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(8) $CH_3-CH=CH-CH_3 \xrightarrow{NBS}$ $CH_3-CH=CH-CH_2Br$ + $CH_3-\overset{*}{C}H(Br)-CH=CH_2$

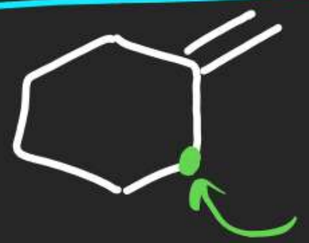
$CH_3-CH=CH-CH_2Br$: 2(Cis+Trans) $\quad$ $CH_3-\overset{*}{C}H(Br)-CH=CH_2$: 2(R+S) $\quad$ 2, 4

(9) $CH_3-CH=CH-CH_2-CH_3 \xrightarrow{NBS}$ CH_2

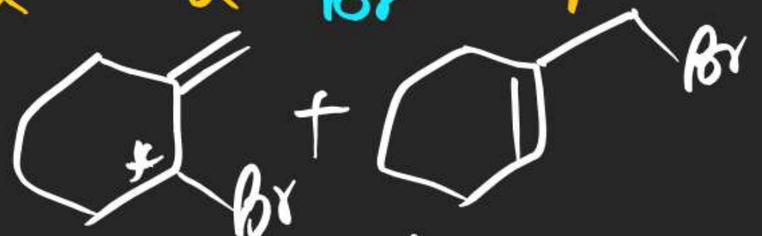
Possible Radical $\left[\bullet\!\!-\!\!=\!\!-\leftrightarrow -\!\!=\!\!-\bullet\right]$ & $\left[\bullet\!\!-\!\!=\!\!-\!\!-\leftrightarrow -\!\!=\!\!-\!\!-\bullet\right]$

Possible product

3, 8

(10) 

$\xrightarrow{NBS}$



2 $\quad$ 1

2, 3

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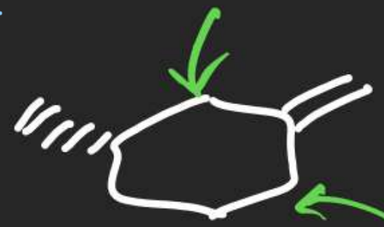
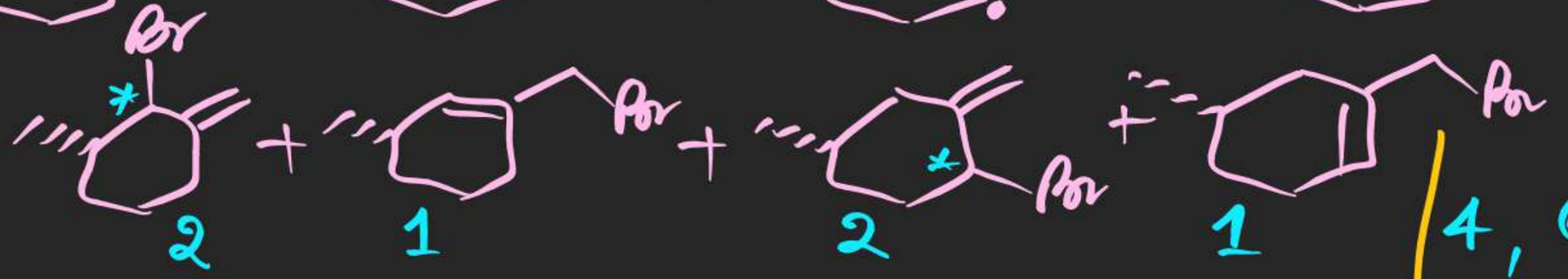
(11)  NBS

