

September 2001 CUME

Organic Chemistry

Department of Chemistry

University of Missouri—Columbia

Saturday, September 8, 2001, @Nine O' Clock, 202 Schlundt

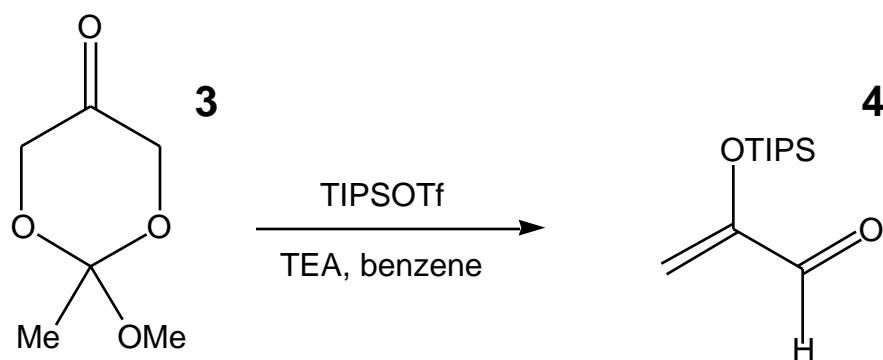
Dr. Rainer Glaser

Announced Reading: "Recent CycLoaddition Chemistry"
60 points to Pass

Question 1. 4+3 Cycloaddition Chemistry. (25 points)

The following questions are based on the lecture by Dr. Harmata in the Organic Chemistry seminar on October 1, 2000. The study has been published, see Harmata, M.; Sharma, U. *Org. Lett.* **2000**, *2*, 2703-2705. All compound numbers are those used in the paper.

(a) The formation of 2-(triisopropylsilyloxy)acrolein **4** was achieved by treatment of the dioxinone **3** with TIPSOTf in the presence of TEA. Provide a mechanism of the formation of **4** from **3** assuming a retro-Diels-Alder reaction. (10 points)



Structure and full name of **TIPSOTf**: (2 p)

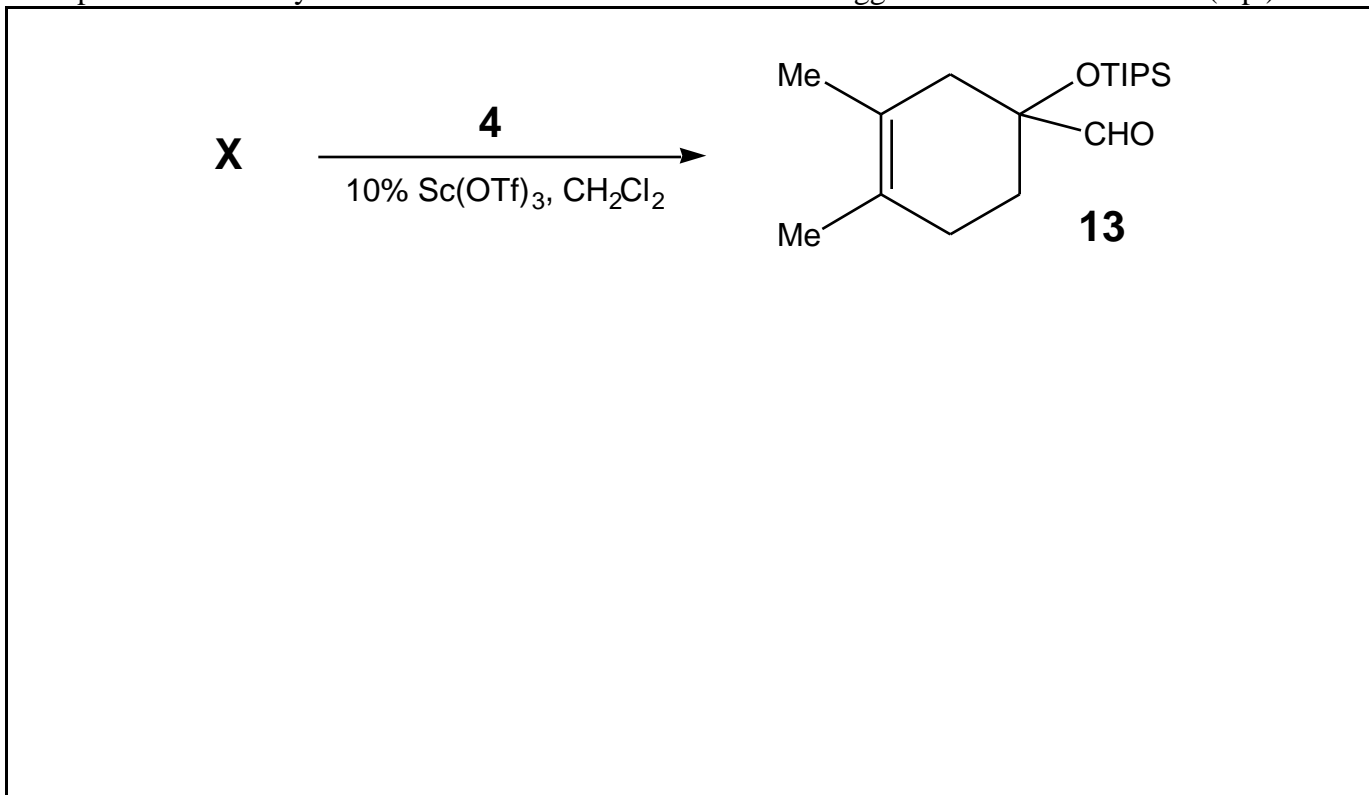
Structure and full name of **TEA**: (2 p)

