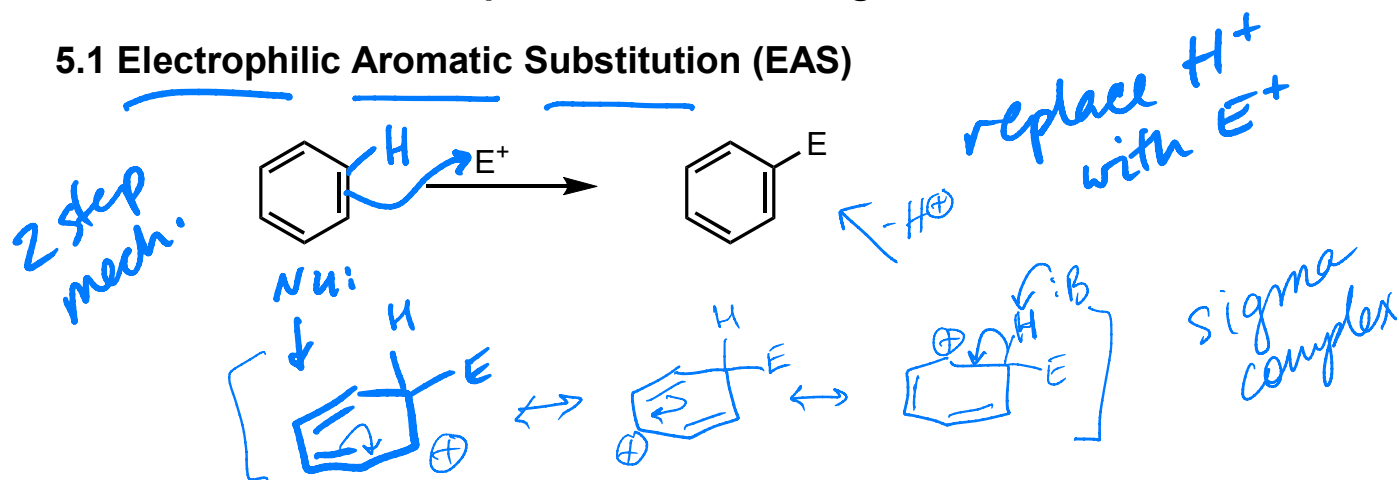


Chapter 5 - Aromatic Target Molecules

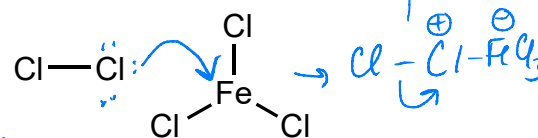
5.1 Electrophilic Aromatic Substitution (EAS)



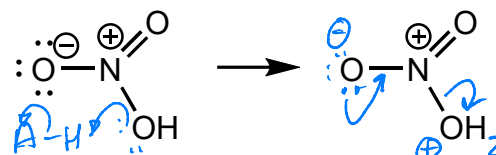
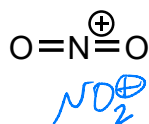
EAS Reaction	Conditions	Electrophile (E^+)
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Mech. to make E^+ (1st steps in EAS)

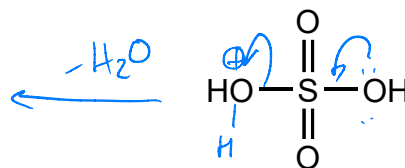
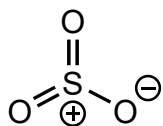
halogenation -X	$Br_2/FeBr_3$ $Cl_2/FeCl_3$	Br^+ ✓ Cl^+ ✓	
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nitration -NO ₂	HNO_3 , H_2SO_4	$O=N^+=O$ NO_2^+	
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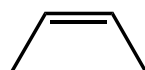
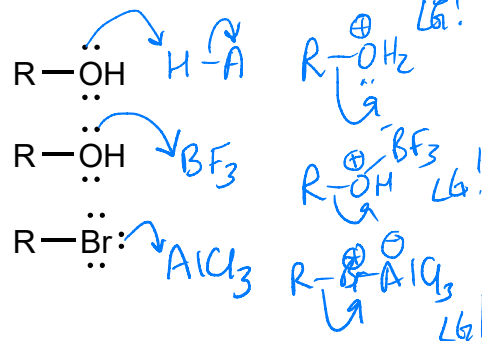
sulfonation* -SO ₃ H	SO_3 , H_2SO_4	$O=S^+=O$ SO_3^+	
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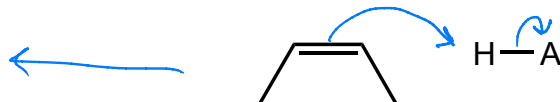
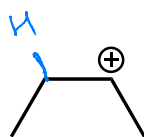
forming sulfuric acid

reaction is reversible (heat removes -SO₃H group)

