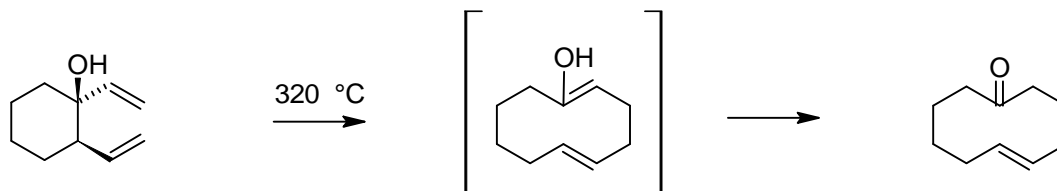


Synthetically interesting variations on Cope rearrangement

Oxy-Cope

Migrating sigma bond is substituted by OH. Initial product is an enol that tautomerizes to ketone. This doesn't affect the rate of the reaction much, but it does make the rearrangement irreversible (and quite sneaky).

Tet. Lett. **1970**, 509

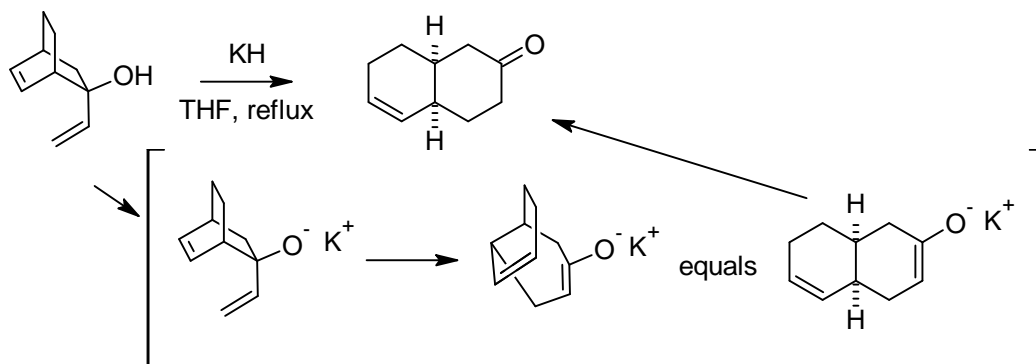


please note: absurd geometry drawn for intermediate/product

Anion-Oxy-Cope

Same as oxy-Cope, but strong base is used to deprotonate OH first. The anion rearranges *very rapidly*, e.g., refluxing THF, and the rearrangement is still irreversible. The product after workup is still a ketone.

JACS **1978**, 100, 8170



The effect of the cation on the reaction rate has been examined. It appears that cations that give more ionic (less covalent) $RO^- M^+$ ion pairs rearrange more quickly. The effect can be quite dramatic with rate enhancements of 10-17 orders of magnitude: 18-c-6(K^+) > K^+ > Na^+ > Li^+ (**18-c-6** is a crown ether that encapsulates potassium ions with 6 oxygen atoms).

JACS **1977**, 99, 4186

