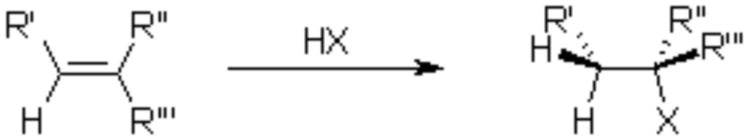
Instructions to the students:

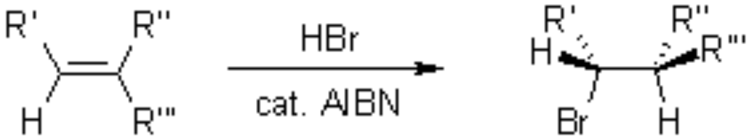
1. Starting January 2026, some questions in chemistry will be posted. The students are to download the questions from the OCS Website and attempt to answer all the questions.
2. They are advised to keep the questions and answer sheets. The OCS may conduct OLYMPIADS for the graduate students.
3. The present questions may be helpful to the students in the Olympiad Examinations.

Q1. Markovnikov's Rule



Markovnikov Rule predicts the regiochemistry of HX addition to unsymmetrically substituted alkenes. The halide component of HX bonds preferentially at the more highly substituted carbon, whereas the hydrogen prefers the carbon which already contains more hydrogens.

Anti-Markovnikov

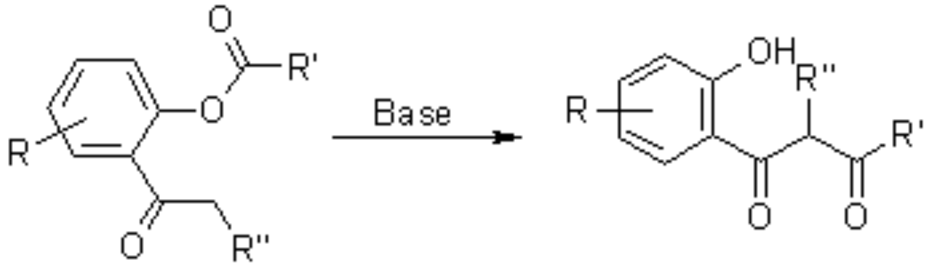


Some reactions do not follow Markovnikov's Rule, and *anti*-Markovnikov products are isolated.

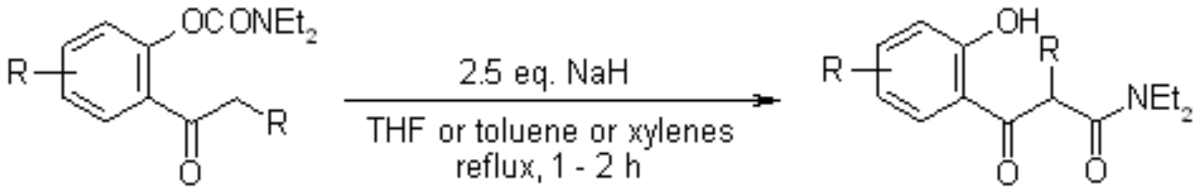
Give the mechanisms of Markovnikov and Anti-Markovnikov Rules.

Q2. The Baker-Venkataraman Rearrangement

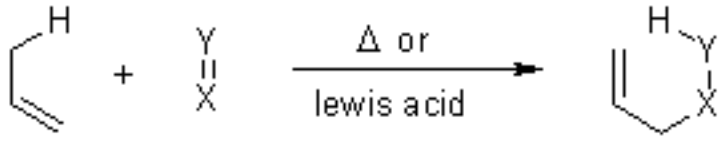
The Baker-Venkataraman Rearrangement is the base-induced transfer of the ester acyl group in an *o*-acylated phenol ester, resulting in a 1,3-diketone. This reaction proceeds through the formation of an enolate, followed by intramolecular acyl transfer



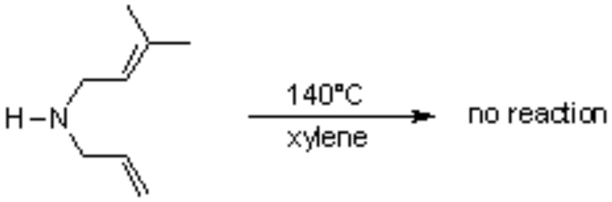
Based on the rearrangement, suggest a mechanism for the following transformation:

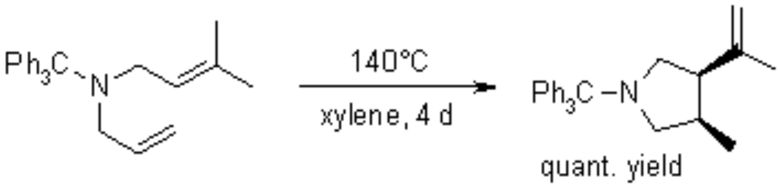


Q3. Alder-Ene Reaction



The four-electron system, including an alkene π-bond and an allylic C-H σ-bond, can participate in a pericyclic reaction in which the double bond shifts and new C-H and C-C σ-bonds are formed.

