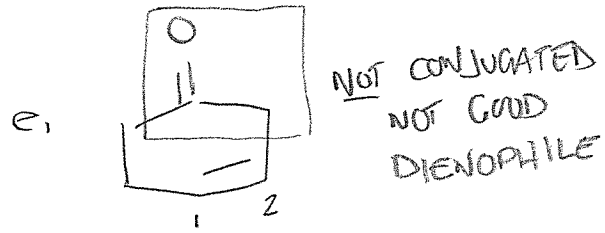
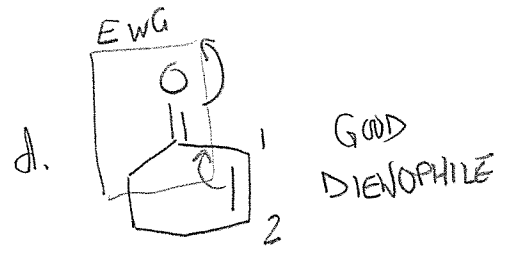
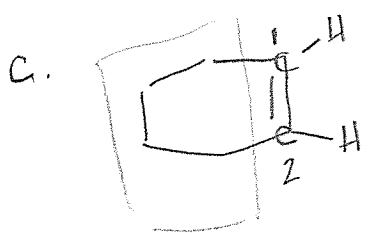
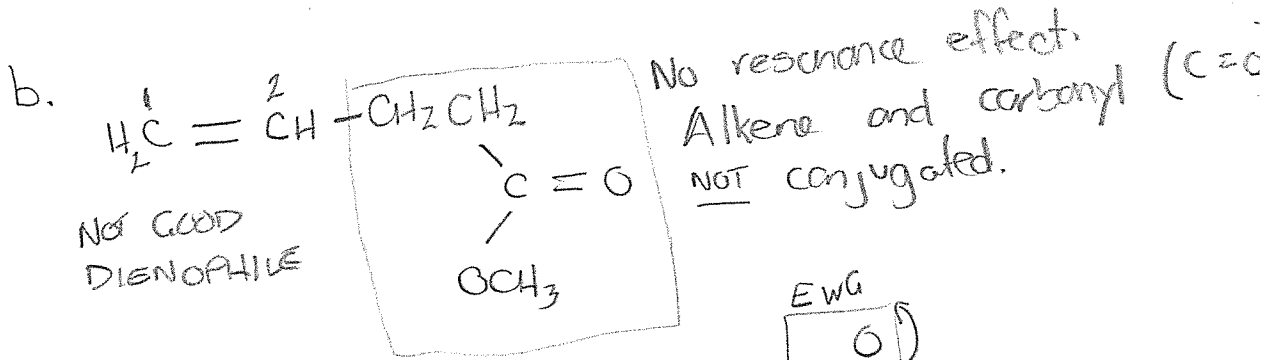
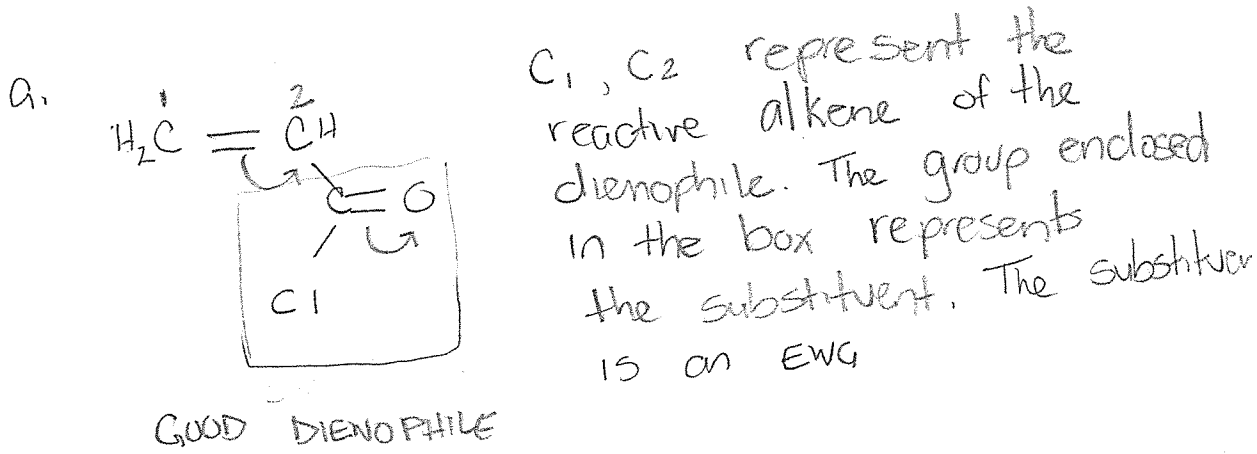
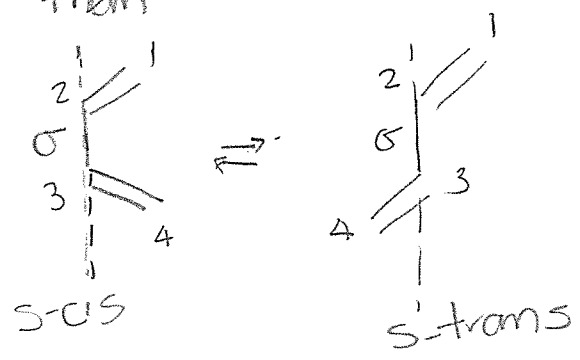