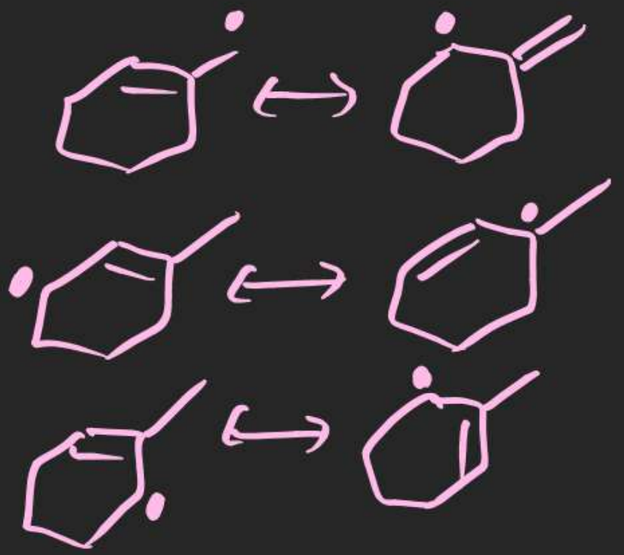
Possible Radical

Possible Product:

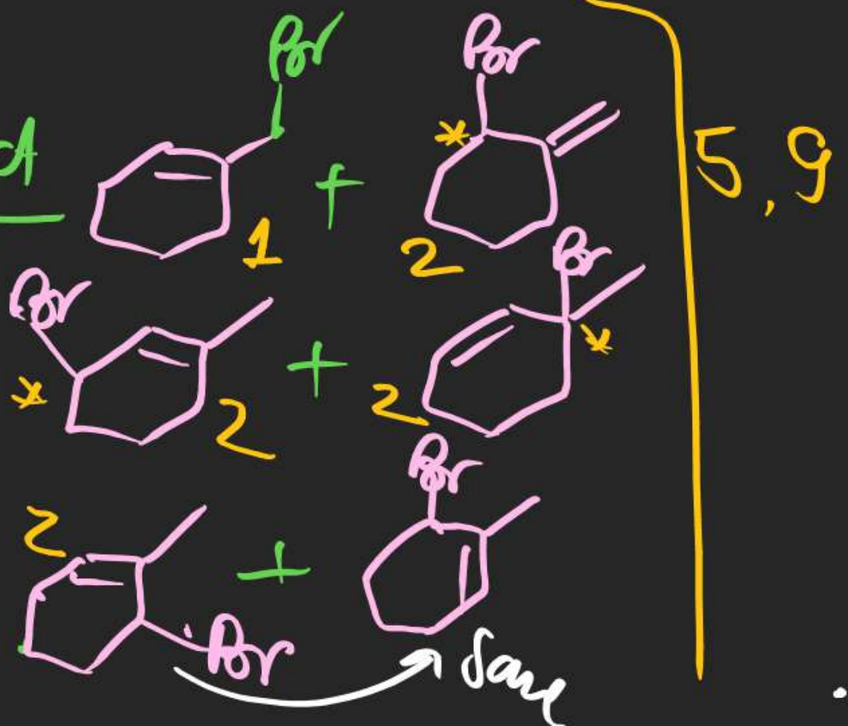


(12)  NBS

Possible Radical:



possible product



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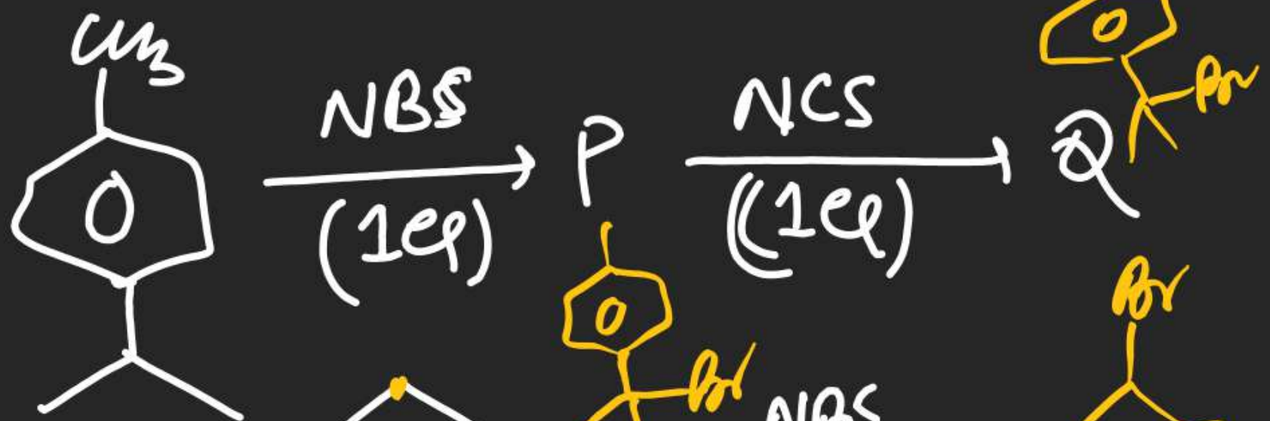
(13)  NBS →

