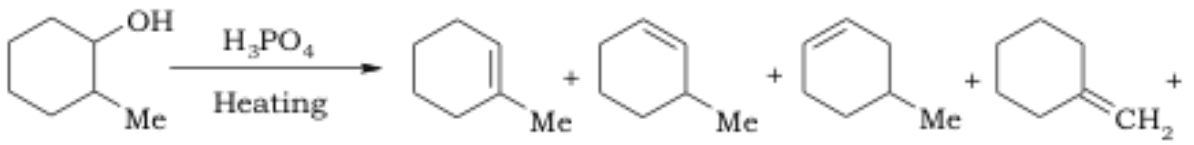
TPO-11 Dehydration of 2-methylcyclohexanol



(1) **(2)** **(3)** **(4)** **(5)**

Place 20 mL of 2-methylcyclohexanol (**1**) and a stirring rod into a 50 mL Claisen-Vigreux flask topped by an additional funnel in which 5 mL of 85% phosphoric acid (handle with care) are introduced. Warm up gently and stir.

Add the phosphoric acid dropwise. Distil out the products by heating the mixture gently. *Do not allow the temperature of the distillate to rise above 115 °C.*

Transfer the distillate to a separating funnel. Wash the organic layer with 10 mL of cold water, then with 10 mL of 5% sodium hydrogencarbonate and then with as many water necessary.

Transfer the organic layer to a clean, dry erlenmeyer flask and dry it.

Purify your product with the appropriate method.

Analyse your product mixture by GC (gas chromatography) and IR (infrared spectroscopy).

Cautions

- 85% phosphoric acid is corrosive to skin and clothing. Neutralise any spills with sodium bicarbonate and quickly wash the affected areas of skin with lots of soap and water.
- Methylcyclohexenes are flammable, volatile and have a noxious odor ; be sure to handle them under your student hood. Keep all containers of methylcyclohexene capped.

Physical data

- 2-methylcyclohexanol (**1**) : FW = 114.2 $g.mol^{-1}$; d = 0.93 ; bp 165-168°C ; purity : 99% ; very sol. in ethanol.
- 1-methylcyclohexene (**2**) : FW = 96.2 $g.mol^{-1}$; d = 0.81 ; bp 110°C ; insoluble in water, soluble in diethylether.
- 3-methylcyclohexene (**3**) : d = 0.80 ; bp 104 °C ;
- 4-methylcyclohexene (**4**) : d = 0.79 ; bp 102 °C ;
- methylenecyclohexane (**5**) : d = 0.80 ; bp 102 °C. All insol. in water, very sol. in diethylether.

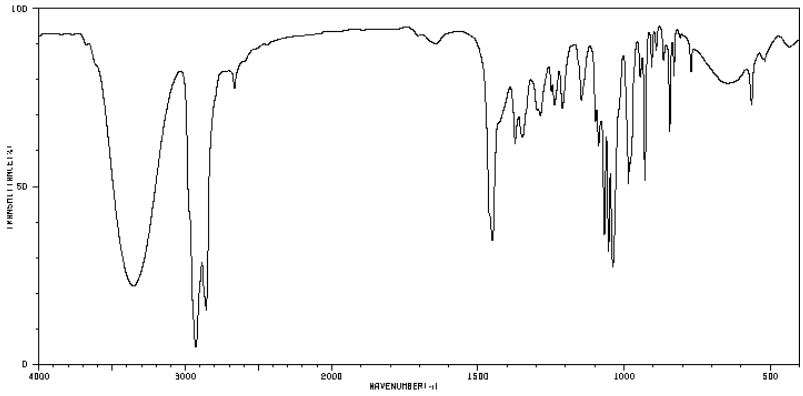
Results

1. Calculate the yield of your synthesis R.
2. Analyse your chromatogram (qualitatively, and then quantitatively with the normalization method).
3. Calculate the yield R_c corrected by your chromatography analysis for each product obtained.
4. Interpret your experimental IR spectra.
5. IR spectra of 2-methylcyclohexanol are recorded as : spectrum **1** a liquid film and spectrum **2** as CCl_4 solution. Interpret the difference between these two spectra.
6. Assign the peaks of the ^{1}H NMR and ^{13}C NMR spectra **3** and **4** below to specific groups of protons and carbon atoms on the molecule.
7. Attribute the MS spectrum **5,** and NMR spectra **6** and **7**.

