CHAPTER 3 LECTURE NOTES FOR ORGANIC CHEMISTRY © MM 2001

STRUCTURE AND STEREOCHEMISTRY OF ALKANES

ALKANES ARE HYDROCARBONS CONTAINING ONLY SINGLE BONDS

THEY ARE "SATURATED" BECAUSE ALL VALENCES ARE FILLED BY HYDROGENS - SATURATED HYDROCARBONS

A HOMOLOGOUS SERIES IS A GROUP OF HYDROCARBONS DIFFERING ONLY IN BY 1 CH_2

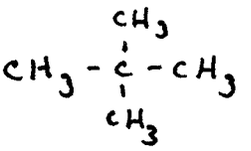
CH_4 METHANE CH_3CH_3 ETHANE $CH_3CH_2CH_3$ PROPANE $CH_3CH_2CH_2CH_3$ BUTANE ETC.

THE MOLECULAR FORMULAS OF ALL ALKANES IS

$C_N H_{2N+2}$ THE "2N+2" RULE

FOR THE ABOVE EXAMPLES ITS CH_4, C_2H_6, C_3H_8, C_4H_{10}

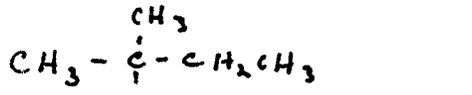
EVEN BRANCHED ALKANES HAVE 2N+2



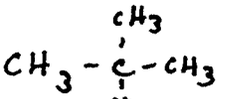
C_5H_{12}

NEO PENTANE

FOR THE SMALLEST ALKANES WE STILL USE A FEW COMMON NAMES



ISO PENTANE



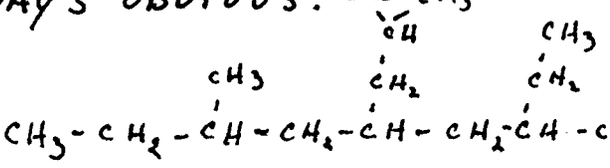
ISO BUTANE

MOST MOLECULES GET STANDARDIZED NAMES CALLED IUPAC

IUPAC NOMENCLATURE

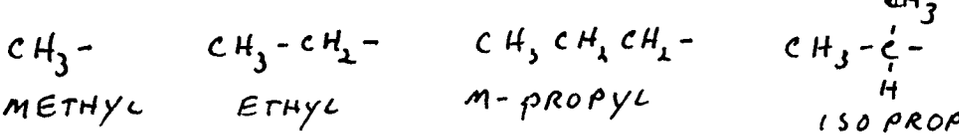
1) FIND THE LONGEST CONTINUOUS CARBON CHAIN THIS IS THE BASENAME
2) NUMBER THE CHAIN, STARTING AT THE END NEAREST A BRANCH
3) NAME THE SUBSTITUENT GROUPS
4) WHEN TWO OR MORE SUBSTITUENTS ARE PRESENT, LIST THEM IN ALPHABETICAL ORDER. IF THERE ARE TWO OR MORE OF THE SAME SUBSTITUENTS USE THE PREFIXES DI, TRI, TETRA FOR 2, 3 OR 4 IN ONTICAL SUBSTITUENTS

FINDING THE LONGEST CHAIN AND NUMBERING IT IS EASY, BUT NOT ALWAYS OBVIOUS.



