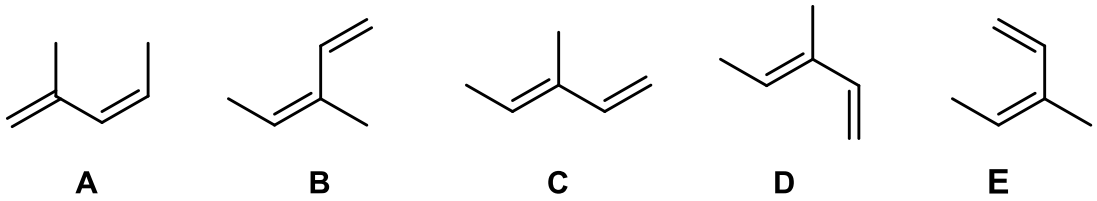
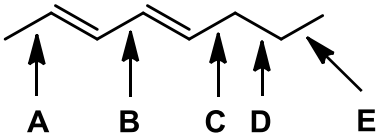
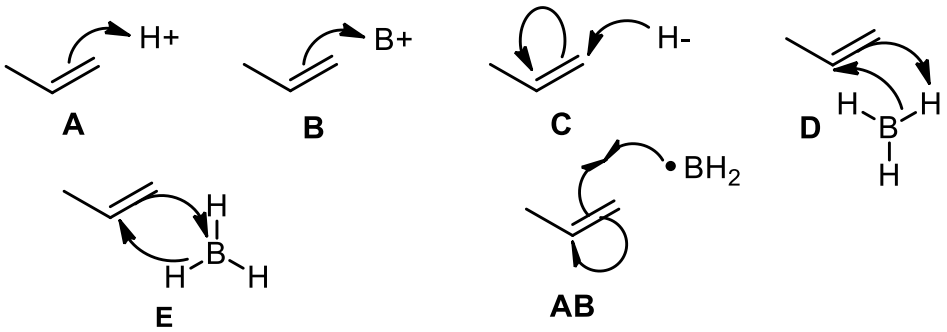
30. Which of the following molecules is the *s-trans* form of (3Z)-3-methylpenta-1,3-diene ? **(select all that apply)**



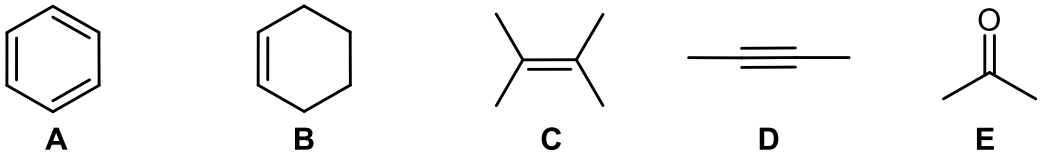
31. Which of the CC bonds indicated is the **shortest** ?



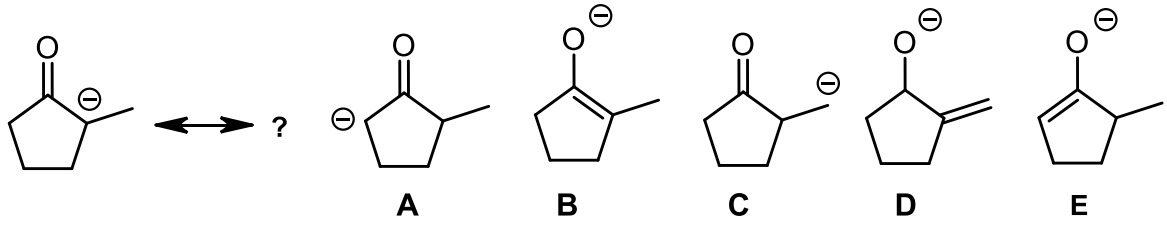
32. Which of the following **best** represents a step in the mechanism of the reaction of propene with BH_3 ?



33. Which of the following systems would be the **most** reactive towards H_2 / Pd ?



34. Which of the following systems are resonance contributors of the anion shown below ? **(select all that apply)**



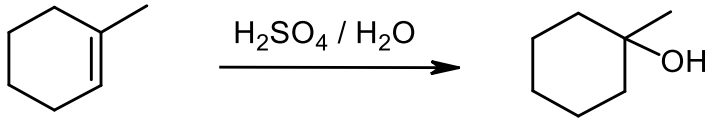
10% **PART 5: MECHANISMS**

ANSWER TWO (2) QUESTIONS, ONE FROM PART A and ONE FROM PART B

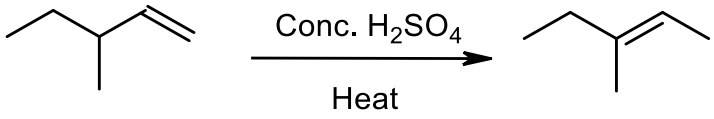
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Draw curly arrow mechanisms to explain the following reactions / observations. No other reagents are required.