Questions

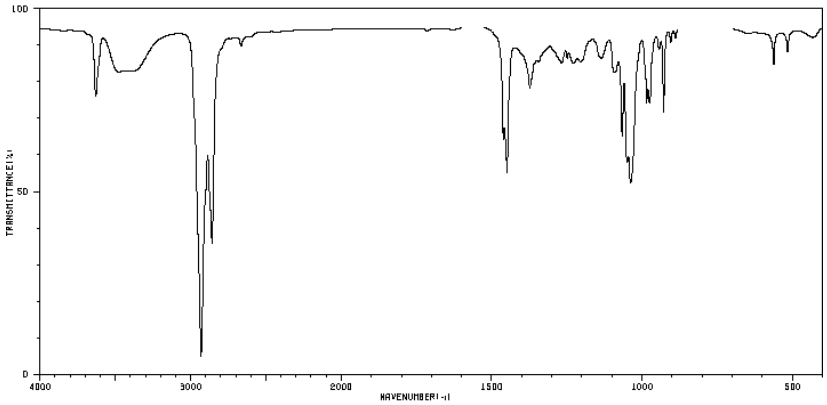
1. Does the E2 mechanism explain the formation of compounds (4) and (5) ?
2. What geometric requirement of the E2 mechanism causes the cis isomer to dehydrate faster ? If the trans isomer undergoes E2 elimination, which product is formed ?
3. How does Saitzev's Rule apply to this experiment ?
4. Show that E1 mechanism accounts for the formation of the by-products (4) and (5).
5. Explain the role of phosphoric acid in this reaction.
6. Explain what would happen if we used hydrochloric acid instead of phosphoric acid ?
7. Explain why the temperature measured at the top of the column (first distillation) must not exceed 115 °C ?
8. Explain the difficulty to purify correctly the 1-methylcyclohexene.

Spectrum 1 : FT-IR Spectrum of (1)



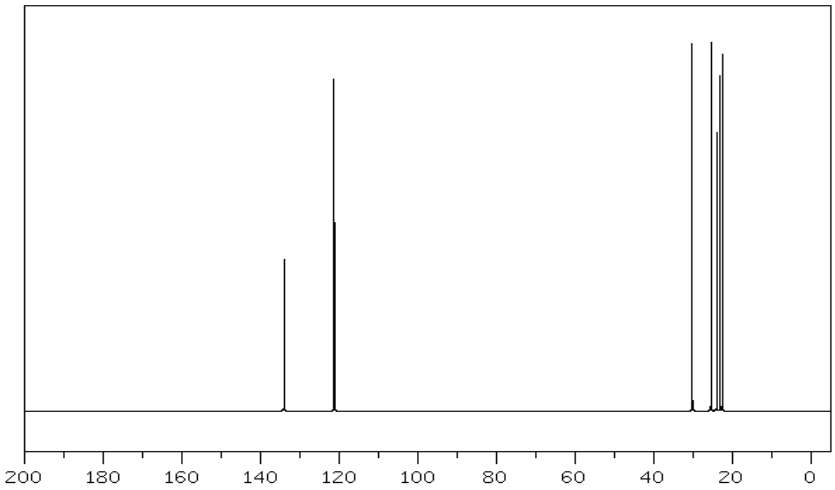
3351	21	1348	62	1098	66	945	77	771	79
2928	4	1298	68	1087	58	929	49	564	70
2858	14	1267	68	1067	35	905	81	524	81
2666	74	1248	74	1053	30	890	84	519	81
1461	41	1239	70	1038	26	868	81	439	86
1450	33	1212	70	986	49	844	62	434	66
1373	60	1146	72	979	63	830	77		

Spectrum 2 : FT-IR Spectrum of (1)



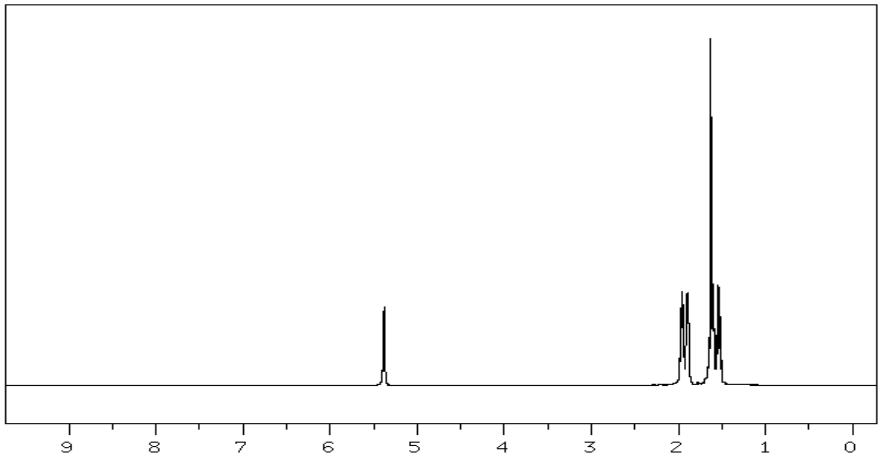
3630	72	1257	81	1066	62	662	81
2930	4	1249	84	1050	55	617	84
2858	34	1228	81	1038	50		
2664	86	1217	84	985	70		
1462	62	1135	84	974	70		
1449	53	1095	79	943	66		
1373	74	1088	79	928	68		

Spectrum 3 : Interpret the Carbon NMR Spectrum of (2)



