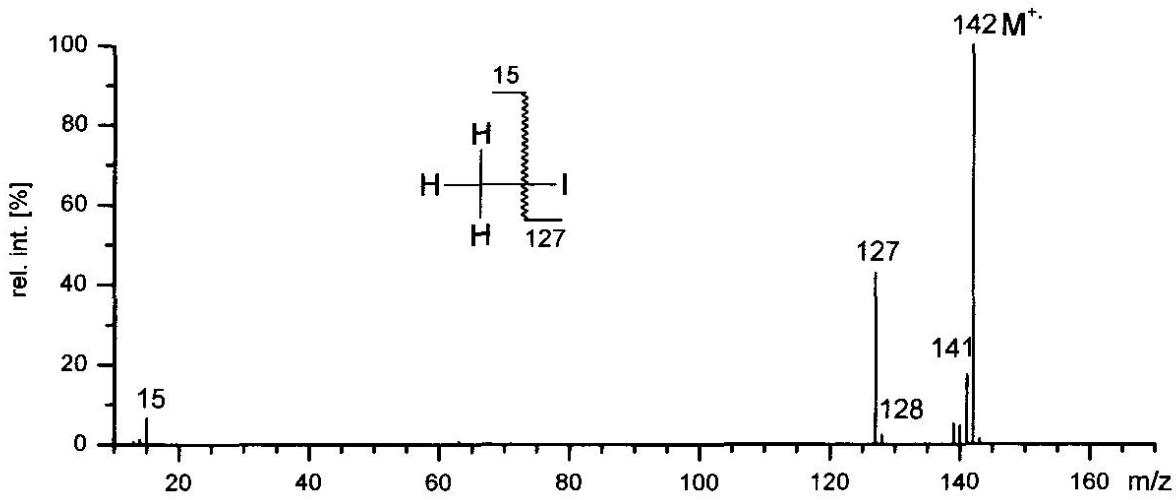
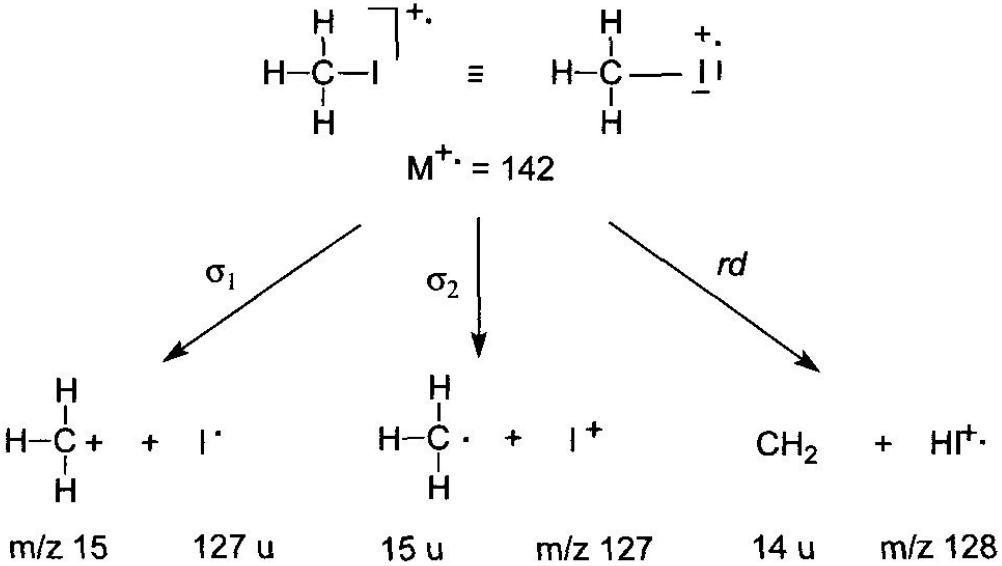
EM de moléculas simples funcionalizadas: clivagem σ

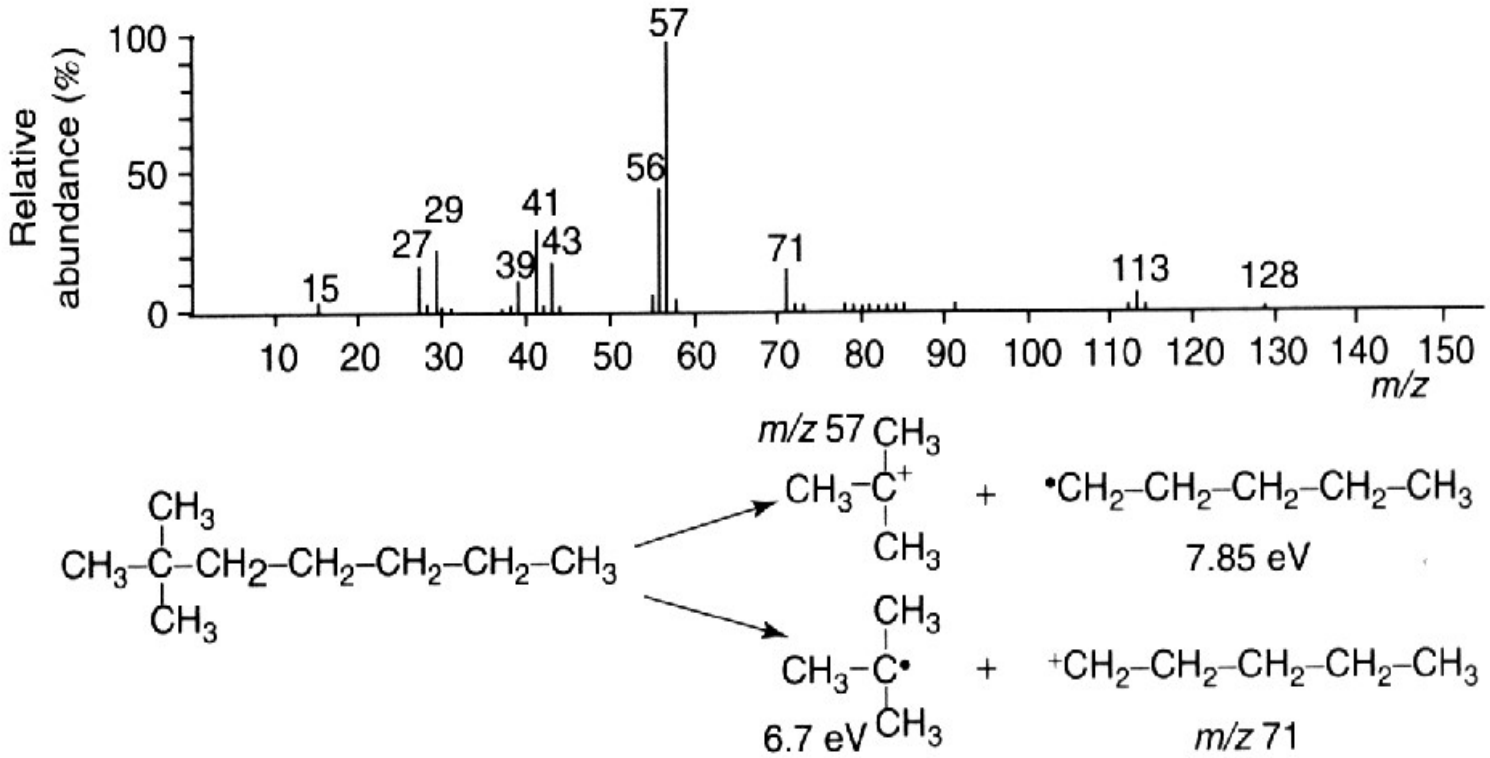
PF1





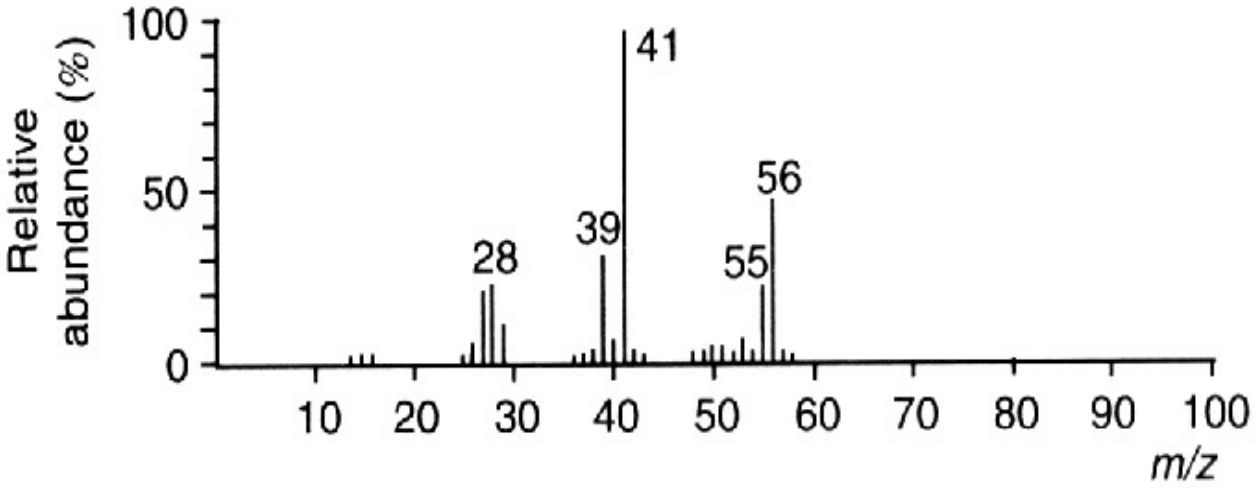
Clivagem do íon molecular: tendência do elétron não emparelhado permanecer com o fragmento de maior energia de ionização