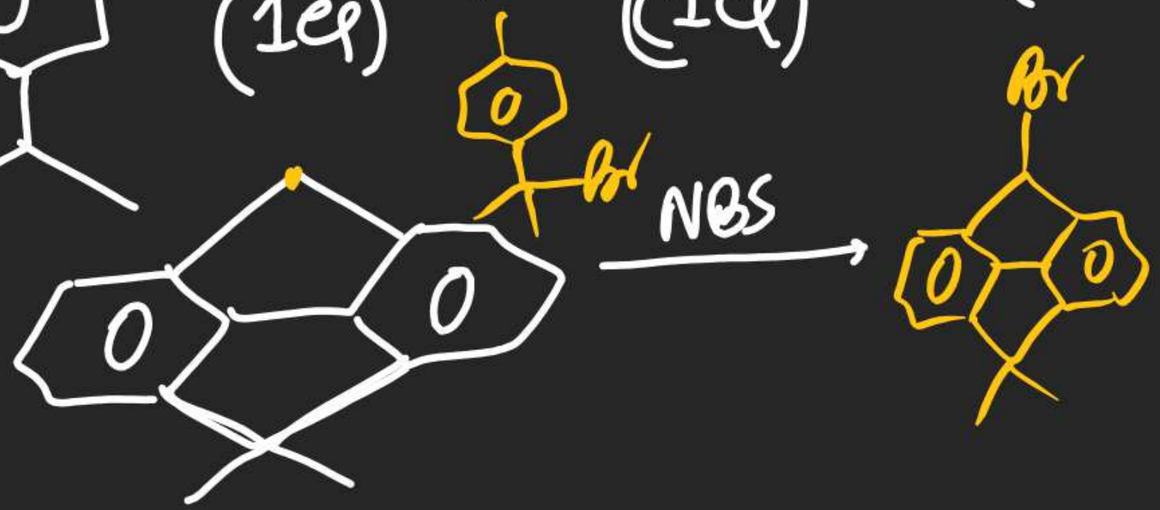
(4, 11)

(#) Write major Product

(14) 

(15) 

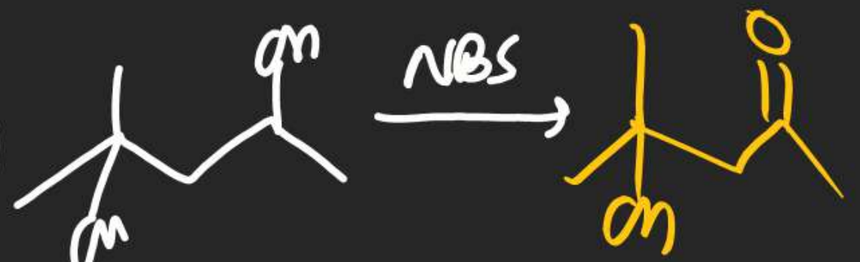
(16) 

(17) 

(18) 

(19) 

(20) 

(21) 

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(#) Reed'ff Reaction!-

$\Rightarrow$ alkane on Reaction with SO_2Cl_2 gives alkyl halide as a Product

(1) $R-H + SO_2Cl_2 \xrightarrow{h\nu} R-Cl + H-Cl + SO_2$

mechⁿ!

