University of Missouri-Columbia
Department of Chemistry
Organic Cume, December 9, 2006
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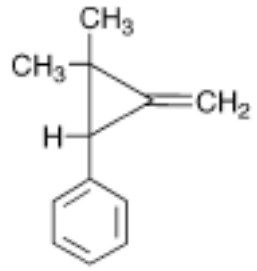
Radical Stabilization

Announced Reading

Creary, X. Super Radical Stabilizers. *Acc. Chem. Res.* **2006**, *39*, 761-771.

Question 1. The 1,1-Dimethyl-2-Methylenecyclopropane Rearrangement. (20 points)

(a) The compound shown rearranges thermally at about 80 °C. Draw the structures of the intermediate and of the product of this reaction.



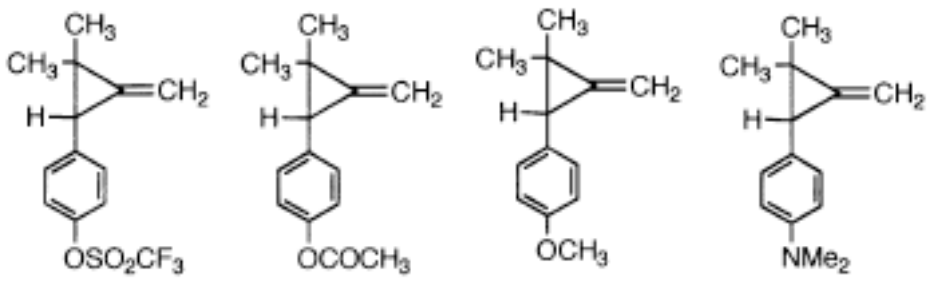
(b) In the *Account*, it is stated that "It is theoretically possible that this reaction is a concerted 1,3-sigmatropic rearrangement proceeding with inversion of stereochemistry at the migrating center." Explain what this means.

Question 2. Synthesis. (20 points)

(a) Suggest a synthesis of the compound shown in Question 1 via carbene addition chemistry to an allene. Give all reagents, specify conditions, catalysts. Argue for the observed preference of the regiochemistry.

(b) Suggest a possible synthesis for 1,1-dimethylallene.

Question 3. *Para*-Substituent Effects. (20 points)



Relative to the rate of rearrangment of the parent compound (see Question 1), indicate whether the above compounds rearrange faster / slower and rank the compounds according to their rates of rearrangement. Briefly explain your answer using resonance structures (show all lone pair, lone electrons, formal and actual charges).

Question 4. Super Radical Stabilizers. (20 points)

Creary discussed three "super radical stabilizers". For two of the three "super radical stabilizers," provide its structure, its name, and explain the electronic mechanism by which the "super radical stabilizers" does its thing.

Question 5. Anionic Radical Stabilizers. (20 points)

(a) Explain how the analysis of the "super radical stabilizers" led to the hypothesis that anionic *para*-substituents might enhance the rate of the rearrangement.

(b) Provide one example of a substrate with an anionic *para*-substituent (draw its structure). Also draw the resulting intermediate and explain the mechanism by which the substituent enhances the rate of reaction (draw resonance forms).

(c) Outline a synthesis for the substrate you cited as an example in (b).