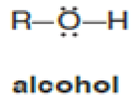
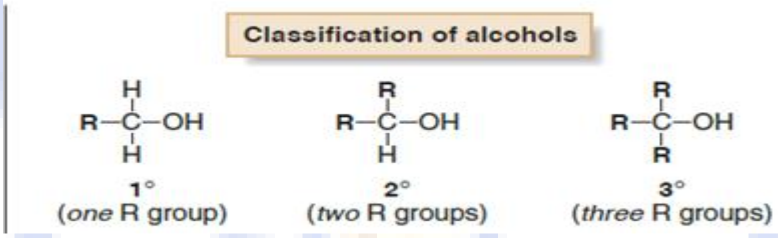
الكلية	كلية التربية للعلوم الصرفة
القسم	قسم الكيمياء
المادة باللغة الانجليزية	**Organic chemistry**
المادة باللغة العربية	الكيمياء العضوية
المرحلة الدراسية	المرحلة الثانية
اسم التدريسي	د. عمر جمال مهدي العسافي
عنوان المحاضرة باللغة الانجليزية	**Alcohols**
عنوان المحاضرة باللغة العربية	الكحولات
رقم المحاضرة	الثانية
المصادر والمراجع	***Organic Chemistry*** 6ed , William H. Brown, Christopher S. Foote, Brent L. Iverson, Eric V. Anslyn, Bruce M. Novak, 2012
	Organic Chemistry 3ed , Janice Gorzynski Smith, 2011
	Organic Chemistry" by Jonathan Clayden, Nick Greeves, and Stuart Warren

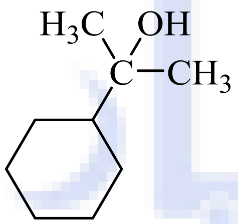
Alcohols is a functional group that contain carbon–oxygen σ bonds.

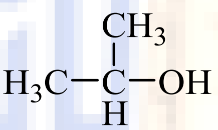


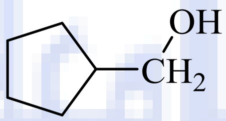
***Alcohols* contain a hydroxy group** (**OH** group) bonded to an *sp*3 hybridized carbon atom. Alcohols are classified as **primary (1°), secondary (2°),** or **tertiary (3°)** based on the number of carbon atoms bonded to the carbon with the OH group.



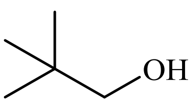
Problem:- Classify each alcohol as primary , secondary or tertiary:

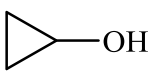
a) 

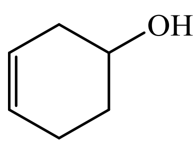
b) 

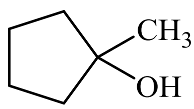
c) 

Problem:- Classify each alcohol as primary , secondary or tertiary:

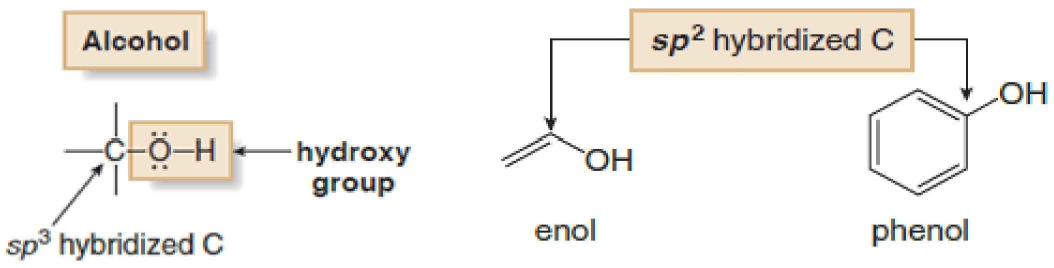
a. 

b. 

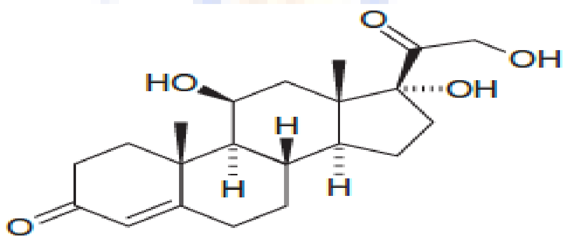
c. 

d. 

- ✓ Compounds having a hydroxy group on an *sp*2 hybridized carbon atom—**enols** and **phenols**— undergo different reactions than. **Enols** have an OH group on a carbon of a C – C double bond. **Phenols** have an OH group on a benzene ring.



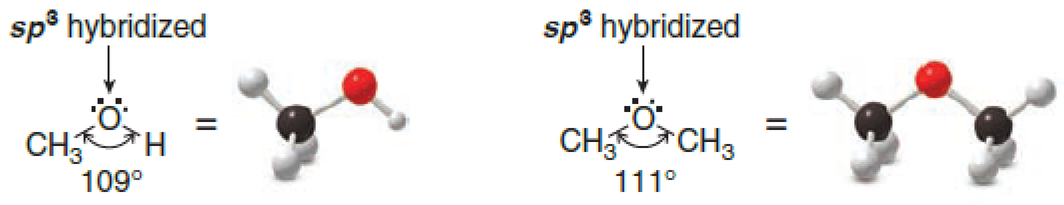
Problem :- Classify each OH group in cortisol as 1°, 2°, or 3°.



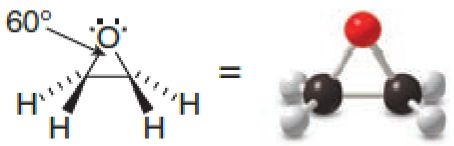
cortisol

2- Structure and Bonding

Alcohols, contain an oxygen atom surrounded by two atoms and two nonbonded electron pairs, making the O atom **tetrahedral** and ***sp***^{3} hybridized. Because only two of the four groups around O are atoms, alcohols and ethers have a **bent** shape like H_2O.



The bond angle around the O atom in an alcohol or ether is similar to the tetrahedral bond angle of 109.5°. In contrast, the C –O– C bond angle of an epoxide must be 60°, a considerable deviation from the tetrahedral bond angle. For this reason, epoxides have angle strain, making them much more reactive than other ethers.



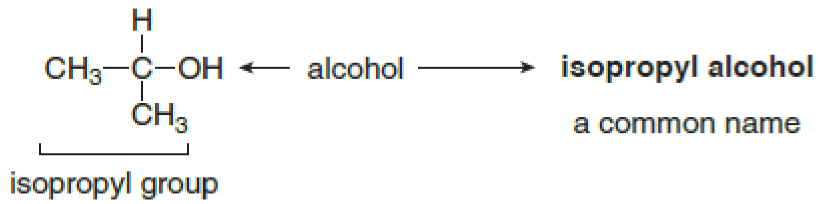
a strained, three-membered ring

Because oxygen is much more electronegative than carbon or hydrogen, the C – O and O – H bonds are all polar, with the O atom electron rich and the C and H atoms electron poor.

3. Naming Alcohols IUPAC system and Common Names

Common names are often used for simple alcohols. To assign a common name:

• Name all the carbon atoms of the molecule as a single **alkyl group.**
• Add the word **alcohol,** separating the words with a space.



In the IUPAC system, alcohols are identified by the suffix ***-ol***

Example Give the IUPAC name of the following alcohol:

$CH_3CH(CH_3)CH_2CH(OH)CH_2CH_3$

Step [1] Find the longest carbon chain containing the carbon bonded to the OH group.

$CH_3CH(CH_3)CH_2CH(OH)CH_2CH_3$

6 C's in the longest chain

6 C's → hexane → hexan*ol*

- Change the **-*e*** ending of the parent alkane to the suffix **-*ol*.**

Step [2] Number the carbon chain to give the OH group the lower number, and apply all other rules of nomenclature.

a. **Number** the chain.

$CH_3CH(CH_3)CH_2CH(OH)CH_2CH_3$

6 5 4 3 2 1

- Number the chain to put the OH group at C3, not C4.

3-hexanol

b. **Name** and **number** the substituents.

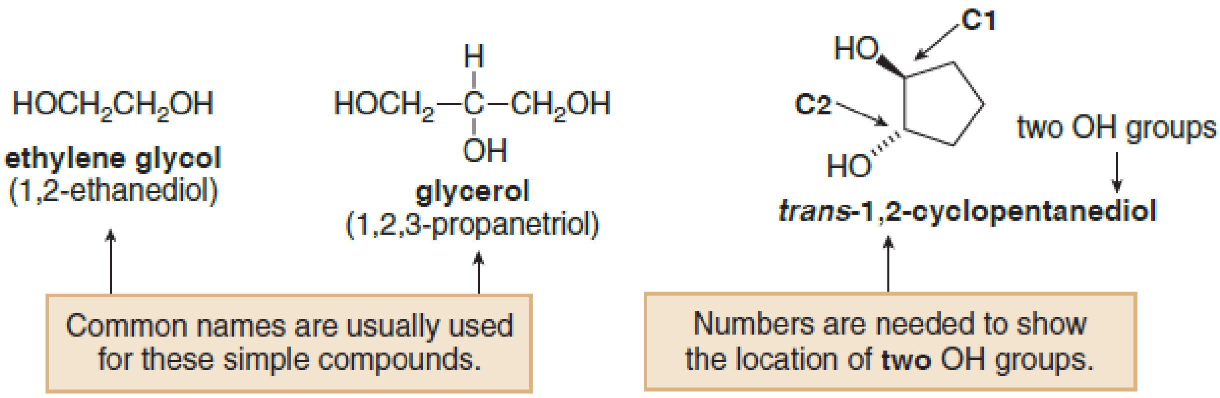
methyl at C5

$CH_3CH(CH_3)CH_2CH(OH)CH_2CH_3$

5 3

Answer: 5-methyl-3-hexanol

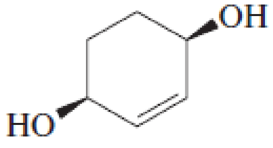
Compounds with two hydroxy groups are called **diols** (using the IUPAC system) or **glycols.** Compounds with three hydroxy groups are called **triols,** and so forth. To name a diol, for example, the suffi x ***-diol*** is added to the name of the parent alkane, and numbers are used in the prefix to indicate the location of the two OH groups.