A. Show the mechanism for **one** of the following reactions:

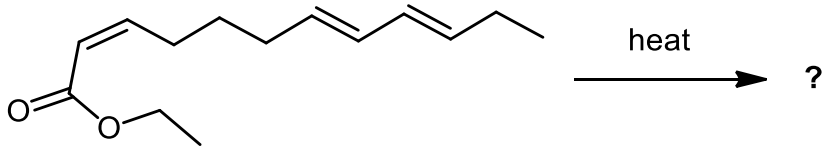


OR

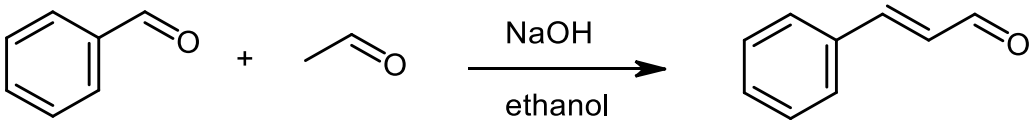


AND

B. Show the mechanism for **one** of the following reactions to give the major product and ***briefly*** justify the product formation :



OR



15% PART 6: SYNTHESIS

ANSWER THREE (3) QUESTIONS, ONE FROM A, ONE FROM B AND ONE FROM C.

WRITE YOUR ANSWERS IN THE BLUE BOOKLET PROVIDED.

Design an efficient synthesis for THREE (3) of the following target molecules

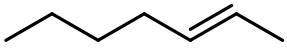
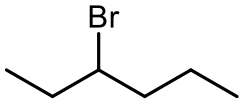
SHOW YOUR ANSWER AS **A STEPWISE REACTION SCHEME** SHOWING THE **REAGENTS REQUIRED AND PRODUCT OF EACH STEP.**

DO NOT SHOW MECHANISMS (*i.e.* curly arrows are NOT required)

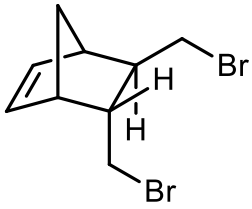
Allowed starting materials and reagents :

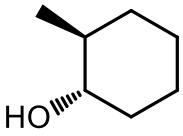
Any hydrocarbons with 5 or less C atoms

Any solvents or reagents that do not contribute carbon atoms to the final structure.

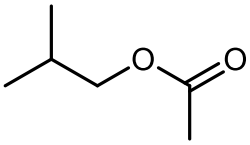
A  or 

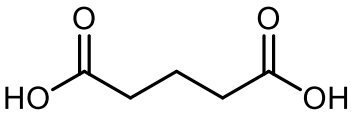
AND

B 

or 

AND

C 

or 

11% PART 7: STRUCTURE DETERMINATION

WRITE YOUR ANSWER IN THE BLUE BOOKLET PROVIDED

Use the information in the following paragraph to answer the questions below.

None of the materials **A - G** are chiral.

When **A**, $C_5H_{11}Br$, was reacted with hot, ethanolic KOH, **B**, C_5H_{10} was obtained, IR :1680 cm^{-1} (w). **B** gave a colourless solution when tested with Br_2 in chloroform. Subsequent reaction of **B** with Br_2 under a uv lamp or with N-bromosuccinimide gave **C**, C_5H_9Br as the major product. When **B** was reacted BH_3 then aq. NaOH / H_2O_2, **D** was the major product. Reaction of **D** with PBr_3 / Et_3N gave **A** as the major product. In contrast, reaction of **B** with aq. H_2SO_4 gave **E** as the major product. **E** spectral data : ^{1}H-NMR: 1.8 ppm (broad, singlet, 1H), 1.5 ppm (quartet, 2H), 1.20 ppm (singlet, 6H) and 0.9 ppm (triplet, 3H), IR : 3500cm^{-1} (very broad).

