

2<sup>ND</sup> YEAR ORGANIC PROBLEM CLASSES 2004/2005

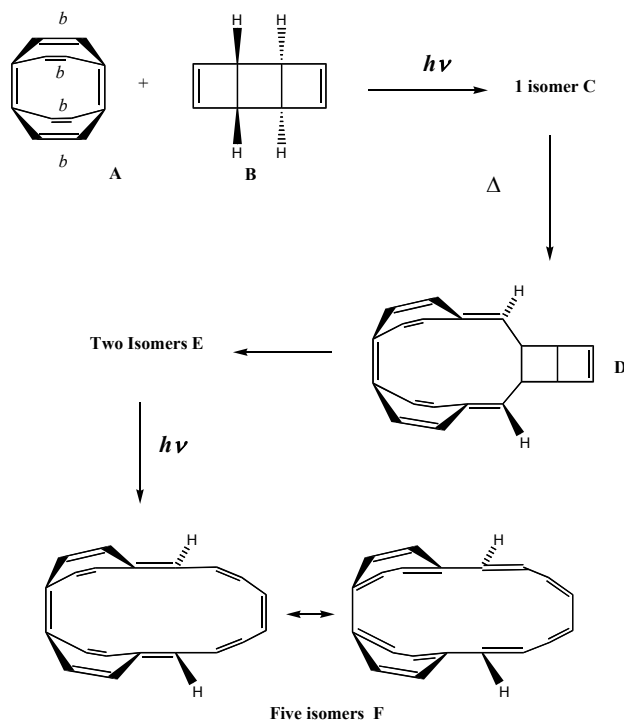
## Class 6. Prof Henry Rzepa &amp; Dr Alan Spivey – Pericyclics &amp; Stereoelectronics

Class to be held at 3pm on Monday 25<sup>th</sup> April 2005 in normal tutors groups

Answers to be handed in to Prof Rzepa's office – C1 Rm 169 before 3 pm on the day of the class. Late scripts will receive no credit.

Please write your own name AND YOUR TUTORS NAME on your script.

1. The following sequence of reactions starting from compounds **A** and **B** was recently reported as the culmination of a "holy grail" target in chemistry.



NB. The four bonds marked *b* are in fact benzo derivatives of the alkene, not shown below to retain clarity in the diagram.

Reaction *via* intermediates **C** and **D** led to an isolable mixture of two isomers **E** (each showing the presence of six alkene C-H <sup>1</sup>H resonances, as well as aromatic resonances resulting from the benzo groups), one of which was claimed to have a structure with an C<sub>2</sub> axis of symmetry and the other a plane of symmetry. Further gentle irradiation led to an equilibrium mixture of five isomers of the [16]-annulene **F**. One of these, after separation by HPLC, proved to be the long sought molecule (which exhibited a C<sub>2</sub> axis of symmetry).

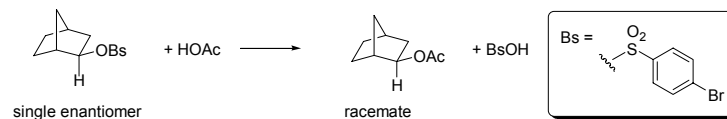
Suggest mechanisms for the various transformations, possible structures for the intermediates **C**, **E** and (only one of) **F** and discuss why a [16]-annulene with a two-fold axis of symmetry might arouse such interest.

[25 marks]

*Hint:* The stereochemistry of the intermediates may not always be unambiguous or necessarily follow selection rules, a point which you might wish to discuss.

2. Answer **ALL THREE** parts of this question.

(a) Consider the following substitution reaction:



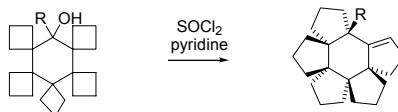
(i) Explain why the product is formed as a racemate.

[5 marks]

(ii) If the carbon atom to which the brosylate (OBs) group is attached had been <sup>13</sup>C labelled what product(s) would be formed?

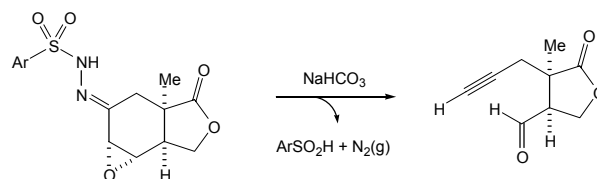
[5 marks]

(b) Write a mechanism for the following transformation:



[5 marks]

(c) The Eschenmoser fragmentation shown below was reported in 1975 by Corey.



(i) Draw a mechanism for this transformation.

[5 marks]

(ii) Draw diagrams of the fragmentation process with the key bonds highlighted, and show the orbitals that are involved.

[5 marks]

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