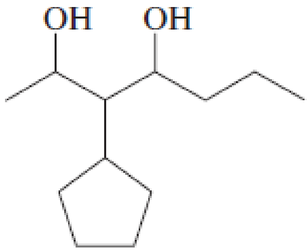


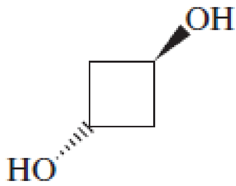
Problem:- Give a systematic (IUPAC) name for each diol.

(a) $CH_3CH(OH)(CH_2)_4CH(OH)C(CH_3)_3$

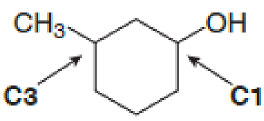
(b) $HO-(CH_2)_8-OH$

(c) 

(d) 

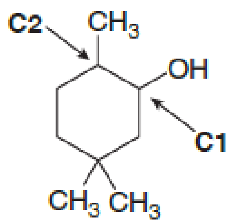
(e) 

When an OH group is bonded to a ring, the ring is numbered beginning with the OH group. Because the functional group is always at C1, the “1” is usually omitted from the name. The ring is then numbered in a clockwise or counterclockwise fashion to give the next substituent the lower number.



3-methylcyclohexanol

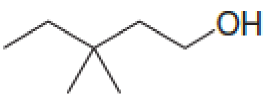
[The OH group is at C1; the second substituent (CH_3) gets the lower number.]

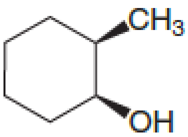


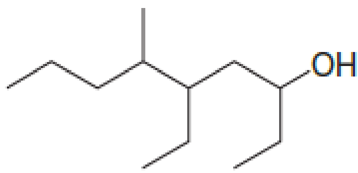
2,5,5-trimethylcyclohexanol

[The OH group is at C1; the second substituent (CH_3) gets the lower number.]

Problem : Give the IUPAC name for each compound.

a. 

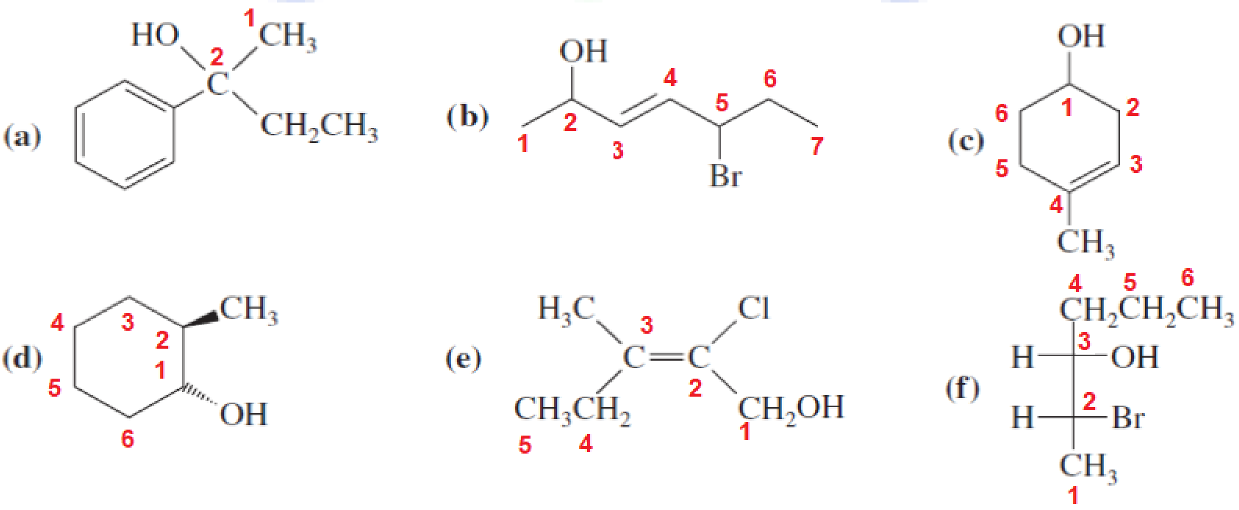
b. 

c. 

Problem : Give the structure corresponding to each name.

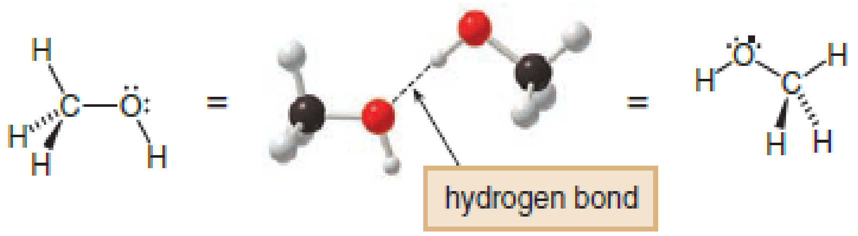
a. 7,7-dimethyl-4-octanol
b. 5-methyl-4-propyl-3-heptanol
c. 2-*tert*-butyl-3-methylcyclohexanol
d. *trans*-1,2-cyclohexanediol

Problem : Give the systematic (IUPAC) names of the following alcohols.



6. Physical Properties

Alcohols, ethers, and epoxides exhibit dipole–dipole interactions because they have a bent structure with two polar bonds. Alcohols are also capable of intermolecular hydrogen bonding, because they possess a hydrogen atom on an oxygen, making alcohols much more polar than ethers and epoxides.



Steric factors affect the extent of hydrogen bonding. Although all alcohols can hydrogen bond, increasing the number of R groups around the carbon atom bearing the OH group decreases the extent of hydrogen bonding. Thus, 3° alcohols are least able to hydrogen bond, whereas 1° alcohols are most able to.

← Increasing ability to hydrogen bond

$RCH_2–OH$	$R_2CH–OH$	$R_3C–OH$
1°	2°	3°

Increasing steric hindrance →

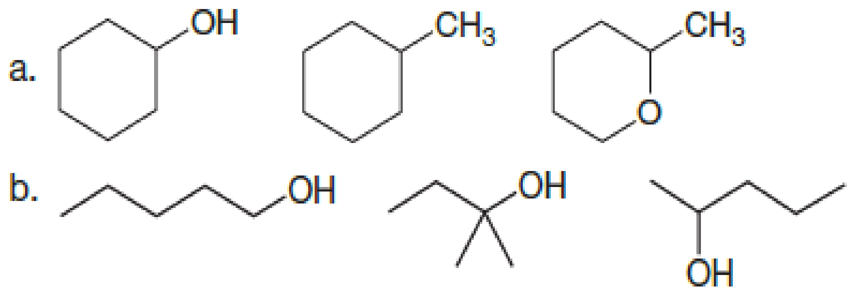
How these factors affect the physical properties of alcohols, ethers, and epoxides is summarized in Table

Table Physical Properties of Alcohols, Ethers, and Epoxides

Property	Observation
Boiling point (bp) and melting point (mp)	• For compounds of comparable molecular weight, the **stronger** the intermolecular forces, the **higher** the bp or mp. $CH_3CH_2CH_2CH_3$ VDW bp 0 °C; $CH_3OCH_2CH_3$ VDW, DD bp 11 °C; $CH_3CH_2CH_2OH$ VDW, DD, HB bp 97 °C Increasing boiling point → • Bp's **increase** as the extent of hydrogen bonding **increases.** $(CH_3)_3C–OH$ 3° bp 83 °C; $CH_3CH_2CH(OH)CH_3$ 2° bp 98 °C; $CH_3CH_2CH_2CH_2–OH$ 1° bp 118 °C Increasing ability to hydrogen bond → Increasing boiling point
Solubility	• Alcohols, ethers, and epoxides having ≤ 5 C's are H_2O soluble because they each have an oxygen atom capable of hydrogen bonding to H_2O • Alcohols, ethers, and epoxides having > 5 C's are H_2O insoluble because the nonpolar alkyl portion is too large to dissolve in H_2O. • Alcohols, ethers, and epoxides of any size are soluble in organic solvents.

