ALKYNES

I. Mechanisms: preparation and use of alkynes

1) Corey-Fuchs alkyne synthesis

\[
\begin{align*}
R^*\text{O} & \quad \text{O} & \quad R^*\text{O} \\
\text{O} & \quad \text{O} & \quad \text{N}_2
\end{align*}
\]

1) CBr₄ (2 equiv.), PPh₃ (4 equiv.)
DCM, 0 °C, 5 min
2) n-BuLi (2 equiv.)
3) hydrolysis

2) Seyferth-Gilbert homologation (with use of the Ohira & Bestmann reagent)

3) Eschenmoser-Tanabe fragmentation

N.B.: The reaction conditions are quite similar to that of a Shapiro reaction.

5) Brown hydroboration and oxidation:

Substitute the boron of a vinyl borane with a hydroxy- or an amino- group. Reagents and mechanisms. Alternatively, how would you get the other regioselectivity for the ketone formation.

6) Electro cyclic reactions:

- Danheiser benzannulation reaction

\[
\begin{align*}
\text{O} & \quad \text{R}^* & \quad \text{R}' \\
\text{R}^* & \quad \text{R}'
\end{align*}
\]

80 - 160 °C
CHCl₃, C₆H₆
or Tol

\[
\begin{align*}
X & \quad \text{OH} & \quad \text{R}^* & \quad \text{R}' \\
\text{R} & \quad \equiv & \quad \equiv & \quad \equiv
\end{align*}
\]

X= OR, OTMS, SR, NR₂

Mechanism. Can you think of another starting material / conditions to afford the same type of reaction.
7) Larock indole synthesis

It is a one-pot Pd-catalysed reaction between an o-iodoaniline and an internal alkyne (needs a source of chloride). Mechanism.

II. Total synthesis


Complete the missing reagents, products and mechanisms.

2) Nakajima, Ogino, Yokoshima and Fukuyama’s synthesis of (-)-Mersicarpine (2010).

Complete the missing reagents, products and mechanism.
III. Retrosynthesis.

This is the retrosynthesis analysis of macbecin I made by Belardi and Micalizio. Draw the synthesis starting with 4 (for the bit between cuts a and b) and with 5 (for the aldehyde bit of 3).