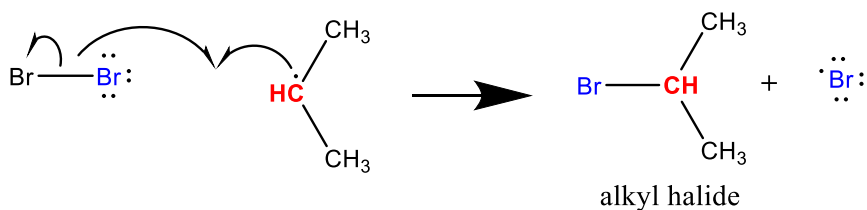
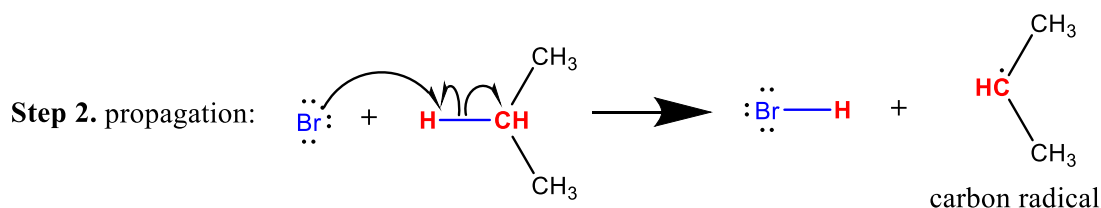
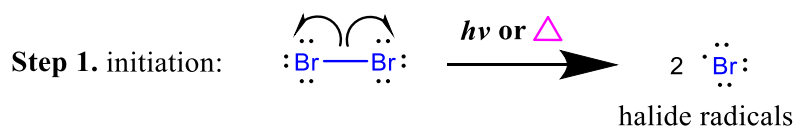
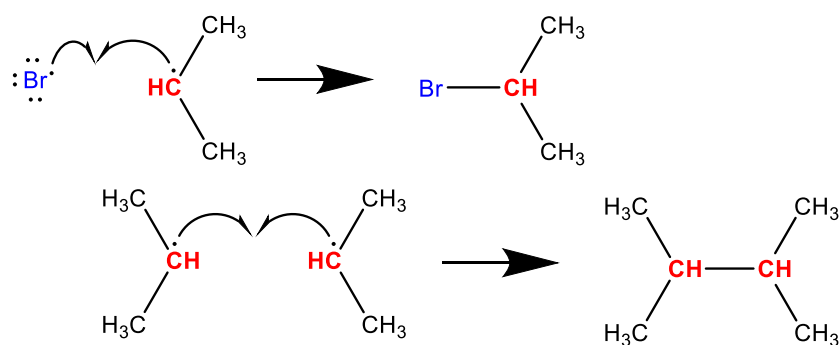


REACTANT(S)	REAGENT(S)	PRODUCT(S)
<p><b>Alkane Radical Halogenation</b> (adding X to an alkane):</p> <p><math>\text{H}-\text{C}(\text{R})_3 + \text{X}_2</math> (X = Cl or Br) (R = H or C group)</p>	<p><math>h\nu</math> or <math>\Delta</math> or ROOR</p>	<p>+ HX</p> <p>X goes on the most stable, or substituted, C. This is always true for X=Br. For X=Cl, you sometimes get a mixture of products. (See below.)</p>