Key: VDW = van der Waals forces; DD = dipole–dipole; HB = hydrogen bonding

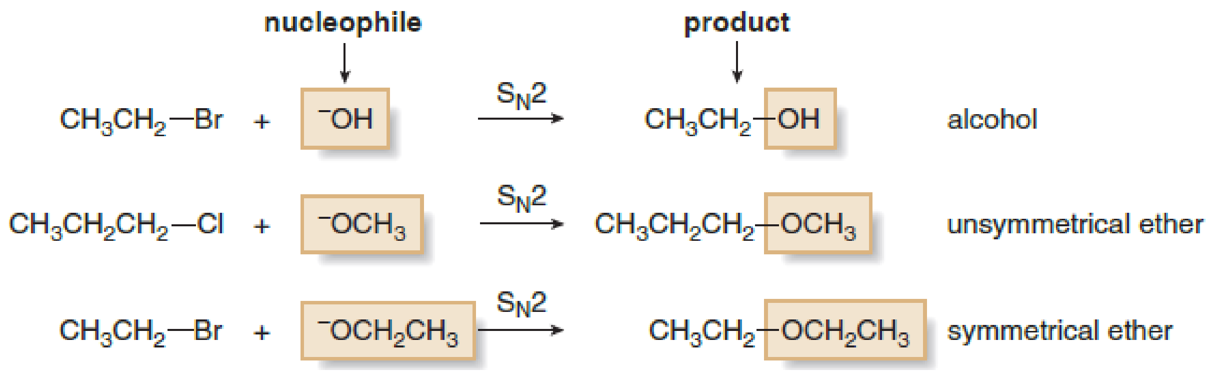
Problem Rank the following compounds in order of increasing boiling point.



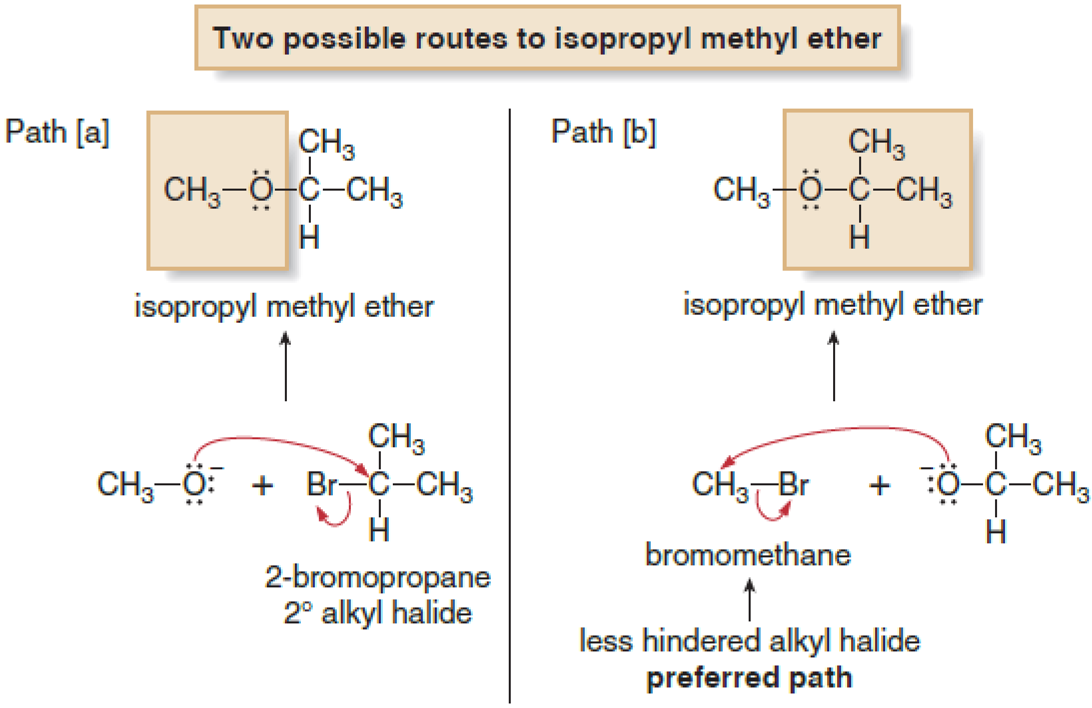
Problem Explain why dimethyl ether $(CH_3)_2O$ and ethanol (CH_3CH_2OH) are both water soluble, but the boiling point of ethanol (78 °C) is much higher than the boiling point of dimethyl ether (–24 °C).

7. Preparation of Alcohols, Ethers

Alcohols and ethers are both common products of nucleophilic substitution. They are synthesized from alkyl halides by SN_2 reactions using strong nucleophiles. As in all SN_2 reactions, highest yields of products are obtained with unhindered methyl and 1° alkyl halides.

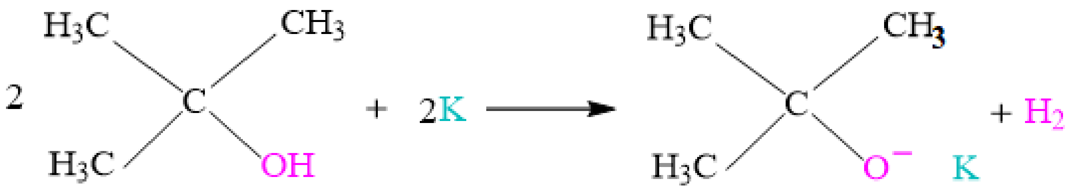


The preparation of ethers by this method is called the **Williamson ether synthesis,** and, although it was first reported in the 1800s, it is still the most general method to prepare an ether. Unsymmetrical ethers can be synthesized in two different ways, but often one path is preferred. For example, isopropyl methyl ether can be prepared from $CH_3O^–$ and 2-bromopropane (Path [a]), or from $(CH_3)_2CHO^–$ and bromomethane (Path [b]). Because the mechanism is SN2, **the preferred path uses the less sterically hindered halide,** CH_3Br—Path [b].



Generating Alkoxides from Alcohols

- **Alcohols are weak acids – requires a strong base to form an alkoxide such as NaH, sodium amide $NaNH_2$, and Grignard reagents (RMgX).**
- **Alkoxides are bases used as reagents in organic chemistry.**



tert-Butyl alcohol
(2-methyl-2-propanol

Potassium tert-butoxide
(potassium-2-methyl-
2-propanolate

$$CH_3OH + NaH \longrightarrow CH_3O^- \; Na^+ + H_2$$

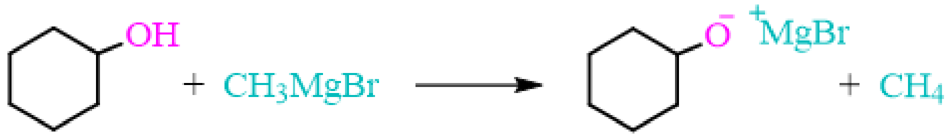
Methanol

Sodium methoxide
(sodium methanolate)

$$CH_3CH_2OH + NaNH_2 \longrightarrow CH_3CH_2O^- Na^+ + NH_3$$

Ethanol

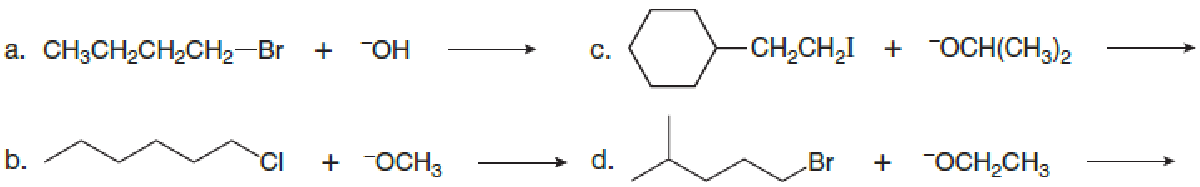
Sodium ethoxide
(sodium ethanolate)



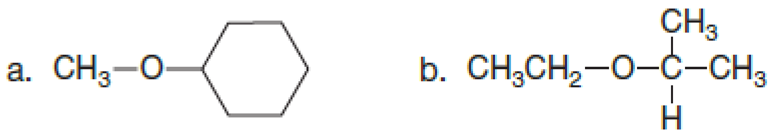
Cyclohexanol

Bromomagnesium
cyclohexanolate

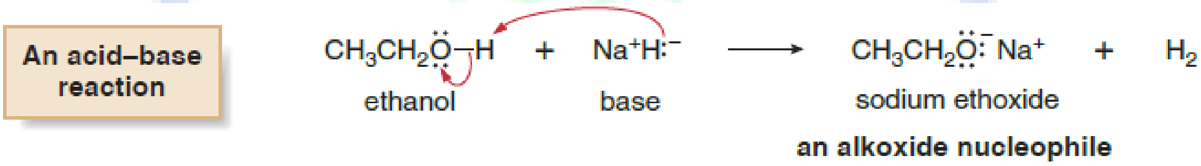
Problem Draw the organic product of each reaction and classify the product as an alcohol, symmetrical ether, or unsymmetrical ether.



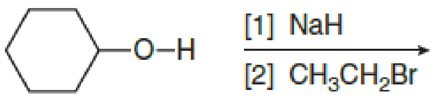
Problem: Draw two different routes to each ether and state which route, if any, is preferred.



