Dr. Steven Pedersen October 29, 2003

Chemistry 3A
Midterm #2

Student name: ____Key____________________

Student signature: ______________________________

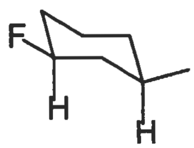
TA's name or section number:______________________________

Problem 1	________	(10 pts)
Problem 2	________	(10 pts)
Problem 3	________	(5 pts)
Problem 4	________	(6 pts)
Problem 5	________	(18 pts)
Problem 6	________	(21 pts)
Problem 7	________	(30 pts)
Total Points	________	(100 pts)

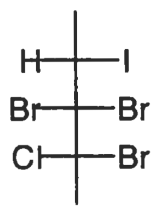
No Calculators Allowed
Be Sure Your Exam has 13 Pages
Be Sure To Try All Parts of Each Problem!

1. 10 pts

A. Provide a systematic name for the following compounds. Use common nomenclature for any branched substituents.



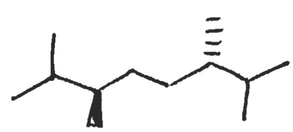
(1S, 3R)-1-fluoro-3-methylcyclohexane



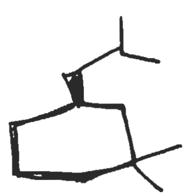
(2R, 4S)-2,3,3-tribromo-2-chloro-4-iodopentane

B. Draw a structure for the following names. For cycloalkanes use flat rings. For all others use bond-line notation.

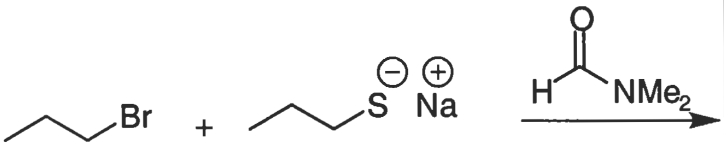
- (3R,6S)-2,3,6,7-tetramethyloctane

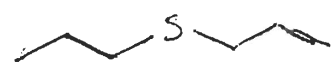


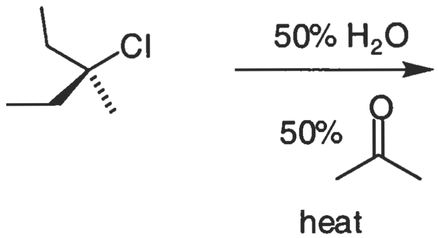
- (S)-1-isobutyl-3,3-dimethylcyclohexane

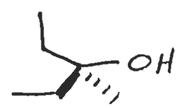


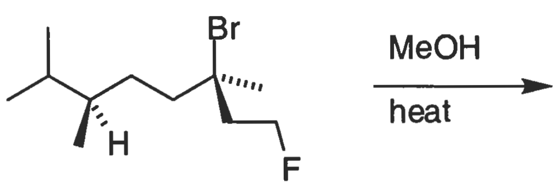
2. Predict the product(s) from the following reactions. Pay attention to any instructions given in the boxes. (10 pts)

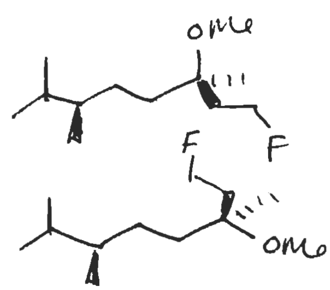




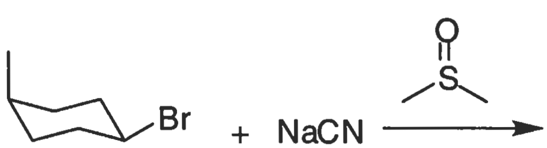


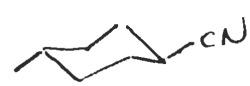






all expected organic products including stereoisomers





draw the product in its most stable conformation

3. Match the molecules shown below with the statements. (5 pts)

a. A symmetrical antiviral. D
b. A racemic insecticide that "unracemizes" (not a real word) in the soil. G
c. Flaming ice cubes. I
d. October 16, 1846, a day to remember if you are into medical history. F
e. A molecule for your sofa that appears too never disappear. B
f. Strawberries and the ozone layer. There is a connection. C
g. Orchids can be masters of chemical mimicry. A
h. If you don't want to be pounced on by a 2-inch wasp while walking in the hills of Japan, avoid wearing a fragrance containing these chemicals. E and H

