

#### 4. Answer all Parts I, II and III.

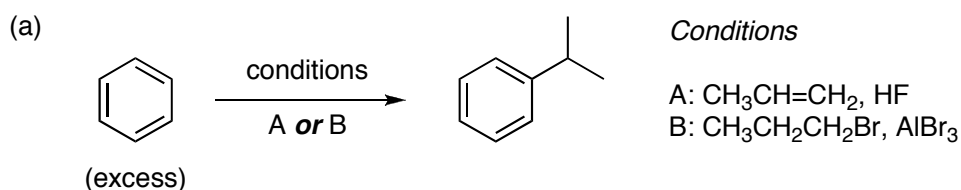
##### Part I

How does the rate and site selectivity of electrophilic aromatic substitution vary in monosubstituted benzene derivatives? In your answer consider inductive and mesomeric effects induced by some or all of the substituents listed below. [7]

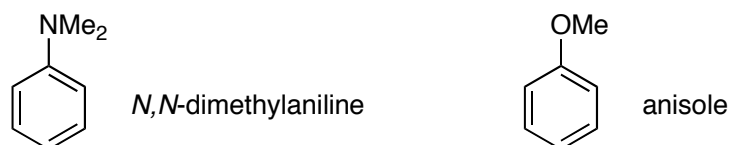


##### Part II

Explain *both* of the following. [2 × 4]

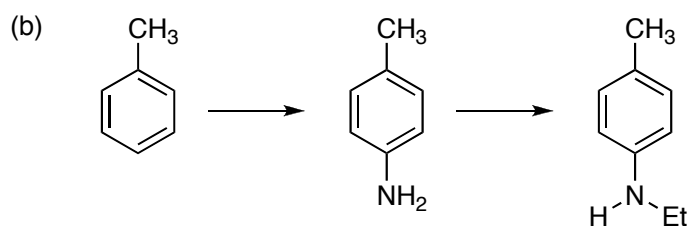
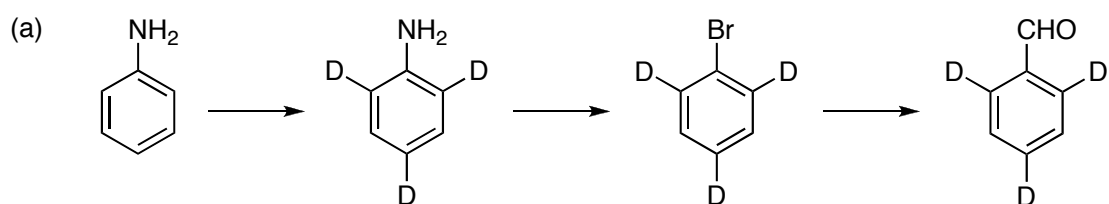


- (b) Nitration of *N,N*-dimethylaniline with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  gives a mixture of *meta*- and *para*- nitro isomers in which the *meta*- isomer is the major product. Under analogous conditions, anisole gives a mixture of *ortho*- and *para*- nitro isomers.



