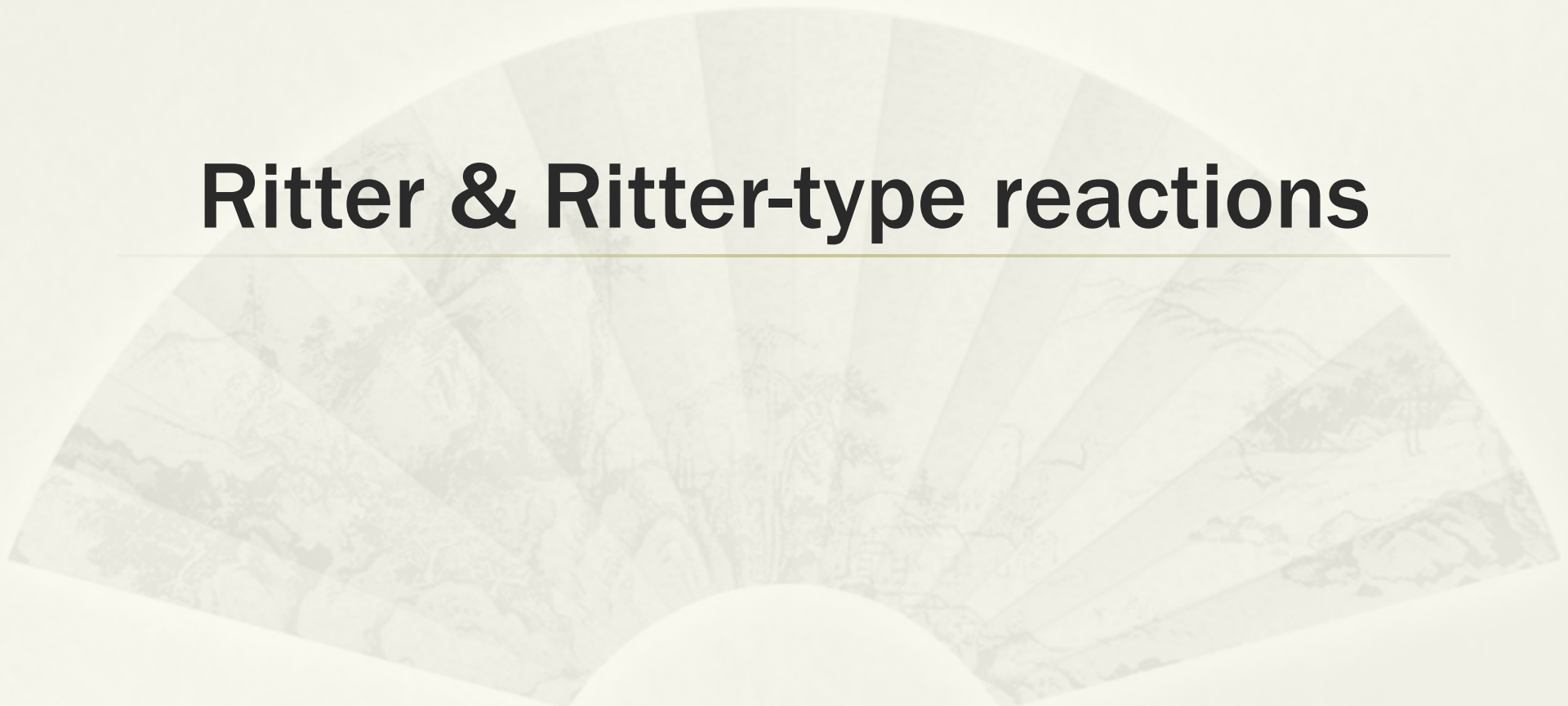
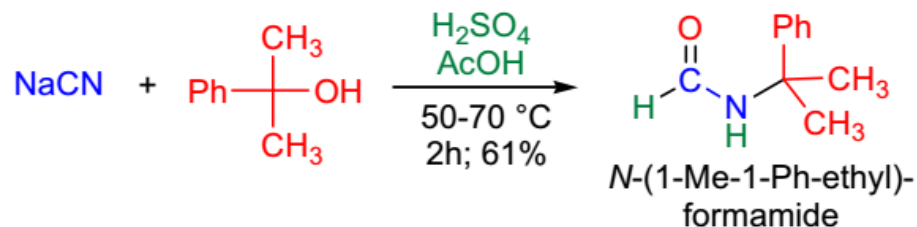
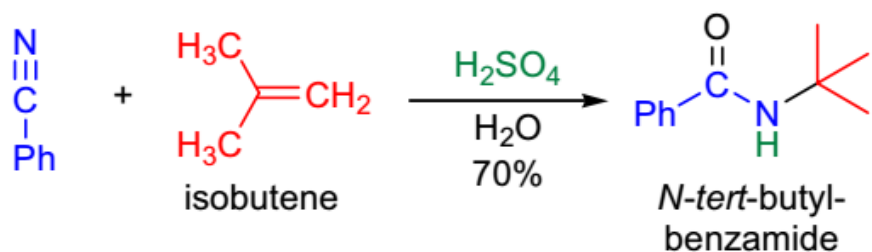


