

E. The Kolbe electrolytic rxn (dimerization of alkyl radicals)

* free radical substitution rxn.
* on electrolysis the alkali metal salts of a carboxylic acid ($\text{RCOOH} \rightarrow \text{RCOO}^-$) gives R-R (coupled product)

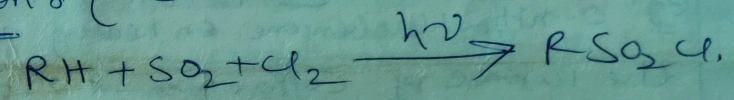
* The alkyl radicals are liberated at anode.

* The sodium liberated at the cathode reacts with the solvent and generate more carboxylate anion.

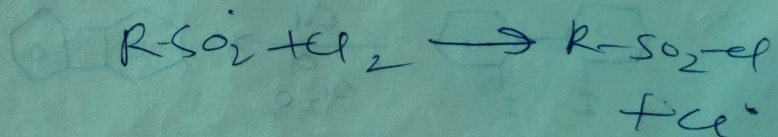
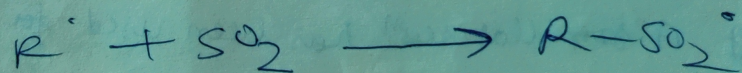
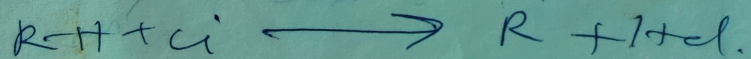
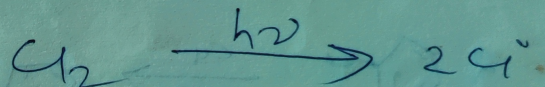
⇒ Platinum foil electrodes used.

⇒ a solⁿ of acid in methanol, containing enough sodium methoxide to neutralize about 2% of the acid.

Reed Reaction: (Chlorosulphonation)

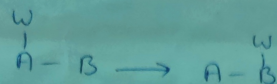


Mechanism:



Free-Radical Rearrangement

Rearrangement: In a rearrangement reaction a group moves from one atom to another in the same molecule.



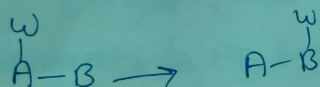
* 1,2 shifts are most common. Rearrangements involve a migration from an atom to another one.

* Most of these rearrangements are intramolecular processes and may occur in -

(1) electron deficient system: called nucleophilic or anionotropic rearrangement

(2) Electron rich system: termed electrophilic or cationotropic rearrangements

(3) The least common of the rearrangements where the migrating group moves with just one electron.



W = migrating gp.

A = migration origin

B = " terminus.

Q. Why nucleophilic 1,2 shifts are much more common than (involving carbocations)

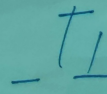
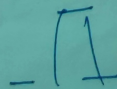
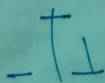
the similar rearrangement that involve Carbanions or free-radicals

Ans. → In rearrangements they involve T.S.

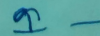


antibonding

Bonding



do antibonding - -



Bonding



Carbocation (nucleophilic)

Carbanion (electrophilic)

Free-radical

Free
*
⇒ For nucleophilic migration one has two electrons, which both can go into the bonding orbital, and it has a low energy. so under this migration, the T.S. is low energy.

⇒ In free-radical migration T.S. has three electrons, one in anti-bonding electron.

and in electrophilic migration T.S. has $2e^-$ excess that are in anti-bonding orbital.

So, in ~~either~~ both cases T.S. are higher energy.

⇒ Thus, we can expect during 1,2 shift of free radicals or 1,2 electrophilic shifts the migrating group is generally an aryl or a similar group which can accommodate the extra electrons and therefore, effectively removes these from the three membered T.S. or intermediate.

* In the case of cationic intermediates migration occurs through a bridged T.S. (or intermediate) which involve a three centre two electron bond.

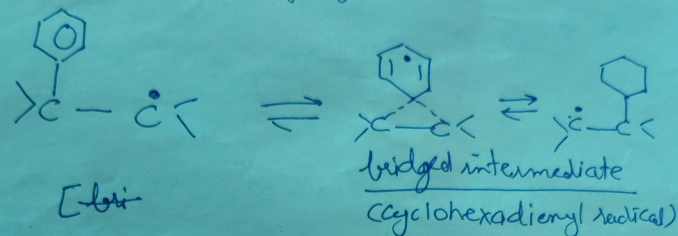
⇒ Free Rad

Free-Radical rearrangement:

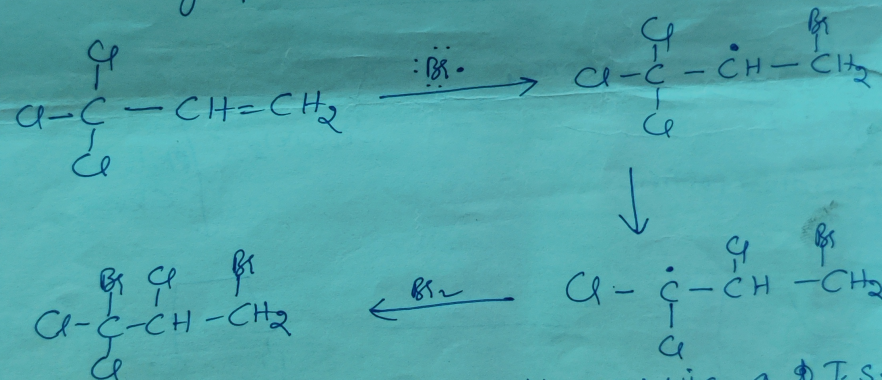
(14)

* In the case of free-radicals, migrations can occur with aryl, vinyl, acyl and other unsaturated groups.

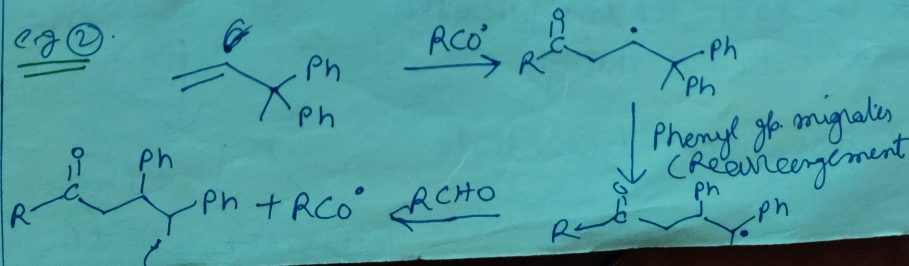
⇒ Migration of aryl group.



e.g. ① ⇒ migrations have also been observed for chloro groups.

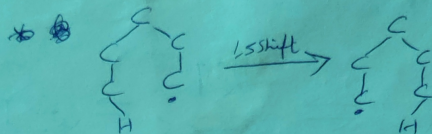


[migration of a halogen could occur via a δ T.S. in which the odd electron is accommodated in a vacant d-orbital of the halogen]



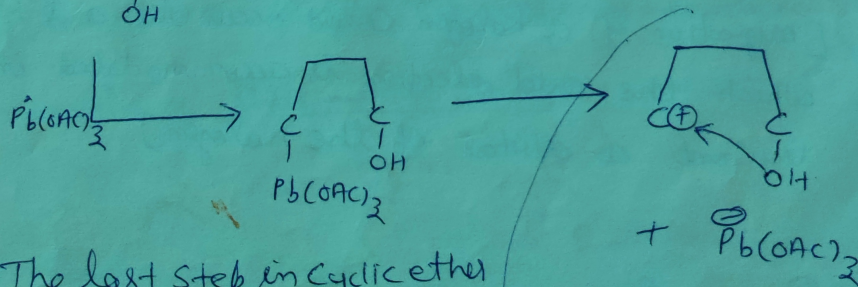
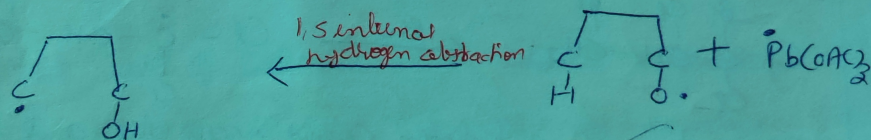
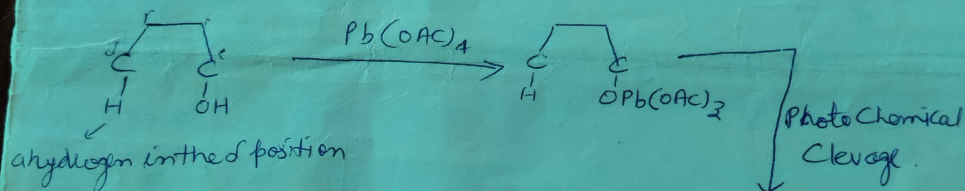
Jerry March 1067

eg 2 Cyclic ether formation (although hydrogen atom do not migrate)
 * longer free radical migrations of hydrogen are known. (1,5 shifts are most common)



* Formation of cyclic ether is an ex. of 1,5 shift of hydrogen atom

⇒ Alcohols having hydrogen atom at δ position can be cyclized with lead tetra acetate.



* The last step in cyclic ether formation is through a Carbocation intermediate.

