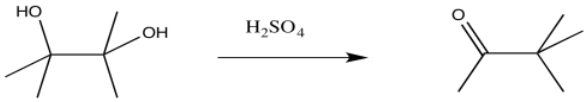
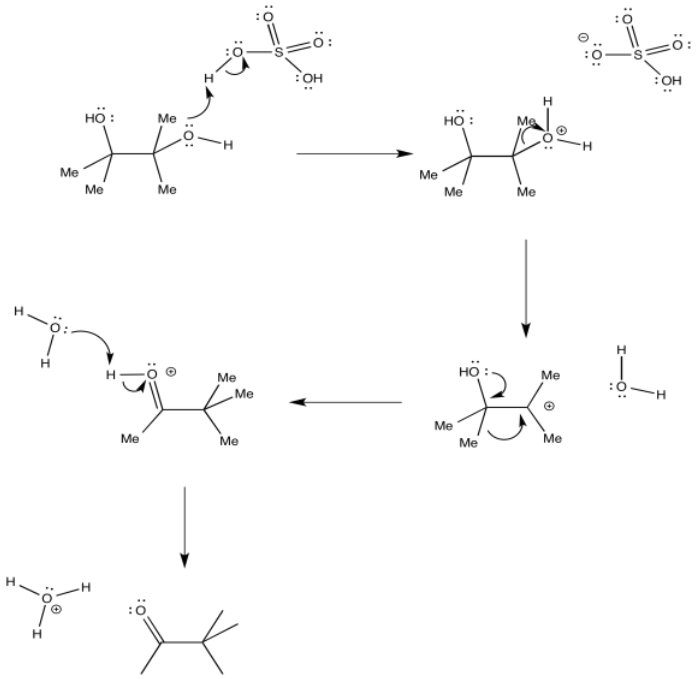
11.2: Pinacol Rearrangement

The pinacol rearrangement is a reaction of 1,2-diols. It takes place under the influence of strong acids, including mineral acids like sulfuric acid. It can also be brought about via the use of Lewis acids. The reaction overall involves the loss of one of the hydroxyl groups, the conversion of the other hydroxyl group into a carbonyl, and the shift of an alkyl group.



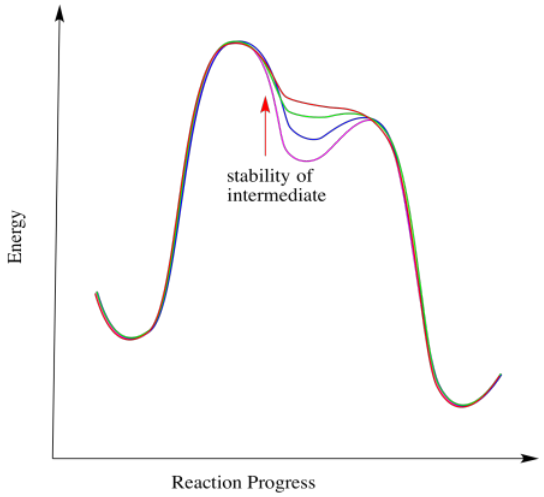
The heart of the rearraction is the 1,2-shift of an alkyl group. This shift is assisted by π-donation from the oxygen, converting the C-O bond into a carbonyl at the same time.

The entire mechanism would look like this:



In many rearrangements, formation of the actual cation is not necessarily involved. The 1,2-shift could occur as the water molecule leaves. The protonated oxygen may draw enough electron density toward itself to induce the shift.

