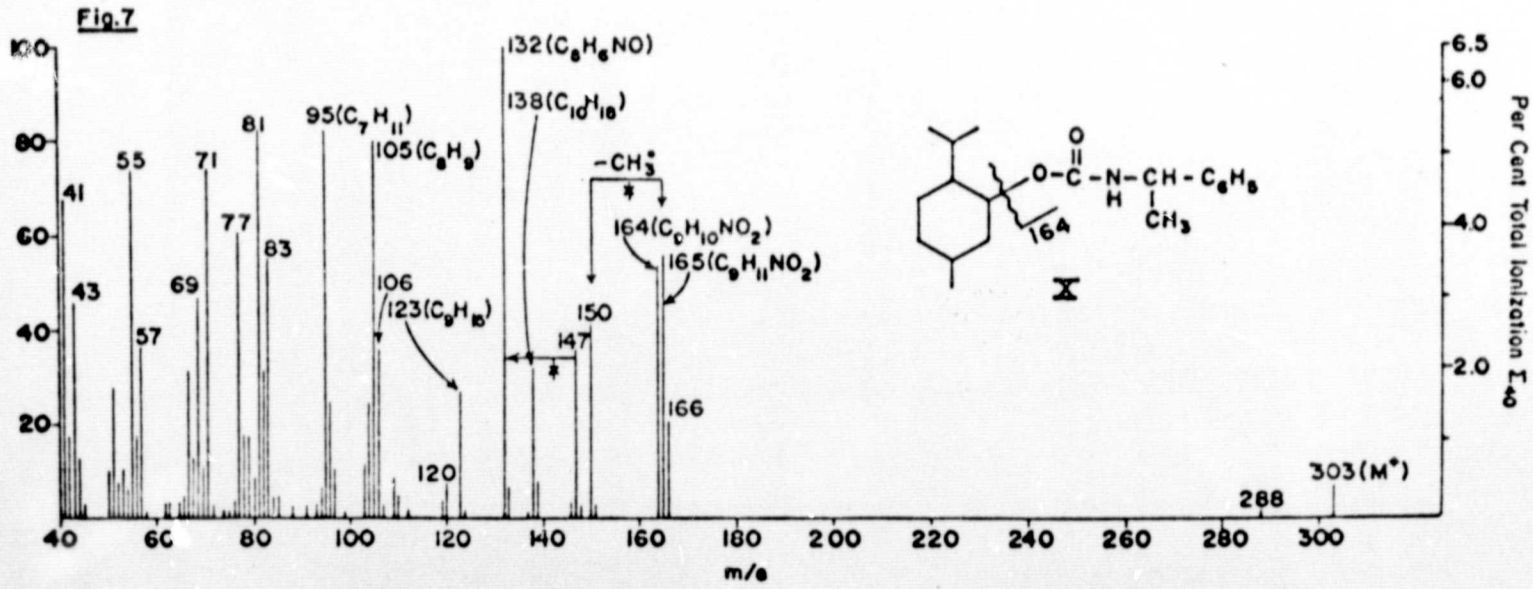


Fig. 8

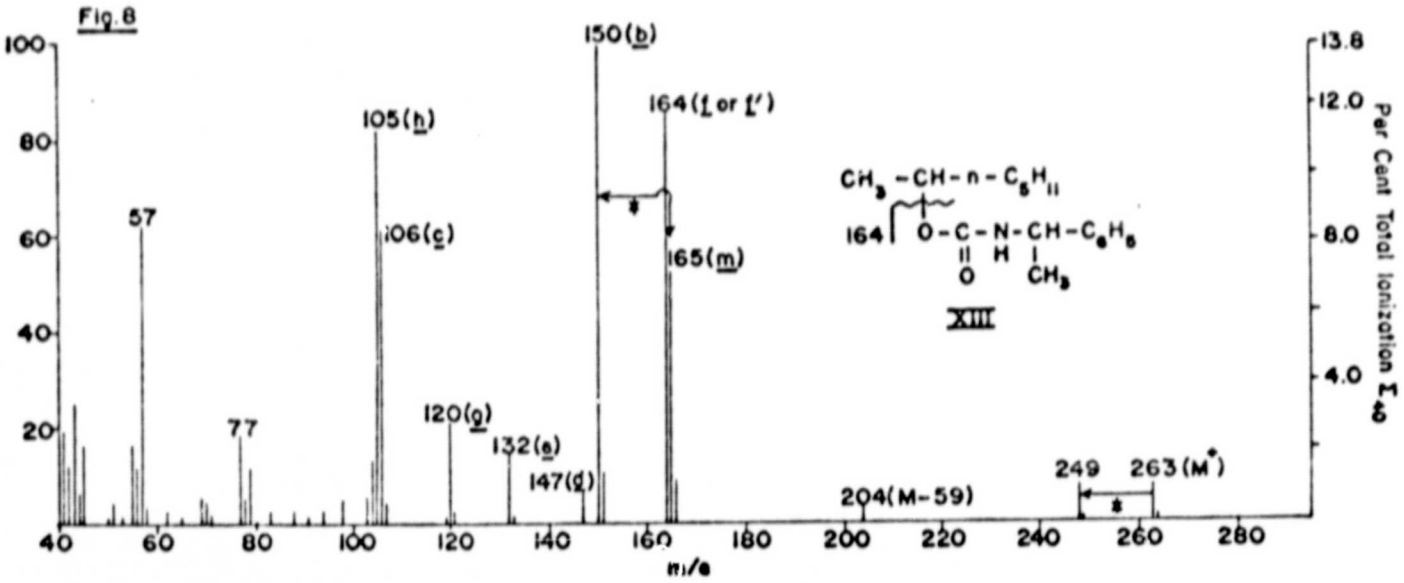


Fig. 9

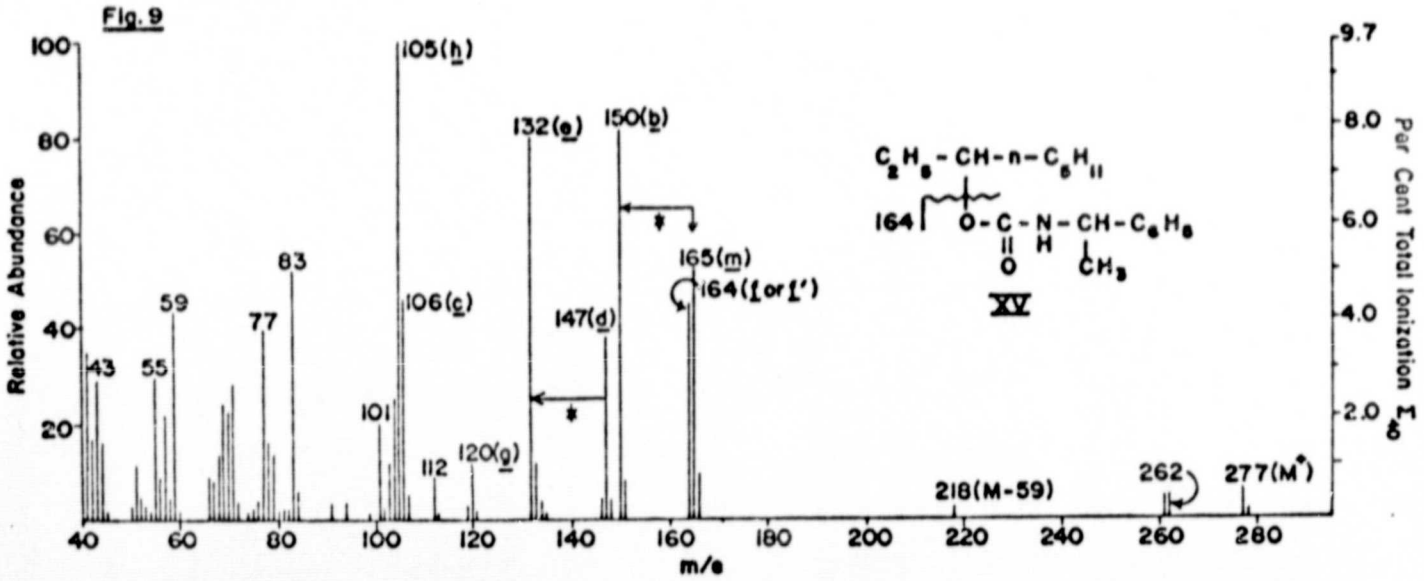


Fig. 9a

