12 AUG. 2020

SYNTHETIC REAGENTS

DEGREE-III (H) LECTURE-7

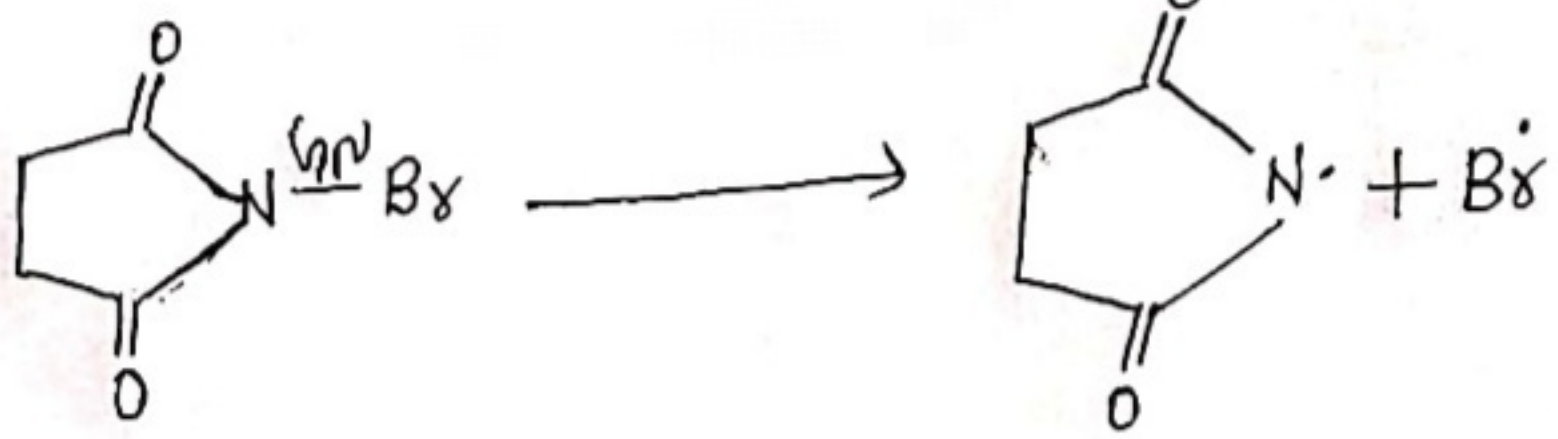
ORGANIC CHEMISTRY, PAPER-VII

Topic :- N-Bromosuccinimide

(Continued...)

Mechanism of allylic bromination proposed by Dauben and MC Coy

Step: 1



Step: 2

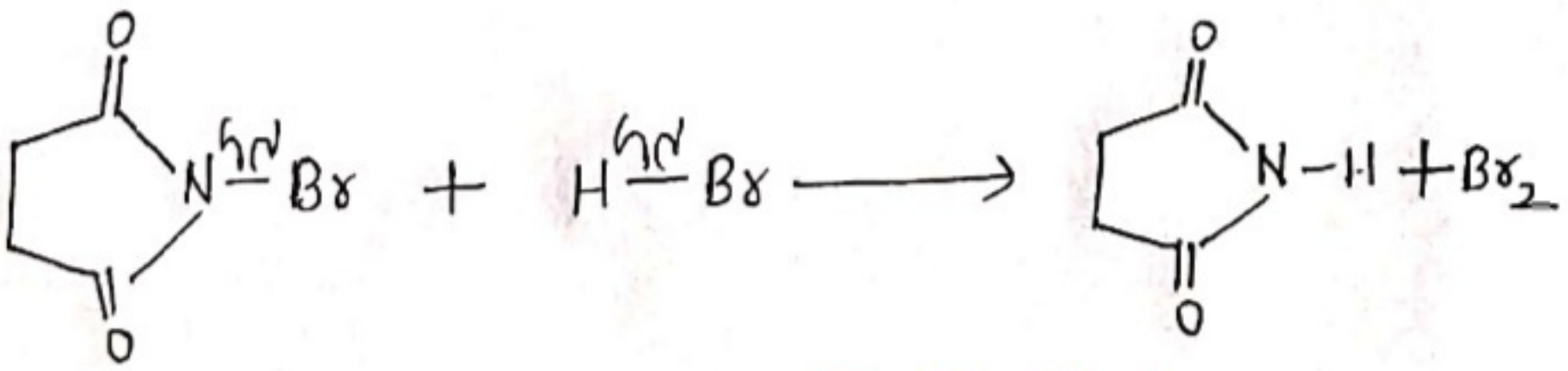
$$Br^{\cdot} + H \overset{h\nu}{=} R \longrightarrow H-Br + \dot{R} \quad (R = -CH_2-CH=CH_2)$$

$$\left(\dot{R} = \dot{C}H_2 - CH \overset{h\nu}{=} CH_2 \longleftrightarrow H_2C = CH - \dot{C}H_2\right)$$

Allyl freeradical

(Resonance stabilised)

