

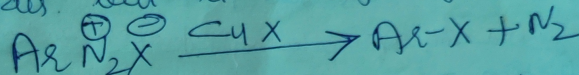
10. Sandmeyer reaction

(12)

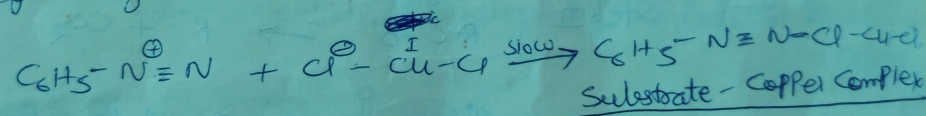
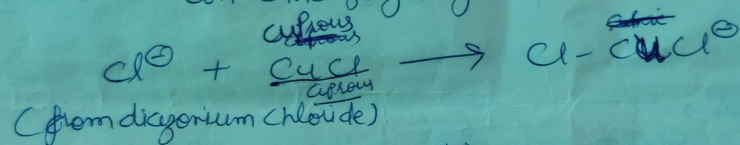
* Treatment of diazonium salts with cuprous chloride or bromide leads to aryl chlorides or bromides respectively. In either case the rxn is called Sandmeyer rxn.

Grattemann rxn: When the similar rxn is carried out with copper and HBr or HCl.

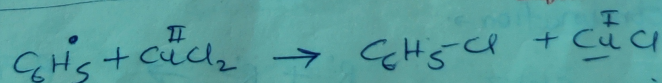
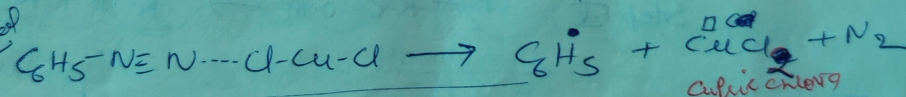
* Sandmeyer rxn is not useful for the preparation of fluorides or iodides, but it is very useful bromides or chlorides.



Mechanism: Copper first acts as a reducing agent and then an oxidizing agent.



Free Radical Form



Note: The mechanism of the rxn is not certain, there are several evidences for the free-radical mechanism.

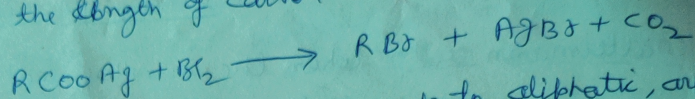
* Cuprous salt facilitates the formation of free-radical via Complex with diazonium salt.

* CuX (CuCl) is regenerated, thus it is true catalyst.

11. Hunsdiecker reaction

* Reaⁿ of a silver salt of a Carboxylic acid with bromine is called the Hunsdiecker reaⁿ.

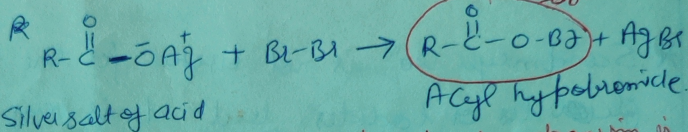
* decreasing the length of Carbon chain by one unit.



* Free radical involve in mechanism. applicable to aliphatic, aromatic and alicyclic comp^s.

Mechanism:

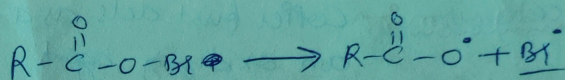
Step I



~~steps not a free radical process and its actual mechanism is not known.~~

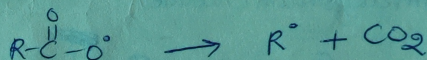
Initiation $\rightarrow$

Step II

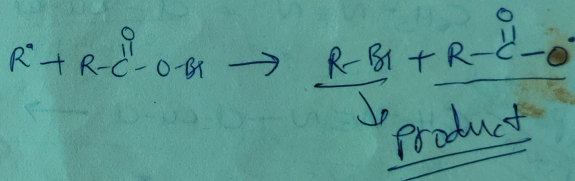


Propagation $\rightarrow$

Step III

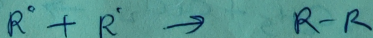


Step IV

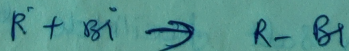
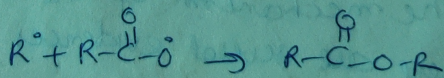


Termination $\rightarrow$

Step V



Step VI



* R = n-alkyl R from 2 to 18 Carbons

R = may be aryl - (but if R is unsaturated, the rxn seldom gives products).