14.8 The best dienophiles are those with electron-withdrawing groups (EWG). The EWG make the dienophile more electron deficient and thus more reactive with the electron rich diene. Each of the dienophiles are evaluated for EWG using resonance effects.

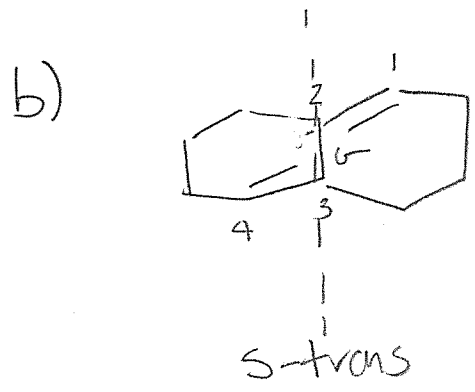
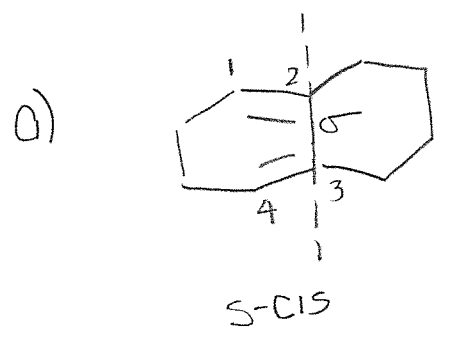


14.9

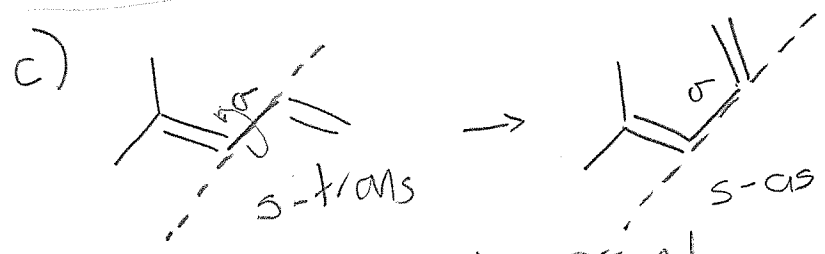
s-cis refers to the conformation where the two alkene groups are oriented on the same side relative to the sigma ( $\sigma$ ) bond separating them



