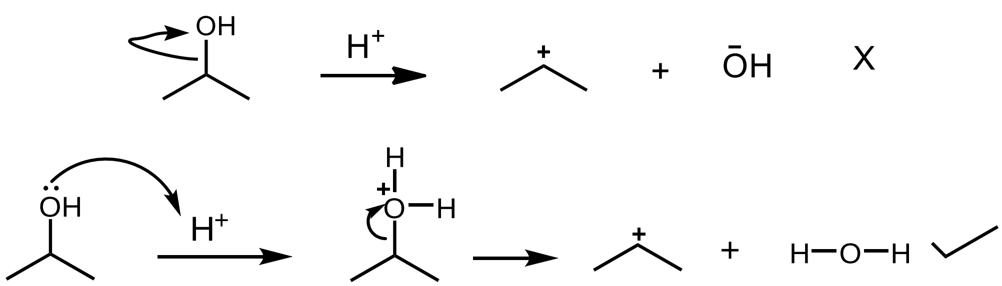
Key points to remember

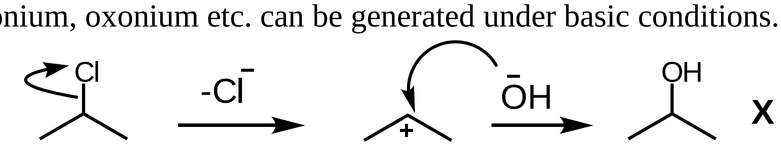
The curved arrow is drawn from the electron rich site to the electron poor site. The arrow points toward the electrophilic (electron poor) site when a bond is made. Electrophilic sites can be identified by the presence of a positive charge or a leaving group. Nucleophilic (electron rich) sites can generally be identified by the presence of a –ve charge, lone pairs or an atom attached to a metal. Since there are only two choices, if you have identified one then the other is evident.

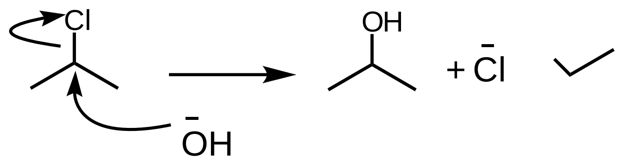
The curved arrow points towards the electronegative atom when a bond is broken. The arrow always originates from the bond (not the atom) and goes to the atom.

For ionic reactions, it is important to know whether the reaction is happening under acidic or basic conditions. Once the conditions are identified remember the following salient points when drawing the mechanism:
Strong bases like: ^{-}H, ^{-}OH, $^{-}OCH_3$ should not be generated under acidic conditions. Conjugate bases of strong acids like Br^{-}, HSO_4^{-} can exist under acidic conditions.

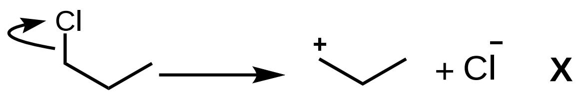


Carbocations should not be generated under basic conditions. You will learn about the exceptions when you will take higher level organic courses. Cations with complete octets such as ammonium, oxonium etc. can be generated under basic conditions.

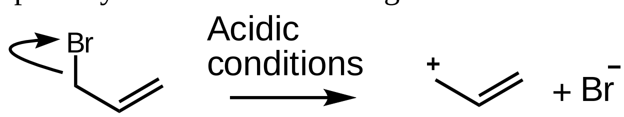




Non stabilized primary carbocations should not be generated under any conditions as they are very high in energy.

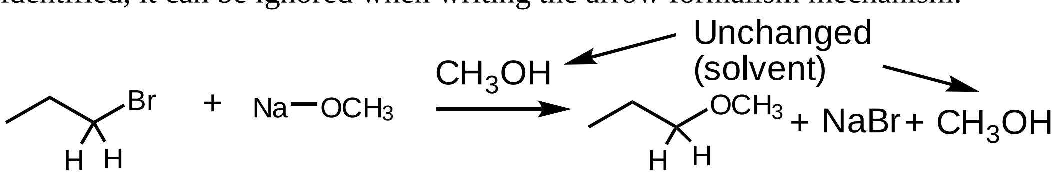


Resonance stabilized primary carbocations can be generated under acidic conditions.

