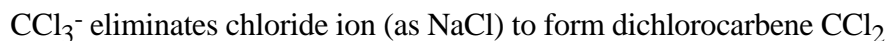
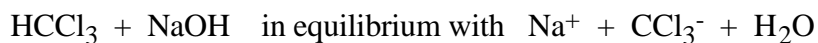


GTQ on Carbenes. (40 points, cyclopropane syntheses, stereochemistry, chirality)

(a) Write down the equations for the formation of **dichlorocarbene** from chloroform. (5 points)

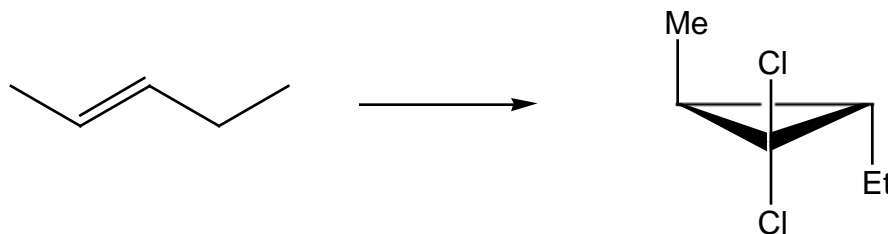


(b) The pK_a value of chloroform is about 25 and the proton can be removed by hydroxide or alkoxide. The C-H bond in chloroform is much more (more/less) acidic as compared to the C-H bonds in methane ($\text{pK}_a > 45$) because the three very electronegative Cl atoms withdraw (withdraw, donate) electron density and thereby stabilize the negative charge in the trichloromethyl anion. (3 p.)

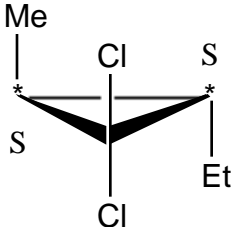
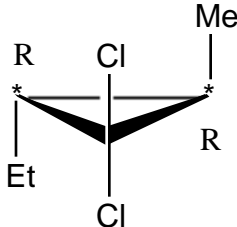
(c) The dichlorocarbene formation is carried out in **tertiary butanol** and this choice of solvent is critical. In water, for example, the dichlorocarbene would not be formed. Can you provide an explanation for this observation? What would happen to the CCl_3^- in water? (4 points)

Water would protonate the CCl_3^- anion and simple back reaction to chloroform occurs
The butanol is less likely to protonate (higher pK_a !) and carbene formation becomes competitive with the protonation.

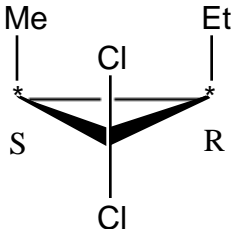
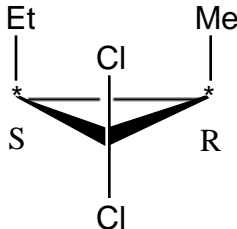
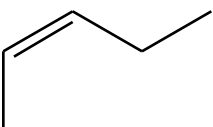
(d) The reaction of chloroform and *trans*-pentene-2 in the presence of tert.-BuOK in the solvent tert.-BuOH stereospecifically yields *trans* cyclopropane. Give the structures for the overall reaction. (4 p.)



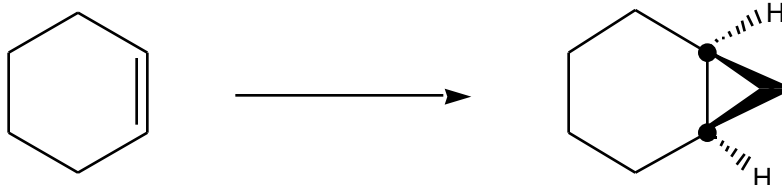
(e) On the left, redraw the cyclopropane product obtained in (d). Mark all asymmetric carbons in this cyclopropane with a star (*) and describe their absolute configurations using the R/S nomenclature. You now realize that the product is chiral! On the right, draw the mirror image of the molecule and indicate the absolute configurations of all of its asymmetric carbons. Finally, state whether the enantiomers are formed as a racemate or whether either of the enantiomers is formed preferentially. Explain your decision by considering what the difference is that leads to each of the enantiomers. (6 points)

<p>The cyclopropane made in (d):</p> 	<p>The mirror image:</p> 
<p>Racemate or not? Explain:</p> <p>Racemate! Of course! The product depends on whether the alkene is attacked from “top” or “bottom” and processes are equally likely!</p>	

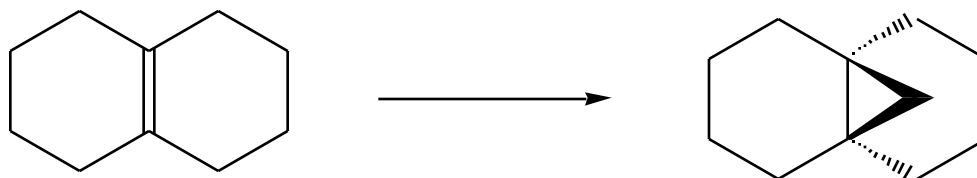
(f) Draw the structure of one cyclopropane that is **diastereoisomeric** in relation to the isomers discussed in part (e). Specify the absolute configuration of all asymmetric carbons of this diastereoisomer with the CIP nomenclature. On the right, draw the mirror image of the diastereoisomer and specify its absolute configuration. Finally, provide a synthesis that yields a racemate of these diastereoisomers. (Yes, understanding the question is part of the test!!) (8 points)

<p>The diastereoisomer:</p> 	<p>The mirror image of the diastereoisomer:</p> 
<p>The synthesis:</p> <p>From the cis alkene!</p> 	

(g) The Simmons-Smith reaction involves the formation of a “carbenoid” by reaction of diiodomethane with the so-called Zn - Cu couple. This carbenoid behaves like a true carbene in that it adds to C=C bonds. For the alkenes shown, complete the reactions and draw the products. The products are **polycyclic** molecules. Provide correct IUPAC names for the product molecules. (Help: Alkanes with 11 C-atoms are called “undecanes”.) (10 points)



The product: bicyclo[4.1.0]heptane



The product: tricyclo[4.4.1.0]undecane

Yes, you guessed it: We need one more number in the [] part!