With no restrictions rotation around the  $\sigma$  bond allows interconversion between s-cis and s-trans conformations



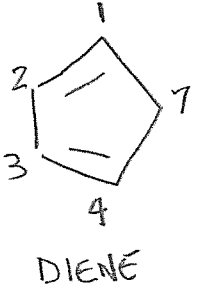
Cannot rotate to s-cis because the ring system locks in the conformation



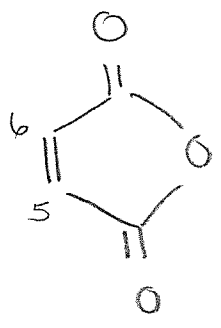
Can rotate around  $\sigma$  bond to generate s-cis conformation.

14. 26

a)

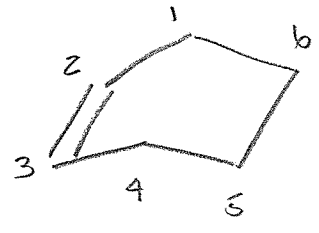


DIENOPHILE

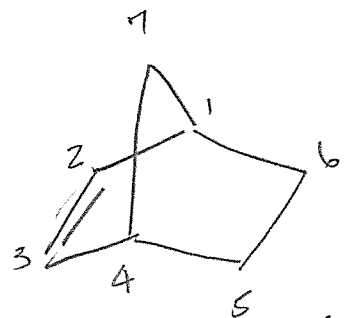


Build the predicted product in steps

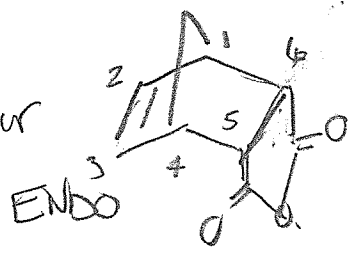
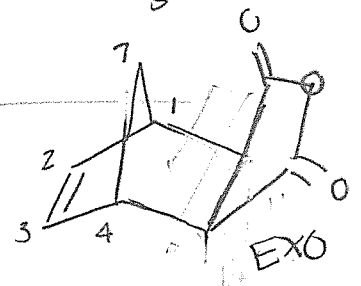
- To predict product first draw a cyclohexene "template" showing formation of 6-membered ring of the product. Since the diene is part of a ring, draw the template cyclohexene "sideways". Number the atoms of the product to show which atoms of the product come from which atoms of the starting diene and dienophile.



- Add the bridge. Since the diene is part of a ring, the C7 carbon becomes a bridge in the product.

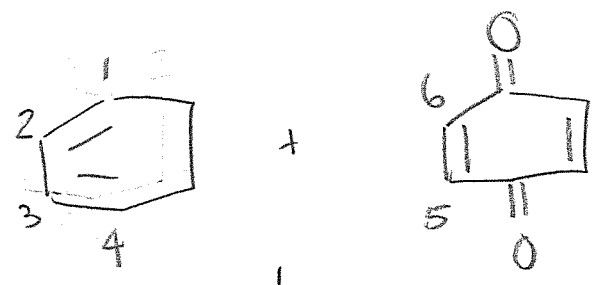


- Fill in the substituents. The substituents of C5 and C6 are also a ring. This ring can be oriented "up" in the product (EXO) or "down" (ENDO). ENDO is favored and gives the major product.

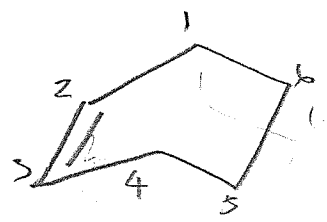


# 14.26 (cont'd)

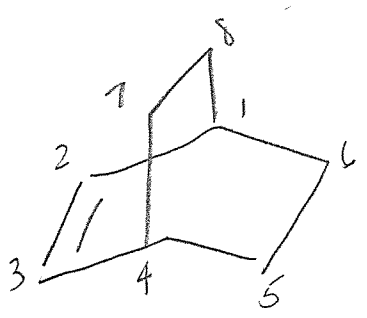
b)



