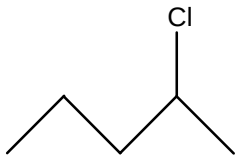
Alkyl Halides

Alkyl Halides (RX)—compounds with a halogen bonded to a saturated carbon (sp^3 hybridized carbon).

Nomenclature

Alkyl halides are named in the same way as alkanes. Treat the halogen as a substituent on the alkane parent chain.

Example



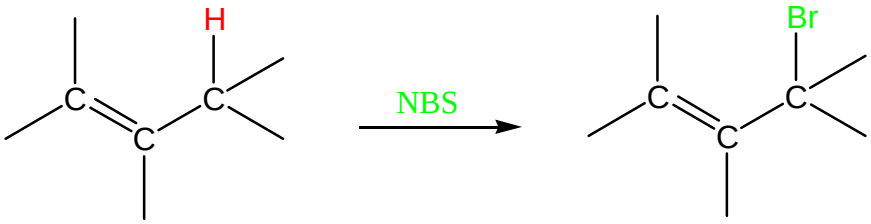
2-chloropentane

Reactions to Know

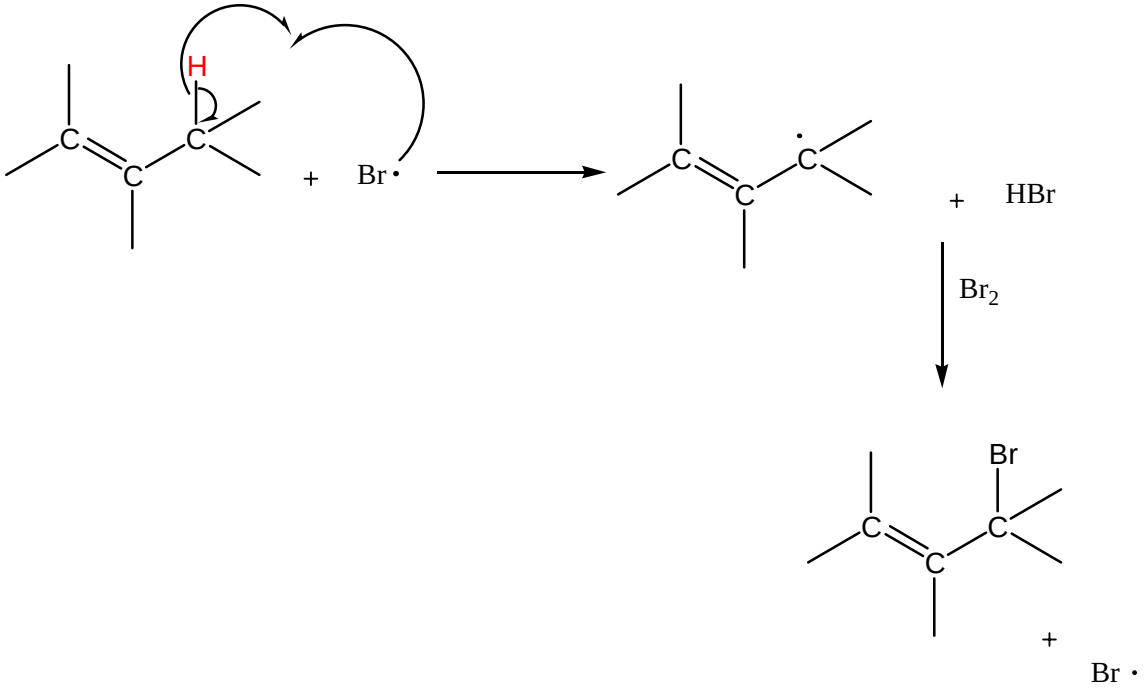
Synthesis of Alkyl Halides

You learned in chapter 5 how to make an alkyl halide by a radical reaction between a halogen and an alkane in uv light.

