

FRAGMENTAÇÕES

Apesar da fragmentação ocorrer em condições altamente energéticas (onde qualquer coisa pode acontecer), podemos prever tipos de fragmentações mais prováveis que são condizentes com a estabilidade de intermediários químicos.

REGRAS GERAIS:

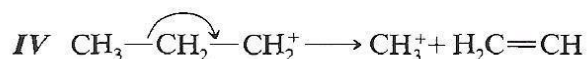
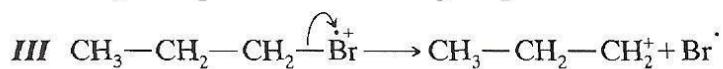
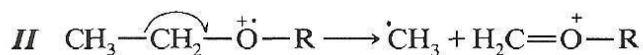
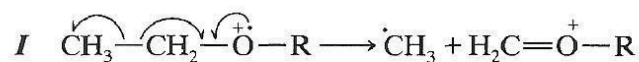
Possibilidade de fragmentações depois de formado o íon molecular (M^+):

I – Clivagem Homolítica – meia flecha

II – Clivagem Homolítica – menos congestionada de flechas

III – Clivagem Heterolítica – Flecha inteira

IV – Clivagem Heterolítica de carbocátion

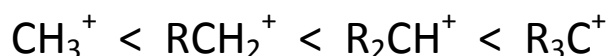


(Sch 1.3)

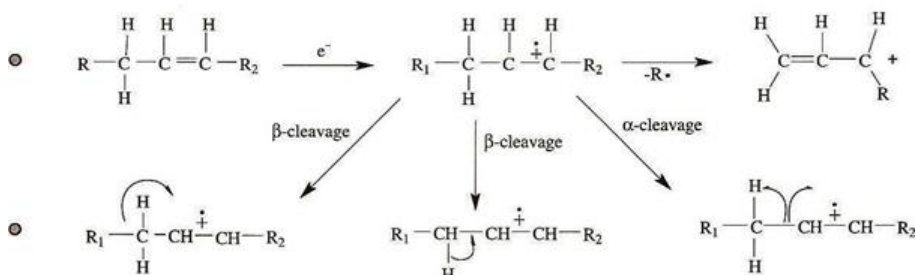
Regras Gerais de Fragmentações

1. A quebra é favorecida nas ligações dos átomos de carbonos ramificados. Segue a ordem de estabilidade dos carbocátions.

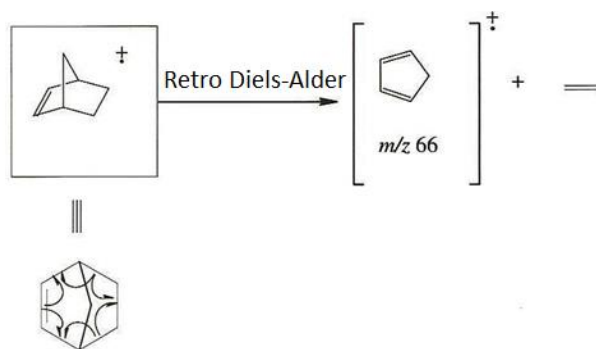
Ordem de estabilidade dos carbocátios



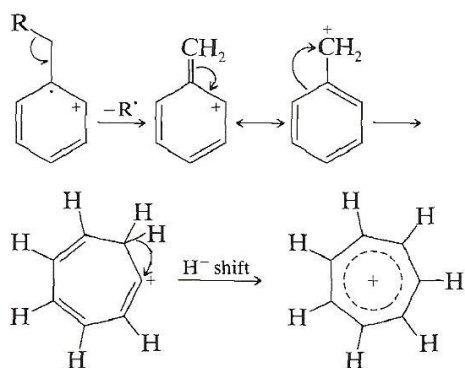
2. As ligações duplas favorecem a quebra alílica e dão um íon de carbônio alílico estabilizado por ressonância.



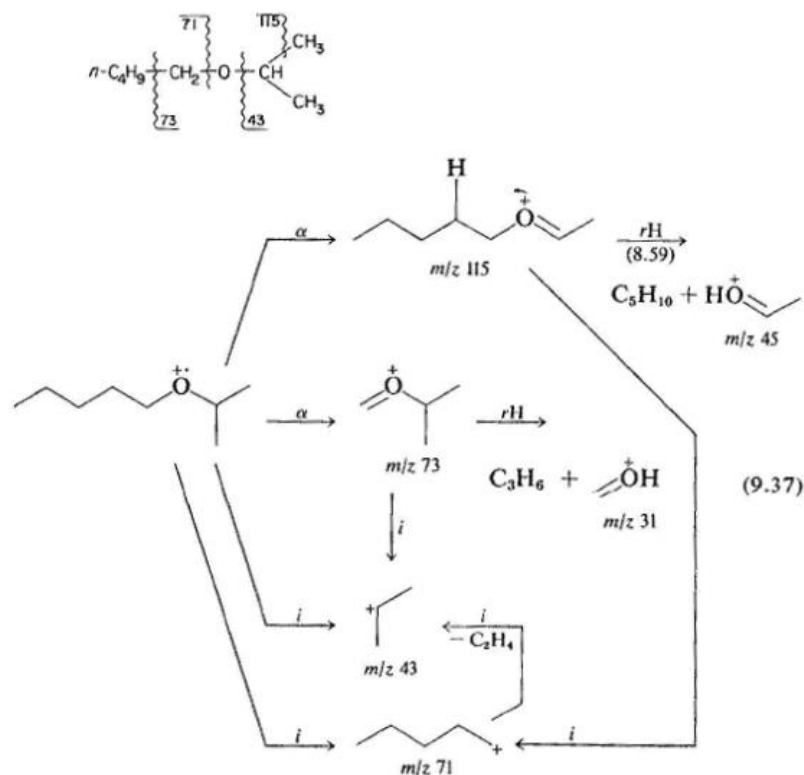
3. Os anéis insaturados podem sofrer reação de Diels-Alder inversa.



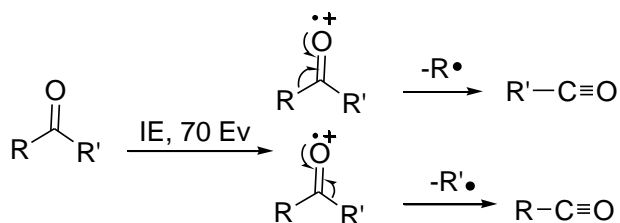
4. Em compostos aromáticos alquil substituídos, a quebra é mais provável na ligação β ao anel, dando o íon benzílico, estabilizado por ressonância ou formação do íon tropílio.



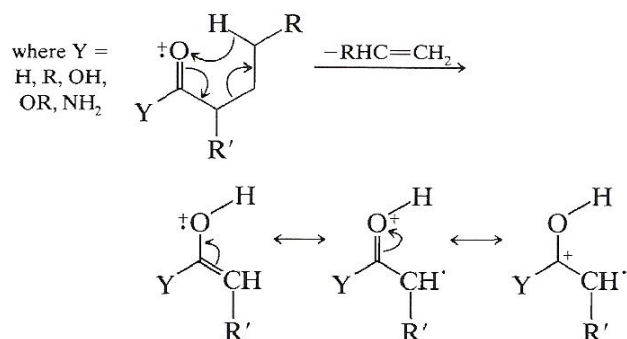
5. As ligações C-C próximas a um heteroátomo frequentemente se quebram deixando a carga no fragmento que contém o heteroátomo, porque os elétrons não-ligantes fornecem estabilização por ressonância.



6. Compostos carbonílicos tem a tendência de quebrar a ligação *alfa*-carbonílica.



7. Compostos carbonílicos que possuem hidrogênio no carbono *gamma* geralmente apresentam o rearranjo de McLafferty como o principal caminho de fragmentação.



8. As molécula neutras mais frequentemente eliminadas são: CO, olefinas, H₂O, NH₃, HS, mercaptanas, cetenos e álcoois.

Espectros de Massas de ALCANOS

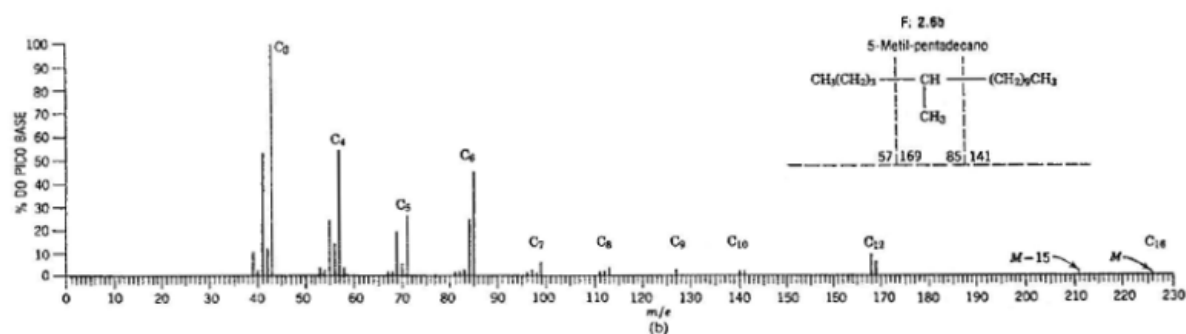
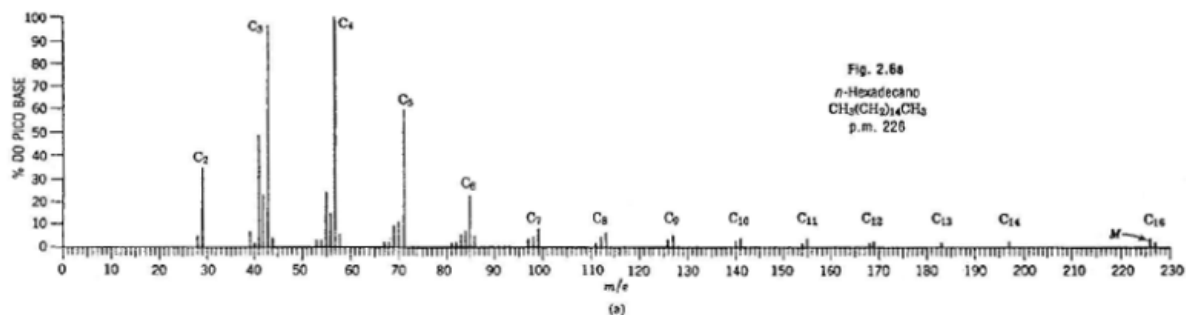
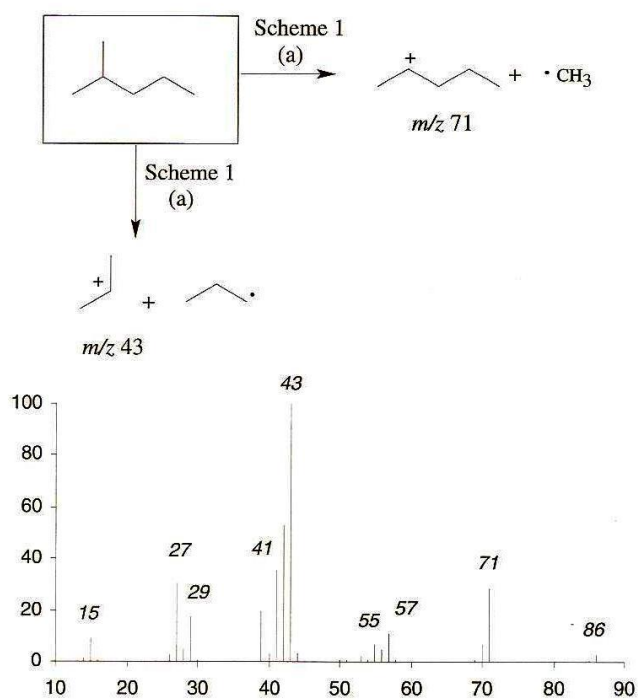


Fig. 2.6 Hidrocarbonetos isoméricos contendo 16 átomos de carbono.

Espectro de massas do 2-metilpentano



Espectro de massas do cicloexano

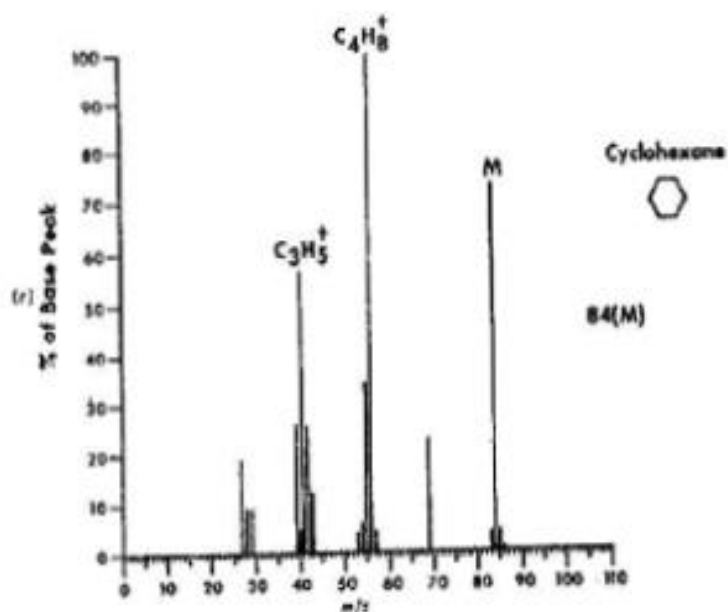
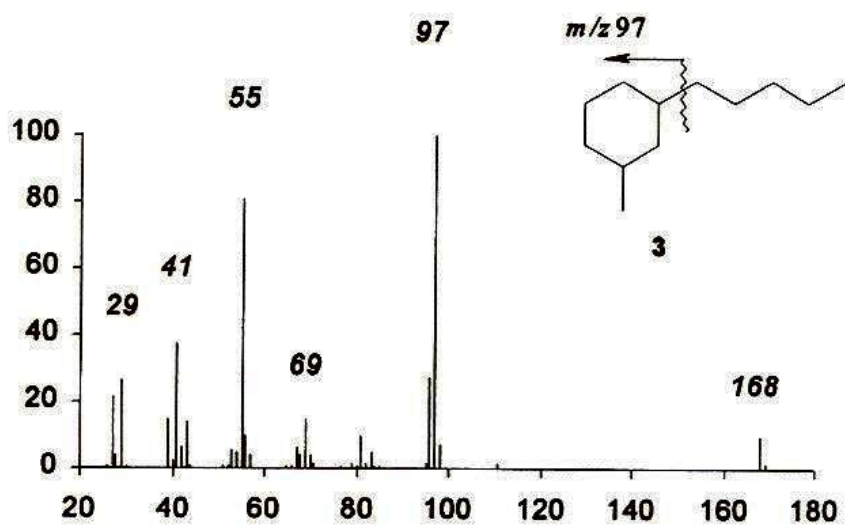
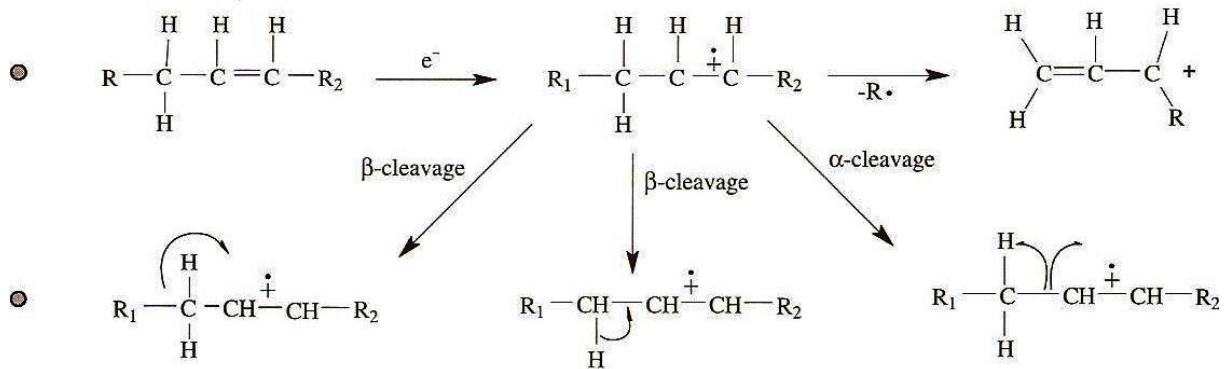
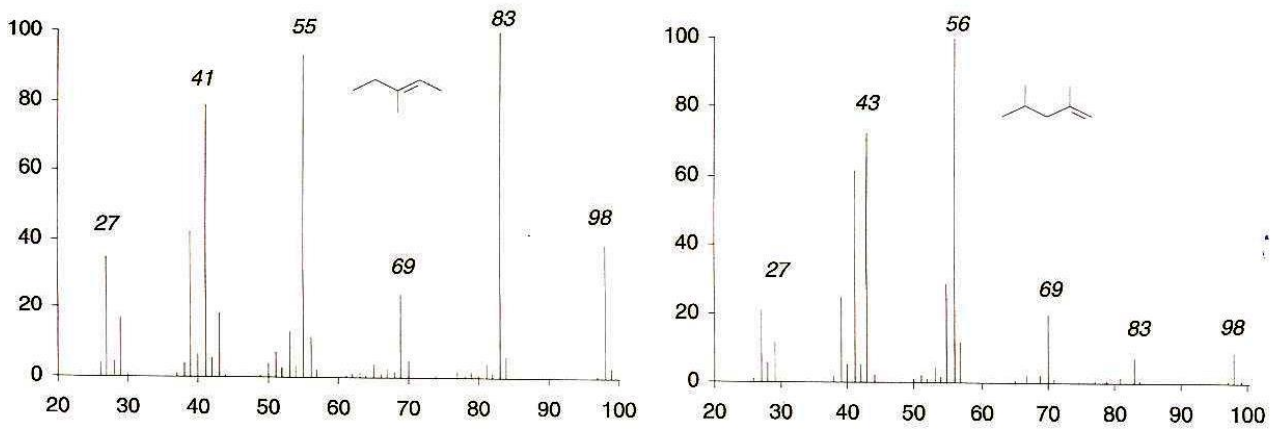