Friedel-Crafts alkylation -R	ROH/HA ROH/BF_3 $RX/AlCl_3$	R^+	
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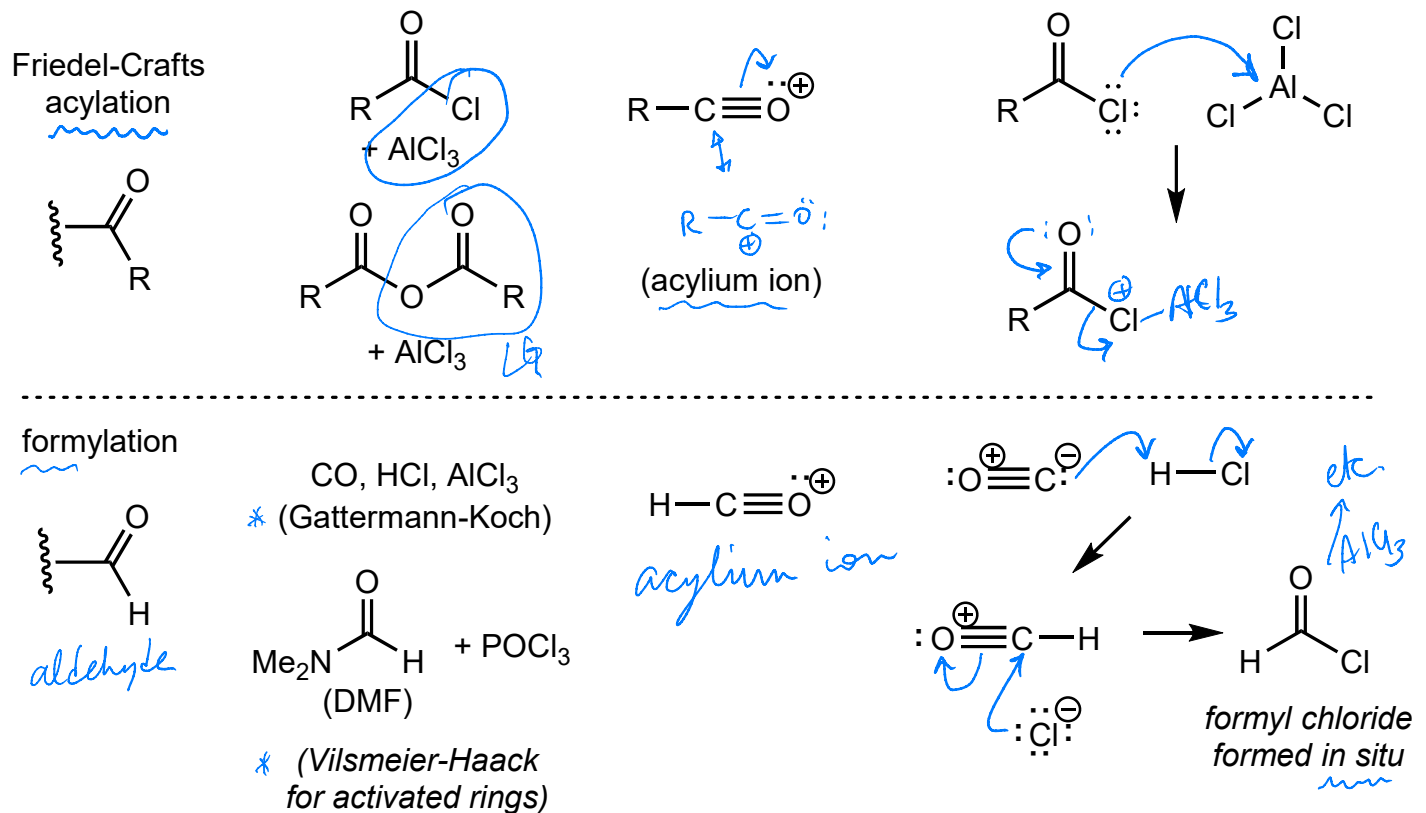


+ HA
(HF)