C_{21}-C_{29} alkanes/alkenes

A

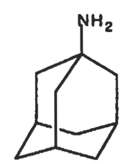
$CF_3(CF_2)_7SO_3H$

perfluorooctanylsulfonate

B

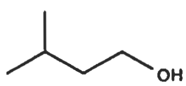
CH_3Br

C



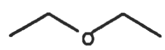
amantadine

D



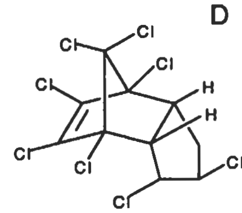
3-methyl-1-butanol

E



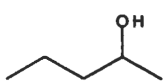
ether

F



trans-chlordane

G



2-pentanol

H

$CH_4(H_2O)_n$

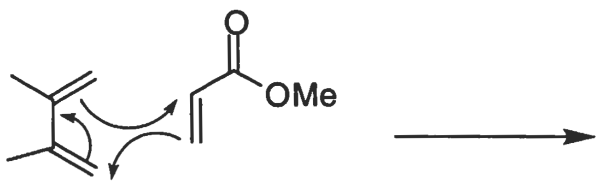
methane hydrate

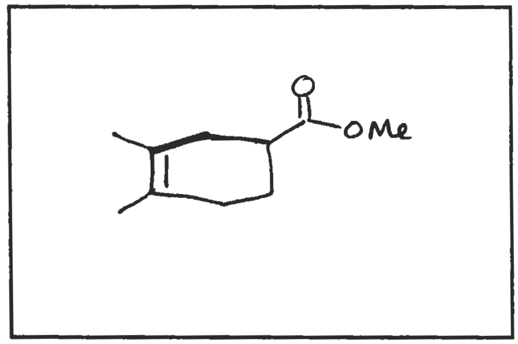
I

A Few More Mechanisms

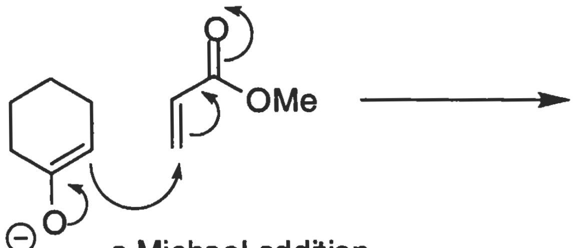
6 pts

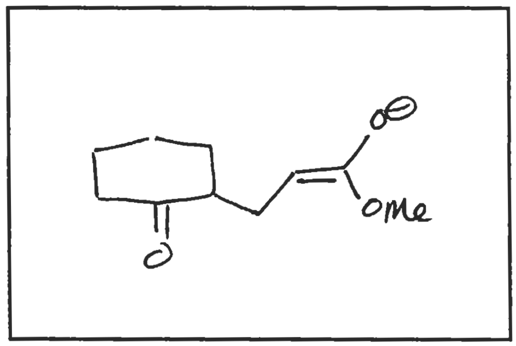
4. A. Show the product(s) you would expect to get from each of the following arrow-pushing mechanisms. Be sure to include all formal charges where relevant.