* Reaⁿ of a silver salt of a Carboxylic acid with bromine.

and way of decreasing the length of a Carbon chain by one unit is called the Hunsdiecker Reaⁿ.

9. Arylation of aromatic Comps by

(10)

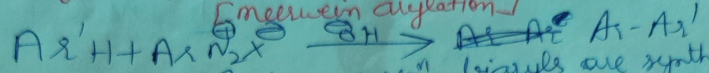
Diazonium salts

① Gromberg - Bachmann re^m

② Pschou re^m or Pschou ring closure

③ Arylation of activated olefines by diazonium salts

Emmelein arylation



* In Gromberg or Gromberg-Bachmann re^m biaryls are synthesized by a radical re^m.

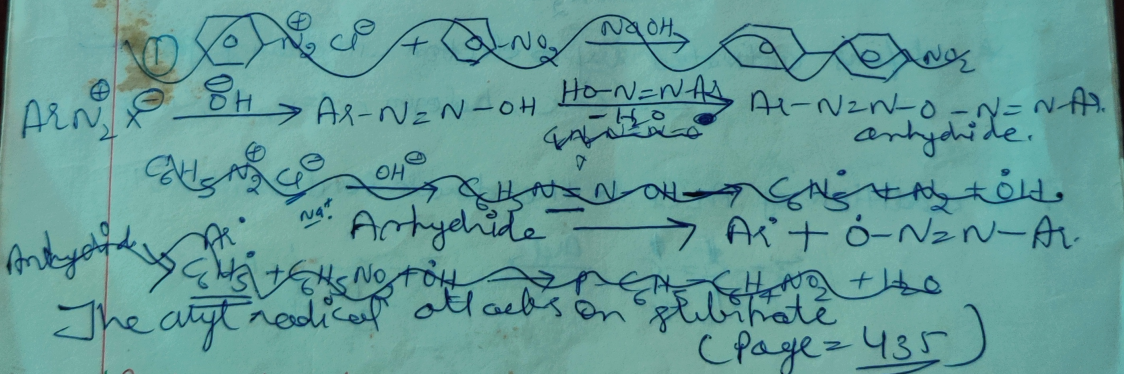
This re^m involves the decomposition of diazonium salt in the pr. of Aromatic substrate in the pr. of aqueous NaOH

* Other Comps having Nitrogen-Nitrogen bonds also used instead of diazonium salts. eg. N-Nitroso amides, $Ar-N(NO)-C(=O)R$

Mechanism:- * Formation of aryl radical.

* This radical attacks on the aromatic substrate

* Abstraction of hydrogen by the radical $Ar-N=N-O$ gives Product



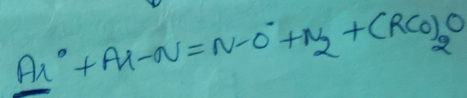
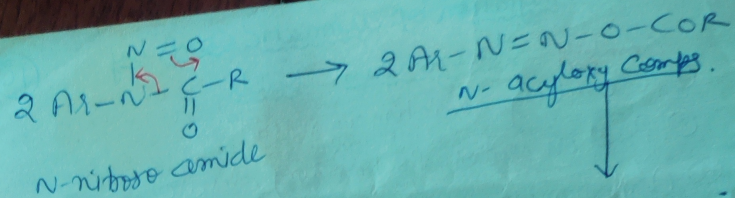
Pschou ring closure:- * when the Gromberg-Bachmann re^m