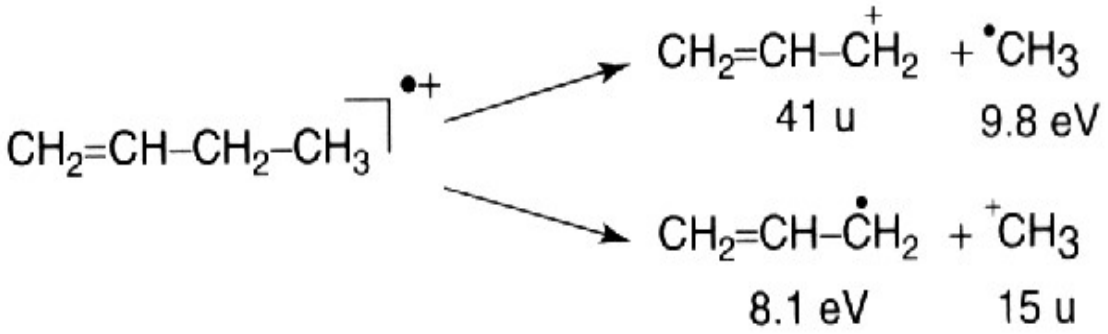
PF2



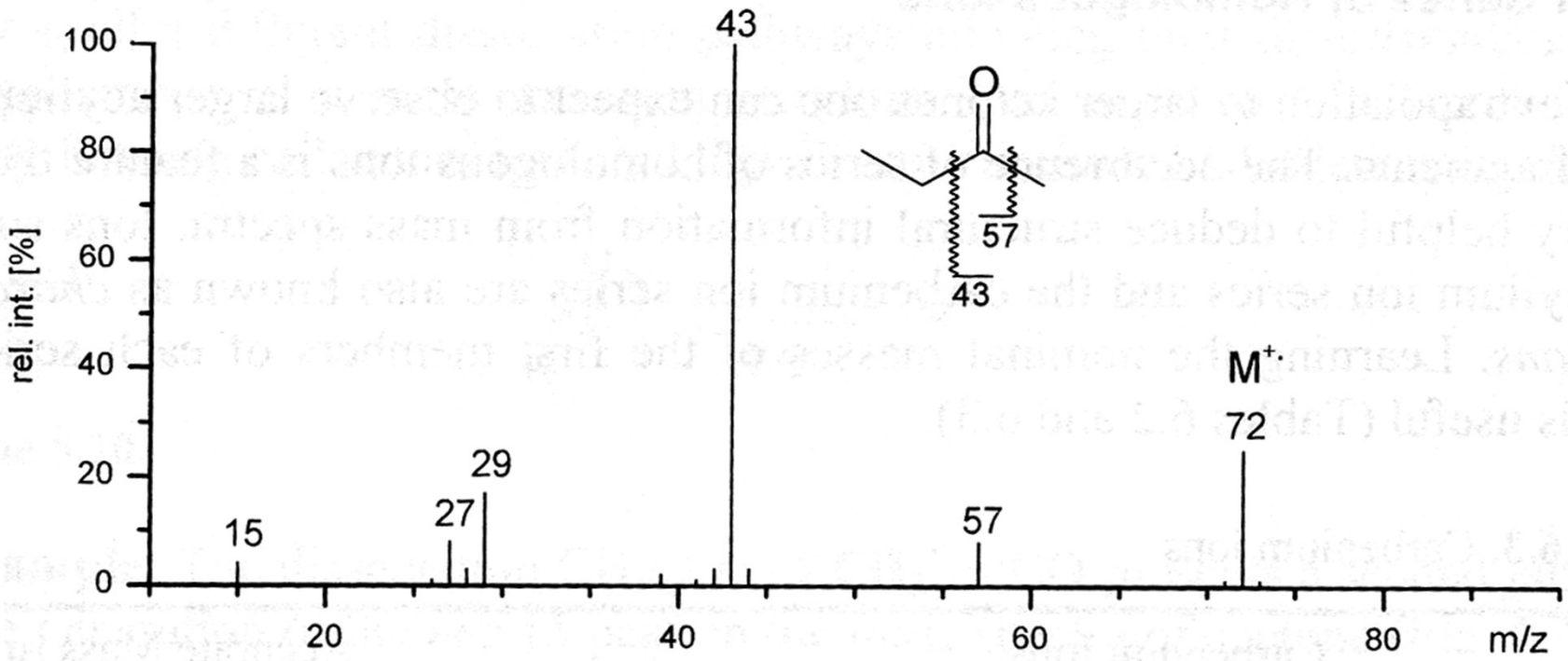
Clivagem do íon molecular: tendência do elétron não emparelhado permanecer com o fragmento de maior energia de ionização