Ritter & Ritter-type reactions

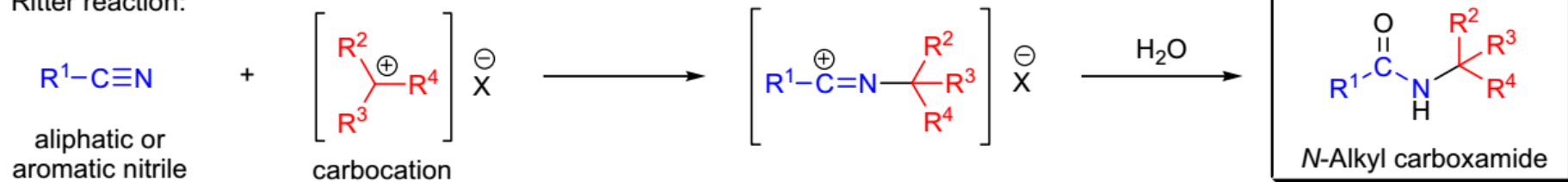


Ritter reaction

* Ritter & Minieri (1948)



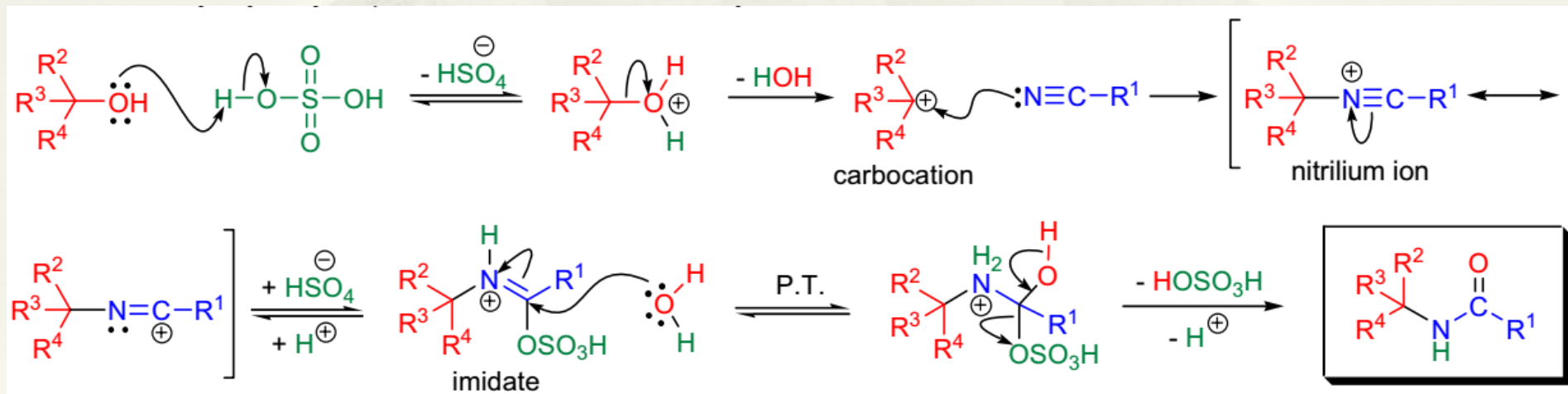
Ritter reaction:



The classical reaction conditions: the nitrile substrate in the mixture of acetic acid and concentrated sulfuric acid followed by the addition of the alcohol or alkene at slightly elevated temperatures (50-100 °C)

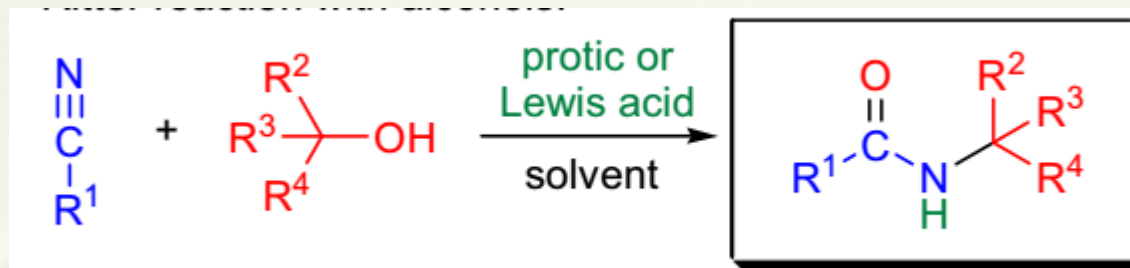
Ritter reaction

Mechanism:



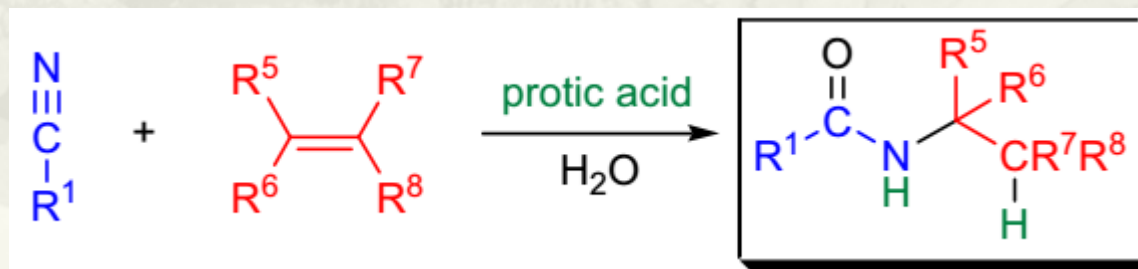
General Features:

- * Alcohols that are easily ionized (e.g., 2° and 3° alcohols, benzylic alcohols) give the best results.