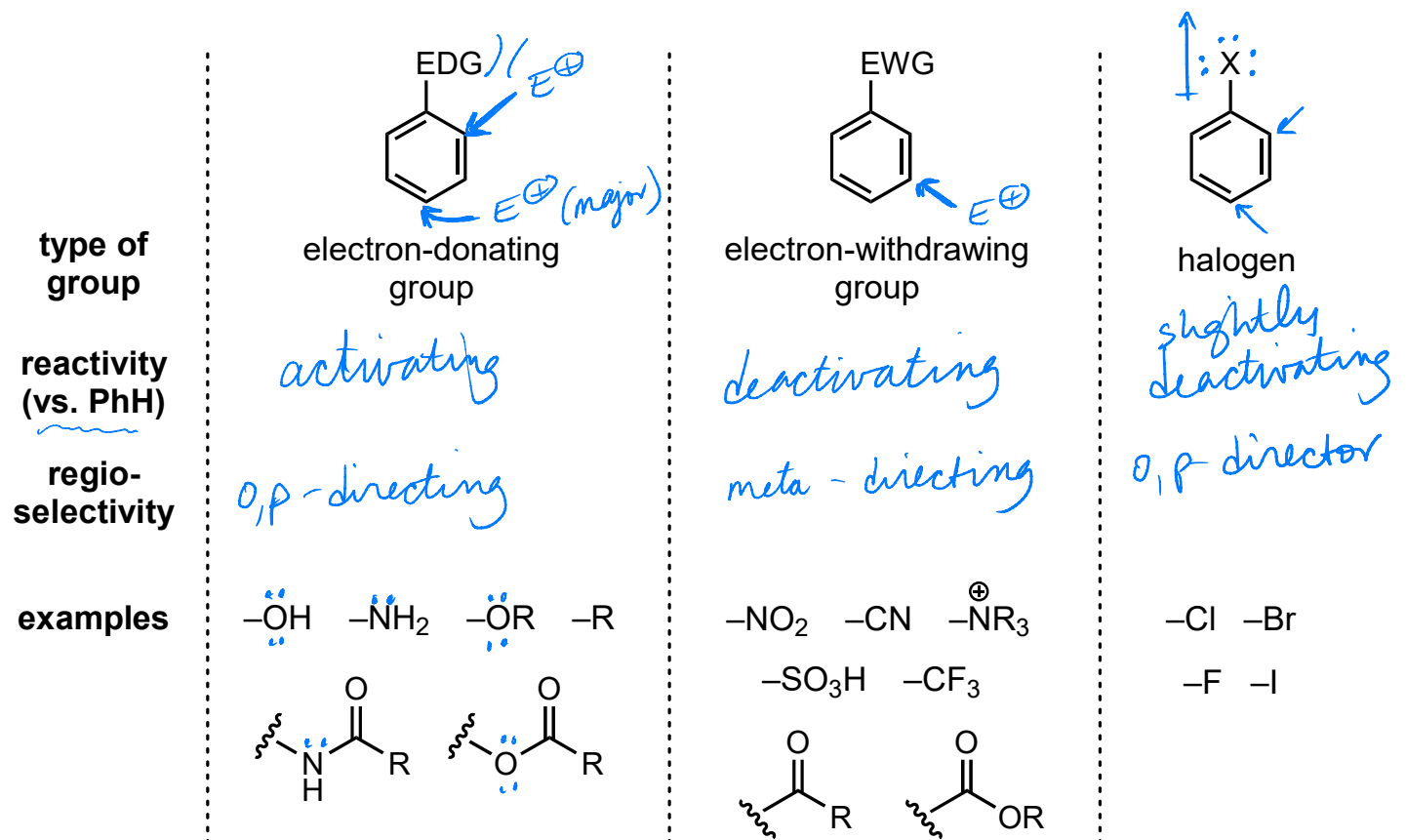


(carbocation)

EAS Reaction Conditions Electrophile (E⁺) Mech. to make E⁺ (1st steps in EAS)

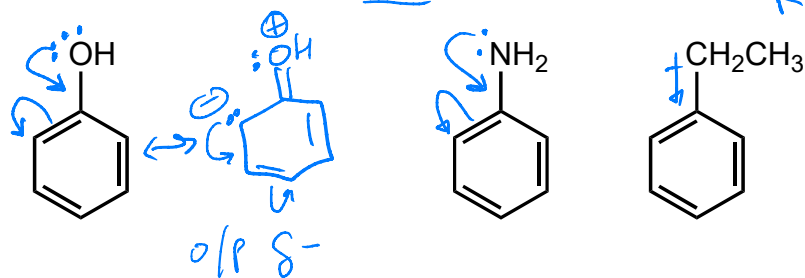


Electrophilic Aromatic Substitution on Substituted Rings



Identifying electron-donating groups (EDG)