##### Part III

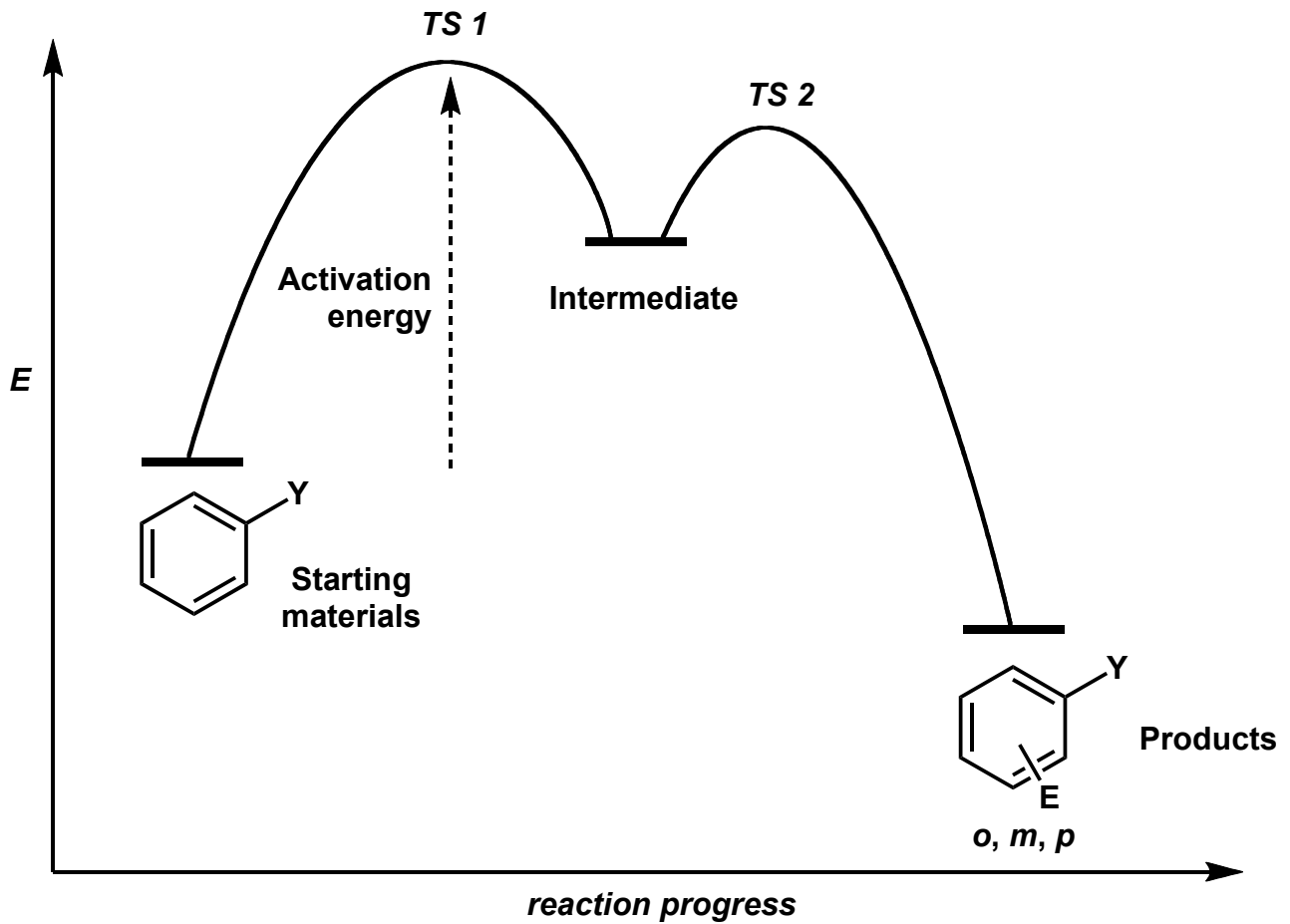
Suggest reagents for the transformations in *one* of the following short sequences [mechanisms are *not* required; more than one step may be necessary for some of the transformations.] [5]



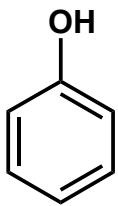
Turn over

(a)

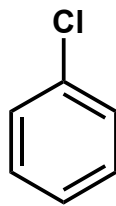
Q4, 2007, Prelim Summer Resit



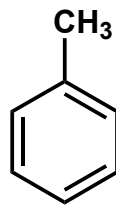
“The transition state looks like an intermediate close to it in energy”



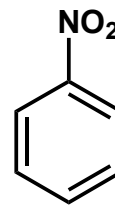
1. Very activated by conjugation
2. direct o,p (conjugation)



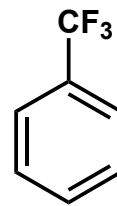
1. deactivated (inductive)
2. direct o,p (conjugation)



1. activating (inductive)
2. direct o, p (hyperconjugation)