STEP 1:  
DRAW CYCLOHEXENE

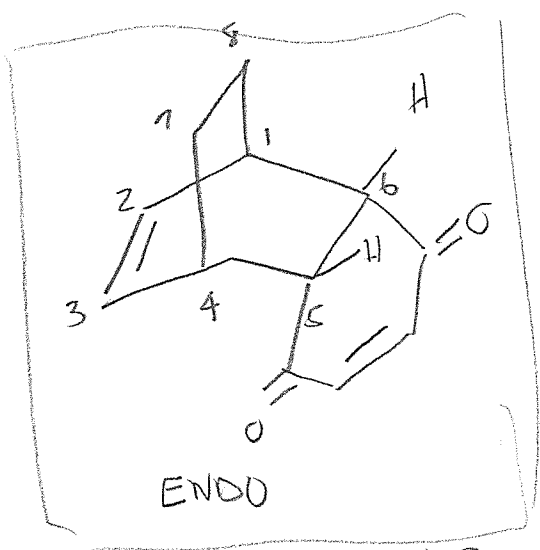


STEP 2:  
FILL IN BRIDGE

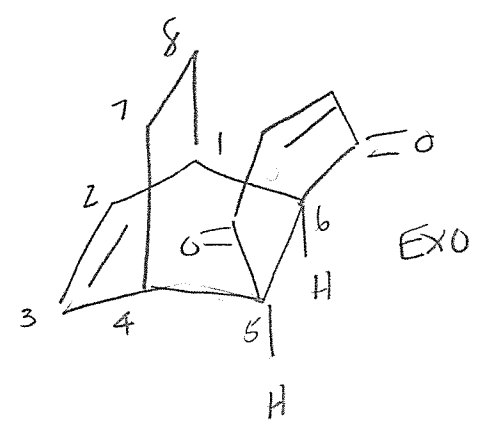


FILL IN

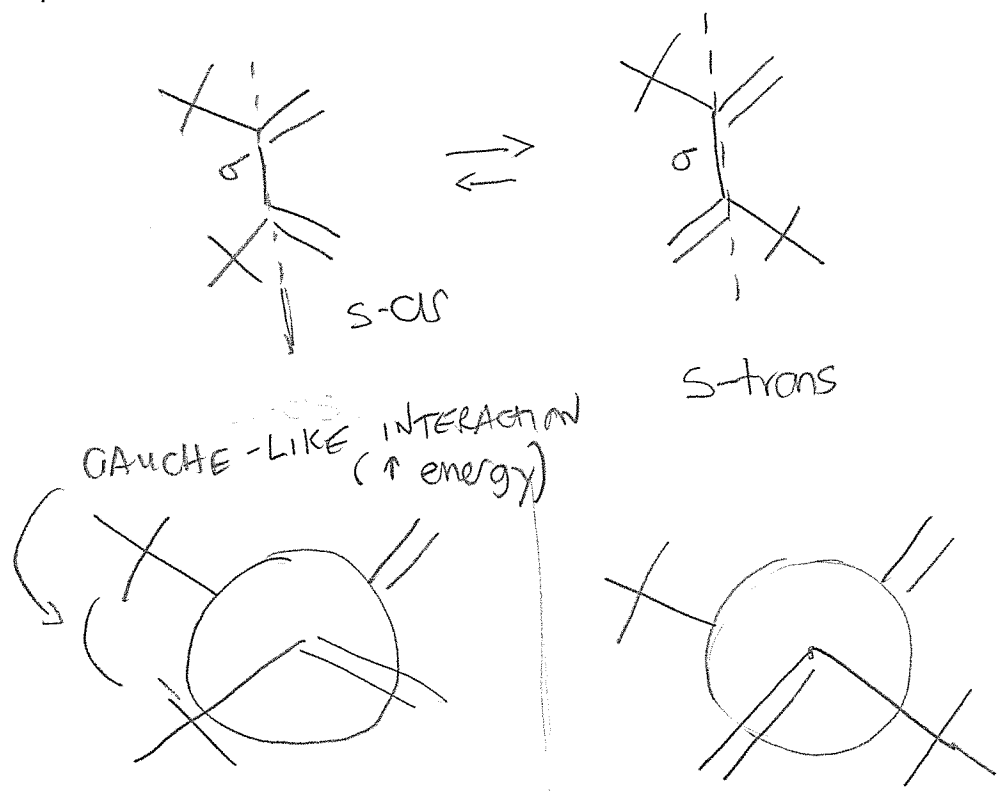