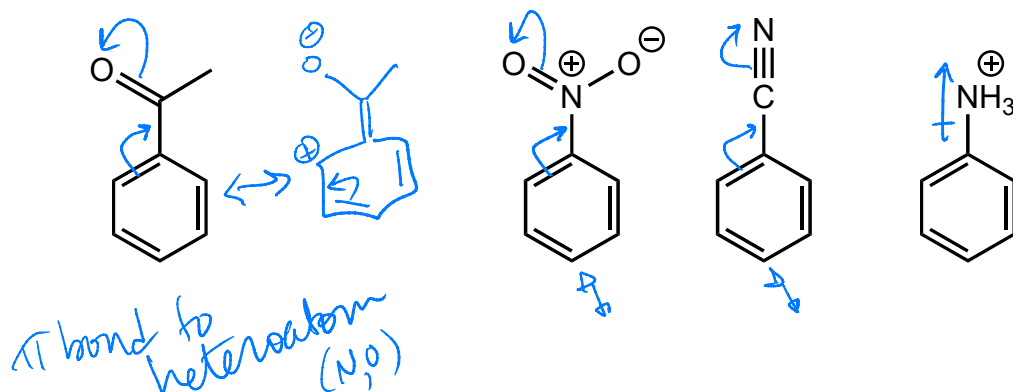
5-3



R = inductively e⁻ donating

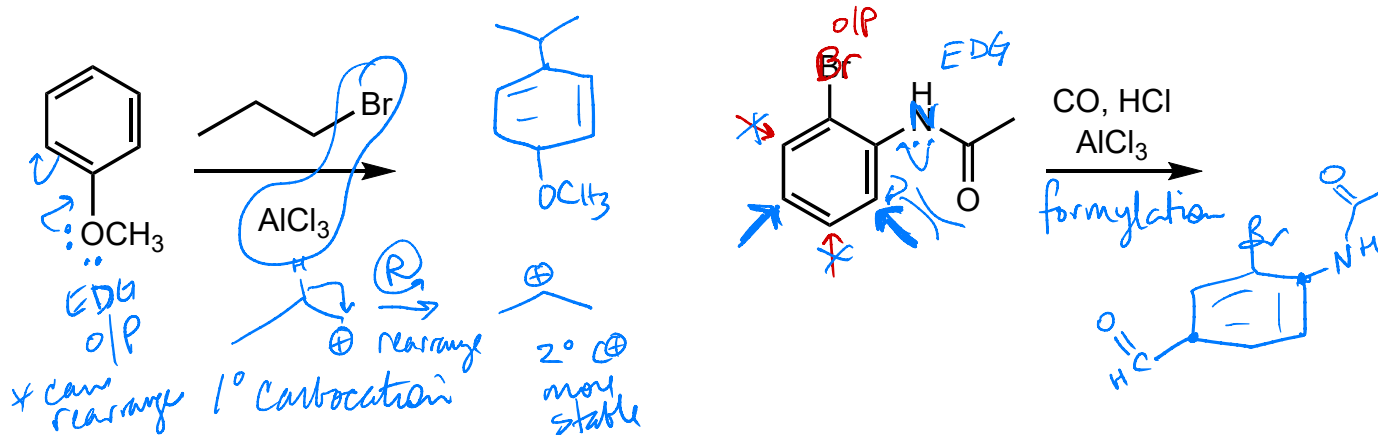
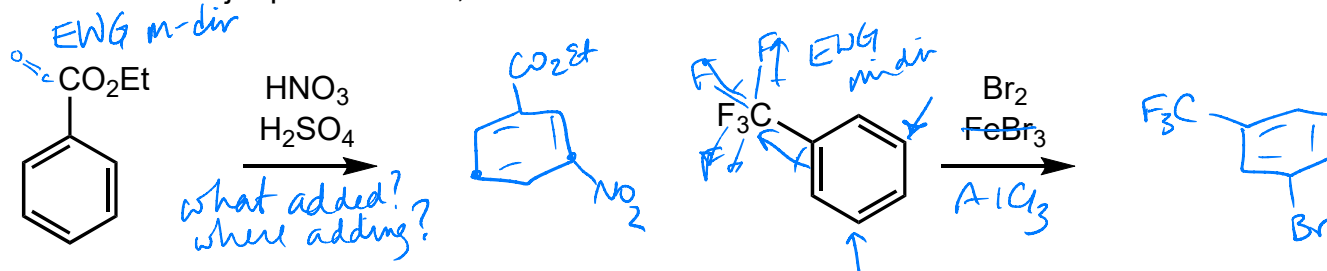
*✓ ring is e⁻ rich
✓ better Nu:
✓ "activated"*

Identifying electron-withdrawing groups (EWG)