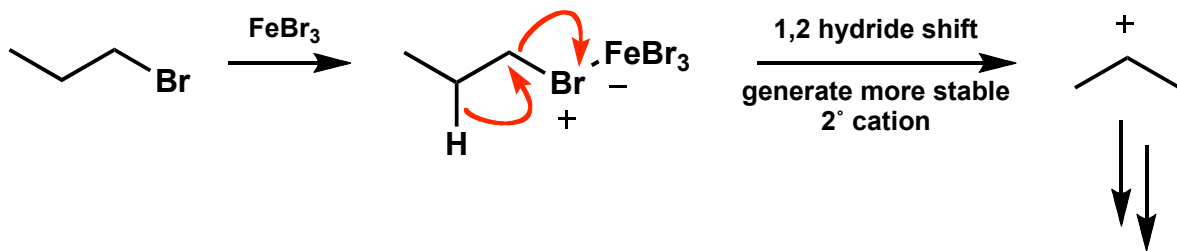
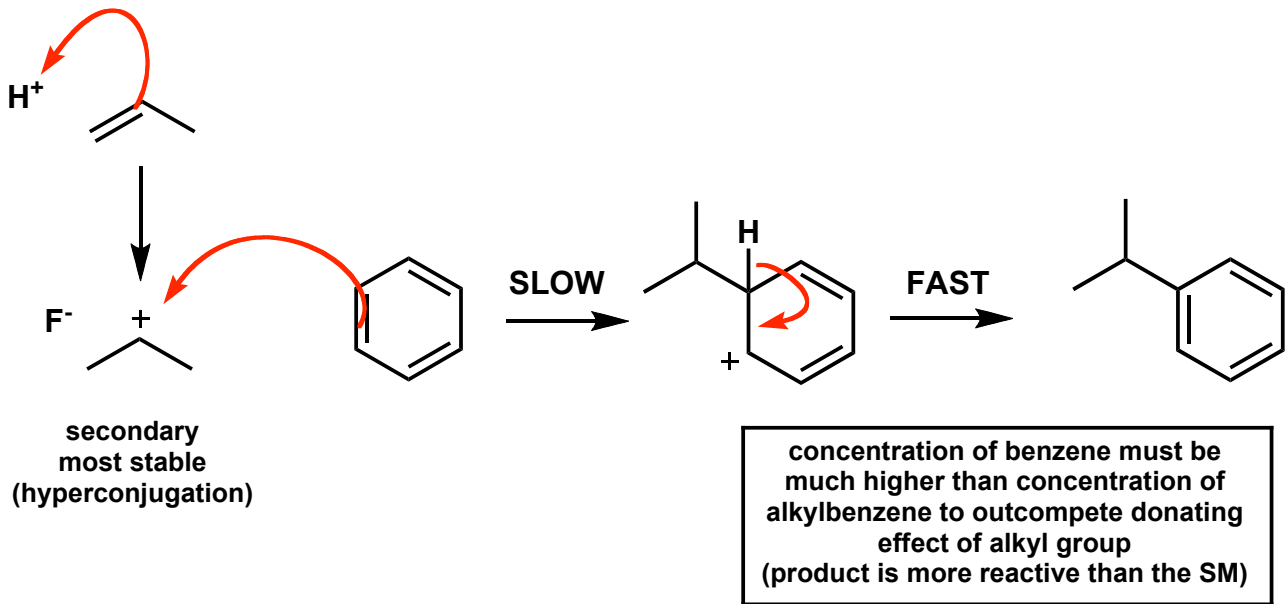


1. deactivated (conjugation)
2. m- directing (conjugation)



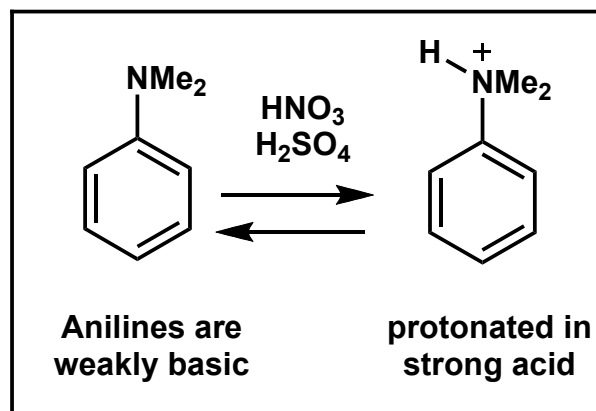
1. deactivated (inductive)
2. m- directing (inductive)

Part II (a)

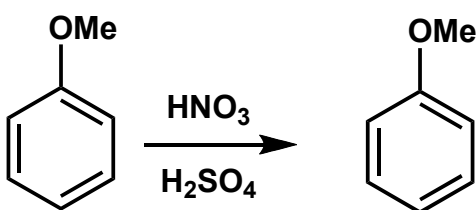


part II (b)

NMe<sub>2</sub> a powerful donor - more reactive than protonated form. Therefore reacts faster even though a minor component of equilibrium



