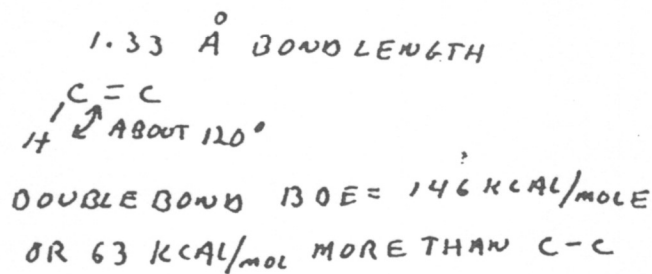
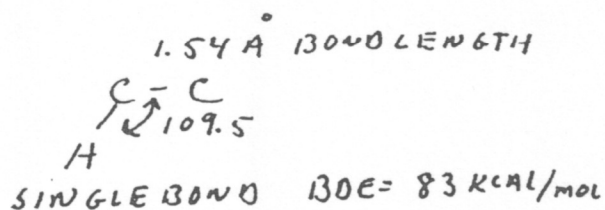


CHAPTER 7 LECTURE NOTES FOR ORGANIC CHEMISTRY ©MM 2001

STRUCTURE AND SYNTHESIS OF ALKENES

ALKENES ARE COMPOUNDS WHOSE PRINCIPAL FUNCTIONAL GROUP IS THE DOUBLE BOND. ITS A SHORTER, TIGHTER BOND THAN A SINGLE BOND WITH sp^2 HYBRIDIZATION AND TRIGONAL PLANAR GEOMETRY

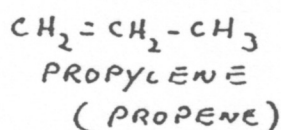
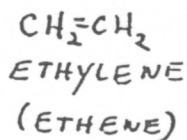


THERE IS NO FREE ROTATION AROUND THIS BOND

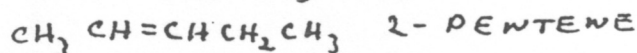
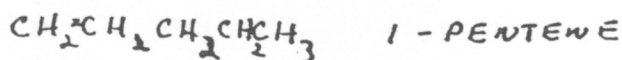
SO CIS/TRANS ISOMERS ARE POSSIBLE

NOMENCLATURE

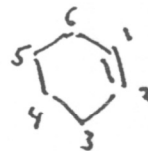
CHANGE THE PARENT ALKANE NAME TO ALKENE



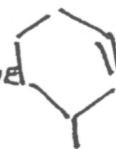
MORE CARBONS MEANS NUMBERING THE POSITION OF THE DOUBLE BOND USING THE CHAIN NUMBER OF THE LOWEST CARBON



THE NUMBER IS NOT NEEDED IN CYCLOHEXENE BUT THATS WHERE THE NUMBERING MUST START IF THERE ARE ANY OTHER GROUPS



3-METHYL CYCLOHEXENE

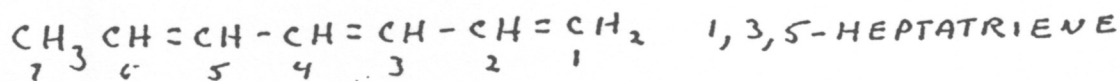


MOLECULES WITH 2 DOUBLE BONDS → DIENE

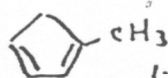
" " 3 " " → TRIENE

" " 4 " " → TETRAENE

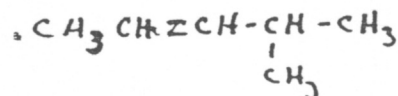
} EACH DOUBLE BOND MUST BE NUMBERED



ALKYL GROUPS ARE NAMED AND NUMBERED AS BEFORE, C=C NUMBER DEFINES THE CHAIN NUMBERING



1-METHYL-1,3-CYCLOPENTADIENE



4-METHYL-2-PENTENE

MOLECULAR FORMULAS

Molecular formulas are relatively easy to obtain :

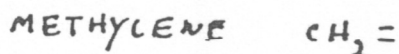
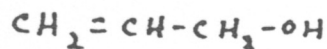
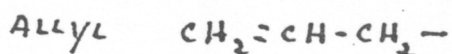
- from mass spectra
- from C,H,N analyses
- any molecular weight determination

