

CHEMISTRY 1B (CHEM1102) - November 2013

NB These answers have not been checked

2013-N-2

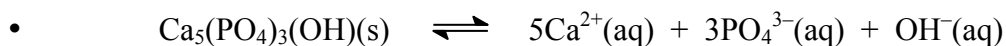
- 2.23



1.70

0.013 mol

2013-N-3



$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})]^5 [\text{PO}_4^{3-}(\text{aq})]^3 [\text{OH}^-(\text{aq})]$$

- tetrahedral O
octahedral Cl, N
octahedral C
linear C

Zn^{2+} is d^{10} system. No unpaired electrons, therefore diamagnetic.

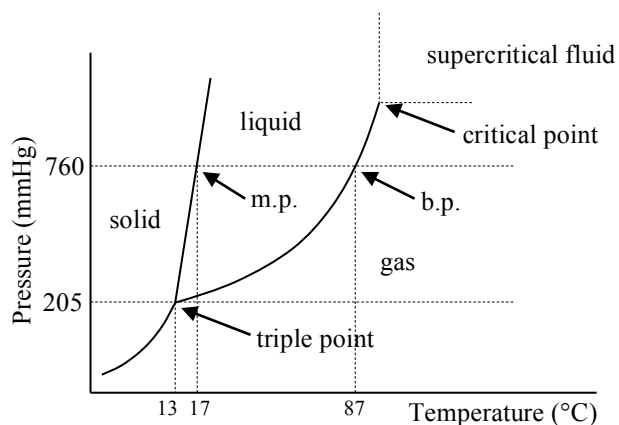
Co^{3+} is d^6 system. 2 paired electrons & 4 unpaired, therefore paramagnetic.

Fe^{2+} is d^6 system. 2 paired electrons & 4 unpaired, therefore paramagnetic.

Ag^+ is d^{10} system. No unpaired electrons, therefore diamagnetic.

2013-N-4

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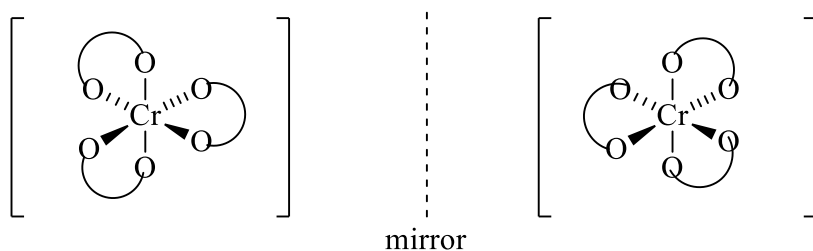
true

true

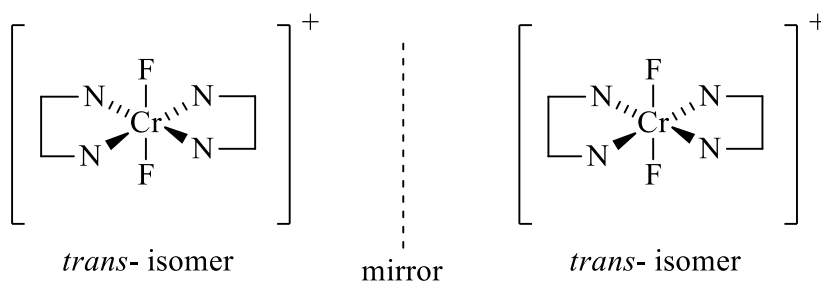
false

2013-N-5

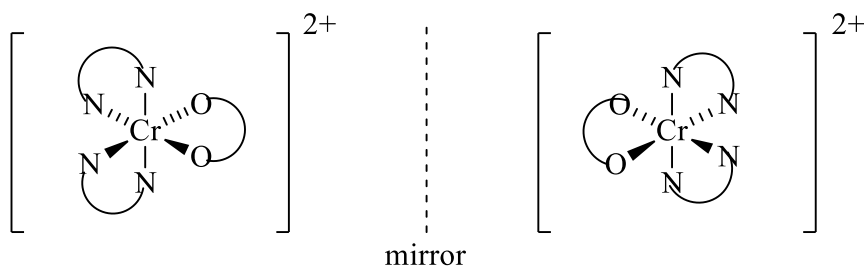
- tris(acetylacetonato)chromium(III) is chiral – mirror images are non-superimposable



trans-bis(ethylenediamine)difluoridochromium(III) ion is not chiral – it is identical to its mirror image.