is performed intramolecularly either by alkaline re^m or

with Copper powder this procedure is termed Pschou ring

closure $\rightarrow$ eg. Pto

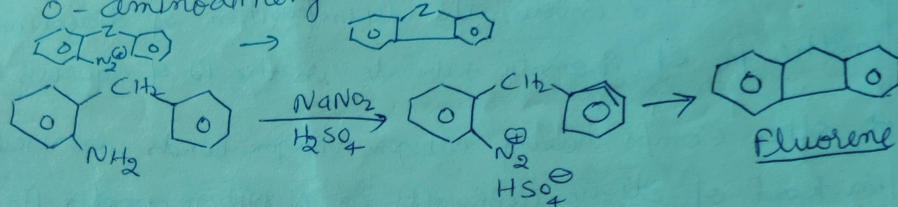
Gromberg Bachmann re^m $\rightarrow$ ② N-Nitroso amides rearrange to N-acyloxy Comps, which cleaves and gives aryl radicals



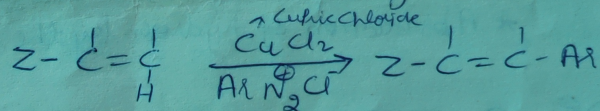
Pischner Synthesis ^{high closure}

Fluorene is prepared starting with

O-aminodiphenylmethane.

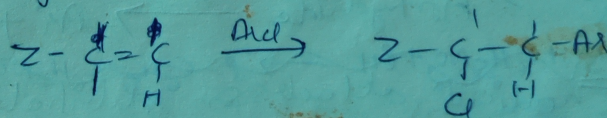


C. Meerwein arylation:- arylation of activated olefins by diazonium salts

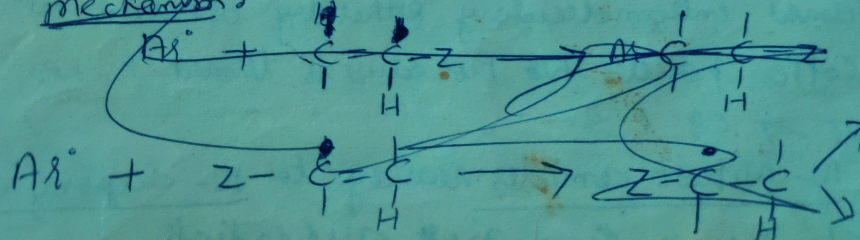


* olefins activated by electron withdrawing groups
 $\text{Z} = \text{C}=\text{C}$, halogen, $\text{C}=\text{O}$, Ar , $\text{C}(\text{NMe}_2)$

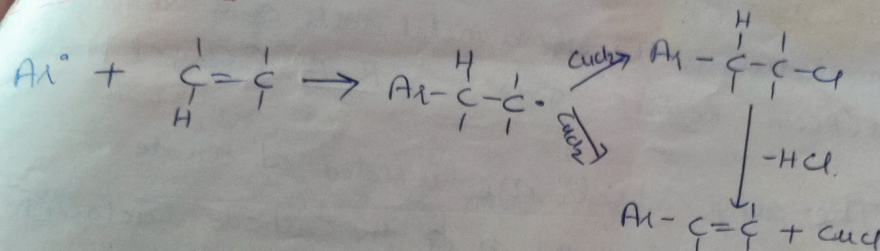
* addition of ArCl to the double bond is side reaction



Improved procedure
mechanism

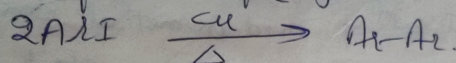


Mechanism:

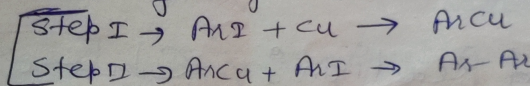


d. The Ullmann reaction (Dimerization of aryl radicals)

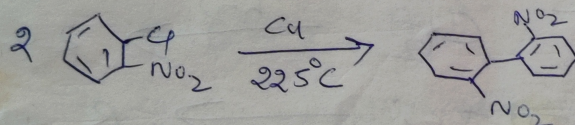
* This reaction is a useful technique for the synthesis of biaryls



* In this rxn two moles of aryl halides react in the presence of Copper.



eg o-nitrochlorobenzene on heating around 225°C in the presence of Copper gives 2,2'-dinitrophenyl.



eg A similar rxn has been used for ring closure.

