

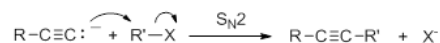
10.9: SYNTHESIS OF LARGER ALKYNES FROM ACETYLIDES

Learning Objective

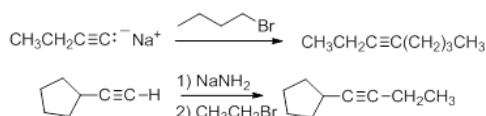
- predict the products and specify the reagents to synthesize larger alkynes with acetylide ions

NUCLEOPHILIC SUBSTITUTION REACTIONS OF ACETYLIDES

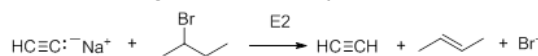
Acetylide anions are strong bases and strong nucleophiles. Therefore, they are able to displace halides and other leaving groups in substitution reactions. The product is a substituted alkyne with a longer, continuous carbon chain.



Because the ion is a very strong base, the substitution reaction follows the S_N2 mechanism and is most efficient with methyl or primary halides without substitution near the reaction center.

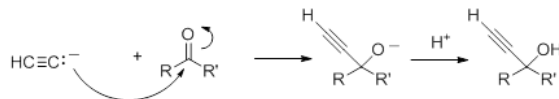


Secondary, tertiary or even bulky primary substrates will give elimination by the $E2$ mechanism.



NUCLEOPHILIC ADDITION OF ACETYLIDES TO CARBONYLS

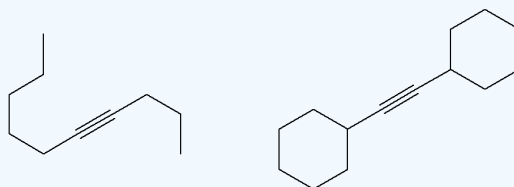
Acetylide anions will add to aldehydes and ketones to form alkoxides that are subsequently protonated to form propargyl alcohols.



With aldehydes and non-symmetric ketones, in the absence of chiral catalyst, the product will be a racemic mixture of the two enantiomers.

Exercise

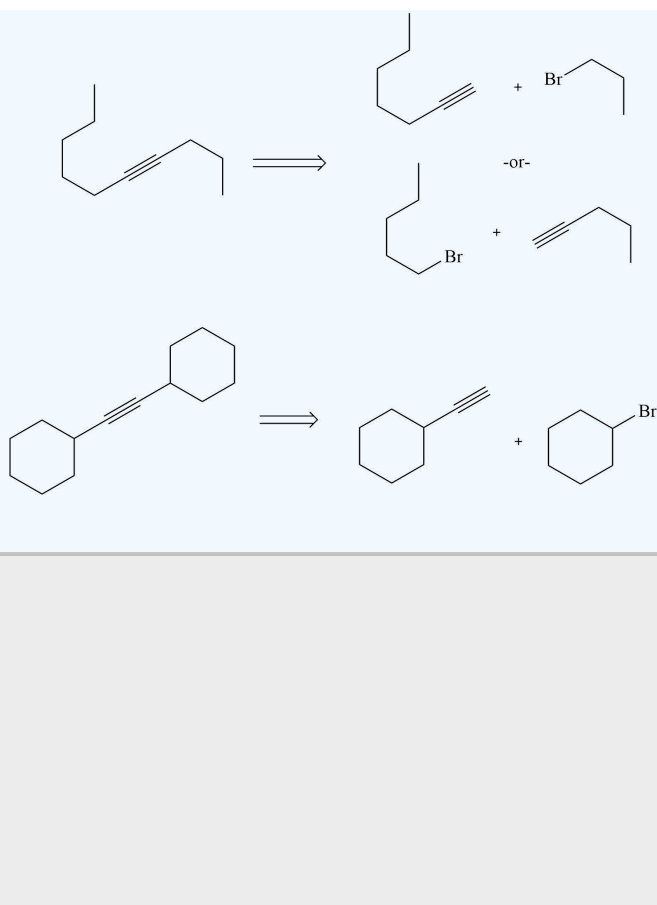
- The pK_a of ammonia is 35. Estimate the equilibrium constant for the deprotonation of pent-1-yne by amide, as shown above.
- Give the possible reactants for the following formations:



- Propose a synthetic route to produce 2-pentene from propyne and an alkyl halide.

Answer

- Assuming the pK_a of pent-1-yne is about 25, then the difference in pK_a s is 10. Since pentyne is more acidic, the formation of the acetylide will be favored at equilibrium, so the equilibrium constant for the reaction is about 10^{10} .
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CONTRIBUTORS AND ATTRIBUTIONS

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