FIGURE 2.6c. Cyclohexane.

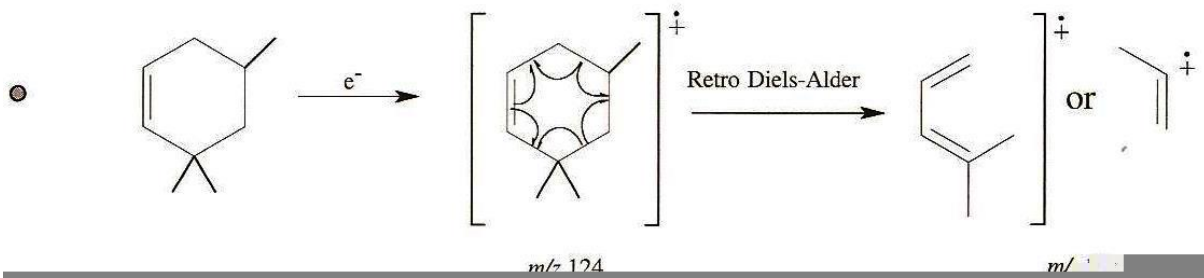
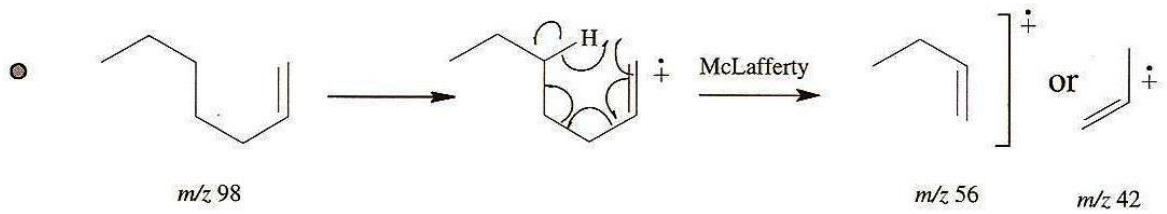
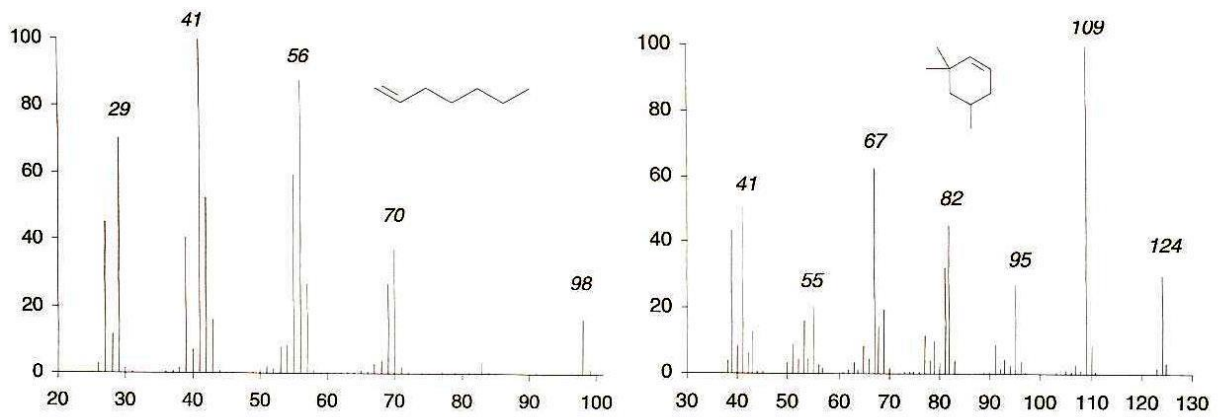
Espectro de massas de um cicloalcano substituído



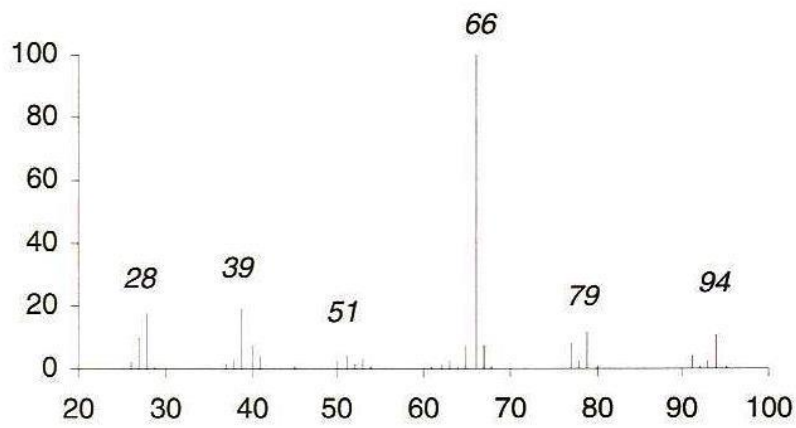
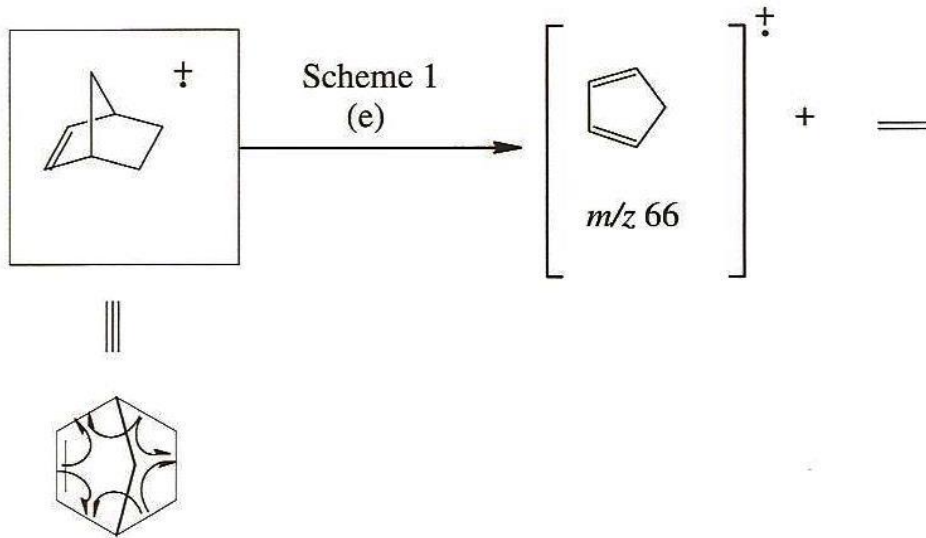
Espectros de massas de alcenos



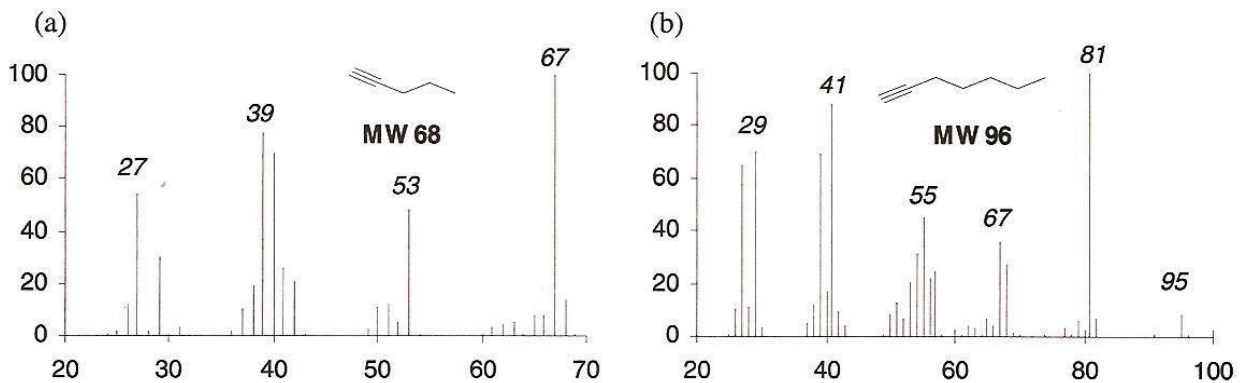
Espectros de massas de alcenos



Espectro de massas de um cicloexeno



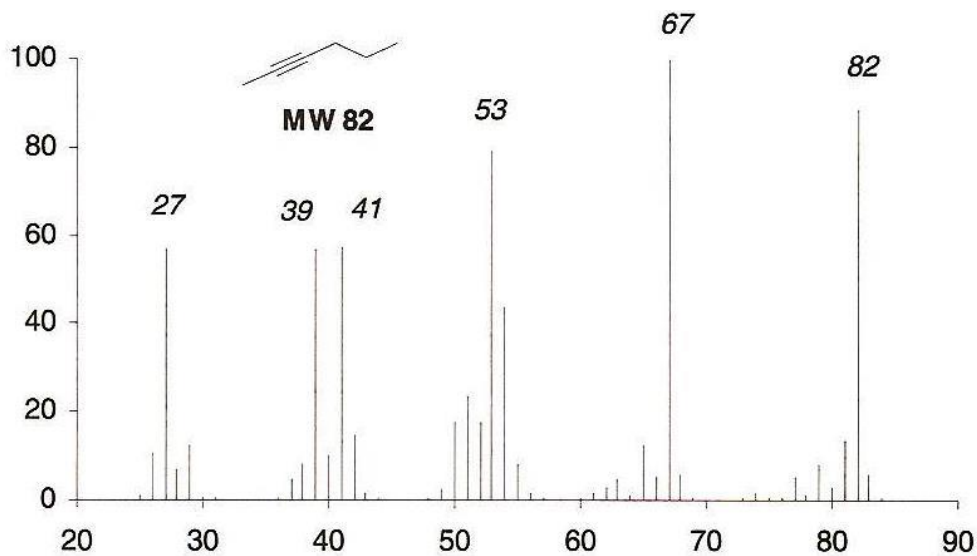
Espectro de massas de alcinos terminais



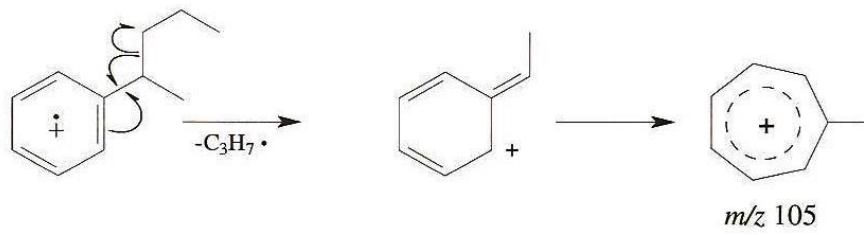
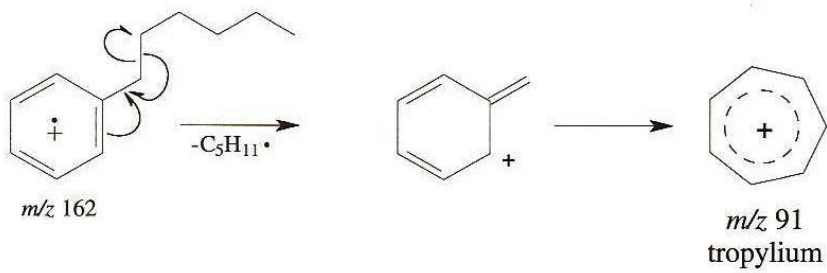
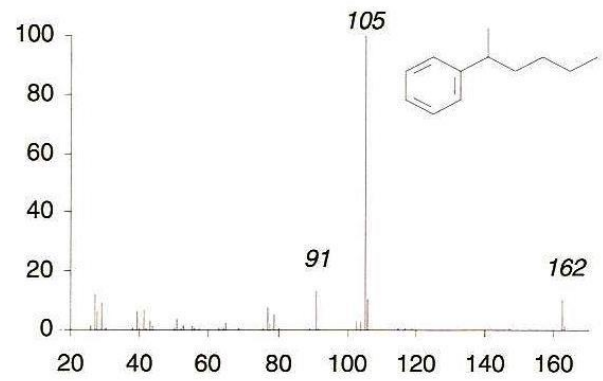
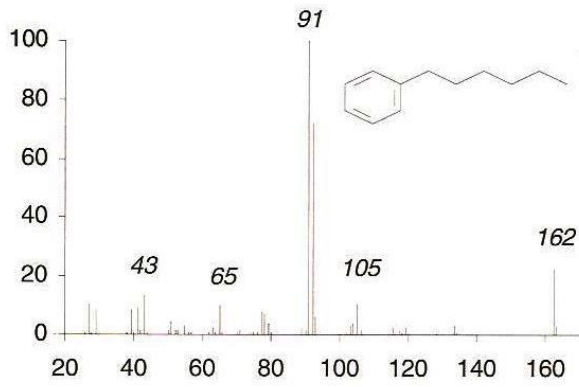
-Alcinos terminais geralmente não fornecem M^+ muito intenso, mas sim o $M-1$

