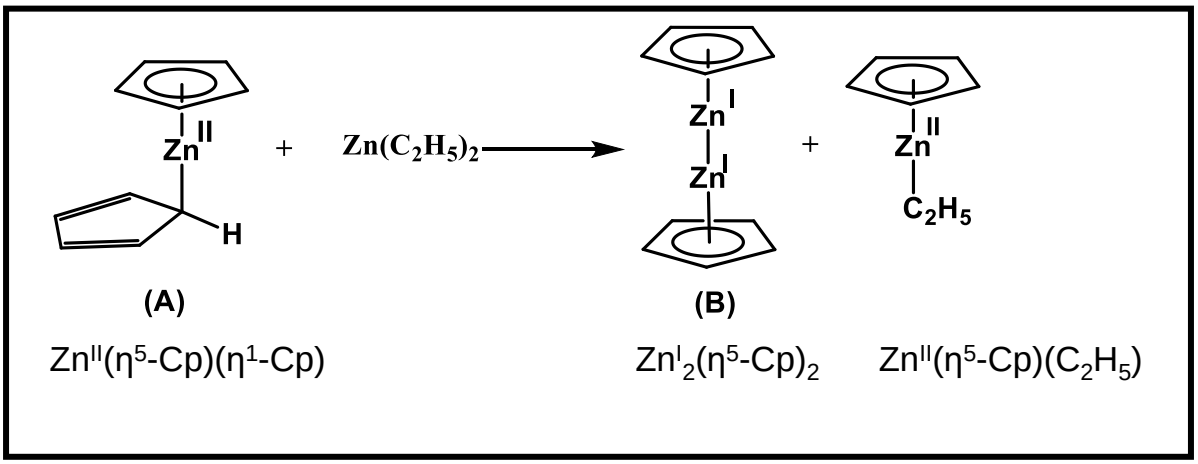
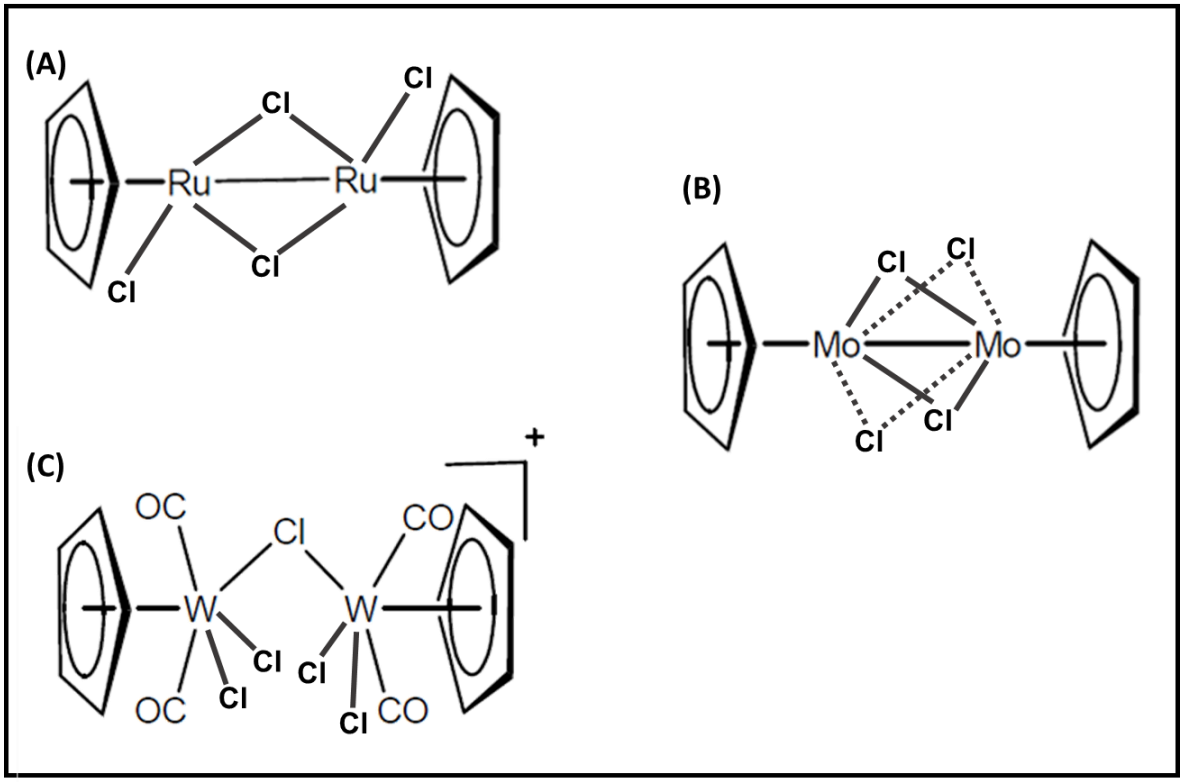
1a. Compounds **A** and **B** in the given equation obey the 18-electron rule.