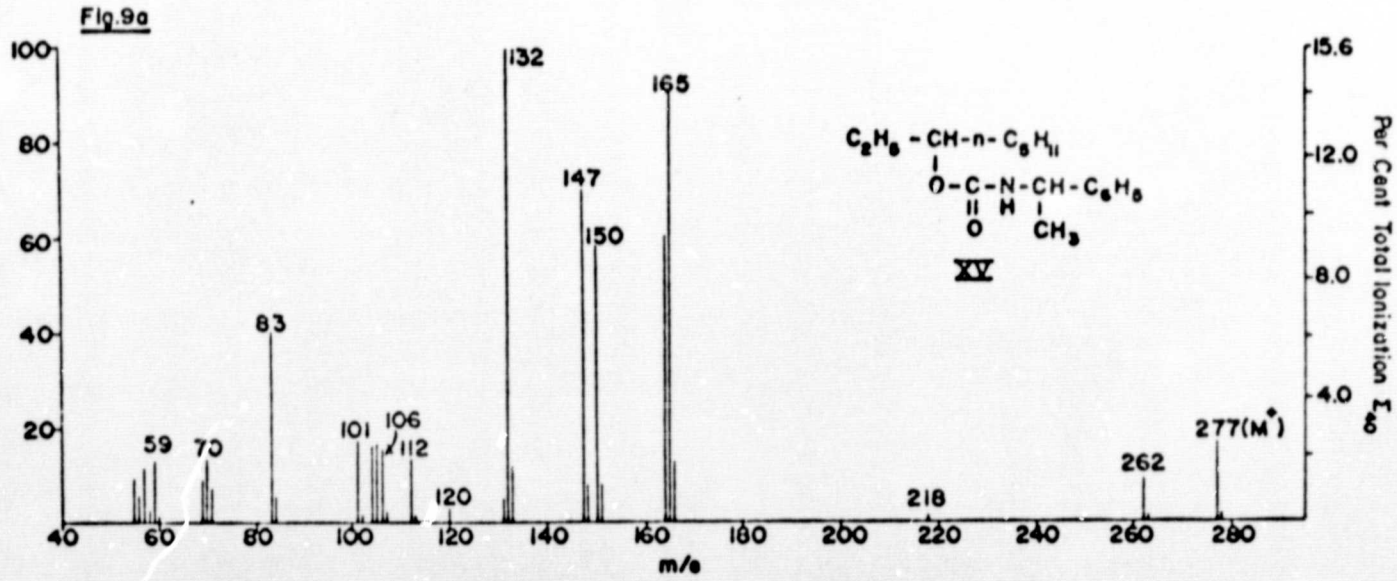


Fig.10

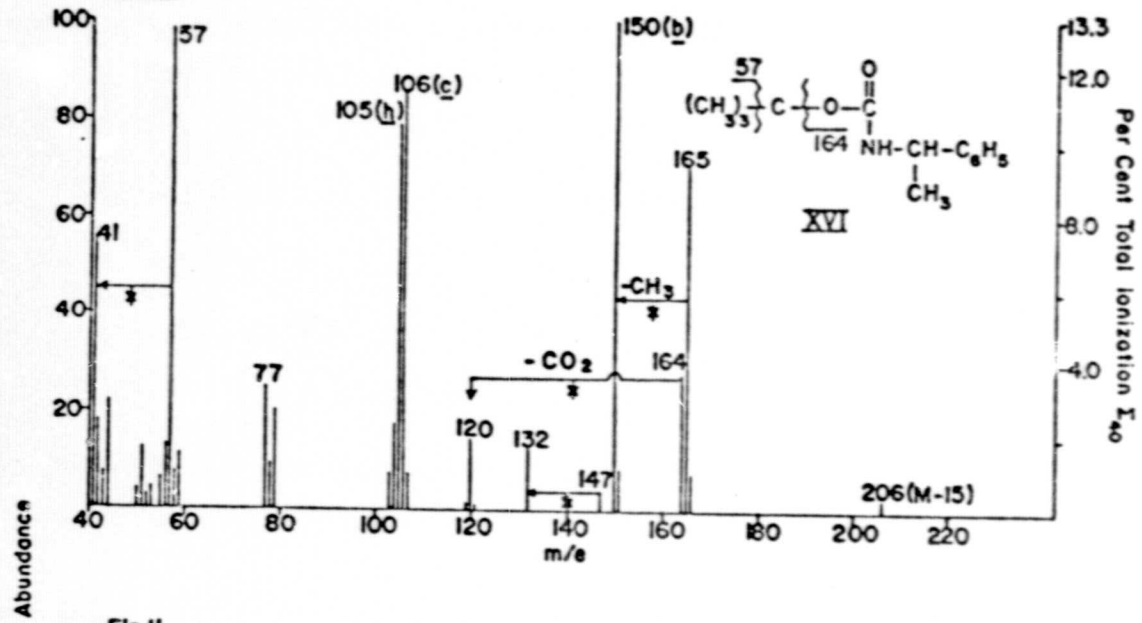

Relative Abundance
Per Cent Total Ionization Σ_{40}
m/e
57