-São geralmente reconhecidos pelo $m/z = 39$

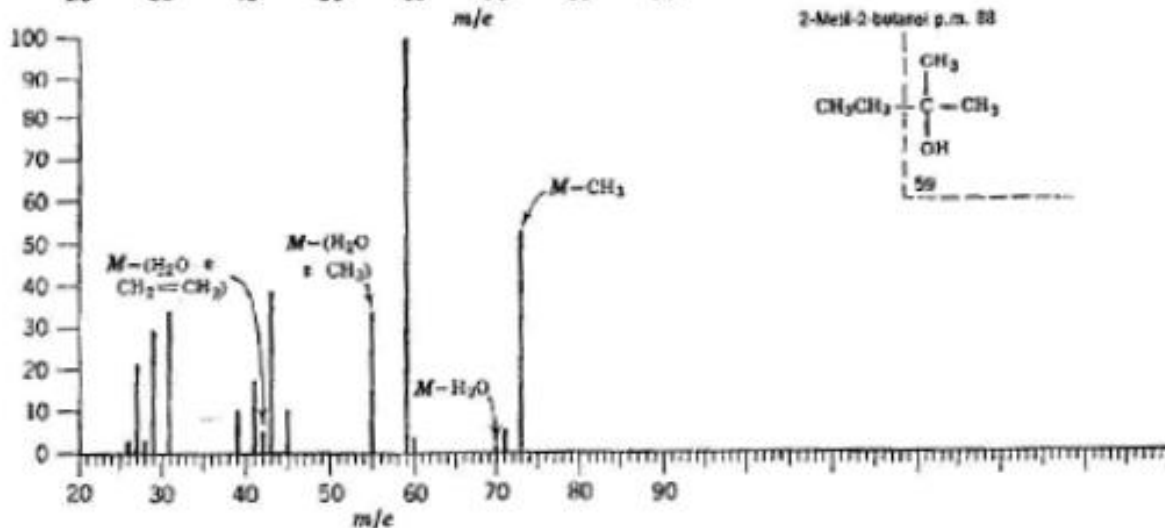
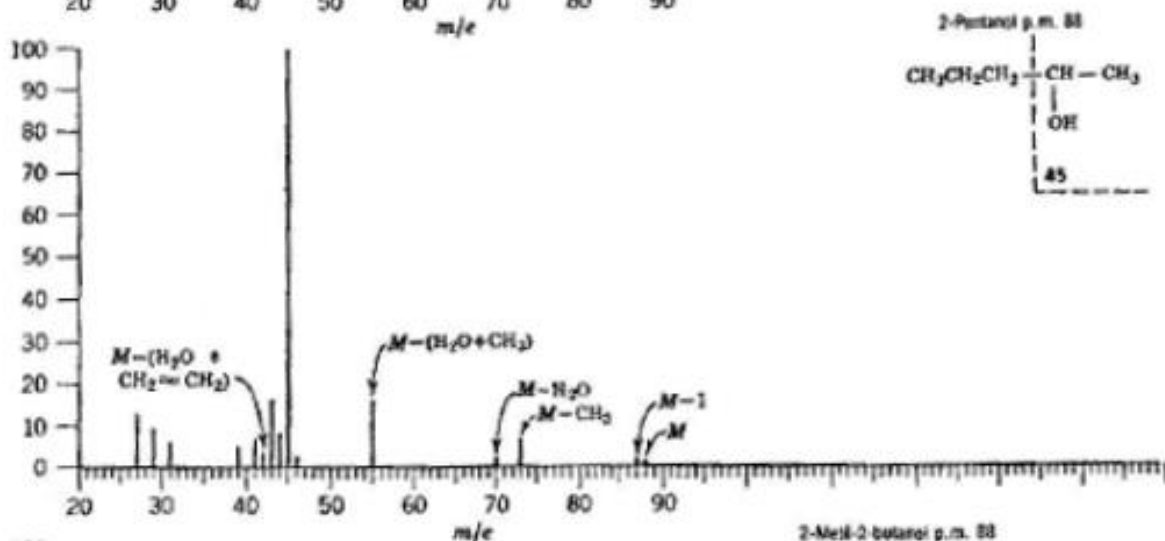
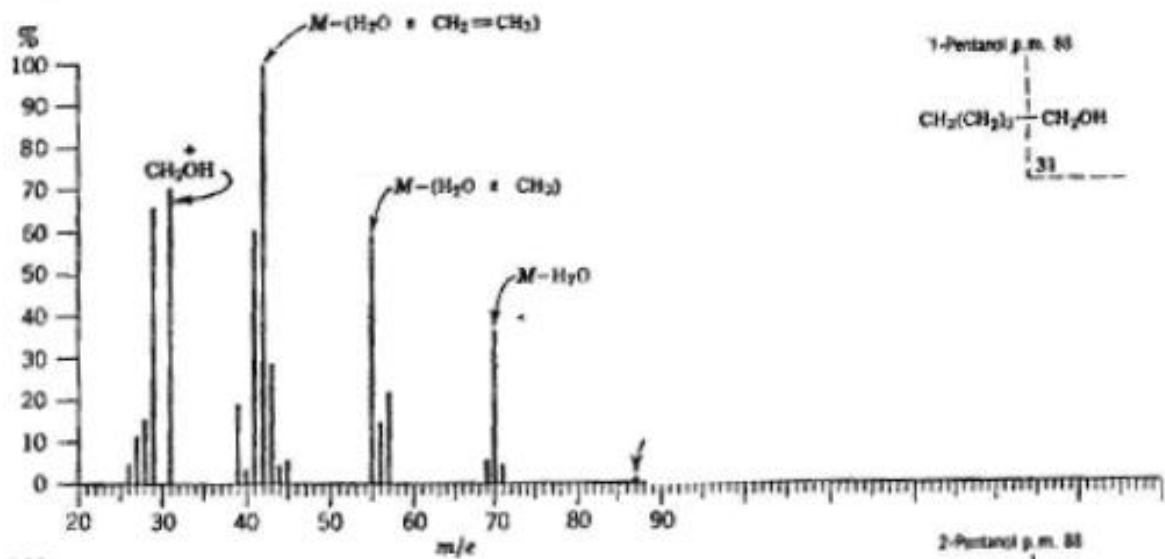
Espectro de massas de alcinos internos



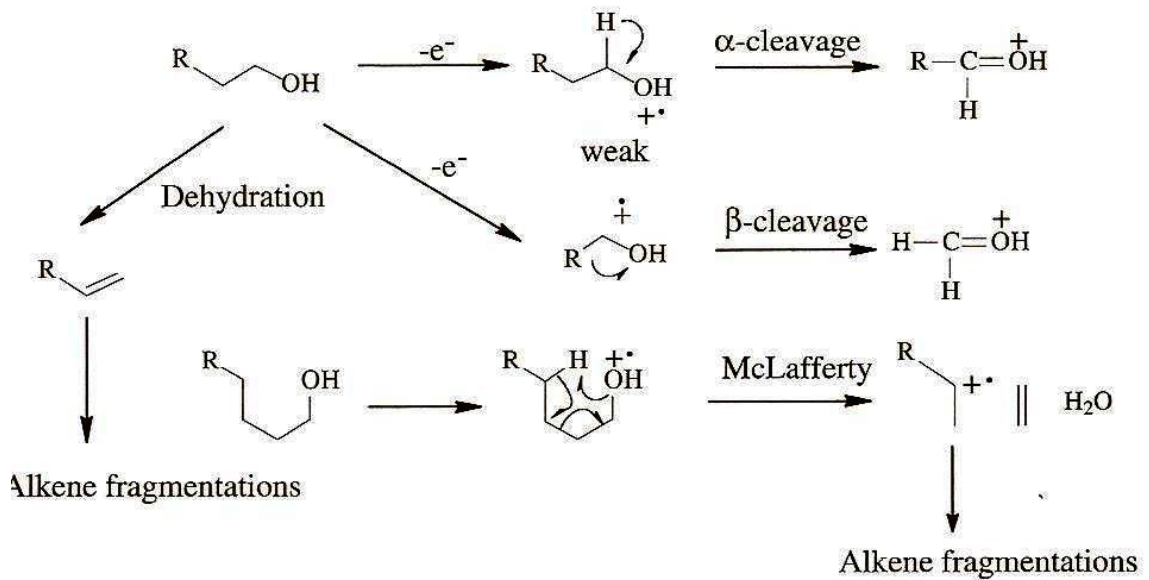
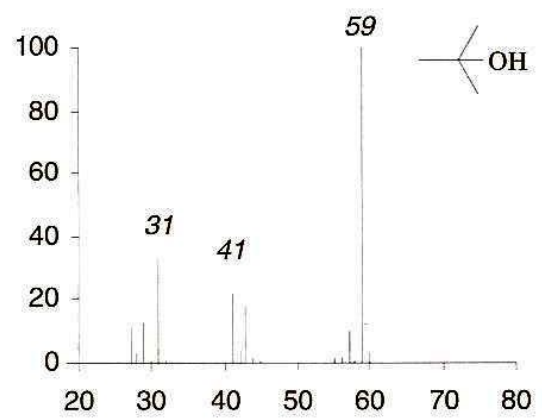
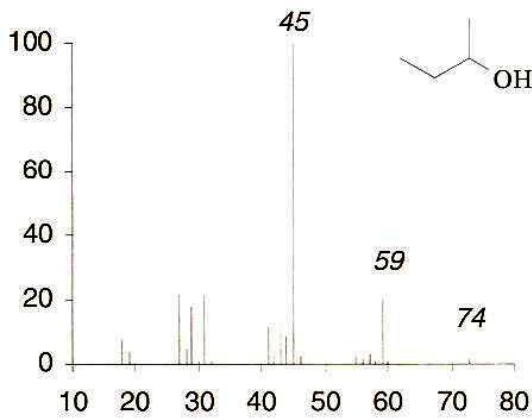
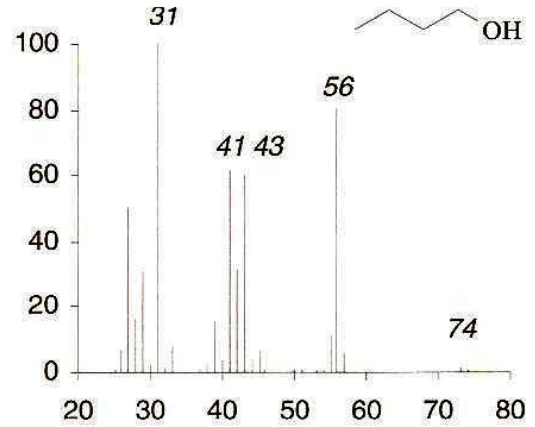
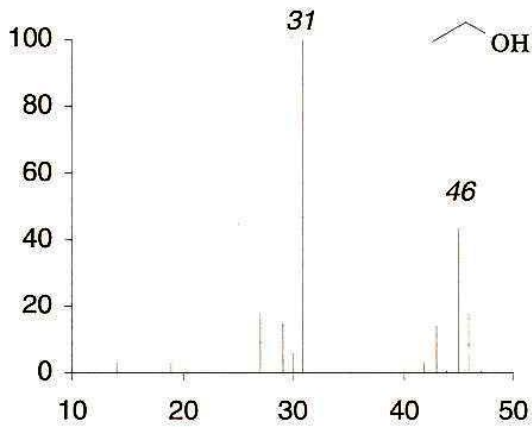
Espectros de massas de alquilbenzenos



Espectro de massas de álcoois

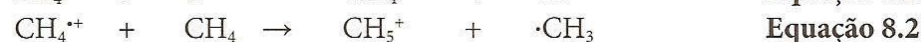
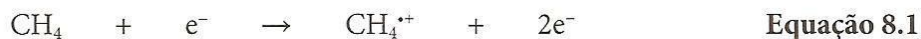


Espectros de massas de álcoois

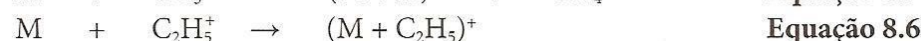


MÉTODOS DE IONIZAÇÃO:

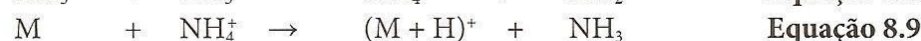
Ionização Química (CI)



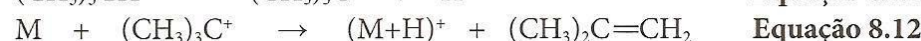
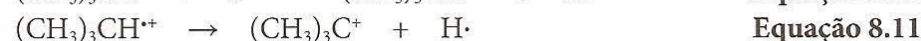
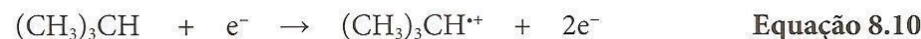
A molécula de amostra M é, então, ionizada, por meio de reação entre moléculas e íons nas Equações 8.5 e 8.6:



Essa situação é muito semelhante para CI tendo a amônia como gás reagente (Equações 8.7 a 8.9):



Usar o isobutano como gás reagente produz cátions *tert*-butila (Equações 8.10 e 8.11), que prontamente protonam sítios básicos na molécula da amostra (Equação 8.12). A formação de adutos também é possível usando o isobutano na CI/MS (Equação 8.13).