$$\underset{\mathbf{A}}{\mathbf{Cp_2Zn}} + Et_2Zn \rightarrow \underset{\mathbf{B}}{\mathbf{[CpZn]_2}} + CpZnEt$$

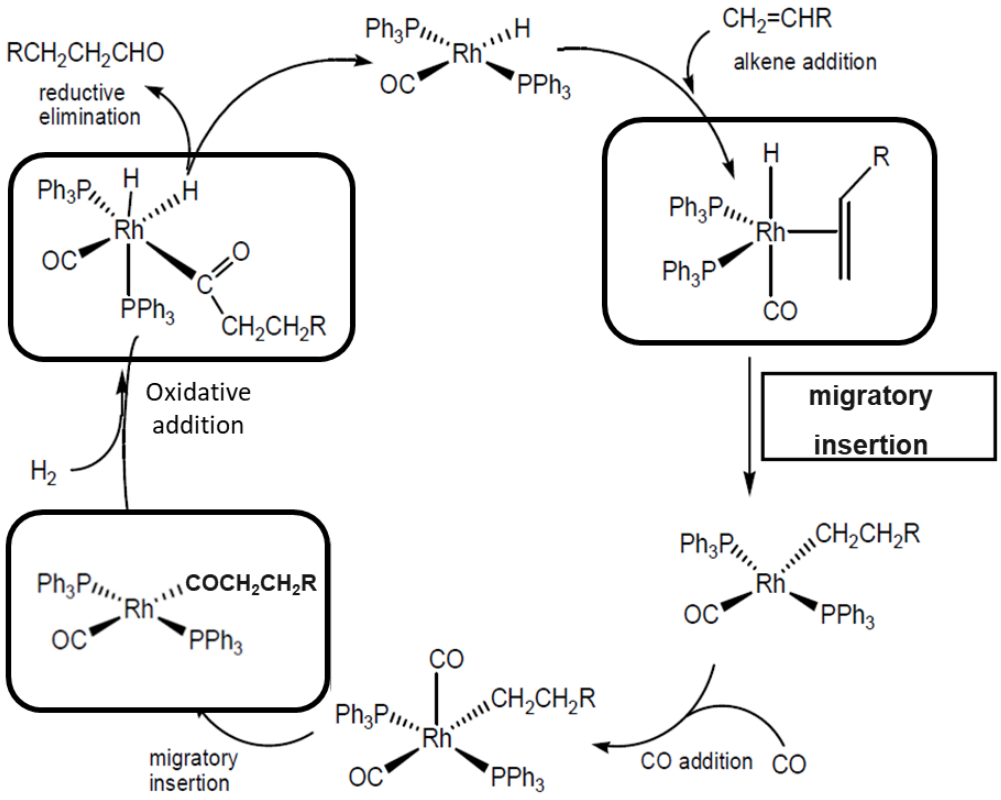
Draw the structures of compounds **A** and **B** clearly indicating hapticity of Cp. Also indicate oxidation state of Zn in both **A** and **B** [The η^3 hapticity can be ruled out as it is rare]. **(1.5 + 1.5 + 1 (OS) marks)**



1b. Four Cl^- ligands are missing in each of the given skeletons of dimeric compounds (**A**), (**B**) and (**C**). Given that all of them obey the 18-electron rule and no additional metal-metal bonds are present, attach the missing Cl^- ligands on the complexes in the most appropriate manner. **(2 + 2 + 2 marks)**



2a. In the given catalytic cycle of hydroformylation, fill in the blanks with the name of the reactions (boxes adjacent to the arrows) and the structure of the specific intermediate with the correct geometry at the given step. **(4 marks, each box one mark)**



2b. Of hypothetical first-row transition metal complexes of general formula $[M(H_2O)_6]^{2+}$, which metals are predicted by the Jahn–Teller theorem to have the distorted complexes? **(4 marks, No partial marking)**

$[Sc(H_2O)_6]^{2+}$, $[Ti(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Cu(H_2O)_6]^{2+}$

This question does not have partial marking. However, we are lenient and give the marking scheme as follows.

Five or more than metals → 4 marks granted.

Less than 5 metals → 2 marks granted.

Even one metal wrong → 0 marks granted.