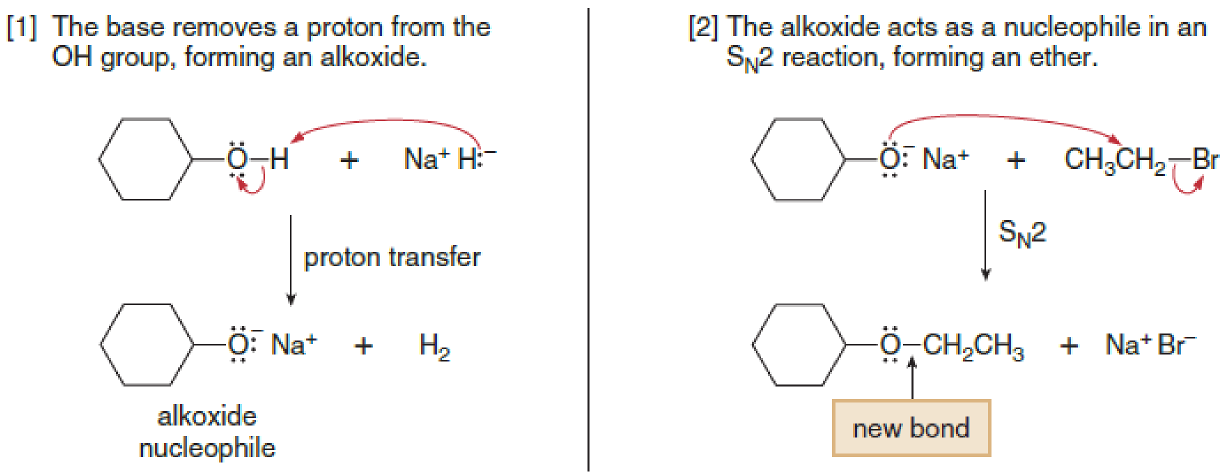
But others are prepared from alcohols by a Brønsted–Lowry acid base reaction. For example, sodium ethoxide (NaOCH2CH3) is prepared by treating ethanol with NaH.



Problem Draw the product of the following two-step reaction sequence.

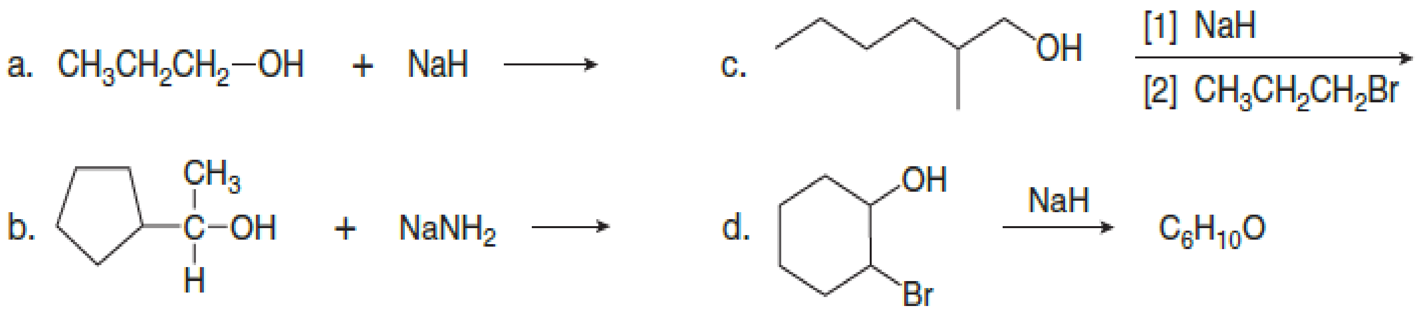


Solution



- This two-step sequence converts an alcohol to an ether.

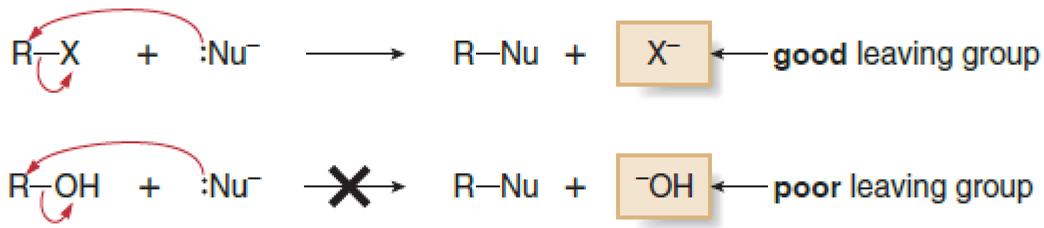
Problem Draw the products of each reaction.



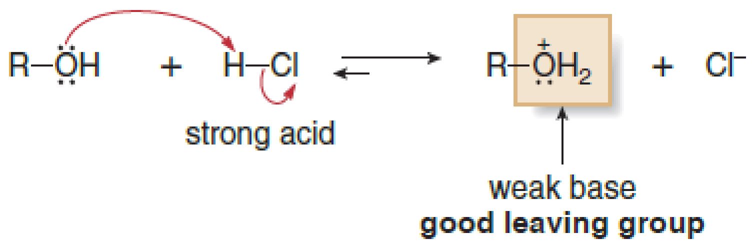
8. Reactions of Alcohols

Unlike many families of molecules, the reactions of alcohols do not fit neatly into a single reaction class. Alcohols are also key starting materials in oxidation reactions, and their polar O– H bond makes them more acidic than many other organic compounds.

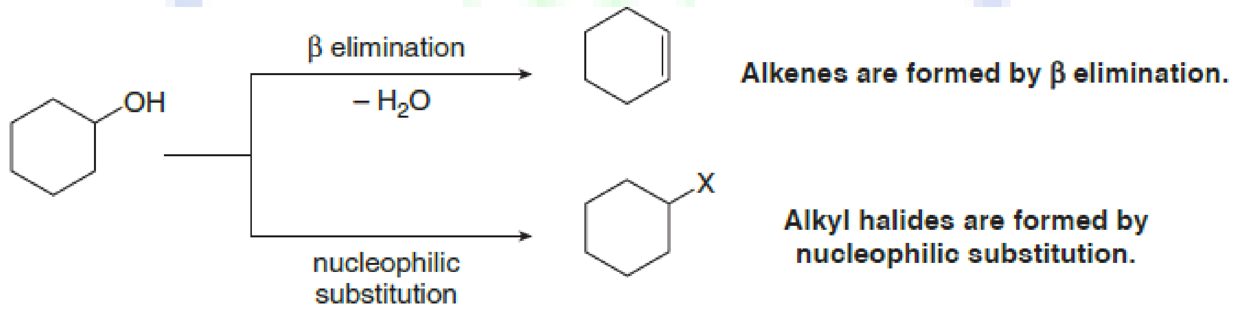
Alcohols are similar to alkyl halides in that both contain an electronegative element bonded to an sp3 hybridized carbon atom. Alkyl halides contain a good leaving group (X–), however, whereas alcohols do not. Nucleophilic substitution with ROH as starting material would displace –OH, a strong base and therefore a poor leaving group.



For an alcohol to undergo a nucleophilic substitution or elimination reaction, the OH group must be converted into a better leaving group. This can be done by reaction with acid. Treatment of an alcohol with a strong acid like HCl or H2SO4 protonates the O atom via an acid–base reaction. This transforms the –OH leaving group into H2O, a weak base and therefore a good leaving group.

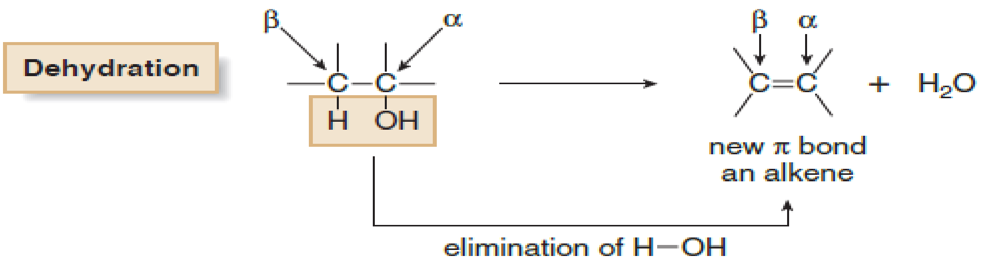


If the OH group of an alcohol is made into a good leaving group, alcohols can undergo β elimination and nucleophilic substitution.

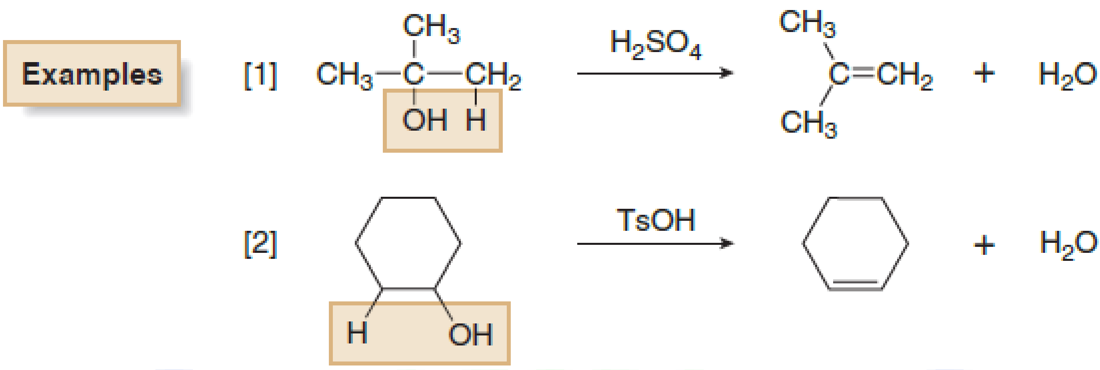


Dehydration of Alcohols to Alkenes

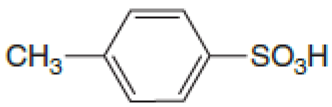
The dehydrohalogenation of alkyl halides, is one way to introduce a π bond into a molecule. Another way is to eliminate water from an alcohol in a dehydration reaction. Dehydration, like dehydrohalogenation, is a β elimination reaction in which the elements of OH and H are removed from the α and β carbon atoms, respectively.