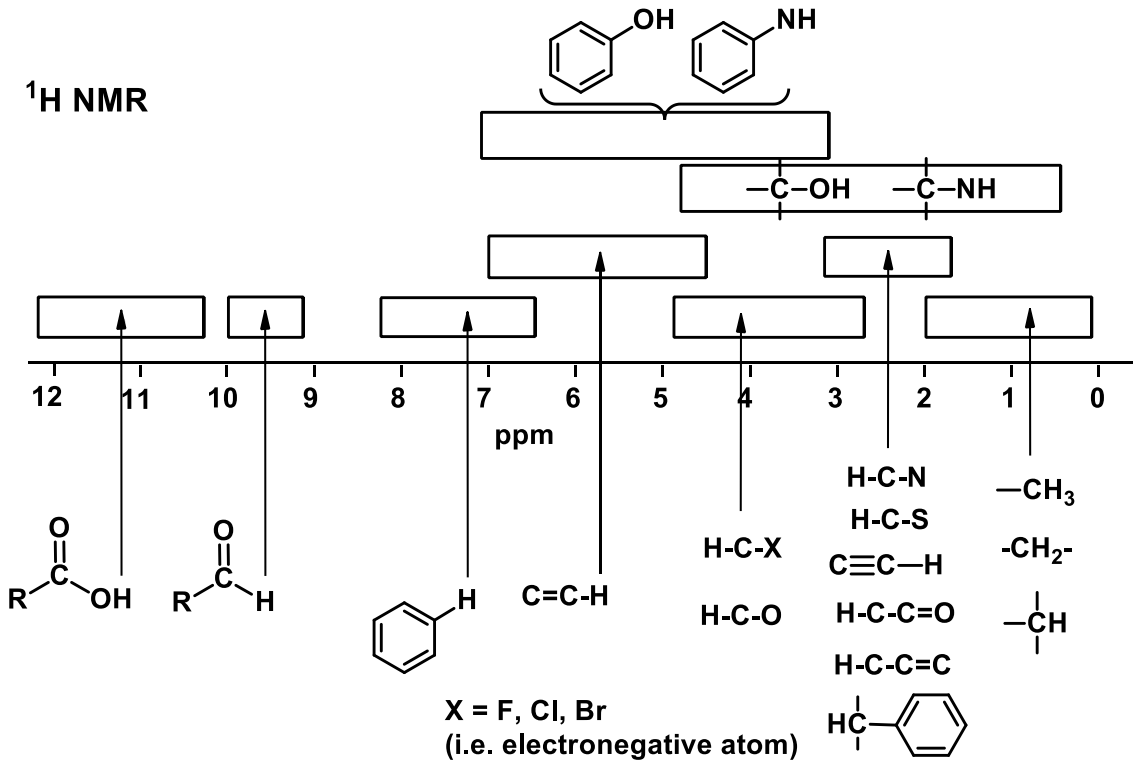
When **C** was reacted with hot, ethanolic KOH, **F**, C_5H_8 was formed. **F** was found to have 5 peaks in the ^{13}C-NMR. When **F** was heated in a sealed tube with ethene, it gave **G**, C_7H_{12}, as the major product. **G**, IR : 1660cm^{-1}, 7 peaks in the ^{13}C-NMR. **G** also gave a colourless solution with Br_2 in chloroform. Subsequent reaction of **G** with ozone followed by hydrogen peroxide work up gave 6-oxo-heptanoic acid.

- Identify the compounds **A - G** (structures are sufficient)

