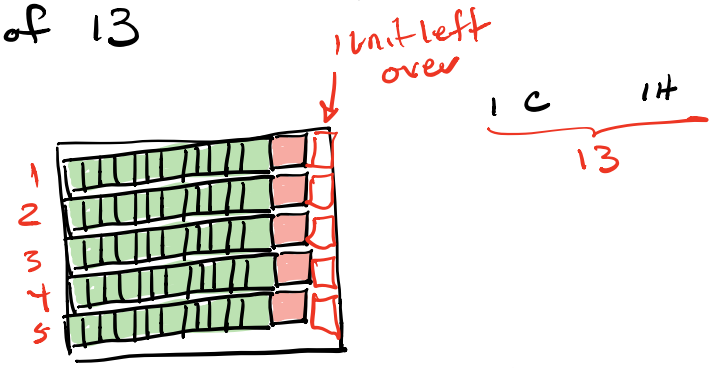
Mass Spec Skill Sets

Formula from $M^{\cdot+}$ Mass/Z Ratio

⇒ Rule of 13

$M^{\cdot+}$



$C_5H_5 + H_5 = C_5H_{10}$

Ex 1 $M^{\cdot+} = 106$ What are possible molecular formulas?

$$13 \overline{)\,106} \quad 8$$
$$-104$$
$$2$$

C_8H_{10} $\frac{96}{10}$ $\frac{}{106}$ ✓

C_7H_6O $\frac{84}{6}$ $\frac{16}{106}$ ✓

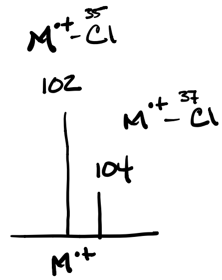
$C_6H_2O_2$ $\frac{72}{2}$ $\frac{32}{106}$ ✓

$C_8H_{8+2} = C_8H_{10}$

$O = 16 = CH_4$

$C_8H_{10} \xrightarrow{-CH_4,\ +O} C_7H_6O \xrightarrow{-CH_4,\ +O} C_6H_2O_2 \xrightarrow{-C,\ +12H} C_5H_{14}O_2$

Ex 2 $M^{\bullet +} = 102$



$$13 \overline{)\,102\,} = 7 \qquad 102 - 91 = 11$$

$C_7H_{7+11} = C_7H_{18}$

$Cl = 35 = C_2H_{11}$

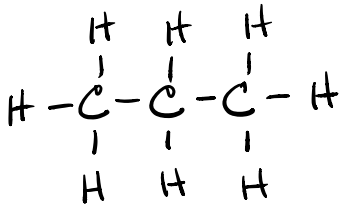
Starting Formula C_7H_{18} $\xrightarrow{-C_2H_{11},\ +Cl}$ C_5H_7Cl $\xrightarrow{-CH_4,\ +O}$ C_4H_3OCl

What to do when there are not enough hydrogens to do the swap

C_7H_8 $\xrightarrow{-C_2H_{11},\ +Cl}$?

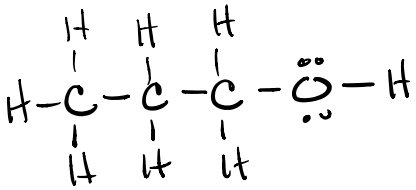
C_6H_{20} $\xrightarrow{-C_2H_{11},\ +Cl}$ C_4H_9Cl ✓

1st Convert a Carbon to hydrogen
2nd Swap for Cl

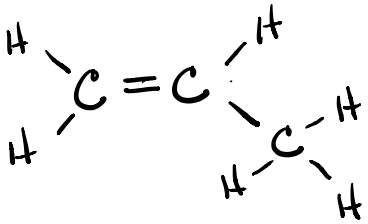


C_3H_8

add oxygen

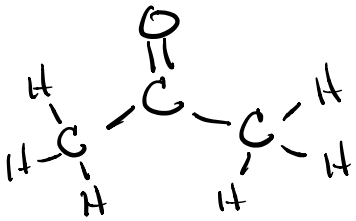


C_3H_8O

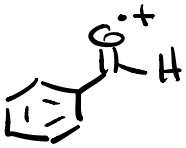
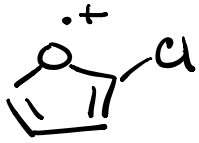
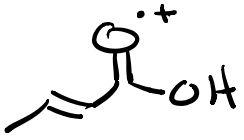
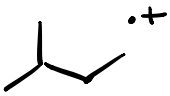


