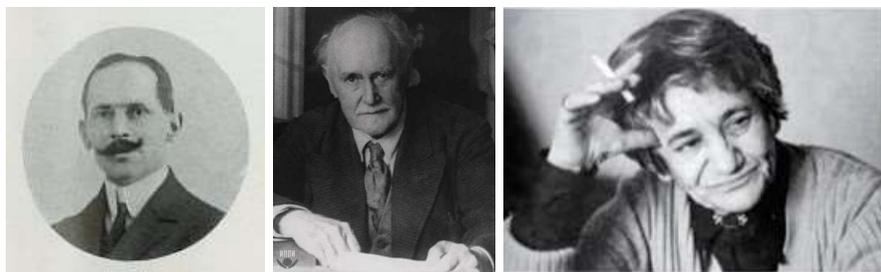


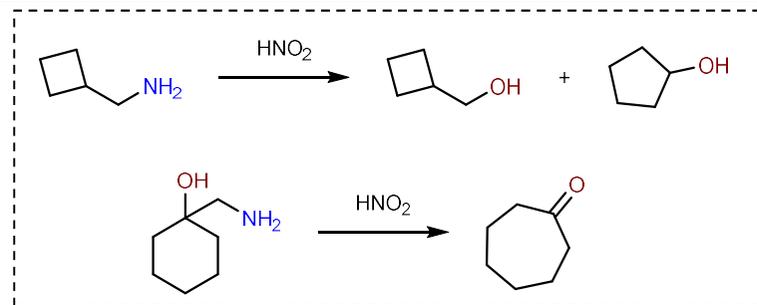
Introduction:



Marc Tiffeneau

Nikolaj Jakovlevič Demjanov

Bianka Tchoubar



Demjanov rearrangement

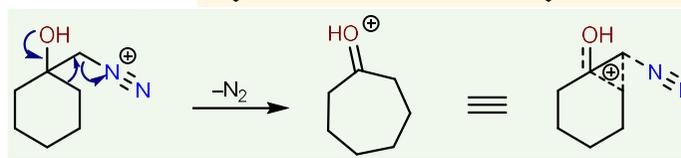
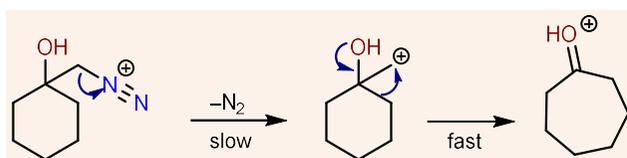
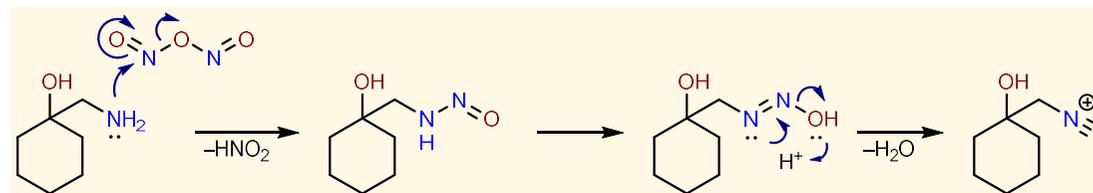
Tiffeneau-Demjanov rearrangement

- Reported by Tiffeneau and Tchoubar, it was later discovered to be a more controllable variation of the original Demjanov rearrangement.
- Used for homologations, ring expansions and contractions.

Tiffeneau, M. and Tchoubar, B. *Comptes Rendus*. 1937, 205, 54–56.

Mechanism:

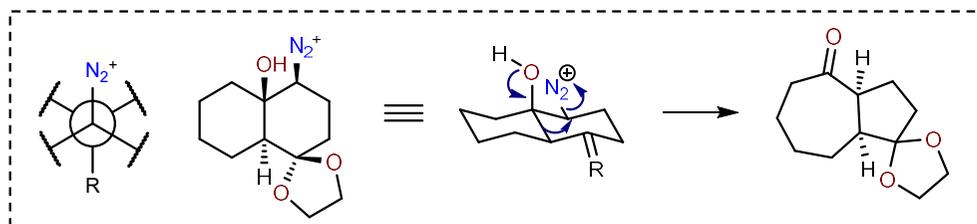
- First step universally accepted to be formation of the unstable alkyl diazonium salt through a classic mechanism.



