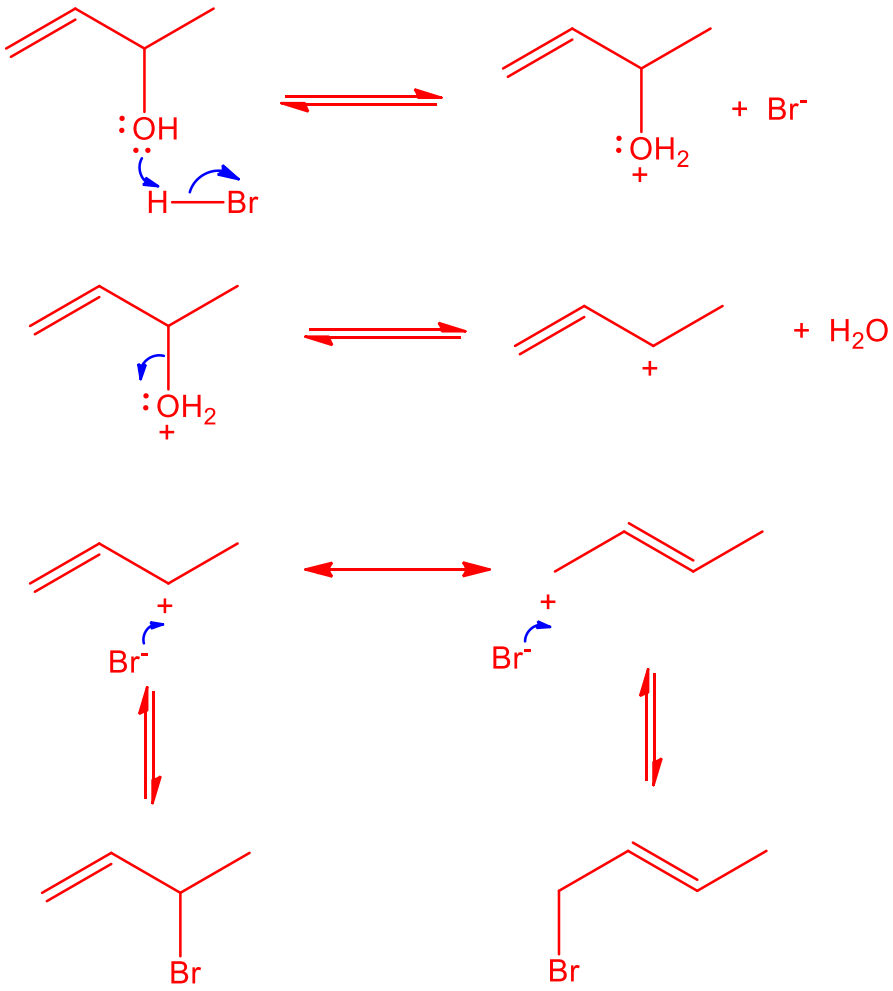
Problem Set 2 – Conjugated Systems

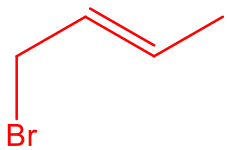
1. 3-Buten-2-ol reacts with cold HBr to give 15% 1-bromo-2-butene and 85% 3-bromo-1-butene. After heating, the major product is 1-bromo-2-butene.

   a. Propose a mechanism to explain the formation of the two products.

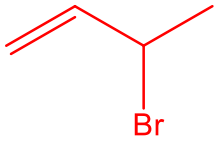


   b. Identify the main product obtained in the reaction that is under thermodynamic control.

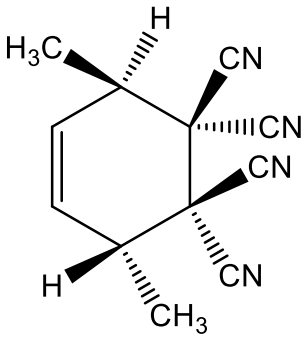
   This is the more stable product which observed after longer reaction times (thereby allowing equilibration to occur) or at higher temperatures:

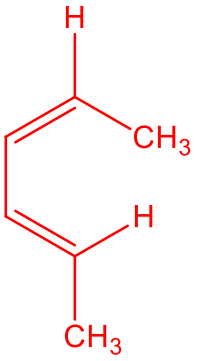


c. Identify the main product obtained in the reaction that is under kinetic control.