C_3H_6

add O

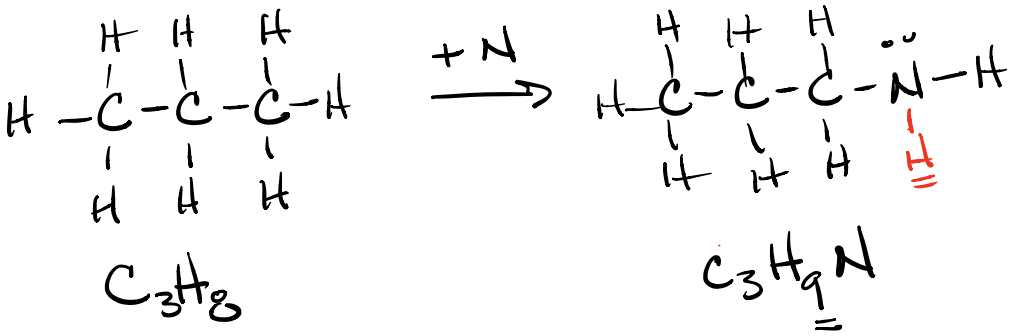


C_3H_6O

	Formula	M/z
	$C_7H_6O^{\cdot+}$	7(12)+6+16 = 106
	$C_4H_3OCl^{\cdot+}$	102
	$C_4H_6O_2^{\cdot+}$	86
	$C_5H_{12}^{\cdot+}$	72
	$C_4H_9NO^{\cdot+}$	87

