

CHEMICAL REACTIONS

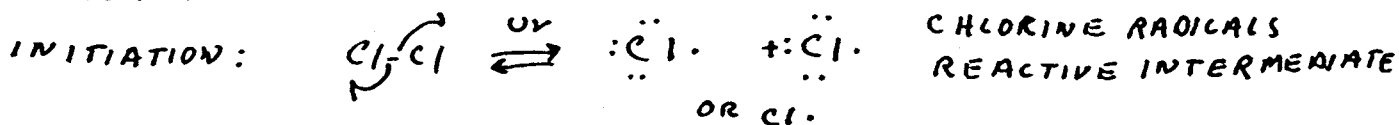
- EQUATION REACTANTS → PRODUCTS
- MECHANISM STEP BY STEP PATHWAY
- THERMODYNAMICS ENERGY FLOW
- KINETICS RATES OF REACTION

THE FREE RADICAL CHLORINATION OF ALKANES



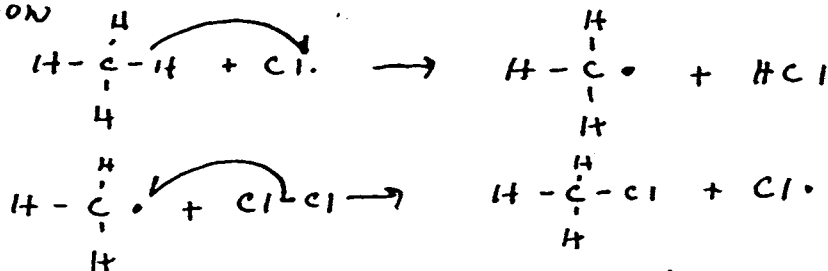
THE REACTION MAY CONTINUE $\text{CH}_3\text{Cl} + \text{Cl}_2 \xrightarrow[\text{OR HEAT}]{\text{UV}} \text{CH}_2\text{Cl}_2 + \text{HCl}$
 AND ON TO CH_3Cl AND CCl_4

A CHAIN REACTION MECHANISM

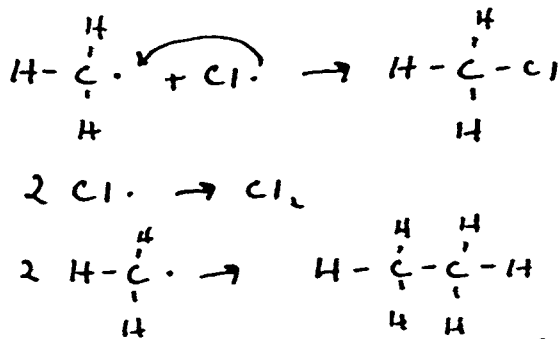


$\text{Cl}\cdot$ IS A FREE RADICAL
 UNPAIRED ELECTRON
 REACTIVE!

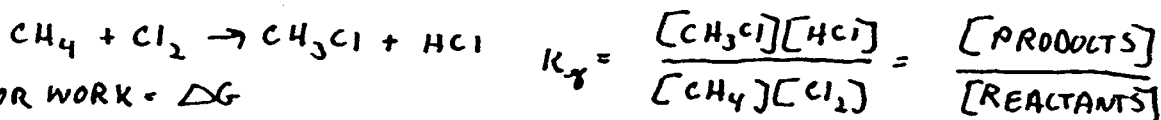
PROPAGATION



TERMINATION:



THIS REACTION HAS A VERY LARGE K_{eq} , 10^{19} , SO IT WILL GO TO COMPLETION



USEFUL ENERGY FOR WORK = ΔG

$$\Delta G = -RT \ln K \quad \text{AT } 25^\circ \text{ -RT} = \approx 2.5$$

$$\Delta G = \Delta H - T\Delta S \quad \Delta H = \text{ENTHALPY CHANGE}$$

$$\Delta S = \text{ENTROPY CHANGE}$$

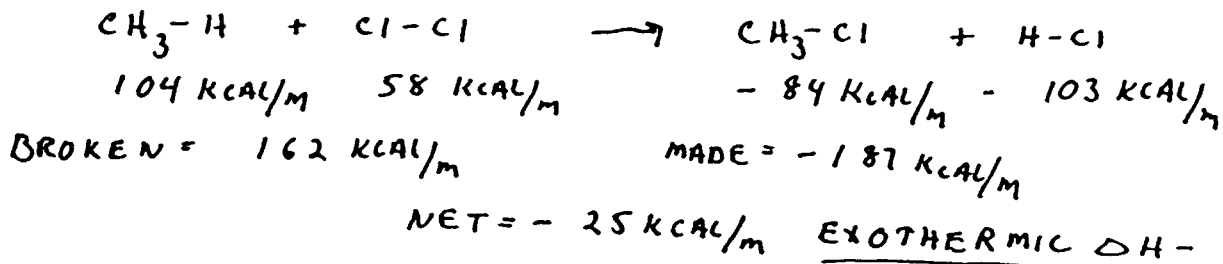
BOND DISSOCIATION ENERGY

ALL BONDS HAVE A CHARACTERISTIC ENERGY (TABLE 4-2)

ENERGY IS RELEASED WHEN BONDS ARE FORMED $\Delta H -$

ENERGY IS CONSUMED IN BREAKING BONDS $\Delta H +$

ΔH FOR A REACTION IS THE SUM OF THE ENERGY REQUIRED TO BREAK BONDS AND THE ENERGY RELEASED BY MAKING BONDS



KINETICS

KINETICS IS THE STUDY OF RATES OF REACTION

RATES ARE EXPRESSED IN A RATE LAW $A + B \rightarrow C + D$

$$\text{RATE} = k [A]^A [B]^B$$

EXPONENTS MUST BE DETERMINED EXPERIMENTALLY

k = RATE CONSTANT

A MOST USEFUL CONCEPT IS THE ORDER OF A REACTION

ZERO ORDER — DOUBLE $[A]$ OR $[B]$ \rightarrow RATE DOES NOT CHANGE

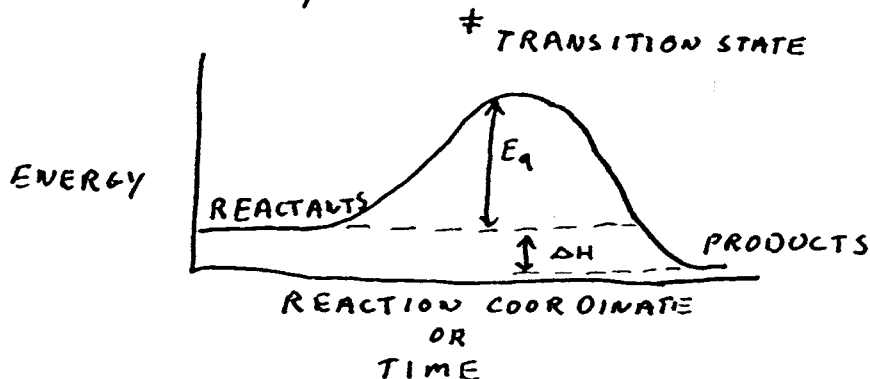
FIRST ORDER — DOUBLE $[A]$ OR $[B]$ \rightarrow RATE DOUBLES

SECOND ORDER — DOUBLE $[A]$ OR $[B]$ \rightarrow RATE QUADROPLES

FOR A REACTION, IF $\text{RATE} = k[A][B]^2$ THATS FIRST ORDER IN A
SECOND ORDER IN B
THIRD ORDER OVERALL

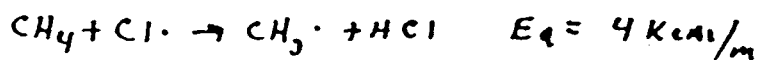
THE ORDER OF A REACTION GIVES INSIGHT INTO ITS MECHANISM

ACTIVATION ENERGY, TRANSITION STATES AND REACTION COORDINATE DIAGRAM



RATES OF MULTI STEP REACTIONS

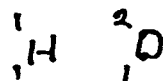
THE STEP WITH THE HIGHEST ENERGY IS RATE DETERMINING FOR THE PROPAGATION STEPS:



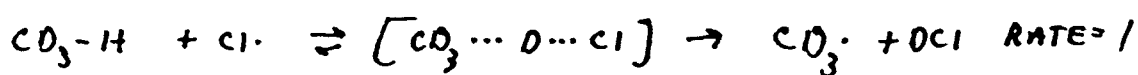
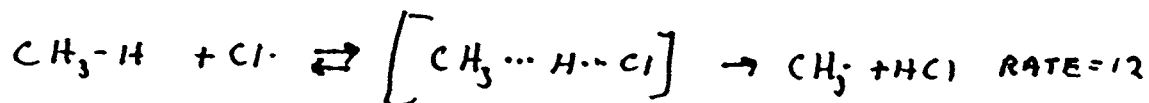
$\text{CH}_3\cdot$ AND $\text{Cl}\cdot$ ARE REACTIVE INTERMEDIATES PRODUCED IN ONE STEP, CONSUMED IN ANOTHER

ISOTOPE EFFECTS

DEUTERIUM IS AN ISOTOPE OF HYDROGEN
ATOMIC NUMBER = 1 ATOMIC WEIGHT = 2



A C-D BOND IS SLIGHTLY STRONGER ($\approx 2 \text{ kcal/m}$) THAN A C-H BOND IN OUR HALOGENATION REACTION:

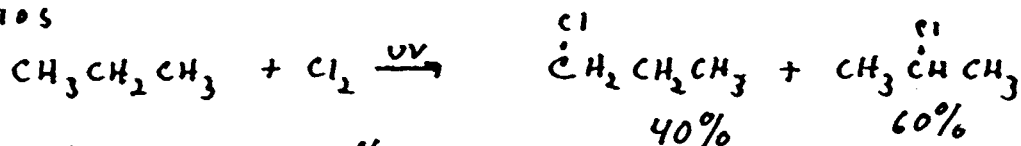


TEMPERATURE DEPENDENCE OF HALOGENATION

REACTION	E_a	RELATIVE RATE
$\text{F}\cdot + \text{CH}_4 \rightarrow \text{HF} + \text{CH}_3\text{F}$	1.2 kcal	140,000
$\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3\text{Cl}$	4 kcal	1300
$\text{Br}\cdot + \text{CH}_4 \rightarrow \text{HBr} + \text{CH}_3\text{Br}$	18 kcal	9×10^{-8}
$\text{I}\cdot + \text{CH}_4 \rightarrow \text{HI} + \text{CH}_3\text{I}$	34 kcal	2×10^{-19}

CHLORINATION OF HIGHER ALKANES

PRODUCT RATIOS



RELATIVE REACTIVITY

$$\frac{40\%}{6 \text{ PRIMARY HYDROGENS}} = 6.67\%/\text{H}$$

$$\frac{60\%}{2 \text{ SECONDARY HYDROGENS}} = 30\%/\text{H}$$

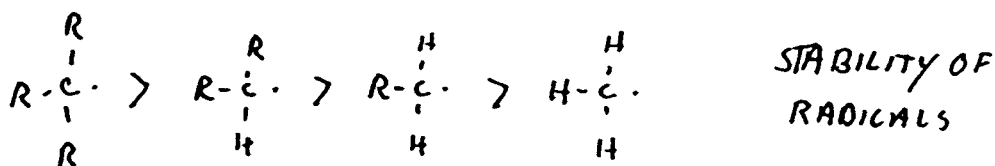
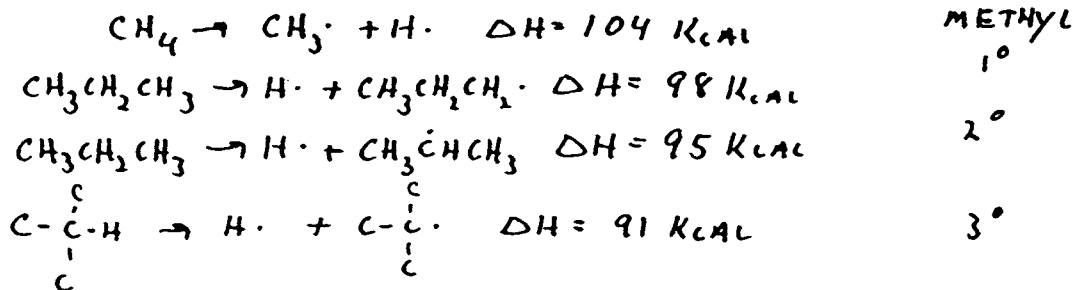
$$\frac{30}{6.67} = 4.5$$

