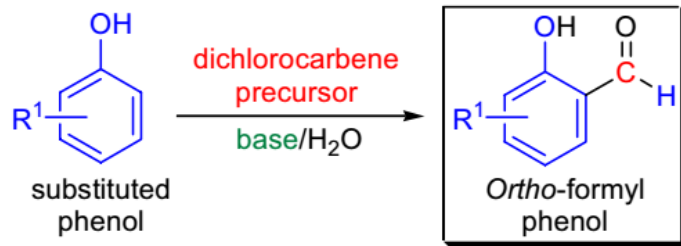
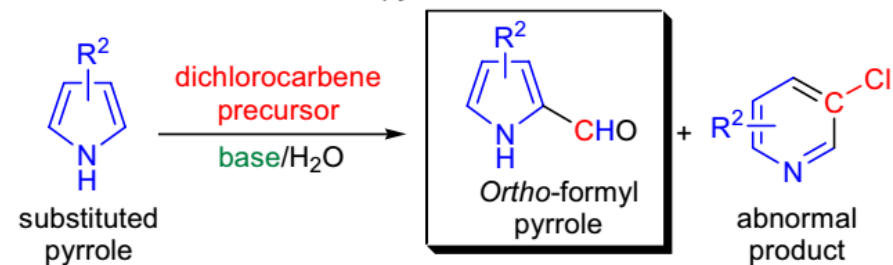


REIMER-TIEMANN REACTION

Reimer-Tiemann reaction of phenols:



Reimer-Tiemann reaction of pyrroles:

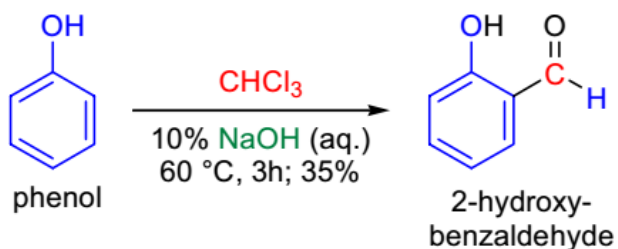


$R^1 = \text{H, alkyl, OH, O-alkyl, CO}_2\text{H, NO}_2, \text{Cl, Br, I}$; $R^2 = \text{H, alkyl}$; dichlorocarbene precursor: $\text{CHCl}_3, \text{Cl}_3\text{CCO}_2\text{H, Cl}_3\text{CCHO, Cl}_3\text{CNO}_2$;
base: NaOH, KOH, CsOH ;

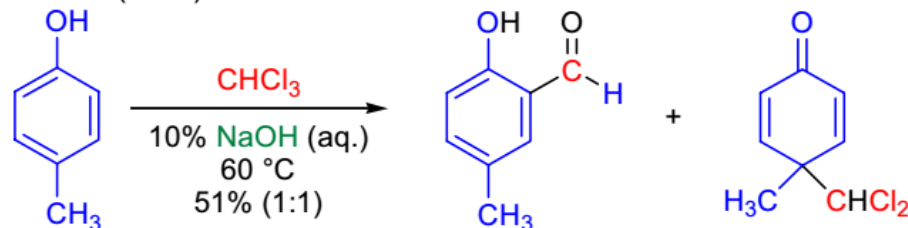
Reimer-Tiemann Reaction

The formylation of phenols and heterocyclic phenols using chloroform in an aqueous alkaline medium is known as the *Reimer-Tiemann reaction*.

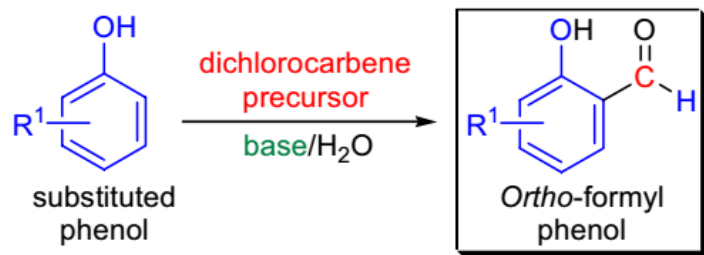
Reimer & Tiemann (1876):