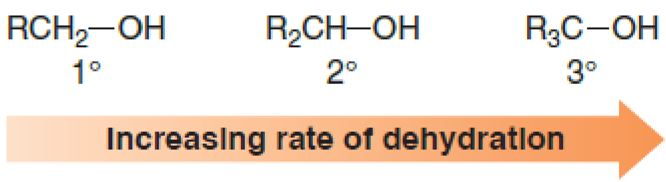
Dehydration is typically carried out using H_2SO_4 and other strong acids, or phosphorus oxychloride ($POCl_3$) in the presence of an amine base.



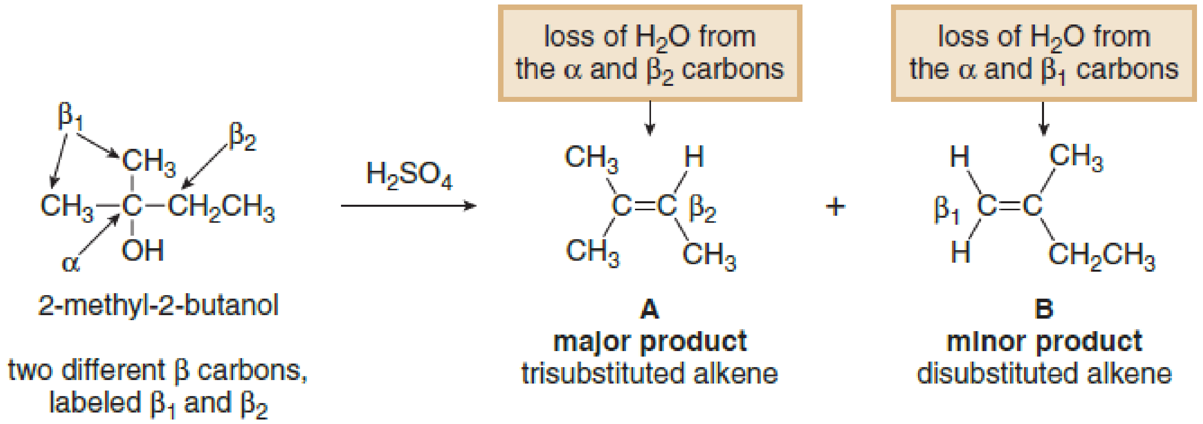
p-toluenesulfonic acid is a strong organic acid (pK_a = −7).



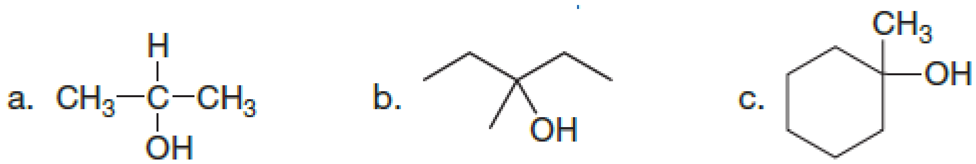
p-toluenesulfonic acid
TsOH



When an alcohol has two or three different β carbons, dehydration is regioselective and follows the Zaitsev rule. The more substituted alkene is the major product when a mixture of constitutional isomers is possible. For example, elimination of H and OH from 2-methyl-2-butanol yields two constitutional isomers: the trisubstituted alkene A as major product and the disubstituted alkene B as minor product.

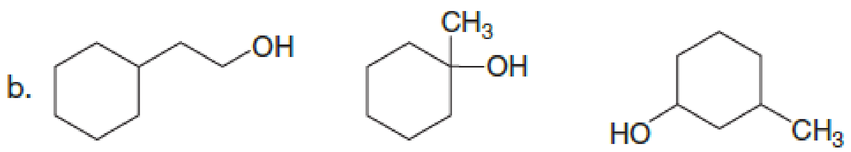


Problem Draw the products formed when each alcohol undergoes dehydration with TsOH, and label the major product when a mixture results.



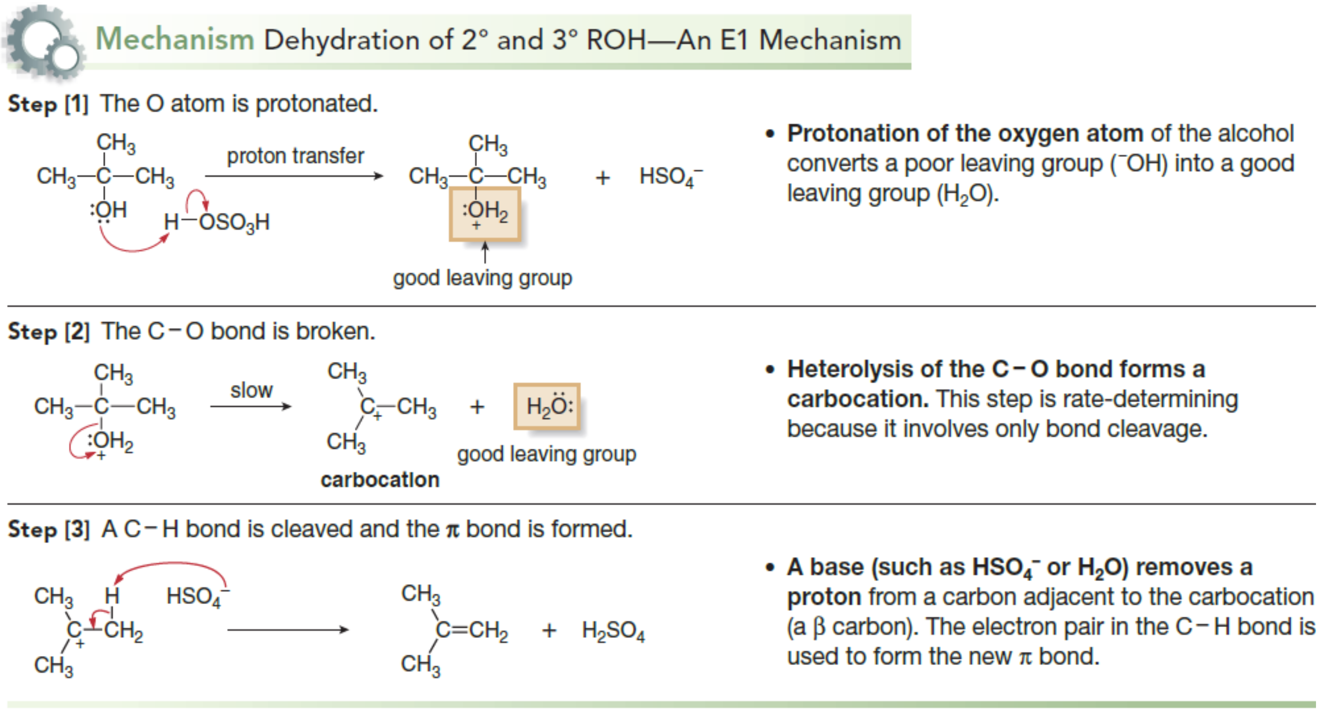
Problem Rank the alcohols in each group in order of increasing reactivity when dehydrated with H2SO4.

a. $(CH_3)_2C(OH)CH_2CH_2CH_3$ $(CH_3)_2CHCH_2CH_2CH_2OH$ $(CH_3)_2CHCH_2CH(OH)CH_3$

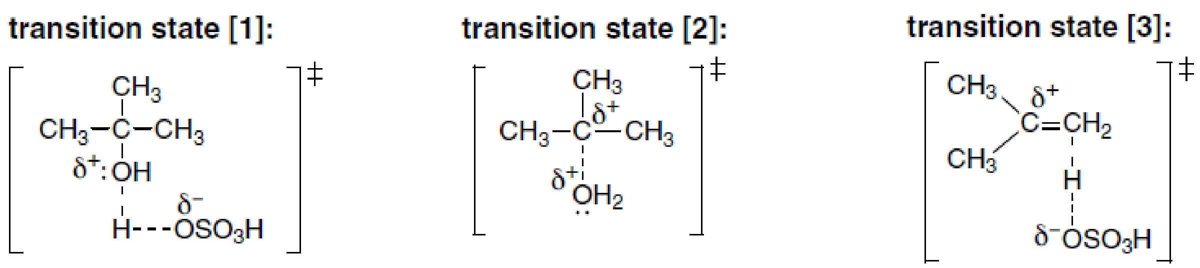


The E1 Mechanism for the Dehydration of 2° and 3° Alcohols

The mechanism of dehydration depends on the structure of the alcohol: **2° and 3° alcohols react by an E1 mechanism, whereas 1° alcohols react by an E2 mechanism.** Regardless of the type of alcohol, however, strong acid is *always* needed to protonate the O atom to form a good leaving group. The E1 dehydration of 2° and 3° alcohols is illustrated with $(CH_3)_3COH$ (a 3° alcohol) as starting material to form $(CH_3)_2C—CH_2$ as product (Mechanism). The mechanism consists of **three steps.**



Problem Draw the structure of each transition state in the three-step mechanism for the reaction, $(CH_3)_3COH + H_2SO_4 \rightarrow (CH_3)_2C{=}CH_2 + H_2O$.