SO A 2° H

IS 4.5 X AS REACTIVE

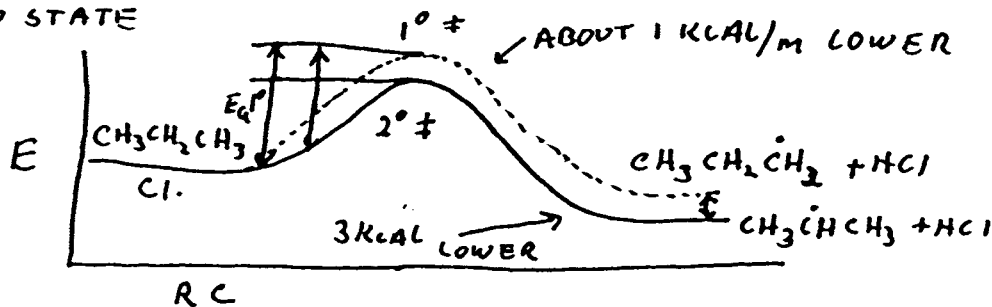
AS A 1° H

THE RELATIVE REACTIVITY OF 1° AND 2° HYDROGENS REFLECTS THE RELATIVE STABILITY OF THE RADICALS



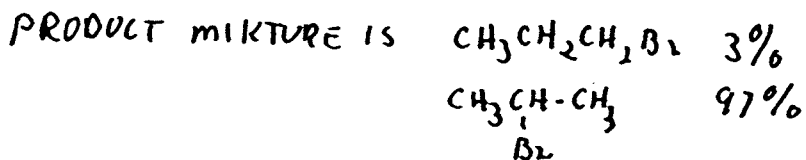
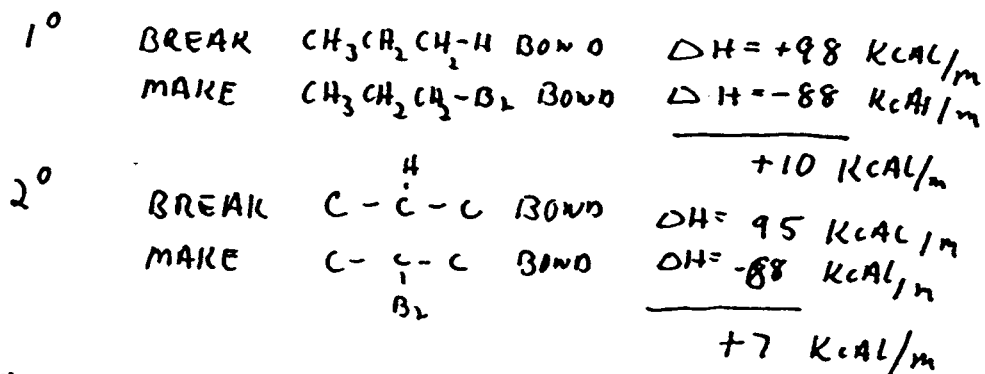
TERTIARY > SECONDARY > PRIMARY > METHYL