Degrees of unsaturation or points of unsaturation

- saturated hydrocarbons C_nH_{2n+2} eg. ethane
- introduction of O to give a saturated compound does not change C/H ratio $C_nH_{2n+2}O_m$
- introduction of double bond or ring requires removal of 2H
- triple bond 4H .
- benzene ring 8H
- any ring 2H
 - eg. C_3H_6O - one double bond C=C or C=O
 - $C_8H_{12}O$ - 3 double bonds or rings or $C\equiv C$, but not benzene ring, therefore not a phenol.
- introduction of X - remove 1H
- $C_nH_{2n+1}X$
- introduction of N - add 1H
- $C_nH_{2n+3}N$
- if a molecule has only CHO it must contain an even number of H
- an odd number of X or N means an odd number of H .
- an even number of X or N means an even number of H

ALKENES AS SUBSTITUENTS

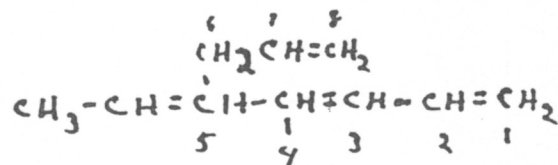
COMMON NAMES



3-METHYLENE CYCLOHEXENE



STYRENE



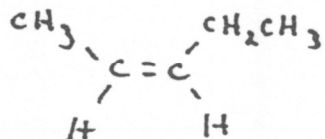
CIS/TRANS NOMENCLATURE

IF 2 SIMILAR GROUPS BOND TO THE DOUBLE BOND CARBONS ARE:

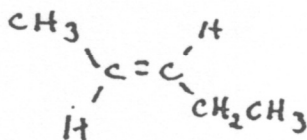
ON THE SAME SIDE \rightarrow CIS

ON OPPOSITE SIDES \rightarrow TRANS

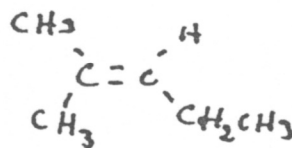
IF THERE ARE 2 IDENTICAL GROUPS ON ONE CARBON \rightarrow NO CIS/TRANS



CIS-2-PENTENE



TRANS-2-PENTENE



NEITHER CIS NOR TRANS

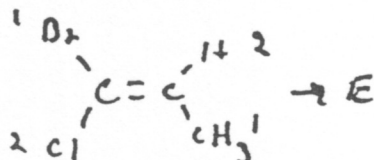
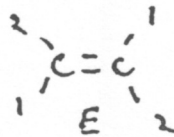
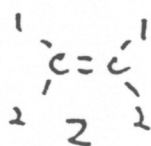
ALL RING DOUBLE BONDS ARE ASSUMED TO BE CIS UNLESS NAMED OTHERWISE

THE E/Z NOMENCLATURE

PRIORITIZE EACH GROUP ON THE DOUBLE BOND (AS IN THE R,S PRIORITIES)

IF THE 1_a ARE ON ONE SIDE, 2_a ON THE OTHER \rightarrow Z = SAME (CIS LIKE)

IF THE 1_a AND 2_a ARE ON OPPOSITE SIDES \rightarrow E = OPPOSITE (TRANS LIKE)



NOMENCLATURE RULES SUMMARIZED ON PG 301

COMMERCIAL USES OF ALKENES

HARD TO IMAGINE HOW MUCH IS IN USE AND MADE EACH YEAR

50 BILLION POUNDS OF ETHYLENE

25 BILLION POUNDS OF PROPYLENE

MOSTLY USED FOR POLYMERS (ABOUT 50%) (FIG 7-4)

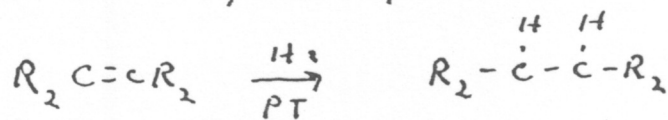
THE REST IS STARTING MATERIAL FOR OTHER SMALL, USEFUL MOLECULES

SEE FIG 7-3

ETHYLENE IS ALSO A PLANT HORMONE (RIPENING FRUITS)

STABILITY OF ALKENES

ALKENES ARE CATALYTICALLY REDUCED WITH H_2 , PRODUCT IS AN ALKANE



THE ENERGY EVOLVED IN THIS EXOTHERMIC REACTION IS USED TO COMPARE THE STABILITY OF VARIOUS ALKENES TABLE 7-1

THE DATA CONFIRM THE SAYTZEFF RULE:

MORE HIGHLY SUBSTITUTED ALKENES ARE MORE STABLE

IN ADDITION, AMONG DI-SUBSTITUTED ALKENES, THE ORDER OF STABILITY IS



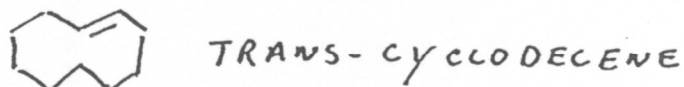
STABILITY OF CYCLOALKANES

BY FAR, DOUBLE BONDS IN RINGS ARE MOSTLY CIS
IN THREE AND FOUR MEMBERED RINGS THERE IS ADDITIONAL RING STRAIN

TRANS ISOMERS ARE RARE AND A MINIMUM OF 8 CARBONS ARE REQUIRED IN THE RING



10 MEMBER AND HIGHER RINGS CAN HAVE STABLE TRANS C=C



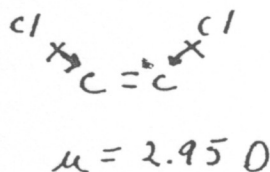
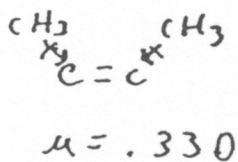
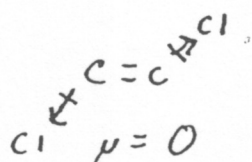
BREITS RULE SAYS THAT BRIDGEHEAD CARBONS MAY ONLY BE IN A DOUBLE BOND IF THEY ARE ALSO IN AN 8-MEMBERED RING