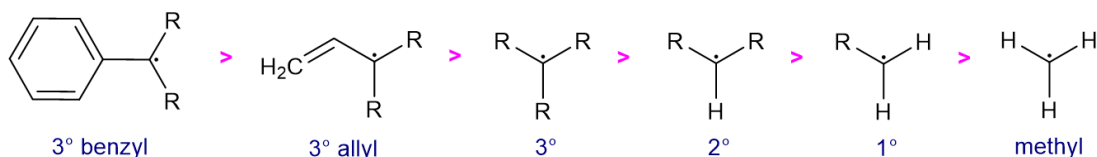
**Mechanism:**



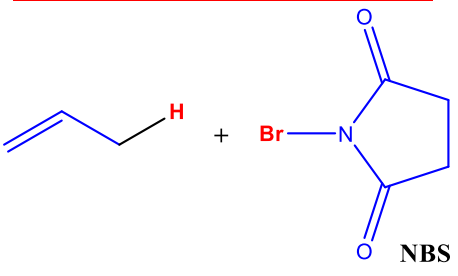
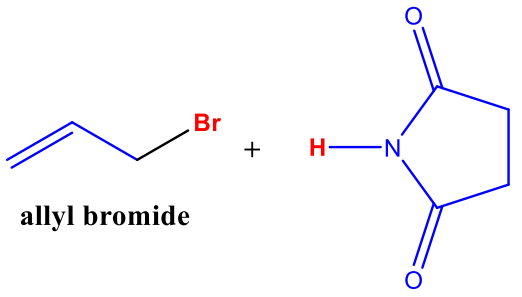
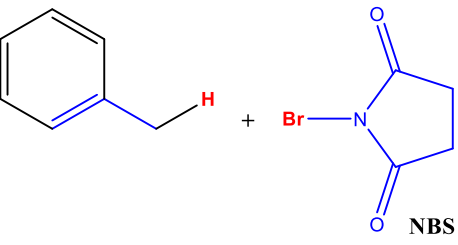
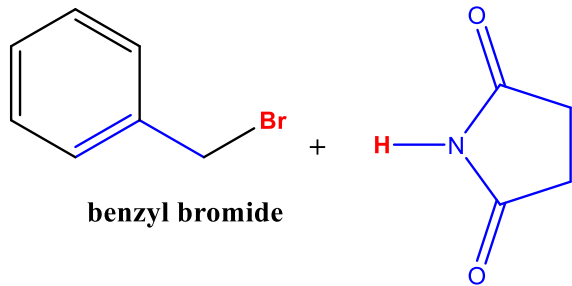
Step 3. termination steps (these get rid of radicals):



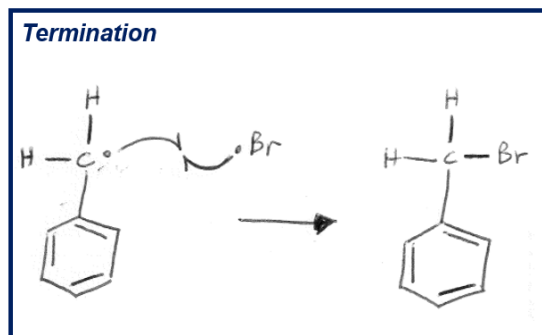
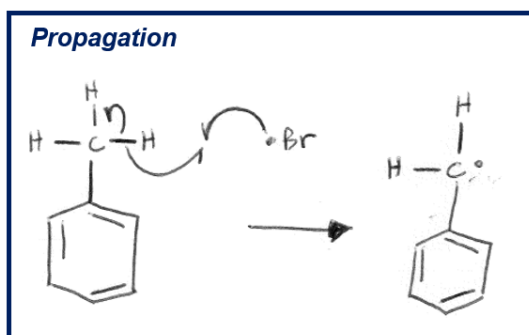
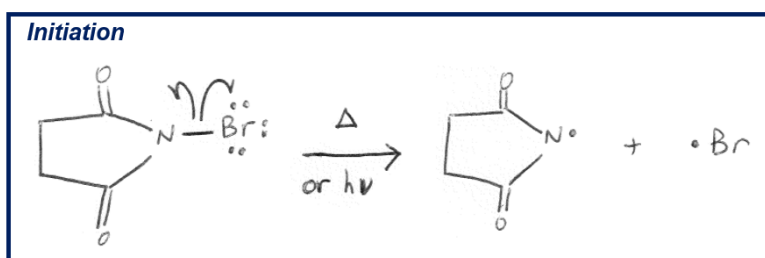
Br **always** ends up on the most substituted C, or (if applicable) on a resonance-stabilized C, due to radical stability (see below). Cl is less selective and sometimes gives mixtures of products.