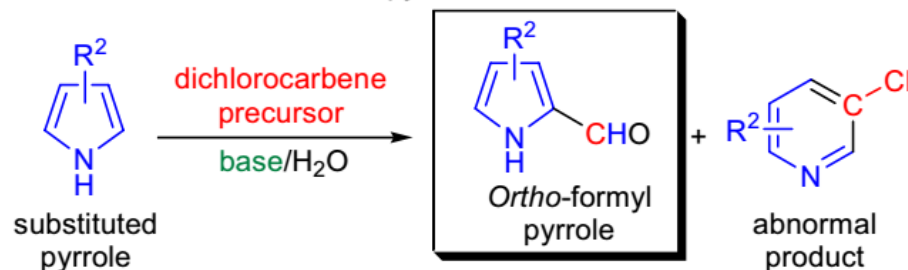
Auwers (1884):



Reimer-Tiemann reaction of phenols:



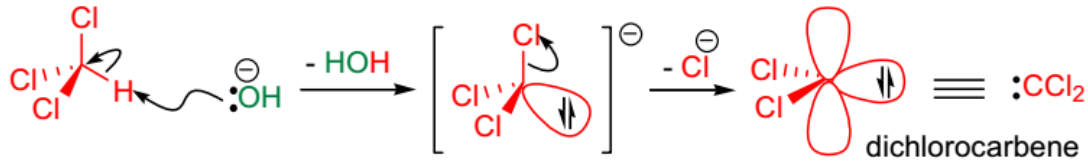
Reimer-Tiemann reaction of pyrroles:



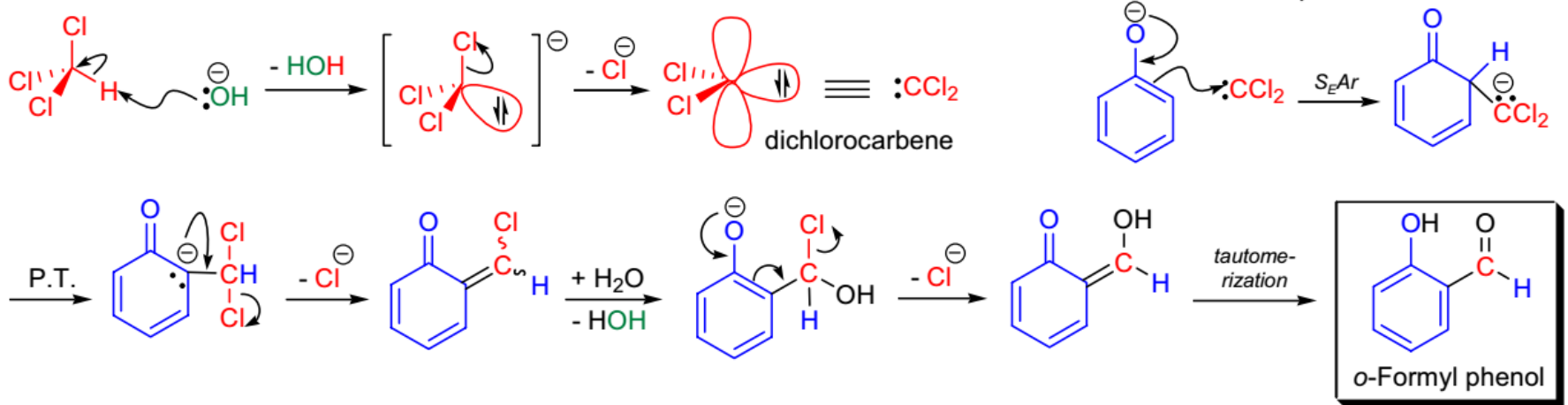
$R^1 = \text{H, alkyl, OH, O-alkyl, CO}_2\text{H, NO}_2, \text{Cl, Br, I}$; $R^2 = \text{H, alkyl}$; dichlorocarbene precursor: $\text{CHCl}_3, \text{Cl}_3\text{CCO}_2\text{H, Cl}_3\text{CCHO, Cl}_3\text{CNO}_2$;
base: NaOH, KOH, CsOH ;

Mechanism

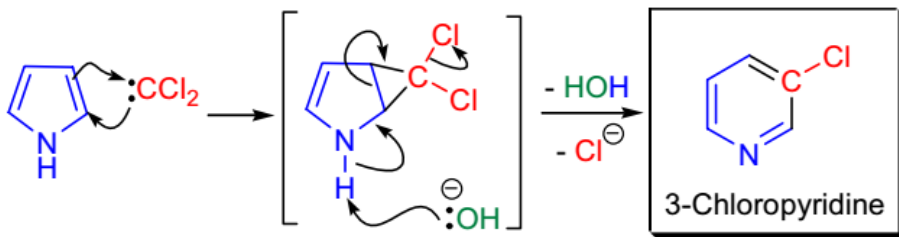
Dichlorocarbene formation:



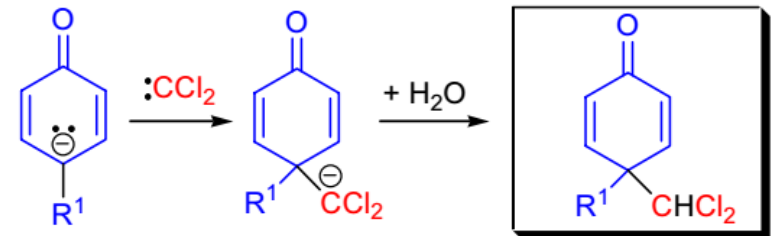
Reaction with the phenol:



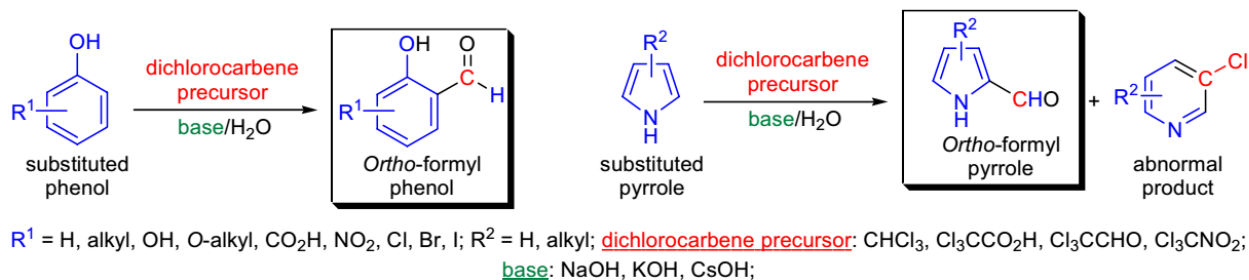
Formation of the abnormal product from pyrrole:



Formation of the abnormal product from alkylphenols:

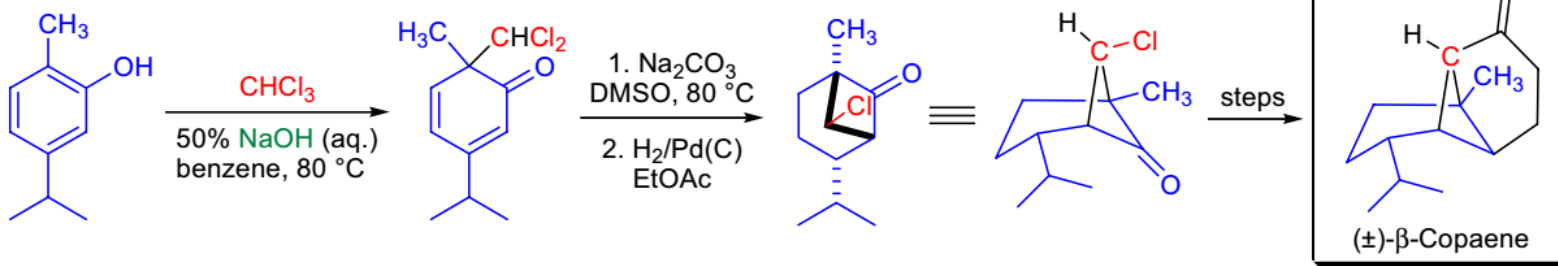
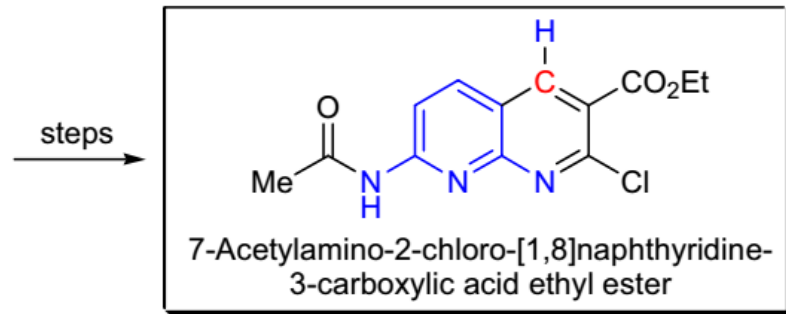
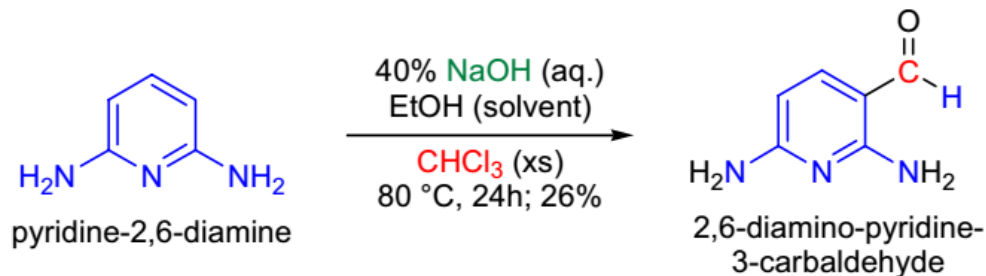