PF3

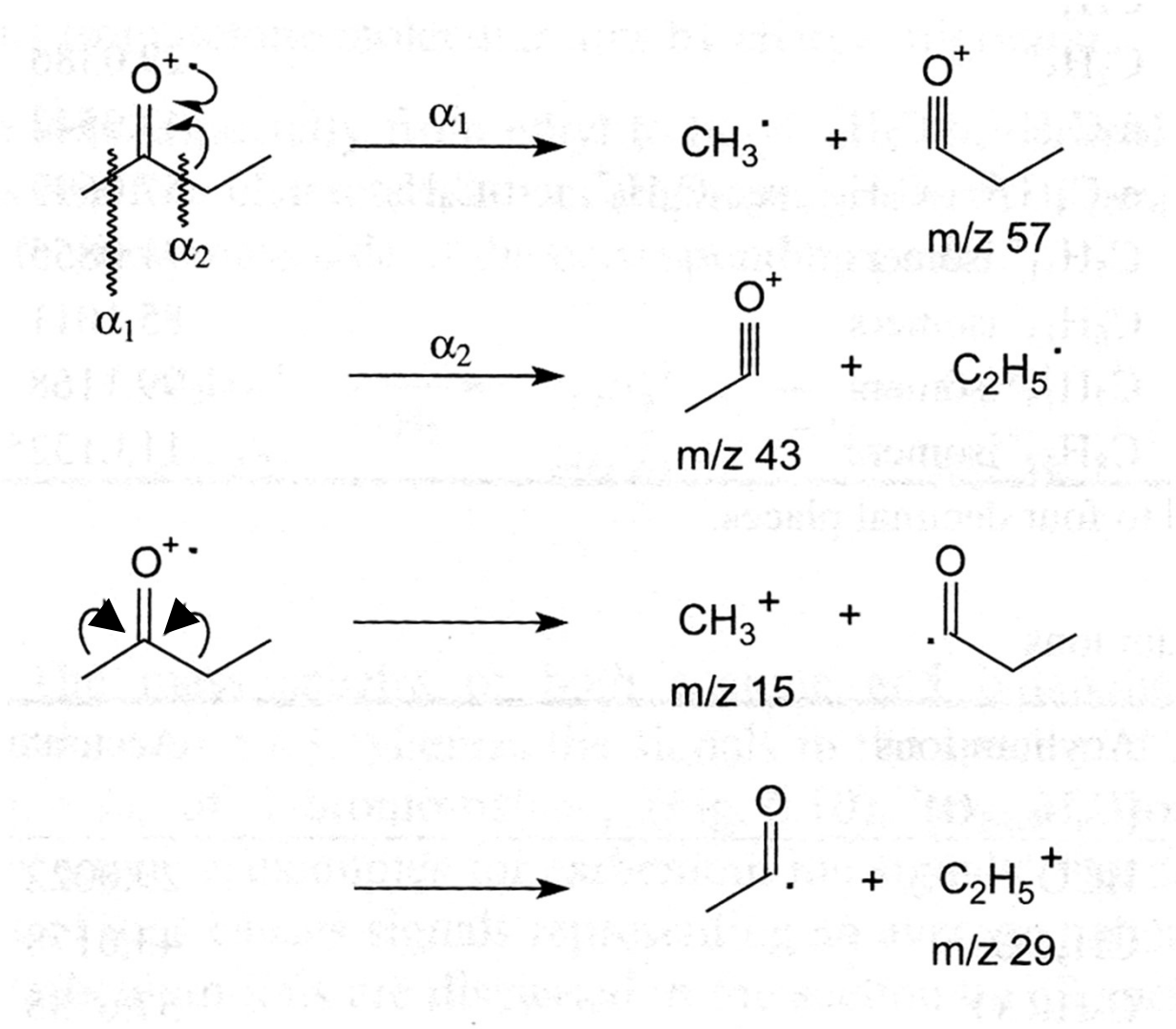




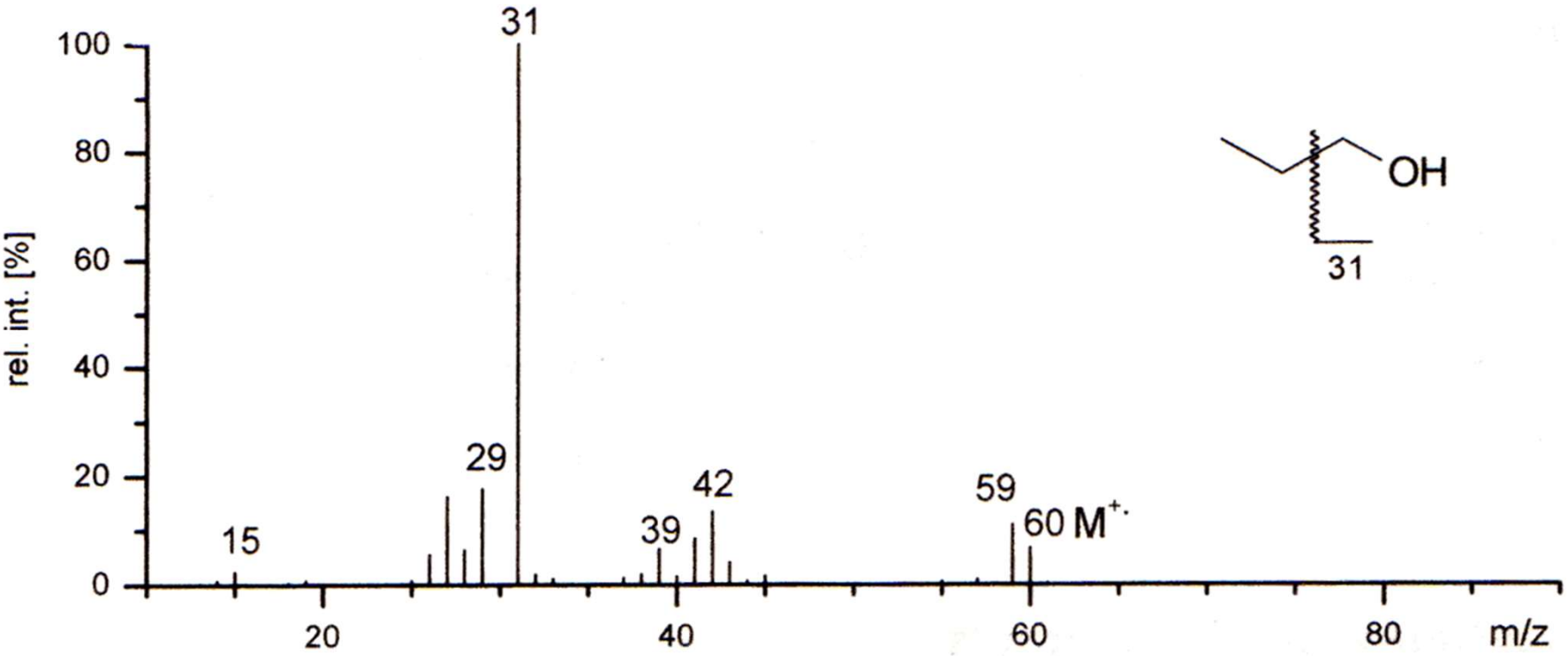
Fragmentação iniciada pelo sítio radicalar em butanona: duas clivagens α possíveis