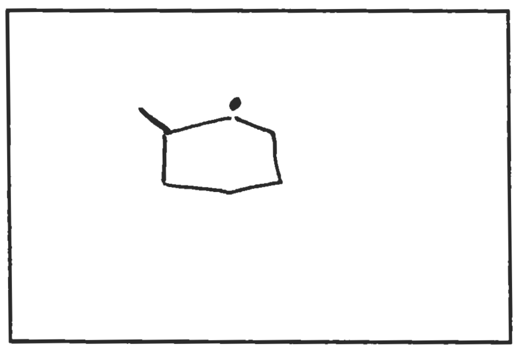


a Diels-Alder reaction



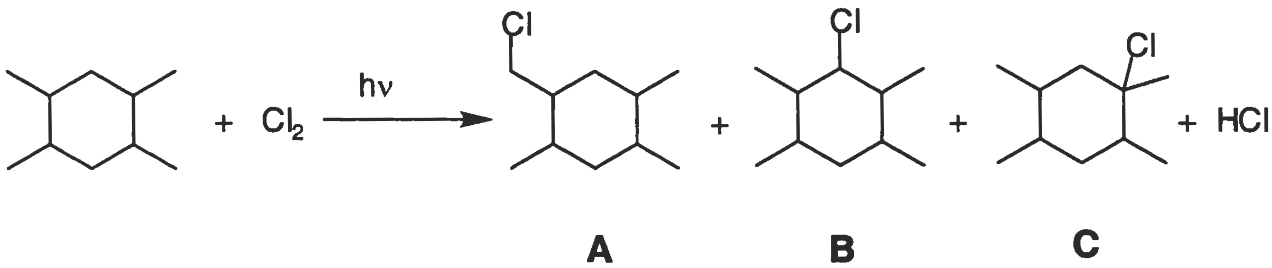


a Michael addition



Radical Chlorination

5. (18 pts)
All of the following questions are related to the reaction shown below.



A. Calculate the statistical product ratio for products A, B and C, expressing your answer as percentages (i.e. the A + B + C = 100%). You must show all of your work below to receive ANY credit for your answer.

Show your final answer here: %A = 60 **%B =** 20 **%C =** 20
Show your work here:

\# of 1° H's = 12
\# of 2° H's = 4
\# of 3° H's = 4
Total H's = 20

$\% A = \frac{12}{20} \times 100 = 60\%$
$\% B = \frac{4}{20} \times 100 = 20\%$
$\% C = \frac{4}{20} \times 100 = 20\%$

B. Based on the known selectivity factors of 5:4:1 (tertiary:secondary:primary respectively) for radical chlorination, predict what percent of product A you would actually expect to get in this reaction. Again, you must show all of your work to receive ANY credit for your answer.

Your final answer: %A = 25
Show your work here:

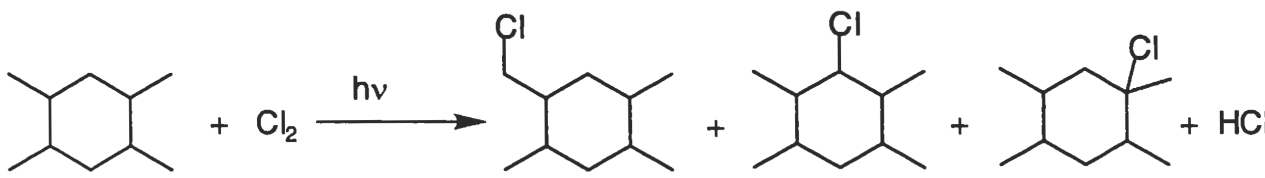
\# of 1° H's x 1 = 12
\# of 2° H's x 4 = 16
\# of 3° H's x 5 = 20
48

$\% A = \frac{12}{48} \times 100 = 25\%$

C. Calculate ΔH for the formation of product ~~A~~ C. You must show your work to receive any credit. A table of bond dissociation energies is provided as a handout.

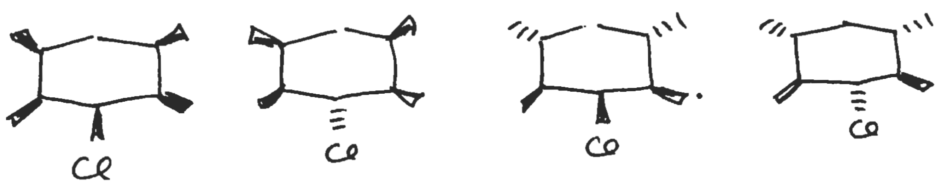
Show your final answer here: ΔH for product C = −33.5 kcals/mole
Show your work here:

ΔH = Σ bonds broken − Σ bonds formed
(96.5 + 58) − (85 + 103)
(154.5) − (188) = −33.5

