oxidation with $KMnO_4$:-

monosubsituted vinylic carbons converts in to carboxylic group by $KMnO_4/\overset{\ominus}{O}H/\Delta$

$$CH_3-CH=CH-CH_3 \xrightarrow[\Delta]{KMnO_4/\overset{\ominus}{O}H} CH_3COOH + CH_3COOH$$

Terminal alkene gives formic acid as one of the product which further undergoes oxidation into CO_2 & H_2O.

$$CH_3-CH=CH_2 \xrightarrow[\Delta]{KMnO_4/\overset{\ominus}{O}H} CH_3-COOH + HCOOH \downarrow CO_2 + H_2O$$

disubsituted vinylic carbon converts in to keto group :-

$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}=C\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow[\Delta]{KMnO_4/\overset{\ominus}{O}H} CH_3-CH_2-\underset{CH_3}{\overset{\overset{\ominus}{O}}{C}} + CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

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Cleavage with $OSO_4/NaIO_4$

(Osmium tetra oxide)

November 2006

S	M	T	W	T	F	S
			1	2	3	4
5	6	7	8	9	10	11
12	13	14	15	16	17	18
19	20	21	22	23	24	25
26	27	28	29	30		

monosubsituted vinylic carbon converts in to carboxylic group while disubsituted

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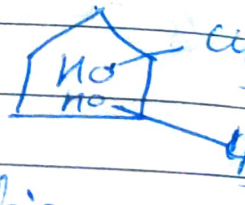
Vinylic carbon converts in to keto groups By this reagents formic acid does not undergoes further oxidation.

$$CH_3-\underset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{OSO_4/NaIO_4} CH_3-\overset{O}{\overset{||}{C}}-CH_3 + HCHO$$

$$C_2H_5-CH=\underset{CH_2-CH_3}{\overset{CH_3}{C}} \xrightarrow{OSO_4/NaIO_4} C_2H_5COOH + \overset{O}{\overset{||}{C}}(H)-CH_3$$

$$\xrightarrow[\text{Baeyers Reagent}]{KMnO_4/NaOH/H_2O}$$



oximeriquration Reduction

$$CH_3-\underset{CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[(ii)\ NaBH_4]{(i)(CH_3COO)_2Hg/H_2O} CH_3-\underset{CH_3}{\overset{OH}{\overset{|}{C}}}-CH_2-CH_3$$

addition of alkene with mercuric acetate in the Presence of H_2O is called oximeriquration Reaction The Reaction Product on

Reduction with $NaBH_4$ gives alcohol. This step is 1,4 demerguration. So the overall reaction is called as oximerguration Reduction.

Ques Complete the following Reaction

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}=CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } Hg(OCOCH_3)_2} \text{Product}$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

Substitution on the allylic & Vinalic ⟹

When an alkene is heated with halogen at 500°C then in place of addition substitution reaction takes place.

$$CH_3-CH=CH_2 \xrightarrow[Cl_2/500^\circ C]{Cl_2/CCl_4} CH_2-\underset{Cl}{CH}-CH_2-Cl$$

$$Cl-CH_2-CH=CH_2 + HCl$$

Allyl chloride

01 Wednesday November 2006

If the allylic groups contain more than one carbon atom then the substitution occurs at the carbon α to the double bonds or at allylic carbon atom due to this the reaction is k/a allylic Substitution

$$CH_3-CH_2-CH=CH_2 + Cl_2 \xrightarrow{500^\circ C} CH_3-\underset{Cl}{CH}-CH=CH_2$$

mechanism :—

(I) $Cl-Cl \longrightarrow Cl^\cdot + Cl^\cdot$

(II) $Cl^\cdot + H-CH_2-CH=CH_2 \longrightarrow -HCl$

$$\dot{C}H_2-CH=CH_2 \longleftrightarrow CH_2=CH-\dot{C}H_2$$

(III) $CH_2=CH-\dot{C}H_2 + Cl-Cl \longrightarrow$

$$CH_2=CH-CH_2-Cl + Cl^\cdot$$

Allylic Substitution are brought about by N-bromosaccinamide (NBS) at room temp in the presence of non polar solvent.

NBS introduces bromine at the allylic & Benzylic position.