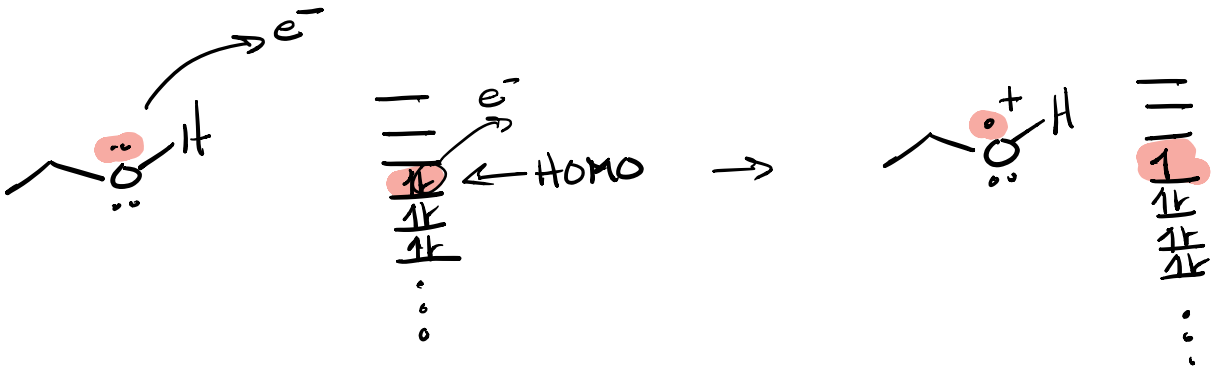
even

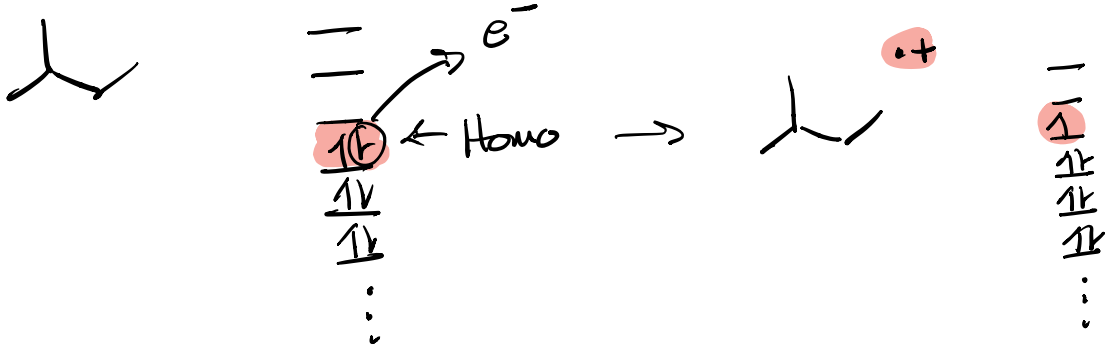
odd



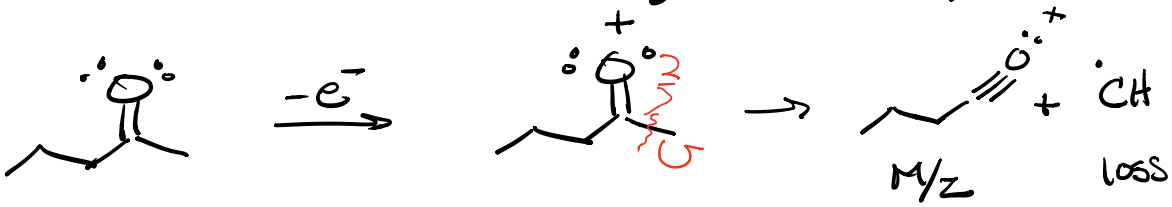
$\Rightarrow$ odd mass = odd # of Nitrogens

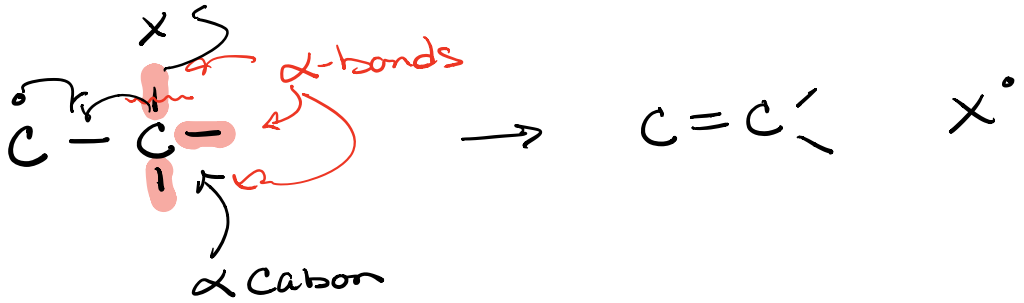
N
P
As
↓ odd mass



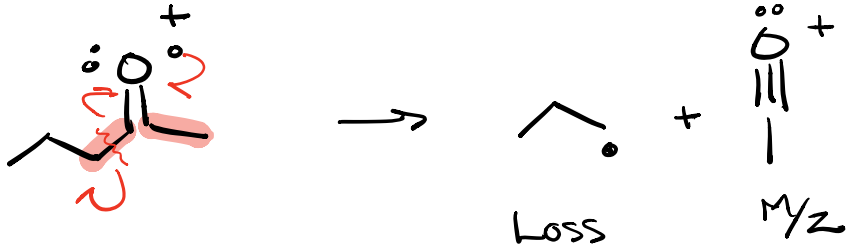


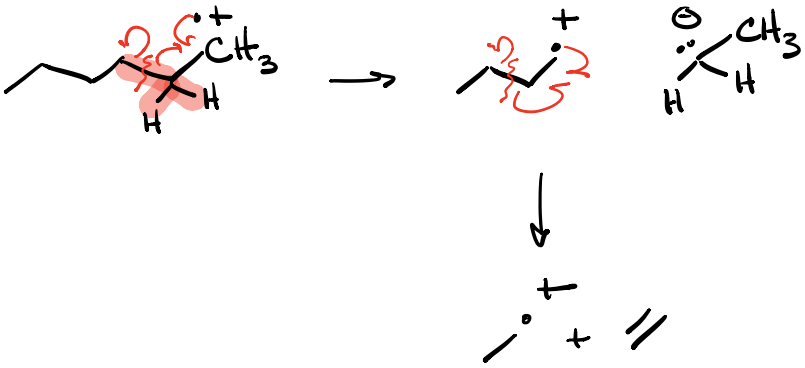
Pattern of α-cleavage (Homolytic)

