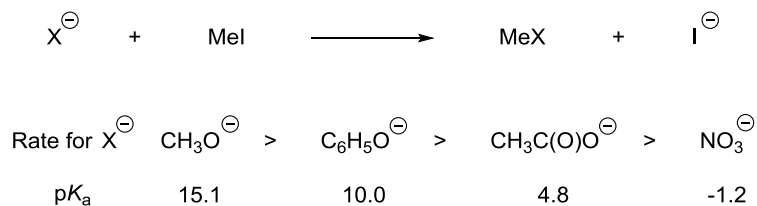
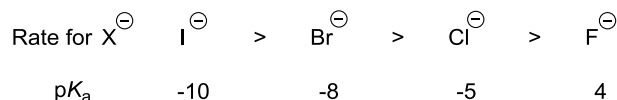


EAA Group Problems - 29/11/16

(a) Suggest an explanation for the trends shown below. The relative rates of reaction of oxygen-centred nucleophiles with MeI, and pK_a data (in water) of the corresponding conjugate acids of these nucleophiles, are as shown below:



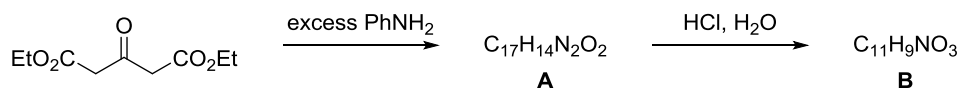
However, for the reaction of halide nucleophiles with MeI, the corresponding data is:



(b) Explain the significance of the following data for carboxylic acid ionisation in water at 298K.

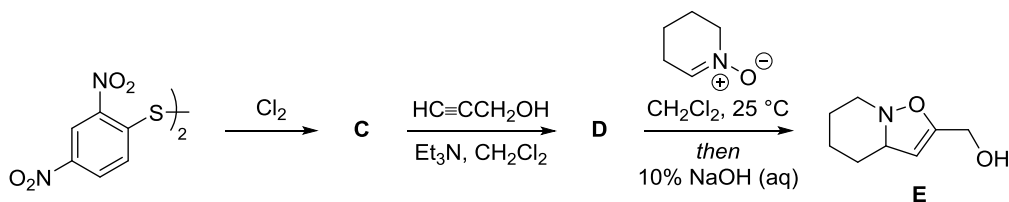
Acid	pK_a	ΔH (kJ mol ⁻¹)
$\text{CH}_3\text{CO}_2\text{H}$	4.8	-0.1
$\text{CCl}_3\text{CO}_2\text{H}$	0.5	+1.2

(c) Using the data provided, identify the product **B**, and suggest a structure for intermediate **A**. Suggest mechanisms for the formation of both **A** and **B**.



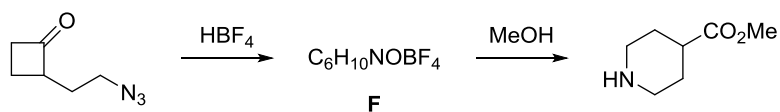
Data for **B**: δ_{H} 17.1 (1H, br. s), 7.6–7.0 (5H, m), 5.42 (1H, s), 3.65 (2H, s)
 δ_{C} 191.2 (C), 165.7 (C), 163.4 (C), 133.8 (C), 128.9 (CH), 128.1 (CH), 128.0 (CH), 98.0 (CH), 38.0 (CH₂)
 ν_{max} (cm⁻¹) 3110, 1711, 1670 and 1640

(d) Using the data provided, identify compounds **C** and **D**, and suggest mechanisms for the formation of **C**, **D** and **E**.



Data for **D**: δ_{H} 9.16 (1H, d, $J = 3$ Hz), 8.82 (1H, dd, $J = 9, 3$ Hz), 8.52 (1H, d, $J = 9$ Hz),
 6.35 (1H, t, $J = 6$ Hz), 5.54 (1H, dd, $J = 13, 6$ Hz), 5.31 (1H, dd, $J = 13, 6$ Hz)
 ν_{max} (cm⁻¹) 1950
 Elemental analysis C, 42.52; H, 2.38; N, 11.02;

(e) Using the data provided, identify compound **F** and propose a mechanism for its formation.



Data for **F**: δ_{C} 174.7, 47.8, 32.3, 22.8
 ν_{max} (cm⁻¹) 3224, 1877 and 1031 (br)