Features

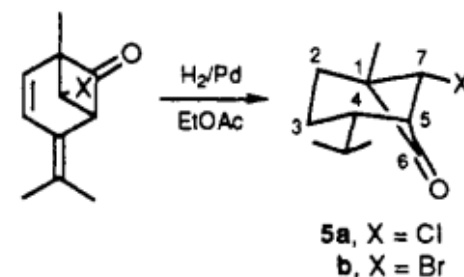
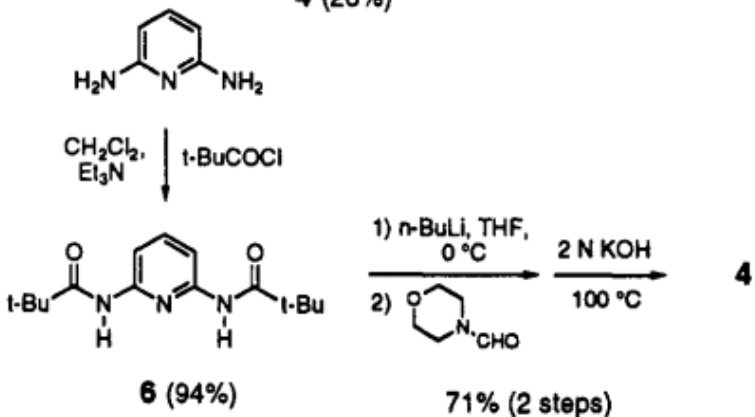
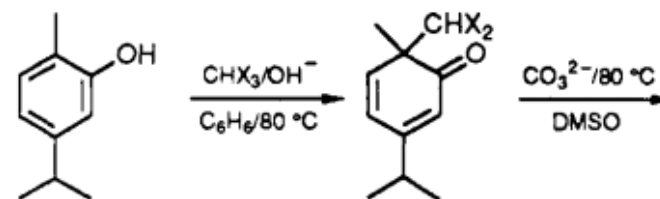
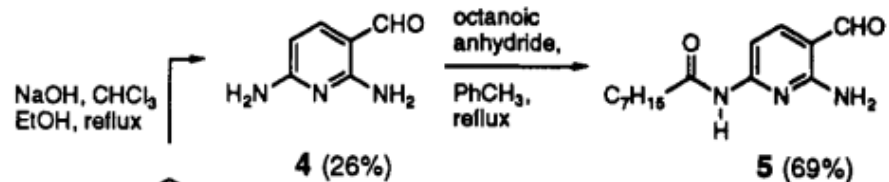


- 1) it is the only electrophilic aromatic substitution reaction that occurs under basic conditions in a protic solvent;
- 2) phenols, naphthols, alkyl-, alkoxy-, and halogenated phenols, salicylic acid derivatives, heterocyclic phenols such as hydroxyquinolines and hydroxypyrimidines, as well as pyrroles and indoles undergo formylation under the reaction conditions;
- 3) besides CHCl_3 , other dichlorocarbene precursors such as chloral, trichloronitromethane, etc. can be used;
- 4) typically the substrate (phenol) is dissolved in 10-40% alkali hydroxide, excess chloroform is added, and the biphasic solution is vigorously stirred at elevated temperatures;
- 5) yields are usually moderate;
- 6) the regioselectivity is not high, but ortho-formyl products tend to predominate;
- 7) when the ortho-position is already substituted, para-formyl phenols are obtained;
- 8) in the case of pyrroles, when the ortho substituent is a CO_2H or CO_2R group, decarboxylation is observed and the o-formyl product is formed (similar findings were reported for an o-alkoxy phenol where the alkoxy group was eliminated to give an o-formyl phenol);
- 9) when the reaction is conducted in the presence of cyclodextrins, the p-formyl product is formed predominantly

Applications



Scheme I



J. Org. Chem. **1993**,58, 6625-6628

J. Am. Chem. SOC. **1992**, 114,644-654

Duff reaction