Resumo dos gases reagentes de ionização química

Tabela 8.1 Resumo dos gases reagentes de ionização química (CI)

Gás Reagente	Afinidade Protônica (kcal/mole)	Íon(s) Reagente(s)	Íon(s) Analítico(s)	Comentários
H ₂	101	H ₃ ⁺	(M + H) ⁺	Produz fragmentação significativa
CH ₄	132	CH ₅ ⁺ , C ₂ H ₅ ⁺	(M + H) ⁺ , (M + C ₂ H ₅) ⁺	Menos fragmentação do que H ₂ , pode formar adutos
NH ₃	204	NH ₄ ⁺	(M + H) ⁺ , (M + NH ₄) ⁺	Ionização seletiva, fragmentação pequena, pouca formação de adutos
(CH ₃) ₃ CH	196	(CH ₃) ₃ C ⁺	(M + H) ⁺ [M + C(CH ₃) ₃] ⁺	Brando, protonação seletiva, fragmentação pequena
CH ₃ OH	182	CH ₃ OH ₂ ⁺	(M + H) ⁺	Grau de fragmentação observado entre o metano e o isobutano
CH ₃ CN	188	CH ₃ CNH ⁺	(M + H) ⁺	Grau de fragmentação observado entre o metano e o isobutano

COMPARAÇÃO ENTRE ESPECTROS REGISTRADOS COM EI e CI

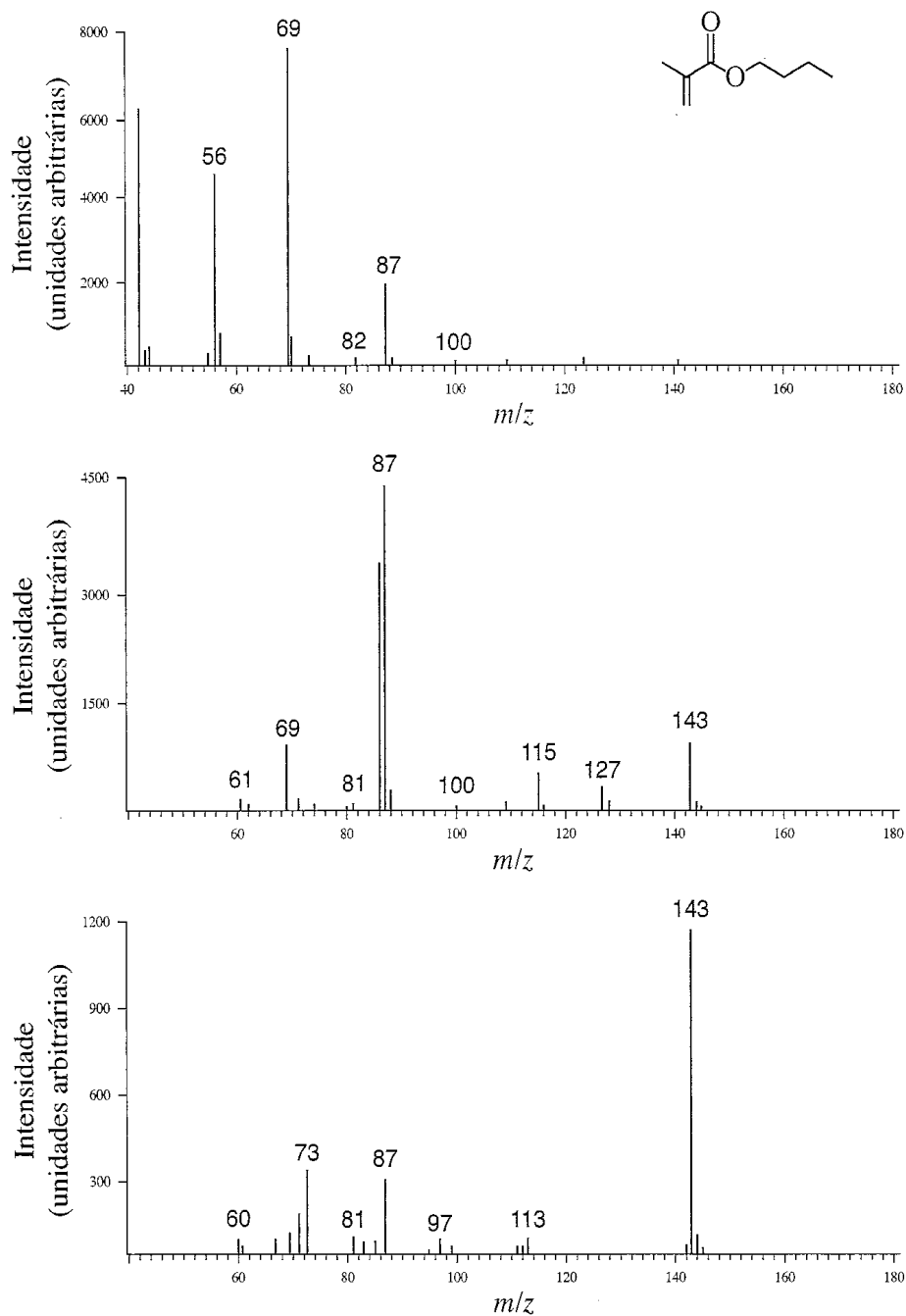


FIGURA 8.4 EM do metacrilato de butila obtido em condições EI (acima) e CI (metano, meio; isobutano, baixo). Fonte: DeHoffmann & Stroobant (1999). Reprodução autorizada.

COMPARAÇÃO ENTRE ESPECTROS REGISTRADOS EM CI USANDO DIFERENTES GASES

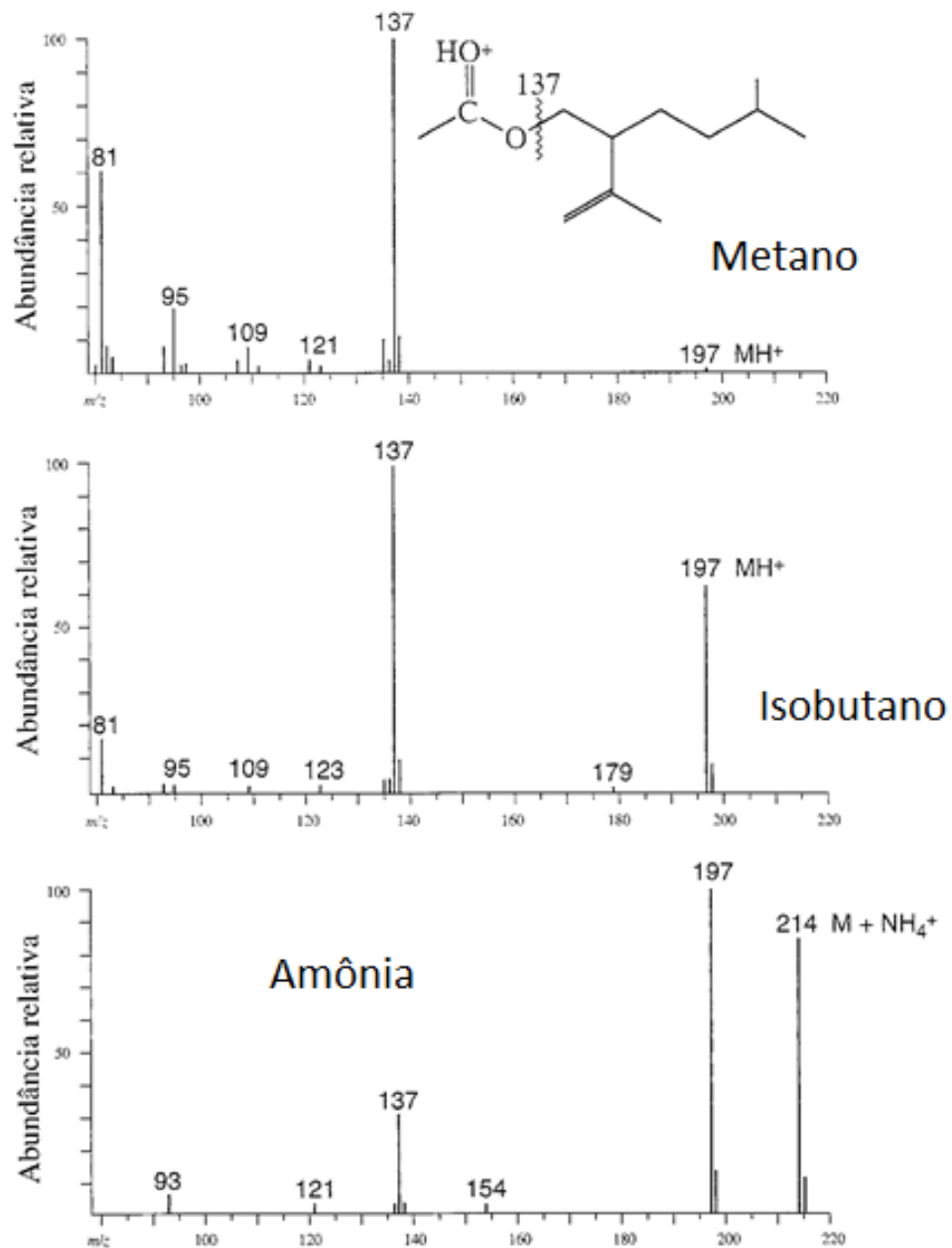
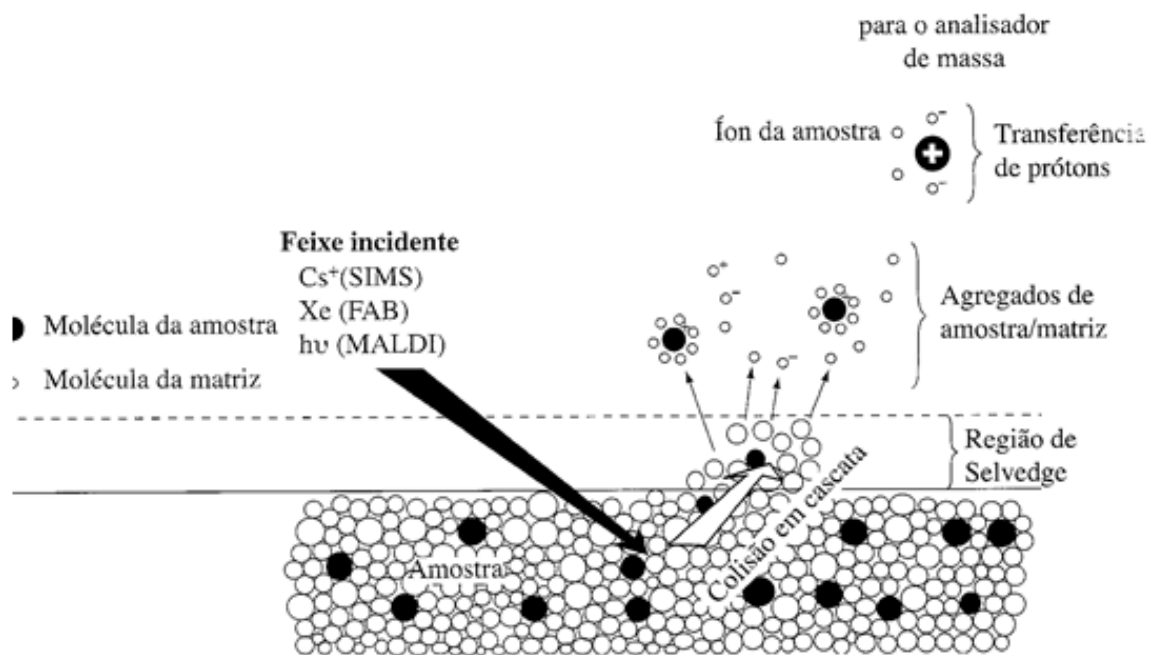


FIGURA 8.3 Comparação de dados CI/MS do acetato de lavandulila usando-se o metano (acima), isobutano (meio) e a amônia (baixo) como gases reagentes. Fonte: McLafferty & Tureček (1993). Reprodução autorizada.

Representação esquemática de técnicas de ionização por dessorção

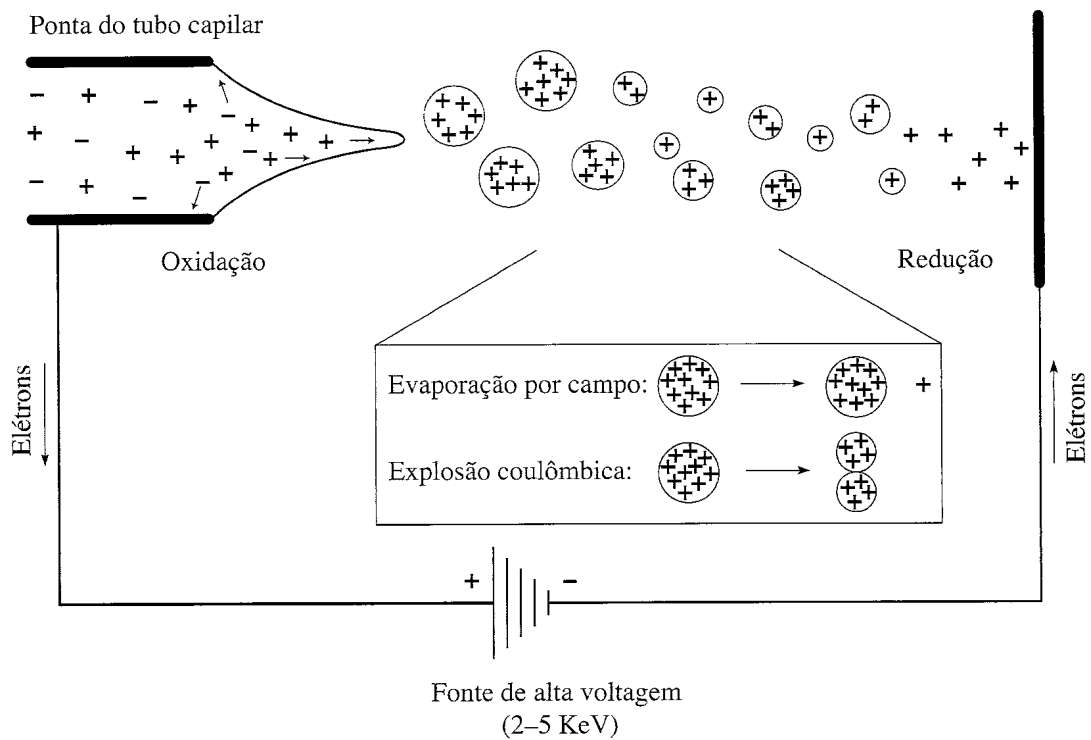


SIMS = (Cs^+) Secondary ion mass spectroscopy - Spectrometria de massa de íons secundários

FAB = (Xe) Fast Atomic Bombardment – Bombardeamento rápido de átomos rápidos

MALDI = ($h\nu$) Matrix Assisted Laser Desorption Ionization – Ionização por Dessorção a Laser Assistido por matriz

Representação esquemática de ionização por eletrospray (ESI)



Evaporação por campo e explosão coulômbica.