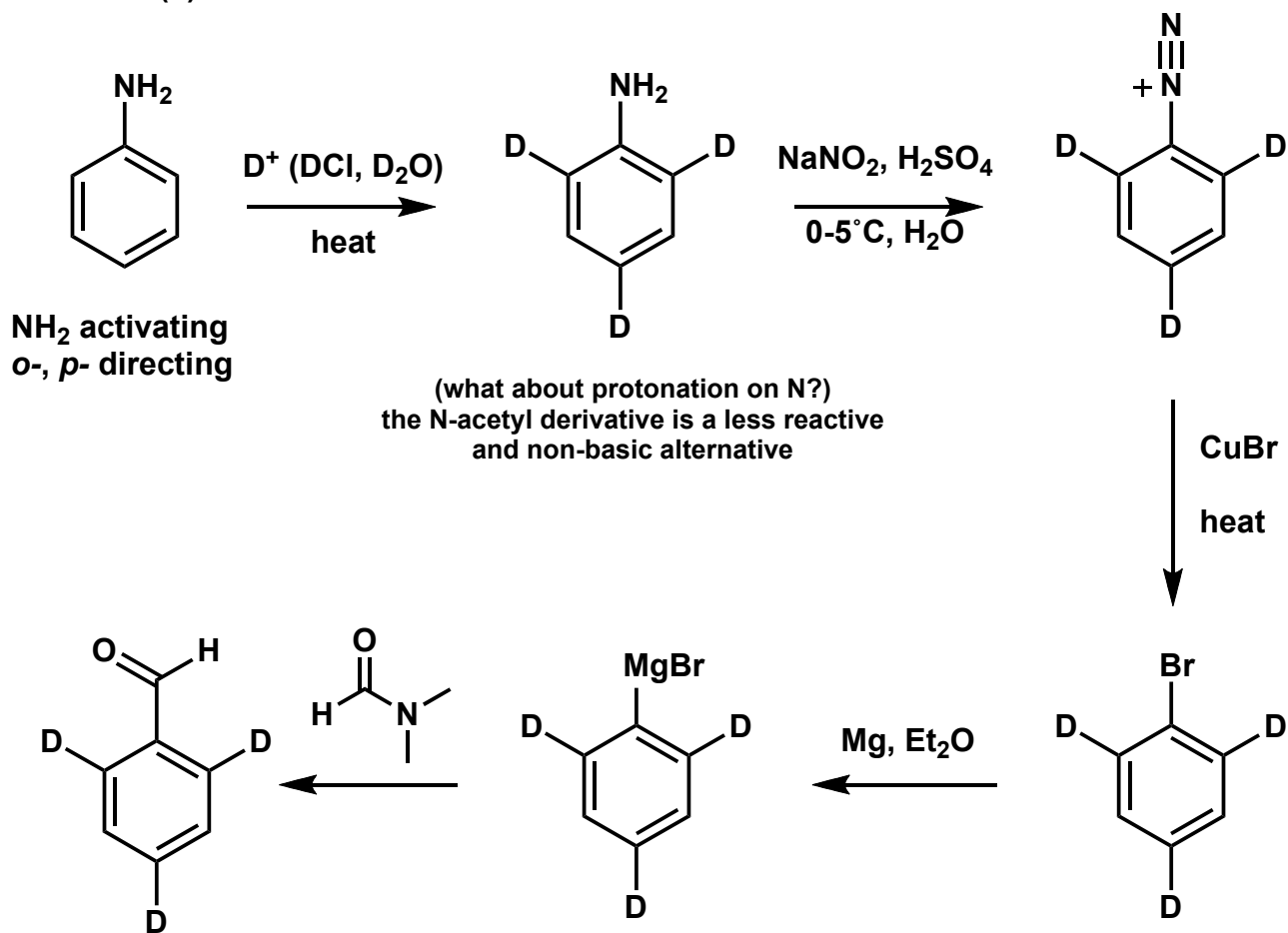
More abundant but less reactive anilinium. Now not a good donor/activator. Mostly inductively withdrawing (deactivated) *meta*- predominates



OMe group not basic  
Not protonated in strong acid  
Therefore: still activating  
ortho- & *para* directing through conjugation of the OMe group.

*direct o,p*

Part III (a)



Part III (b)