Mechanism: (8 p)

(b) 2-(Triisopropylsilyloxy)acrolein, **4**, undergoes 4+3 cycloaddition to furan in 90% yield in the presence of 10% Sc(OTf)₃ in methylenechloride. Provide the structure of the cycloaddition product and suggest a likely reaction mechanism for the formation of the cycloaddition product. (8 points)

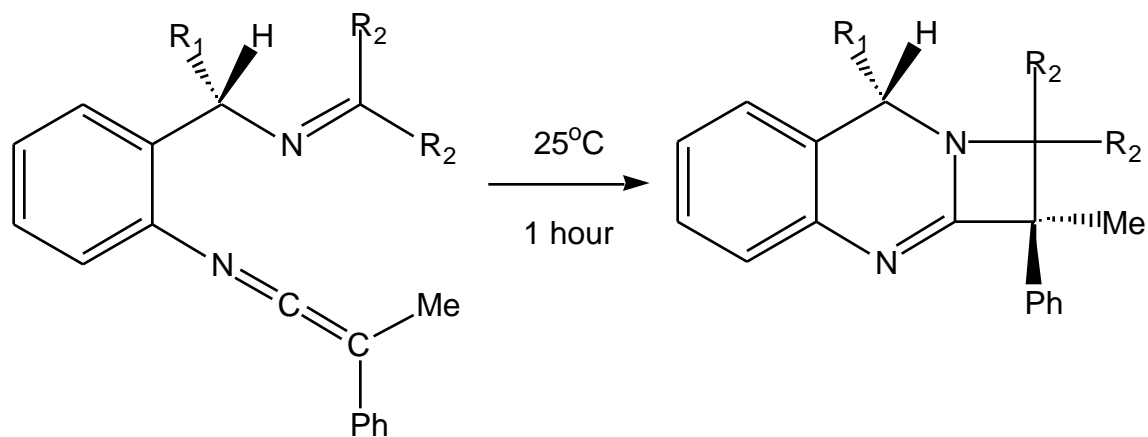


(c) The reaction of **X** with **4** in the presence of 10% Sc(OTf)₃ in CH₂Cl₂ resulted in the formation of compound **13** in low yield. Provide the structure of the **X** and suggest how **13** was formed. (7 p.)