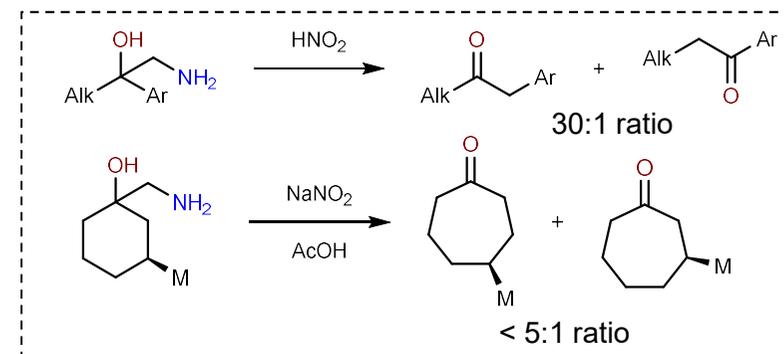
- At first an ionic pathway was proposed.
- It was not until the '80s that a concerted mechanism was proposed and accepted thanks to careful kinetic studies.

Cooper, J. J. *Chem. Soc., Perkin Trans.* 1982, 2, 605-611. <https://doi.org/10.1039/P29820000605>

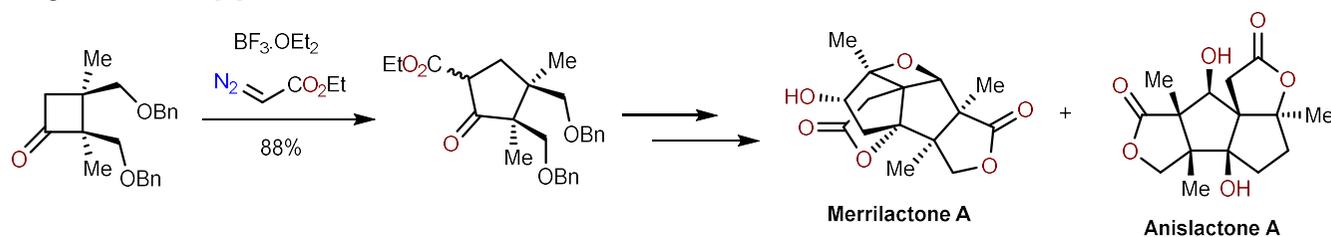
- Different studies suggested from time to time a different explanation for migration.
- Those rules are only valid for very specific cases and are less general than analogous reactions (e.g.: Bayer-Villiger).



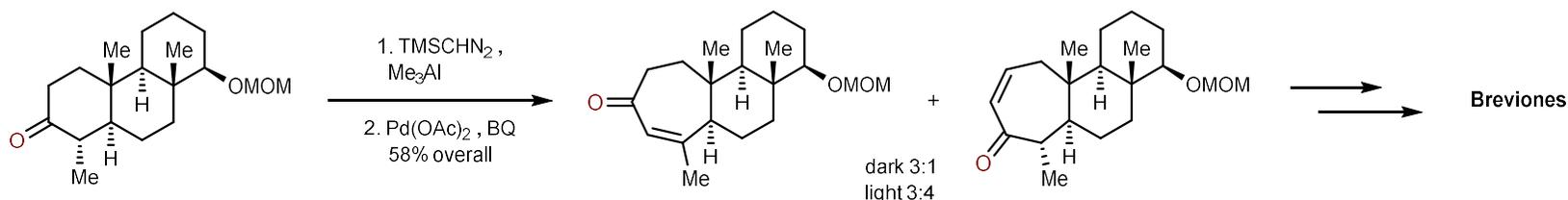
- Eventually it has been accepted that significant factors include: electronic and steric effects of the substrate, electronic and steric effects of the transition state, number of moving atoms, and activation volume.
- Since all these factors can have similar weight, it is difficult for non-limit situations to predict the migrating substituent.