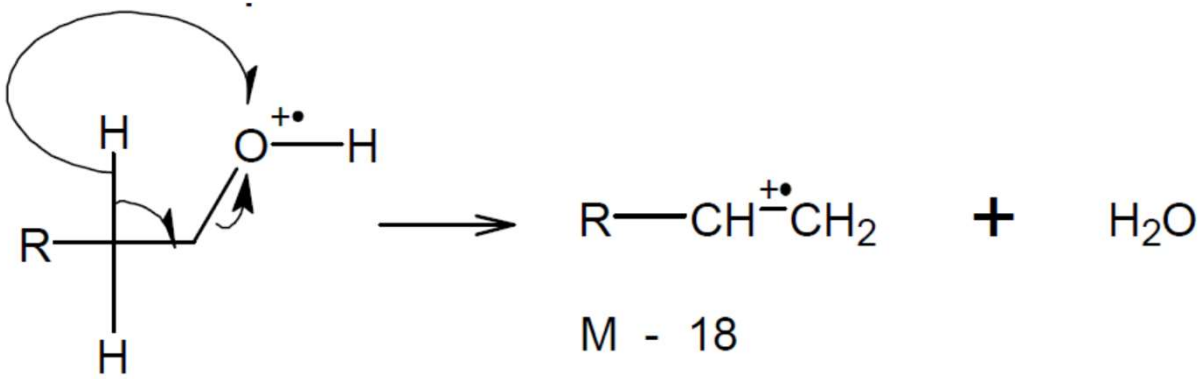


Mecanismos de fragmentação da butanona

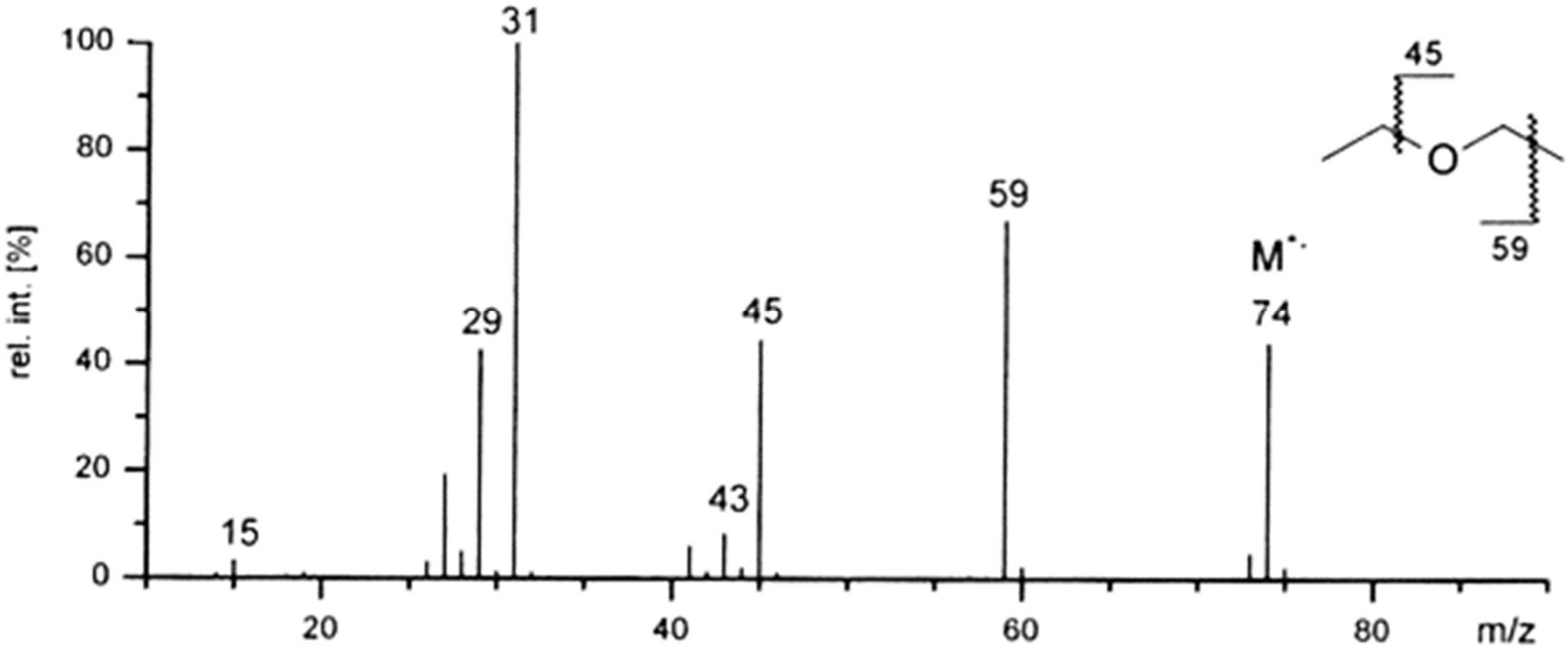


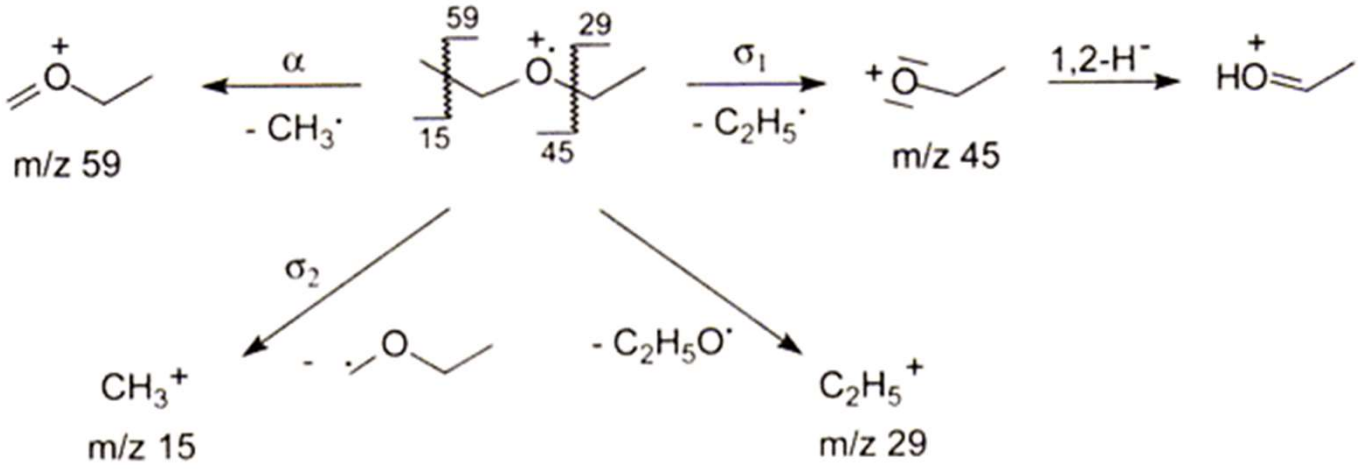
Clivagem α em éteres e álcoois

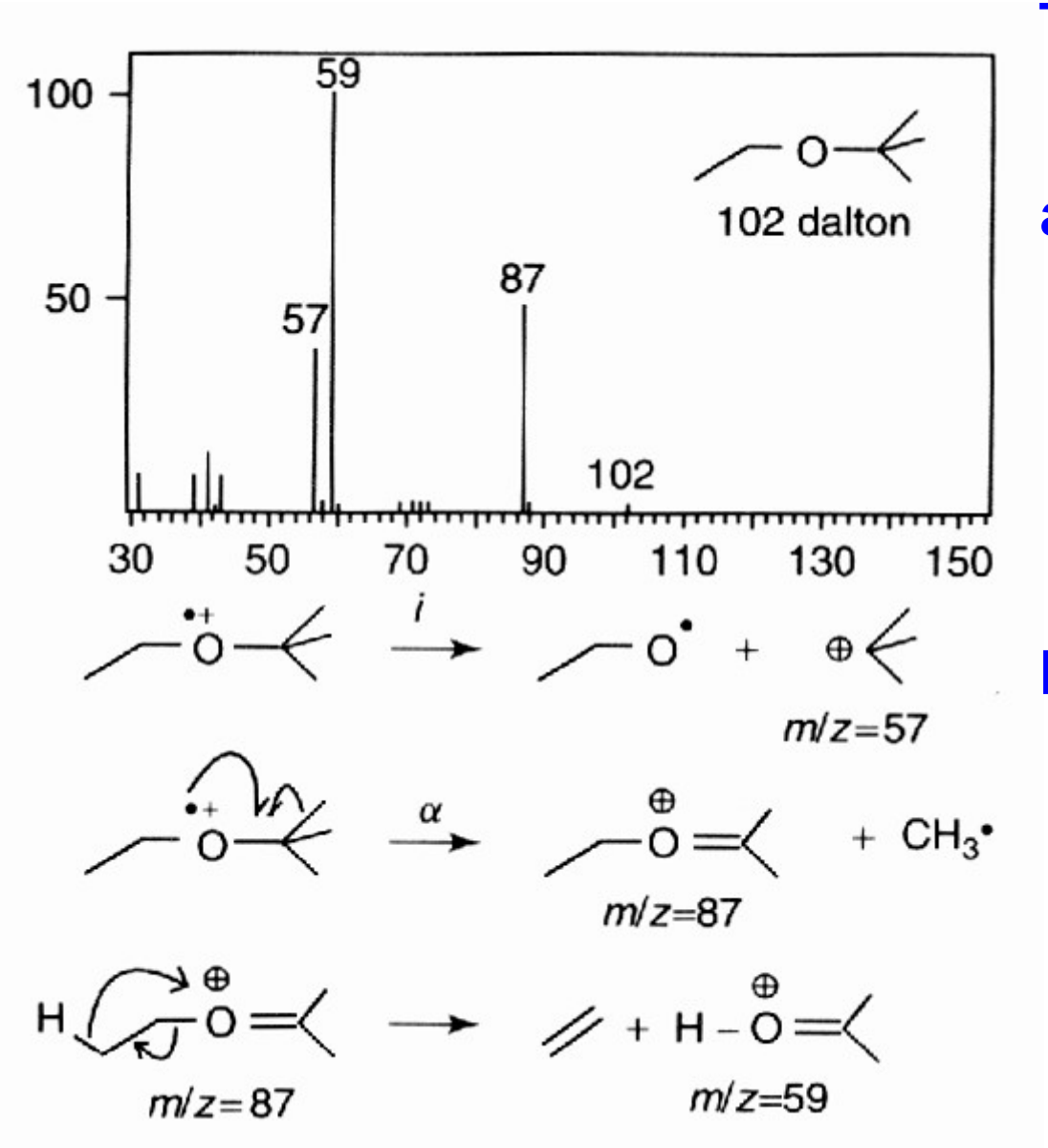




Um estudo mais detalhado das fragmentações primárias no éter dietílico



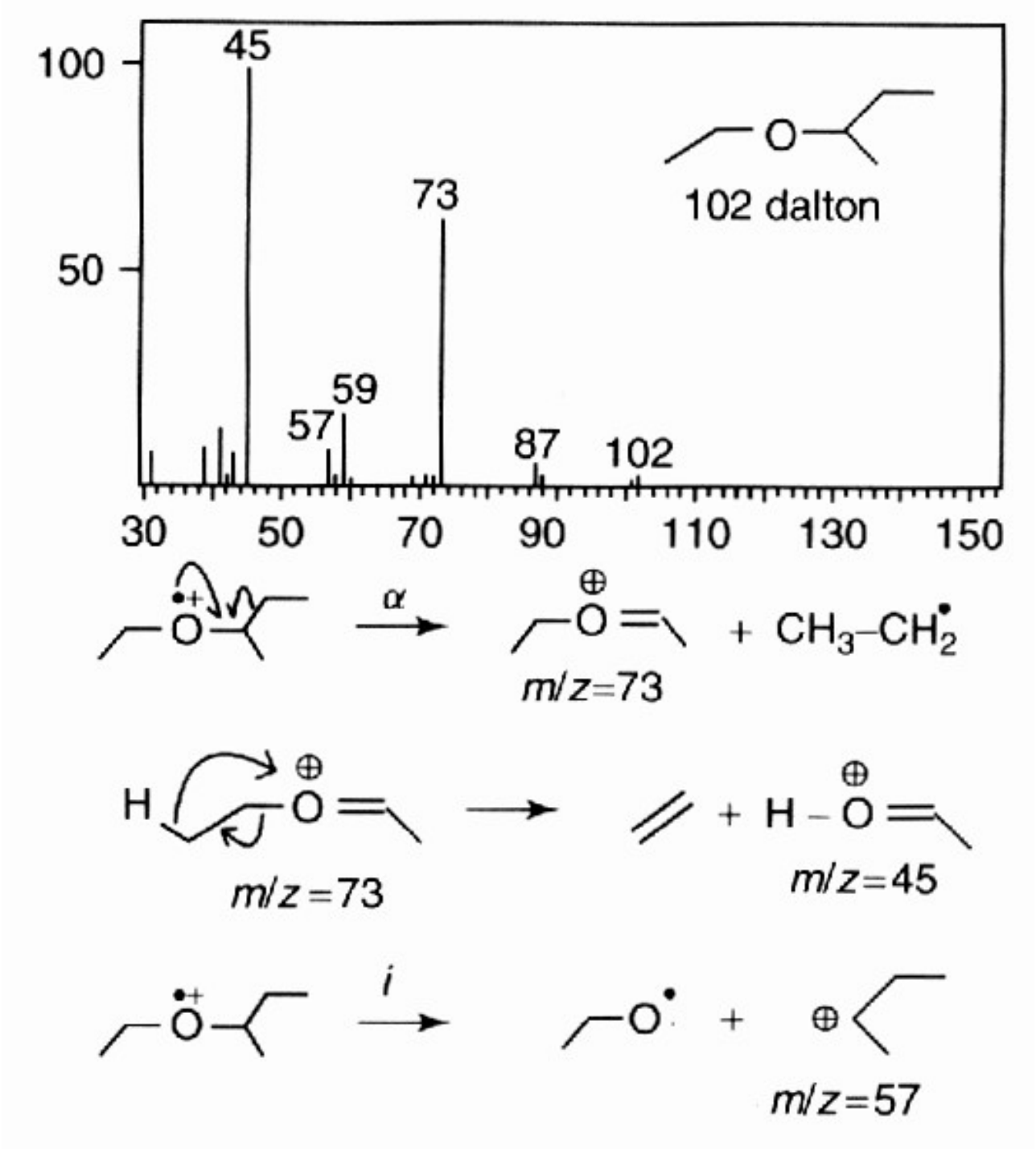




Dois mecanismos de fragmentação: caso do Et-O-*t*-Bu

a) Clivagem induzida pelo sítio da carga, e formação do íon de menor energia de ionização, m/z *57*;

b) Clivagem induzida pelo sítio radicalar numa ligação em posição α (*m/z* 87), seguida de um rearranjo (*m/z* 59).