*** THE END ***

IRH / JvH / W22

SPECTROSCOPIC TABLES

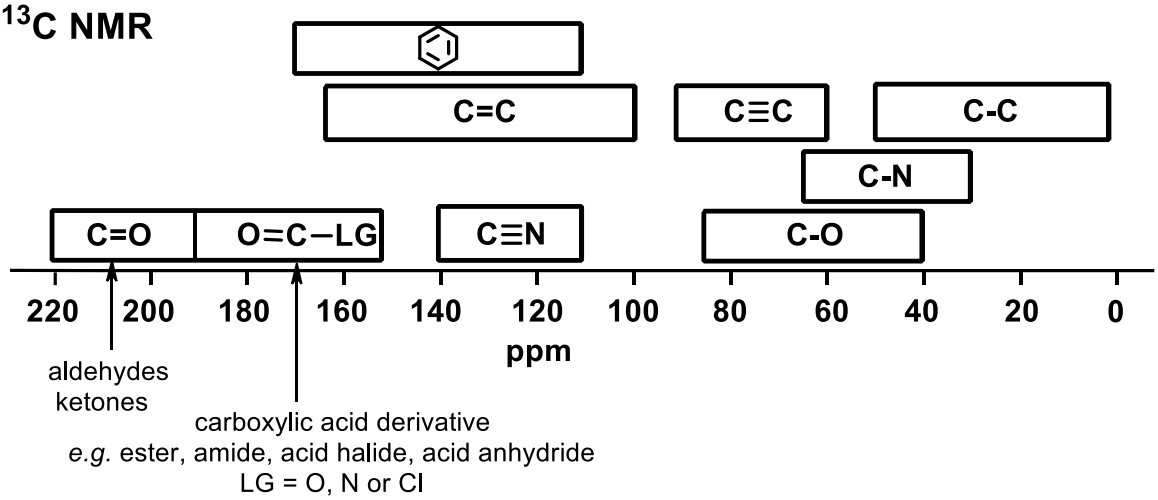


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

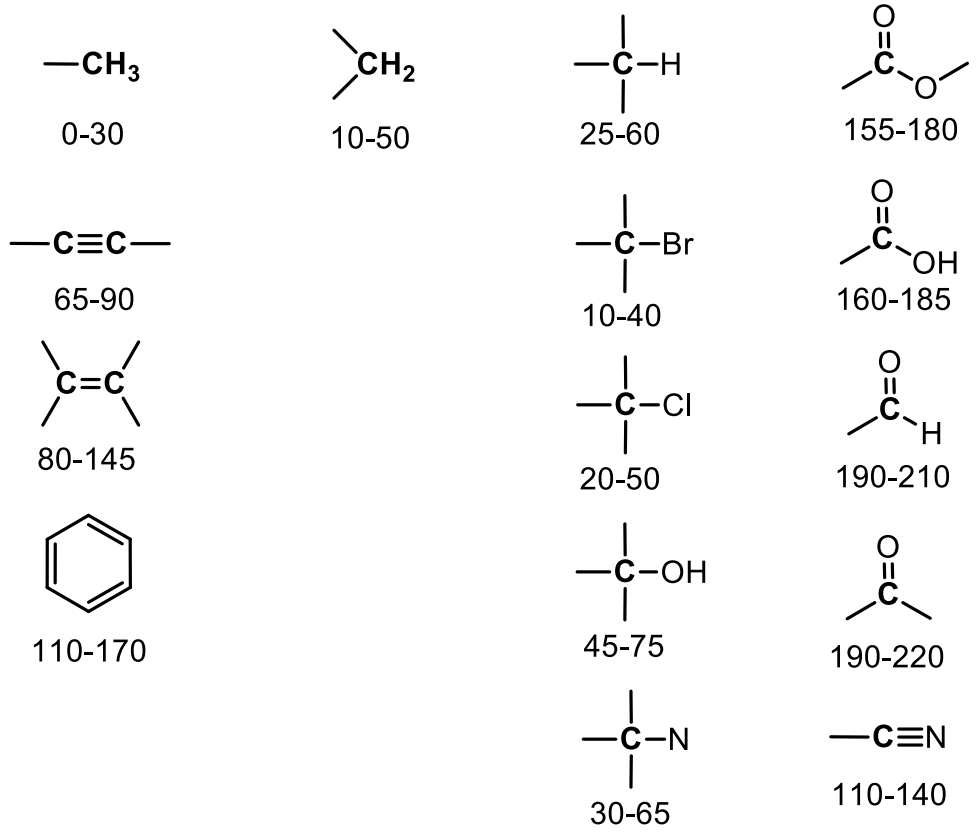
R =	methyl —CH_3	methylene -CH_2-	methyne —CH
R—C—	0.9	1.4	1.5
R, C=C	1.6	2.3	2.6
R—C(=O)—	2.1	2.4	2.5
R—N	2.2	2.5	2.9
R—Ar	2.3	2.7	3.0
R—Br	2.7	3.3	4.1
R—Cl	3.1	3.4	4.1
R—O—	3.3	3.4	3.7

other	
sp^3C-OH	1-5
sp^3C-NH	1-3
C≡CH	2.5
C=C(H)—	4.5-6.5
H—Ar	6.5-8
R—C(=O)—H	9-10
R—C(=O)—OH	9-12

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	$-CH_3$	(bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad.

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)