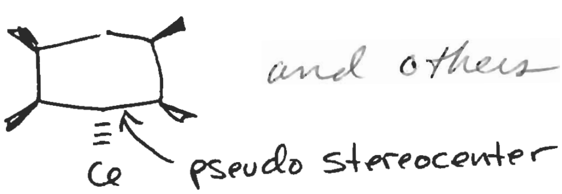


A **B** **C**

D. Draw one meso product you would expect to be formed in the above chlorination reaction.



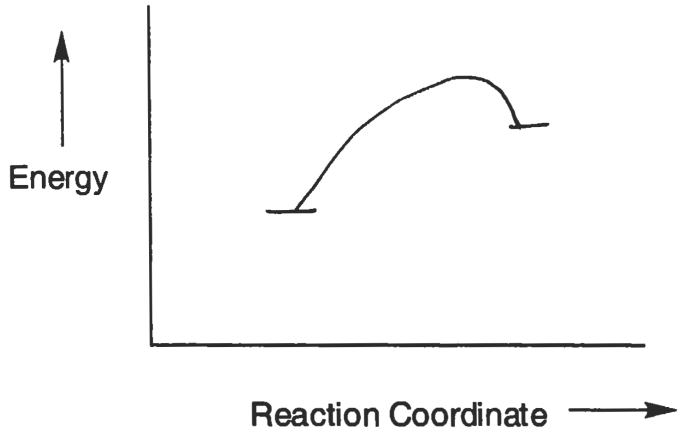
E. Draw one product from the above chlorination reaction that has a pseudo-stereocenter. **This molecule must be different from the one you drew in part D. Label the pseudo-stereocenter.**



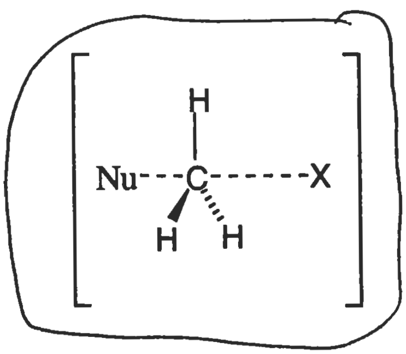
Nucleophilic Substitution

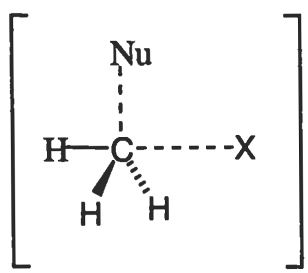
6. (21 pts)

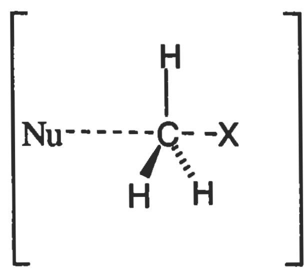
A. On the graph below, draw a reaction coordinate diagram that best represents an S_N2 reaction with a late transition state.

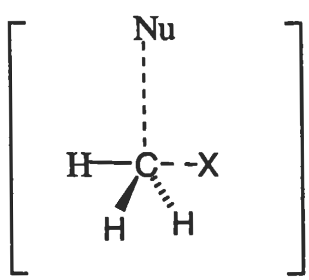


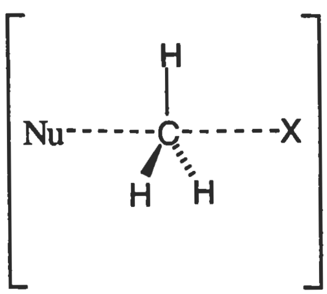
B. Which picture below best represents a late transition state for the $S_N2$reaction between a nucleophile, Nu, and an electrophile, CH_3X, where X is the leaving group. Circle your answer.