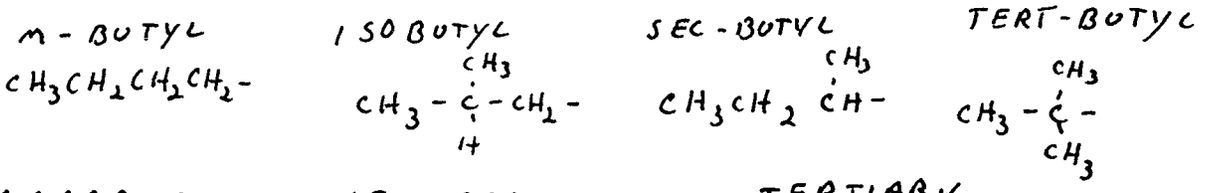
NAMING SUBSTITUENTS

HYDROCARBON GROUPS ARE NAMED AS ALKYL GROUPS

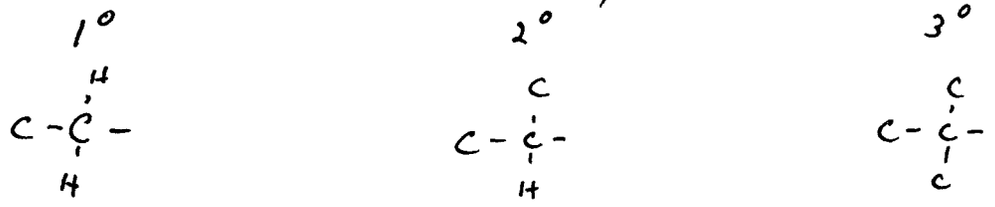


METHYL ETHYL M-PROPYL ISOPROPYL

4 CARBON GROOPS M- INDICATES STRAIGHT CHAIN



PRIMARY CARBON SECONDARY TERTIARY

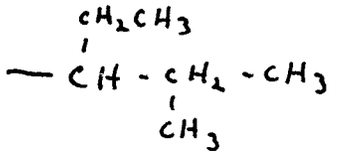


DEGREE OF ALKYL SUBSTITUTION

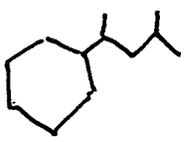
PREFIXES FOR IDENTICAL GROUPS

di-	2	tetra-	4	HEXA-	6
tri-	3	Penta-	5		

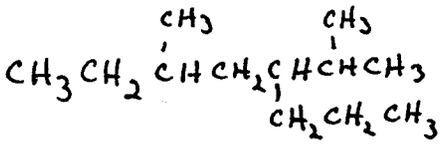
OCCASIONALLY, QUITE COMPLEX ALKYL GROUPS ARE ENCOUNTERED THEY ARE NAMED BY TAKING THE LONGEST CHAIN IN THE GROUP AS A BASE NAME, NUMBERING THIS CHAIN FROM ITS BRANCH POINT WITH THE MAIN CHAIN, LISTING THE ALKYL SUBSTITUENTS WITH NUMBERS FOR THEIR POSITION AND PUTTING EVERY THING IN PARENTHESES



A (1-ETHYL-2-METHYLPROPYL) GROUP



(2,4-DIMETHYLBUTYL) CYCLOHEXANE



3-METHYL-5-ISOPROPYLOCTANE

PHYSICAL PROPERTIES OF ALKANES

ALKANES ARE VERY NONPOLAR, SOLUBLE IN NONPOLAR SOLVENTS
WE CALL THEM "HYDROPHOBIC"

ALKANES ARE LESS DENSE THAN WATER, DENSITY $\tilde{=}$ 0.7 g/mL
ALKANES ARE GENERALLY LOW BOILING. BP INCREASES WITH MOLECULAR WEIGHT

LARGER ALKANES BECOME SOFT SOLIDS, EVEN LARGER → WAX

USES OF ALKANES

AS FUELS AND LUBRICANTS FROM BUTANE LIGHTERS TO GASOLINE, HOME HEATING OIL (DIESEL FUEL) LUBRICANTS FROM LIGHT MACHINE OIL TO HEAVY GEAR GREASE TO ASPHALT

SOURCES

FROM PETROLEUM BY DISTILLATION INTO FRACTIONS

SOME HEAVY PETROLEUM IS "CRACKED" INTO SMALLER MORE VALUABLE PRODUCTS

REACTIONS OF ALKANES

COMBOSTION - THE MOST COMMON REACTION

$$C_n H_{2n+2} + xs\,O_2 \longrightarrow n\,CO_2 + (n+1)H_2O$$

$$CH_3CH_2CH_3 + 5\,O_2 \rightarrow 3CO_2 + 4H_2O$$

CRACKING

LONGER CHAIN ALKANES ARE SPLIT IN A CATALYTIC PROCESS

$$C_{20}H_{42} \xrightarrow[\text{CATALYST}]{} \text{MIXTURE OF SMALLER ALKANES}$$

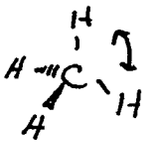
HALOGENATION

ALKANES REACT WITH HALOGENS

$$CH_4 + Cl_2 \xrightarrow[\text{OR LIGHT}]{\text{HEAT}} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$

STRUCTURE AND CONFORMATION

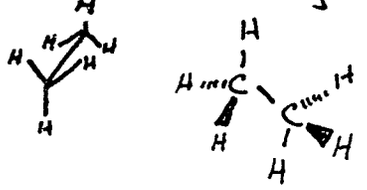
METHANE - A SIMPLE TETRAHEDRON



109.5° THE TETRAHEDRAL ANGLE

BOND LENGTH 1.09 Å

ETHANE - CH_3-CH_3



BOND ANGLES 109.5

C-C BOND LENGTH 1.54 Å

CONFORMATIONS

FREE ROTATION ABOUT THE C-C BOND LEADS TO DIFFERENT ARRANGEMENTS OF ATOMS IN SPACE CALLED CONFORMATIONS

SOME CONFORMATIONS ARE ESPECIALLY STABLE, SOME UNSTABLE.