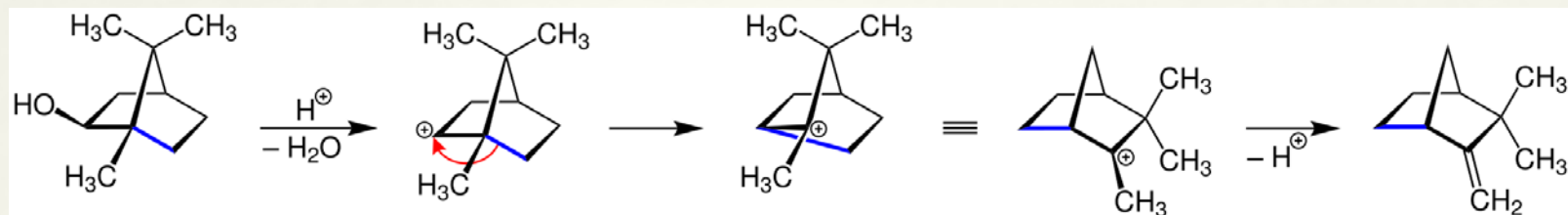
Carbocation Stability $\text{CH}_3^{(+)} < \text{CH}_3\text{CH}_2^{(+)} < (\text{CH}_3)_2\text{CH}^{(+)} \approx \text{CH}_2=\text{CH}-\text{CH}_2^{(+)} < \text{C}_6\text{H}_5\text{CH}_2^{(+)} \approx (\text{CH}_3)_3\text{C}^{(+)}$

- * 1,1-disubstituted alkenes give rise to regioisomerically pure products, but with 1,2-disubstituted alkenes a mixture of regioisomers may be formed.



General Features :

- * The initially formed carbocation may undergo a **Wagner-Meerwein rearrangement** to give rise to the most stable carbocation before reacting with the nitrile.

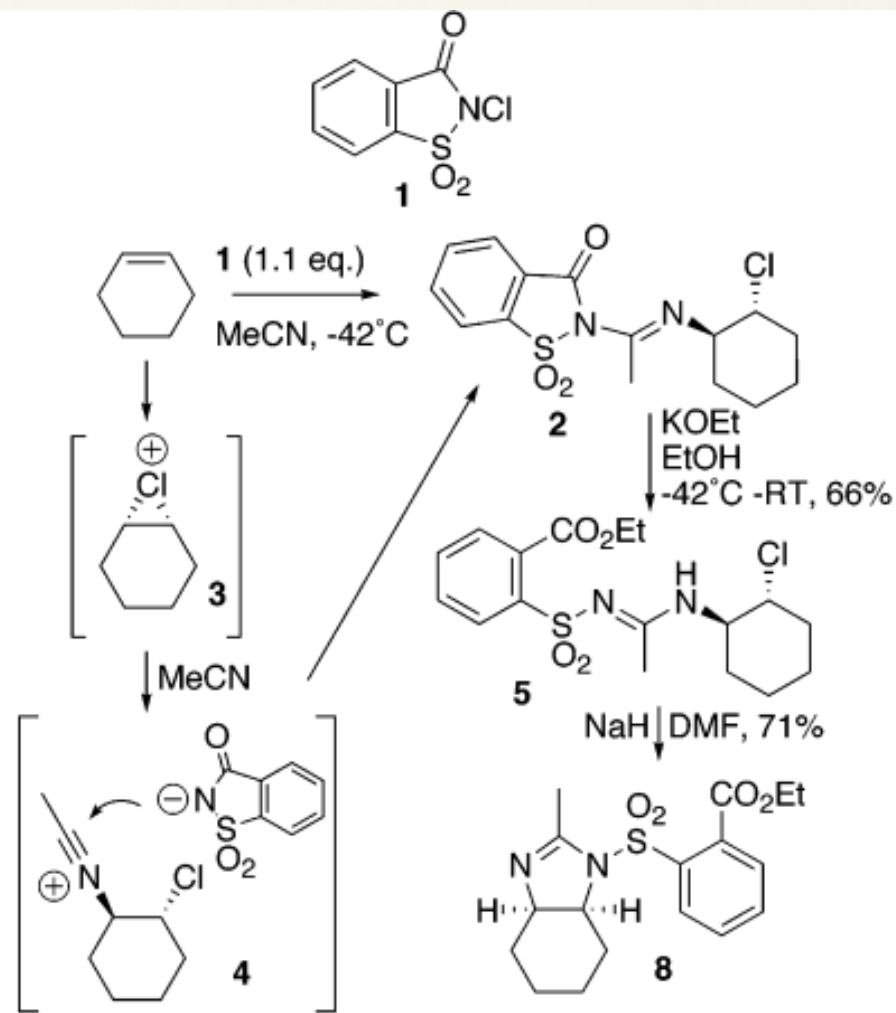
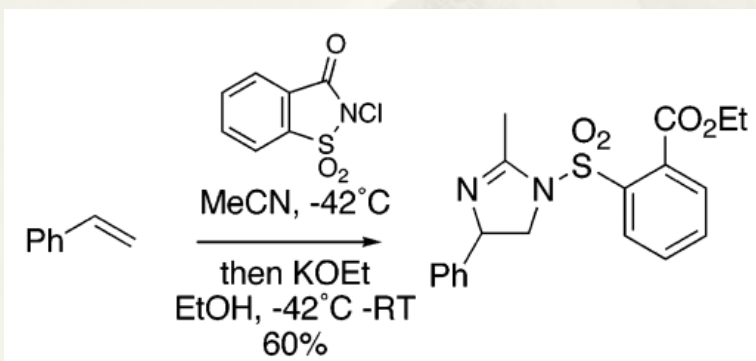