2c. How many unpaired electrons are there in $[IrBr_6]^{4-}$? (hint: Br^- is a weak-field ligand, **Ir forms low spin complexes, Ir is a 5d-metal**) **(1 mark)**

(i) 4 (ii) 3 (iii) 2 **(iv) 1** (v) 0

2d. Which of the following ligand(s) are capable of showing linkage isomerism? **(1 mark, No Partial marking)**

(i) N_3^- (ii) $NH_2CH_2CH_2NH_2$ **(iii) CH_3SOCH_3** (iv) CH_3COO^- **(v) OCN^-** (vi) HO^-

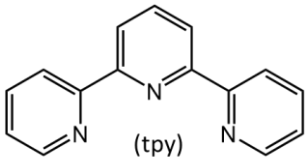
3a. What is the spin-only magnetic moment of oxy-myoglobin? Briefly justify your answer. **(2 marks)**

Oxy-myoglobin **Fe(III)-$O_2^{-\bullet}$** (an iron(III)-superoxo species)

Fe(III) is in low spin configuration → 1 unpaired electron

Superoxo has one unpaired electron. Due to anti ferromagnetic coupling their spins cancel out, hence, the spin-only magnetic moment is 0 BM.

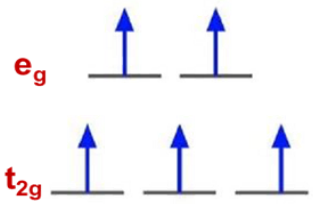
3b. For $[Fe(tpy)Cl_3]$, μ_{eff} = 5.85 BM at 298 K.



(i) Determine the number of unpaired electrons and comment on whether there will be orbital contribution to μ_{eff}. **(2 marks)**

(ii) Can this complex exist in the *fac*-form? Briefly justify. **(2 marks)**

Oxidation state of iron is +III. High μ_{eff} value indicate the high spin nature of the Fe(III). Due to absence of asymmetric electron filling, there will be no orbital contribution to μ_{eff}.



This complex can't exist in the *fac*-form. It can only exist in the *mer*-form. The ligand 'tpy' does not allow three chloride ligands to bind to metal facially.

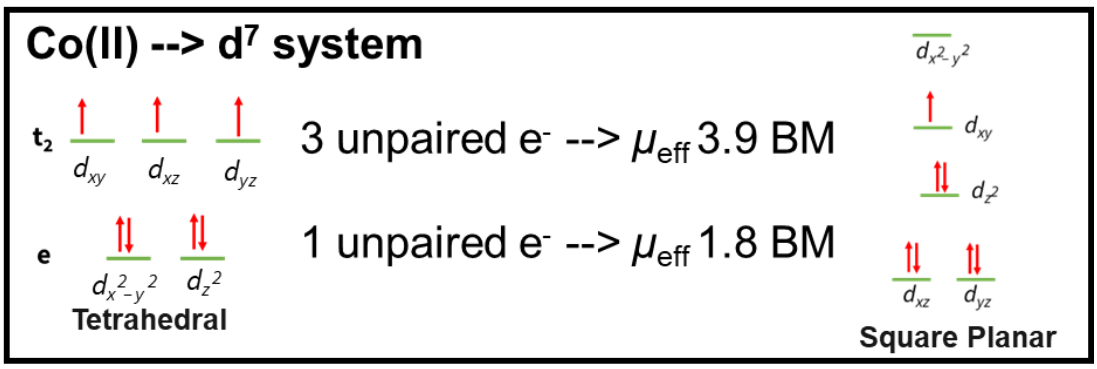
3c. Which of the following statement(s) about the complex ion $[Co(en)_2Cl_2]^+$ is/are **true**? **(1 mark, No Partial marking)**

(i) The secondary valency of the complex is four.
(ii) The complex ion exhibits geometric isomers, but no optical isomers.
(iii) This complex does not exhibit Jahn–Teller distortion.
(iv) Because en is a strong field ligand (large Δ_o), the complex ion is diamagnetic.
(v) The geometric isomers of the cobalt complex ion have identical chemical properties.