ESI = Electron Spray Ionization

Espectro de massas de fenóis

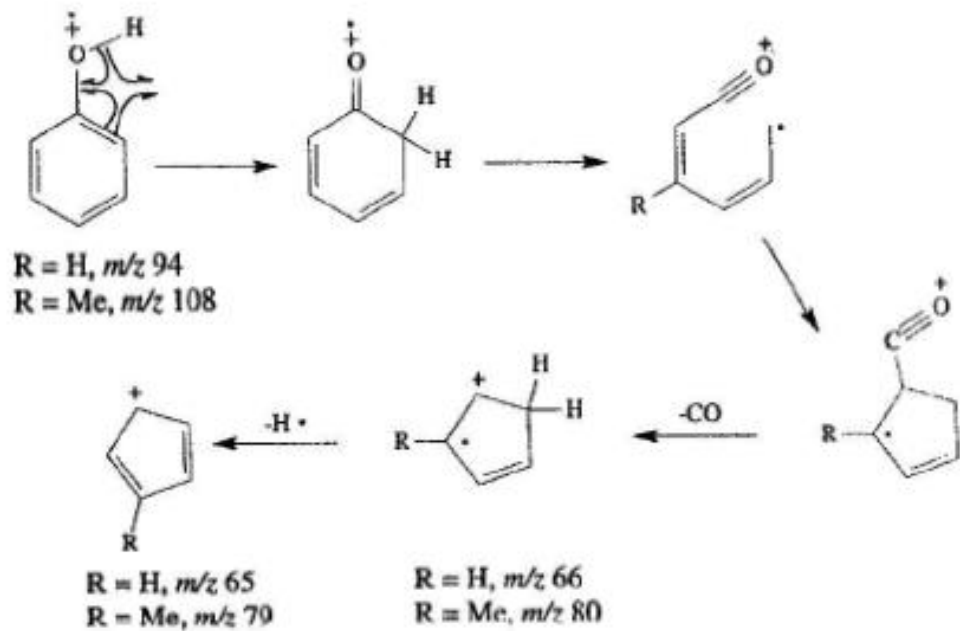
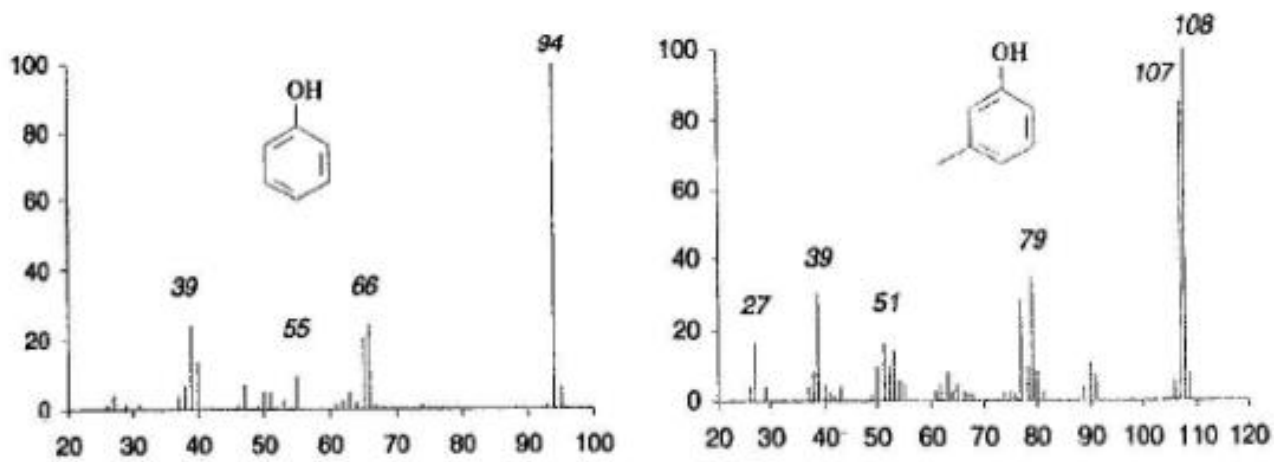
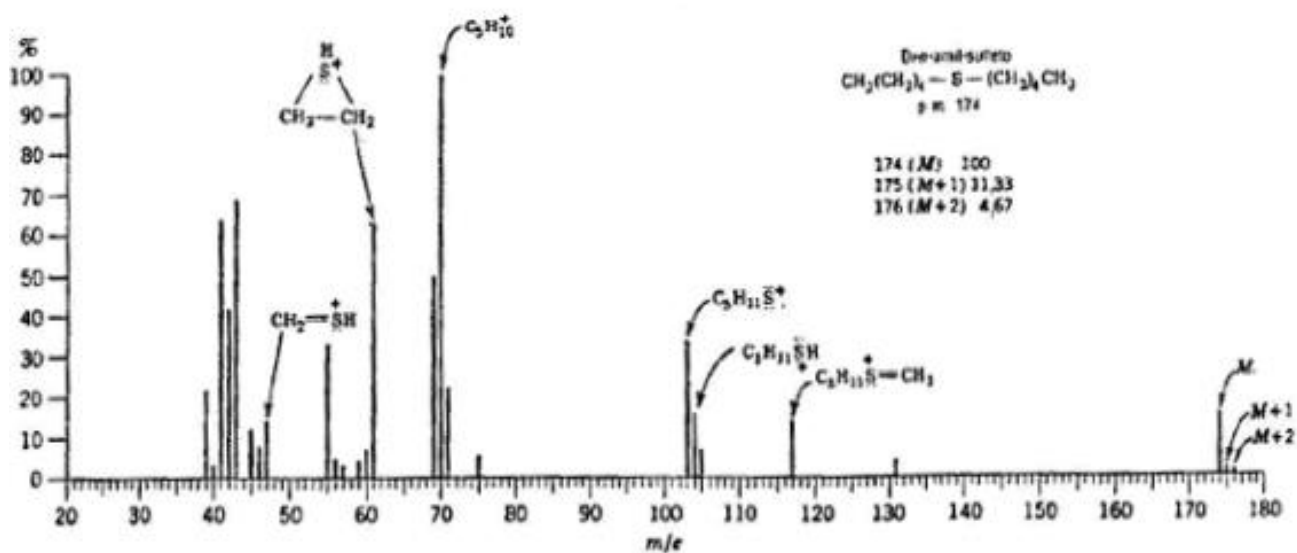
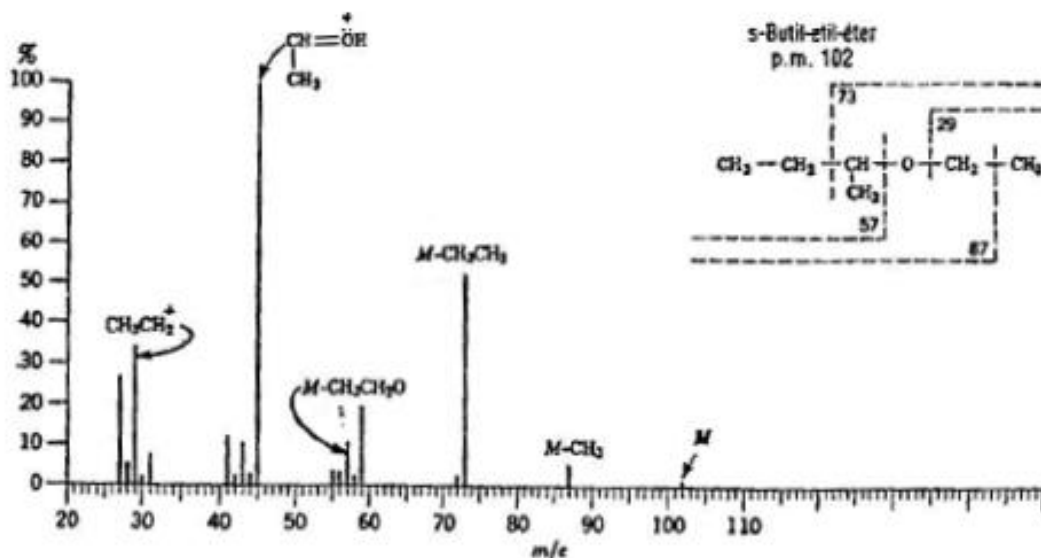


FIGURE 6.27 EIMS of phenols.

Espectro de massas de éteres e tioéteres



Mecanismo de fragmentação de um éter

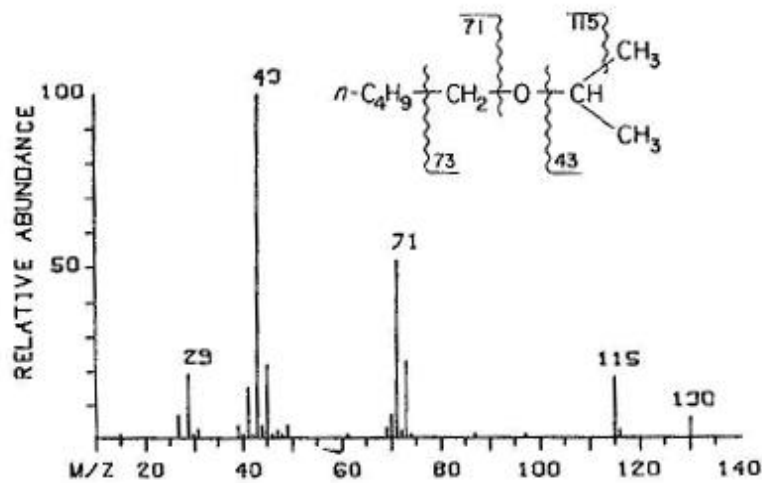
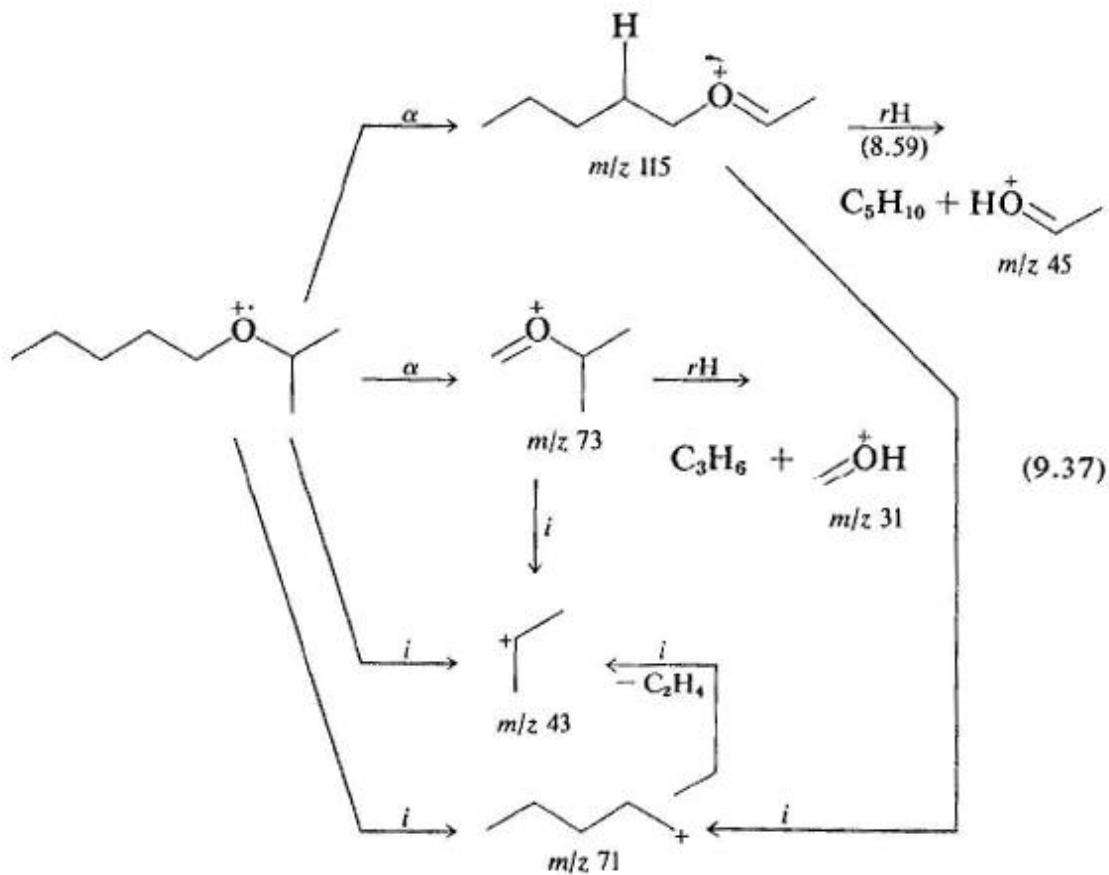


Figure 9N. Mass spectrum of isopropyl *n*-pentyl ether. (The relative abundance of *m/z* 131 increases with increasing sample pressure.)



Mecanismo de fragmentação de um tio éter

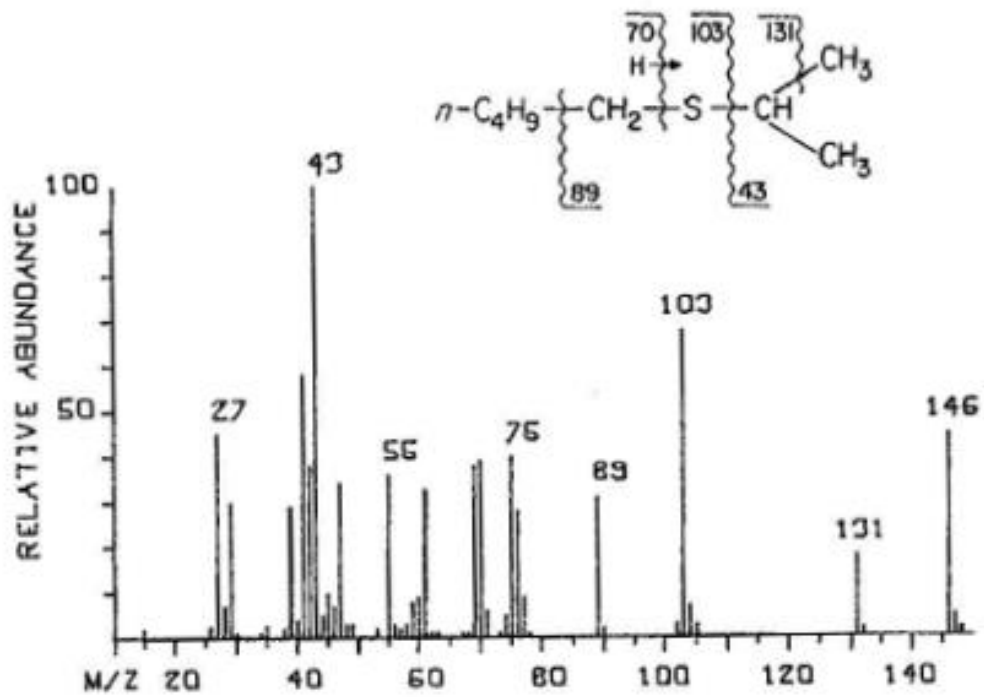


Figure 9Q. Mass spectrum of isopropyl *n*-pentyl sulfide.

Espectros de massas de aminas

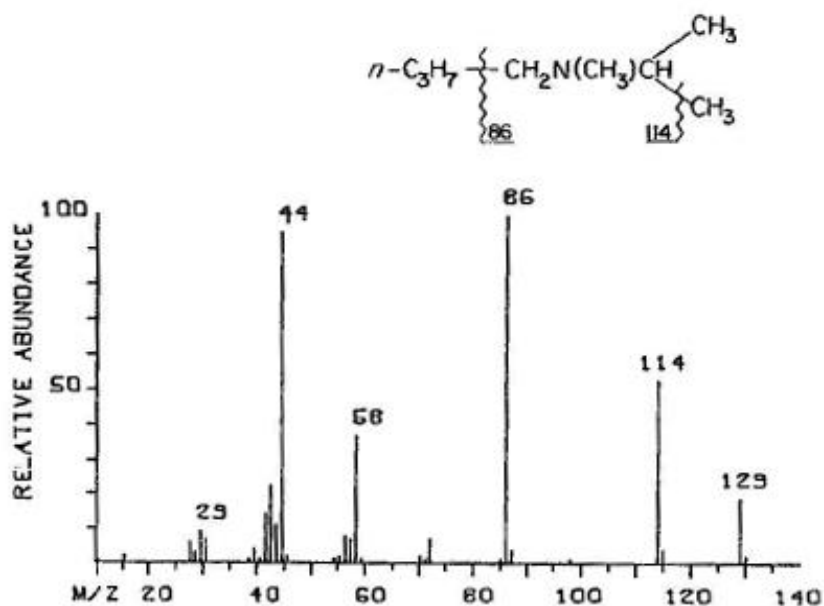


Figure 9R. Mass spectrum of *N*-methyl-*N*-isopropyl-*N*-*n*-butylamine. (Relative abundance of the *m/z* 130 peak increases with increasing sample pressure.)