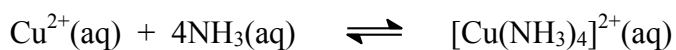


acetylacetonatobis(ethylenediamine)chromium(III) ion is chiral – mirror images are non-superimposable



2013-N-6

- $3.4 \times 10^{-7} \text{ M}$



$$1.6 \times 10^{-6} \text{ M}$$

No. Equilibrium constant K is very small so the reaction lies heavily in favour of reactants.

2013-N-7

- Rate = $k[\text{I}^-][\text{H}_2\text{O}_2]$

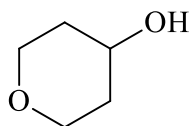
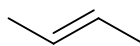
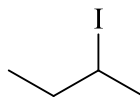
$$k = 0.0102 \text{ L mol}^{-1} \text{ s}^{-1}$$

A catalyst provides a reaction pathway of lower activation energy and hence increases the rate of the reaction. It is unchanged at the end of the reaction and does not change the equilibrium position.

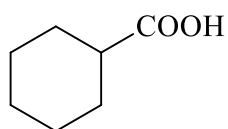
2013-N-8

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1. LiAlH_4 in dry ether
2. $\text{H}^+ / \text{H}_2\text{O}$

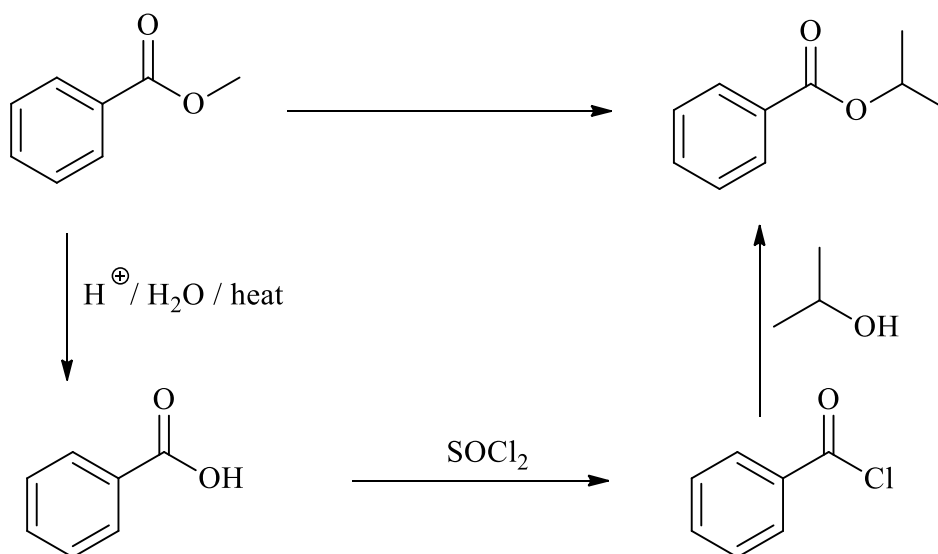


SOCl_2

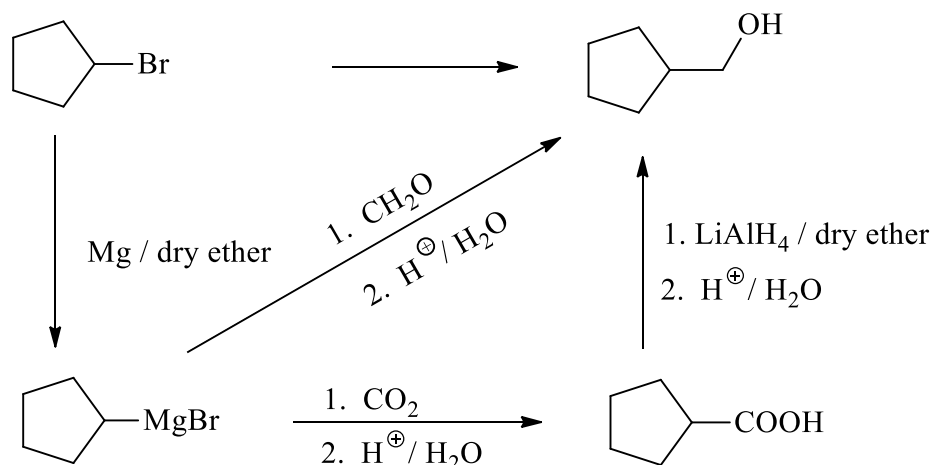


2013-N-9