Step: 3



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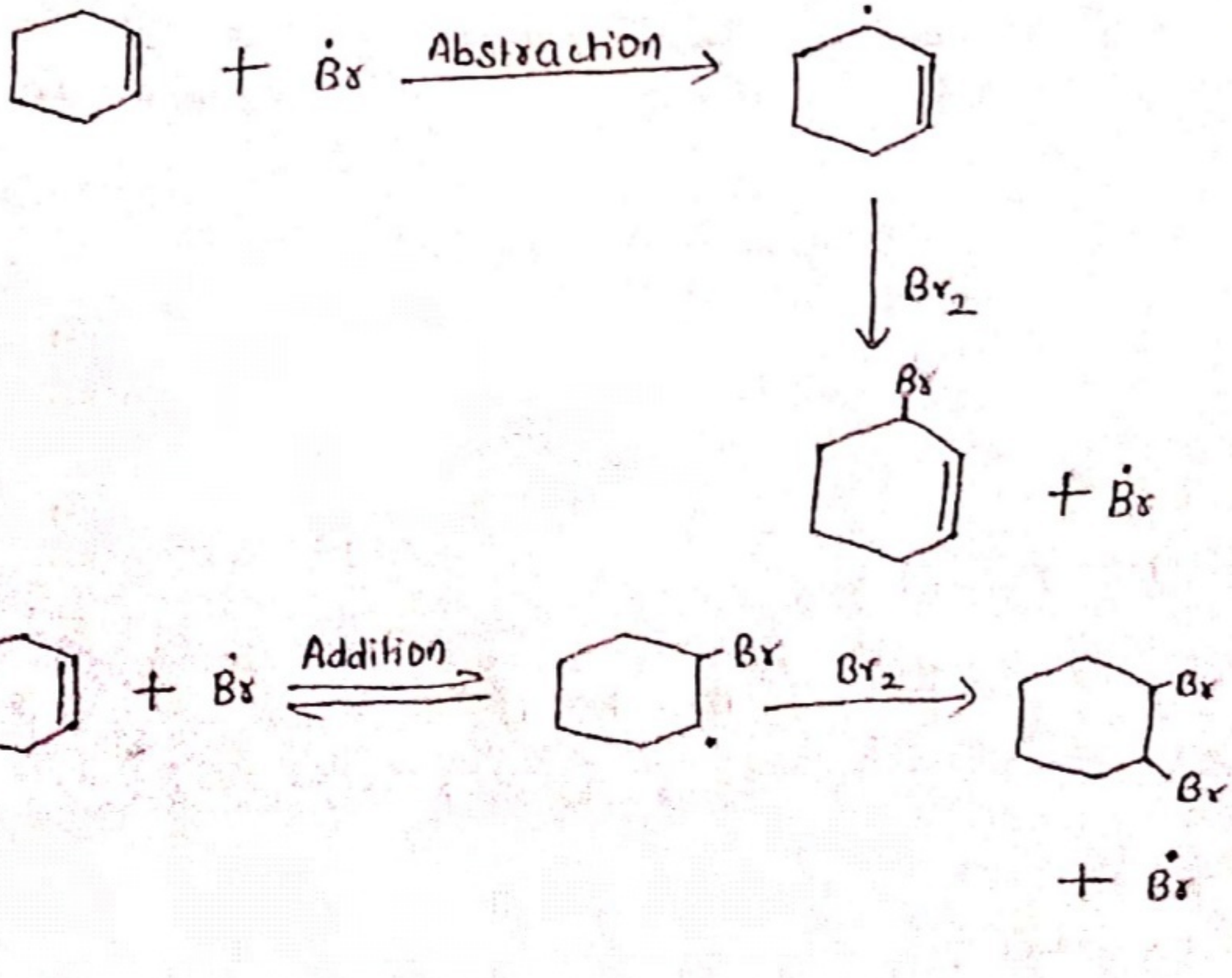
Step·4 $Br\overset{\curvearrowleft}{-}Br + \dot{R} \longrightarrow R-Br + \dot{Br}$

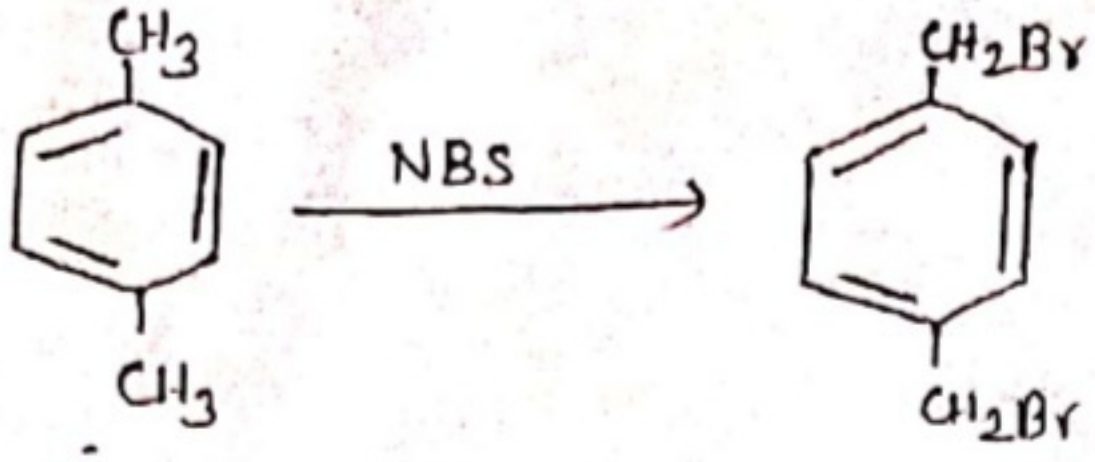
$R-Br = Br-CH_2-CH=CH_2$)

* The allylic bromination of alkenes occurs in preference to addition to the double bond. The addition of bromine atoms to a double bond is reversible and a low bromine concentration favours hydrogen abstraction.