STEP 3:  
FILL IN  
SUBSTITUENTS



MAJOR PRODUCT



14.21

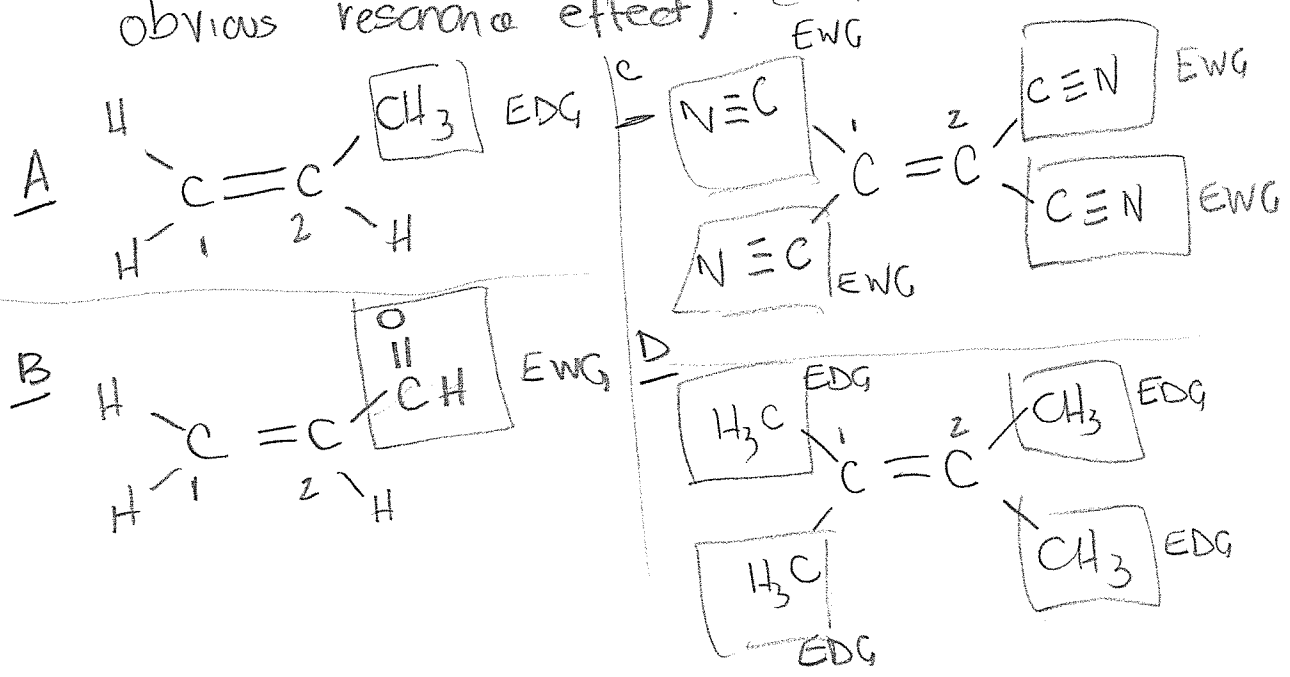


The *s-cis* conformation is required for the Diels-Alder reaction to occur.