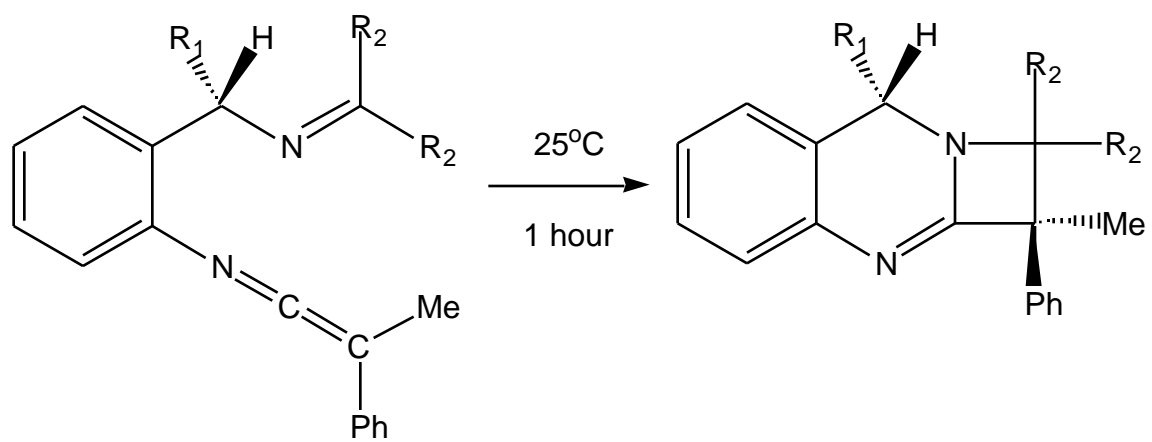
Question 2. 2+2 Cycloadditions between Ketenimines and Imines. (15 points)

This question is based on a paper published in the *Journal of Organic Chemistry* under the title “New Stereoselective Intramolecular [2+2] Cycloadditions between Ketenimines and Imines on an *ortho*-Benzylic Scaffold: 1,4-Asymmetric Induction.”; see Alajarin, M. et al. *J. Org. Chem.* **2000**, *65*, xxx-xxx.



The reaction is stepwise. First, the imine N atom adds to the ketenimine to form a zwitterion. Next, the zwitterion is transformed into the cycloadduct by electrocyclic reaction. Show this mechanism on the following page. Below, argue whether the electrocyclic reaction involves a conrotatory or a synrotatory ring closure.