Initiation! $SO_2Cl_2 \xrightarrow{h\nu} SO_2 + 2Cl^{\cdot}$

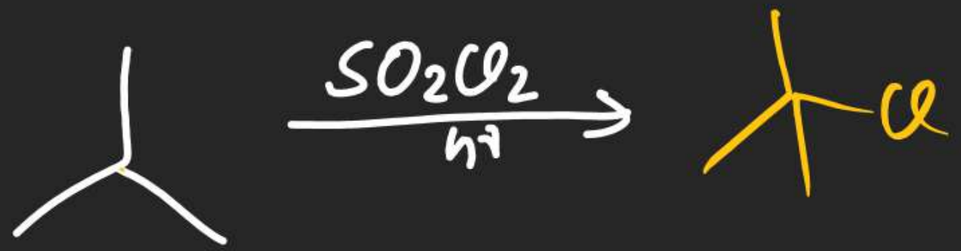
Propagation! $Cl^{\cdot} + R-H \longrightarrow R^{\cdot} + HCl$

$R^{\cdot} + SO_2Cl_2 \longrightarrow R-Cl + SO_2 + Cl^{\cdot}$

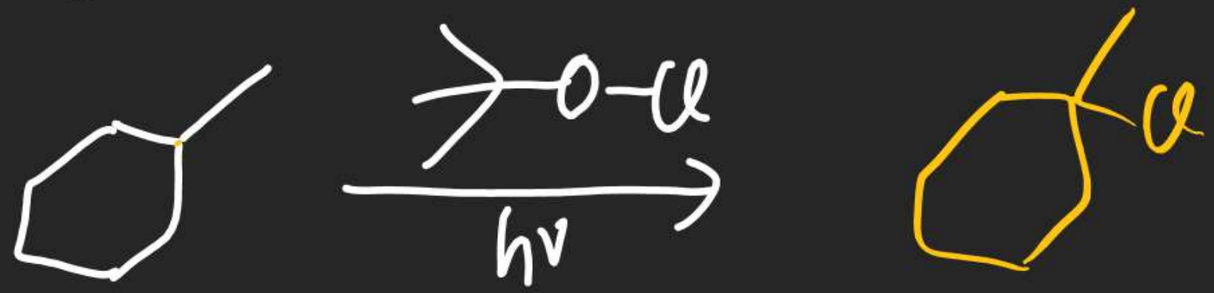
Termination! $Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$

Note

(i) Free Radical intermidiate
(ii) Chain Rxn
(iii) Oxidation of alkane

(2) 

(3) 

(4) 

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(#) Photohalogenation :-

$\Rightarrow$ halogenation of Alkane By using X_2 & photon's Energy of UV rays.

(1) $R-H + X_2 \xrightarrow{h\nu} R-X + H-X$

mechanism :-

Initiation: $X-X \xrightarrow{h\nu} 2X^{\bullet}$

Propagation: $X^{\bullet} + R-H \xrightarrow{Y\cdot d\cdot s} R^{\bullet} + H-X$

$R^{\bullet} + X-X \longrightarrow R-X + X^{\bullet}$

Termination: $X^{\bullet} + X^{\bullet} \longrightarrow X_2$

$\therefore$

Note

(i) Free Radical intermidiate

(ii) Chain Reaction

(iii) Oxidation of Alkene

(iv) Formation of $R^{\bullet}$ is r.d.s

(v) order of rate of reaction for $>C-H$

$3^{\circ}\ >C-H > 2^{\circ}\ >C-H > 1^{\circ}\ >C-H$

(vi) order of rate of rxn for X_2

$F_2 >> Cl_2 > Br_2 >> I_2$

Fastest — Slowest

Flvorination:- Flvorination is highly Exothermic & Explosive phenomenon & it gives Carbon Black.

(2) $CH_4 + 2F_2 \longrightarrow C_{Black} + 4HF$

Chlorination:- Chlorination is highly Exothermic & Explosive phenomenon & it gives Carbon Black in B.S.L

(3) $CH_4 + 2Cl_2 \xrightarrow{BSL} C_{Black} + 4HCl$

(*) **Chlorination** can be carried out in D.S.L (diffused sunlight)

(4) $\underset{1}{CH_4} + Cl_2 \xrightarrow{h\nu} CH_3-Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + \cdots\cdots$

$1 : 1$

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mechanism:

Initiation step:-

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$

Propagation step:

$$Cl^{\bullet} + CH_4 \longrightarrow \dot{C}H_3 + HCl$$
$$\dot{C}H_3 + Cl\text{-}Cl \longrightarrow CH_3\text{-}Cl + Cl^{\bullet}$$

$$Cl^{\bullet} + CH_3\text{-}Cl \longrightarrow \dot{C}H_2Cl + HCl$$
$$\dot{C}H_2Cl + Cl\text{-}Cl \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

$$Cl^{\bullet} + CH_2Cl_2 \longrightarrow \dot{C}HCl_2 + HCl$$
$$\dot{C}HCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl^{\bullet}$$

$$Cl^{\bullet} + CHCl_3 \longrightarrow \dot{C}Cl_3 + HCl$$
$$\dot{C}Cl_3 + Cl_2 \longrightarrow CCl_4 + Cl^{\bullet}$$