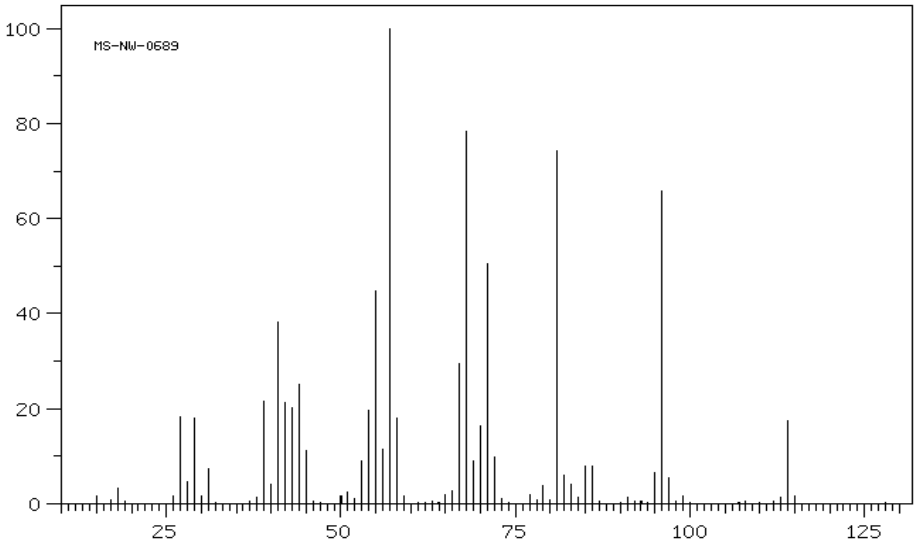
Seven signals / ppm : 134 ; 121 ; 30 ; 25 ; 24 ; 23 ; 22

Spectrum 4 : Interpret the Proton NMR Spectrum of (2)

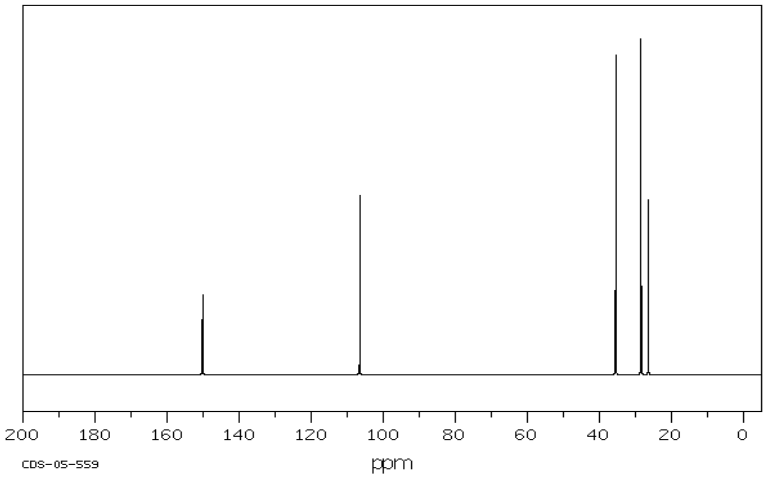


5.4 ppm : I = 1 ; 1.9 ppm : I = 4 ; 1.63 ppm : I = 3 ; 1,55 ppm : I = 4

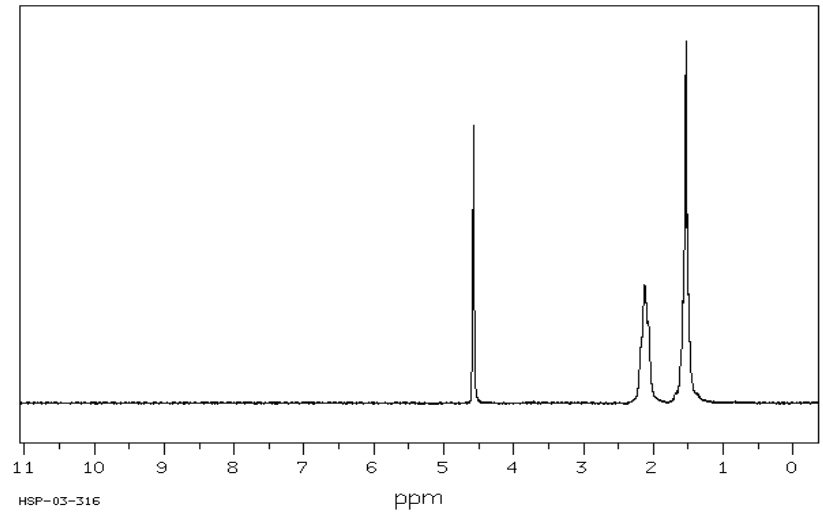
Spectrum 5 : Mass Spectrum of Unknown Compound



Spectrum 6 : Carbon NMR Spectrum of (3), (4) or (5) ?



Spectrum 7: Proton NMR Spectrum of (3), (4) or (5) ?



4.6 ppm : I = 2 ; 2.1 ppm : I = 4 ; 1.5 ppm : I = 5