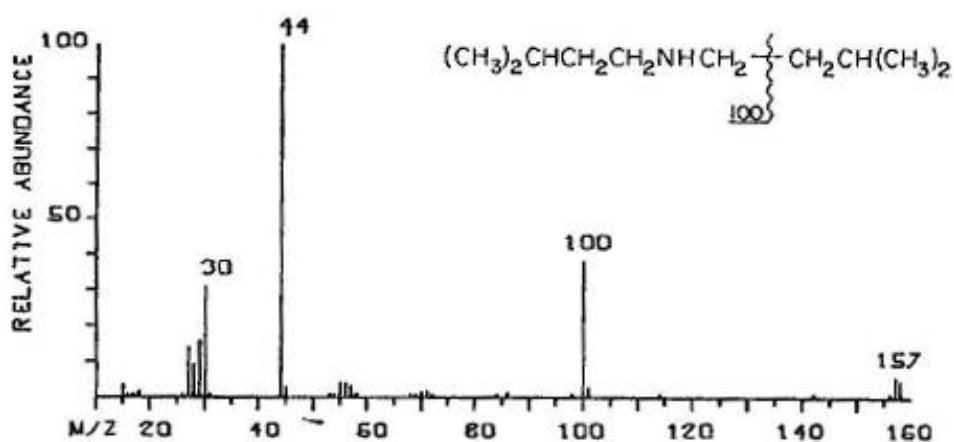
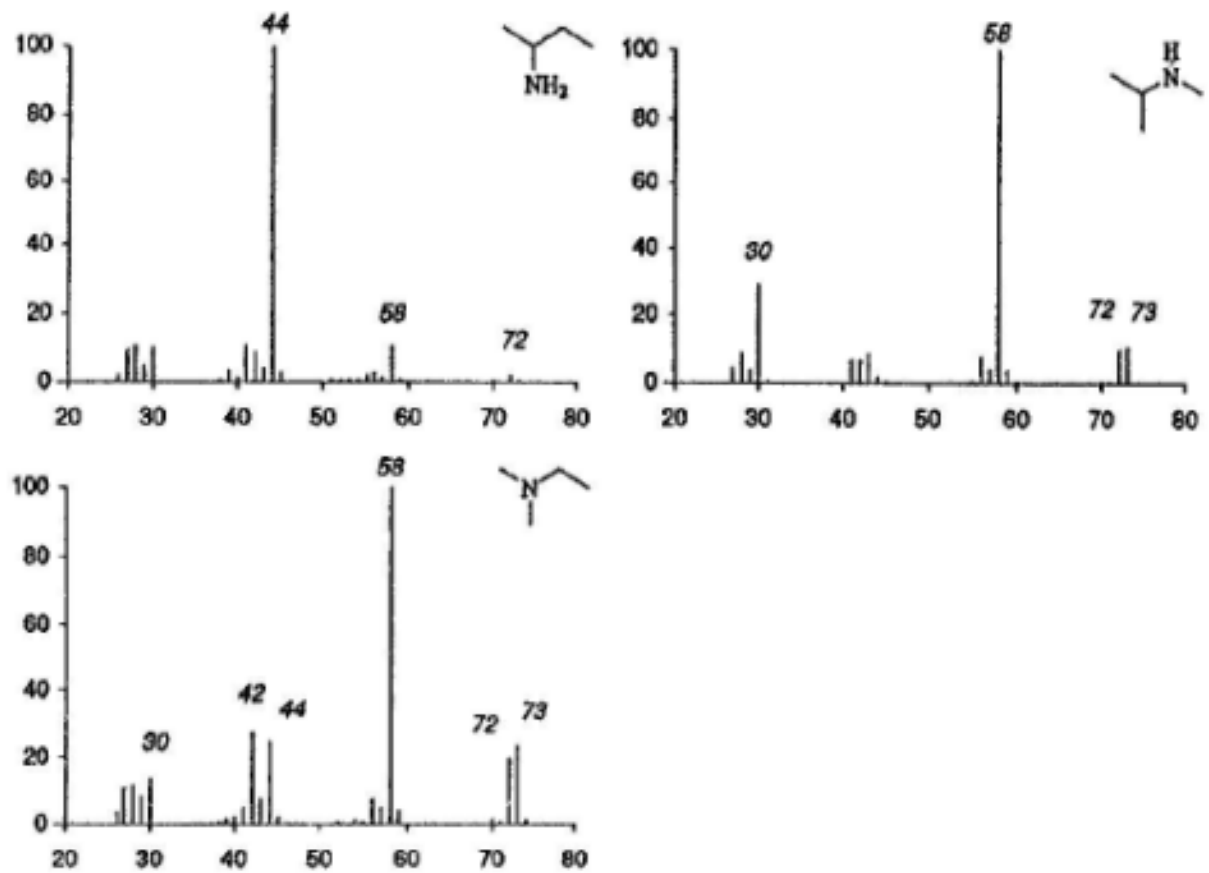
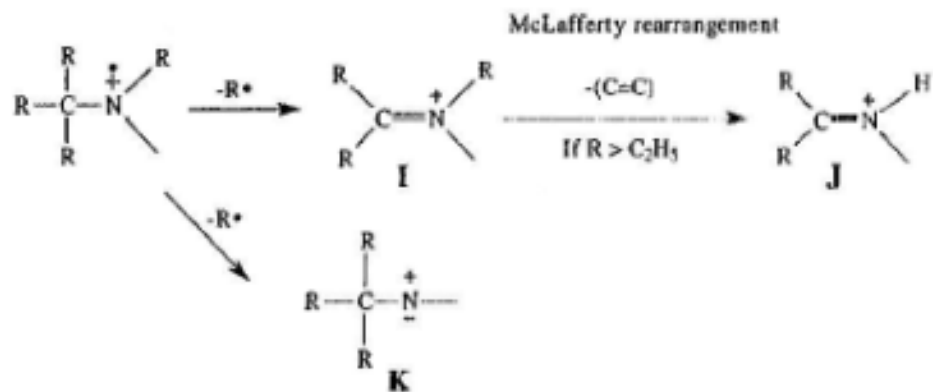


Figure 9S. Mass spectrum of *bis*(3-methylbutyl)amine. (Relative abundance of the *m/z* 158 peak increases with increasing sample pressure.)

Espectro de massas de aminas



Typical fragments in acyclic amines.



Espectro de massas de aminas cíclicas

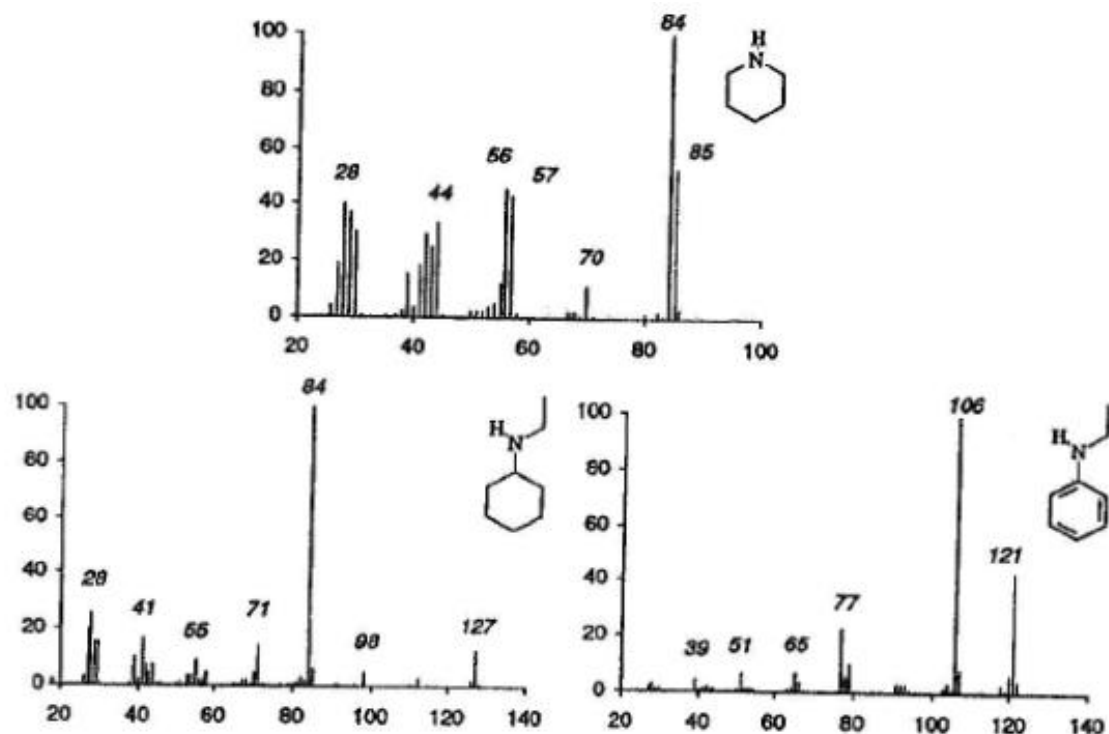
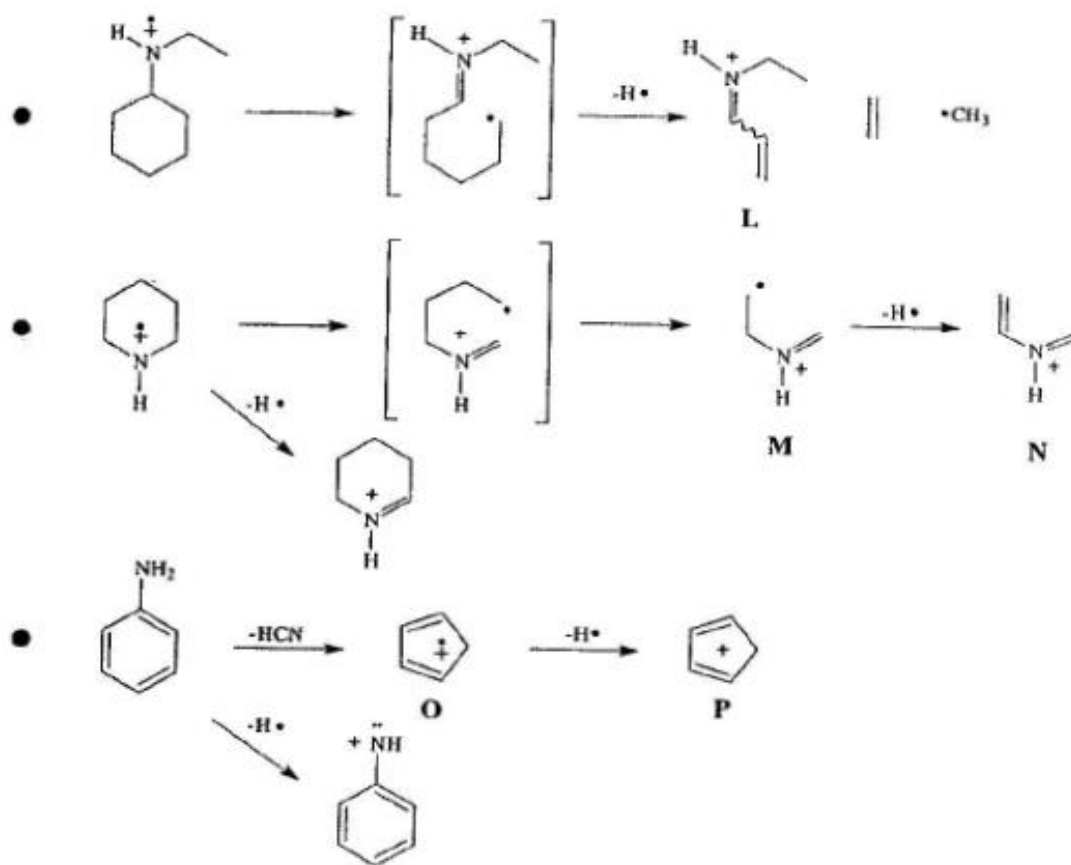


FIGURE 6.30 EIMS of amines.



Espectro de massas de aldeídos

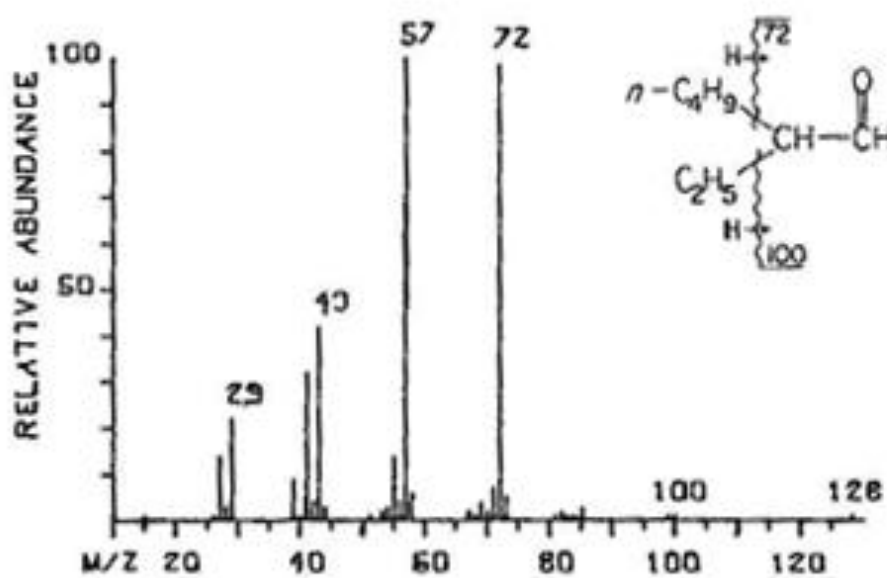
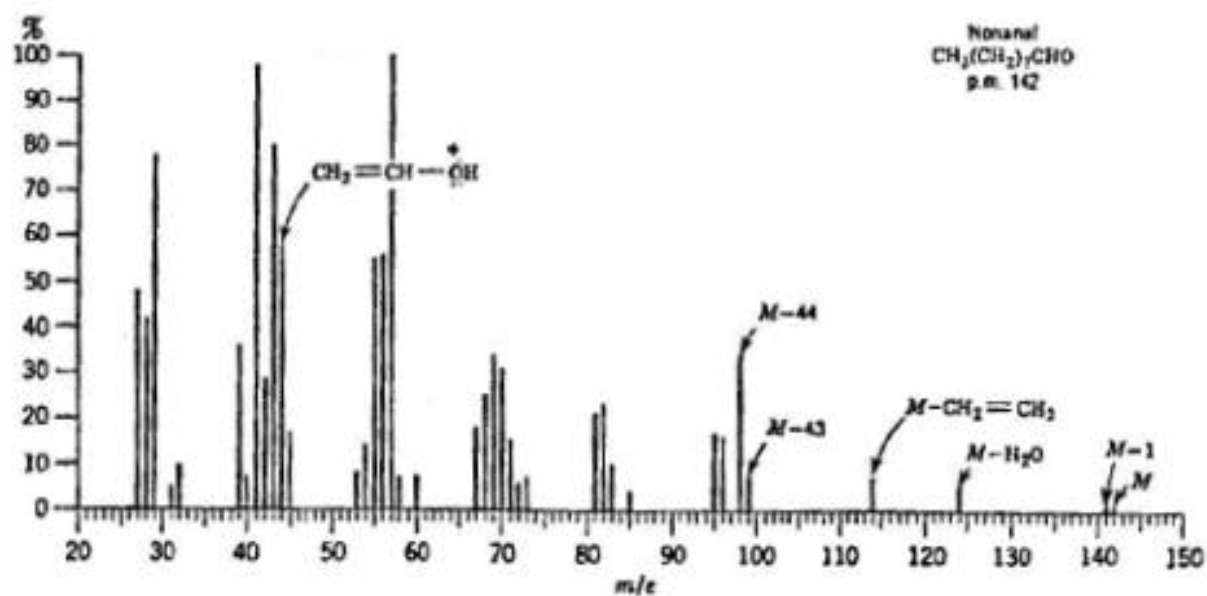


Figure 9H. Mass spectrum of 2-ethylhexanal.

