

## Alkenes (elimination) and Arenes

### Reading

Sykes; Clayden & co. and Maitland Jones; Meakins, Maskill and Sainsbuty primers; also Chapter 3 of Stereochemistry at a Glance. will cover all of the topics listed below, some Primers are also suggested.

### Notes:

1. Elimination to give alkenes: E1, E2 and E1cB mechanisms and cyclic eliminations.
2. Aromatic electrophilic substitution: nitration, sulfonation, halogenation, Friedel-Crafts and related reactions.
3. Simple aromatic nucleophilic substitution by addition/elimination mechanism.
4. Diazotisation; substitution via diazonium salts; use in synthesis.

Please make your own notes on these topics, but do not give them in. Do all the problems and hand in your answers by 6pm on the day before your tutorial.

### Elimination

Elimination is an alternative and sometimes competitive pathway to substitution that involves loss of a proton from the  $\alpha$  carbon to the one that the leaving group is attached to. Cover the basic E1 and E2 mechanisms. See how they compare with the  $S_N1$  and  $S_N2$  mechanisms.

Again emphasize any stereochemical consequences (particularly E2) and include the effects of the reactants and the base.

Cover the following topics (in the form of SHORT revision notes). As always do not write long essays and try to use examples to illustrate any worthwhile points.

Mechanisms E1, E2, E1cB Stereochemistry and regiochemistry (Hoffmann vs. Saytzev elimination) Elimination vs substitution - factors affecting (See Norman for a good account)

Syn Eliminations (e.g. Cope Elimination, cyclic transition states).

### Aromatic Electrophilic Substitution

The alkene reactions we have just seen occur by ADDITION whereas aromatic compounds commonly react via SUBSTITUTION. Summarise aromatic electrophilic substitution by using the following standard reactions as models, making sure that you can draw out the mechanisms in each case.

1. Nitration.
2. Bromination, Chlorination etc.
3. Friedel-Crafts alkylation and acylation and related reactions.
4. Sulfonation.
5. Diazo-coupling.

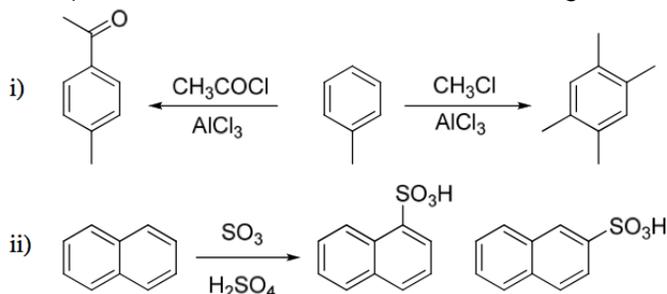
Look carefully at the directing effects of substituents around the ring due to inductive/mesomeric electron donation/withdrawal, steric effects, etc. Be able to explain how these affect rate, orientation and the product composition; see also kinetic and thermodynamic

control.

Also look briefly at nucleophilic aromatic substitution, both by use of diazonium salts,  $\text{ArN}_2^+$ , and by addition/elimination (e.g. ammonia and 4-nitro chlorobenzene).

### Problems

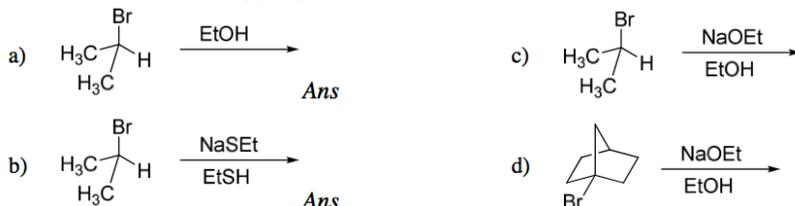
1a) Explain the difference between the following reactions.



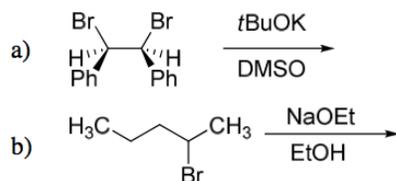
One product predominates at high temperature while the other at low temperature. Which one is which and why? Hint Look at KINETIC and THERMODYNAMIC control.

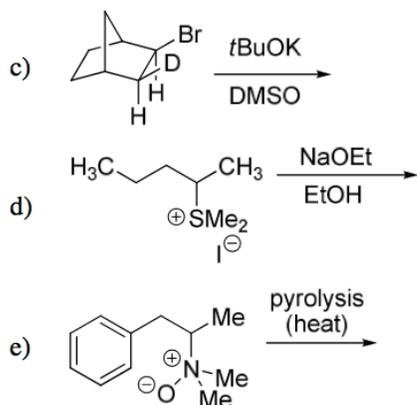
b) State concisely the mechanistic and stereochemical differences between the E1 and the E2 reactions. In which cases are syn eliminations 'allowed' when we know that the E2 mechanism prefers an anti-periplanar alignment of orbitals? Give an example of the E1cb mechanism and state why this mechanism is preferred for that particular substrate.

2. In many reaction of alkyl halides there is competition between substitution and elimination. Predict the major products of the following reaction and explain your reasoning giving mechanisms where appropriate.

