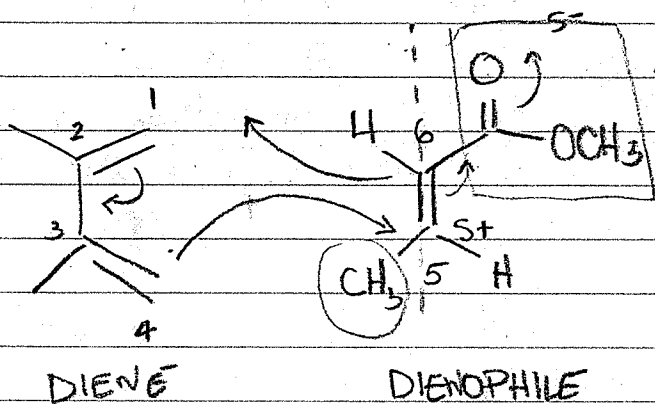


PROBLEM SET #9

SOLUTIONS

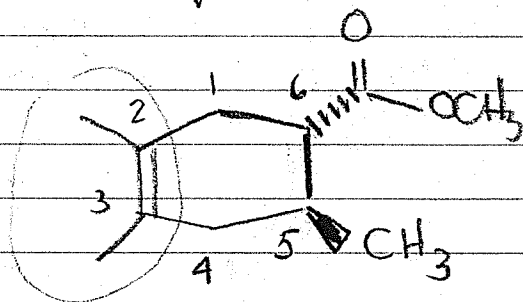
14.7, 14.22 (a,c,e), 14.23

14.7 Diels-Alder occurs between e^- rich DIENE and e^- deficient DIENOPHILE. Identify and number the diene and dienophile.