2. Identify the diene and the dienophile that you would use to synthesize the following compound:





diene

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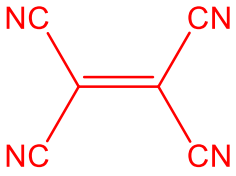
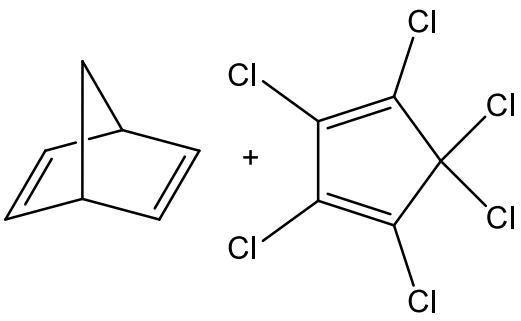
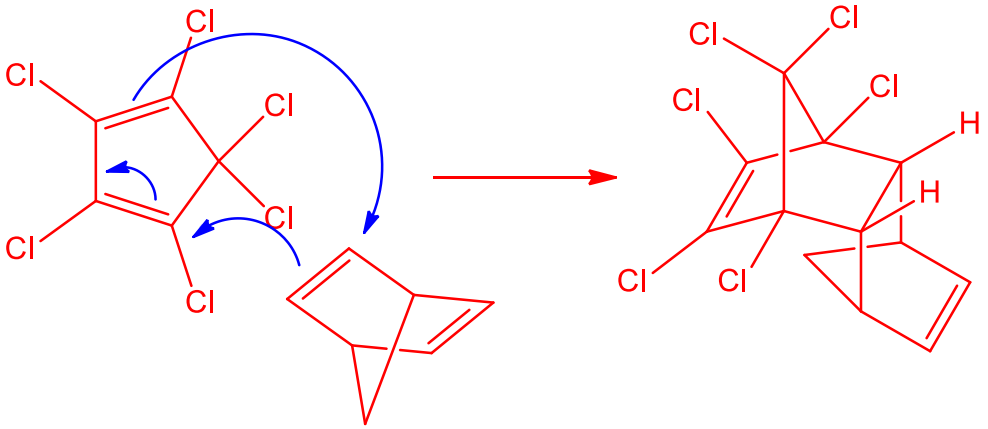