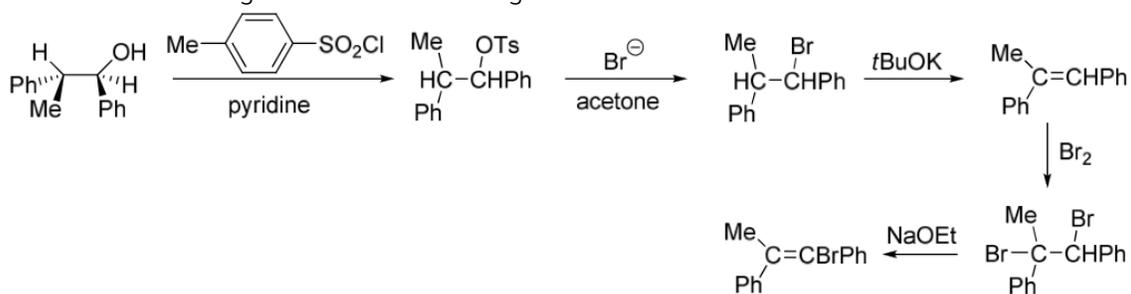


3. Predict the products in the following elimination reactions. Give mechanisms and reasons for your answers.



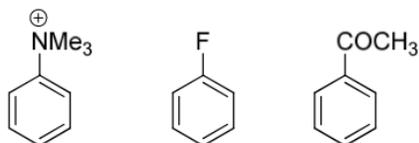


4. Trace the following transformations using 3-D structures.



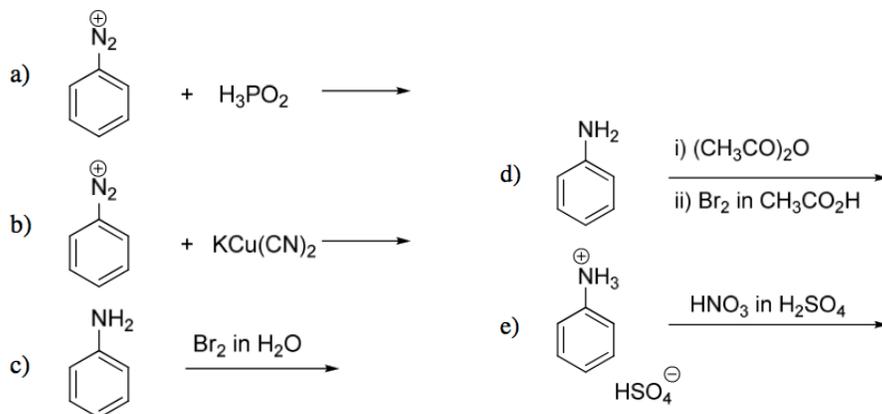
5. Discuss each of the following:

a) The relative rates of nitration of

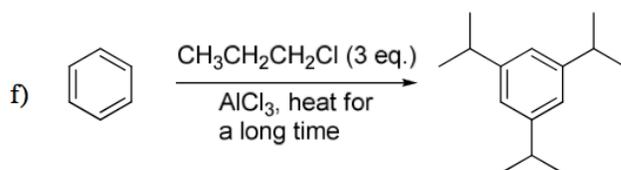
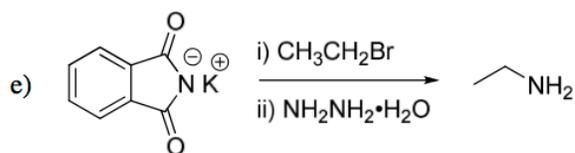
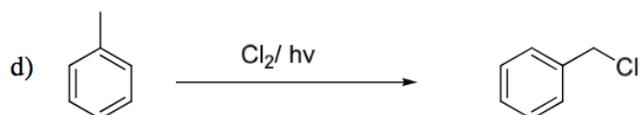
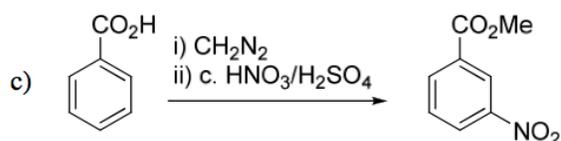
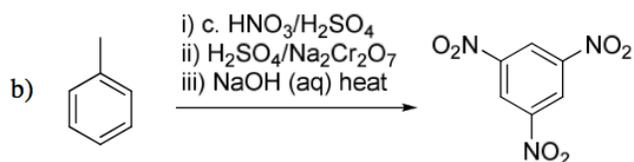
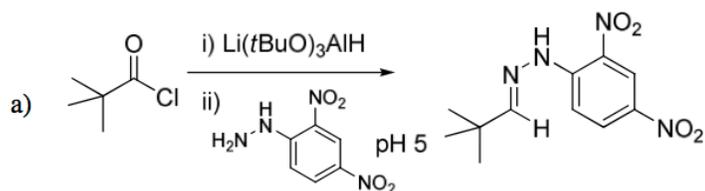


b) The finding that dilute  $\text{HNO}_3 + \text{HNO}_2$  will nitrate phenol whereas concentrated  $\text{HNO}_3$  / concentrated  $\text{H}_2\text{SO}_4$  mixtures are needed to nitrate benzene.

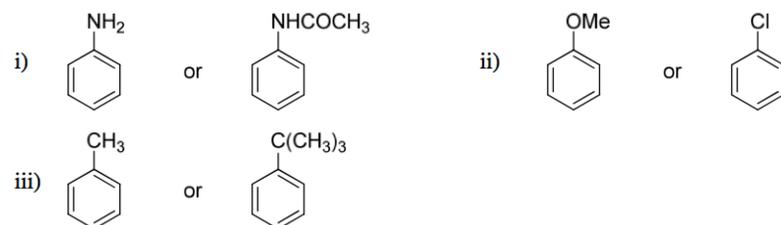
6. Give products of the following reactions



7. Provide mechanistic rationalisation for all of the following conversions:



8. For each of the following pairs of compounds explain which would be expected to undergo nitration more readily. For ALL six compounds indicate the expected position of nitration using conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$



Now check your work:

[http://paton.chem.ox.ac.uk/teaching/files/Y1\\_Alkenes\\_Elimination\\_Notes.pdf](http://paton.chem.ox.ac.uk/teaching/files/Y1_Alkenes_Elimination_Notes.pdf)