1. From Alkenes by Allylic Bromination:



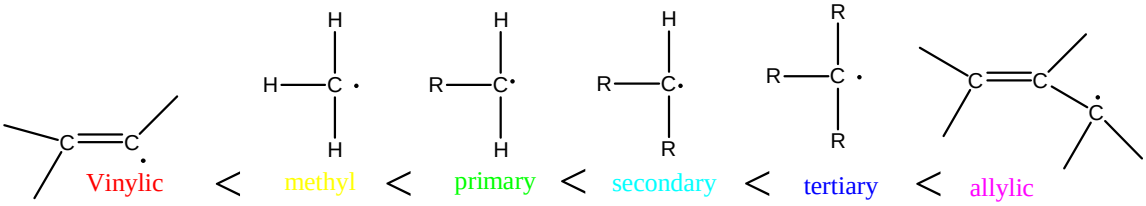
Allylic Bromination with NBS is analogous to the radical reaction with an alkane, a halogen and uv light (Ch. 5). The NBS can be thought of as producing a Br radical. The Br radical removes a hydrogen, leaving an allylic radical and forming HBr. This allylic radical reacts with Br_2 (which is formed from NBS reacting with the HBr formed from the removal of a hydrogen from the alkene) to give the product.



Why does the reaction only occur at the allylic position?

Allylic radicals are more stable than alkyl or vinylic radicals:

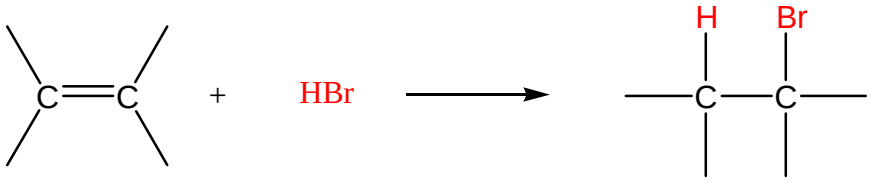
Stability of Radicals



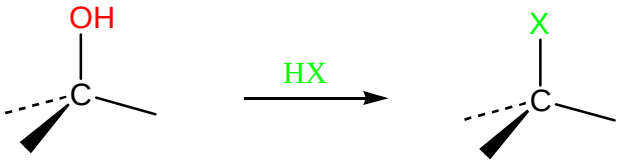
Allylic radicals are so stable because they are resonance stabilized.

Because the allylic radical is more stable, it has a lower energy of activation and more collisions per unit of time result in a successful reaction at the allylic position.

2. From Alkenes (Chapters 6 & 7):



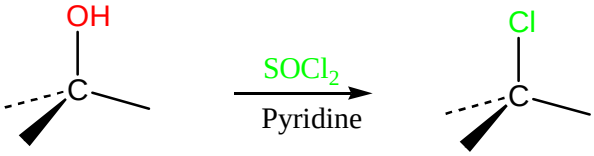
3. From Alcohols (a):



Reactivity of alcohols: 3º > 2º > 1º

You'll learn the mechanism for this reaction in Ch. 11.

4. From Alcohols (b):



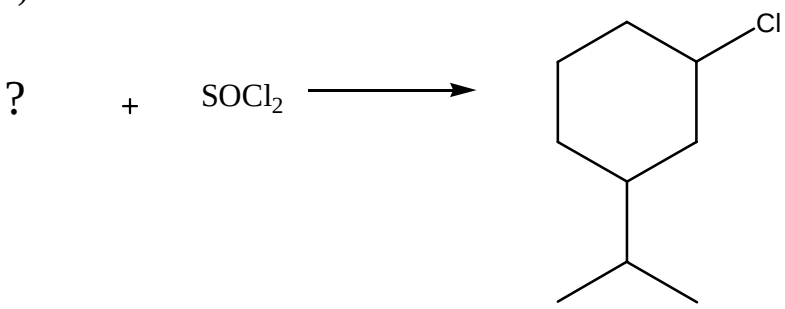
1º and 2º alcohols (PBr_3 PCl_3 and PCl_5 halogenate similarly).

