SEM II 08/09 APRIL 2009

1 (a)

(S)-(+)-l-chloro-2-methylbutane




IV

v

(b) I $=$ (S)-1,1-dichloro-2-methylbutane is chiral

II $\quad=\quad 1,2$-dichloro-2-methylbutane is achiral
III (a) $\quad=\quad(\mathrm{R})$-1,2-dichloro-2-methylbutane
III (b) $\quad=\quad(\mathrm{S})$-1,2-dichloro-2- methylbutane


IV $\quad=\quad(2 R, 3 R)$-1,3-dichloro-2-methylbutane
$\mathrm{V} \quad=\quad(2 \mathrm{R}, 3 \mathrm{~S})$-1,3-dichloro-2-methylbutane
VI $\quad=\quad(\mathrm{S})$-1,4-dichloro-2-methylbutane is chiral

2 (a) $\mathrm{NH}_{3}<\mathrm{H}_{2} \mathrm{O}<\mathrm{HF}$
When determining relative acidity, it is often useful to look at the relative basicity of the conjugate bases. The stronger the acid, the weaker (more stable, less reactive) the conjugate base. In this case, one would look at the relative basicity of $\mathrm{F}^{-}, \mathrm{OH}^{-}$, and $\mathrm{NH}_{2}{ }^{-}$. The relative strengths of these species can be gauged based on the electronegativity of the charged atom in each. Since fluorine is the most electronegative, $\mathrm{F}^{-}$is the most stable, least reactive base in the group. This means that its conjugate acid, HF, is the strongest.
(b) (i) The single carbon-carbon sigma bond present in $\mathrm{CH}_{3} \mathrm{CH}_{3}$ is formed by the overlap of two $\mathrm{C} \mathrm{sp}{ }^{3}$ hybrid atomic orbitals. The overlap of these orbitals is not disrupted by rotation about the carbon-carbon bond axis. In the case of $\mathrm{CH}_{2} \mathrm{CH}_{2}$, the carbon-carbon bond is a double bond with both a sigma and pi bond present. Rotation about the carbon-carbon bond axis disrupts the overlap of the two carbon p orbitals forming the pi bond.
(ii)

(c) (i) 2,2-dimethyl-5-(1-methylpropyl)nonane
(ii) 1-ethyl-2-(2,2-dimethylpentyl)cyclopentane
(iii) 4,4-dichloro-6-isopropyl-3-methylnonane
(d)


3
(a)

pent-1-ene


3-methylbut-1-ene

(E)-pent-2-ene


2-methylbut-1-ene

(Z)-pent-2-ene


2-methylbut-2-ene
(b) (i)




(ii)

(iii)


(c)



4 (a) Ethylacetylene is an alkyne compound with the following structure:

$$
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{C} \equiv \mathrm{C}-\mathrm{H}
$$

I With $\mathrm{H}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{HgSO}_{4}$, electrophilic addition of H and OH places the H atom on the less substituted carbon on the alkyne to form a ketone after tautomerization


II In contrast, addition of $\mathrm{BH}_{3}$ places the $\mathrm{BH}_{2}$ group on the less substituted terminal carbon of the alkyne. Oxidation and tautomerization yield an aldehyde.


The relationship between both of the product: Both compounds are constitutional isomers.
(b) Identification of the compounds $\mathbf{A}$ and $\mathbf{B}$ in the given reaction.

Note: The starting compound is an alkyne with two terminal H atoms. In each step, $-\mathrm{NH}_{2}$ removes an $s p$ hybridized proton, and the resulting acetylide anion reacts as a nucleophile with an alkyl halide to yield an $\mathrm{S}_{\mathrm{N}} 2$ product.

## Answer

i. The first two-step reaction sequence forms the terminal alkyne $\mathbf{A}$ by nucleophilic attack of the acetylide anion on $\mathrm{CH}_{3} \mathrm{Br}$.


Therefore,
Compound A is a terminal alkyne named as:
propyne or methyl acetylene or prop-1-yne
ii. The second two-step reaction sequence forms the internal alkyne $\mathbf{B}$ by nucleophilic attack of the acetylide anion on $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Cl}$.

(B)

## Therefore,

Compound B is an internal alkyne, named as:

## 2-pentyne or ethylmethylacetylene or pent-2-yne.

(c) The expected product from the reaction of 1-ethylcyclopentene with:
(a) $\mathrm{BH}_{3}$, THF followed by $\mathrm{H}_{2} \mathrm{O}_{2}, \mathrm{OH}^{-}$
(b) $\mathrm{Hg}(\mathrm{OAc})_{2}, \mathrm{H}_{2} \mathrm{O}$ followed by $\mathrm{NaBH}_{4}$

Apparently, the two methods are about the hydration-hydroboration/oxidation and oxymercuration, and both will give complimentary products. Hydroboration/oxidation occurs with syn stereochemistry and gives the nonMarkovnikov addition product, while oxymercuration gives the Markovnikov products.

## The first reaction:



The second reaction:



Markovnikov addition of $\mathrm{H}_{2} \mathrm{O}$

