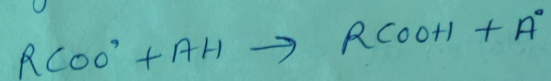


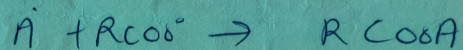
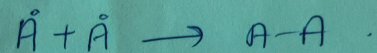
arrested by the addition of antioxidants like
Phenol or Secondary aromatic amines.

The antioxidants (AH) destroy the chain-carrying radicals by Parting with a hydrogen atom.



⇒ Radical ($A^{\bullet}$), which is not capable of initiating fresh chain, is resonance stabilized and relatively unreactive.

⇒ These are destroyed either by Combination with a similar radical or with a peroxy radical.



Importance of autooxidation:-

- (a) It is involved in the hardening of Paints
- (b) It is involved in the rancidity of fats and Perishing of rubber.

Neighbouring group assistance in free-radical

(18)

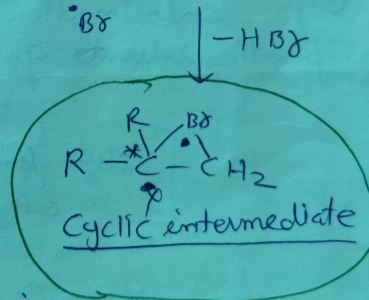
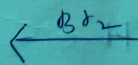
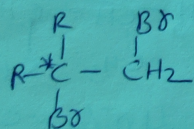
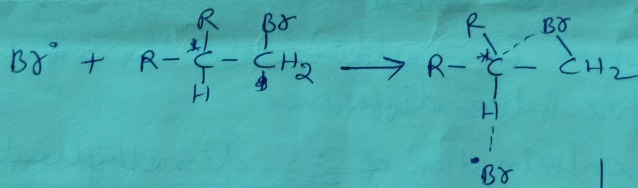
⇒ Photolytic halogenation is a process that normally leads to a mixture of many products.

⇒ but bromination of allyl bromide gave 84 to 94% substitution at the carbon adjacent to the bromine already in the molecule.

↓
⇒ This result is surprising because the position close to the polar group (such as Br_2) should actually be deactivated by the electron-withdrawing field effect of the Br_2 .

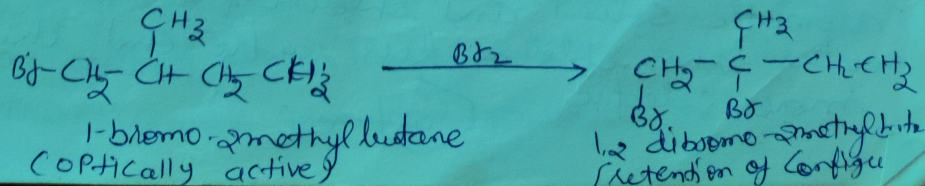
∴ The unusual regioselectivity is explained by a mechanism in [neighbouring gp. assistance]

~~First step~~ ⇒ $\text{Br}^\bullet$ abstracts a hydrogen from RH.



Evidence in favour of this mechanism:-

① If this mechanism is correct, then the configuration at substituted carbon^(C*) should be retained. and it was for we take a ex. ~~1-bromo-2-methylbutane~~



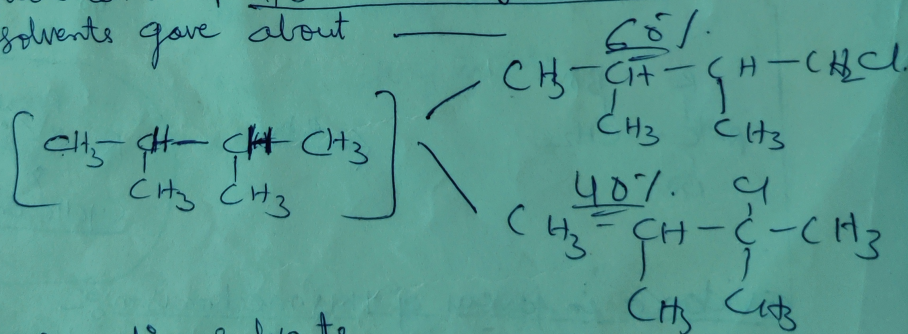
② Further, when the same rxnⁿ was carried out in the presence of DBI, the recovered "1-bromo-2-methylbutane" was found to be deuterated at position 2.