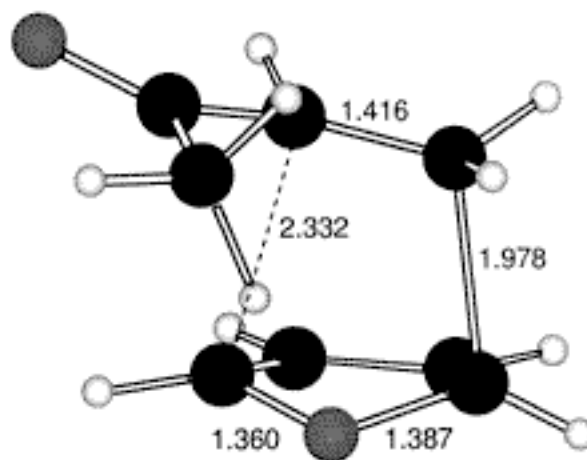
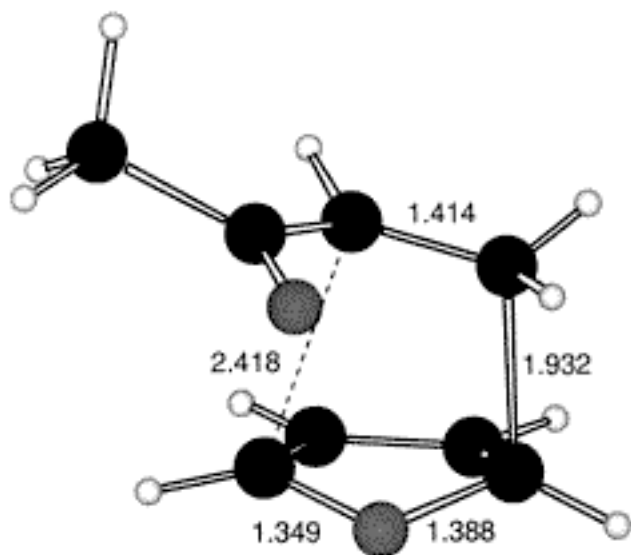
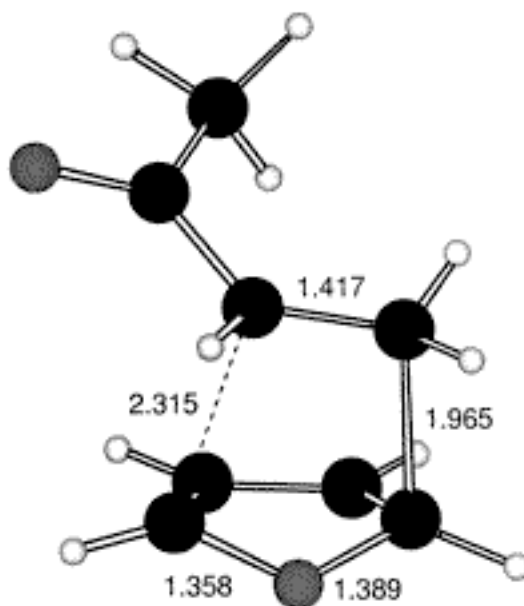
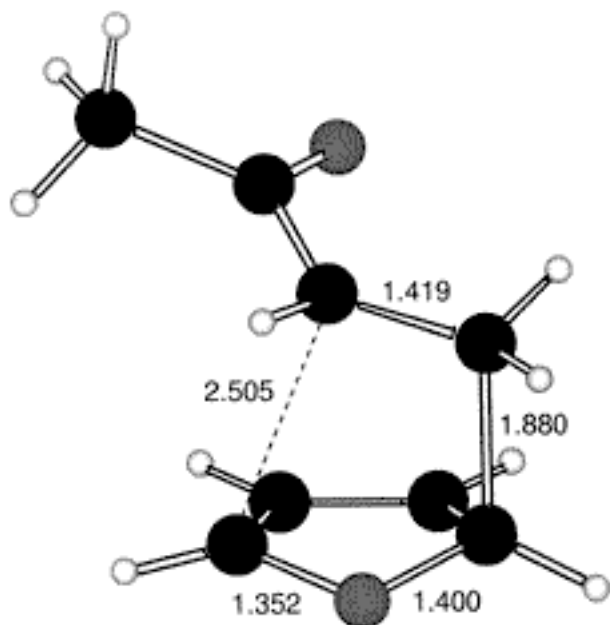
Conrotatory or synrotatory?



Mechanism:

Question 3. Transition States of Cycloaddition of Furan with Methyl Vinyl Ketone. (30 points)

This question is based on a paper published in the *Journal of Organic Chemistry* under the title “Computational Studies on the BF_3 -Catalyzed Cycloaddition of Furan with Methyl Vinyl Ketone: A New Look at Lewis Acid Catalysis.”; see Babiano, R. et al. *J. Org. Chem.* **2000**, *65*, 6613-6619.