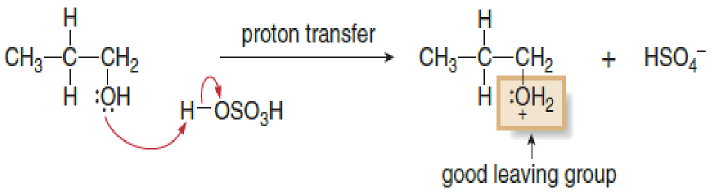


The E2 Mechanism for the Dehydration of 1° Alcohols

Because 1° carbocations are highly unstable, the dehydration of 1° alcohols cannot occur by an E1 mechanism involving a carbocation intermediate. With 1° alcohols, therefore, dehydration follows an E2 mechanism. This two-step process for the conversion of $CH_3CH_2CH_2OH$ (a 1o alcohol) to $CH_3CH—CH_2$ with H_2SO_4 as acid catalyst is shown in Mechanism.

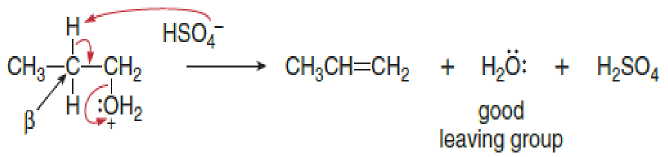
Mechanism Dehydration of a 1° ROH—An E2 Mechanism

Step [1] The O atom is protonated.



- **Protonation of the oxygen atom** of the alcohol converts a poor leaving group (^{-}OH) into a good leaving group (H_2O).

Step [2] The C–H and C–O bonds are broken and the π bond is formed.

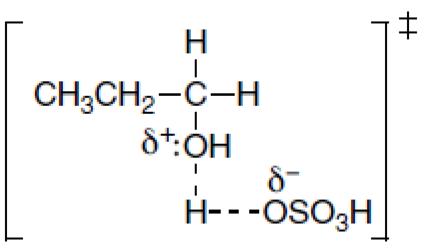


- **Two bonds are broken and two bonds are formed in a single step:** the base (HSO_4^- or H_2O) removes a proton from the β carbon; the electron pair in the β C–H bond forms the new π bond; the leaving group (H_2O) comes off with the electron pair in the C–O bond.

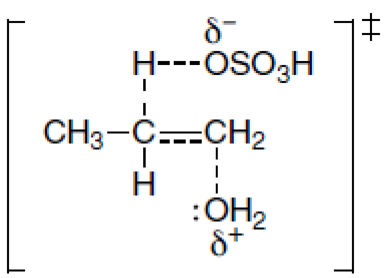
Problem Draw the structure of each transition state in the two-step mechanism for the reaction,

$$CH_3CH_2CH_2OH + H_2SO_4 \rightarrow CH_3CH{=}CH_2 + H_2O.$$

transition state [1]:

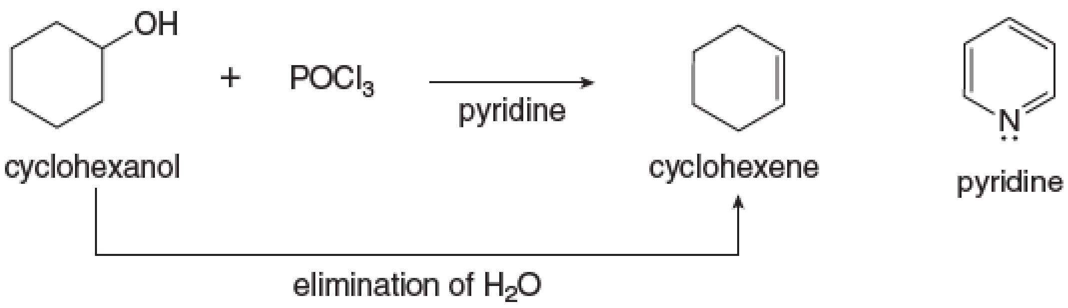


transition state [2]:



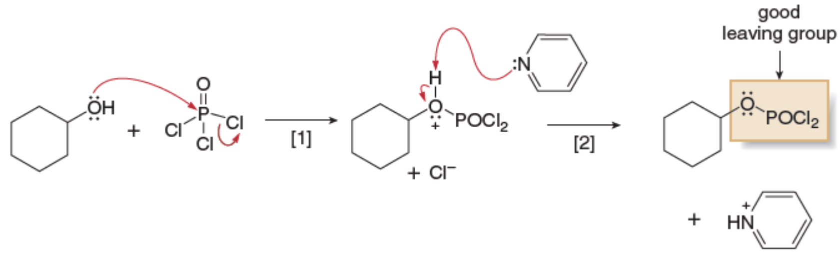
Dehydration Using $POCl_3$ and Pyridine

Because some organic compounds decompose in the presence of strong acid, other methods that avoid strong acid have been developed to convert alcohols to alkenes. A common method uses phosphorus oxychloride ($POCl_3$) and pyridine (an amine base) in place of H_2SO_4 or TsOH. For example, the treatment of cyclohexanol with POCl3 and pyridine forms cyclohexene in good yield.



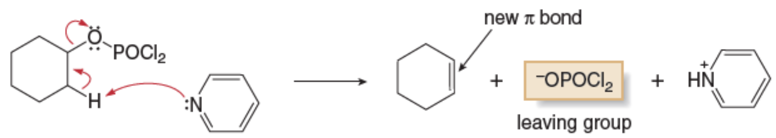
Mechanism Dehydration Using $POCl_3$ + Pyridine—An E2 Mechanism

Steps [1] and [2] Conversion of OH to a good leaving group



- A two-step process converts an OH group into $OPOCl_2$, **a good leaving group:** reaction of the OH group with $POCl_3$ followed by removal of a proton.

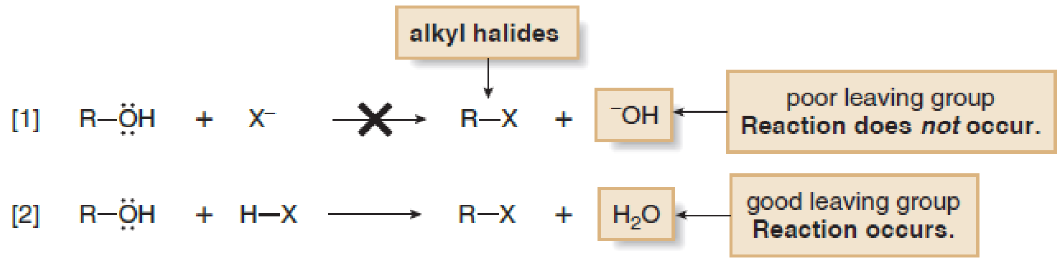
Step [3] The C–H and C–O bonds are broken and the π bond is formed.



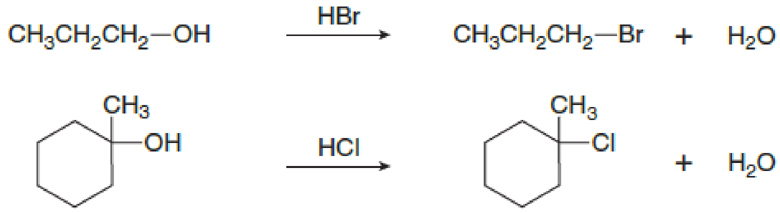
- **Two bonds are broken and two bonds are formed in a single step:** the base (pyridine) removes a proton from the β carbon; the electron pair in the β C–H bond forms the new π bond; the leaving group ($^{-}OPOCl_2$) comes off with the electron pair from the C–O bond.

Conversion of Alcohols to Alkyl Halides with HX

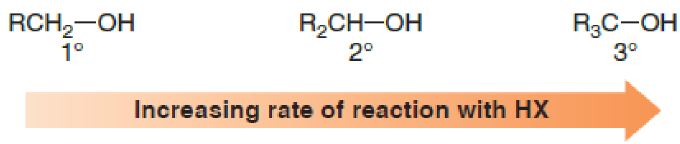
Alcohols undergo nucleophilic substitution reactions only if the OH group is converted into a better leaving group before nucleophilic attack. Thus, substitution does *not* occur when an alcohol is treated with X– because –OH is a poor leaving group (Reaction [1]), but substitution *does* occur on treatment of an alcohol with HX because H_2O is now the leaving group (Reaction [2]).



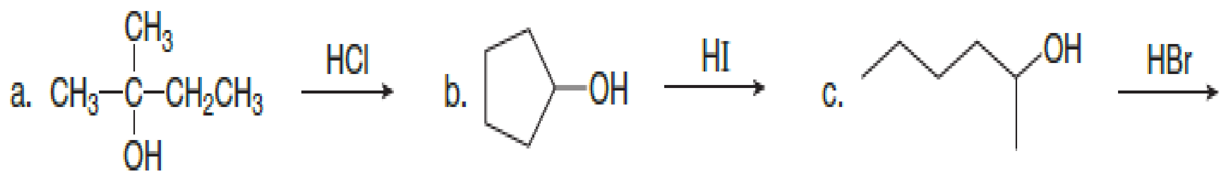
The reaction of alcohols with HX (X = Cl, Br, I) is a general method to prepare 1°, 2°, and 3° alkyl halides.