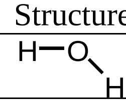
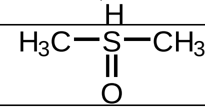
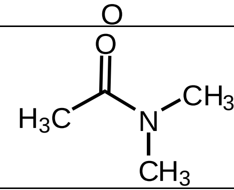
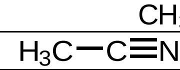
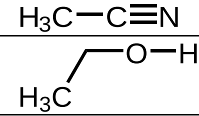
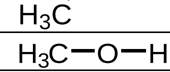


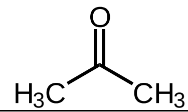
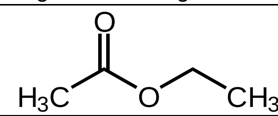
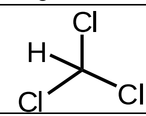
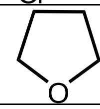
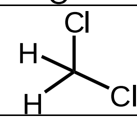
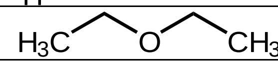
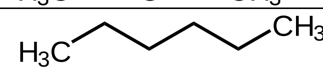
Initially, it may be confusing to draw a mechanism when solvents are written in the equation. Solvents mostly do not participate in the mechanism. When they do, they are commonly used in the protonation or deprotonation step of a mechanism. In this book these steps will be shown without the help of solvents. This is an acceptable practice.

Solvents can be identified after the balancing of the equation as they remain unchanged on both sides of the equation. They can be differentiated from catalysts because they do not carry the abbreviation cat. or mol% before them. Once the solvent has been identified, it can be ignored when writing the arrow formalism mechanism.



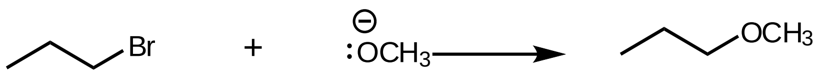
Some common solvents according to the descending order of polarity are mentioned below.

Abbreviation	Name	Structure
	Water	
DMSO	dimethylsulfoxide	
DMF	*N*, *N*-dimethylformamide	
	acetonitrile	
EtOH	ethanol	
MeOH	methanol	

	acetone	
EtOAC	ethyl acetate	
	Chloroform	
THF	tetrahydrofuran	
DCM	dichloromethane	
Ether	diethyl ether	
Hex	hexane	

Problem 1

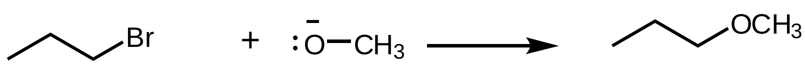
Consider the following transformation that is an example of Williamson ether synthesis.



The arrow formalism mechanism for this transformation can be drawn by keeping in mind the points mentioned in the previous section and by following the steps mentioned below.

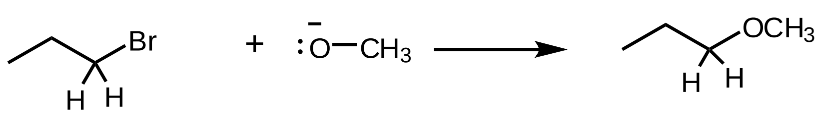
ANALYSIS

Draw all of the bonds at the reactive atoms in the starting materials



This step will keep analysis neat.

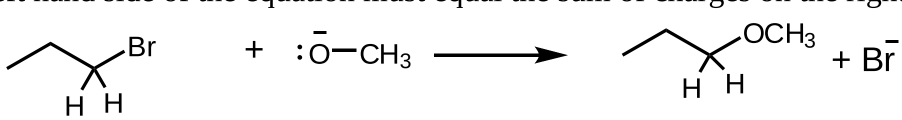
Draw all of the H-atoms at or near the reactive sites of the starting materials and the products



This will help avoid drawing too many bonds, keeping track of charges and numbering the atoms (see below).