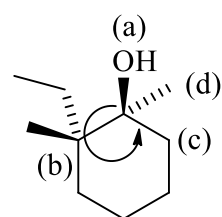
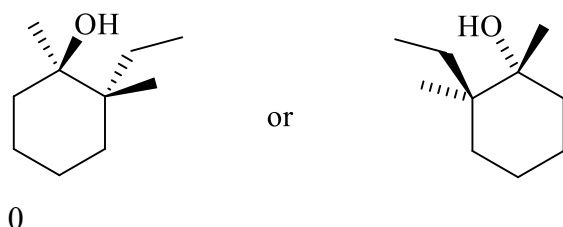
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2013-N-9 (cont.)



2013-N-10

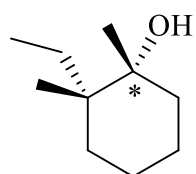


The order of priority is:



With lowest priority (d) at back, the order of the groups goes anticlockwise as shown. Therefore the stereochemistry is (*S*).

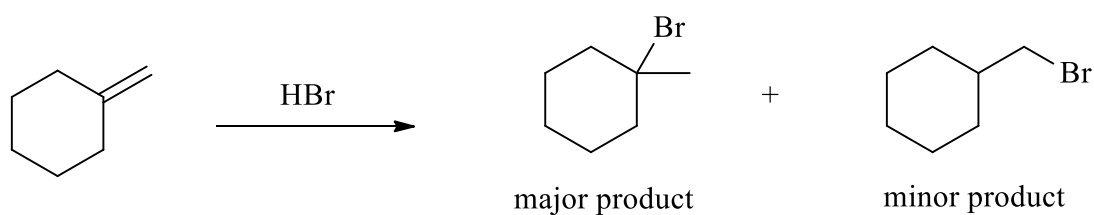
The molecule is still chiral as the molecule still contains a stereogenic centre.



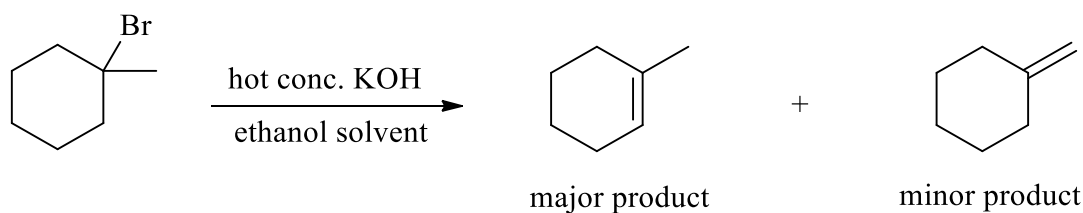
Ratio A : diastereomer is approximately 1 : 1.

The tertiary carbocation intermediate has trigonal planar geometry, so the attacking nucleophile (H_2O) is equally likely to attack from above or below the plane of the ring.

2013-N-11

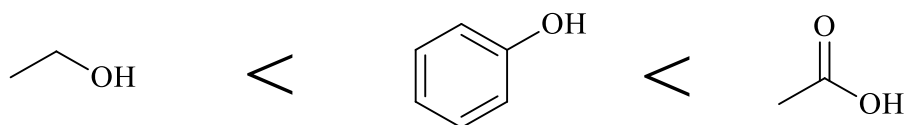
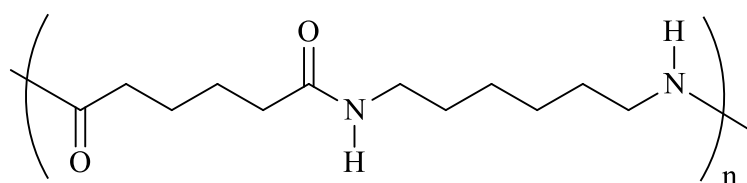


Electrophilic addition follows Markovnikov's rule. There are two possible intermediates, a primary and a tertiary carbocation. The tertiary is more stable so is formed preferentially.