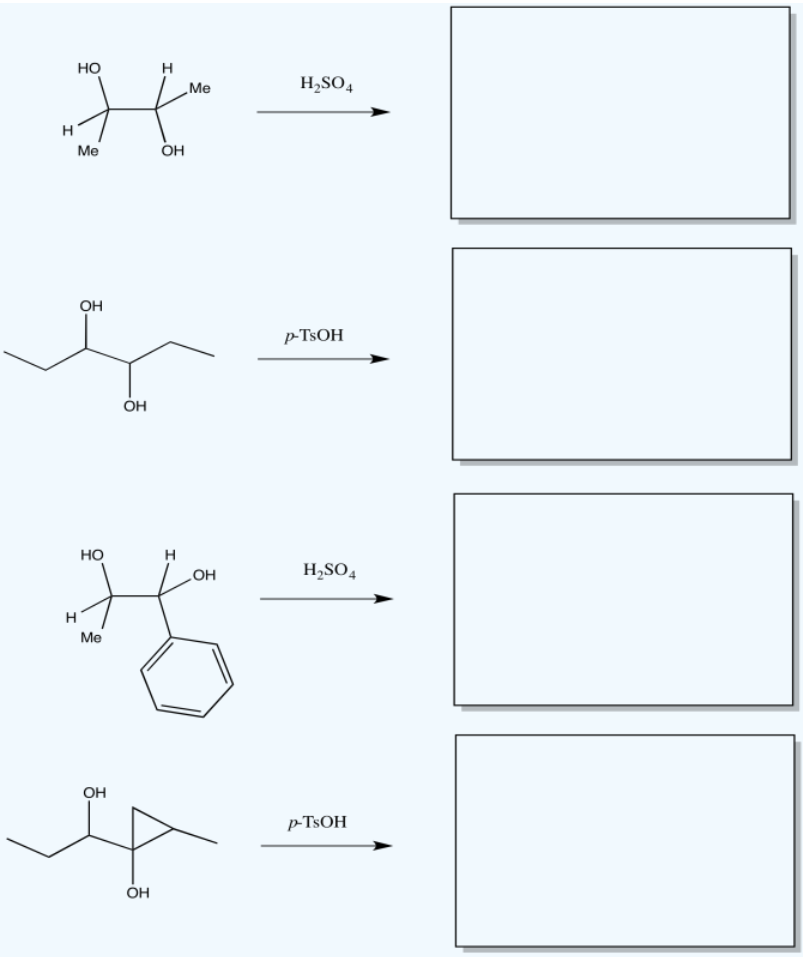
Frequently there is a fine line between alternative reaction pathways. In many cases, the stability of an intermediate determines whether a reaction happens in stages or in one step. If the intermediate is relatively stable, the reaction will happen in steps. The less stable the intermediate, the more likely the reaction will proceed in a concerted manner.



Exercise 11.2.1

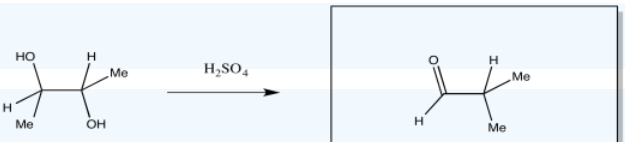
Fill in the products of the following pinacol rearrangements.

https://chem.libretexts.org/@go/page/190074



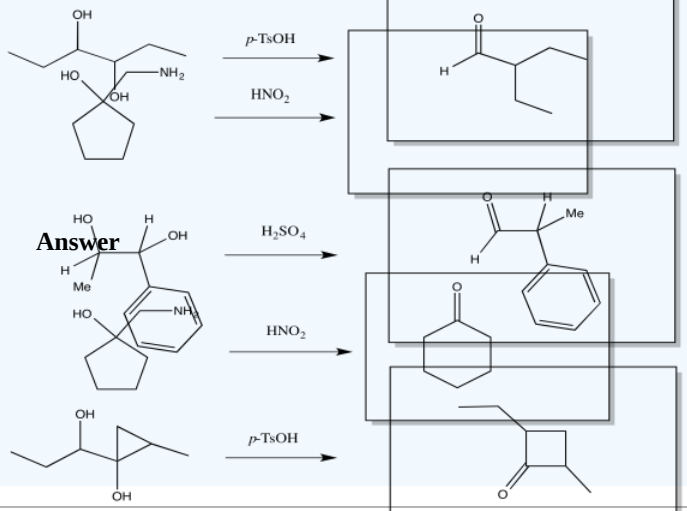
Answer

https://chem.libretexts.org/@go/page/190074



Exercise 11.2.2

The Tiffeneau Demjanov rearrangement is superficially similar to a pinacol rearrangement. It occurs when a β-amino alcohol is treated with nitrous acid. The reaction results in loss of the amino group with rearrangement of the molecule. Predict the product of the reaction.



Answer

This page titled 11.2: Pinacol Rearrangement is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller via source content that was edited to the style and standards of the LibreTexts platform.