Enantioselective Synthesis of Iboga Alkaloids and Vinblastine Via Rearrangements of Quaternary Ammoniums
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1) C, THF, reflux
2) H₂, Pd/C (10% mol)
3) isobutyl chloroformate, NMO, then D, Et₃N
4) t-butylthiol, 270W sun lamp
5) Boc₂O
6) LDA, propargyl bromide
7) TFA
8) Me₂O⁺BF₄⁻, then NaBH₄
9) PPh₃AuNTf₂ (cat.), E, MsOH, AgOTf (cat.) then NaHCO₃ (aq.), Et₃N
10) t-BuOK, Ph₃PEtBr

Step 1: What is the name of the amino acid that the starting material comes from? Name the reaction.

Step 4: Name the reaction

Step 9: During the basic treatment a second reaction happens followed by a rearrangement. Name the rearrangement and provide a mechanism.

Step 10: Name the reaction

(+)-Dihydrocatharanthine
Step 11: Propose a mechanism for this step

11) \( \text{H}_2, \text{PtO}_2 \)

12) \( \text{F}, \text{FeCl}_3, 0.1\text{N HCl-CF}_3\text{CH}_2\text{OH} \)
then \( \text{Fe}_2(\text{ox})_3, \text{O}_2, \text{NaBH}_4 \)

\(+\)-Dihydrocatharanthine

Vinblastine
Step 9: [1,2]-Stevens rearrangement. Proposed mechanism:

\[
\begin{align*}
\text{Et}_3\text{N} & \quad \rightarrow \\
\text{intramolecular} & \quad \text{alkylation} \\
\end{align*}
\]

Note: radical mechanism also plausible

Step 12: Oxidative coupling to vinblastine. Proposed mechanism.

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