(a) The reaction between furan and methyl vinyl ketone may involve four possible transition states. The approach of the diene with respect to the carbonyl group of the dienophile can be *endo or exo*. And the conformation of the methyl vinyl ketone can be *s-cis or s-trans*. The computed transition states for these four situations are displayed on the previous page. For each TS, clearly indicate whether it is *endo or exo* and *s-cis or s-trans*. (8 points)

(b) Draw the products obtained by the reactions via the 4 transition states shown on the previous page. Draw the products in the corresponding quadrant; top left TS gives top left product etc. (12 points)

(c) Note that one CC bond is much shorter than the other CC bond in all of the transition state structures shown in (a). Explain this structural feature. Keep it simple. [Why are the CC bonds not about equal? Or why are the relative bond lengths not the other way around?] (10 points)

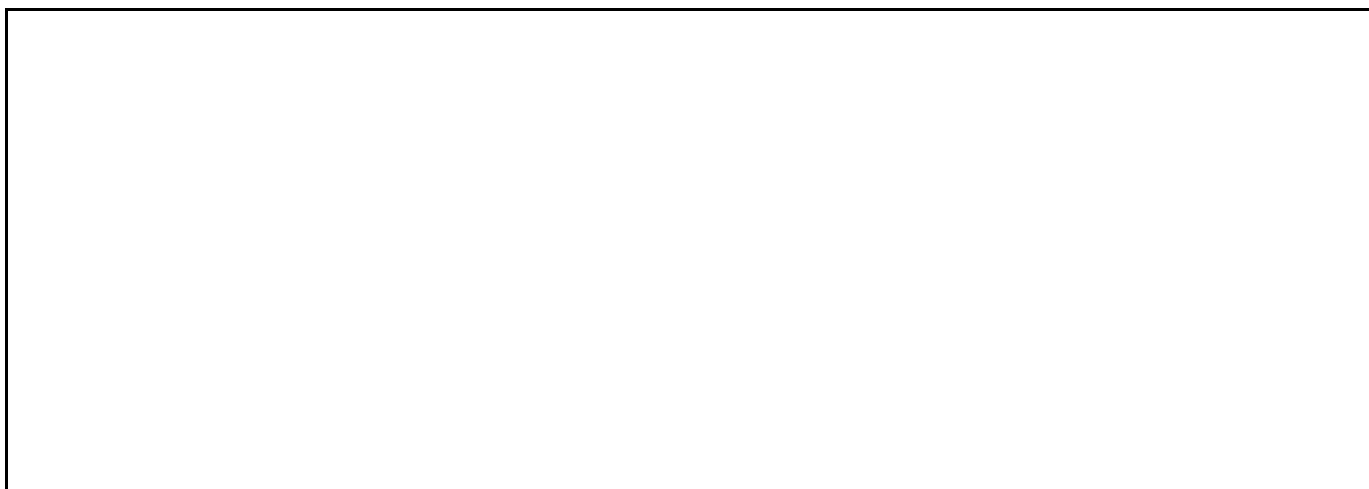
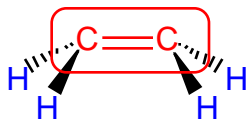
Question 4. 2+2 Cycloaddition Chemistry with Semiconductor Surfaces. (30 points)

The following questions are inspired or based on an account in the September 2000 issue of *Accounts of Chemical Research* with the title “Cycloaddition Chemistry of Organic Molecules with Semiconductor Surfaces”; see Greenlief, M. C. et al. *Acc. Chem. Res.* **2000**, 33, 617-624.

