

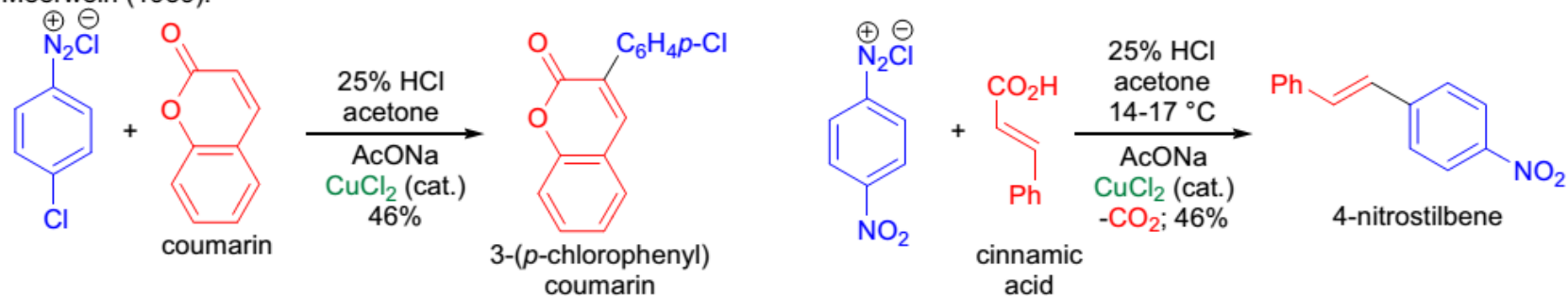
# MEERWEIN ARYLATION

Liu Hongjuan

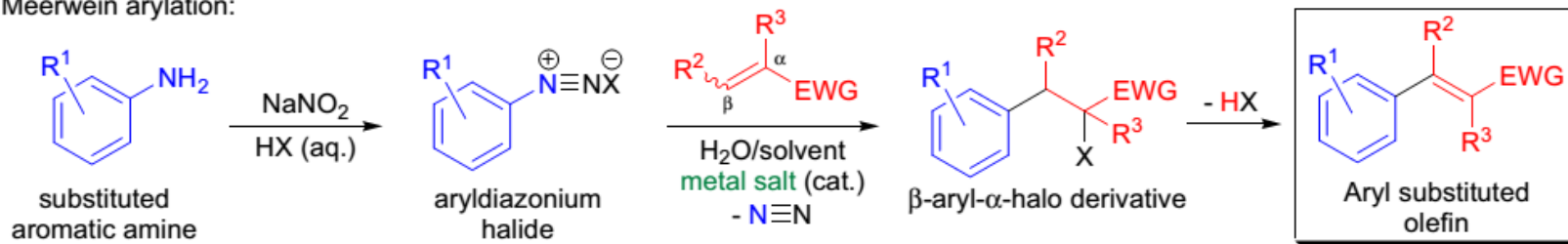
2016-5-17

# Introduction

Meerwein (1939):



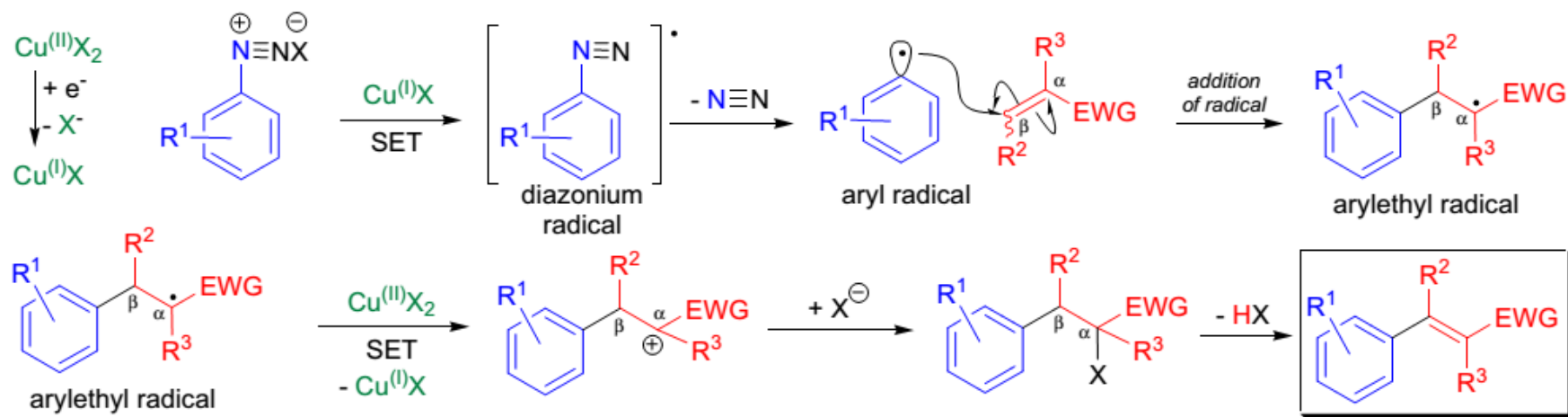
Meerwein arylation:



$\text{R}^1$  = H, alkyl, aryl, O-alkyl, Cl, Br, I,  $\text{CO}_2$ -alkyl, CONHR,  $\text{SO}_2\text{R}$ ,  $\text{NO}_2$ ,  $\text{CF}_3$ ;  $\text{R}^{2-3}$  = H, alkyl, aryl; EWG = CHO, CO-alkyl,  $\text{CO}_2$ -alkyl,  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{NH}_2$ ,  $\text{CO}_2\text{NR}_2$ , CN, alkenyl, Cl, Br; HX: HCl, HBr; solvent: acetone, acetonitrile; metal salt:  $\text{CuCl}_2$ ,  $\text{CuBr}_2$

# Mechanisms

The mechanism of the *Meerwein arylation* is not completely understood. In his seminal paper, Meerwein proposed the involvement of aryl cations, however, this hypothesis was soon eliminated when J.K. Kochi suggested that aryl radicals are formed under the reaction conditions.<sup>22</sup> The actual catalyst is a copper(I) species, which is formed *in situ* from copper(II) salts and carbonyl compounds (e.g., acetone which is often used as a solvent).<sup>23</sup>



# Common features

- the procedure is simple; no special laboratory equipment is needed;
- the aryldiazonium halides are prepared by the diazotization of aromatic amines using sodium nitrite and aqueous hydrohalic acids and are not isolated, rather immediately reacted with the alkenes in the presence of an organic solvent (e.g., acetone, acetonitrile);
- the presence of electronwithdrawing substituents on the aromatic ring tends to increase the yield, whereas electron-donating groups often give lower yields;
- the alkene component usually has an electron-withdrawing substituent and mostly  $\alpha,\beta$ -unsaturated carbonyl compounds are used;
- if there are two electron-withdrawing substituents on the double bond, and they are attached to the same carbon and then the aryl group will add to the other  $sp^2$  hybridized carbon atom;

# Common features

- when each of the olefin carbon atoms has an electron-withdrawing substituent, regioisomeric products may be formed; however, the major product will arise from the most resonance stabilized radical intermediate;
- cinnamic acids and maleic acids are arylated at the  $\alpha$ -carbon, and the reaction is accompanied by decarboxylation which is a pH-dependent process;
- alkynes with electron-withdrawing substituents also react, but the yields are often poor;
- furan derivatives are arylated with ease under the reaction conditions;
- the initial product of the reaction is a substitution product (alkyl halide), which can be dehydrohalogenated under basic conditions to afford the corresponding aryl substituted olefin.

# Synthetic applications