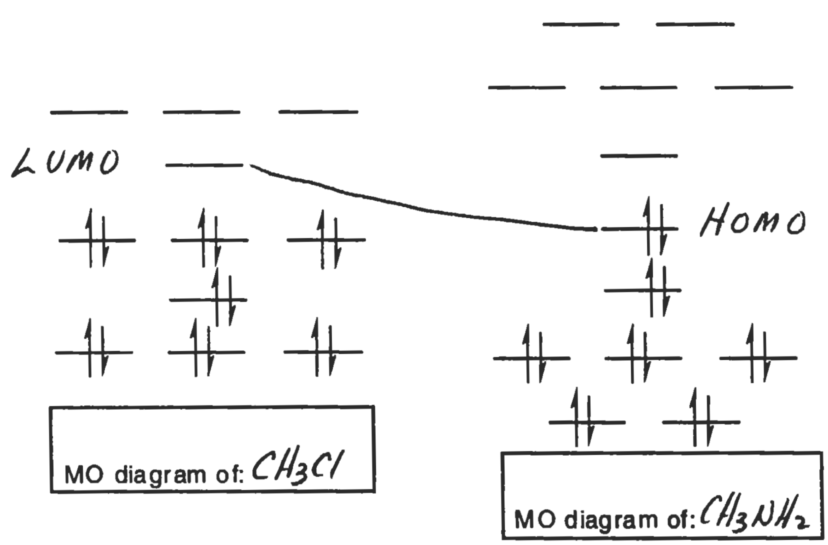








C. Below are the molecular orbital diagrams for methylamine, CH_3NH_2, and methyl chloride, CH_3Cl. In the box below each diagram label which molecule belongs to which diagram.



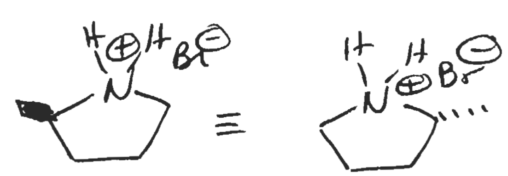
D. Considering Frontier Molecular Orbital Theory, which molecular orbital of the nucleophile will interact with which molecular orbital of the electrophile in an S_N2 reaction between these two molecules. On the diagram above, show this interaction by drawing a line between the two levels that are interacting.

E. For the intramolecular substitution reaction shown below, a normal kinetic study of the molecularity of this reaction would not allow you to determine whether this is a S_N1 or S_N2 reaction. Explain.

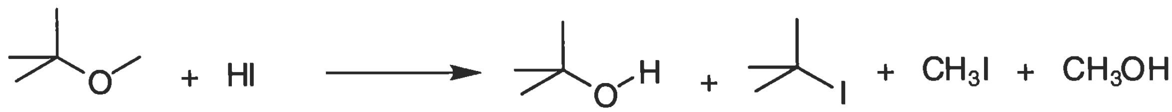
In order to determine if a reaction rate is bimolecular, you must vary the concentration of both the electrophile and nucleophile. That is not possible in this case since they are both in the same molecule.

F. If the reaction in part E proceeded via a S_N2 type mechanism, show the structure of the product, including any relevant stereochemistry.

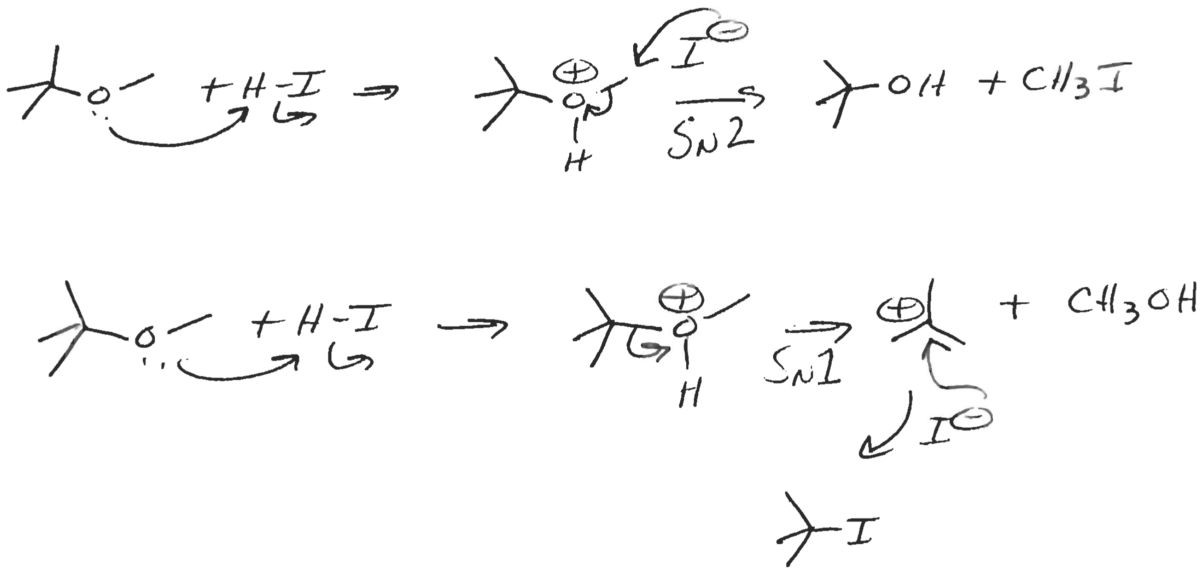
Structure of $C_5H_{12}N^{\oplus}$ $Br^{\ominus}$