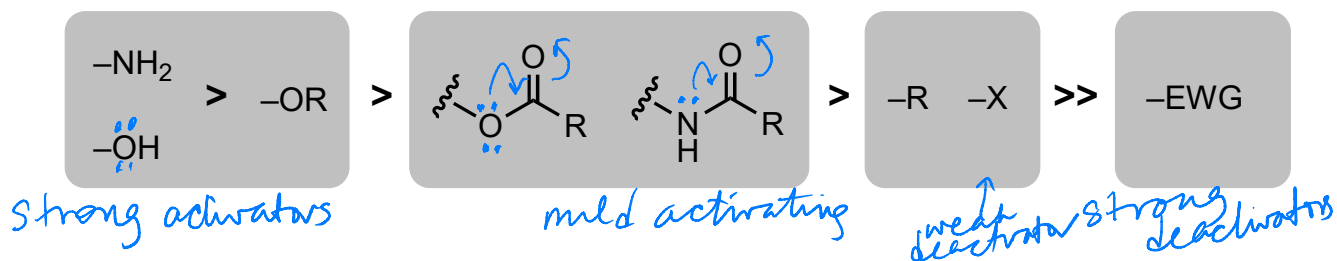


*✓ ring is e⁻ poor
✓ poor Nu:
✓ "deactivated"*

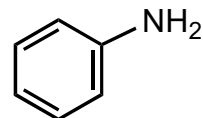
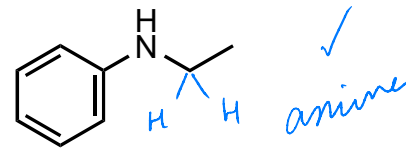
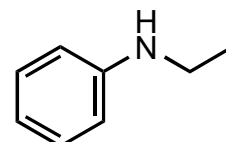
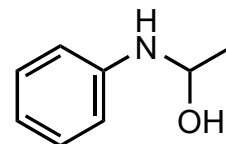
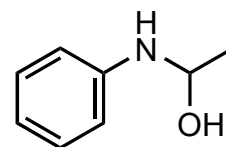
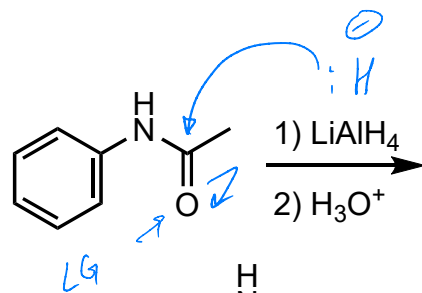
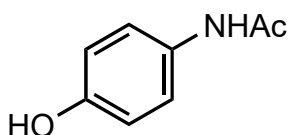
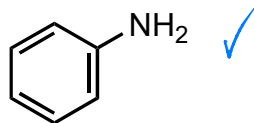
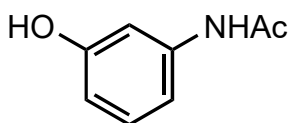
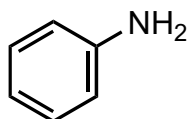
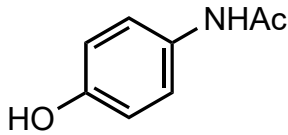
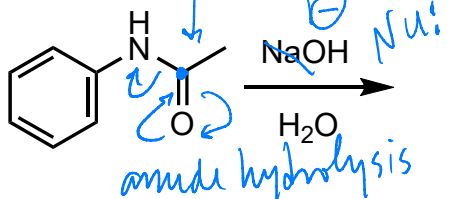
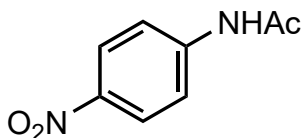
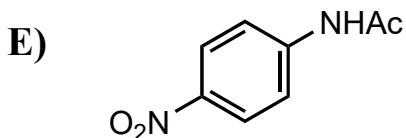
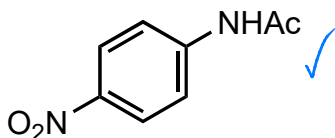
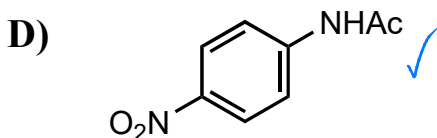
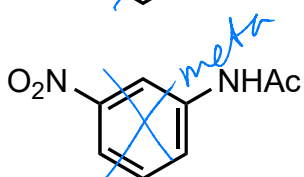
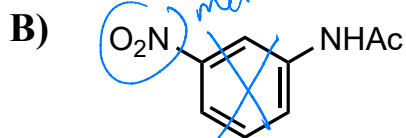
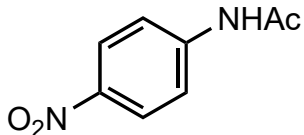
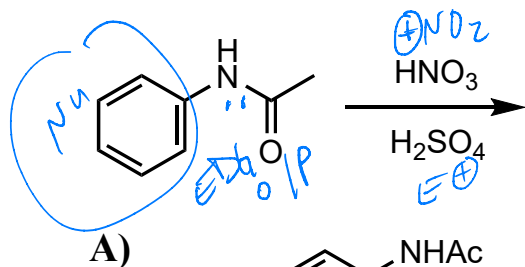
Predict the major product. First, determine whether substituent is an EDG or EWG.



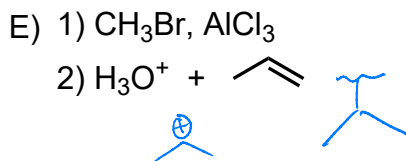
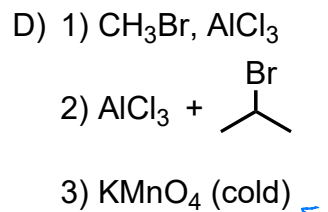
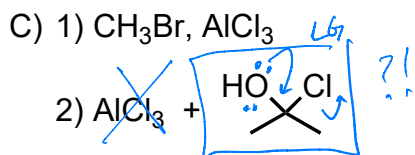
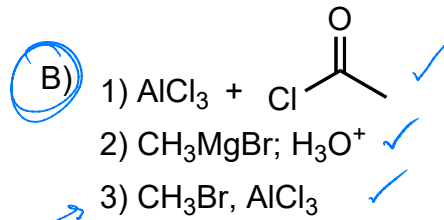
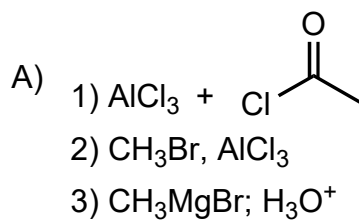
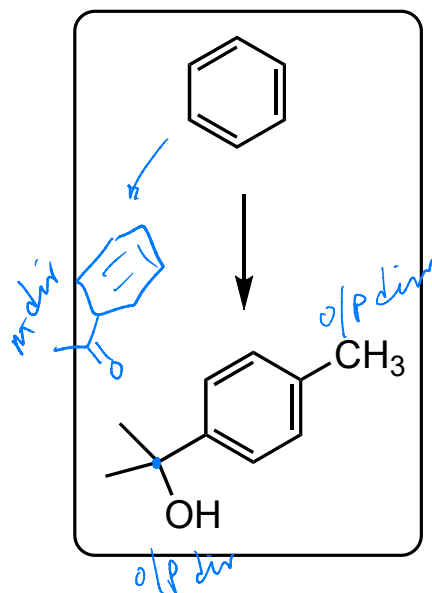
Directing power of substituents