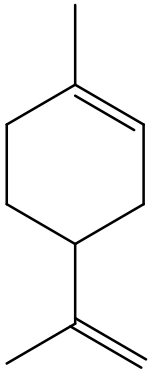
dienophile

3. Draw the structure of the following Diels-Alder reaction:



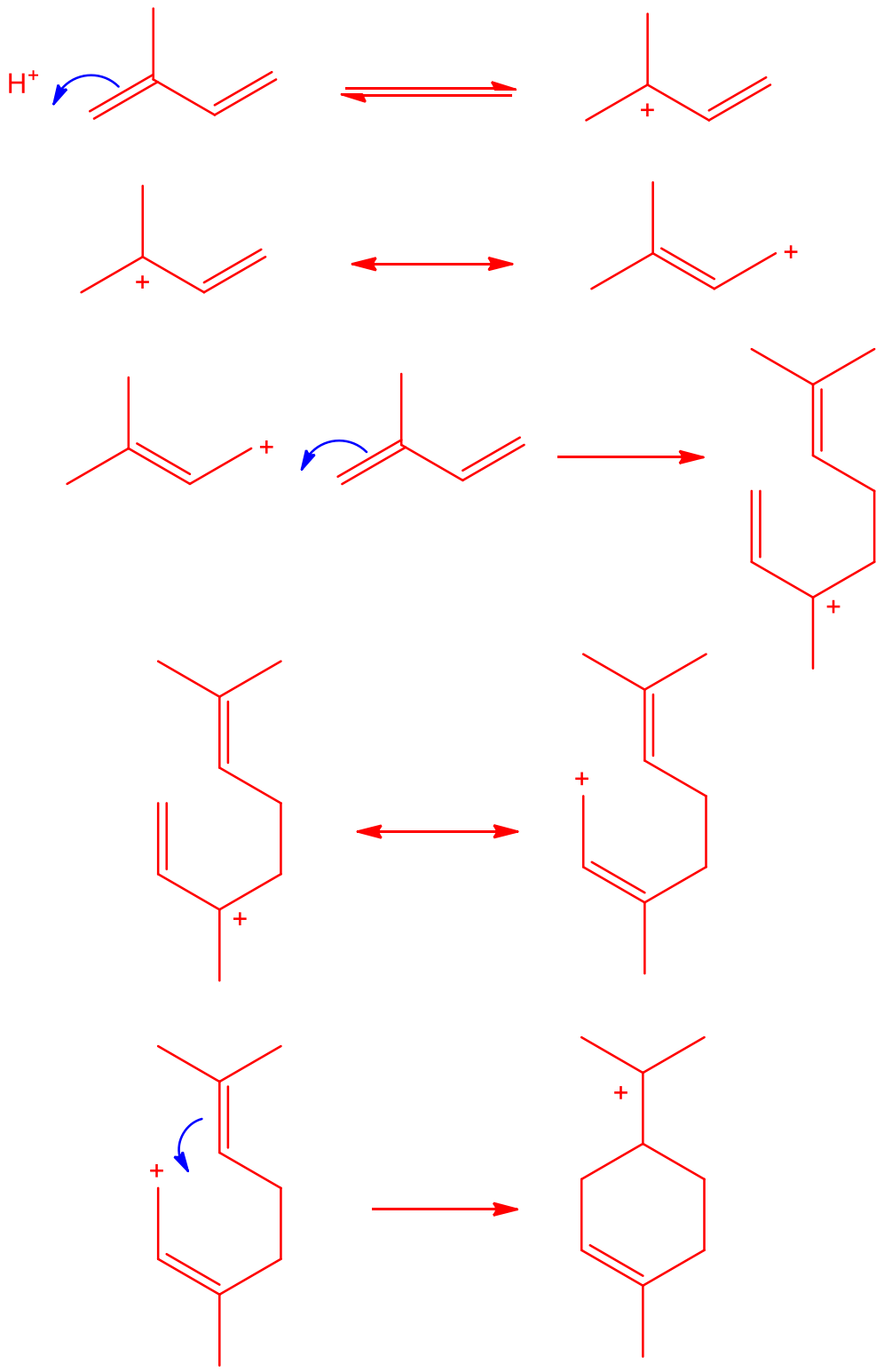


4. Treatment of isoprene (2-methyl-1,3-butadiene) with catalytic amounts of acid leads to a variety of oligomeric products, one of which is limonene:



limonene

a. Devise a detailed mechanism for the acid-catalyzed conversion of two molecules of isoprene into limonene.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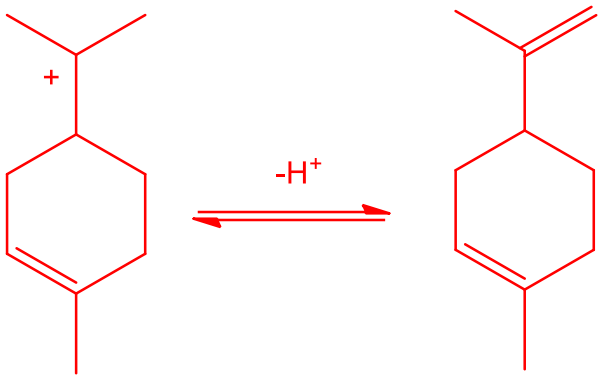
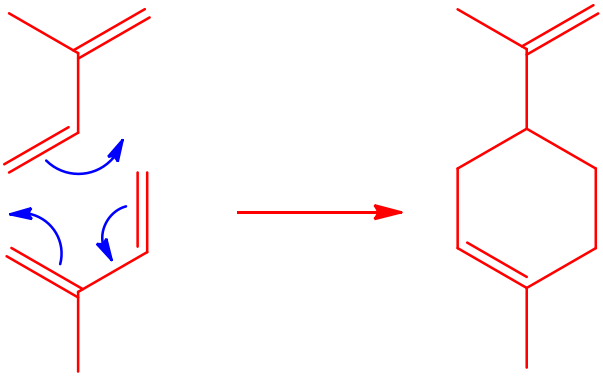


b. Two molecules of isoprene may also be converted into limonene by a completely different mechanism, which takes place in the strict absence of catalysts of any kind. Describe this mechanism.



c. What is the name of the reaction?

The Diels-Alder reaction