A RCO SHOWS A LOWER E_a FOR 2° RADICALS AND A MORE EASILY ACHIEVED TRANSITION STATE



BROMINATION OF PROPANE

THE RATE DETERMINING STEP IS ENDOOTHERMIC

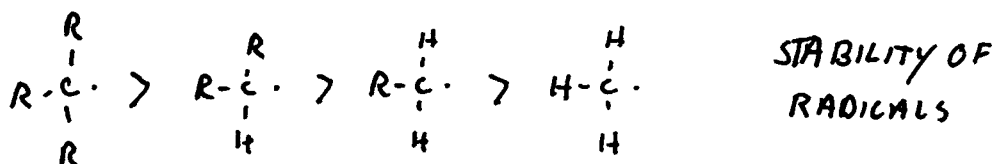
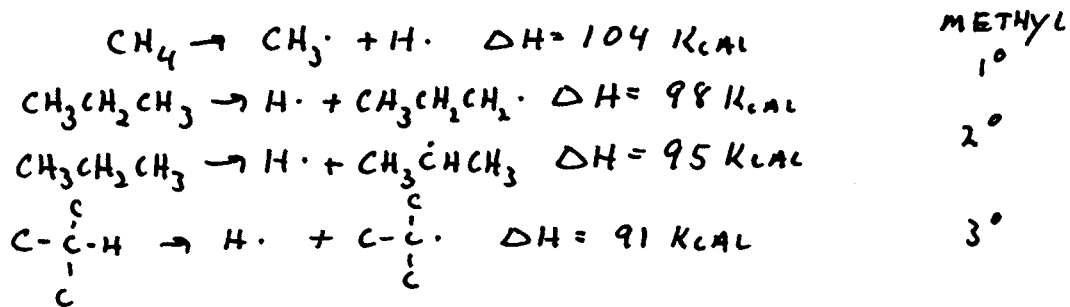


$$\frac{3\%}{3} = 0.5\%/\text{H}$$

$$\frac{97}{2} = 48.5$$

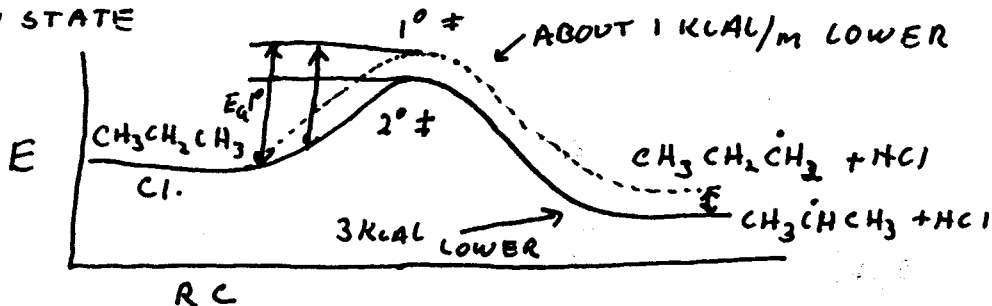
SO 2° H ARE $\frac{48.5}{.5} = 97$ X AS REACTIVE

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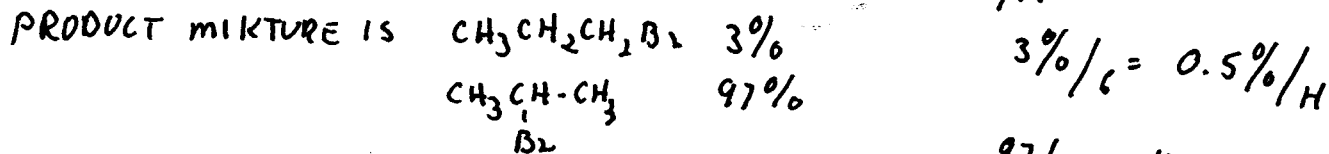
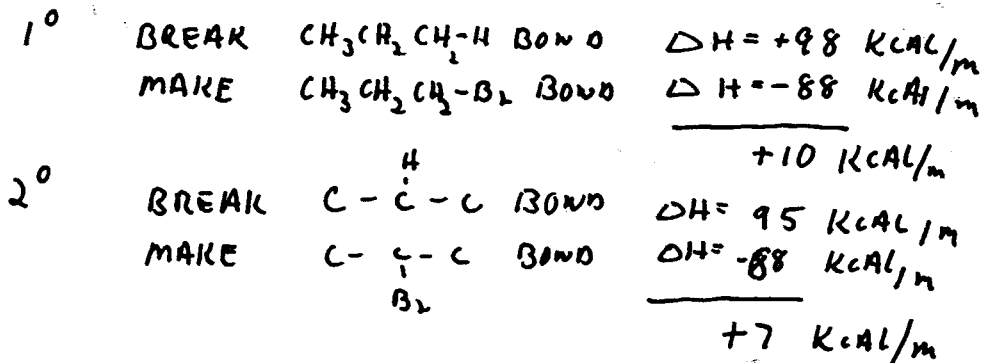
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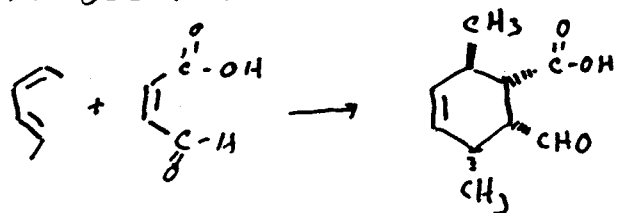
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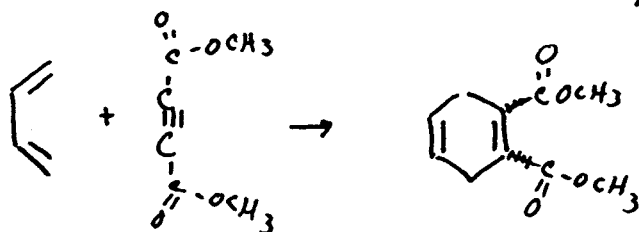
SO 2° H ARE $\frac{48.5}{.5} = 97 \times$ AS REACTIVE