PHYSICAL PROPERTIES OF ALKENES RESEMBLE THE RELATED ALKANE

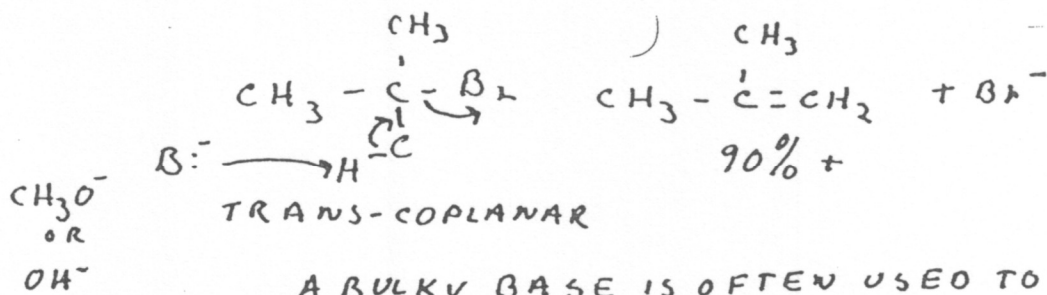
SYMMETRICALLY DISUBSTITUTED TRANS ALKENES HAVE A DIPOLE MOMENT OF ZERO

CIS DI-SUBSTITUTED ALKENES MAY BE POLAR



ALKENE SYNTHESIS BY ELIMINATION

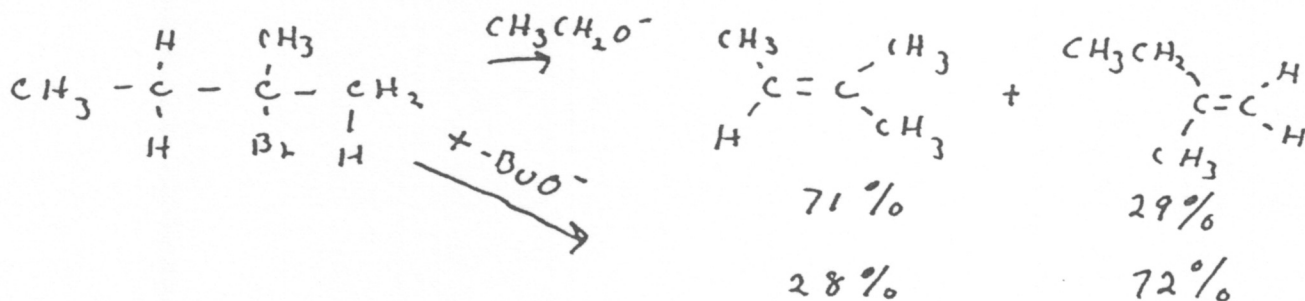
E2 - STRONG BASE + HINDERED HALIDE



A BULKY BASE IS OFTEN USED TO MINIMIZE SUBSTITUTION



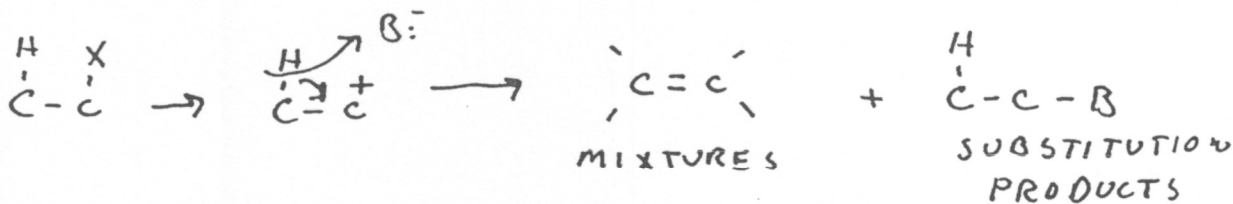
BULKY BASES HAVE A PREFERENCE FOR LESS HINDERED PROTONS



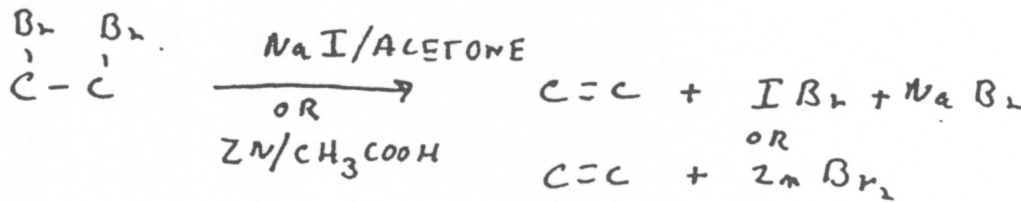
E1 → NO STRONG BASE

GOOD IONIZING SOLVENT

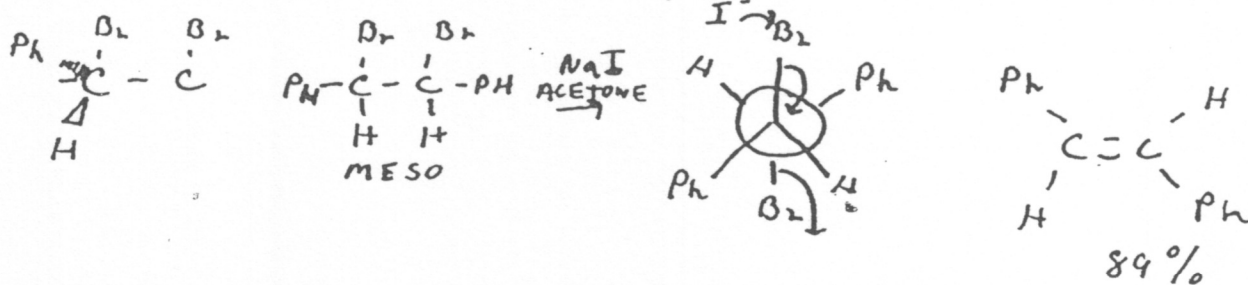
ACCOMPANIED BY S_N1, LESS USEFUL SYNTHETICALLY



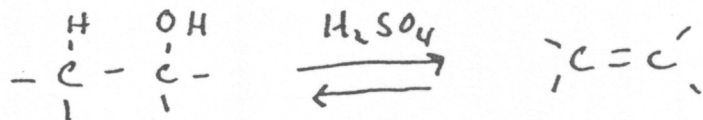