Termination:

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

⇒ monohalogented product dominates when alkane is taken in Excess

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{(major)}}{CH_3-Cl} + HCl$$

(Excess)

⇒ If X_2 is taken in Excess polyhalogented product dominates

$$CH_4 + 2Cl_2 \xrightarrow{h\nu} \underset{\text{(major)}}{CCl_4} + 4HCl$$

Excess

$$C_2H_6 + 3Cl_2 \longrightarrow \underset{\text{(major)}}{C_2Cl_6} + 6HCl$$

Excess

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⇒ **Bromination:-** Bromination is slightly Reversible phenomenon.

$$R-H + Br_2 \xrightleftharpoons{h\nu} R-Br + H-Br$$

⇒ **Iodination:** It is highly Reversible & can be carried out only in presence of oxidising agent like HIO_3, HNO_3 ……

$$R-H + I_2 \rightleftharpoons R-I + H-I$$

Reduction — Reducing agent — Oxidation

$$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$

Oxidising agent — Reducing agent

⇒ Chlorination is highly Reactive & less selective in nature.

⇒ Bromination is less Reactive & highly selective in nature.

⇒ Stability $\propto \frac{1}{\text{Reactivity}} \propto$ selectivity

⇒ Relative Reactivity Of chlorination towards $1^\circ, 2^\circ$ & 3° C–H

$= 1 : 3.8 : 4.5$

⇒ Relative Reactivity Of Bromination towards $1^\circ, 2^\circ$ & 3° C–H

$= 1 : 80 : 1600$

⇒ Relative yeild of Product = Relative Reactivity × Probability factor

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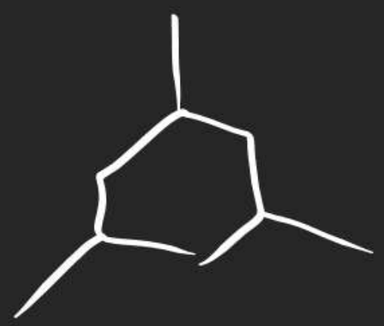
Ex-1: At Temp "T" on monochlorination of Propane, two products 1-chloro propane (46%) & 2-chloro propane (54%) is obtained & on monochlorination of iso Butane at same Temp two products 1-chloro-2-methyl Propane (66.5%) & 2-chloro 2-methyl propane (33.5%) is obtained. Calculate % yeild of products formed on monochlorination of following compounds at same Temp "T".

(i) 

(ii) 

(iii) 

(iv 

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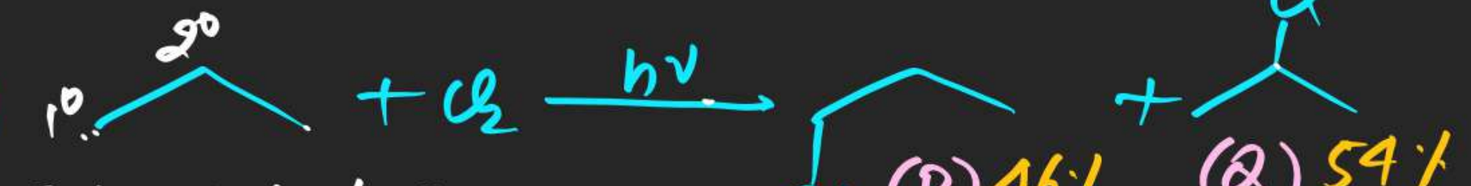
Sol: Relative yeild = Rel. Reactivity × Prob. factor