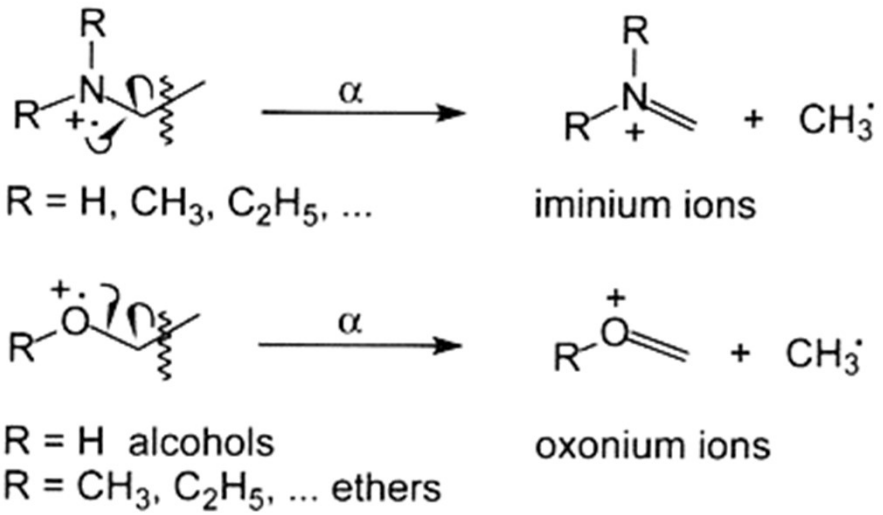


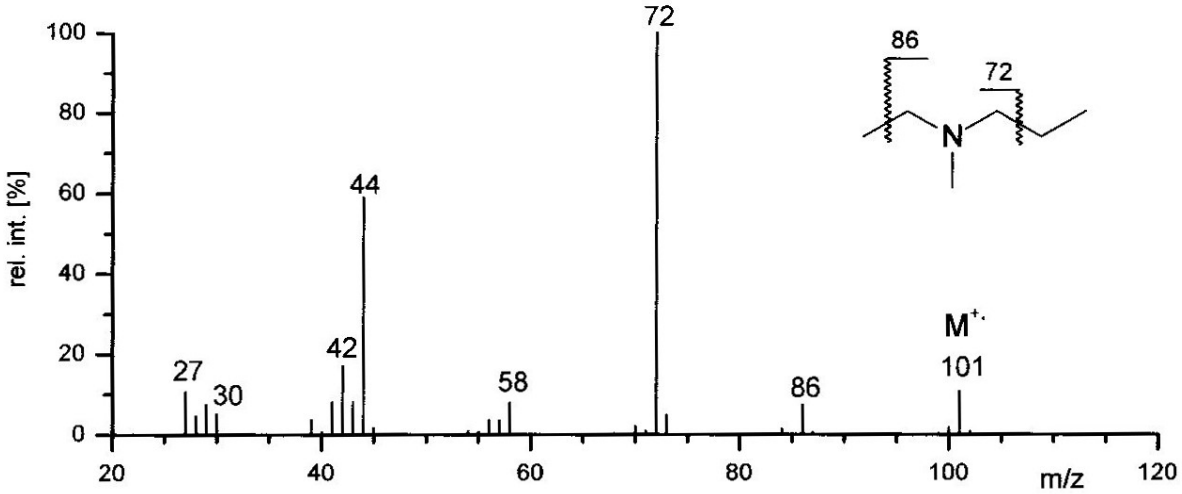
Mecanismos de fragmentação: Et-O-2-Bu

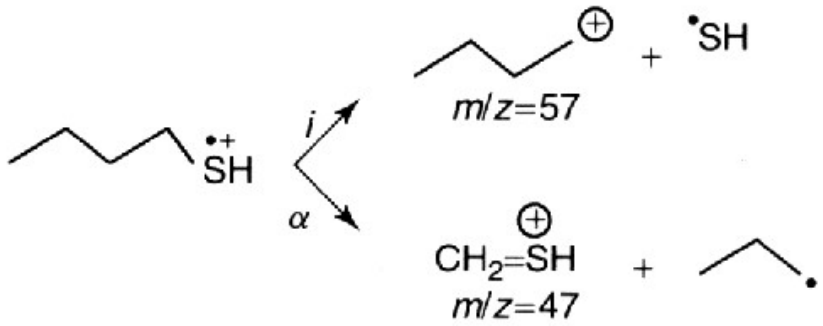
a) Duas possibilidades de clivagem α induzidas pelo sítio radicalar;

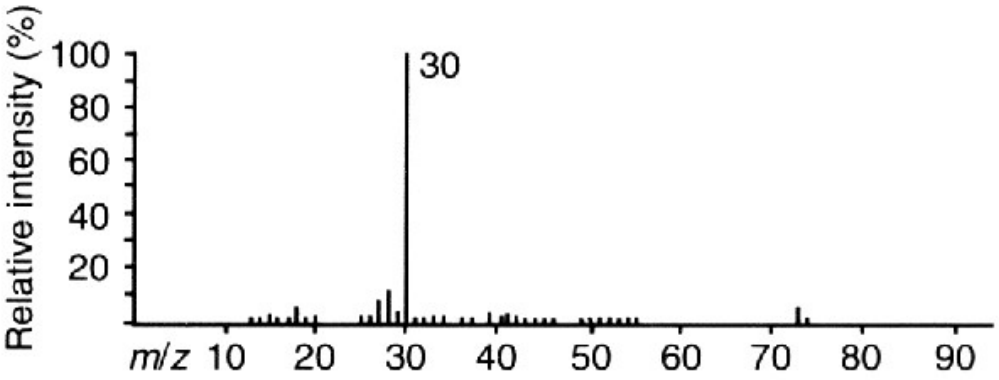
b) Clivagem da ligação adjacente à carga.

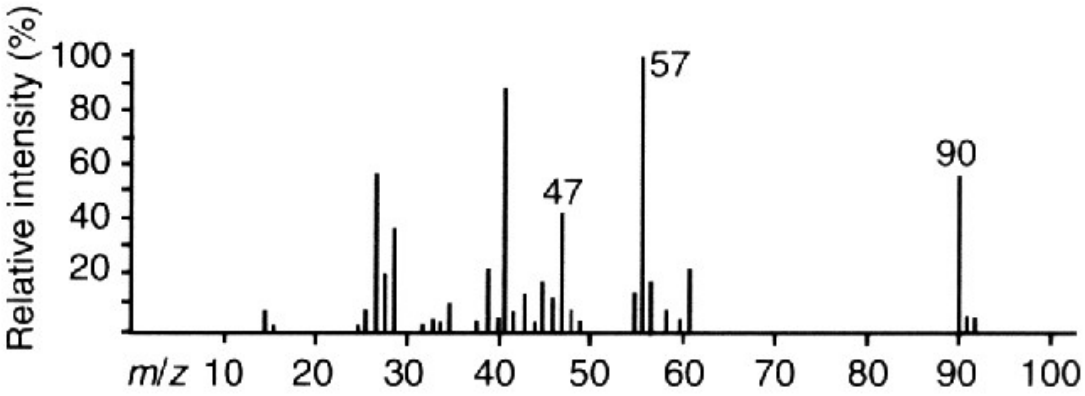
Clivagem α em aminas e éteres









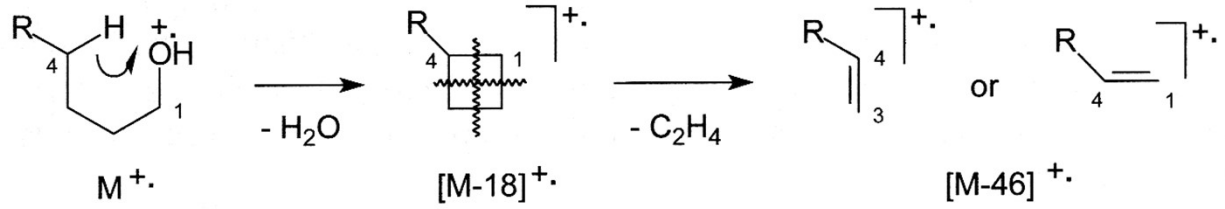


Competição entre clivagem na ligação adjacente e na ligação α.

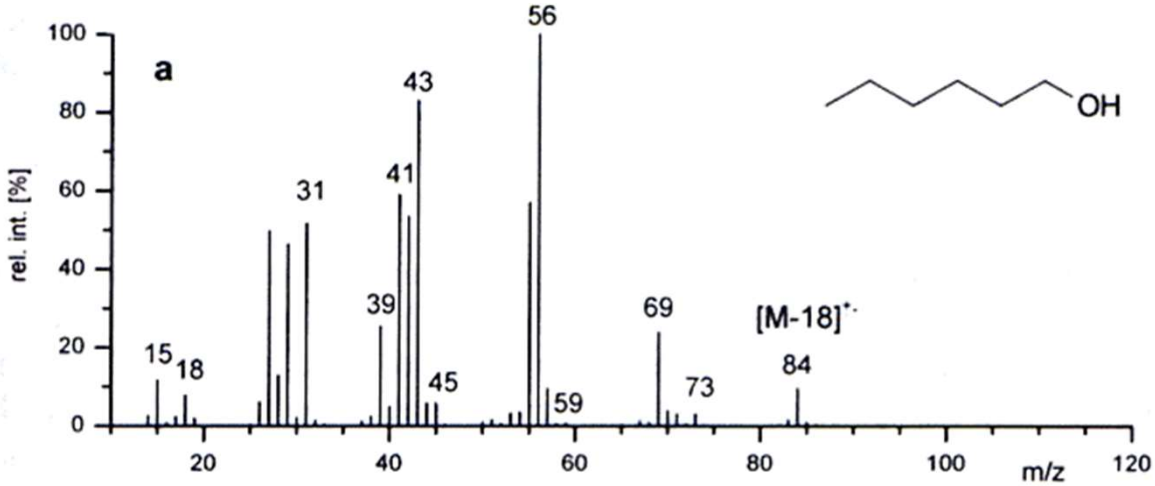
a) $BuNH_2$, clivagem α é favorecida pela doação de elétrons do N.