The presence of the two tert-butyl groups at C<sub>2</sub> and C<sub>3</sub> of the diene make the *s-cis* conformation very high energy. The tert-butyl groups are large bulky groups that create significant steric strain energy when in the *s-cis* conformation as illustrated by the gauche-like interactions in the Newman projection shown above. These interactions are sufficiently unfavorable to prohibit formation of the *s-cis* conformation.

14, 32

MOST REACTIVE dienophiles are those that are most electron-deficient, created by the presence of EWG. Methyl groups are EDG (although there is no obvious resonance effect).



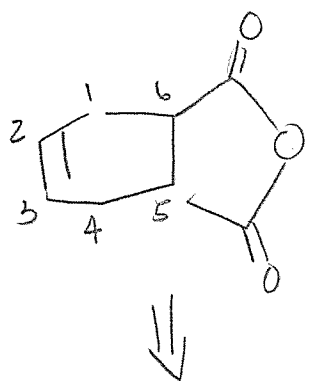
C > B > A > D

(MOST REACTIVE) (LEAST REACTIVE)

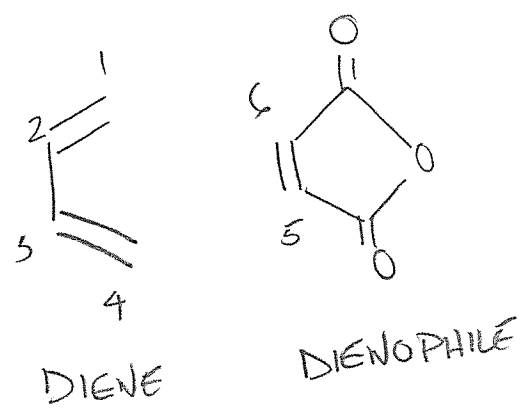
14.35

Work backwards to identify possible starting dienes/dienophiles.  
First find the "cyclohexene" in the product and number it, making the alkene the C<sub>2</sub>-C<sub>3</sub> bond.

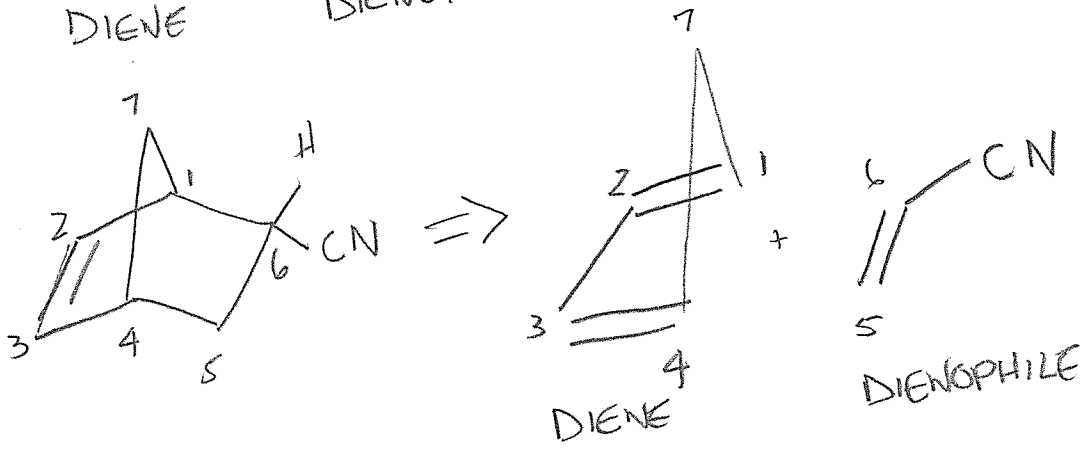
a.