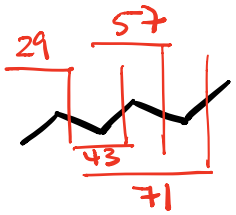




two α-bonds = 2 possible α-cleavages

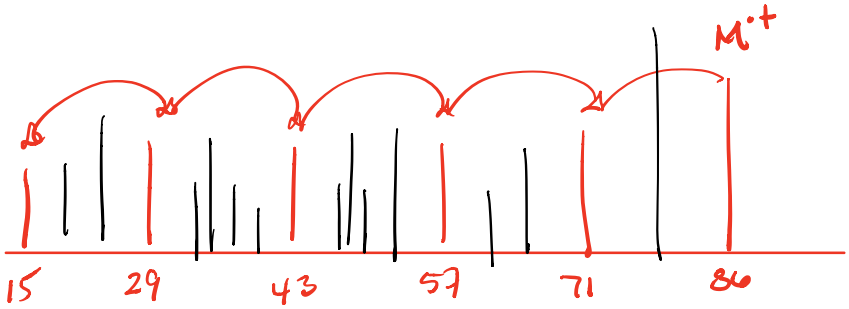


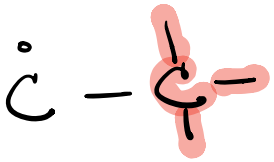




$M/z = C_6H_{14} = 86$

Alkyl loss Series





α carbon
1-position away

odd mass ⇒ odd # of N

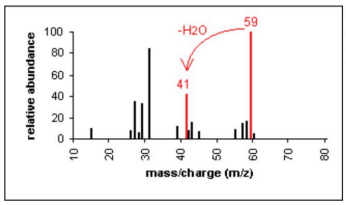
M/z = 73 Give me a possible molecular formula

C_5H_{13}

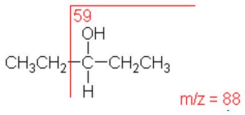
$C_4H_{11}N$

Cleavage notation

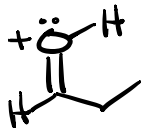
An alcohol's molecular ion is small or non-existent. Cleavage of the C-C bond next to the oxygen usually occurs. A loss of H_2O may occur as in the spectra below.