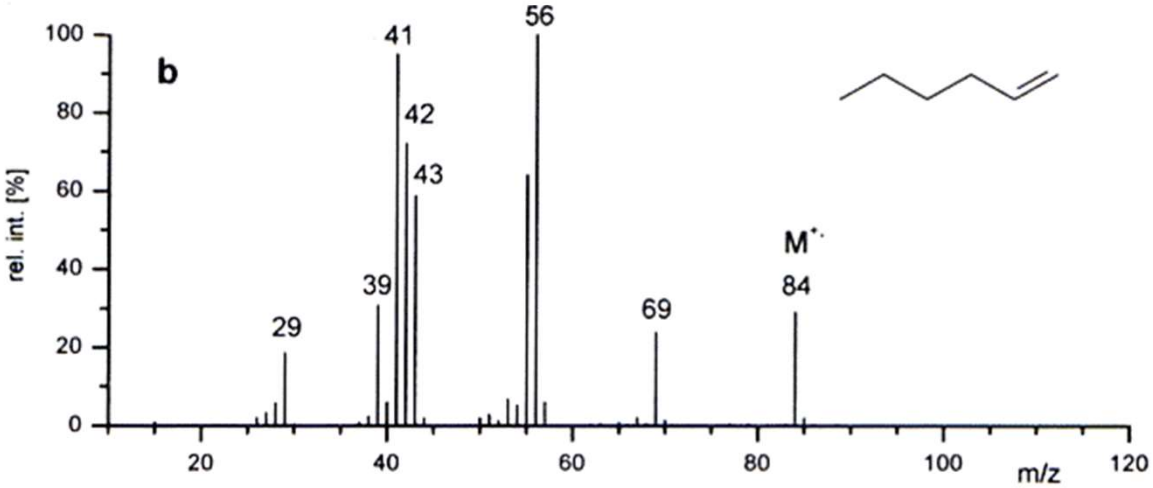
b) BuSH, prevalece a clivagem induzida pela carga e formação de *m/z* 57.

Perda de H_2O pelos íons moleculares de álcoois

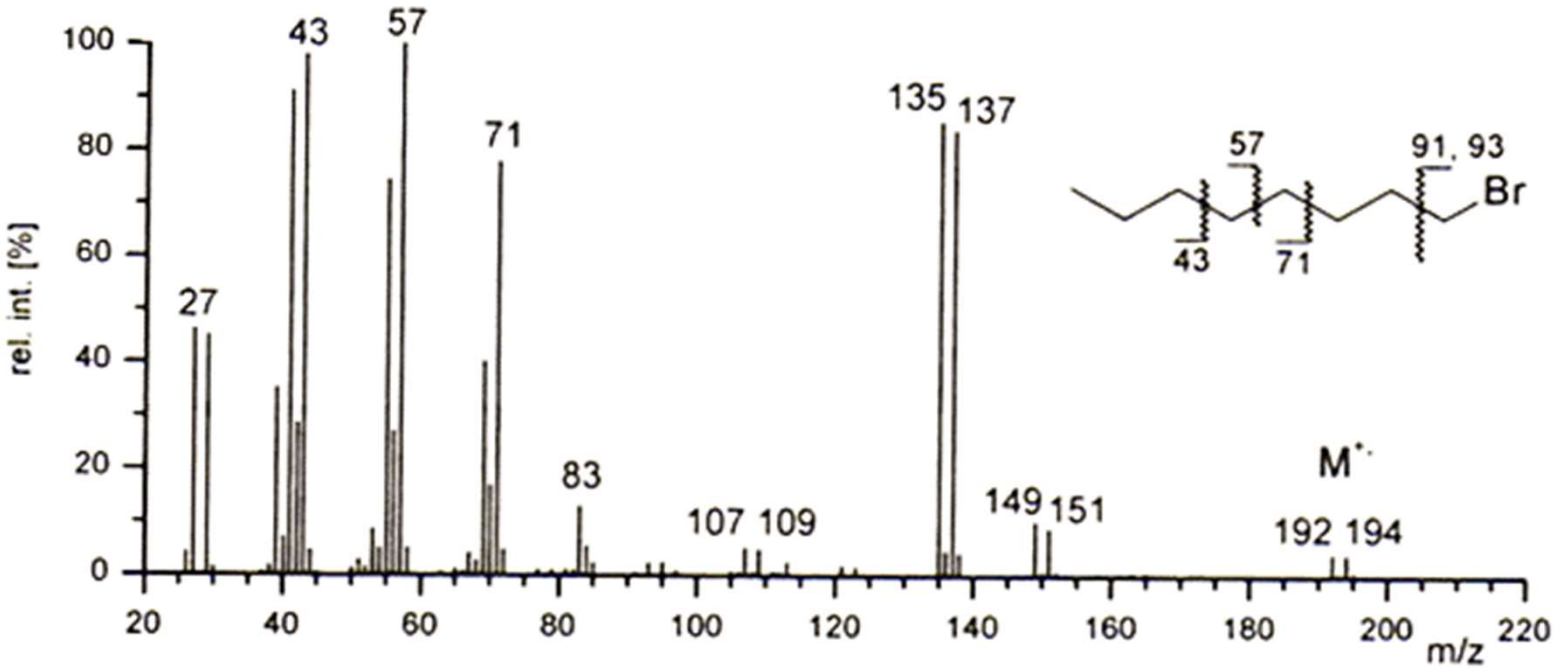


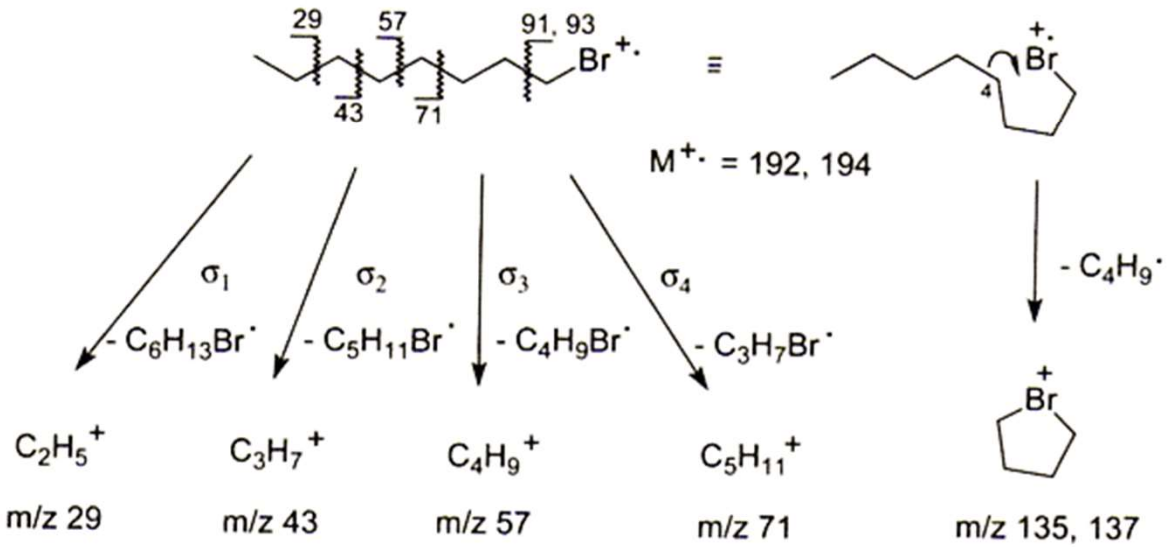
O espectro de massas do hexanol revela grandes semelhanças com o espectro do 1-hexeno devido a formação inicial de (M-18)+