Espectro de massas de cetona

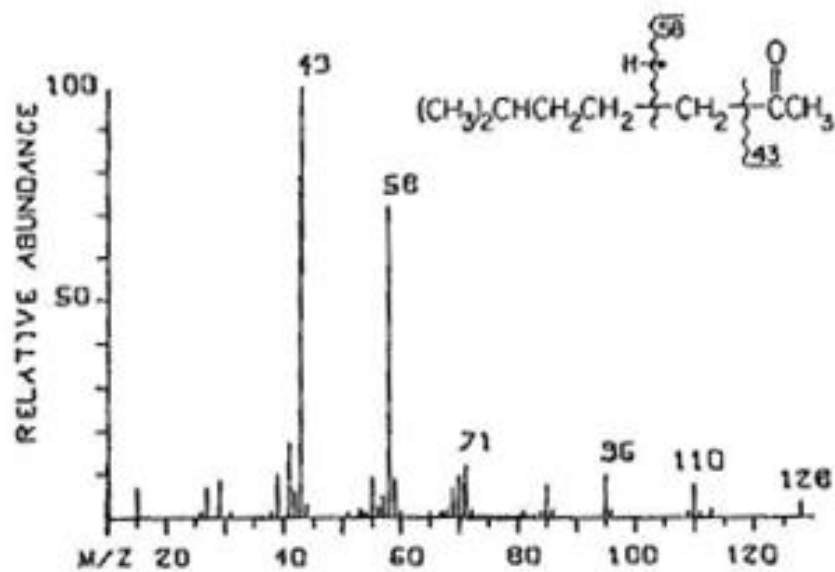


Figure 9I. Mass spectrum of 6-methyl-2-heptanone.

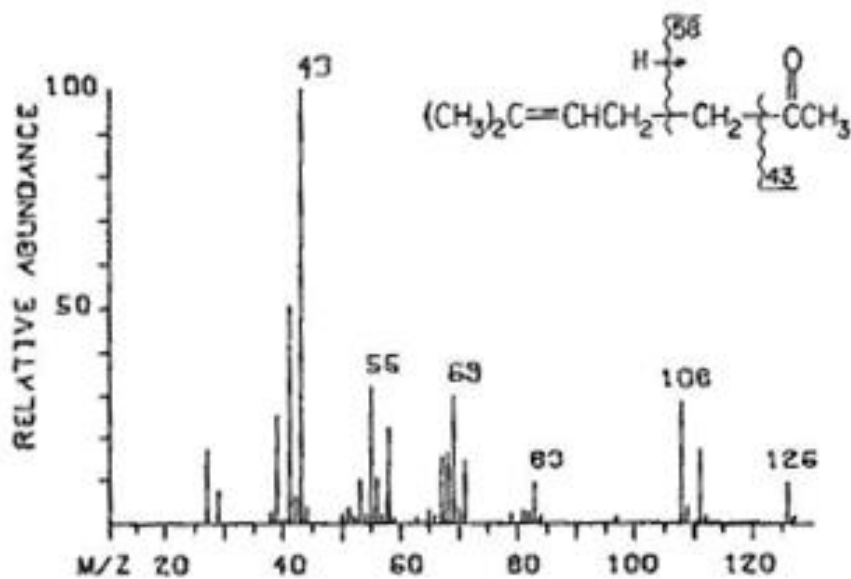
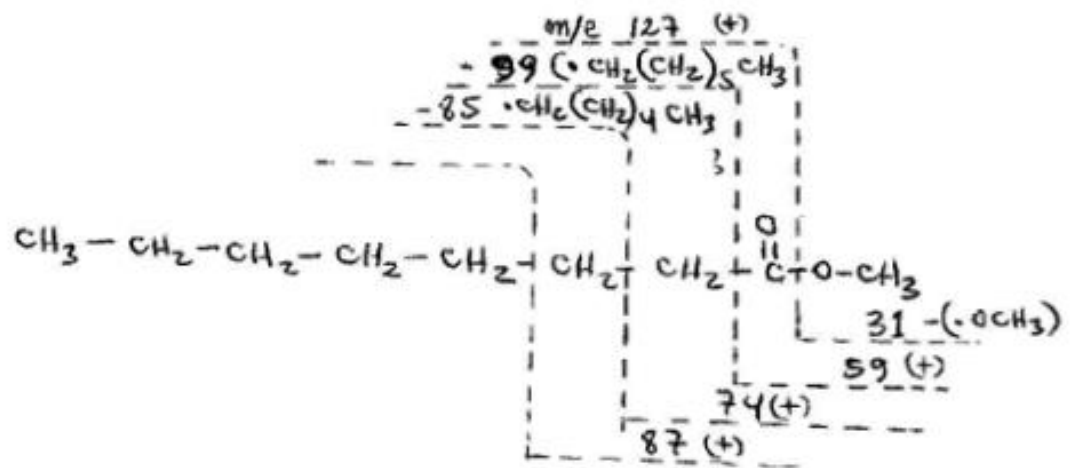
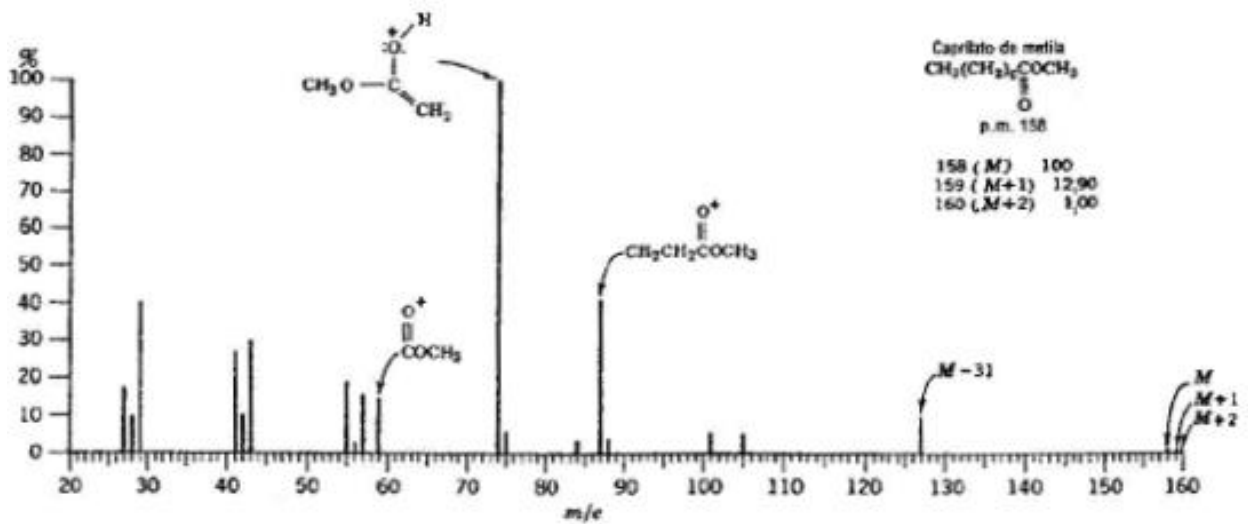
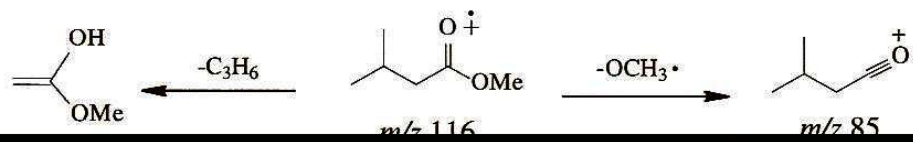
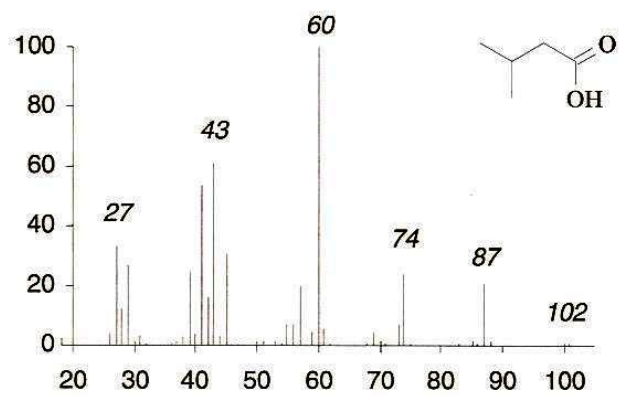
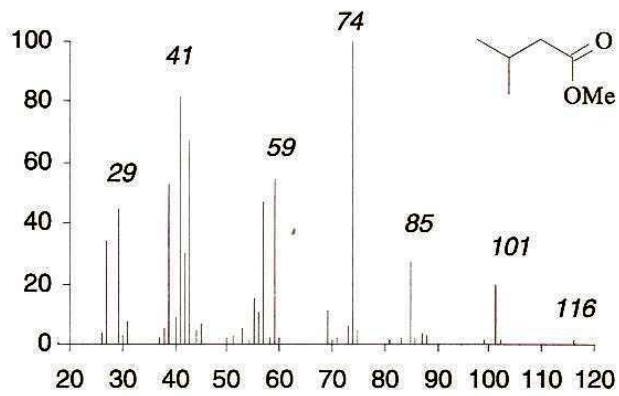


Figure 9J. Mass spectrum of 6-methyl-5-heptene-2-one.

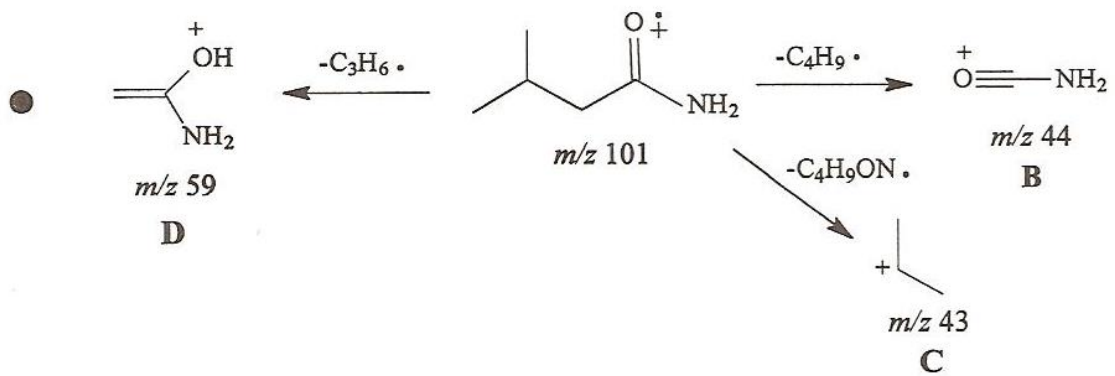
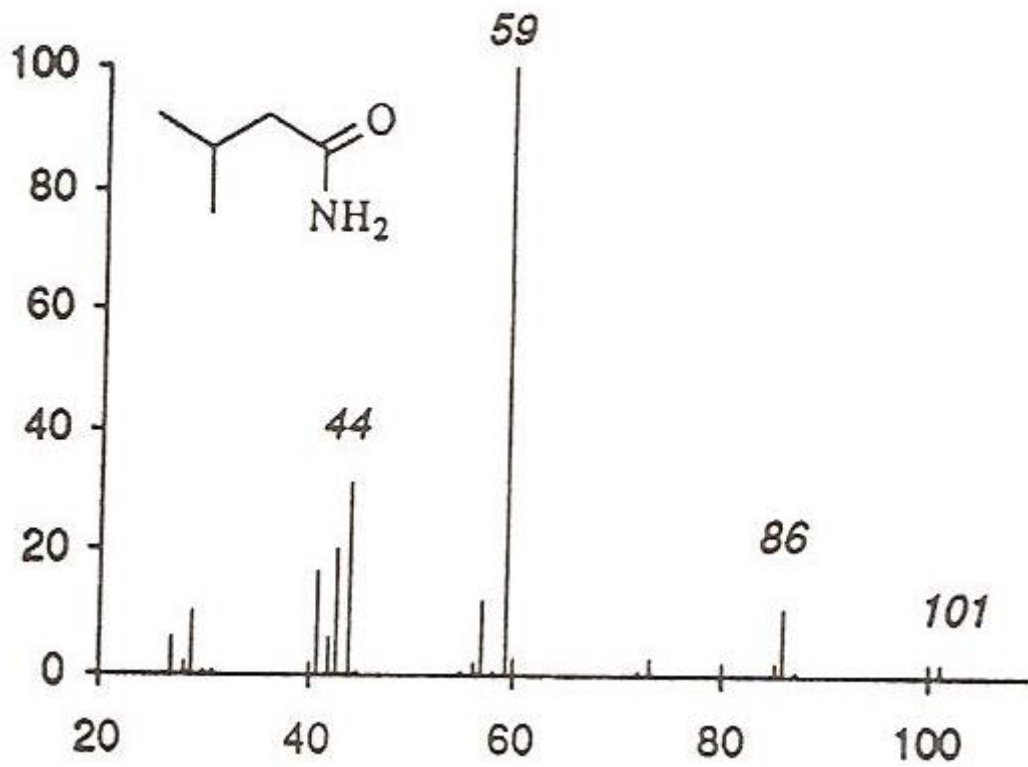
Espectro de massas de um éster