Wagner-Meerwein rearrangement

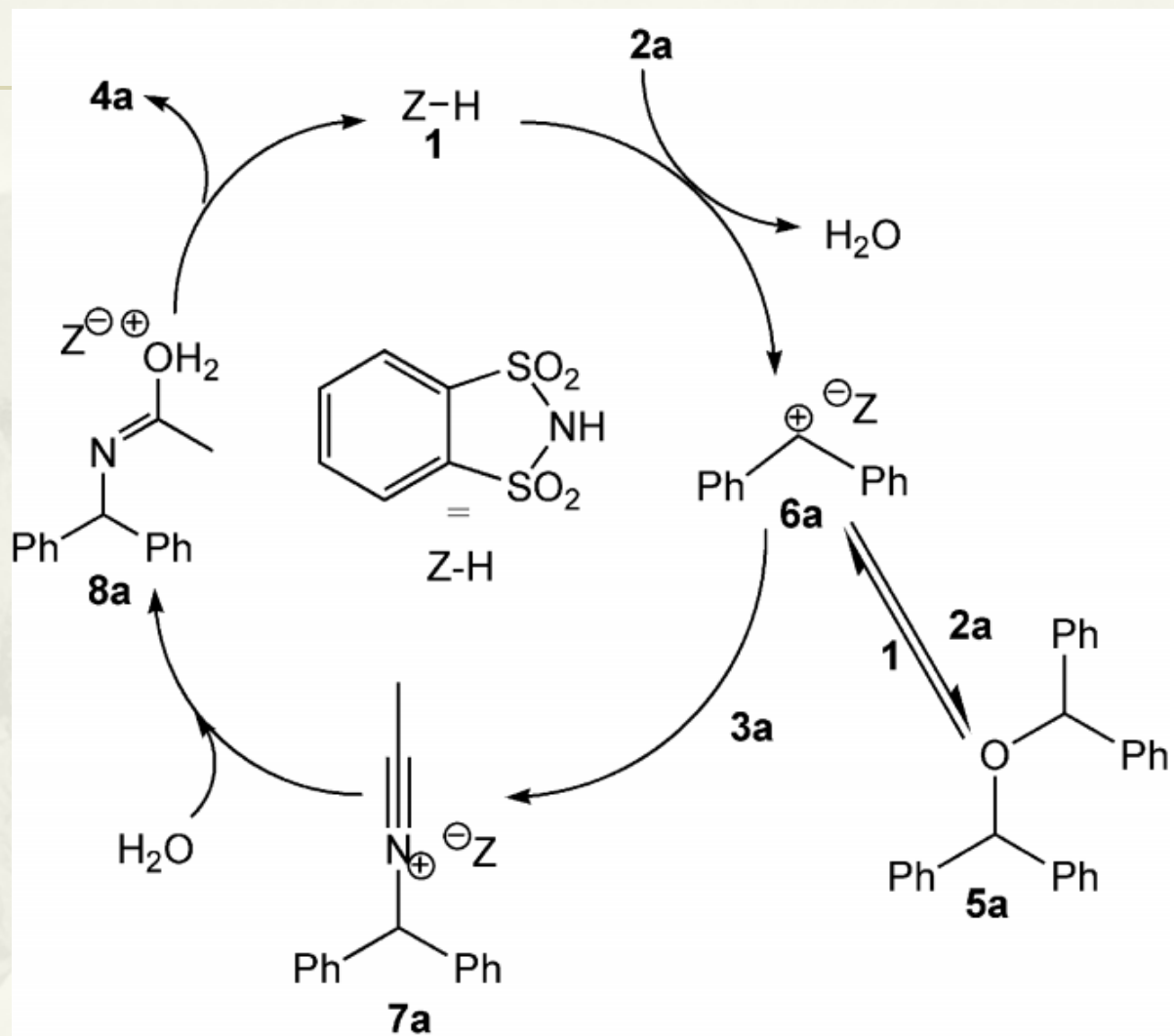
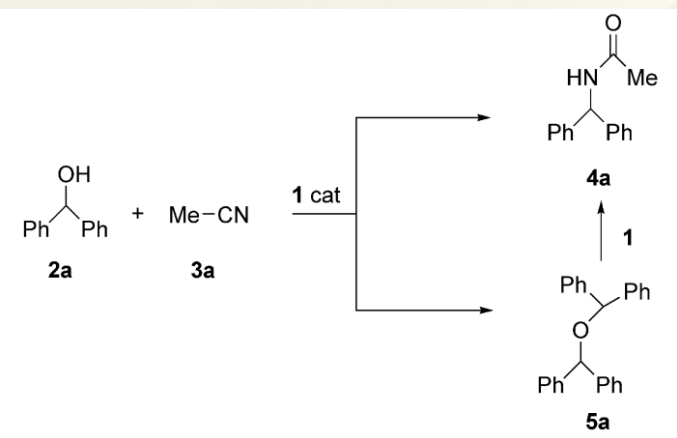
- * Besides **protic acids**, **Lewis acids** (e.g., SnCl_4 , $\text{BF}_3 \cdot \text{OEt}_2$, AlCl_3 , etc.) have been successfully employed in the Ritter reaction to generate the required carbocations.
- * the nitrile substrate **may not contain acidsensitive functional groups** that would be destroyed under the strongly acidic reaction conditions