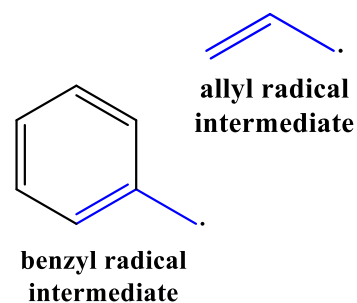
←  
**increasing radical stability**

REACTANT(S)	REAGENT(S)	PRODUCT(S)
<p><b>Radical bromination with NBS:</b></p>  <p>allyl bromide + NBS</p>	<p><math>h\nu</math> or <math>\Delta</math> or ROOR</p>	 <p>allyl bromide + NBS</p> <p><b>NBS adds to the carbon that's <u>one position away from the double bond</u> (the <b>allylic</b> carbon).</b></p>
 <p>benzyl bromide + NBS</p>	<p><math>h\nu</math> or <math>\Delta</math> or ROOR</p>	 <p>benzyl bromide + NBS</p> <p><b>NBS adds to the carbon that's <u>one position away from the double bond</u> (the <b>benzylic</b> carbon).</b></p>

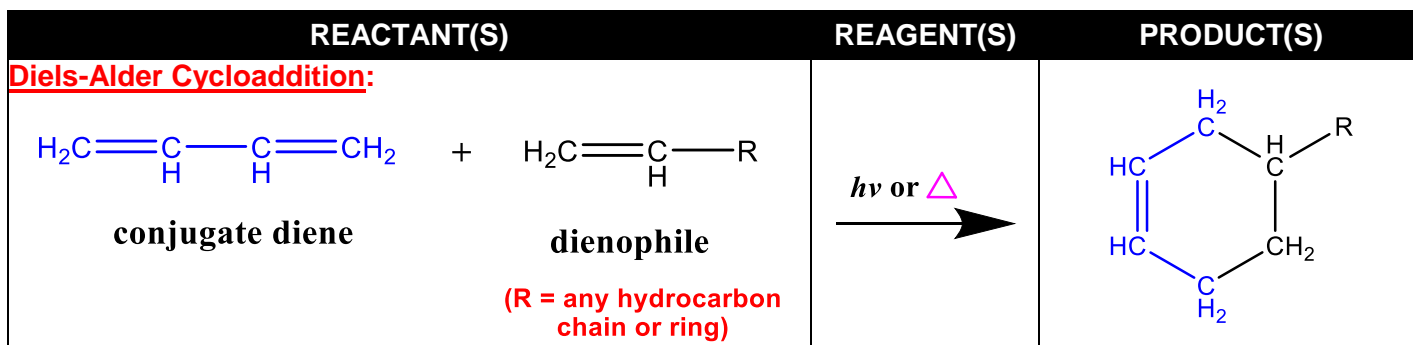
**Mechanism:**



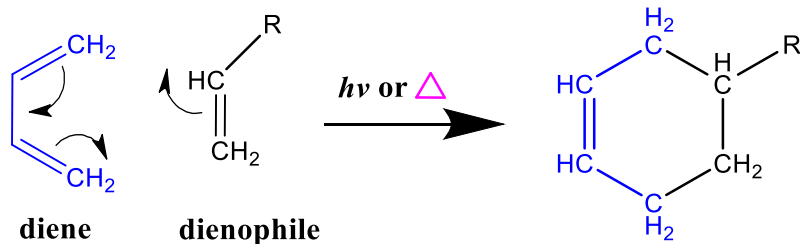
**NBS** adds to the carbon that's one position away from the double bond (the **allylic** carbon) because that's where the most stable **radical** is located. Allylic radicals are stabilized by resonance delocalization:



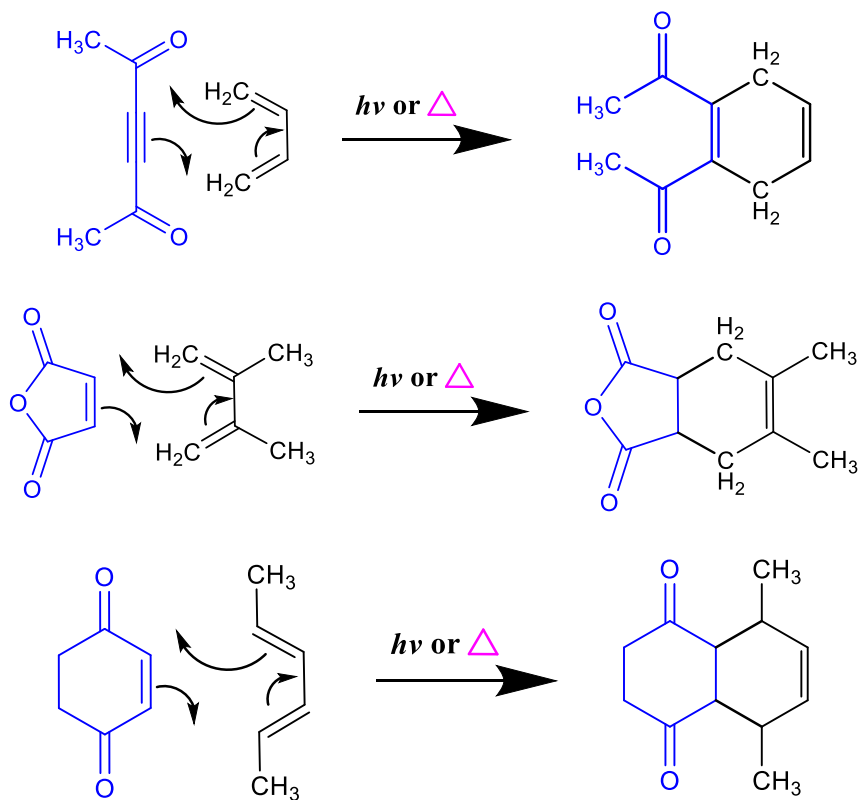
**NBS** adds to the carbon that's one position away from the double bond (the **benzylic** carbon) because that's where the most stable **radical** is located. Benzylic radicals are stabilized by resonance delocalization:

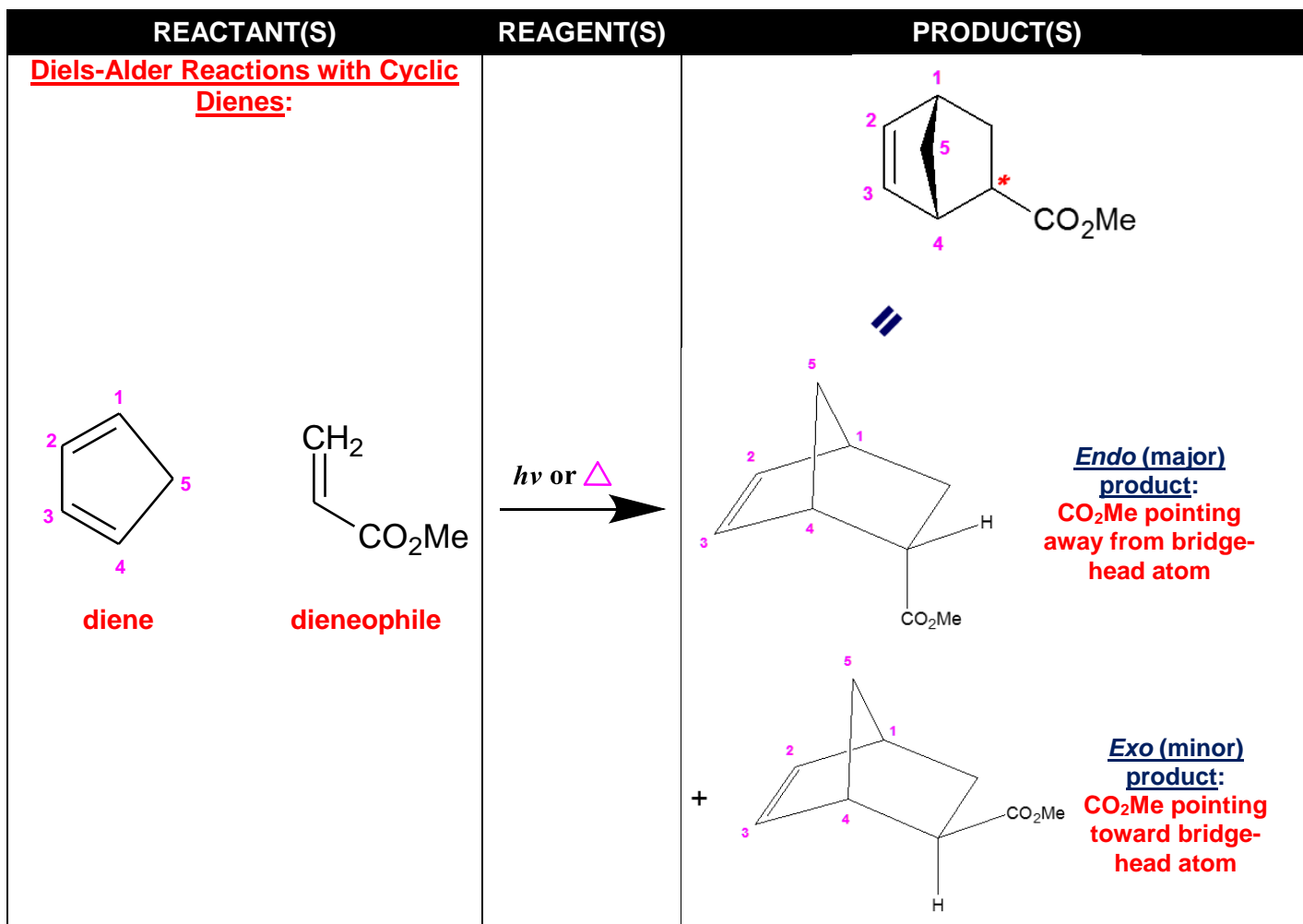


**Mechanism:**

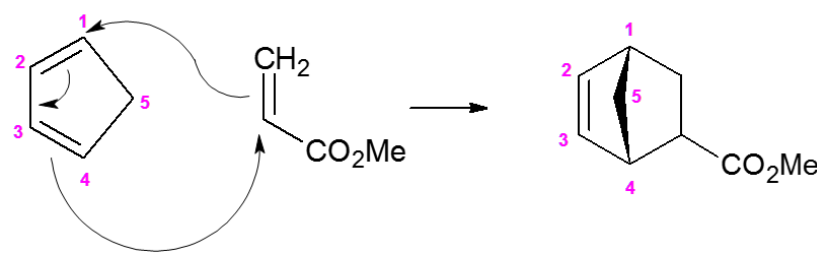


**Examples:**

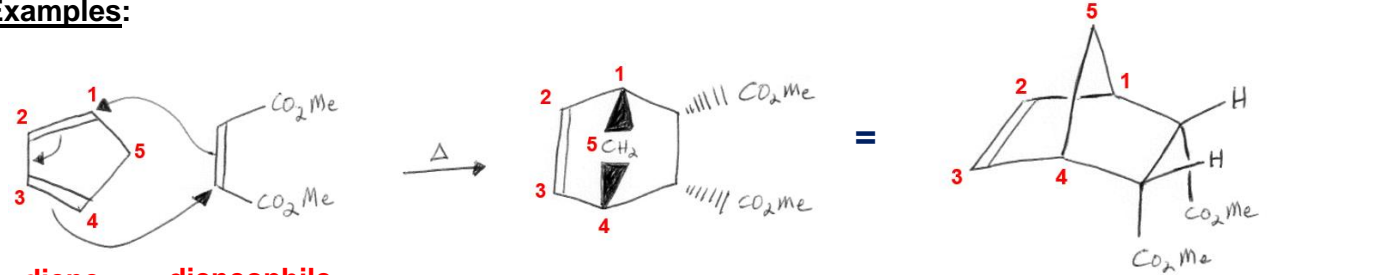




**Mechanism:**

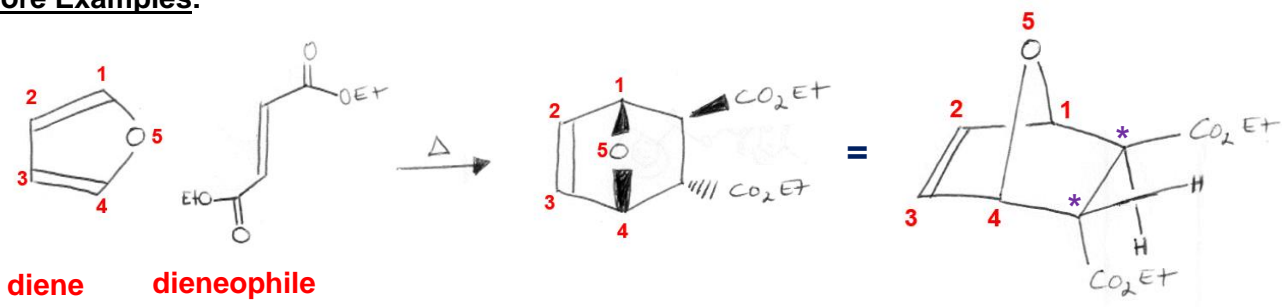


**Examples:**

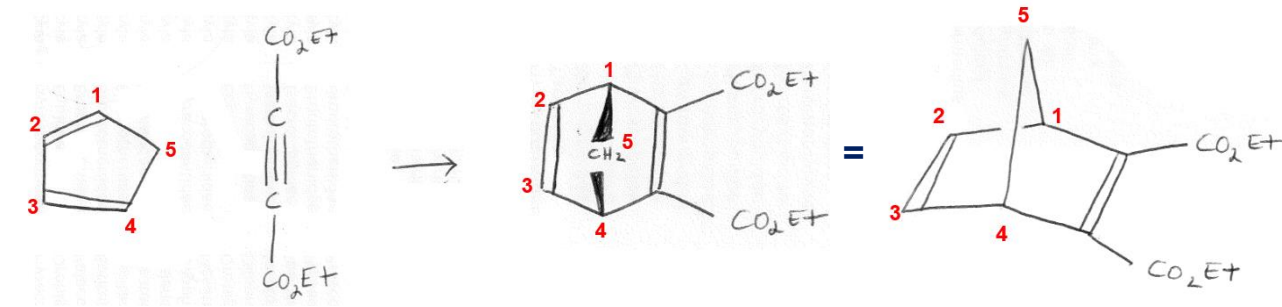


**Endo (major) product:**  
CO<sub>2</sub>Me's pointing away from bridge-head atom – CO<sub>2</sub>Me's both go in the same direction in the product because they are *cis* to each other in the original dieneophile.

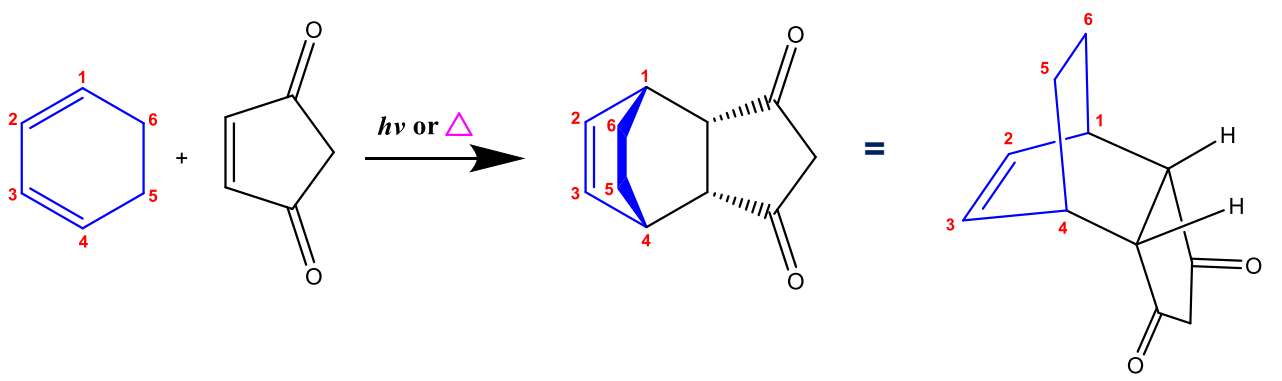
**More Examples:**



**Endo product is not possible:**  
 Because the CO<sub>2</sub>Me's are *trans* to each other in the original dieneophile, they end up *trans* in the product – not possible to have both CO<sub>2</sub>Me's pointing away from the bridgehead atom. Reversed isomer at the \* positions will also be formed.



**Endo product is not possible:**  
 Because the dieneophile is an alkyne, the product has a C=C bond where the CO<sub>2</sub>Et groups are – not possible to have CO<sub>2</sub>Et's pointing away from the bridgehead atom, due to planar geometry around C=C.



**Endo (major) product:**  
 Because the diene here has 6 C's, the product has a two-carbon bridge – as usual, the major *endo* product has its lower ring pointing away from the bridge. The *exo* (minor) product is not shown.