3-Pentanol
$C_5H_{12}O$
MW = 88.15



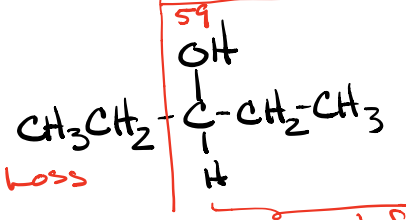
Loss = 29



M/z = $C_3H_7O^+$ = 59

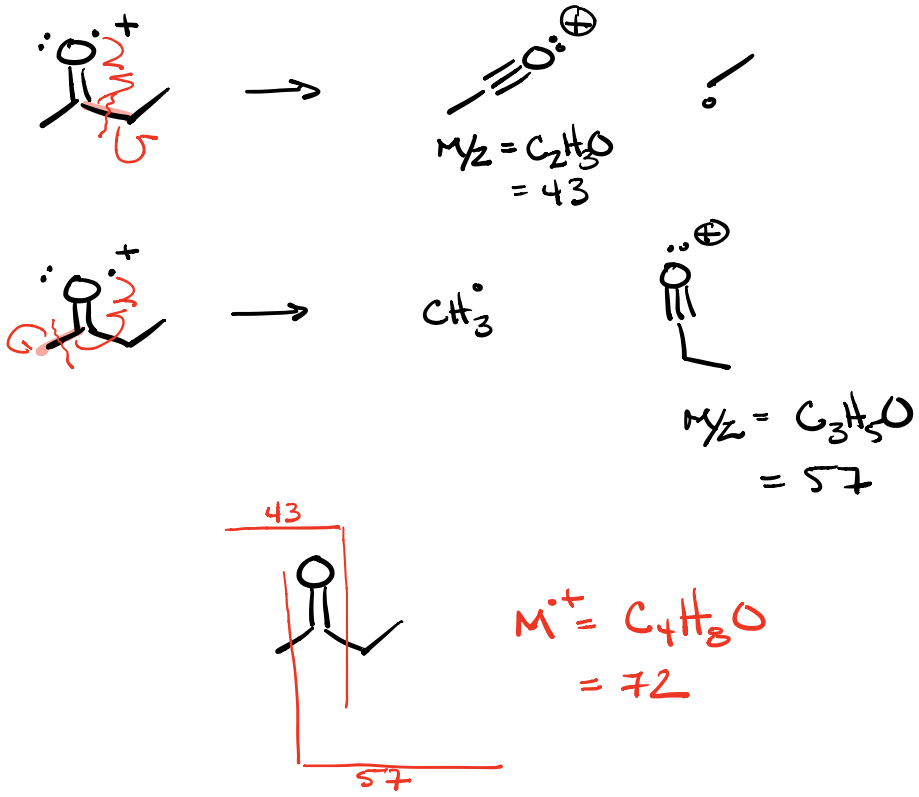
observable

59



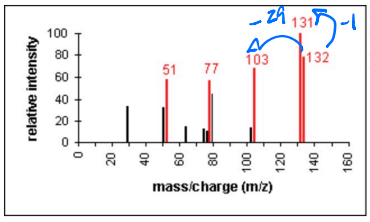
Loss

charged fragment = 59 M/z



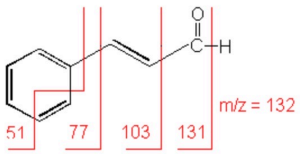
Aldehyde

Cleavage of bonds next to the carboxyl group results in the loss of hydrogen (molecular ion less 1) or the loss of CHO (molecular ion less 29).



3-Phenyl-2-propenal
C_9H_8O
MW = 132.16

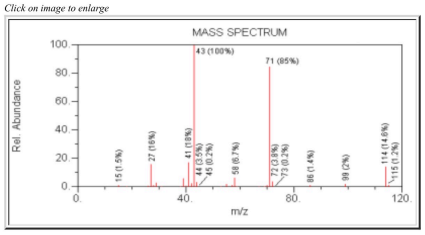
loss of 29 = CHO
loss of 1 = H
= aldehyde



4. ***Choose the compound that this spectrum represents.***

Hint

Click on image to enlarge



- a) 2-heptanone
- b) 4-heptanone
- c) 3-pentanone
- d) 4-methyl-2-heptanone
- e) 2,4-dimethyl-3-pentanone