3d. For the process $[Co(NH_3)_5Cl]^{2+} + Cl^- \rightarrow [Co(NH_3)_4Cl_2]^+ + NH_3$, what would be the ratio of *cis* to *trans* isomers in the product? **(1 mark)**

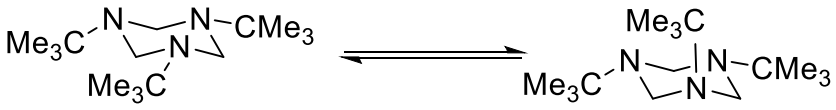
(i) 1:1 (ii) 1:2 (iii) 1:4 **(iv) 4:1** (v) 2:1

3e. The square-planar and tetrahedral complexes of cobalt(II) exhibit magnetic moments (μ_{eff}) in the range ca. 2 and ca. 3.9 BM, respectively. Justify these observations using orbital splitting diagram with their labels. **(3 marks)**



4a. Among the following equilibrium structures write the stable conformer in the box provided.
(5 marks, *all must be correct; no partial marks will be given)

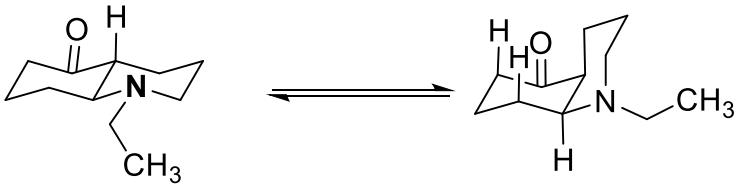
(i)



(A) (B)

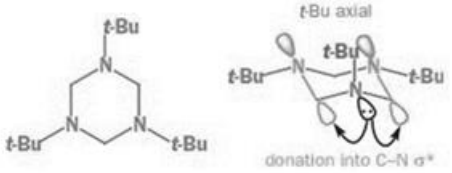
B

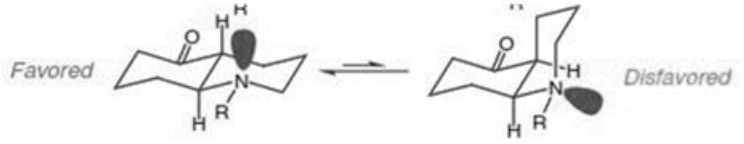
(ii)



(C) (D)

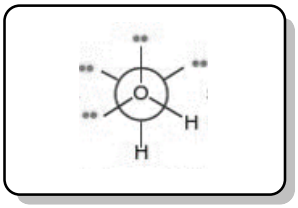
C



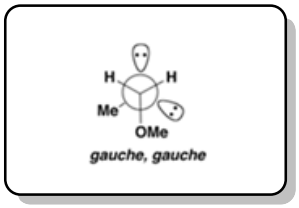


4b. Draw the most stable conformer of H_2O_2 and $CH_3OCH_2OCH_3$ in Newman projection and explain why is it more stable in one sentence in the given box? **(5 marks)**

H_2O_2

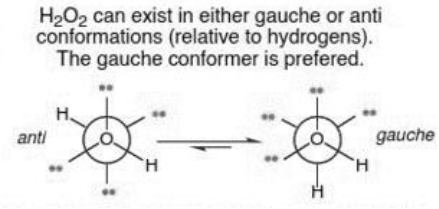


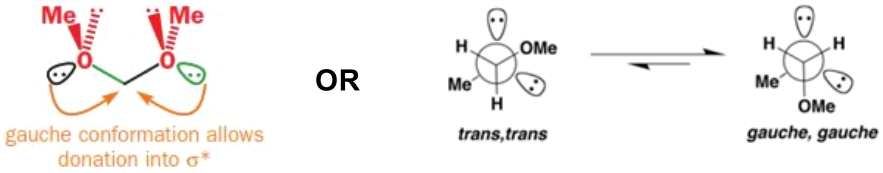
$CH_3OCH_2OCH_3$



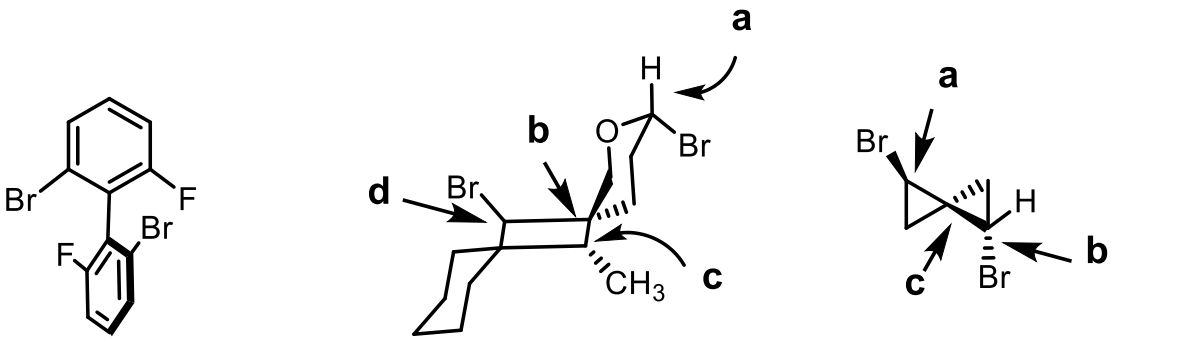
Explanation

σ^*–orbital of O-H in H_2O_2 and O-Me in $CH_3OCH_2OCH_3$ are stabilized by lone-pair electrones from other oxygen of the same compounds.