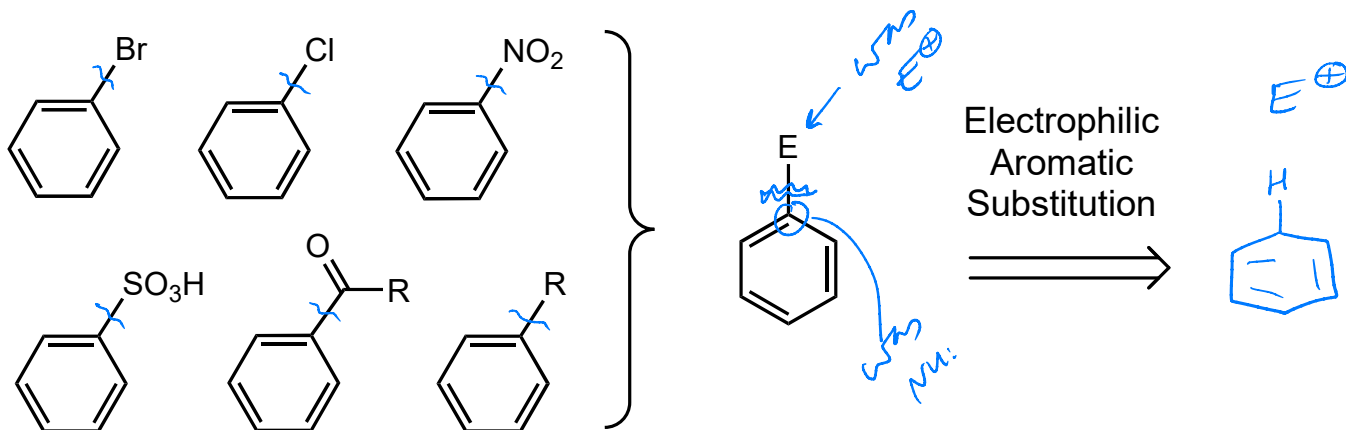


Predict the major products for the following reactions.



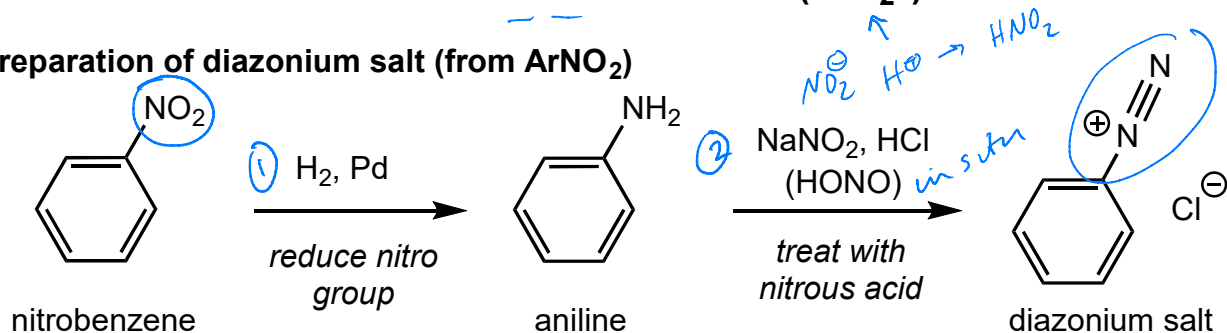
Provide the reagents necessary to transform the given starting material into the desired product.