More substituted alcohols usually react more rapidly with HX:

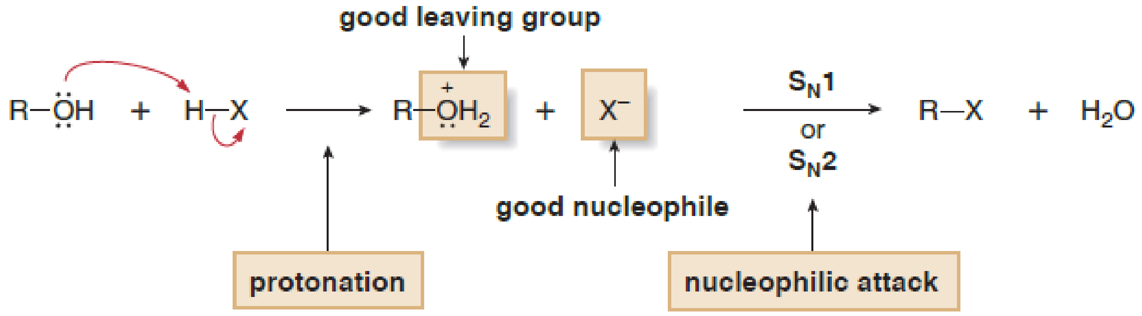


Problem Draw the products of each reaction.



Two Mechanisms for the Reaction of ROH with HX

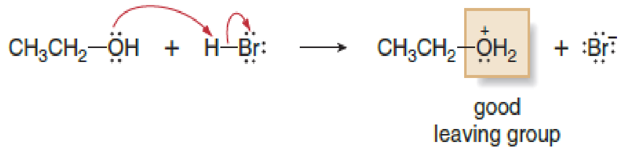
How does the reaction of ROH with HX occur? Acid–base reactions are very fast, so the strong acid HX protonates the OH group of the alcohol, forming a **good leaving group** (H_2O) and a **good nucleophile** (the conjugate base, X–). Both components are needed for nucleophilic substitution. The mechanism of substitution of X– for H_2O then depends on the structure of the R group.



- Methyl and 1° ROH form RX by an S_N2 mechanism.
- Secondary (2°) and 3° ROH form RX by an S_N1 mechanism.

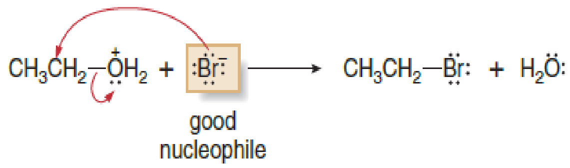
Mechanism Reaction of a 1° ROH with HX—An S_N2 Mechanism

Step [1] The O atom is protonated.



- **Protonation of the OH group** forms a good leaving group (H_2O).

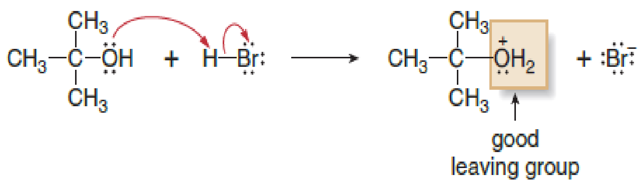
Step [2] The C–O bond is broken as the C–Br bond is formed.



- **Nucleophilic attack of Br^- and loss of the leaving group** occur in a single step.

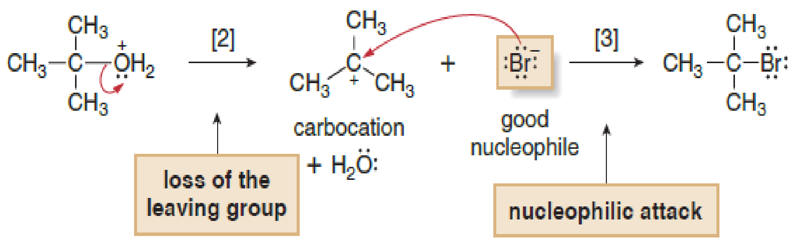
Mechanism Reaction of 2° and 3° ROH with HX—An S_N1 Mechanism

Step [1] The O atom is protonated.



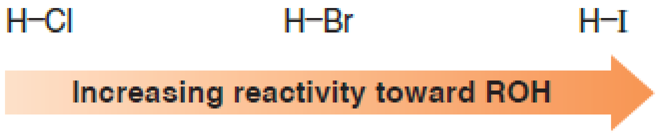
- **Protonation of the OH group** forms a good leaving group (H_2O).

Steps [2] and [3] The C–O bond is broken, and then the C–Br bond is formed.

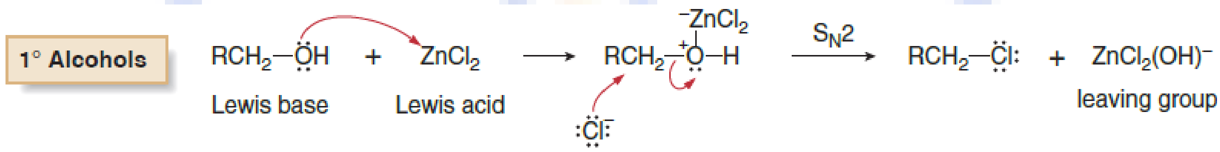


- Loss of the leaving group in Step [2] forms a **carbocation,** which reacts with the nucleophile (Br^-) in Step [3] to form the substitution product.

The reactivity of hydrogen halides increases with increasing acidity:



Because Cl– is a poorer nucleophile than Br– or I–, the reaction of 1° alcohols with HCl occurs only when an additional Lewis acid catalyst, usually **ZnCl2,** is added. ZnCl2 complexes with the O atom of the alcohol in a Lewis acid–base reaction, making an especially good leaving group and facilitating the SN2 reaction.



Conversion of Alcohols to Alkyl Halides with $SOCl_2$ and PBr_3

Primary (1°) and 2° alcohols can be converted to alkyl halides using $SOCl_2$ and PBr_3.

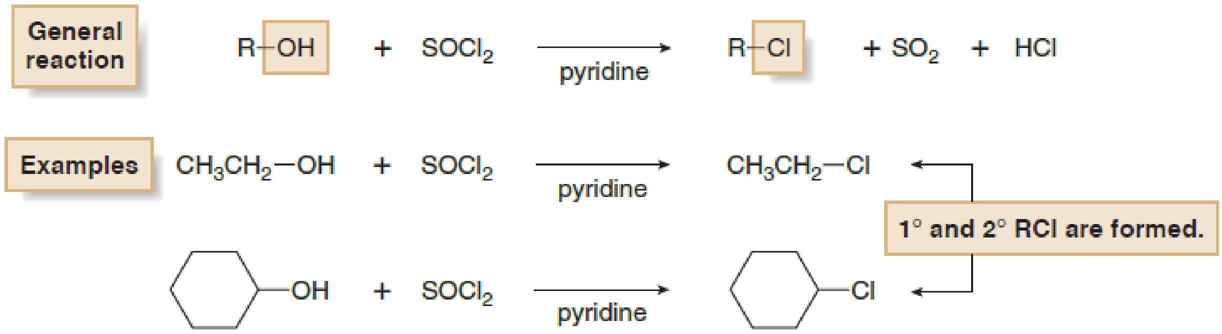
• **$SOCl_2$ (thionyl chloride) converts alcohols into alkyl chlorides.**

• **PBr_3 (phosphorus tribromide) converts alcohols into alkyl bromides.**

Both reagents convert –OH into a good leaving group *in situ*—that is, directly in the reaction mixture—as well as provide the **nucleophile,** either Cl– or Br–, to displace the leaving group.

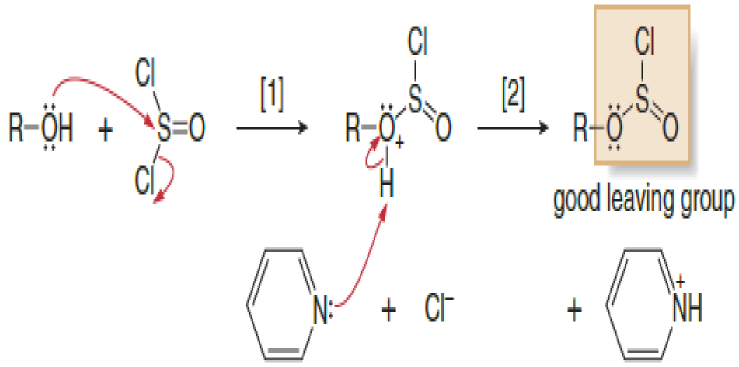
Reaction of ROH with SOCl2

The treatment of a 1° or 2° alcohol with thionyl chloride, $SOCl_2$, and pyridine forms an alkyl chloride, with SO2 and HCl as by-products.



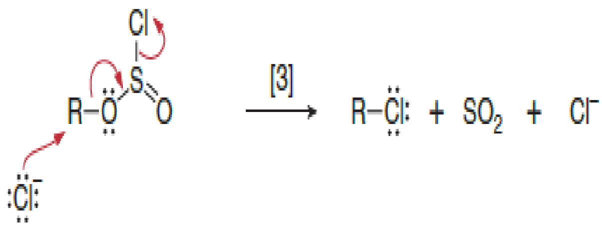
Mechanism Reaction of ROH with $SOCl_2$ + Pyridine—An S_N2 Mechanism

Steps [1] and [2] The OH group is converted into a good leaving group.



- Reaction of the alcohol with $SOCl_2$ forms an intermediate that loses a proton by reaction with pyridine in Step [2]. This two-step process converts the OH group into OSOCl, a **good leaving group,** and also generates the **nucleophile (Cl^-)** needed for Step [3].