General Features:

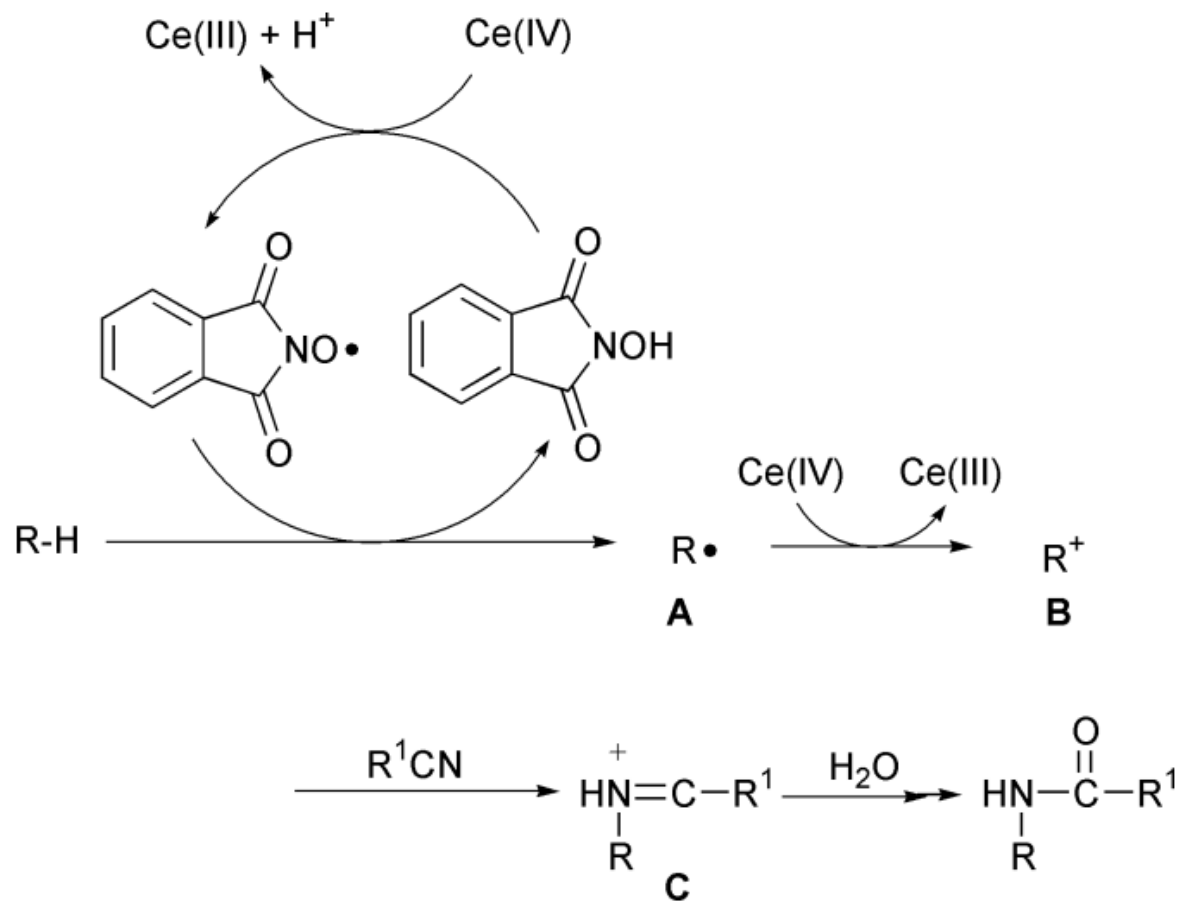
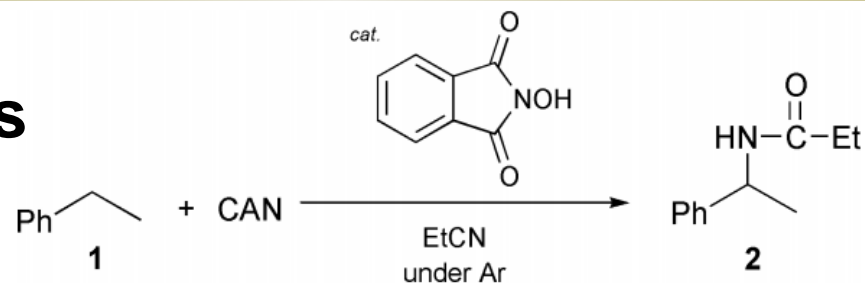
- * **Ritter-type reactions** that proceed under neutral conditions expanded the scope of the substrates.