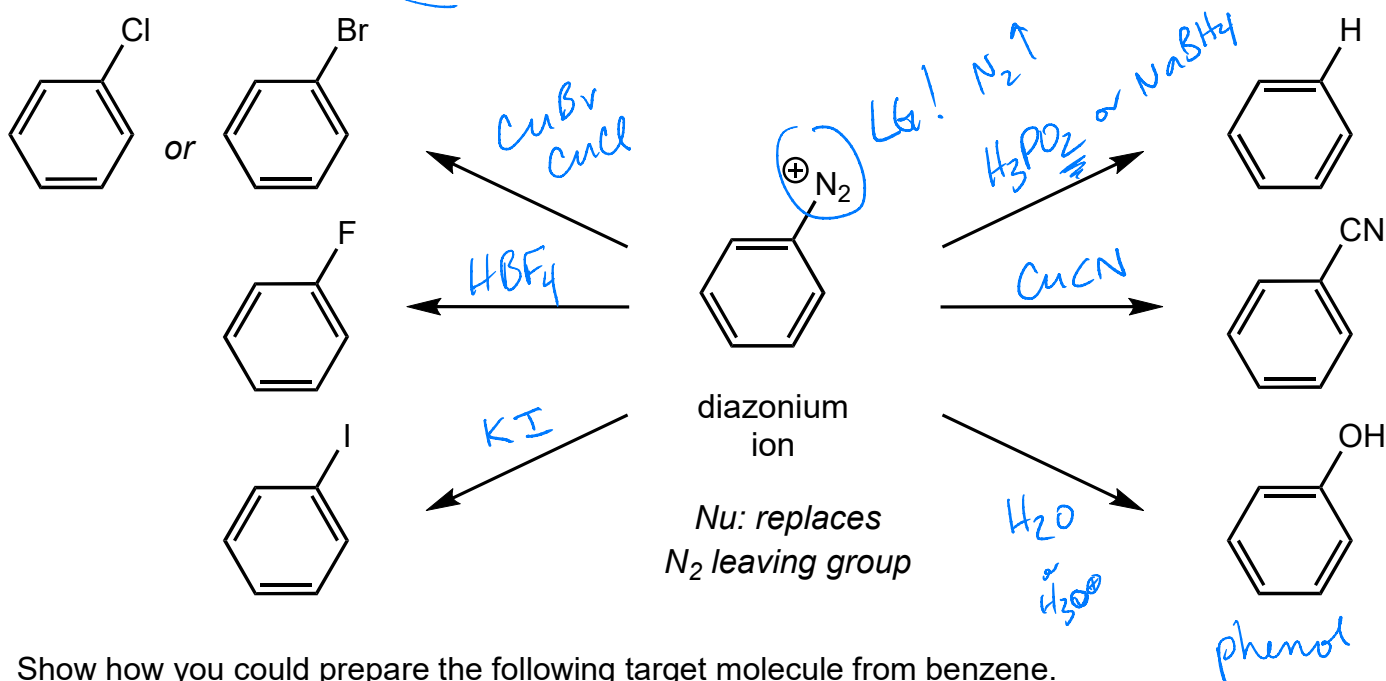


5.2 Aromatic Substitution via Diazonium Salts (ArN_2^+)

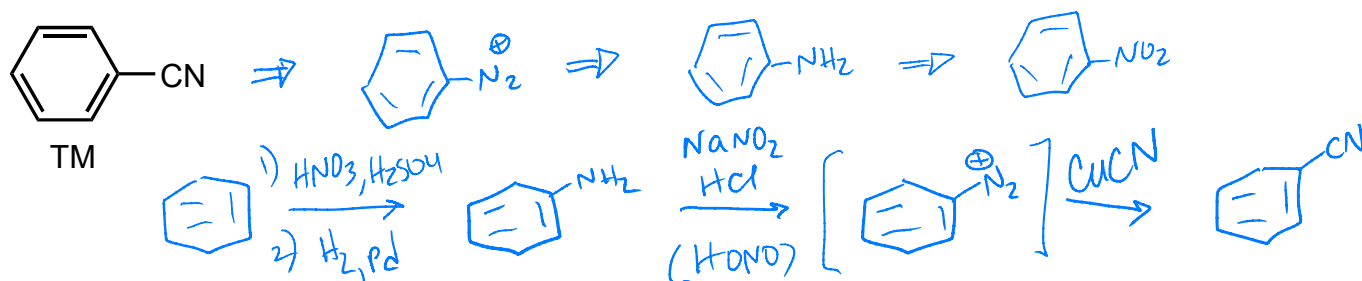
Preparation of diazonium salt (from ArNO_2)



Use of diazonium salts (copper reagents = Sandmeyer reaction)



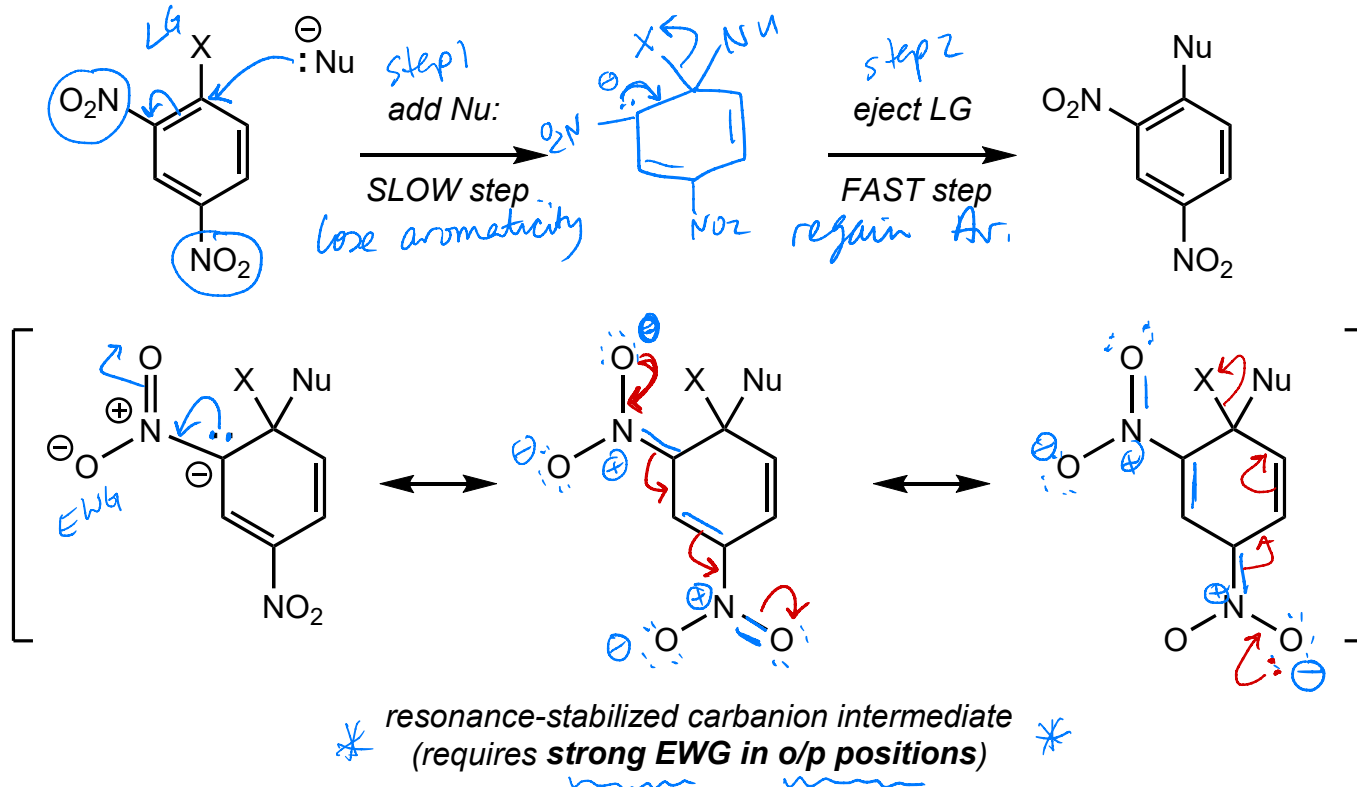
Show how you could prepare the following target molecule from benzene.



