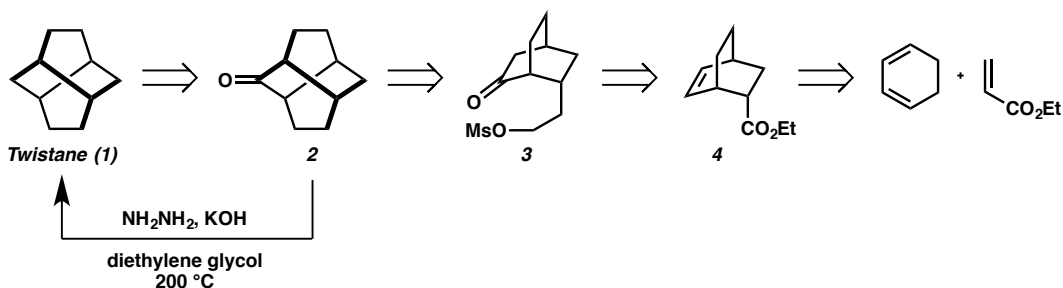


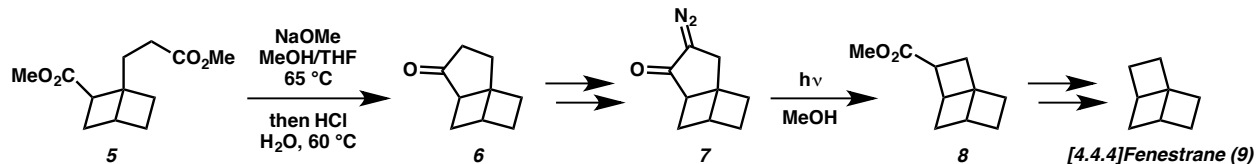
Attempt all questions. Present your answers **clearly** and **legibly** in the order that they appear below. Label each section in your answer book according to the problem numbering. **(100 total points)**

Structurally complex organic hydrocarbons present particularly interesting synthetic challenges owing to the lack of functional groups to serve as synthetic “handles.” A great deal of effort has been directed toward the preparation of highly strained and highly symmetrical hydrocarbons that test the limits of C–C bond formation. Consider the following transformations that have been employed in the course of these endeavors.

1. Most syntheses of hydrocarbons rely on the strategic addition of functional groups in the retrosynthetic analysis to facilitate bond construction. A consequence of this strategy is that these functional groups must be removed to access the final hydrocarbon. For example, Whitlock’s synthesis of twistane (**1**) involves a straightforward enolate alkylation and Diels–Alder reaction to construct the carbon skeleton. Deletion of the carbonyl in ketone **2** under the shown conditions was the final step of the synthesis. (*J. Am. Chem. Soc.* **1962**, *84*, 3412)



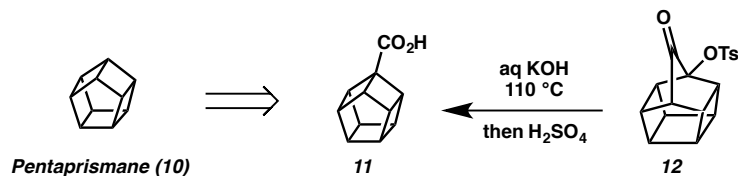
- Provide a detailed arrow-pushing mechanism for conversion of ketone **2** into twistane (**1**). **(12 points)**
  - What is the name associated with this reaction? **(2 points)**
  - Suggest an alternative method to reduce ketone **2** to the saturated hydrocarbon (you may use multiple steps). **(5 points)**
  - Suggest conditions to convert ester **4** into ketone **3** (multiple steps are required). **(18 points)**
2. Ring contractions are a powerful method for generating strained, small-ring compounds. This is particularly useful when coupled with well-established methods of ring closure. An example of such a sequence is found in Wiberg’s synthesis of [4.4.4]fenestrane (**9**). (*J. Am. Chem. Soc.* **1980**, *102*, 7467)



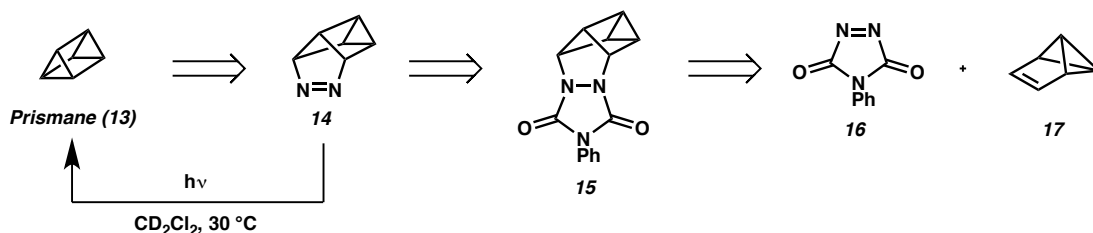
- Provide a detailed arrow-pushing mechanism for the cyclization of diester **5** to cyclopentanone **6**. **(12 points)**
- What is the name associated with the reaction in part a? **(2 points)**
- Provide a detailed arrow-pushing mechanism for photochemical ring contraction reaction of diazoketone **7** to ester **8**. **(12 points)**
- What is the name associated with the reaction in part c? **(2 points)**

(over)

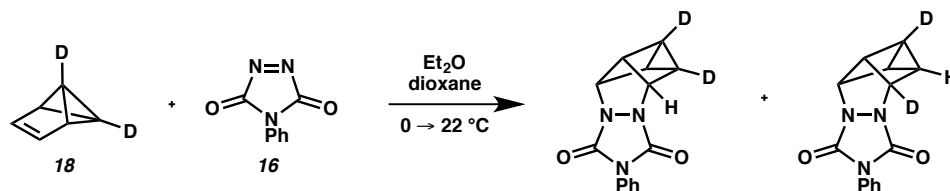
3. A related ring contraction reaction was used by Eaton toward the synthesis of pentaprismane (**10**). In this case a diazoketone could not be used due to the tertiary centers flanking the carbonyl.  
(*J. Am. Chem. Soc.* **1981**, *103*, 2134)



- Provide a detailed arrow-pushing mechanism for ring contraction reaction of tosylate **11** to acid **12** under basic conditions. (12 points)
  - What is the name associated with this reaction? (2 points)
4. Katz described the first synthesis of prismane (**13**) utilizing azo intermediate **14** as a precursor. This azo compound was prepared readily using a remarkable transformation of the strong electrophile 4-phenyltriazolinedione (**16**) and benzvalene (**17**), another highly strained hydrocarbon which Katz had synthesized in 1971. Although prismane and benzvalene are constitutional isomers and both are very strained, prismane is considerably more stable as a pure compound.  
(*J. Am. Chem. Soc.* **1973**, *95*, 2738)



- Provide a detailed arrow-pushing mechanism for conversion of diazene **14** into prismane (**13**). (9 points)
- The azo compound precursor **15** was prepared in one step from 4-phenyltriazolinedione (**16**) and benzvalene (**17**). To understand the mechanism of this transformation, deuterated benzvalene isotopologue **18** was employed, leading to the indicated deuterated products:



Taking this result into account, provide a detailed arrow-pushing mechanism for reaction of 4-phenyltriazolinedione (**16**) and benzvalene (**17**) to form the adduct **15**. (12 points)