41
77
105(h)
106(c)
120
132
147
150(b)
165
164
206(M-15)
-CH3
-CO2
XVI

Fig.11

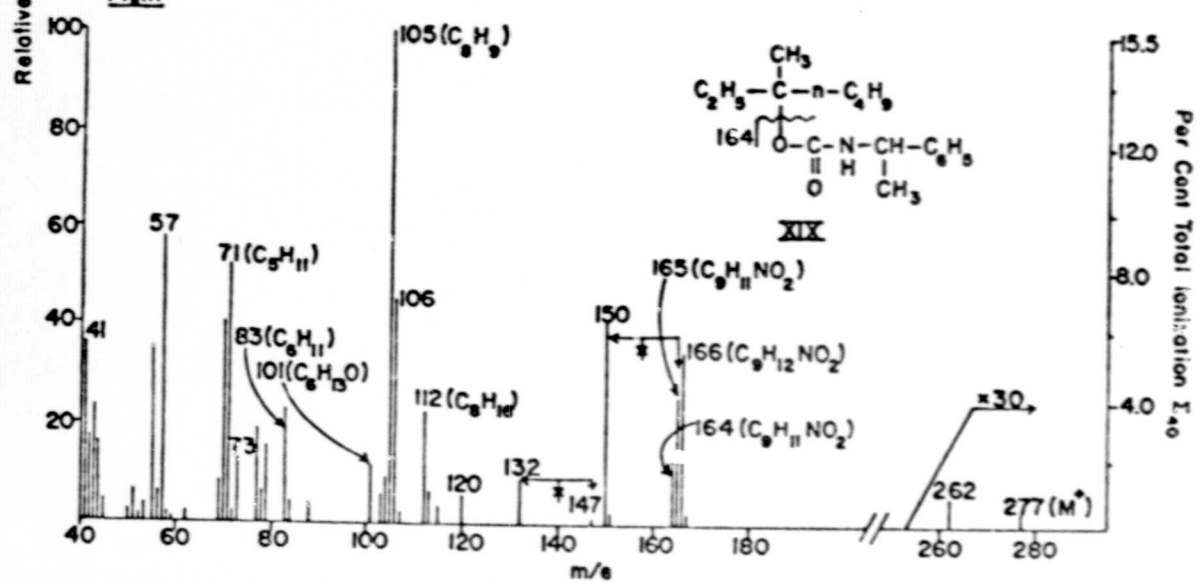

Per Cent Total Ionization Σ_{40}
m/e
41
57
71(C5H11)
73
83(C6H11)
101(C6H13O)
105(C8H9)
106
112(C8H16)
120
132
147
150
165(C9H11NO2)
166(C9H12NO2)
164(C9H11NO2)
×30
262
277(M+)
XIX