H. Write a rational arrow-pushing mechanism(s) for the following reaction.



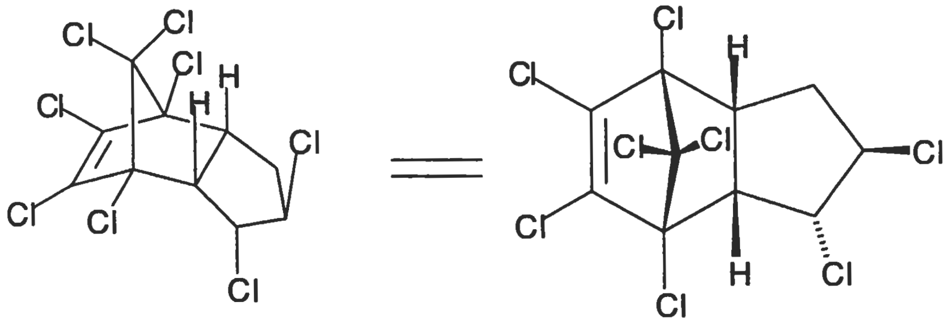
your mechanism(s) must account for all of the products formed



You will not need the whole page for this mechanism(s). I just didn't want to start a new problem on the same page.

trans-Chlordane

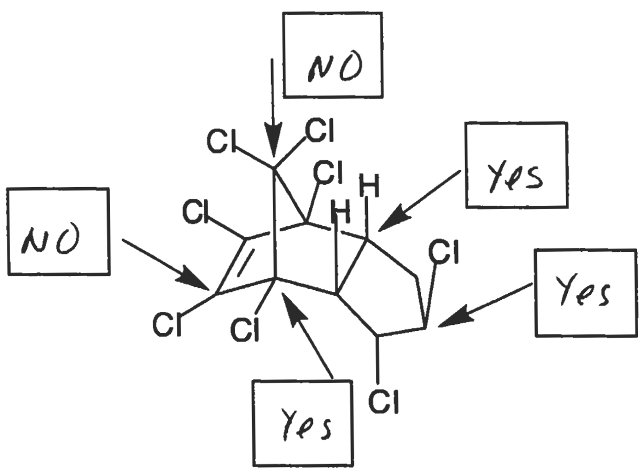
7. Two views of trans-chlordane, an organochlorine insecticide, are shown below. Keep these in mind when working on the rest of the parts of this problem. (30 pts)