(*) Relative Reactivity for $1^0, 2^0, 3^0$ C–H = 1 : P : Q at Temp T

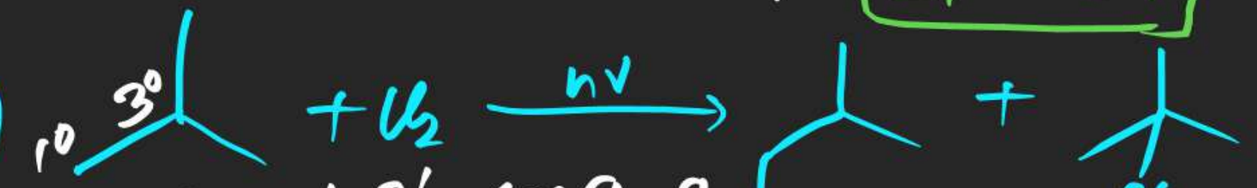
(i) 

(P) 46% (Q) 54%

Rel. yeild of $P = 1 \times 6 = 6$

$Q = P \times 2 = 2P$

$\frac{6}{2P} = \frac{46}{54}$

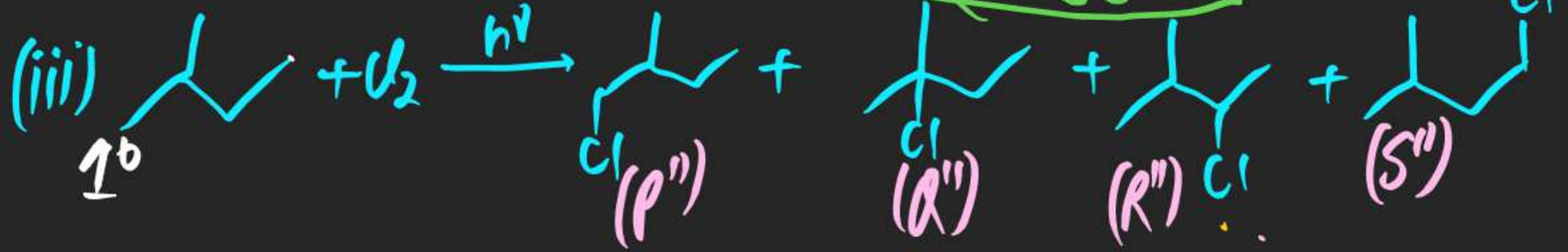
(ii) 

(P') 66.5% (Q') 33.5%

Rel. yeild of $P' = 1 \times 9 = 9$

$Q' = Q \times 1 = Q$

$\frac{9}{Q} = \frac{66.5}{33.5}$

(iii) 

Rel. yeild of $P'' = 1 \times 6 = 6$

$Q'' = Q \times 1 = Q$

$R'' = P \times 2 = 2P$

$S'' = 1 \times 3 = 3$

$g + 2P + Q$

$\% P'' = \frac{6}{g+2P+Q} \times 100$

$\% Q'' = \frac{Q}{g+2P+Q} \times 100$

$\% R'' =$

$\% S'' =$

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(2) Calculate following

(a) Total no. of products obtained on monochlorination Ex. stereo.
(b) Total no. of products obtained on monochlorination _____.
(c) Total no of chiral product obtained _____.
(d) Total no. of Enantiomeric pair _____.
(e) Total no. of fraction obtained on fractional distillation of product mixture obtained on monochlorination.

(1)  $+ Cl_2 \xrightarrow{h\nu}$ 

$2(d+l)$ — T_1 ; 1 — T_2 ; $2(d'+l')$ — T_3 ; 1 — T_4

(a) 4
(b) 6
(c) 4
(d) 2
(e) 4

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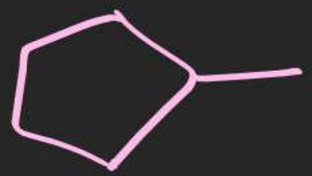
(2) 

(3) 

(4) 

(5) 