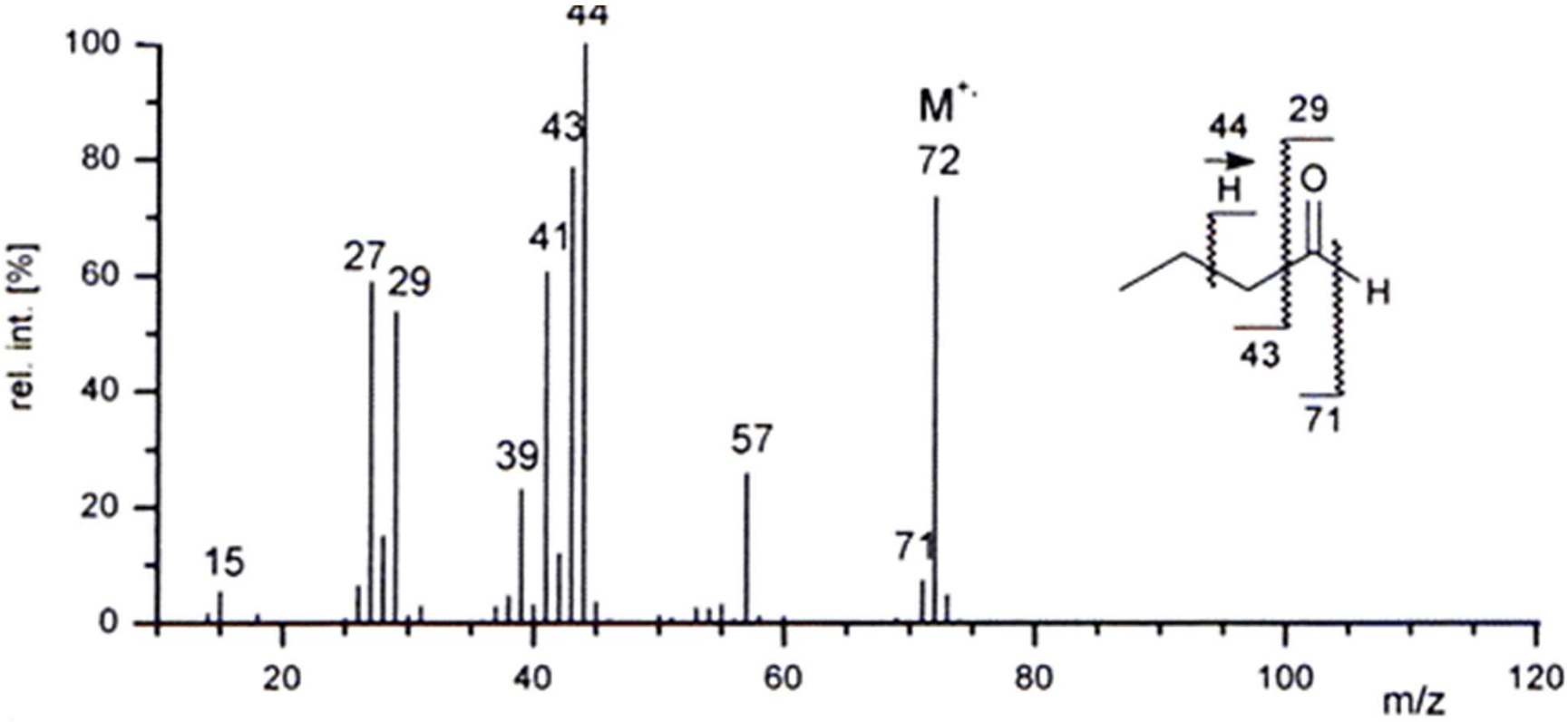


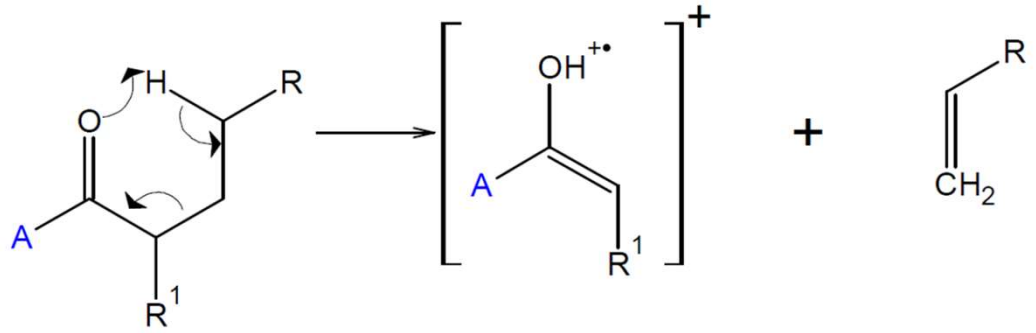
Espectro de 1-bromooctano: clivagem α e clivagens σ



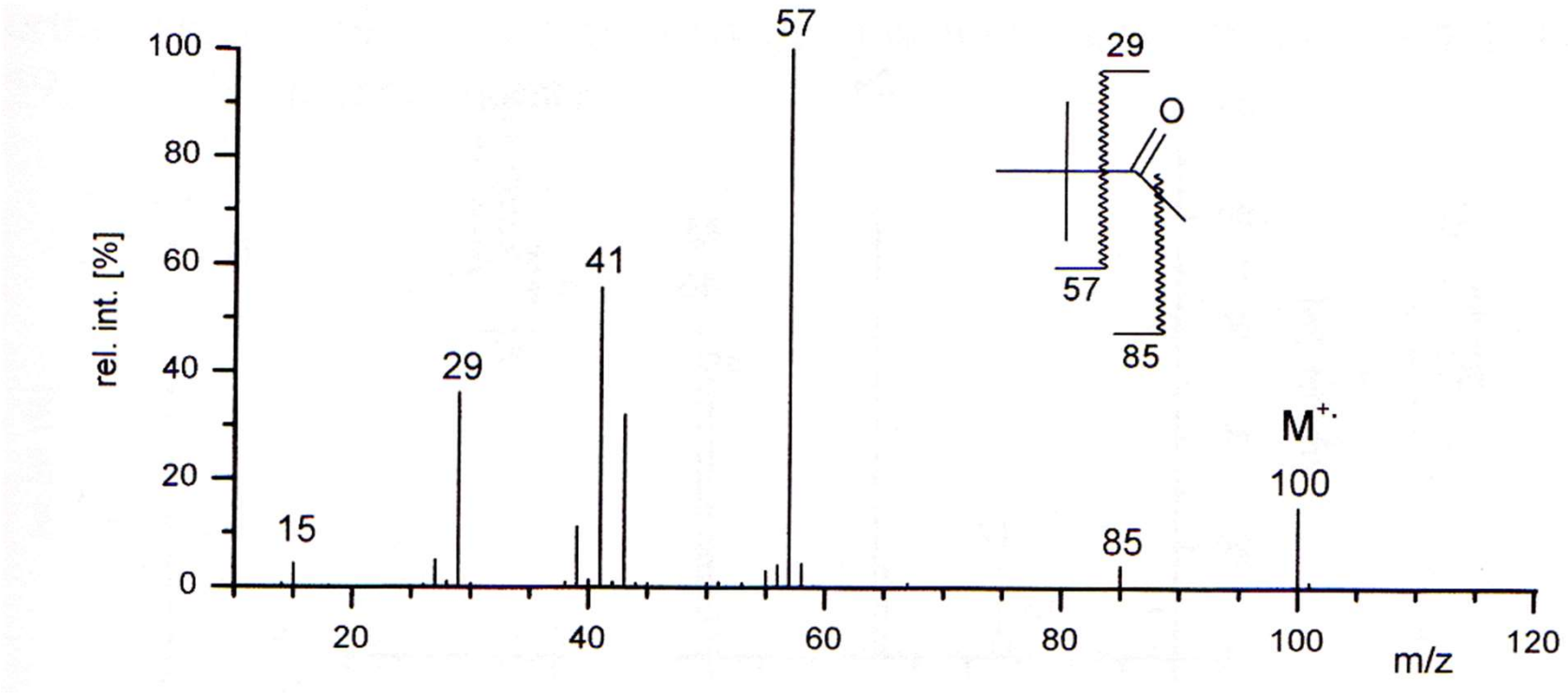


Rearranjo de McLafferty em aldeídos e cetonas



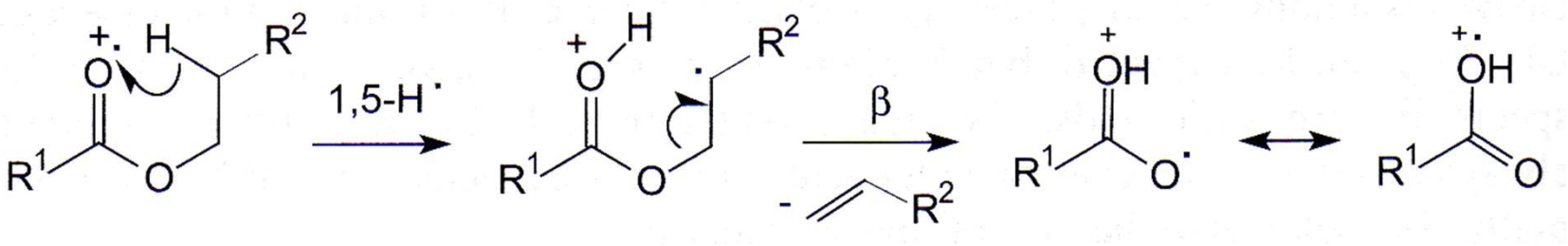


Efeito do hidrogênio γ e rearranjo de McLafferty

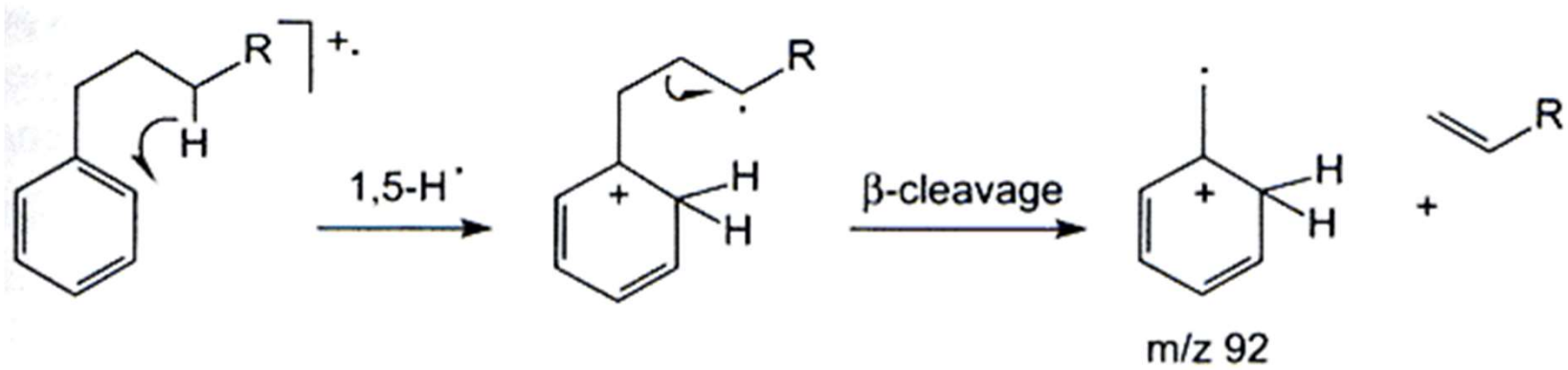


Na ausência de um hidrogênio em posição γ, o rearranjo de McLafferty não é observado, e o espectro de massa pode ser interpretado conforme clivagens convencionais.