DIELS-ALDER REACTION

SEE PROBLEM 51 FOR AN APPROACH TO THE ENDO RULE



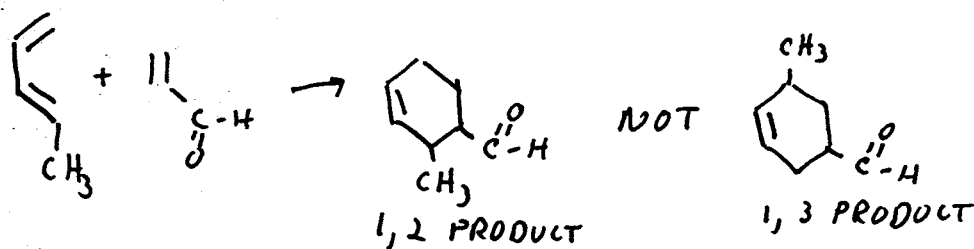
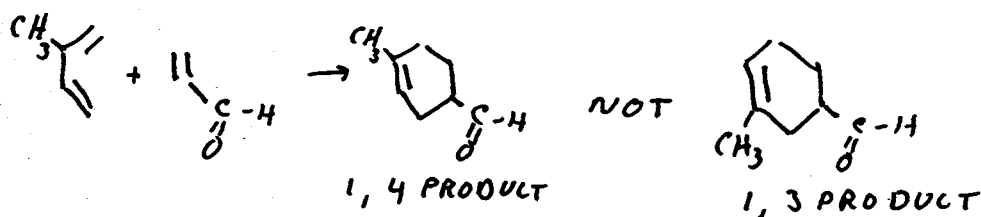
THE REACTION WORKS WELL WITH ALKYNES AS DIENOPHILES



RING IS FUNCTIONALIZED FOR FURTHER REACTIONS, WHICH MAY INCLUDE RING OPENING

REACTIONS WITH UNSYMMETRICAL REAGENTS

THE ELECTRON WITHDRAWING GROUPS OF THE DIENOPHILE AND THE ELECTRON DONATING GROUPS OF THE DIENE USUALLY HAVE A 1, 4 OR A 1, 2 RELATIONSHIP IN THE PRODUCT, BUT NOT A 1, 3 RELATIONSHIP



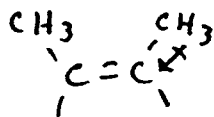
MOLECULAR ORBITALS AND PERICYCLIC REACTIONS

WHEN ATOMIC ORBITALS OVERLAP TO FORM BONDS, MOLECULAR ORBITALS ARE FORMED BY A LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO) SO, IN ETHYLENE, 2 p ORBITALS COMBINE TO FORM 2 MOLECULAR ORBITALS AND IN BUTADIENE, 4 p ORBITALS COMBINE TO FORM 4 MOLECULAR ORBITALS

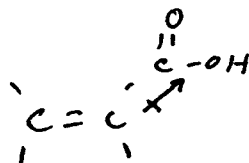
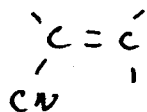
THE + AND - SIGNS REFER TO THE PHASE OF THE WAVE FUNCTION AND LOBES OF THE SAME SIGN OVERLAP CONSTRUCTIVELY. LOBES OF OPPOSITE SIGN OVERLAP DESTRUCTIVELY - CALLED ANTI BONDING.