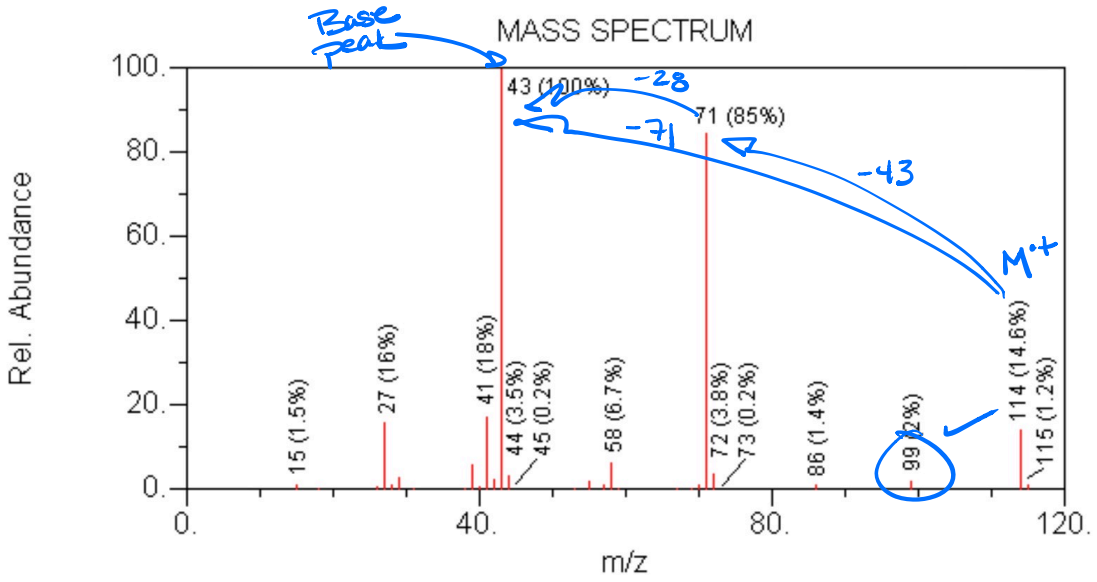
2-heptanone $C_7H_{14}O$ 114

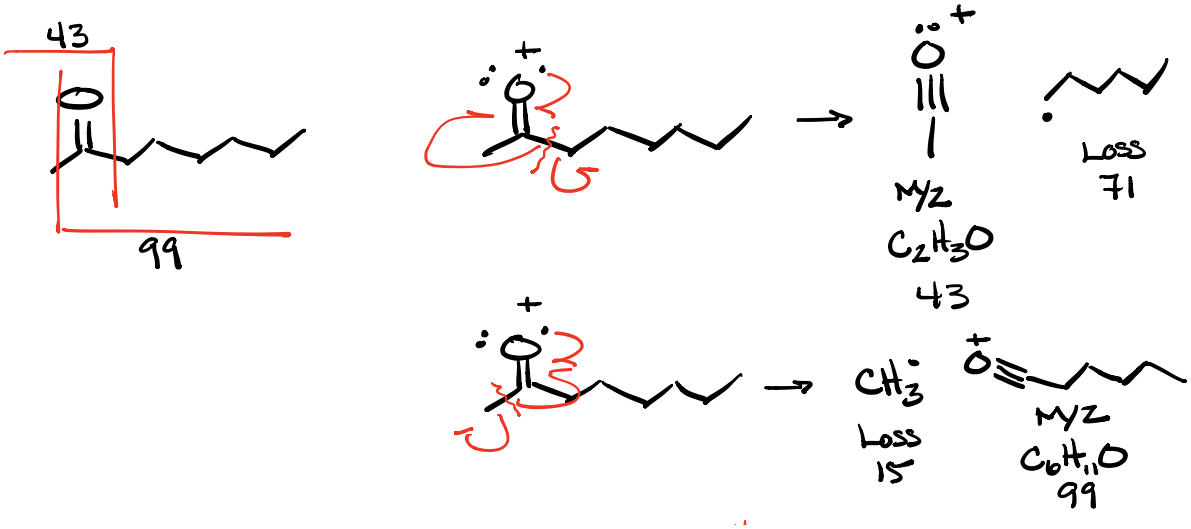
4-heptanone $C_7H_{14}O$ 114

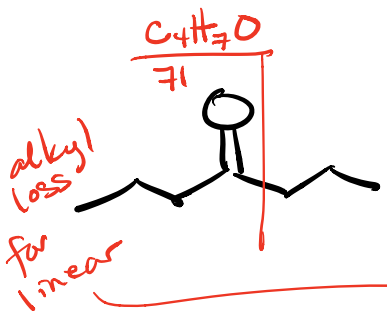
~~3-pentanone~~ $C_5H_{10}O$ 86

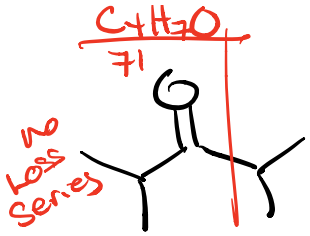
~~4-methyl-2-heptanone~~ $C_8H_{16}O$ 128

2,4-dimethyl-3-pentanone $C_7H_{14}O$ 114







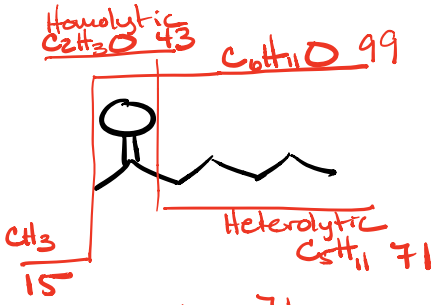


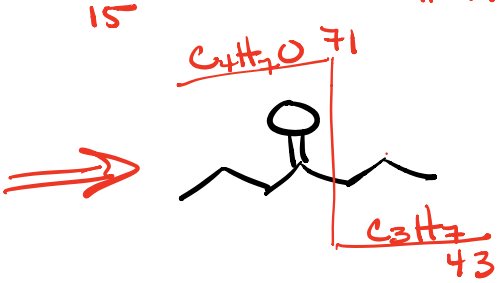
Don't give 43!

C_3H_7 43

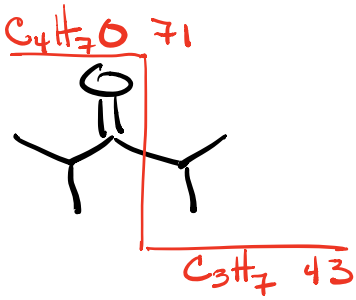
$CH_3-CH_2^{\bullet+}$ C_2H_5 29

CH_3 15





Loss Series



Heterolytic (asymmetrical) α-Cleavage