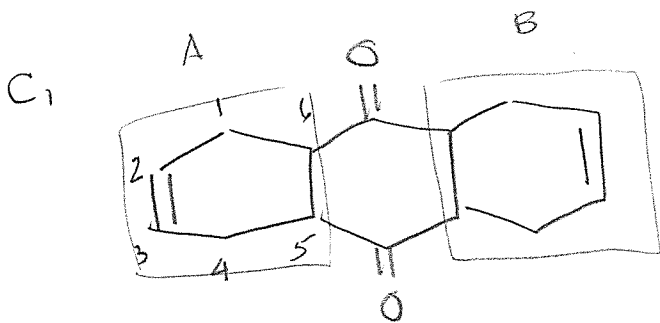
The C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> must be derived from the diene, C<sub>5</sub> and C<sub>6</sub> from the dienophile



b.



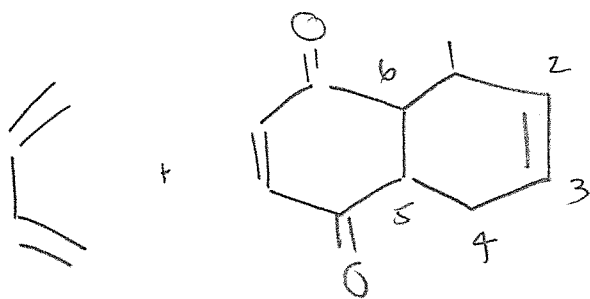
14.35 (cont'd)



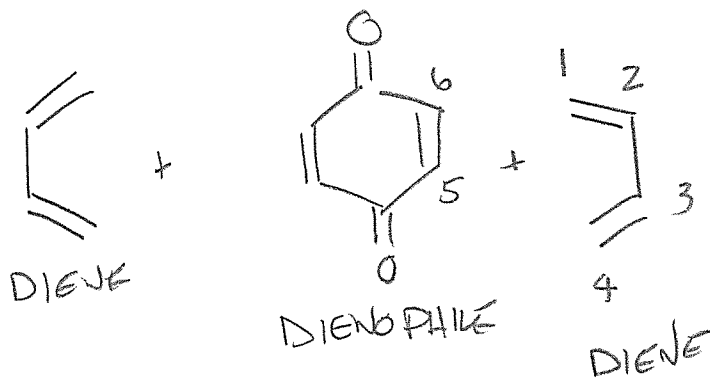
There are two cyclohexenes labeled as A and B

This is a Diels-Alder product that could result from reaction of 2 equivalents of diene reacting with a dienophile that contains two reactive alkenes

For formation of A...

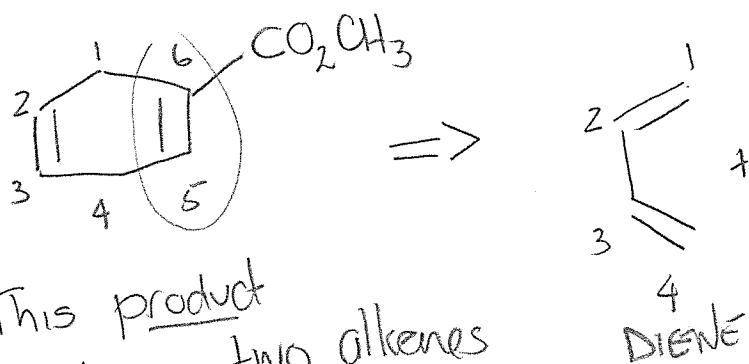


For formation of B...



So there would be two 1,3-butadienes for each one dienophile.





This product contains two alkenes in the 6-membered ring. The  $\text{C}_2\text{-C}_3$  alkene is formed from the diene reacting with a  $\pi$  bond from  $\text{C}_5\text{-C}_6$  of the dienophile. The dienophile must have two  $\pi$  bonds (triple bond is  $2\pi + 1\sigma$ ). One of the  $\pi$  bonds reacts with the diene to form the ring and the other ends up as an alkene in the product ( $\text{C}_5\text{-C}_6$  alkene in product).