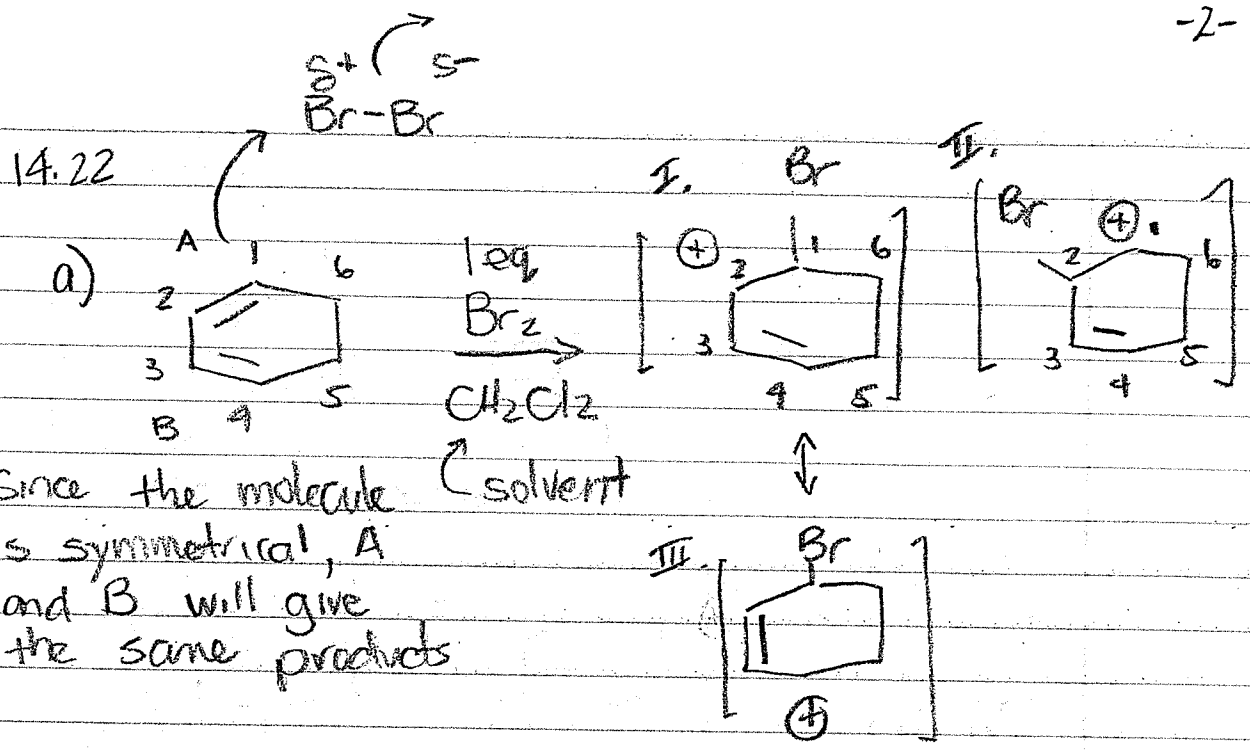


← Electron-withdrawing group (EWG)
- induces δ^+ at C_5

Since the methyl ester at C_6 and the methyl at C_5 are E (trans) in the DIENOPHILE they are trans- in the cyclohexene product

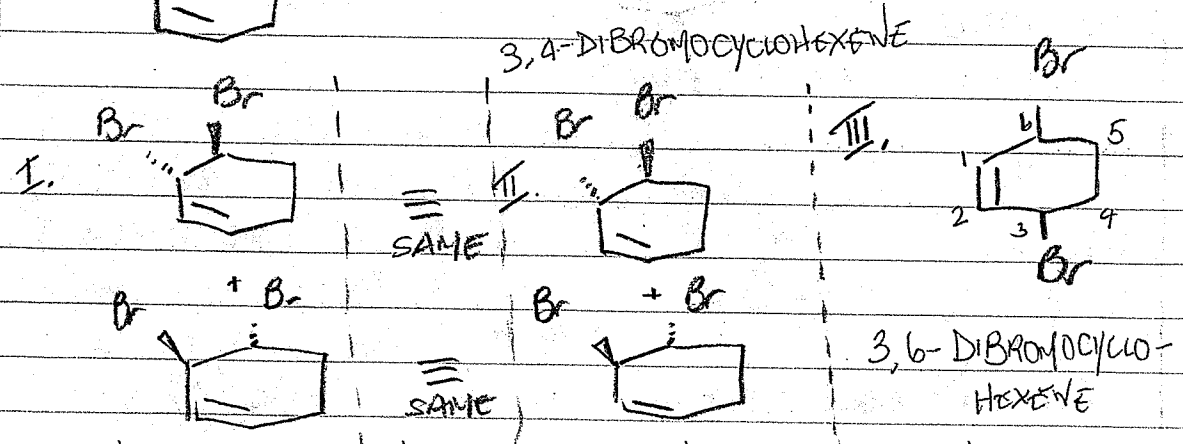
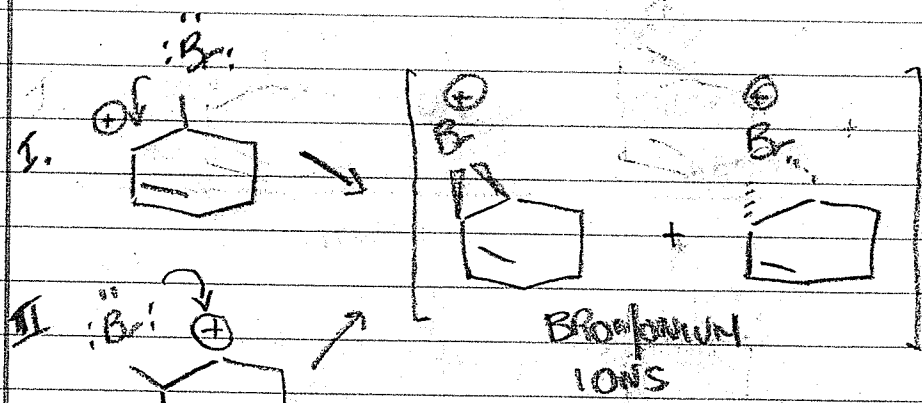


The methyl groups at C_2, C_3 are bonded to sp^2 carbons (flat, trigonal planar) so no cis/trans stereochemistry