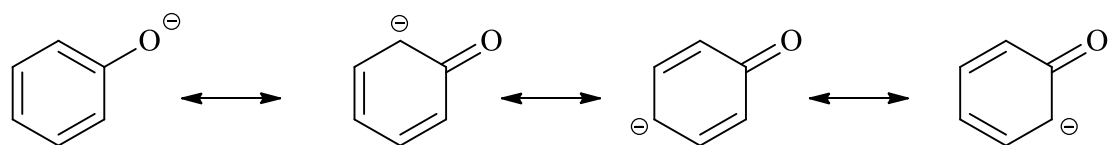


Base catalysed elimination of HBr follows Saytzev's rule – the more highly substituted product will predominate.

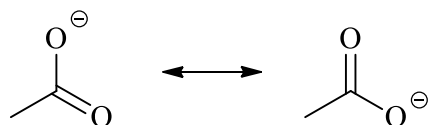
2013-N-12



Ethanol is the weakest acid as its conjugate base is not resonance stabilised. Phenol is a stronger acid as its conjugate base is resonance stabilised – the negative charge can be delocalised into the aromatic ring as shown below.

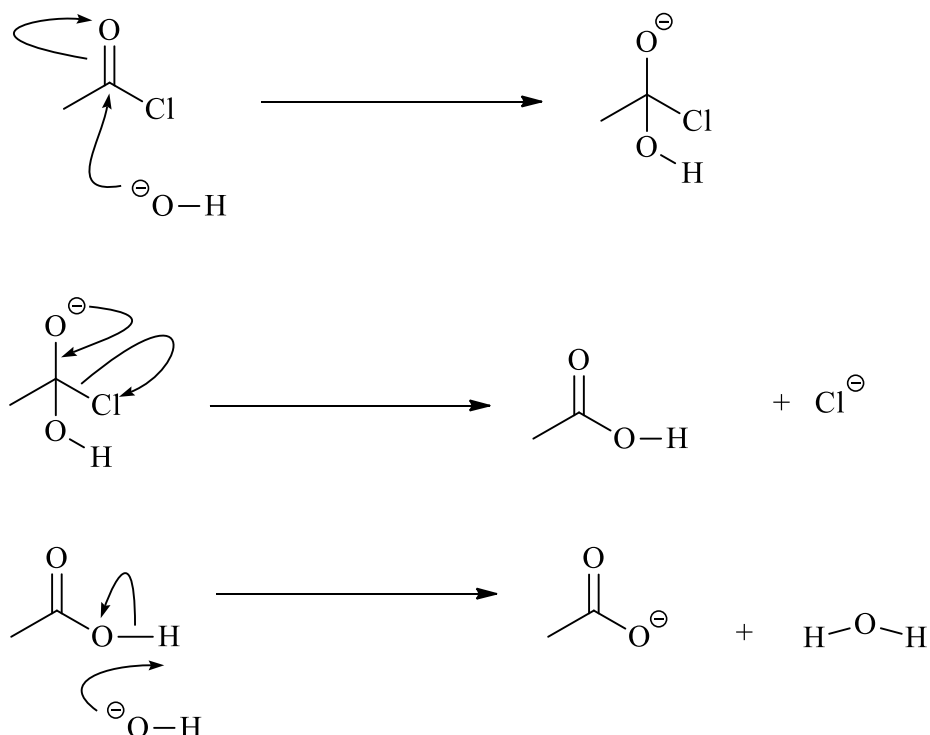


There is even greater resonance stabilisation for the acetate ion (the conjugate base of acetic acid), as the negative charge is delocalised onto the electronegative oxygen atoms (as opposed to the carbon atoms in the case of phenol).



2013-N-13

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2013-N-14

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Electrophilic addition of H^+ to the $\text{C}=\text{C}$ double bond gives 2 possible carbocations. Due to polarisation, the carbon of the carbonyl $\text{C}=\text{O}$ double bond has a partial positive charge. The H^+ electrophile will not attack that carbon (like charges repel), so the carbocation on the left in the scheme below is formed preferentially. This carbocation then leads to the acid chloride as the major product.