4c. Assign all the possible R/S configuration(s) in the given molecules. **(10 marks = 2 + 4 + 4 marks)**



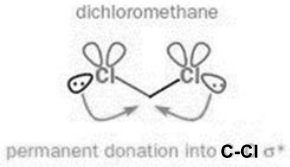
R	

a =	R
b =	R
c =	R
d =	R

a =	R
b =	S
c =	S

5a. Methyl chloride reacts with NaOH to provide the product methanol. However, dichloromethane exhibits considerably weak reactivity with NaOH. Sate the reason with a proper conformation for the poor reactivity of dichloromethane in the given boxes. **(5 marks)**

Conformation

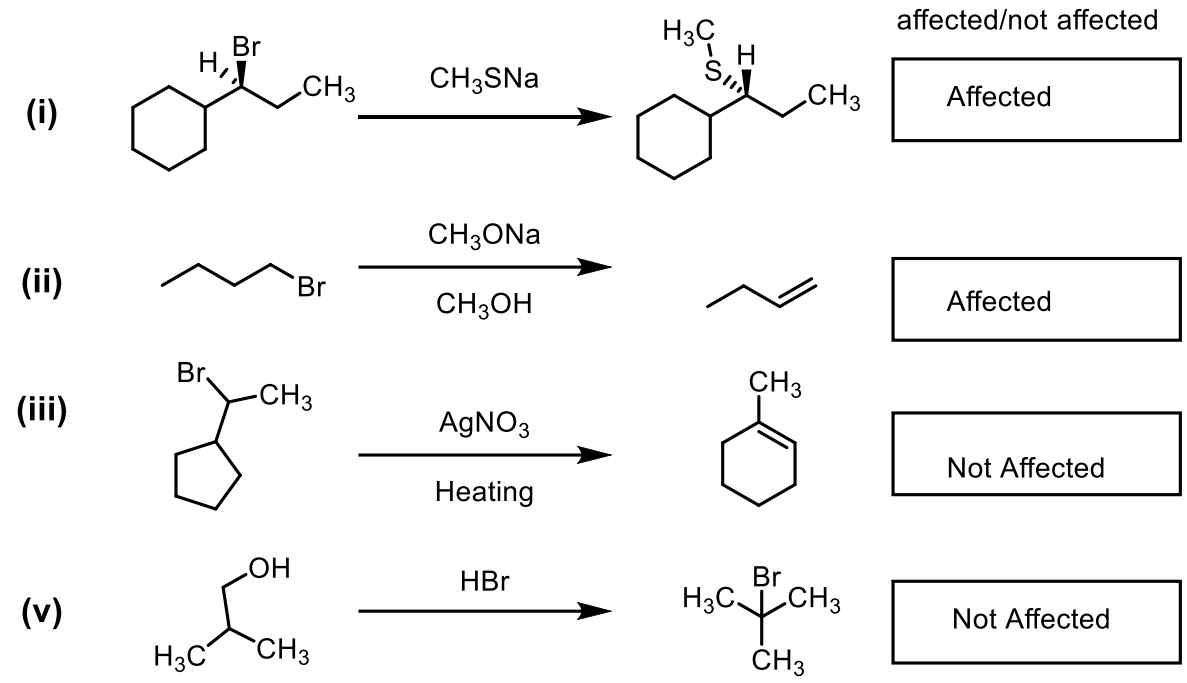


Explanation

C-Cl σ^*-orbital is already stabilized by a lone pair of another Chlorine atom which makes it less prone to accept electrons from incoming nucleophiles, making it unreactive in the S_N2 reaction

5b. Identify the rate of the reactions, that will be affected upon increasing the concentration of the nucleophile to more than one equivalent?

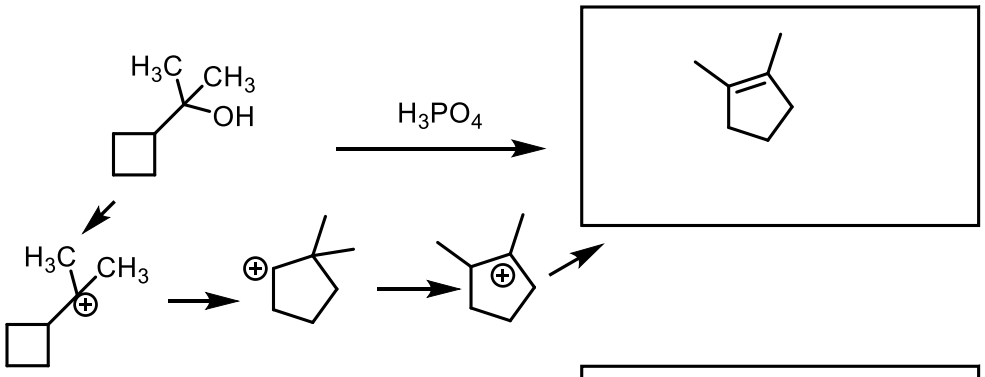
(5 marks, *all must be correct; no partial marks will be given)