Practice Problems

1)

Answer

2)

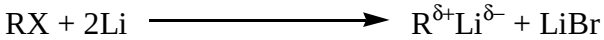


Answer

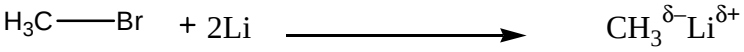
<u>Reactions of Alkyl Halides</u>

1) Organometallic Reactions–Formation of Gilman Reagents

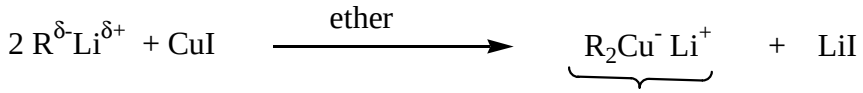
a. General Reaction:



Example:

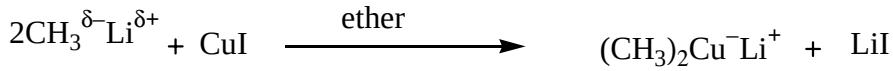


b. General Reaction:



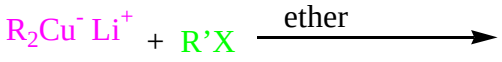
Gilman Reagent

Example:

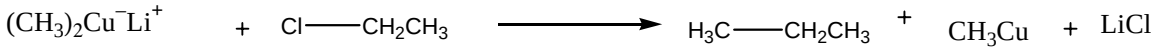


2) Corey-House (Formation of Gilman Reagent)

General Reaction:



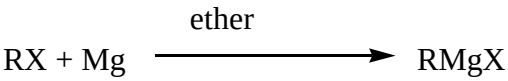
Example:



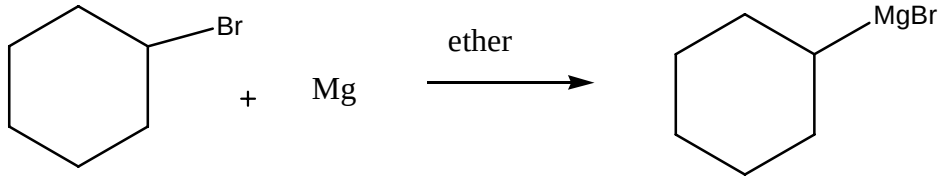
This reaction is useful because it forms new carbon-carbon bonds, lengthening the carbon chain. The alkyl halide loses a halogen and gains the alkyl group from the Gilman Reagent.

3) Formation of Grignard Reagent

General Reaction:



Example:

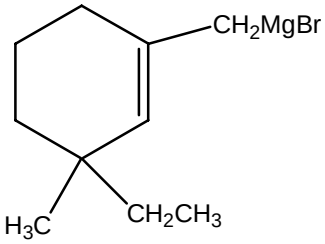


Like Gilman Reagents, Grignard Reagents are useful because they can be used to lengthen a carbon chain. You'll study Grignard reagents and the reactions they are involved in during the second semester of organic chemistry.

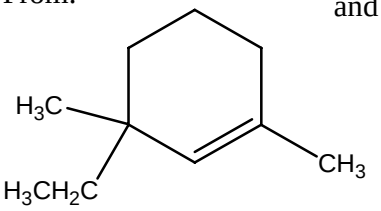
Practice Problems

3)

Prepare:



From:

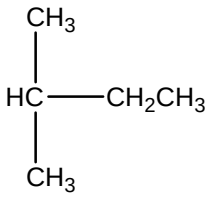


and any other needed reagents

Answer

4)

Prepare:

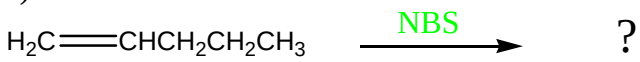


From: $ClCH_2CH_3$ and any other needed reagents

Answer

Answer

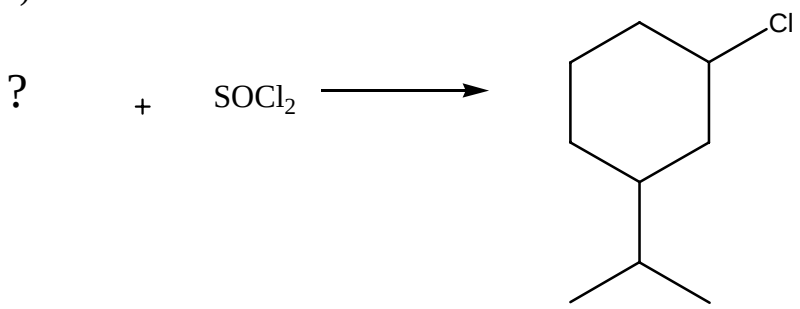
1)