Ritter-type reactions

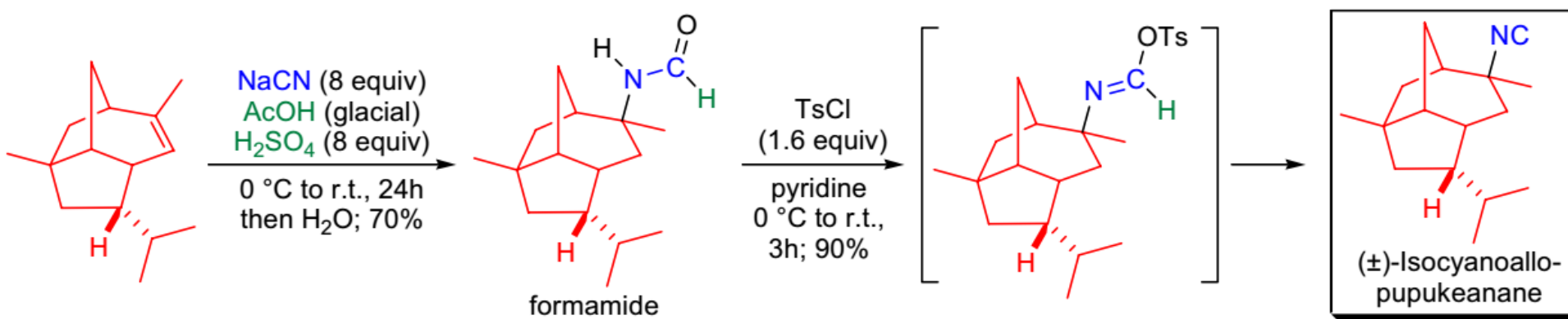
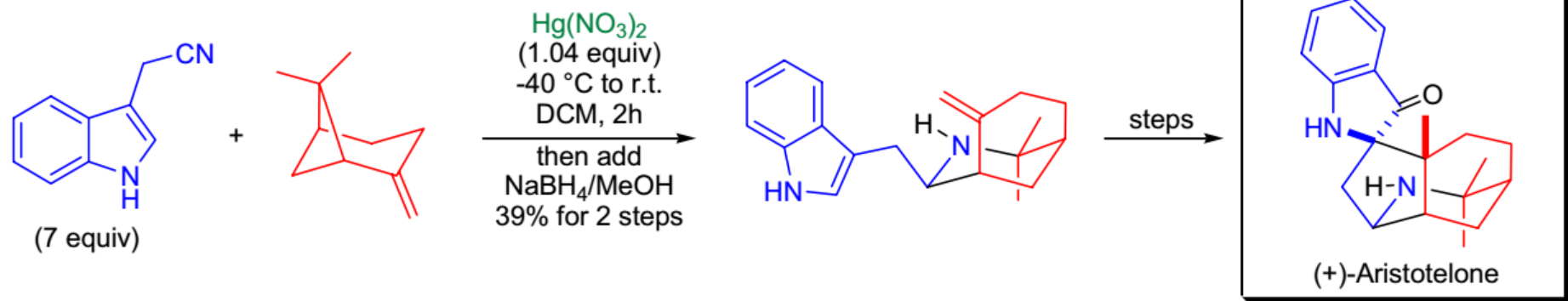
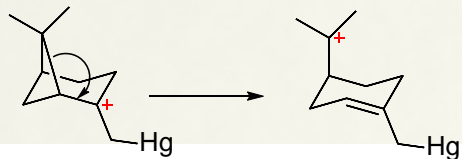


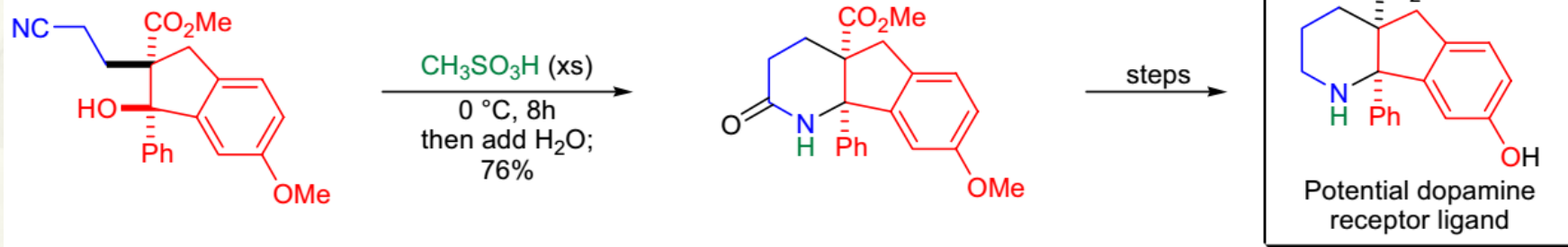
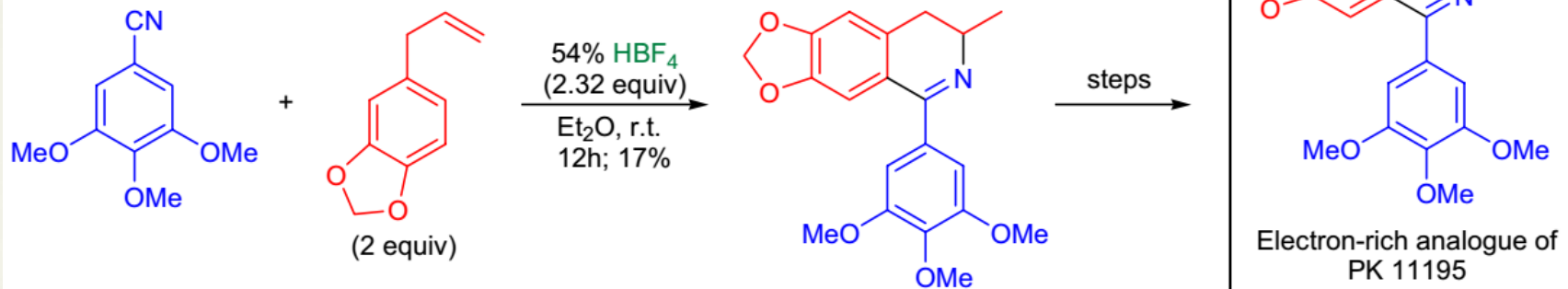
Ritter-type reactions