Synthetic applications:

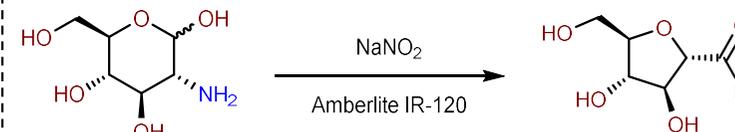
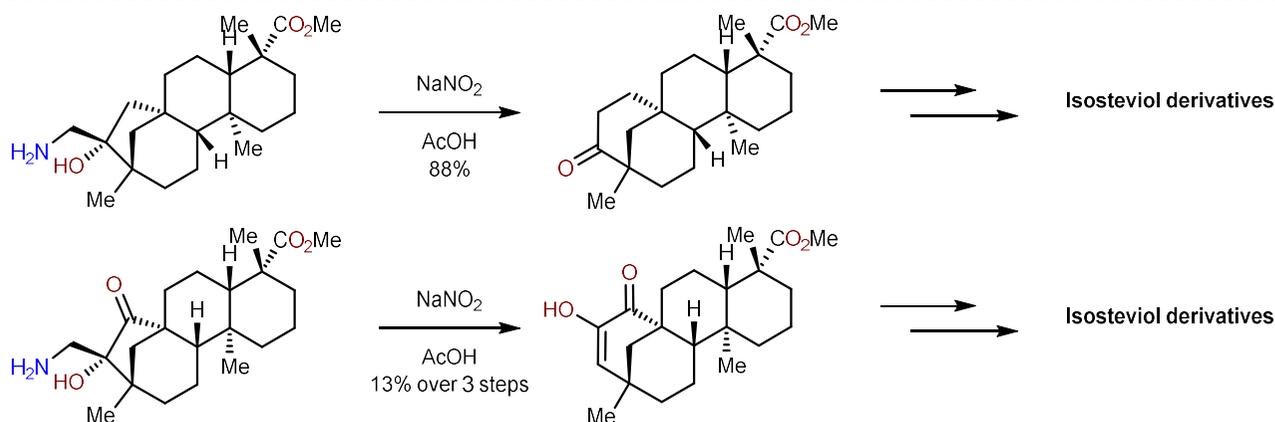


- Several modifications of the reagents used exist.
- As a “general” rule, the less substituted carbon usually migrates preferentially.
- An example in which light changes the regioisomeric ratio is shown, but no mechanistical consideration have ever been taken into account.



Greaney, M. F. *Angew. Chem.* **2010**, *122*, 9436–9439. <https://doi.org/10.1002/ange.201005156>

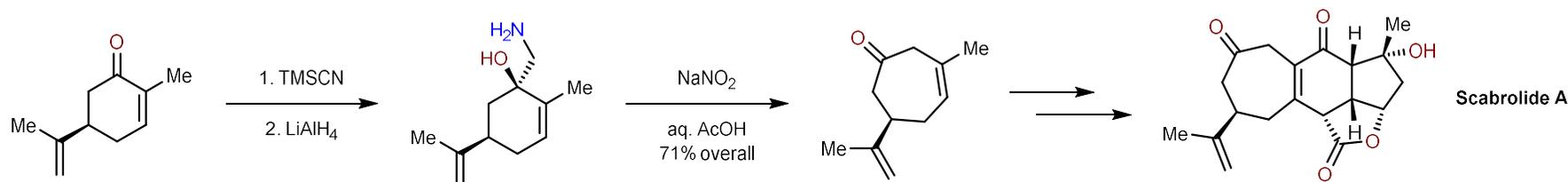
Macias, F. A. *Tetrahedron* **2010**, *66*, 4125–4132. <https://doi.org/10.1016/j.tet.2010.03.116>



- Waldvogel gives a perfect example for migration selectivity based on electronics.
- As mentioned, it can also be used as an efficient way for ring contractions.

Waldvogel, S. R. *Eur. J. Org. Chem.* **2012**, *32*, 6364–6371. <https://doi.org/10.1002/ejoc.201200970>

McQuade, D. T. *Beilstein J. Org. Chem.* **2013**, *9*, 2022–2027. <https://doi.org/10.3762/bjoc.9.238>



Fürstner, A. *J. Am. Chem. Soc.* **2022**, *144*, 1528–1533. <https://doi.org/10.1021/jacs.1c12401>