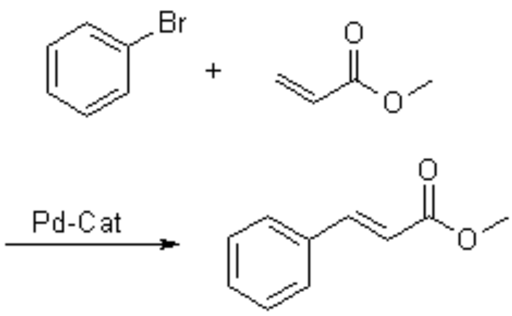




cis-isomer above 95% (NMR)

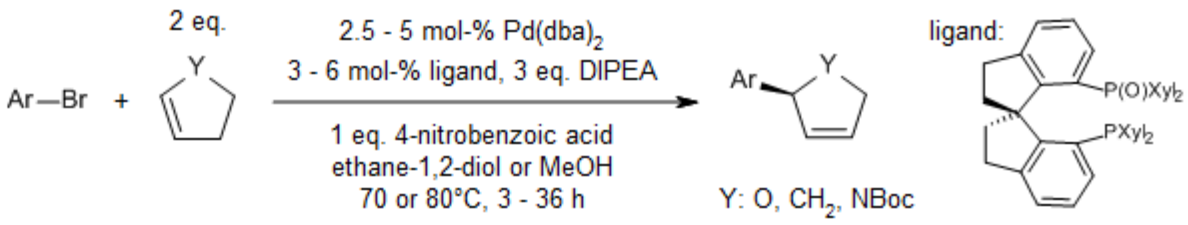
Give the reasons for the above and suggest a mechanism.

Q4. Heck Reaction



The palladium-catalyzed $[Pd(PPh_3)_2]$ C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base is referred to as the "Heck Reaction". One of the benefits of the Heck Reaction is its outstanding *trans* selectivity.

The following is an asymmetric intermolecular Heck Reaction of aryl halides.

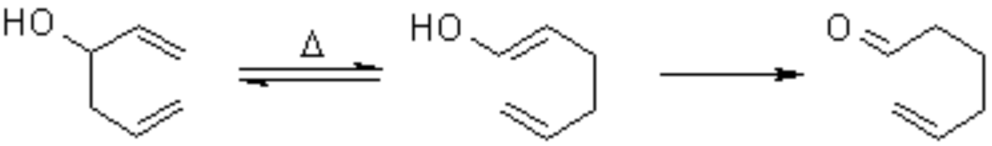


What are $Pd(dba)_2$, DIPEA, and NBoc? Present a mechanism of the reaction.

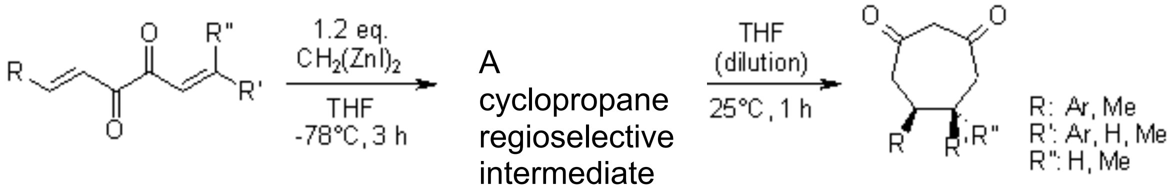
Q5. Cope Rearrangement
(Anionic) Oxy-Cope Rearrangement

The Cope Rearrangement is the thermal isomerization of a 1,5-diene leading to a regioisomeric 1,5-diene. The main product is the thermodynamically more stable regioisomer.

The Oxy-Cope has a hydroxyl substituent on an sp^3-hybridized carbon of the starting isomer.



Based on the above, give the structure of the intermediate and suggest a mechanism for the following :



Recognise the importance of low temperatures (-78 °C) during cyclopropanation to prevent premature Cope rearrangement. Gradual warming to 25 °C promotes the rearrangement efficiently.

OPEN ACCESS SOURCE CREDITS:
https://www.organic-chemistry.org/namedreactions