Chemistry 2301

Workshop 19 Solutions Interfering Functional Groups

$$H_3C$$
 H_2O/OH H_3C H_3C H_3C

KMnO₄ will react with the alkyne too. Permanganate cleaves triple bonds. It's not clear whether that would occur before or after oxidation of the double bond, but it's certainly a risk.

$$H_3C$$
 \longrightarrow H_3C \longrightarrow H_3C

HBr will add Markovnikov to the alkyne, just like it will to the alkene. The recipe doesn't say how many equivalents of HBr were added, but in principle, any number of HBr molecules could add to the starting material:

The problem here is that the molecule will react with itself—or, more accurately, as soon as alkynyl ions are generated, they will immediately react with other molecules of the same type:

H NaNH₂

$$\begin{array}{c}
 & 1. \text{ NaNH}_2 \\
 & \bigcirc \text{ C} = \text{ C}
\end{array}$$

$$\begin{array}{c}
 & \bullet \\
 & \bullet$$

The anion never gets the chance to react with CH₃I. Take-home message: avoid creating synthetic intermediates that will react with themselves. In principle, the NH₂⁻

anion could also serve as a nucleophile to open the epoxide, but NH_2^- is a much stronger base than it is a nucleophile, so it probably will take the proton first.

$$H-C\equiv C-H$$

$$1. NaNH2$$

$$2. Br OH$$

$$OH$$

Here, the problem is that the alkynyl anion would more rapidly deprotonate the alcohol than it would do S_N2 on the halide—because acid-base reactions are extremely rapid, and the alcohol is a stronger acid (pK_a \approx 16) than the alkyne (pK_a \approx 25).

$$H-C \equiv C-H$$

$$1. \text{ NaNH}_2$$

$$H-C \equiv C \xrightarrow{\Theta} \text{ Na}^{\oplus}$$

$$2. \text{ Br} \xrightarrow{Q-H}$$

I'm sure the hydroboration will succeed, but the OH in the second step could not only help convert the borane into the alcohol, but it could also open the epoxide:

HO
$$\bigcirc$$
 HO \bigcirc OH

$$H_3C$$
 Br
 Na/NH_3
 H_3C
 H
 Br

Amines are great nucleophiles, and because this reaction is run in liquid ammonia (condensed amine), there would be no way to stop the ammonia from attacking the bromide:

$$H_3C$$
 \longrightarrow H_3C \longrightarrow \longrightarrow H_3C \longrightarrow \longrightarrow H_3C \longrightarrow \longrightarrow