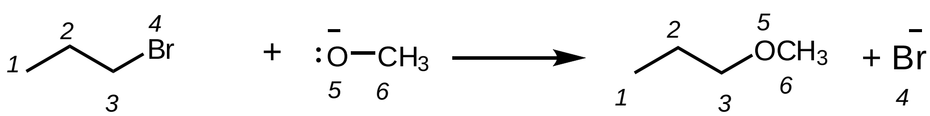
Balance the equation

Balance the atoms and the charges. When balancing the charges, the sum of charges on the left hand side of the equation must equal the sum of charges on the right.



Number the non-H atoms

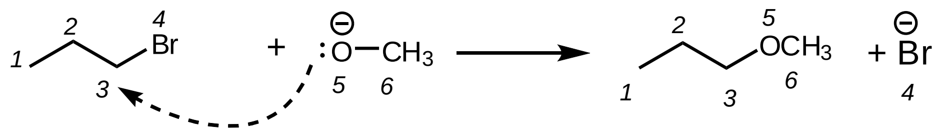
Number the non-H atoms in the starting materials. The order does not matter. Mark the corresponding atoms in the product(s) with the same numbers.



Identify the bonds made and broken

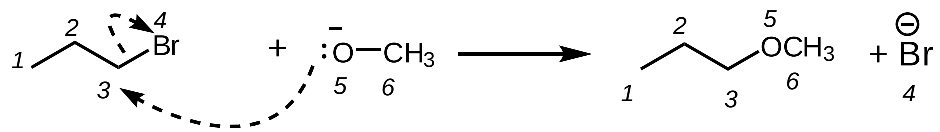
Write the bonds made, and draw a dotted line between the two atoms making sure that the arrow points to the electrophile. This dotted line will help you immensely in the drawing of the mechanism.

Bonds Made: 5-3



Identify the broken bonds. Draw another dotted line between the two atoms making sure that the arrow points to the electronegative atom.

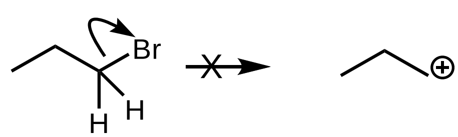
Bonds Broken: 3-4



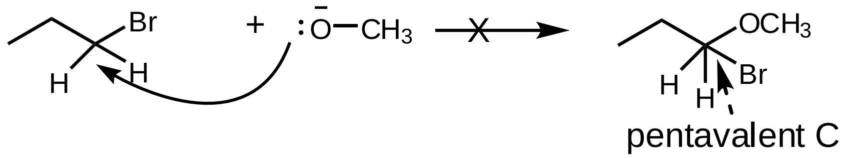
Identify the conditions:
Basic (do not generate strong acids)

Draw the Mechanism:
All arrows that will be used in this mechanism are already shown above with the dotted lines. This will be the case with all the problems that you will encounter in this book. Most arrows if not all will be visible in the analysis of all the problems.

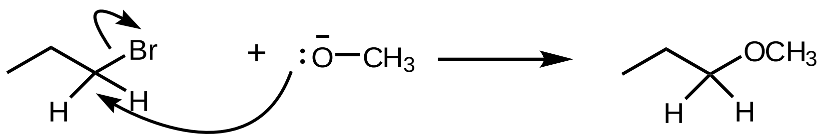
Initially it may be difficult to identify which arrow should be drawn first for any problem. Do the following: draw any one arrow and see what you will get. If the arrow produces an intermediate that cannot exist under the reaction conditions, then the arrow must be incorrect. Thus, for the above transformation, the top arrow will produce a carbocation. Carbocations should not be generated under basic conditions, thus this arrow must not be the first one.



Now try the second arrow and analyze the intermediate. In this particular case, it will generate a pentavalent carbon.



For this situation, draw the other arrow present on the reaction site as well. If there is no other arrow in the initial analysis, then this step must also be incorrect. However, in this particular case, the second arrow is present and can be drawn. Thus, the complete reaction mechanism is as follows:



How to tell when a step is complete?

1. Initially, it may be difficult to know when a step is complete. You will know when the step is complete when the minimum number of arrows will give an intermediate that can exist under the reaction conditions. So, for example, in the above case, when the first correct arrow was drawn it generated a pentavalent C. This indicated that the step was incomplete and needed the second arrow. The second arrow gave the product that can exist under the reaction conditions.

2. It is customary to write the organic products only. Thus, Br^- is not shown in the mechanism.