Fig. 12

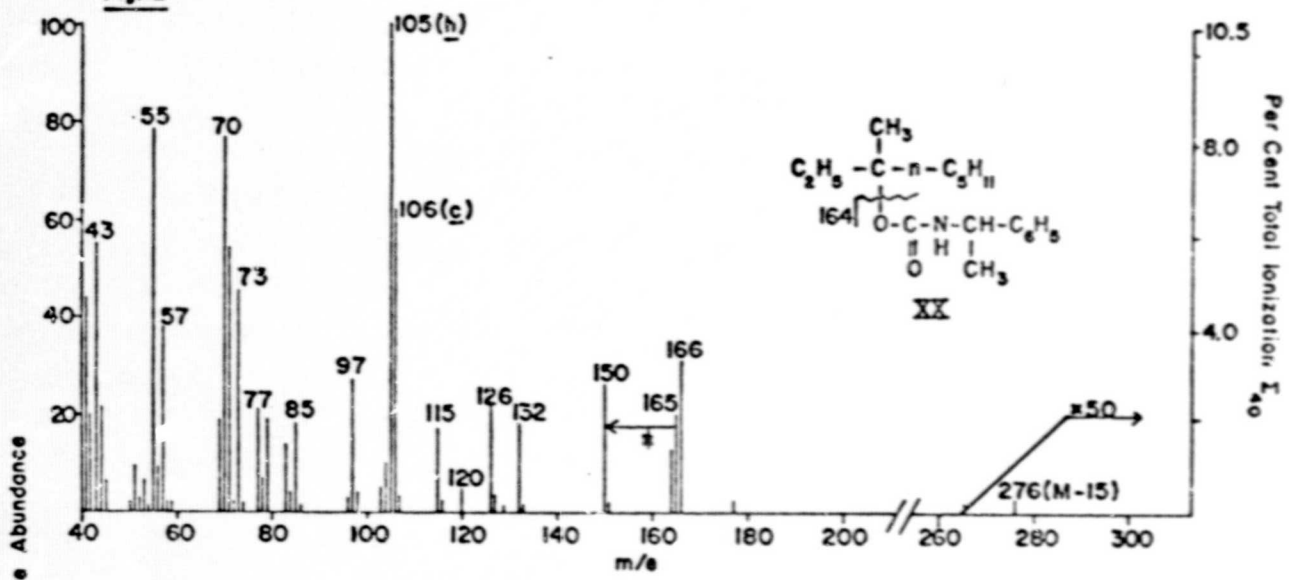
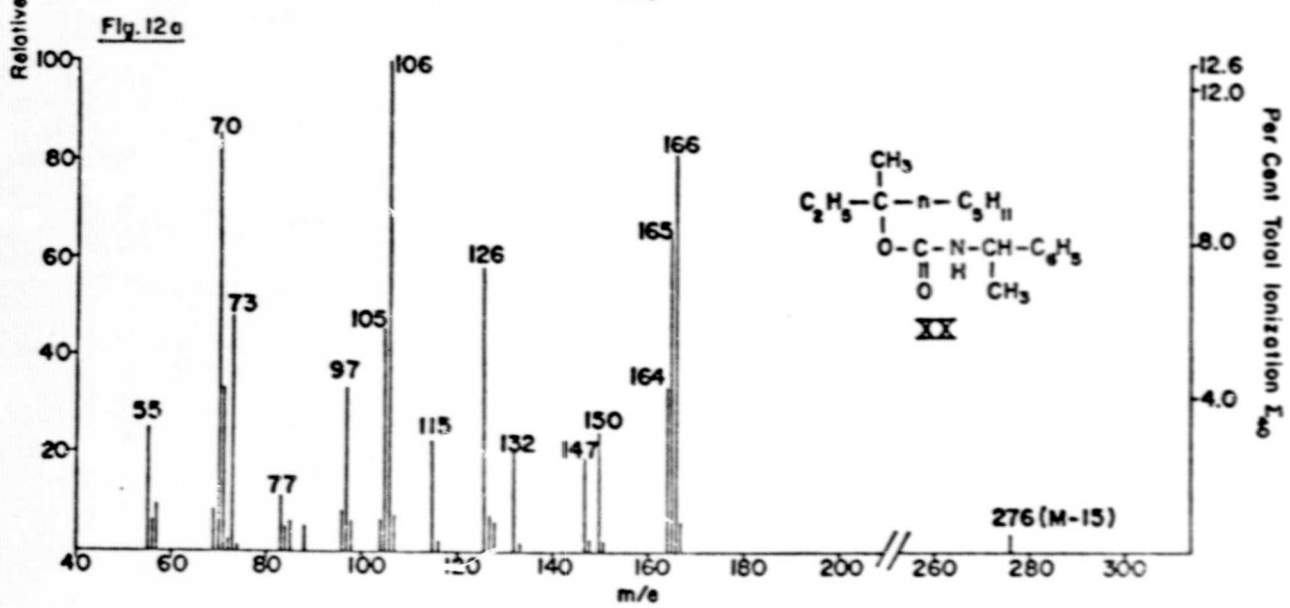



Fig. 12a