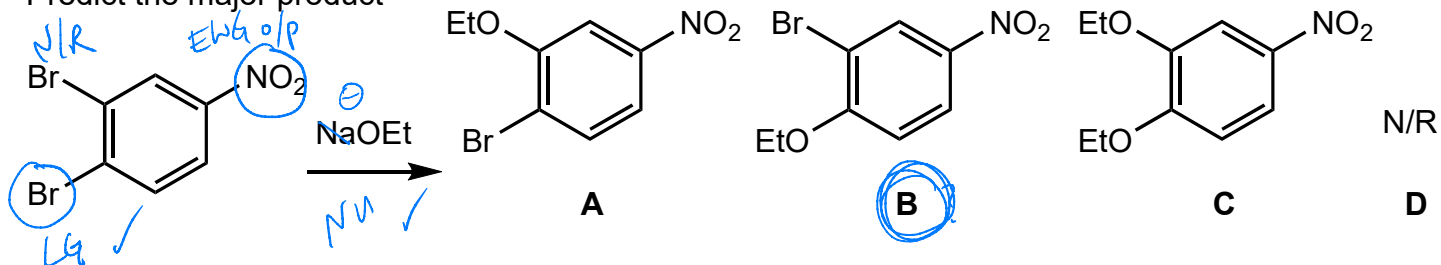
5.3 Nucleophilic Aromatic Substitution (S_NAr)

5-5

F is best LG

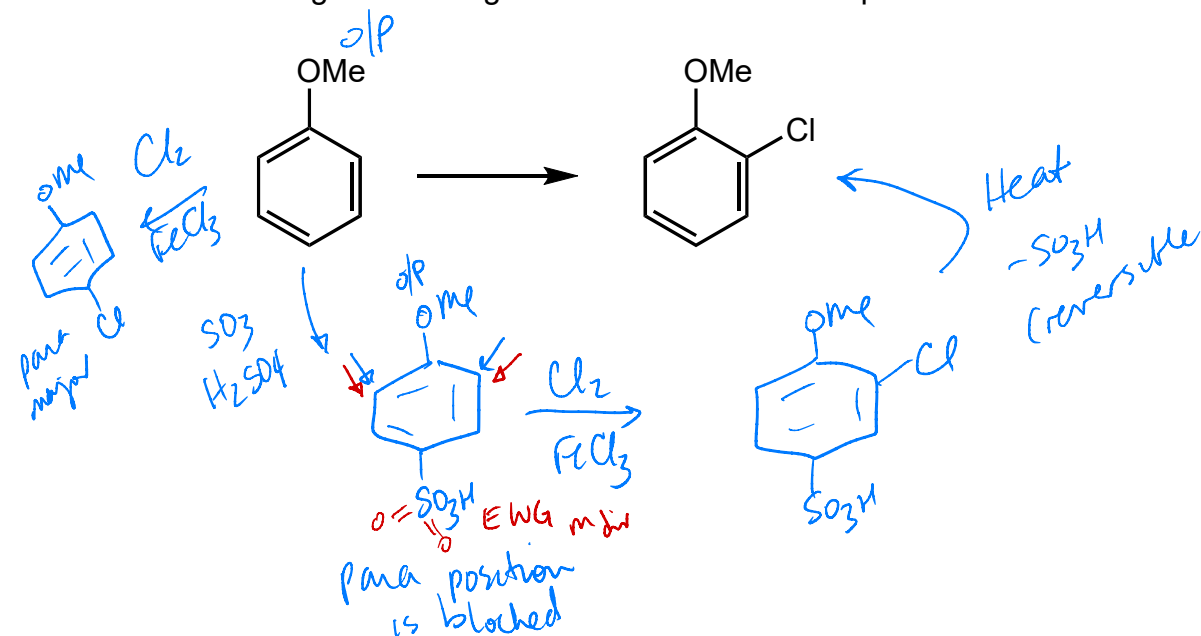


Predict the major product



Additional Synthetic Strategies: Protecting Groups and Blocking Groups

Transform the given starting material into the desired product.





Provide the structures **A – J** and missing reagent(s) **A – E**.