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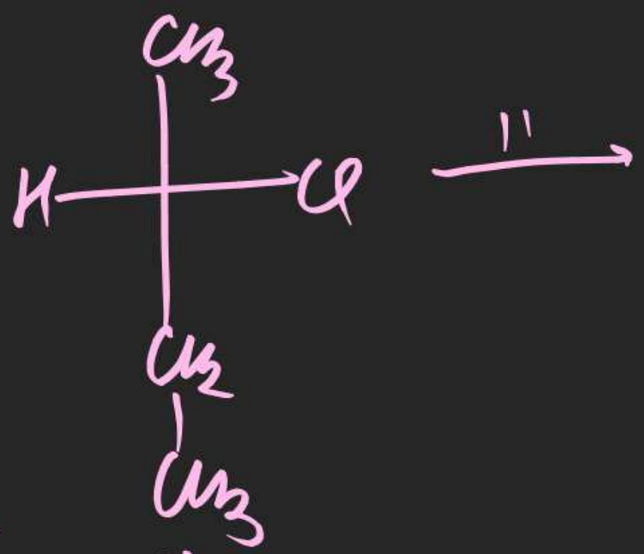
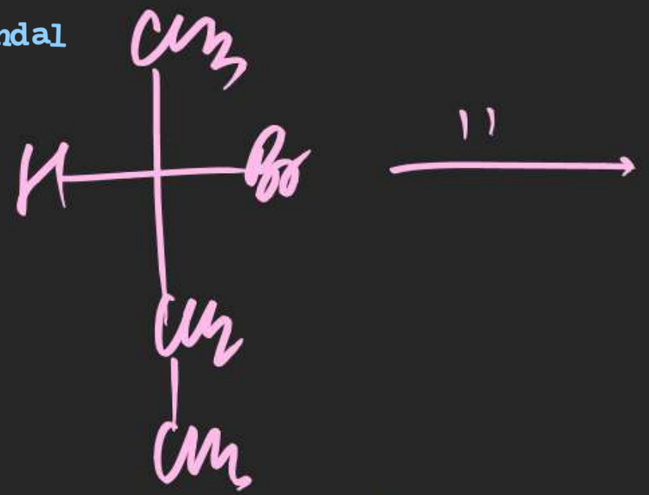
(6)  $\xrightarrow[h\nu]{Cl_2}$

(7)  $\xrightarrow{\quad}$

(8)  $\xrightarrow{\quad}$

(optically pure)

(9)

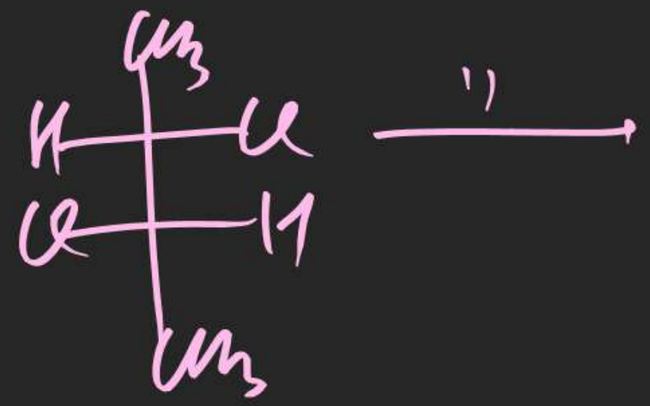


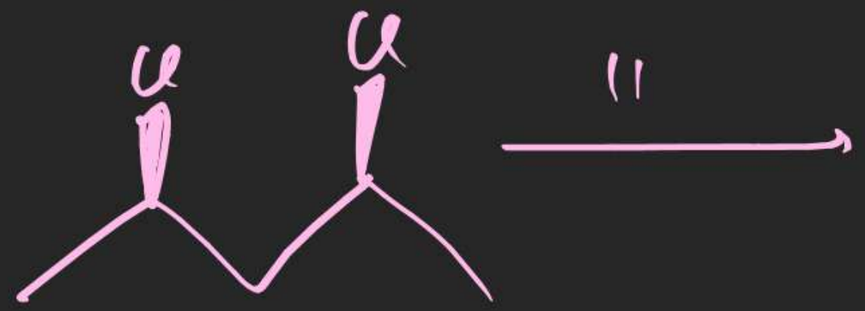
(optically pure)

(10)

(11)

(12) 

(13) 

(14) 

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Substitution Reaction

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Sheet Ex-1 Complete

Ex-2 (1-30)

Alkyl halide, Alcohol, Ether
- Substitution Rxn
- Elimination Rxn

Carbonyl Compound
- Nu. addn, neighbouring effect
- Reduction Rxn
- Oxidation Rxn
- Named Rxn

Hydrocabon	1
Acid derivative	3
Amines	3
Aromatic	6

Biomolecule, POC, Polymer 6-7