Guillaume George – Problem Session – January 2011

REARRANGEMENTS

Mechanisms, missing reagents, synthesis ideas, analogies, advantages, drawbacks, stereochemistry… The number of steps is not given on purpose.

I. Anionic

Benzilic acid rearrangement

A cyclic α-diketone treated with hydroxide anion yields a ring contracted α -hydroxy acid.

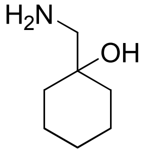
Hofmann rearrangement

Primary amides treated with alkali hypohalite afford an intermediate isocyanate. For base sensitive substrate, the reaction can be carried out with Koser's reagent (PhI(OH)OTs) under slightly acidic conditions.

II. Cationic

Tiffeneau-Demjanov rearrangement

Nitrosonium reacted with the following β-amino alcohol affords the ring-expanded cyclic ketone.



Schmidt rearrangement

Carboxylic acids, aldehydes and ketones can be treated with hydrazoic acid under fairly acidic conditions to afford amine, nitrile and amide respectively.

III. Concerted

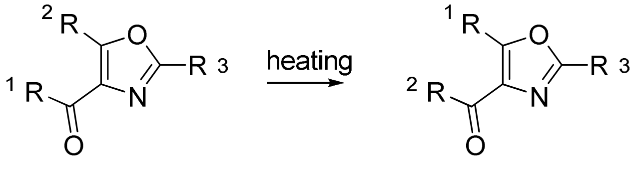
Baeyer-Villiger

Cyclic ketones are turned into ring-expanded lactones by treatment with peroxyacids.

IV. (AN)RORC

Cornforth rearrangement

Account for this.

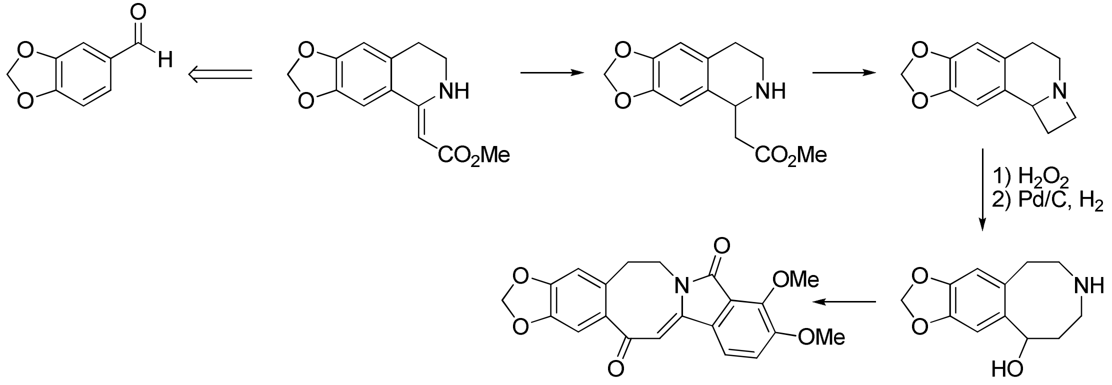


V. Neutral

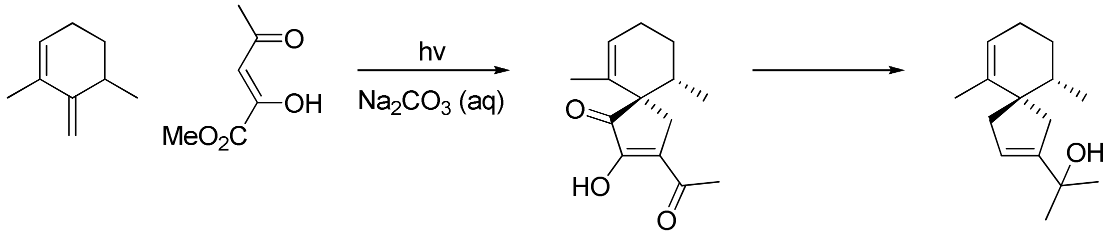
Curtius rearrangement

Carboxylic acids react with diphenylphosphoryl azide to afford the intermediate isocyanate.

VI. Megallanesine



VII. Hinesol



VIII. Dendrobatid alkaloid 251F