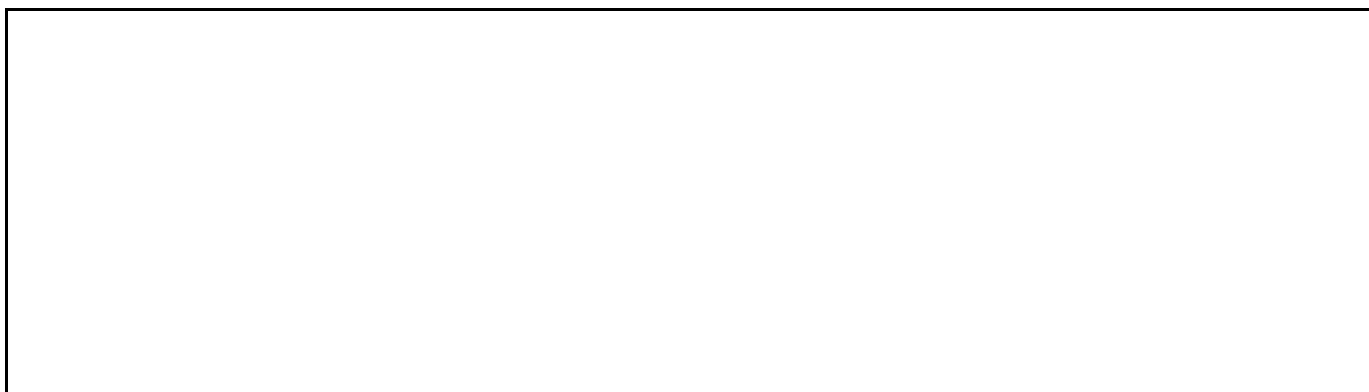
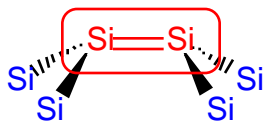
(a) Draw the σ - and π^* -MOs of ethene for the (planar) equilibrium structure of ethene. Of course, the hybridization at C is _____. (5 points)



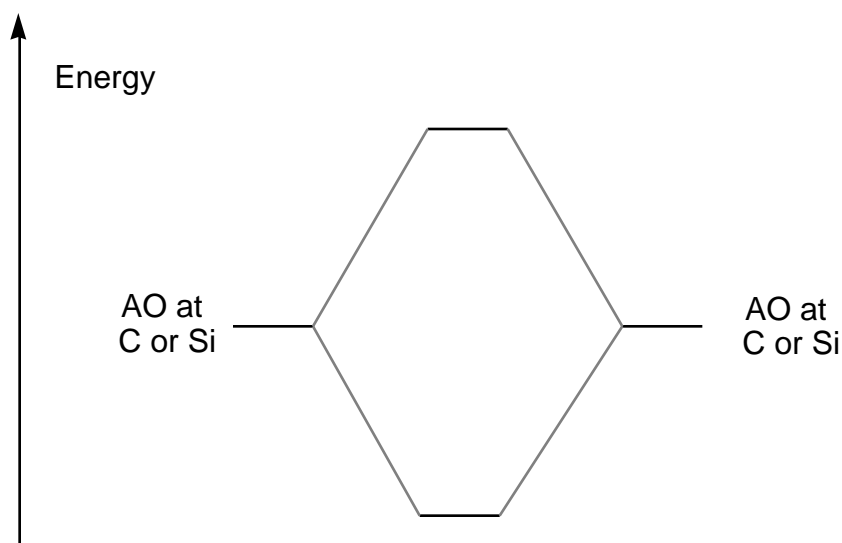
(b) Imagine that ethene is being distorted as shown, both C-atoms are pyramidal and the molecule maintains one plane of symmetry (the plane of the paper). Now the hybridization at the C-atoms is sp^n where n is greater than 2. For simplicity, let's just assume that the C-atom hybridization now is sp^3 . Draw the σ - and the π^* -MOs of this distorted structure of ethene. (5 points)



(c) The (001) surface of silicon contains units that look very much like distorted silenes. The red silicon atoms are exposed on the surface and these so-called Si-dimers are connected to the blue tetravalent Si atoms in the bulk Si crystal. Draw the “ σ ”- and the “ π^* ”-MOs of this Si dimer. For simplicity, let's assume again that the Si-atom hybridization is sp^3 . (5 points)



(d) The diagram shows the relative positions of the σ - and π^* -MOs of ethene in its equilibrium structure relative to the AOs. Indicate schematically where you would expect to find the “ σ ”- and the “ π^* ”-MOs of the distorted ethene, as in (b), and the “ σ ”- and the “ π^* ”-MOs of this Si dimer, as in (c). (5 points)



(e) The thermal 2+2 reaction between ethene and cyclopentene is symmetry-forbidden and does not occur. On the other hand, the thermal 2+2 reaction between the Si-dimers on the (001) surface of silicon and cyclopentene occurs readily. Explain. (10 points)