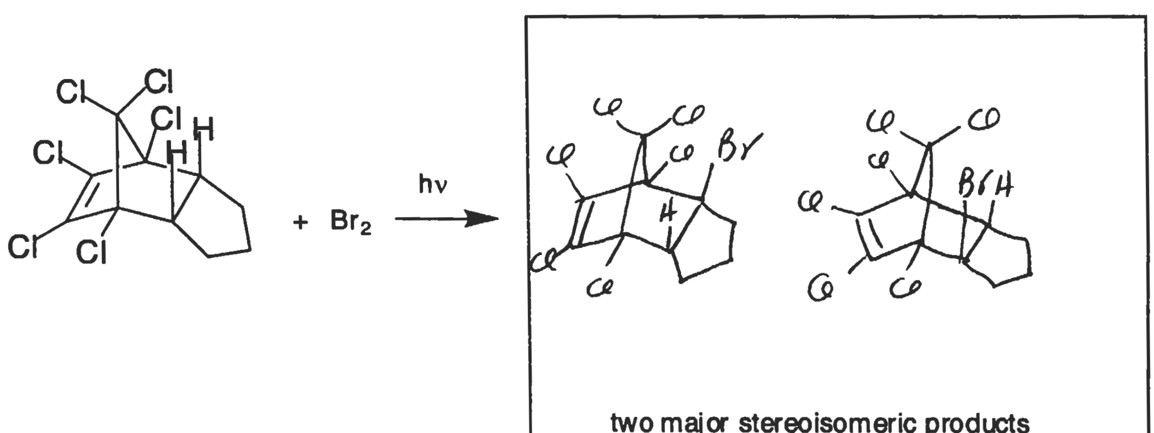
trans-chlordane

trans-chlordane (redrawn)

A. On the structure below, write a YES in the box at the beginning of each arrow if the carbon being pointed to is a stereocenter. Write NO if it is not a stereocenter.



B. Predict the two MAJOR stereoisomeric products from the reaction shown below.

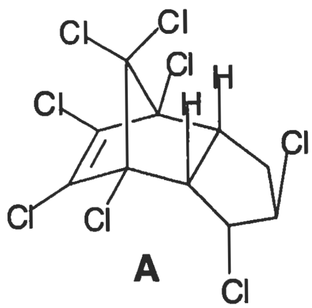


two major stereoisomeric products

C. For each of the following molecules below, indicate whether they are chiral or achiral by circling the appropriate answer underneath the structure.

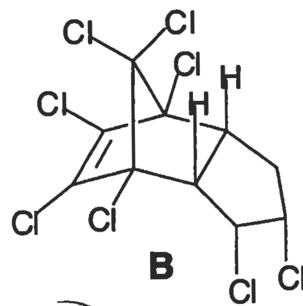
D. Using the letters underneath each compound, indicate in the box below, which compound(s) are meso. If there are none, then say none. This is an all or nothing question, there is no partial credit.