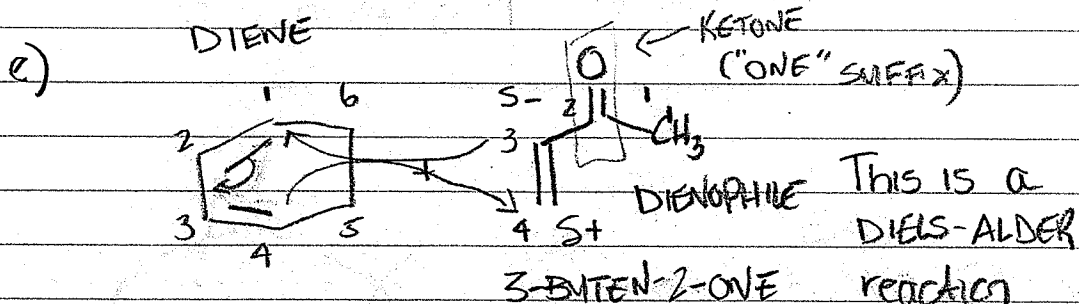
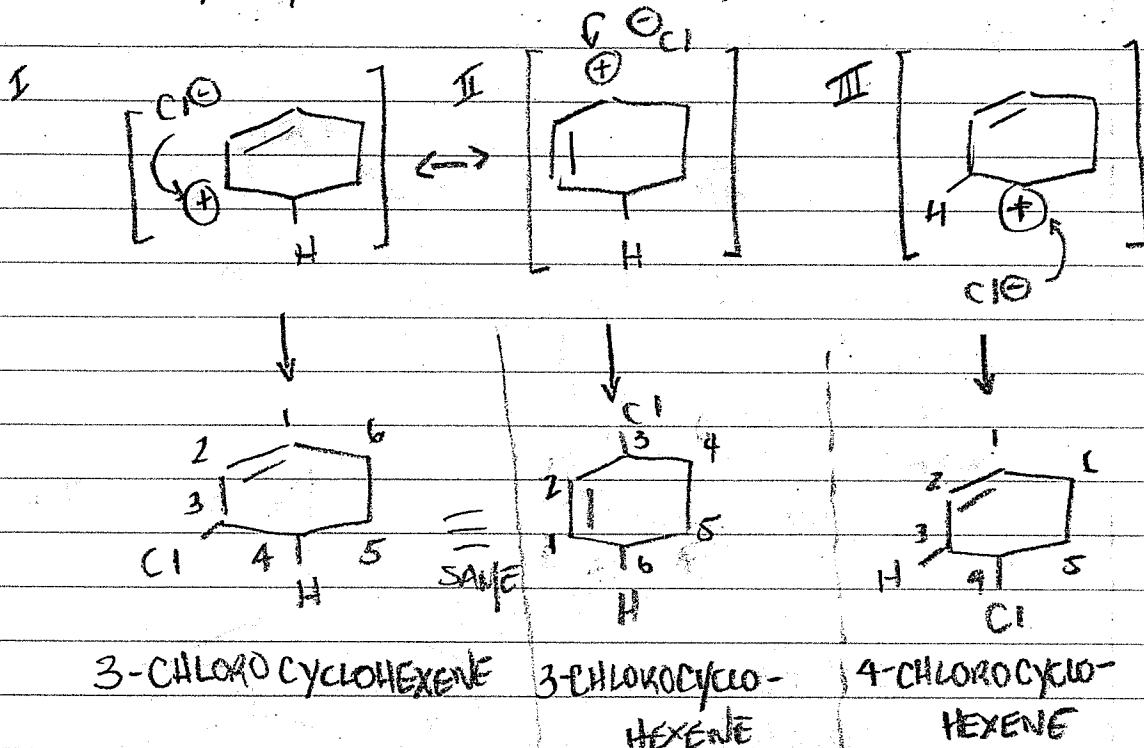
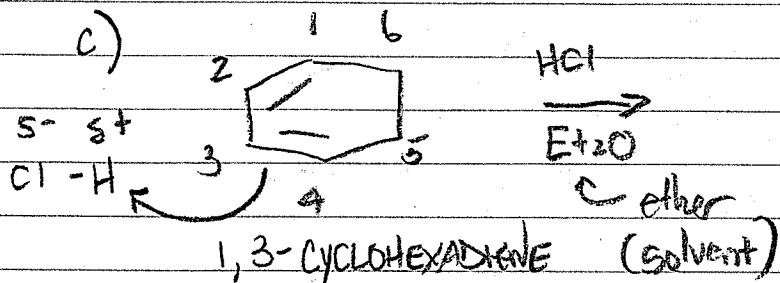