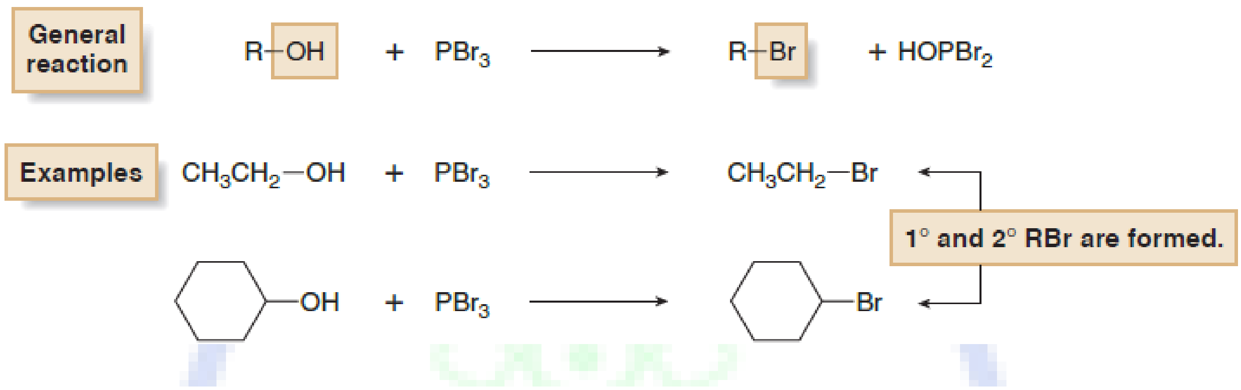
Step [3] The C–O bond is broken as the C–Cl bond is formed.



- **Nucleophilic attack of Cl^- and loss of the leaving group ($SO_2 + Cl^-$) occur in a single step.**

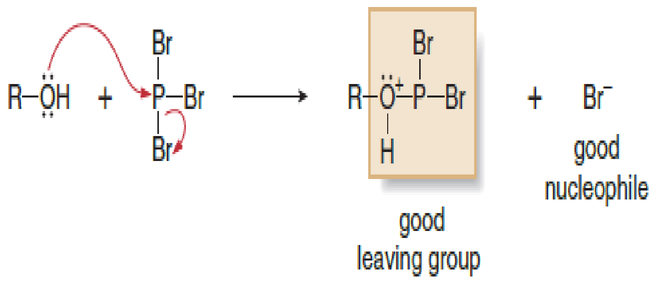
Reaction of ROH with PBr_3

In a similar fashion, the treatment of a 1° or 2° alcohol with phosphorus tribromide, PBr3, forms an alkyl bromide.



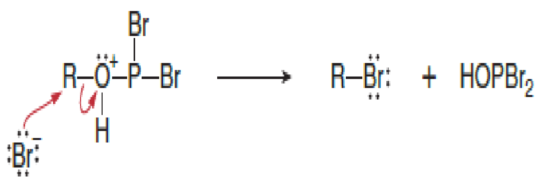
Mechanism Reaction of ROH with PBr_3—An S_N2 Mechanism

Step [1] The OH group is converted into a good leaving group.



- Reaction of the alcohol with PBr_3 converts the OH group into a **better leaving group,** and also generates the **nucleophile (Br^-)** needed for Step [2].

Step [2] The C–O bond is broken as the C–Br bond is formed.



- **Nucleophilic attack of Br^- and loss of the leaving group ($HOPBr_2$)** occur in a single step.

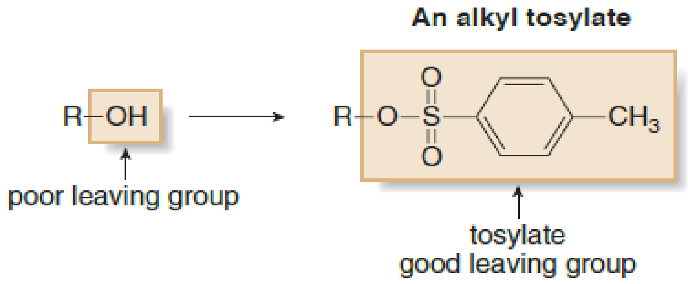
Summary of Methods for ROH → RX

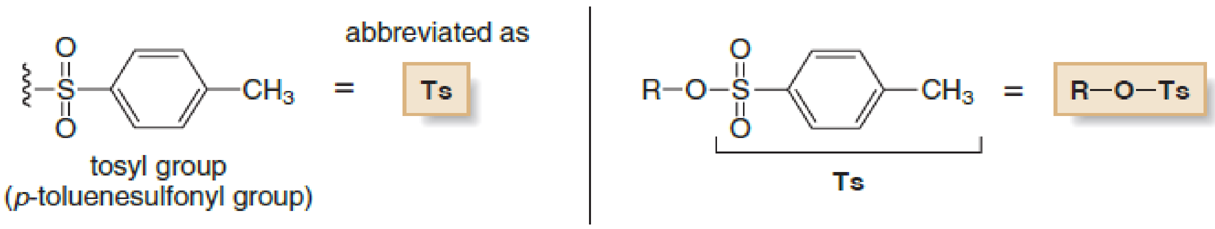
Overall reaction	Reagent	Comment
ROH → RCl	HCl	• Useful for all ROH • An S_N1 mechanism for 2° and 3° ROH; an S_N2 mechanism for CH_3OH and 1° ROH
	$SOCl_2$	• Best for CH_3OH, and 1° and 2° ROH • An S_N2 mechanism
ROH → RBr	HBr	• Useful for all ROH • An S_N1 mechanism for 2° and 3° ROH; an S_N2 mechanism for CH_3OH and 1° ROH
	PBr_3	• Best for CH_3OH, and 1° and 2° ROH • An S_N2 mechanism
ROH → RI	HI	• Useful for all ROH • An S_N1 mechanism for 2° and 3° ROH; an S_N2 mechanism for CH_3OH and 1° ROH

Tosylate—Another Good Leaving Group

We have now learned two methods to convert the OH group of an alcohol to a better leaving group: treatment with strong acids , and conversion to an alkyl halide , Alcohols can also be converted to alkyl tosylates**.**

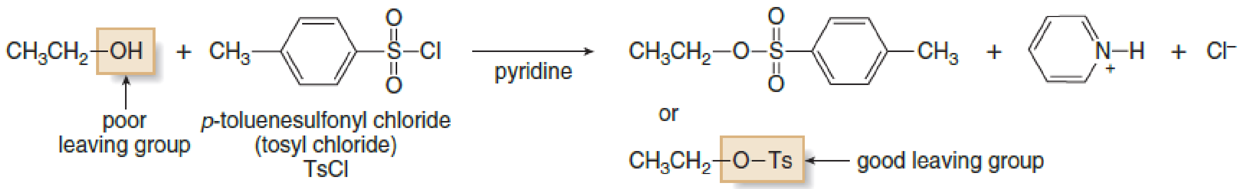
An **alkyl tosylate** is composed of two parts: the **alkyl group R,** derived from an alcohol; and the **tosylate** (short for ***p*****-toluenesulfonate**), which is a good leaving group. A tosyl group, CH3C6H4SO2 – , is abbreviated as **Ts,** so an alkyl tosylate becomes **ROTs.**

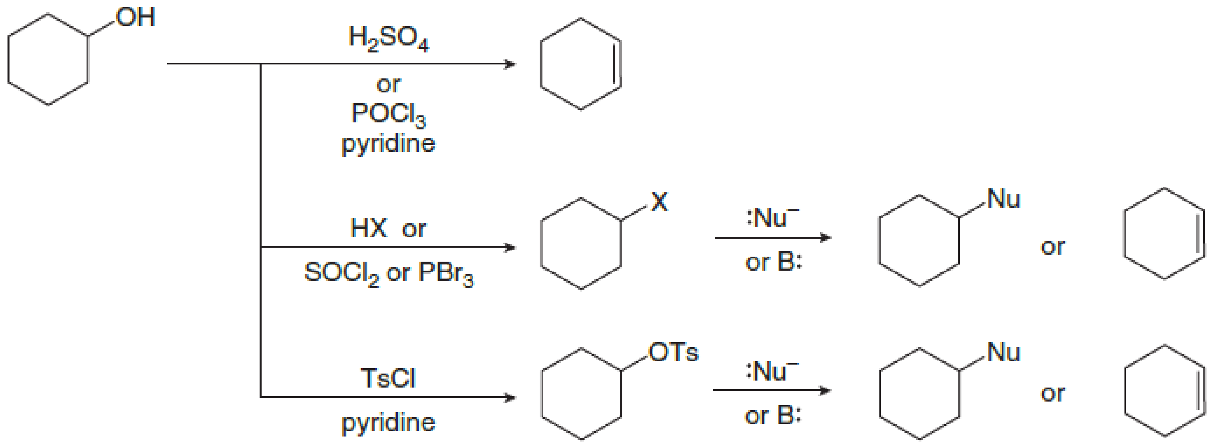




Conversion of Alcohols to Alkyl Tosylates

Alcohols are converted to alkyl tosylates by treatment with p-toluenesulfonyl chloride (TsCl) in the presence of pyridine. This overall process converts a poor leaving group (–OH) into a good one (–OTs). A tosylate is a good leaving group because its conjugate acid, p-toluenesulfonic acid (CH3C6H4SO3H, TsOH), is a strong acid (pKa = –7).





Problem Draw the product formed when $(CH_3)_2CHOH$ is treated with each reagent.

a. $SOCl_2$, pyridine
b. TsCl, pyridine
c. H_2SO_4
d. HBr
e. PBr_3, then NaCN
f. $POCl_3$, pyridine