November 2006

S	M	T	W	T	F	S
			1	2	3	4
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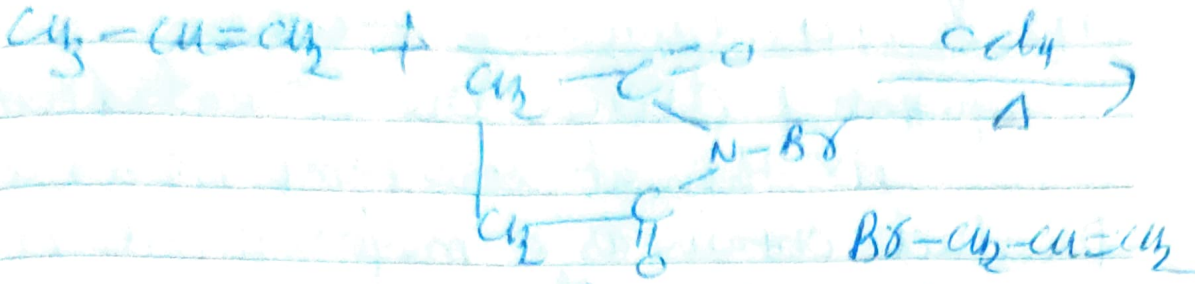
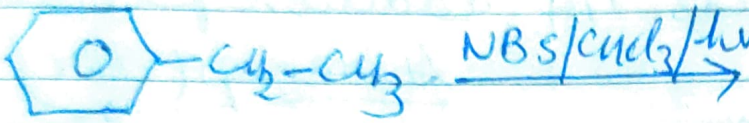
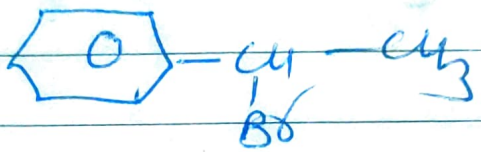
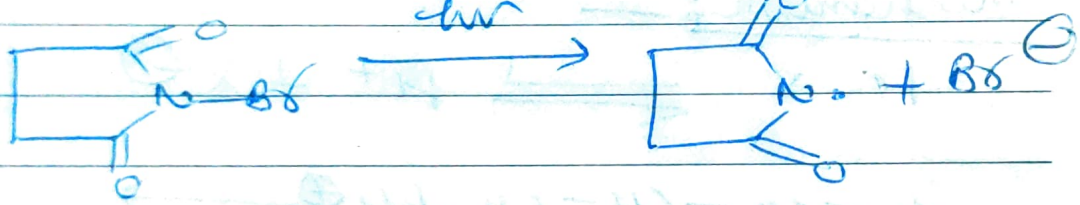
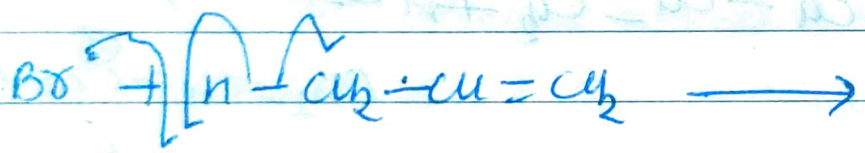


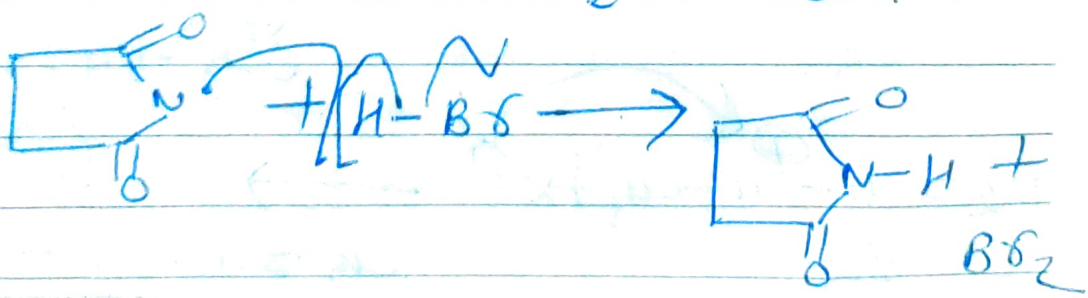


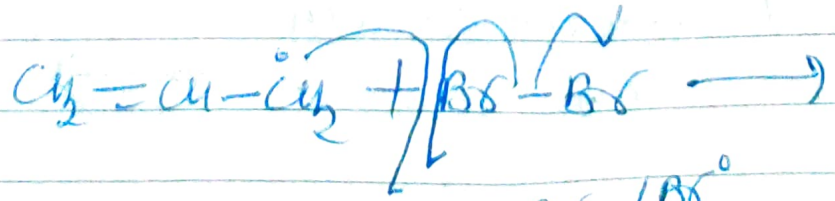


Mechanism :—









03 Friday November 2006

1,2 & 1,4 addition :— when conjugated dienes are treated with HX then at low temp 1,2 addition product obtain as a major product while at higher temp. the major product is 1,4 addition product.

$CH_2=CH-CH=CH_2$ —
- At low temp (−80°C) → $CH_2-CH(X)-CH=CH_2$ (1,2 addition)
- At high temp → $CH_2-CH=CH-CH_2X$ (1,4 addition)

Mechanism :—

$H-X \rightleftharpoons H^+ + X^-$ (1)

$CH_2=CH-CH=CH_2 + H^+ \longrightarrow$

$CH_2=CH-\overset{\oplus}{C}H-CH_3$ (A)

$\overset{\oplus}{C}H_2-CH=CH-CH_3$ (B)

$CH_2=CH-CH(X)-CH_3$

$X^- + CH_2-CH=CH-CH_3$ (B) $\longrightarrow$

$CH_2-CH=CH-CH_3$

Reaction with Conjugated dienes with halogen :—

$CH_2=CH-CH=CH_2 + Br_2$ → at low Temp 0°C; At light Temp 60°C

$CH_2(Br)-CH=CH-CH_2$ (Br)

1, 4 addition

method of formation of butadiene

(i) $HO-CH_2-CH_2-CH_2-CH_2-OH \xrightarrow[Conc.\ H_2SO_4]{P_2O_5} CH_2=CH-CH=CH_2$

(ii) $Cl-CH_2-CH_2-CH_2-CH_2-Cl \xrightarrow[EtOH]{NaOH} CH_2=CH-CH=CH_2$

(iii)  $\xrightarrow{\Delta}$ [ ] + H_2

SUNDAY 5