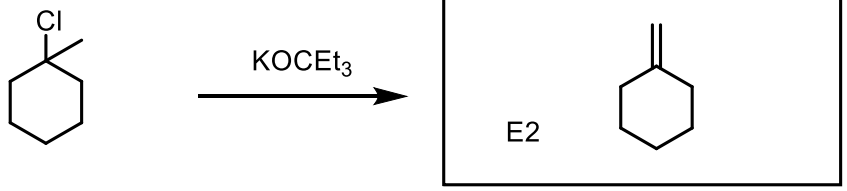
S_N2 and E_2 are second order reactions with respect of substrate and nucleophile(base)

6. Based on the chemical reactions discussed in the classes, draw the major product formed in the following reactions: **(10 marks = 2 + 1 + 1 + 2 + 2 + 2 marks)**

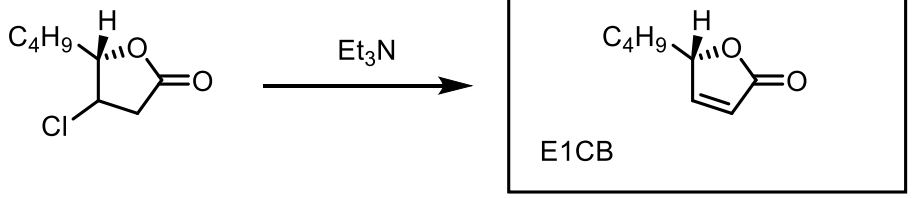
(i)



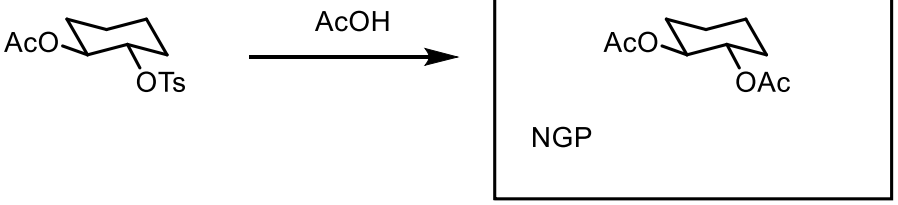
(ii)



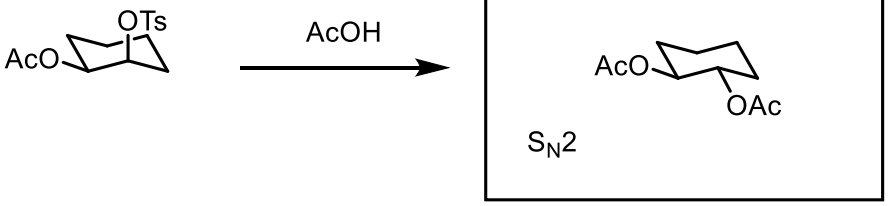
(iii)



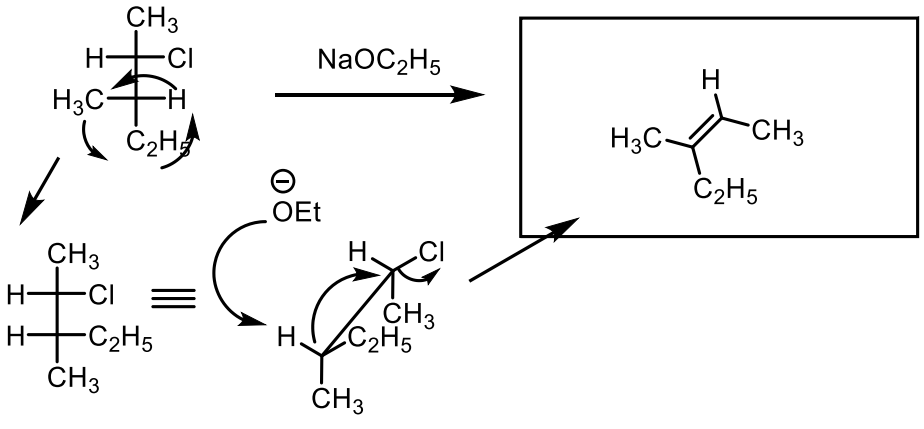
(iv)