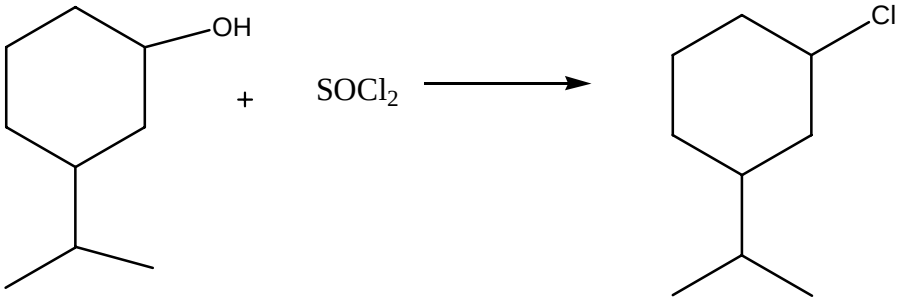


Return to Problem

Answer

2)



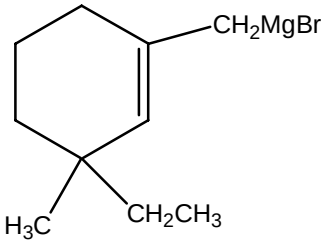


Return to Problem

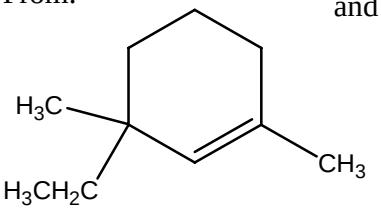
Answer

3)

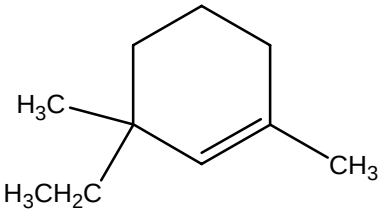
Prepare:

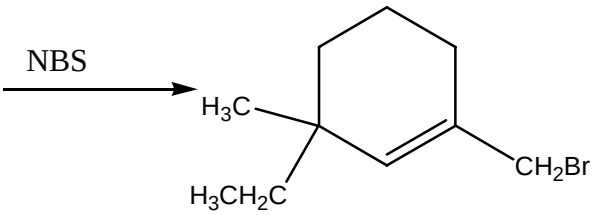


From:



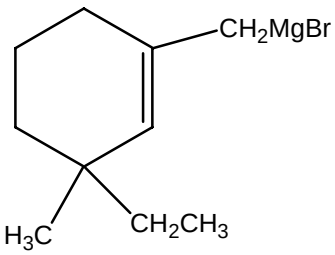
and any other needed reagents





\+ Mg

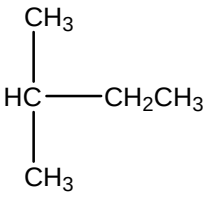
ether



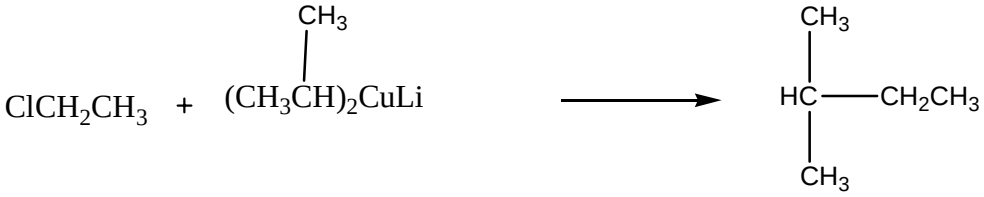
Return to Problem

Answer

4)
Prepare:



From: $ClCH_2CH_3$ and any other needed reagents



Return to Problem