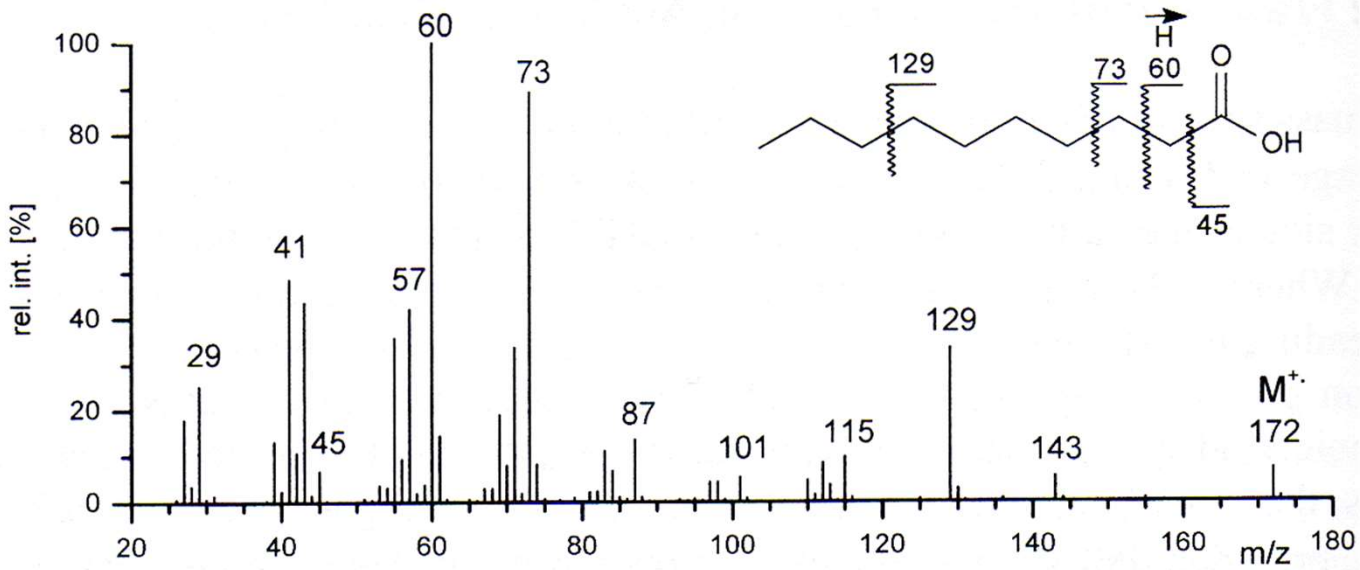
Rearranjos de McLafferty num éster com um grupo alquila com hidrogênio γ

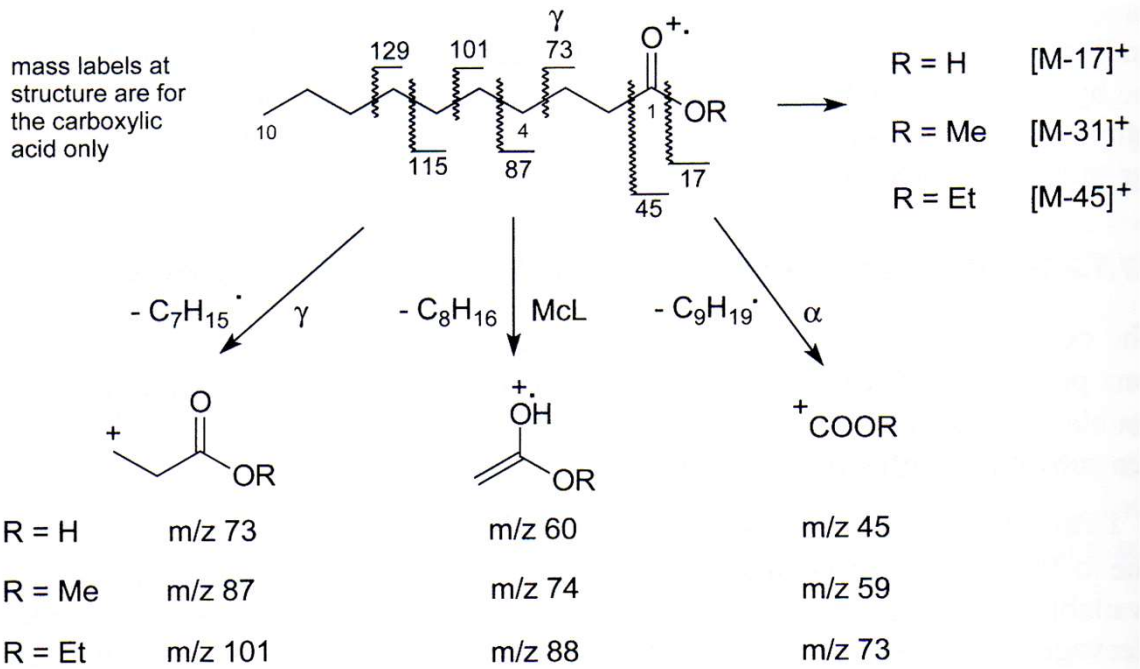
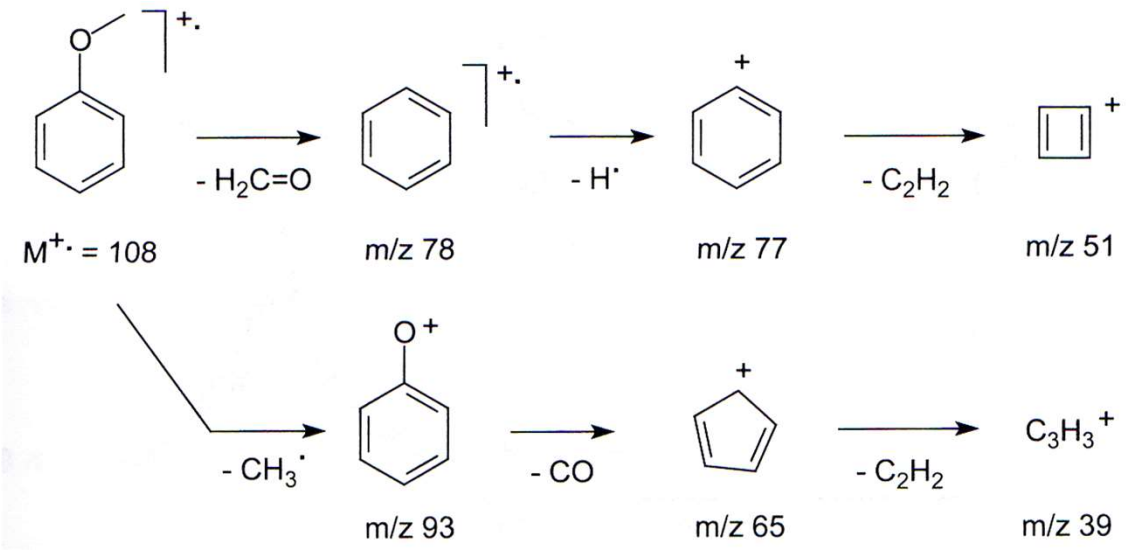
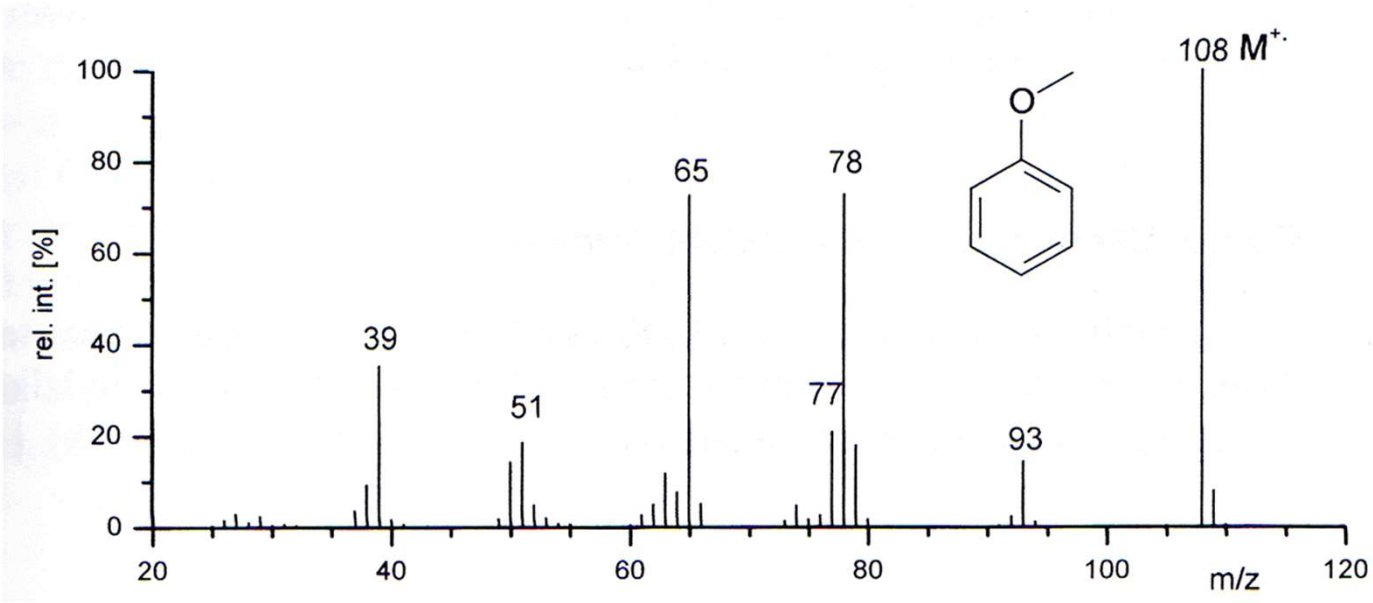


Rearranjos de McLafferty em sistemas aromáticos



Fragmentações no ácido decanóico e no ester





Alquil Aril Éter: o caso do anisol e perdas de H_2CO e CO