② From ESR spectra that Cl and Br can form bridged radicals.

The effect of solvent on reactivity:

- * Unlike ionic substitutions the solvent usually has little effect on free radical substitutions.
- * Free radical reactions in solution are quite similar in character to those in the gas phase, where there is no solvent.
- * However in certain cases the solvent can make an appreciable difference.

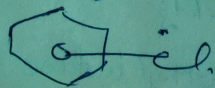
eg chlorination of 2,3-dimethylbutane in aliphatic solvents gave about —



While in aromatic solvents

the ratio become 10:90

- * This is due to complex formation between the aromatic solvent and chlorine free radical which makes the chlorine less reactive and thus more selective.



8. Coupling of Alkynes

[Eglinton rxn]

* Terminal alkynes can be coupled by heating with stoichiometric amount of cupric salts in pyridine or a similar base.
[CuO or Cu(II) acetate]

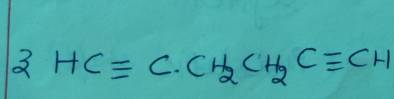
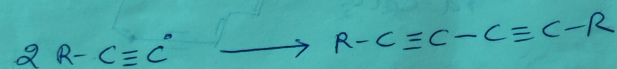
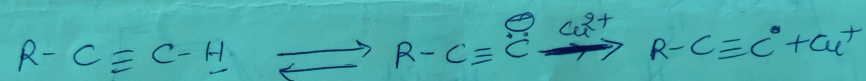
* When catalytic amounts of cuprous salts in the presence of ammonia or ammonium chloride is used, this method is called the Glaser rxn.

Mechanism:-

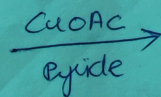
⇒ loss of proton by the base, since acetylenic protons are acidic.

⇒ one electron oxidation of acetylide anion by Cu(I) ion -

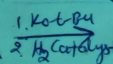
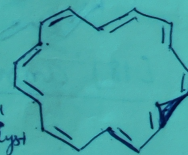
⇒ dimerization.



1,5 hexadiyne



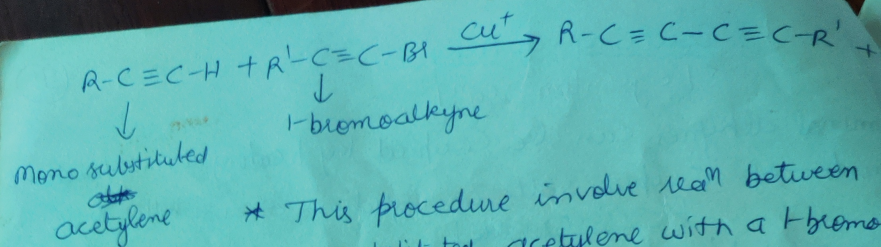
cyclic trimer of 1,5 hexadiyne



* Cadiot-Chodkiewicz Coupling:-

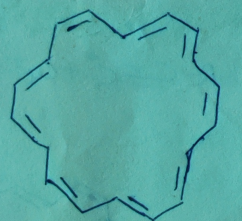
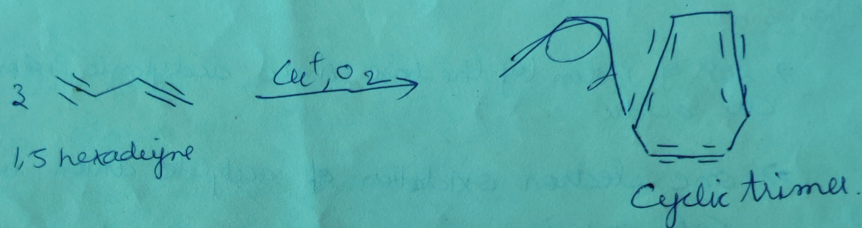
* Generally a mixture of two monosubstituted benzene give on coupling gives a mixture of three products.

* This Procedure give one product.

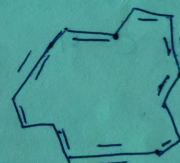
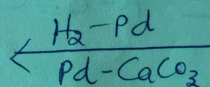


* This procedure involve rxn between monosubstituted acetylene with a 1-bromoalkyne in the presence of COPPER (I) ion.

* This method is used to synthesize [18] annulene. Starting from 1,5-hexadiyne.



[18] annulene



The fully conjugated system
(Prototropic shift)