Carbocations I and II form bromonium ions, which lead to TRANS products. III cannot form bromonium ion (Br and C⁺ too "far" away)

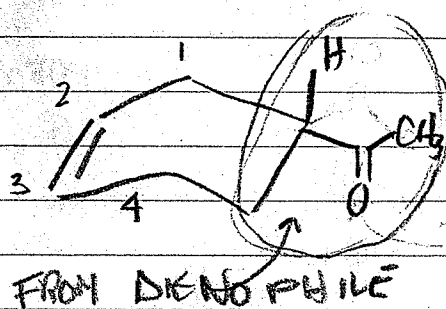
Carbocations I; II generate the same bromonium ions and the same products



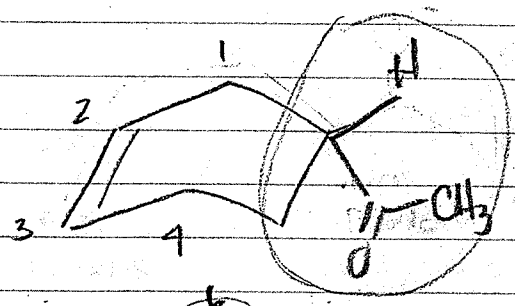
14.22 (cont'd)



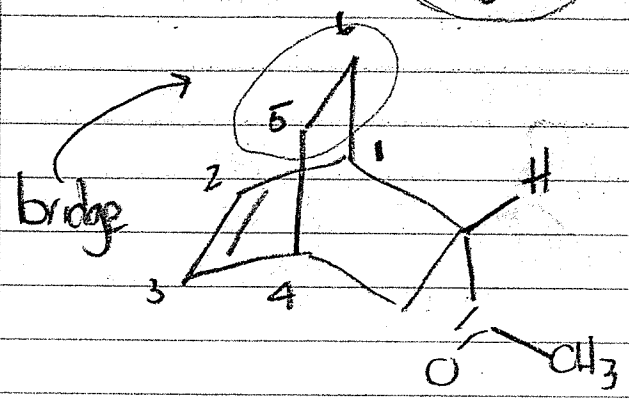
To draw cyclohexene products from a DIELS-ALDER when the diene is part of a ring, 1st draw the cyclohexane, "flatten"



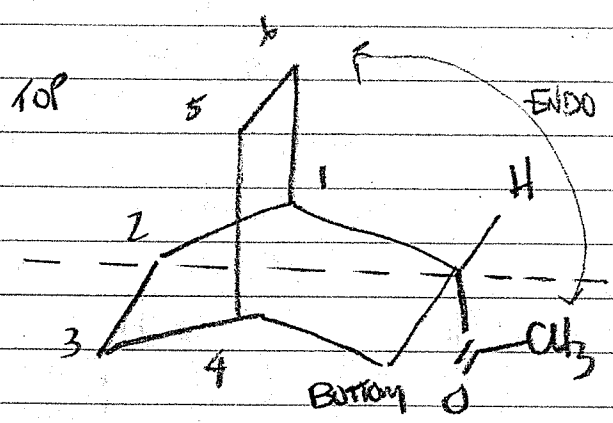
14.22e (cont'd) From dienophile



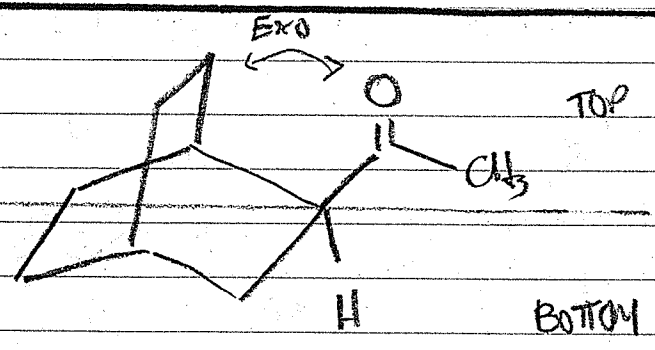
Then, fill in the "bridge", i.e. the C5, C6 carbons of the 1,3-cyclohexadiene starting material