THE DIELS-ALDER REACTION

A DOUBLE BOND CAN BE ELECTRON-RICH

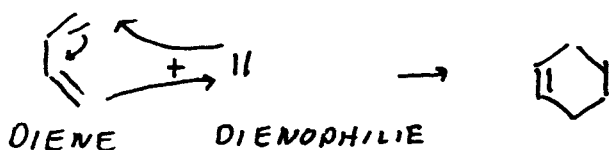


OR ELECTRON-POOR

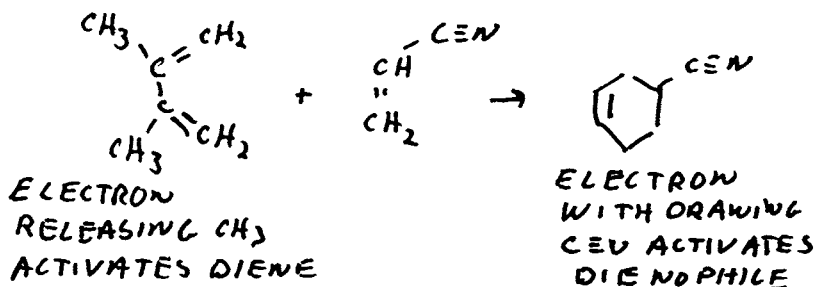


A VERY EFFECTIVE WAY TO MAKE 6-MEMBERED RINGS IS THE DIELS-ALDER REACTION

IN WHICH WE COMBINE AN ELECTRON-RICH DIENE WITH AN ELECTRON-POOR ALKENE (OR ALKYNE), CALLED THE DIENOPHILE

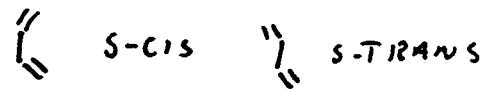


CONCERTED REACTION
SYN ADDITION

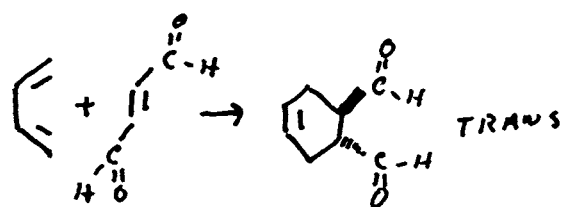
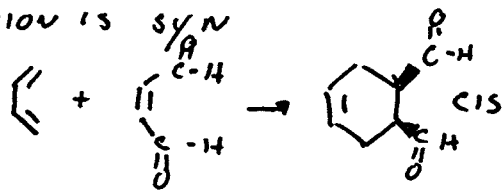


STEREO CHEMISTRY

1) DIENE IS IN S-CIS CONFORMATION

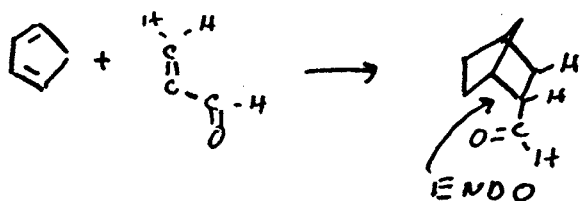


2) ADDITION IS SYN



ENDO RULE

IF THERE IS A π BOND IN THE ELECTRON WITHDRAWING GROUP IT IS "ENDO" IN THE PRODUCT



CHAPTER 21

RANK STABILITY OF
CATIONS AND RADICALS

30, 31, 32, 4, 3, 2, 1

MECHANISM OF FREE
RADICAL REACTIONS

23, 26

REACTIVITY VS SELECTIVITY

7, 8

UNDERSTAND HAMMOND
POSTULATE

7

SKIP SECTION 7, 10, 9, 8

CHAPTER 22

SECTION 6

DIELS-ALDER SYNTHESIS

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