(v)

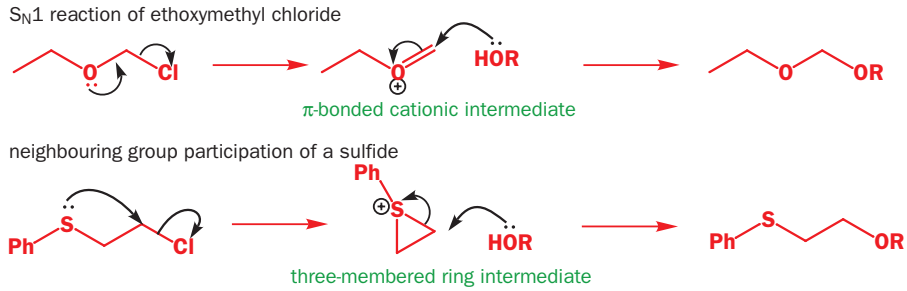


(vi)



▶ Neighbouring group participation is occasionally called **anchimeric assistance** (Greek *anchi* = neighbouring; *mer* = part).

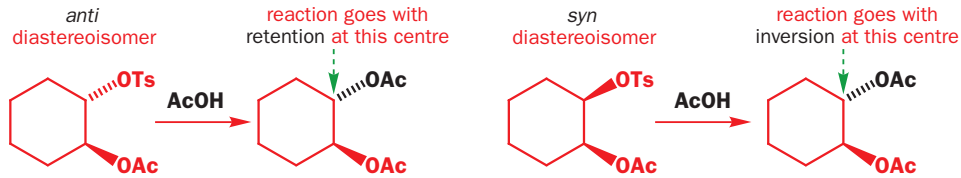
The mechanism by which they speed up the reactions is known as **neighbouring group participation**. Compare the reaction of this ether and this sulfide with an alcohol.



In both cases, ionization of the starting material is assisted by the lone pair of an electron-rich functional group. The ether in the first example assists by forming a π bond, the sulfide assists by forming a three-membered ring, and a common feature of all mechanisms involving neighbouring group participation is the formation of a cyclic intermediate.

Stereochemistry can indicate neighbouring group participation

How do we know that neighbouring group participation is taking place? Well, the first bit of evidence is the *increase in rate*. The neighbouring groups will become involved only if they can increase the rate of the substitution reaction—otherwise the mechanism will just follow the ordinary S_N2 pathway. But more important information comes from reactions where stereochemistry is involved, and one of these is the last of the four examples above. Here it is again in more detail. Not only does the first of these reactions go faster than the second—its stereochemical course is different too.

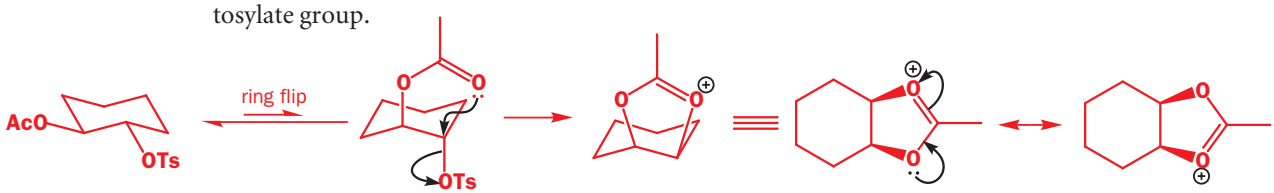


■ If you are unsure what we are talking about, go back and read Chapter 18 now!

Although one starting material has *syn* and the other *anti* stereochemistry, the products have the same (*anti*) stereochemistry: one substitution goes with retention and one goes with inversion. Again, neighbouring group participation is the reason. To explain this, we should first draw the six-membered rings in their real conformation. For the *anti* compound, both substituents can be equatorial.

both substituents equatorial

However, not much can happen in this conformation—but, if we allow the ring to flip, you can see immediately that the acetate substituent is ideally placed to participate in the departure of the tosylate group.