Scheme 1 A possible reaction path.

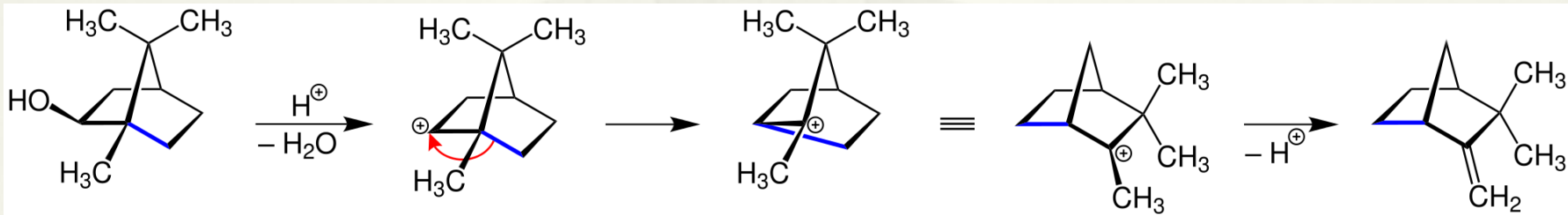
Synthetic Applications:





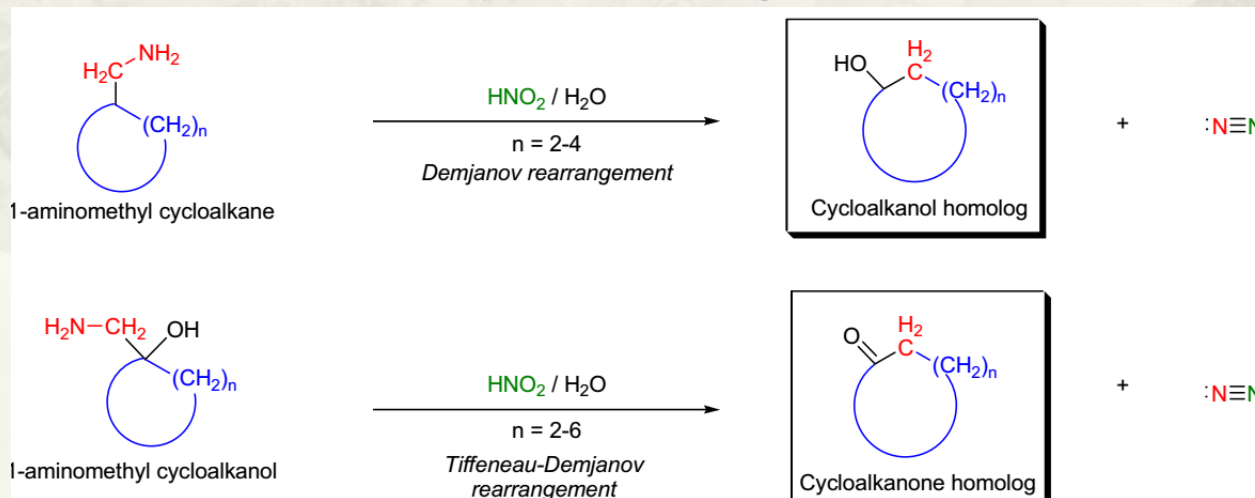
Cationic Rearrangements

* Wagner-Meerwein Rearrangements



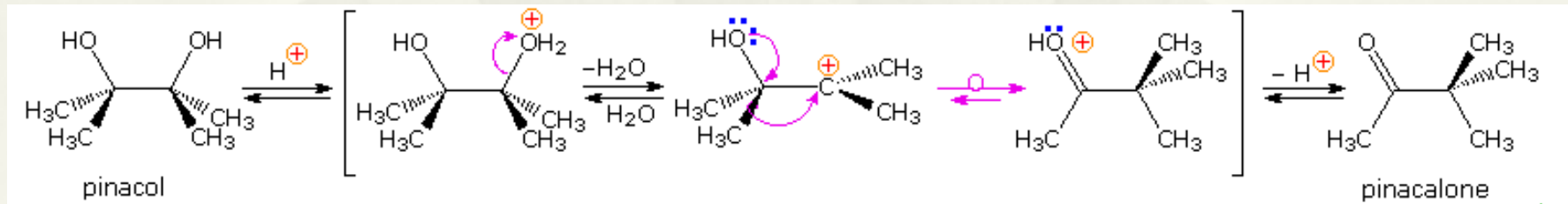
Carbocation Stability $\text{CH}_3^{(+)} < \text{CH}_3\text{CH}_2^{(+)} < (\text{CH}_3)_2\text{CH}^{(+)} \approx \text{CH}_2=\text{CH}-\text{CH}_2^{(+)} < \text{C}_6\text{H}_5\text{CH}_2^{(+)} \approx (\text{CH}_3)_3\text{C}^{(+)}$

* Demjanov and Tiffeneau–Demjanov rearrangements

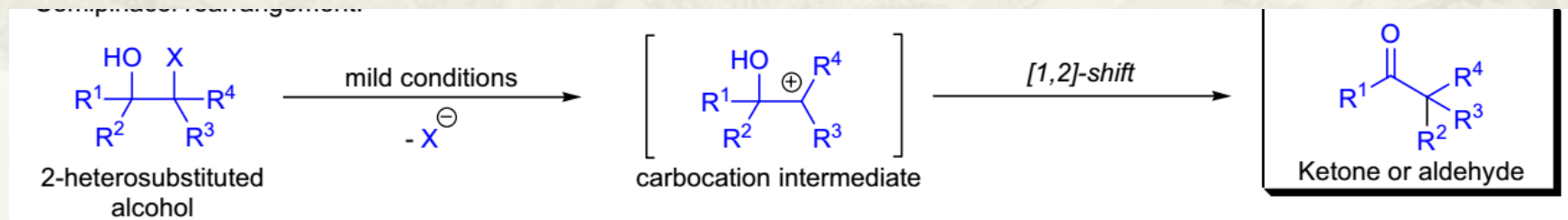


Cationic Rearrangements

* Pinacol Rearrangement

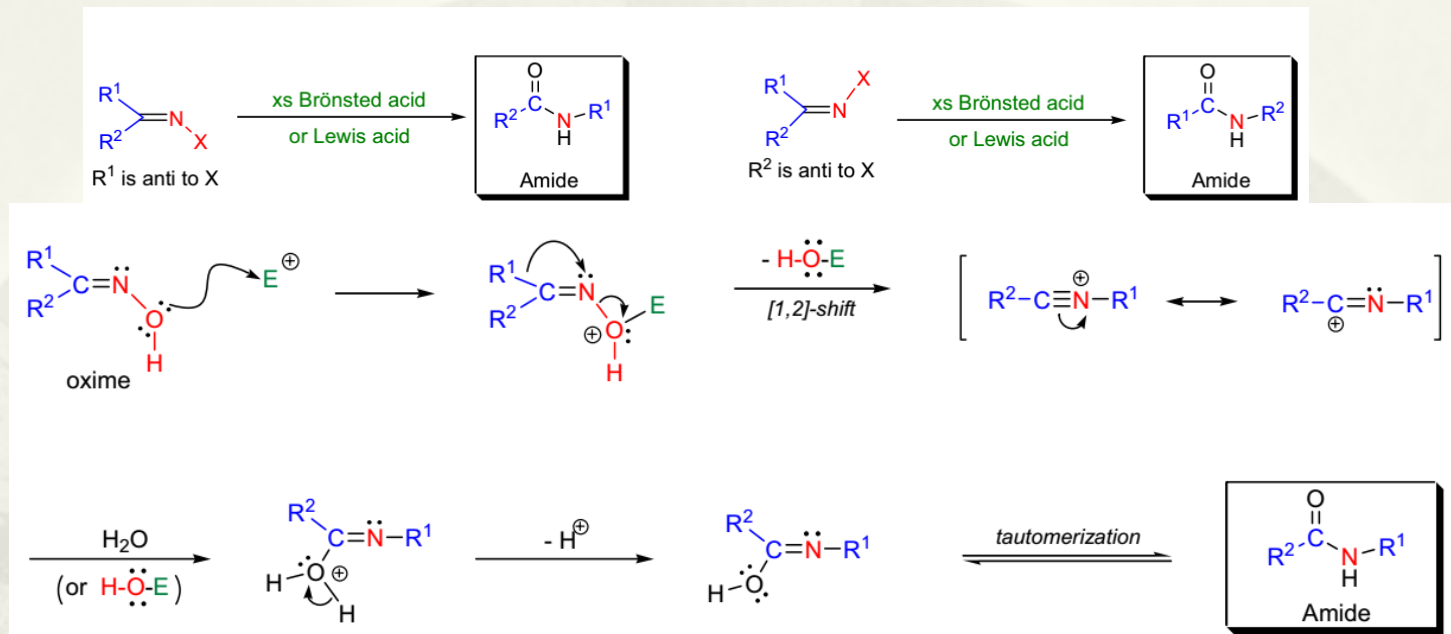


* Semipinacol rearrangement



Cationic Rearrangements

* Beckmann rearrangement



* Stieglitz rearrangement

