

11.11: Reaction of Acetylide Anions

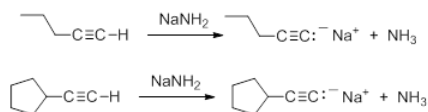
Acidity of Terminal Alkynes: Formation of Acetylide Anions

Terminal alkynes are much more acidic than most other hydrocarbons. Removal of the proton leads to the formation of an acetylide anion, $\text{RC}\equiv\text{C}^-$. The origin of the enhanced acidity can be attributed to the stability of the acetylide anion, which has the unpaired electrons in an sp hybridized orbital. The stability results from occupying an orbital with a high degree of s -orbital character.

There is a strong correlation between s -character in the orbital containing the non-bonding electrons in the anion and the acidity of hydrocarbons. The enhanced acidity with greater s -character occurs despite the fact that the homolytic C-H BDE is larger.

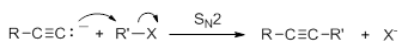
Compound	Conjugate Base	Hybridization	"s Character"	pKa	C-H BDE (kJ/mol)
CH_3CH_3	CH_3CH_2^-	sp^3	25%	50	410
CH_2CH_2	CH_2CH^-	sp^2	33%	44	473
HCCH	HCC^-	sp	50%	25	523

Consequently, acetylide anions can be readily formed by deprotonation using a sufficiently strong base. Amide anion (NH_2^-), in the form of NaNH_2 is commonly used for the formation of acetylide anions.

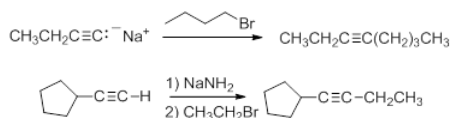


Nucleophilic Substitution Reactions of Acetylides

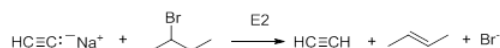
Acetylide anions are strong bases and strong nucleophiles. Therefore, they are able to displace halides and other leaving groups in substitution reactions. The product is a substituted alkyne.



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

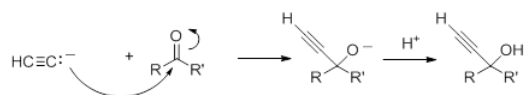


Secondary, tertiary or even bulky primary substrates will give elimination by the $\text{E}2$ mechanism.



Nucleophilic Addition of Acetylides to Carbonyls

Acetylide anions will add to aldehydes and ketones to form alkoxides, which, upon protonation, give 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.

Problems

1. The pK_a of ammonia is 35. Estimate the equilibrium constant for the deprotonation of pent-1-yne by amide, as shown above.

Answers

1. 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}

Contributors

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