meso: F



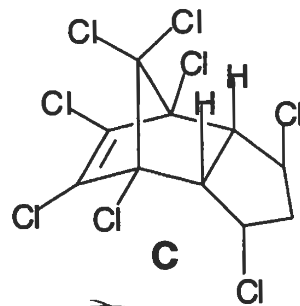
A

Chiral Achiral



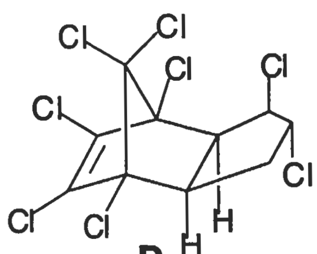
B

Chiral Achiral



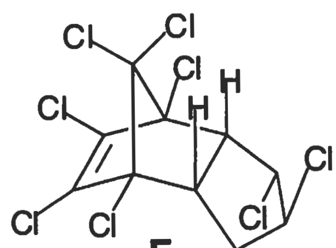
C

Chiral Achiral



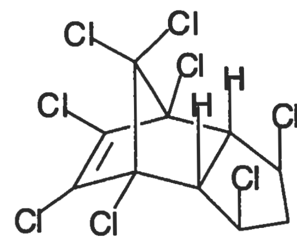
D

Chiral Achiral



E

Chiral Achiral



F

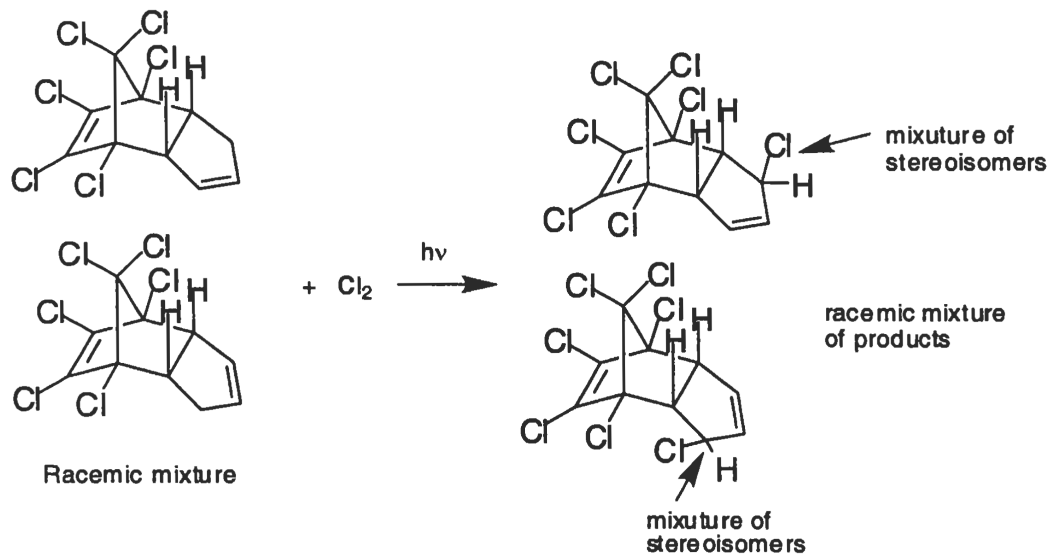
Chiral Achiral

E. For each pair of molecules above use one term (and only one) that best describes their relationship to one another. The terms to choose from are: (you may use the abbreviations shown)

identical **(I)** enantiomers **(E)** diastereomers **(D)** none of these **(N)**

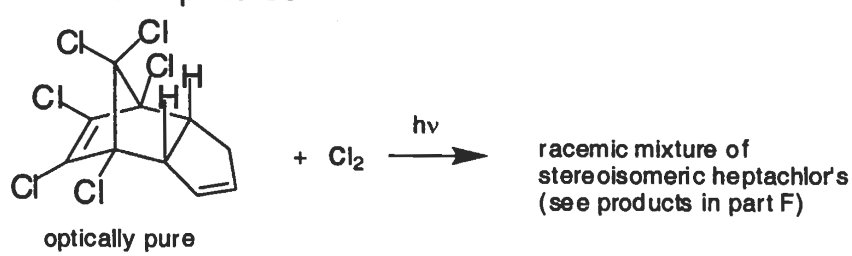
A and B: D	B and C: N	C and E: N
A and C: N	B and D: D	C and F: D
A and D: D	B and E: D	D and E: D
A and E: E	B and F: N	D and F: N
A and F: N	C and D: N	E and F: N

F. Heptachlor is a "relative" of trans-chlordane and was at one point used to vanquish the cotton bollweevil. It can be prepared by radical chlorination of a racemic mixture of hexachlor as shown below. As can be seen from the results, secondary hydrogens are more reactive than the tertiary hydrogens in this molecule. Explain this reverse in selectivity. NOTE: This experimental fact has nothing to do with steric effects or ring strain.

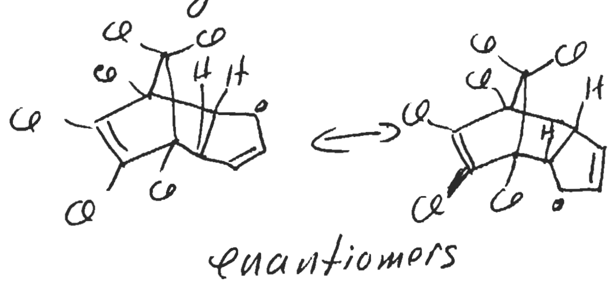


The secondary radical generated in this reaction is resonance stabilized, which apparently is more stable than a tertiary radical that is not resonance stabilized.

H. When OPTICALLY PURE hexachlor was chlorinated the same racemic mixture of stereoisomeric heptachlor's shown in part F was obtained. Explain how this is possible using words and pictures.



The secondary radical can resonate as shown below, leading to two enantiomeric resonance structures.



Cl_2 → racemic mixture of enantiomeric heptachlor's

enantiomers