The rxn occurs to preferentially give the ENDO product where the ketone is "ANTI" (trans) to the bridge

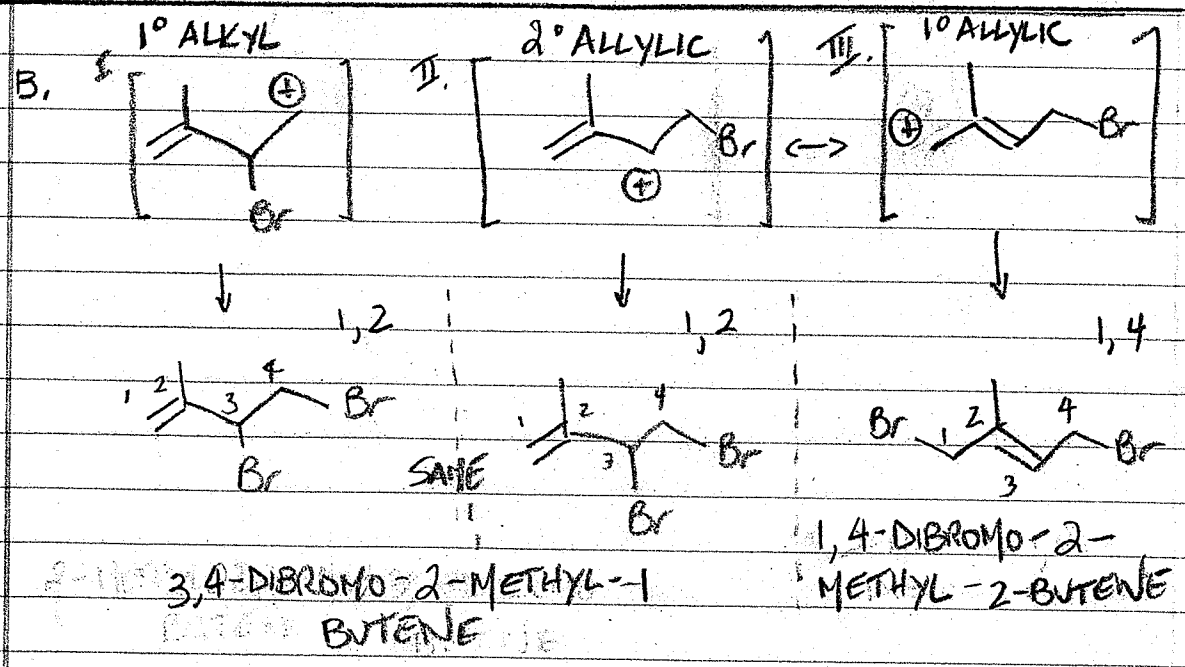
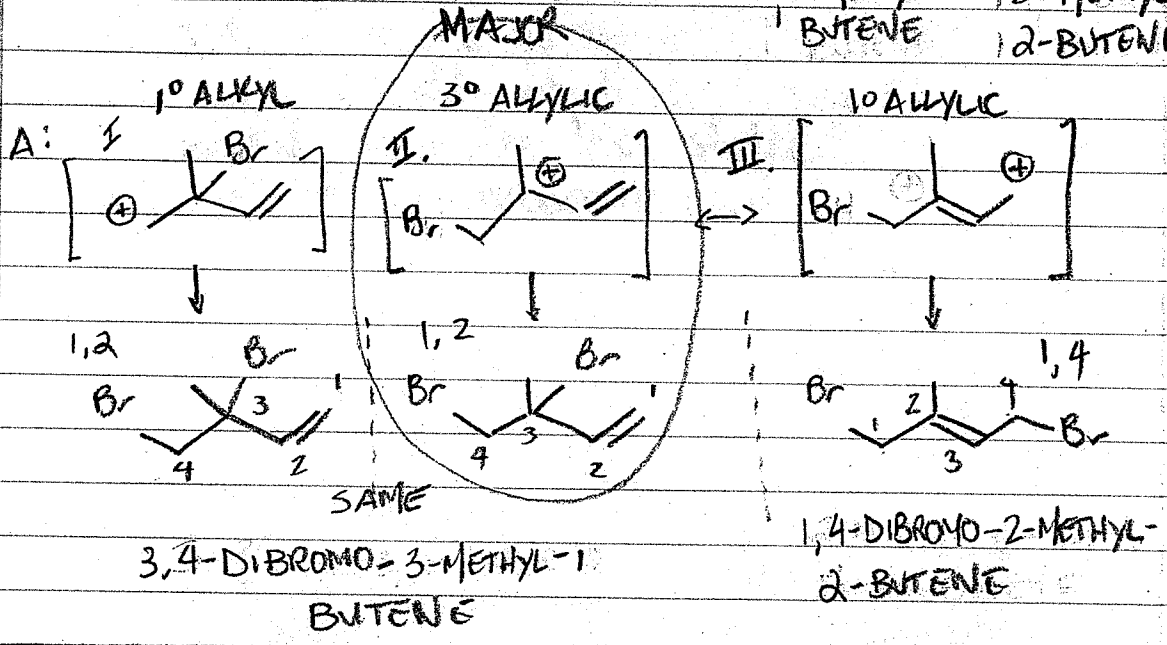
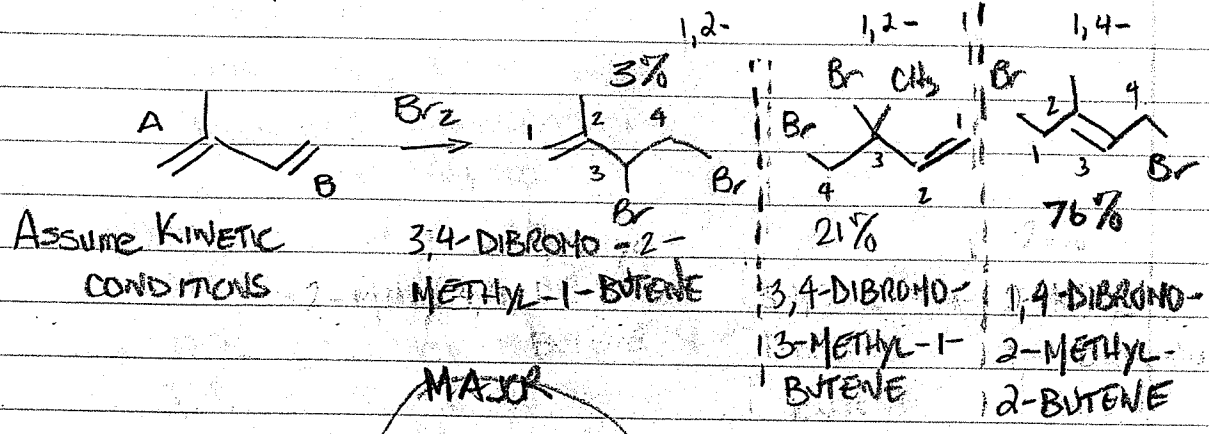


ENDO (MAJOR PRODUCT)



EXO (MINOR PRODUCT)

14.23 USE APPROACH OUTLINED IN LECTURE



14.23 (cont'd)

-6-

3,4-DIBROMO-3-METHYL-
1-BUTENE IS DERIVED
FROM THE MOST STABLE
POSSIBLE CARBOCATION

i.e., 3° ALLYLIC

Therefore, it is the
MAJOR KINETIC PRODUCT

and predominates over
3,4-DIBROMO-2-METHYL-1-
BUTENE which is
derived from the less stable
2° ALLYLIC carbocation.