DEHALOGENATION OF VICINAL DIBROMIDES



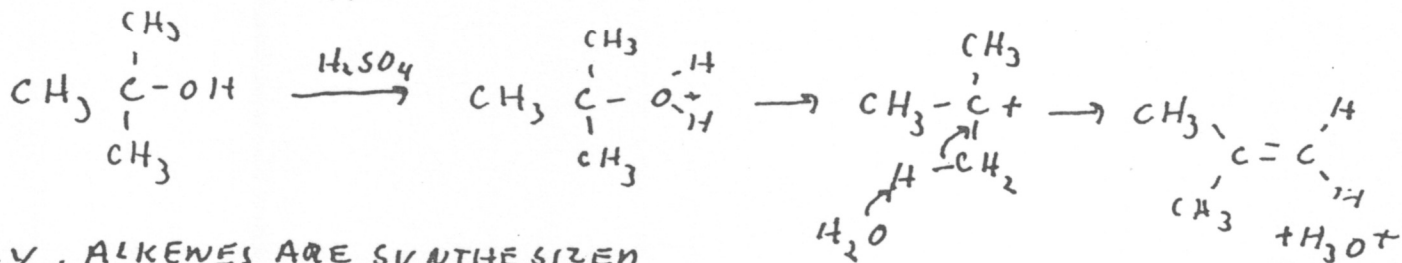
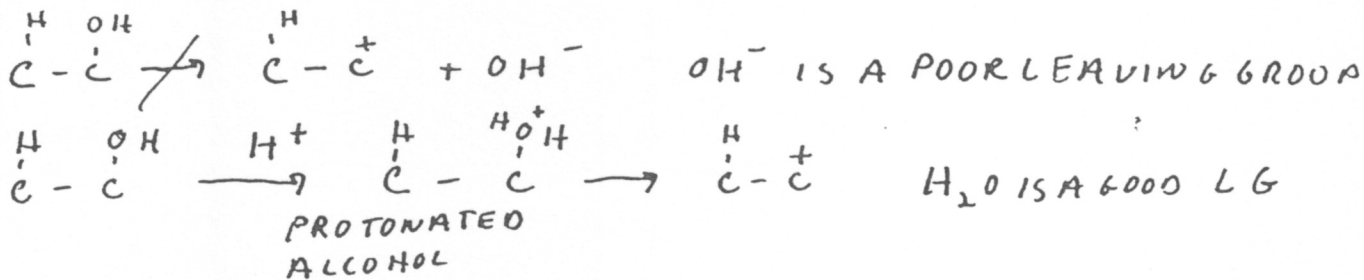
E2 MECHANISM, ANTI COPLANAR, STEREO SPECIFIC PRODUCTS



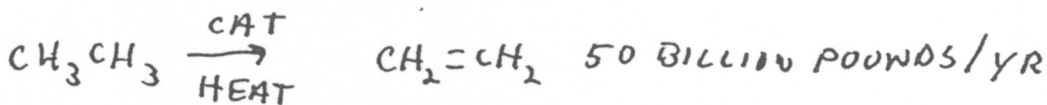
DEHYDRATION OF ALCOHOLS



THE MECHANISM INVOLVES A CARBOCATION



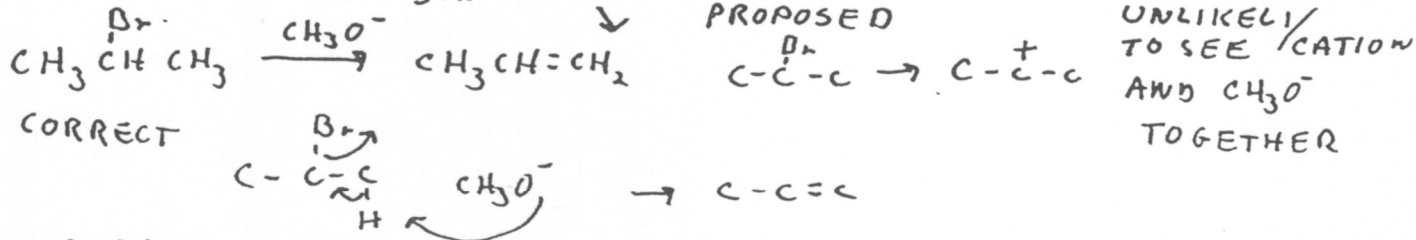
FINALLY, ALKENES ARE SYNTHESIZED BY CATALYTIC CRACKING OF ALKANES
THIS IS A CHEAP, INDUSTRIAL PROCESS



MECHANISMS PG 318-321

LOOK AT REACTANTS AND SUBSTRATES - STRONG BASE? NUCLEOPHILE?
ELECTROPHILE? HINDERED BASE?
DRAW ALL BONDS NEEDED, CONDENSE ONLY PERIPHERAL STRUCTURES
HINDERED OR 1° SUBSTRATE?

SHOW 1 STEP AT A TIME STRONG NUCLEOPHILES



ELECTROPHILES → INTERMEDIATES WILL BE H⁺ AND ELECTROPHILES

