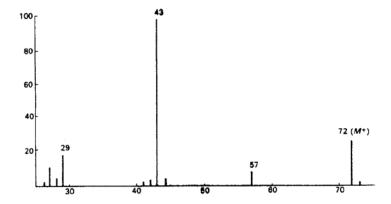
Dr. H.M. Muchall

- 1. (5 points) For the butanal with signals in the mass spectrum at m/z 72, 57, 44, 43, 41 and 29, show (put + and \cdot on the more likely species)
 - a) an α -cleavage (both fragments).

b) a McLafferty rearrangement (both fragments).

2. (6 points) Give the species from the fragmentations (labeled masses) in the mass spectrum of butanone. Make sure you indicate radical cations, cations or radicals where appropriate. Include the masses of all fragments in the scheme.



3. The ether below shows a fragmentation m/z $102 \rightarrow 87$. Three pathways are possible.

a) (6 points) Show all three possible fragmentations. Include all +, · and masses. Which of these fragmentations is unlikely?

$$(102) \qquad (87) \qquad 15u$$

$$\rightarrow \qquad \stackrel{\uparrow}{\longrightarrow} \qquad + \cdot CH_3$$

$$(87) \qquad 15u$$

$$\rightarrow \qquad + \cdot CH_3$$

$$(87) \qquad + \cdot CH_3$$

$$15u \qquad This would be unlikely: primary carbocation.$$

b) (4 points) Knowing that m/z 87 further fragments to give m/z 31 in an onium reaction, which of the two remaining fragments from a) do you pick? Show the fragments from the onium reaction.

4. (3 points) Which of the following shows correct retro-Diels-Alder fragments for the indicated compound? Which fragment carries the +· preferentially?

+· is preferentially on the more highly conjugated fragment: that molecule is easier to ionize.