Under certain circumtances di- or poly-bromination has been found to occur.

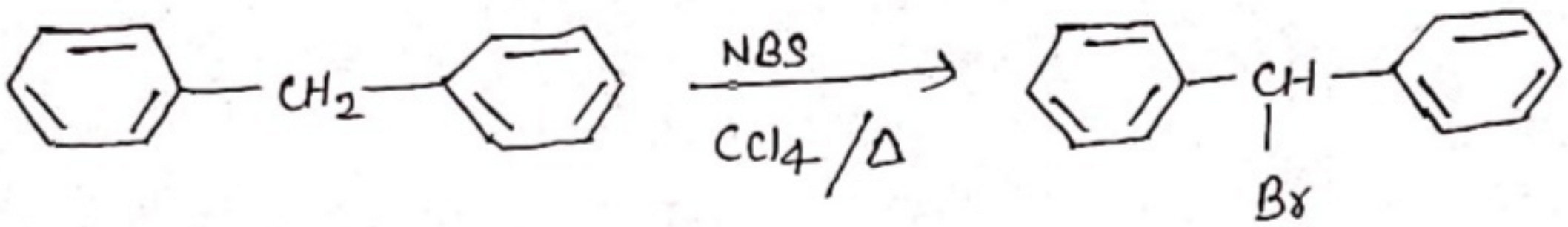


3.



P – xylene

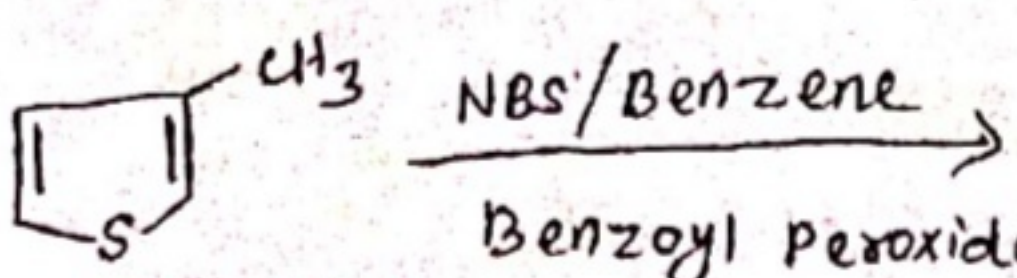
α,α'-dibromoparaxylene



(81%)

* The reaction of heterocyclic compounds with NBS occurs either in a side chain or in the nucleus or a mixture may be formed depending upon the structure of the compound and on the reaction conditions.

* The effect of free radical initiators is very well shown in the reaction of NBS with 3-methylthiophene, where nuclear bromination takes place in the absence of an initiator and side bromination occurs in the presence of benzyl peroxide.

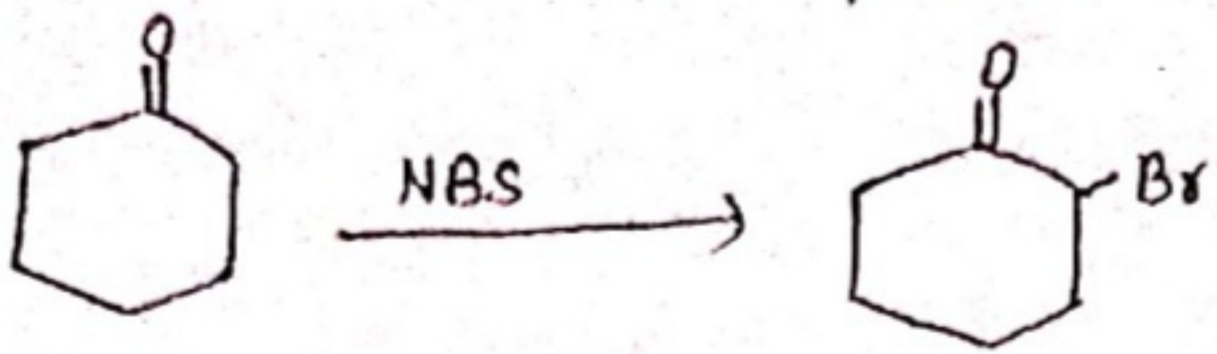


3-methyl thiophene

3-bromomethyl thiophene
(75%)

α - Bromination of Carbonyl derivatives

Ketones, containing an enolisable hydrogen can be brominated at the α-position with NBS.



Cyclohexanone

2-bromocyclohexanone

To be continued in next lecture..

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