Espectro de massas de um éster



Espectro de massas de uma amida



Espectro de massas de uma amida

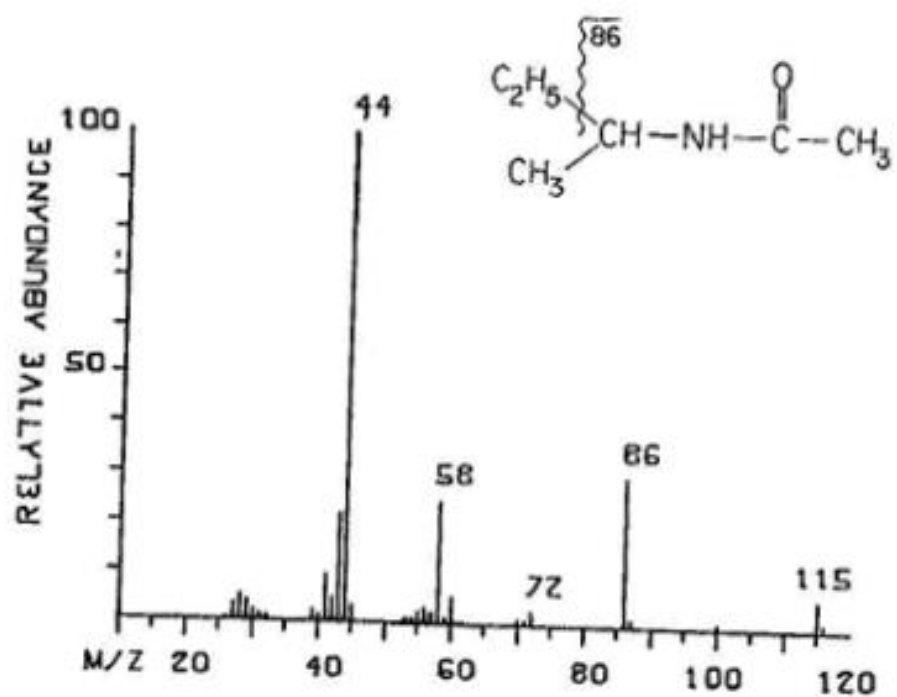
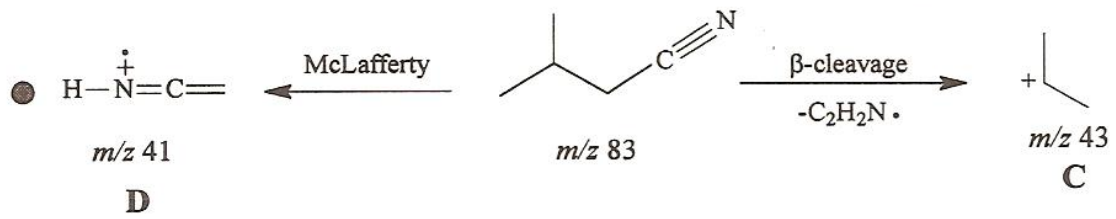
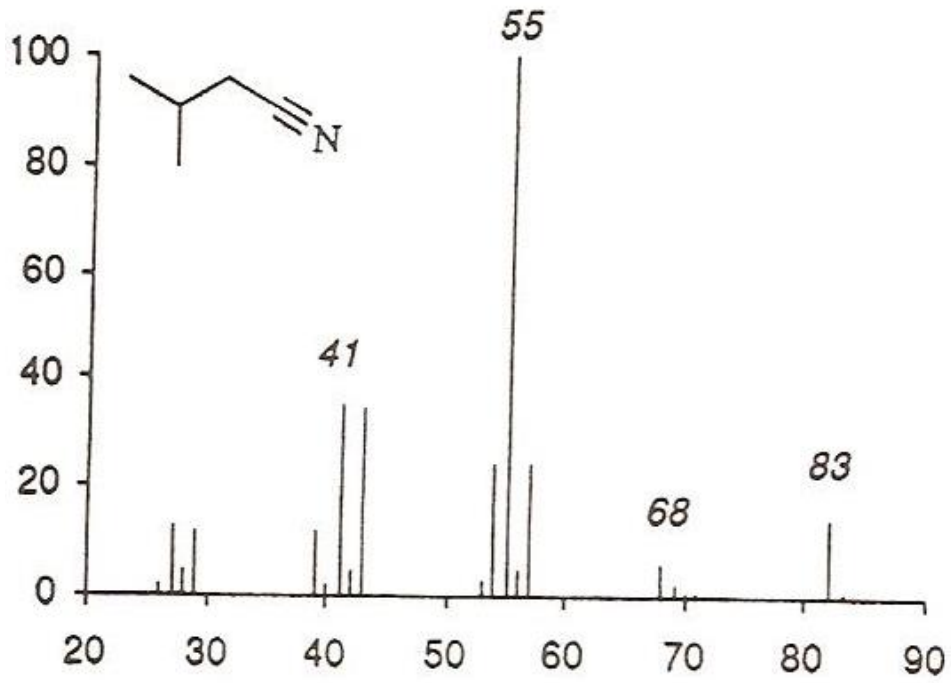
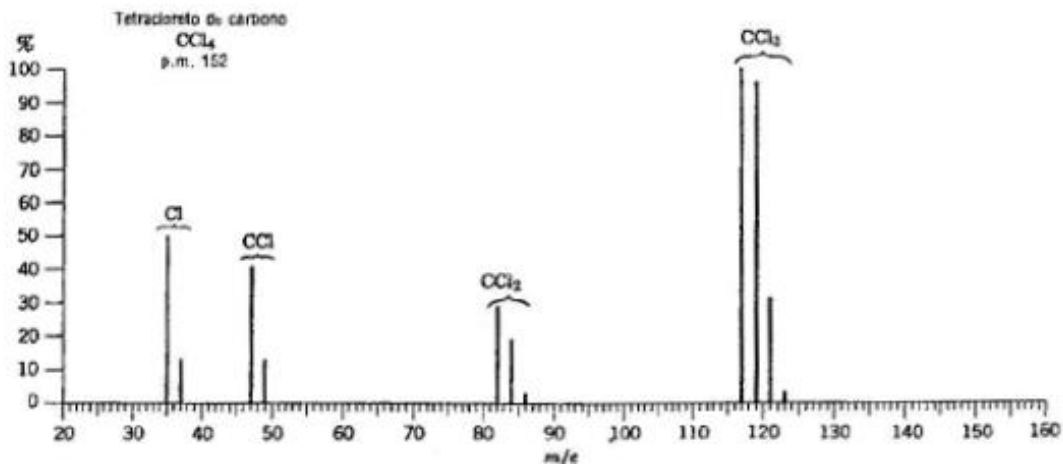


Figure 9T. Mass spectrum of *sec*-butyl acetamide.

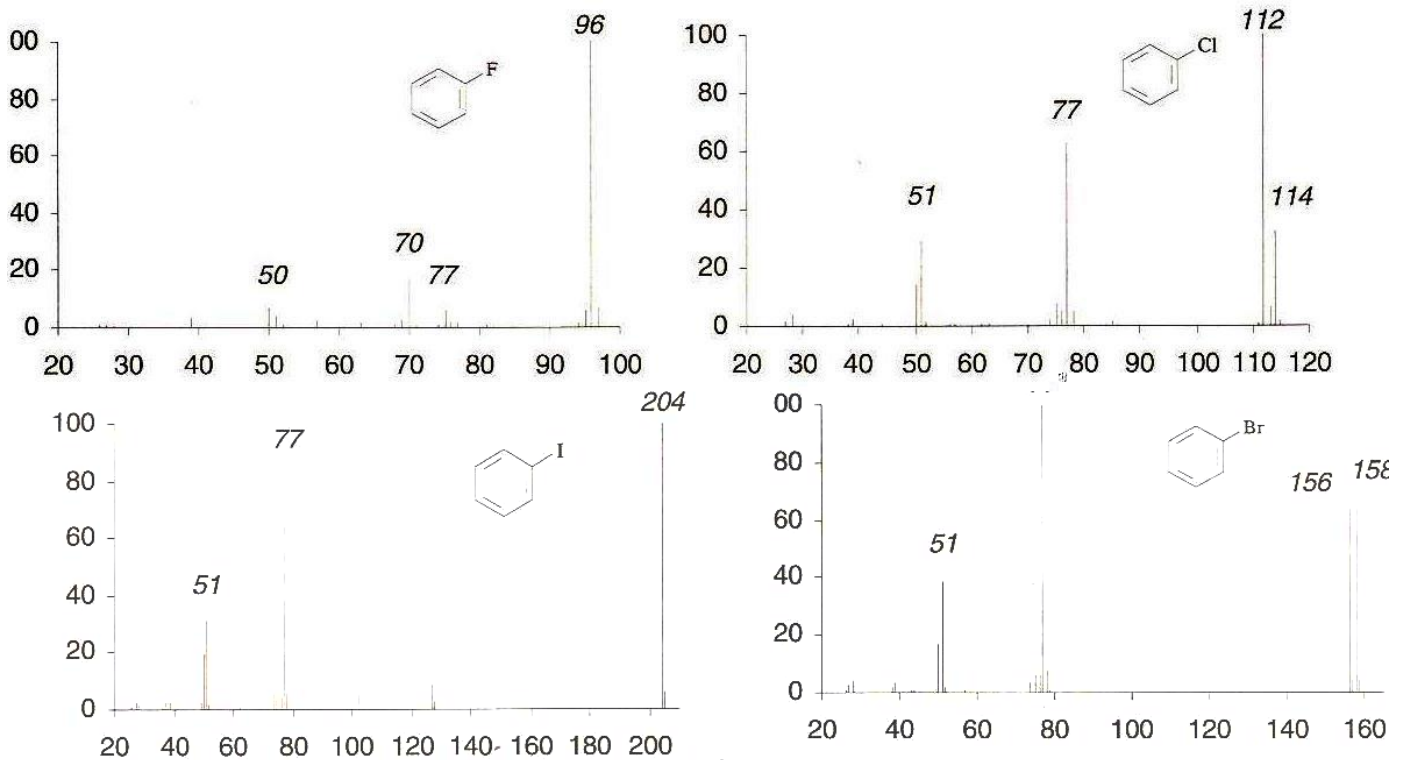
Espectro de massas de uma nitrila



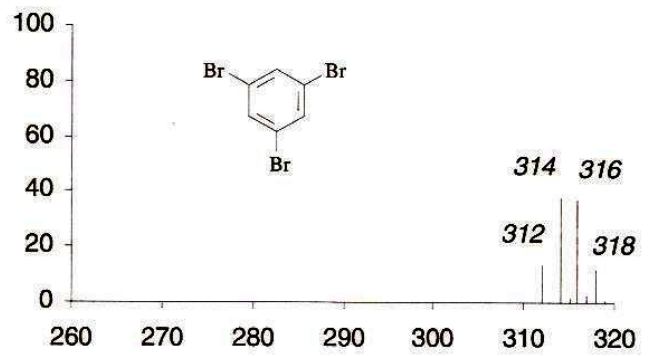
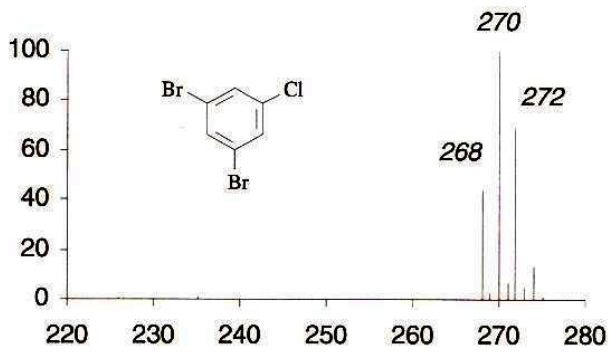
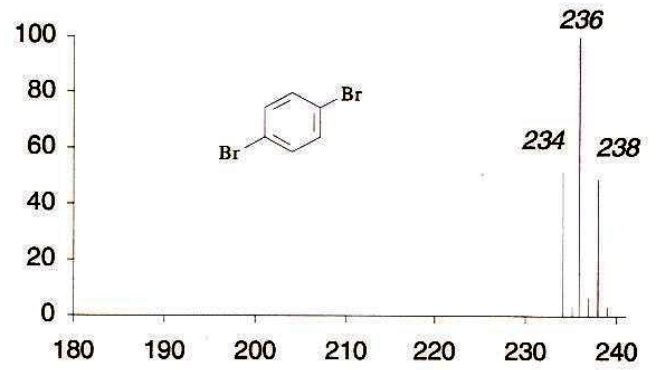
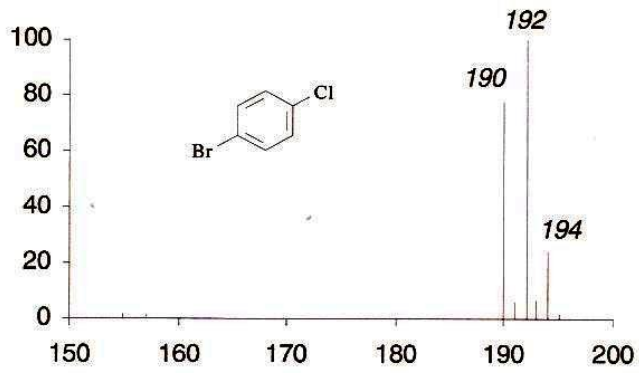
Espectro de massas do Tetracloreto de carbono



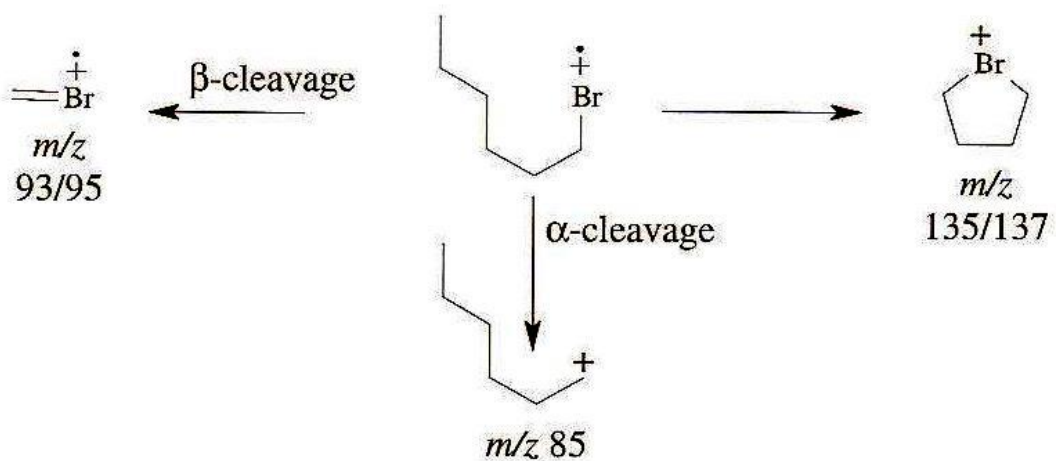
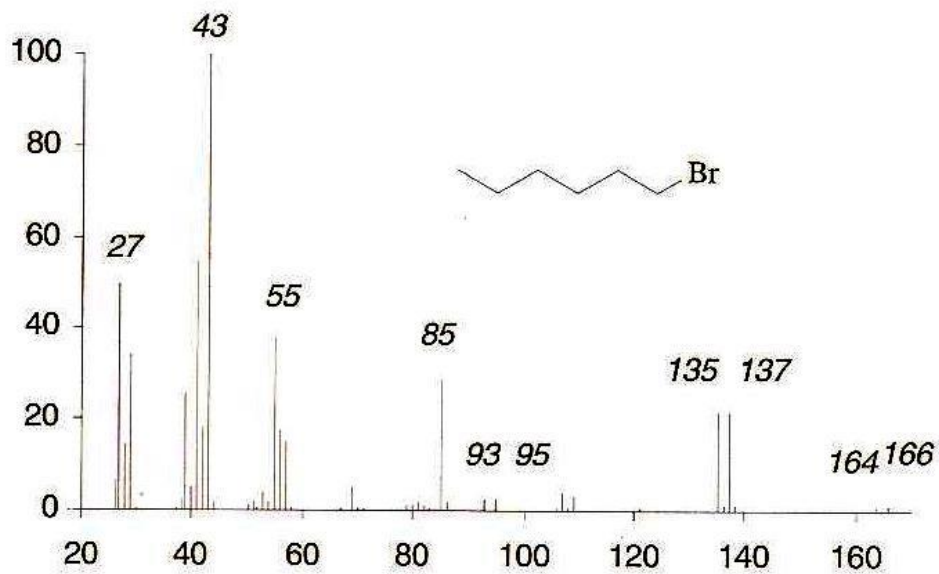
Espectros de massas de compostos halogenados



Espectro de massas de compostos halogenados



Espectro de massas de compostos halogenados



Espectro de massas de um éster halogenado