both substituents equatorial

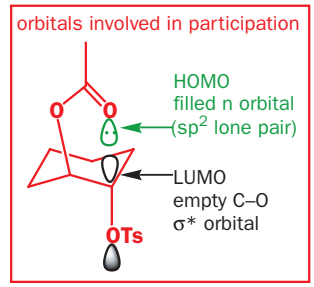
both substituents axial

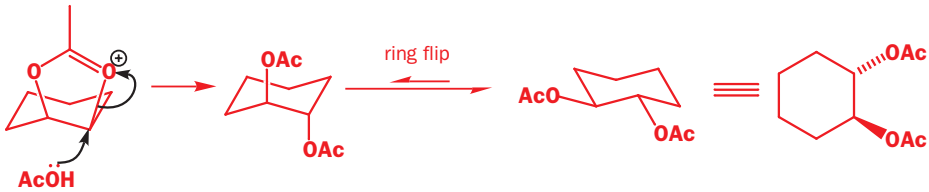
symmetrical intermediate

▶ While the mechanism of this first step of the substitution reaction is S_N2 in appearance—a nucleophile (the acetate group) arrives just as a leaving group (the tosylate group) departs—it is also, of course, only unimolecular.

What results is an entirely symmetrical intermediate—the positive charge on one of the oxygens is, of course, delocalized over both of them. The intramolecular S_N2 reaction takes place with inversion, as required by the orbitals, so now the junction of the two rings is *cis*.

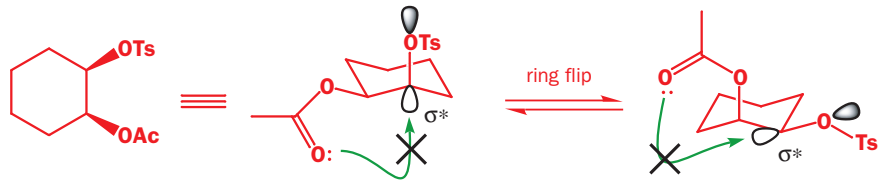
The next step is attack of acetic acid on the intermediate. This is another S_N2 reaction, which also proceeds with inversion and gives back a *trans* product.



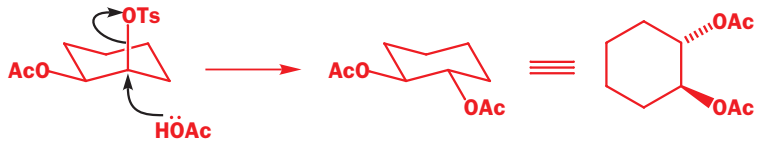


Overall, we have *retention* of stereochemistry. As you know, S_N2 reactions go with inversion, and S_N1 reactions with loss of stereochemical information—so this result is possible only if we have two sequential S_N2 reactions taking place—in other words neighbouring group participation.

Why, then, does the other diastereoisomer react with inversion of stereochemistry? Well, try drawing the mechanism for intramolecular displacement of the tosyl group. Whether you put the tosylate or the acetate group equatorial doesn't matter; there is no way in which the acetate oxygen's lone pair can reach the σ* orbital of the tosylate C–O bond.

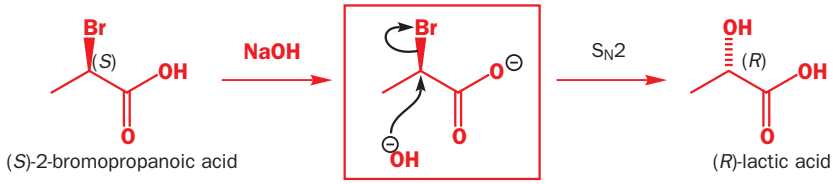


Neighbouring group participation is impossible, and substitution goes simply by intermolecular displacement of OTs by AcOH. Just one S_N2 step means overall inversion of configuration, and no participation means a slower reaction.



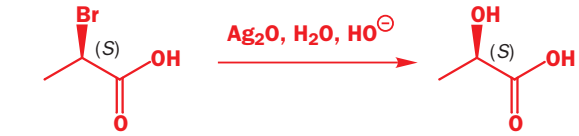
Retention of configuration is an indication of neighbouring group participation

Enantiomerically pure (*S*)-2-bromopropanoic acid reacts with concentrated sodium hydroxide to give (*R*)-lactic acid. The reaction goes with inversion and is a typical S_N2 reaction—and a good one too, since the reaction centre is adjacent to a carbonyl group (see Chapter 17).



(*S*)-2-bromopropanoic acid (*R*)-lactic acid

If, on the other hand, the reaction is run using Ag_2O and a low concentration of sodium hydroxide, (*S*)-lactic acid is obtained—there is overall *retention* of stereochemistry.



(*S*)-2-bromopropanoic acid (*S*)-lactic acid

Nucleophilic substitution reactions that go with retention of stereochemistry are rather rare and mostly go through two successive inversions with neighbouring group participation, like the example you saw in the last section. This time the neighbouring group is carboxylate: the silver oxide is important because it encourages the ionization of the starting material by acting as a halogen-selective Lewis acid.