SPECIFIC CONFORMATIONS ARE CALLED CONFORMERS

NEWMAN PROJECTIONS

DRAW THE MOLECULE LOOKING STRAIGHT DOWN THE C-C BOND

FRONT CH_3 

BACK CH_3 

PROJECTIONS  

A STABLE CONFORMER

USUALLY HAS ALL ATOMS AS FAR APART AS POSSIBLE

"STAGGERED"

LESS STABLE

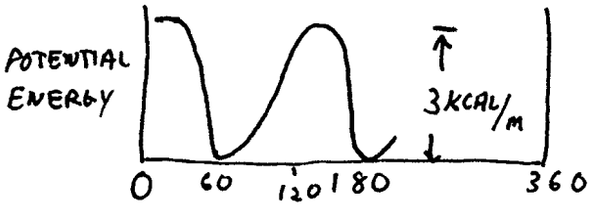
"ECLIPSED" 

"SKEW" IS ANYTHING IN BETWEEN

CONFORMATIONAL ANALYSIS

STUDY OF THE ENERGETICS OF CONFORMATION CHANGE

PLOT POTENTIAL ENERGY VS DIHEDRAL ANGLE (ANGLE OF BOND ROTATION)



0 = 120 = ECLIPSED

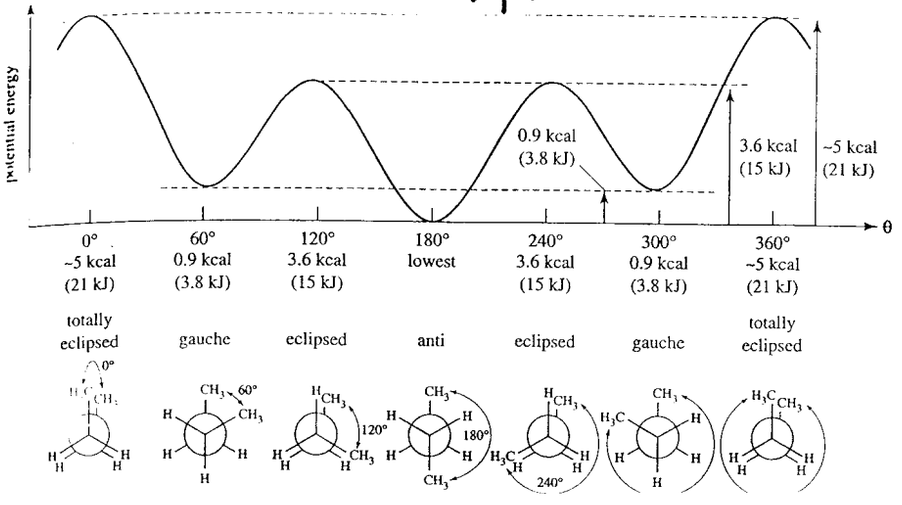
180 = 60 = STAGGERED

FOR BUTANE THERE ARE A FEW NEW POSSIBILITIES

TOTALLY ECLIPSED

GAUCHE

ANTI



CONFORMATIONS OF MONOSUBSTITUTED CYCLOHEXANES

SUBSTITUENT EQUATORIAL IS MORE STABLE, 1.7 KCAL/MOLE FOR CH_3

5.4 KCAL/MOLE FOR T-BUTYL

SEE TABLE 3-5

DISUBSTITUTED - THE 1,3-DIAXIAL INTERACTION IS PARTICULARLY UNSTABLE

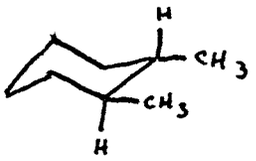
IN CIS 1,3-DIMETHYLCYCLOHEXANE THE DIEQUATORIAL CONFORMER MORE STABLE THAN THE DIEQUATORIAL

IF ONE SUBSTITUENT IS LARGER THAN ANOTHER, IT WILL FAVOR EQUATORIAL

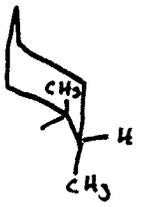
REMEMBER THAT EACH CARBON HAS 2 AVAILABLE BONDS, ONE UP ONE DOWN

CIS MEANS TWO UP BONDS

TRANS MEANS ONE UP, ONE DOWN



TRANS-1,2-DIMETHYLCYCLOHEXANE

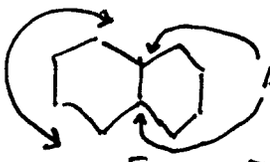


BICYCLIC ALKENES

PREFIX BICYCLO

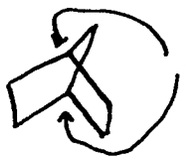
BRACKETS WITH 3 NUMBERS INDICATING HOWMANY CARBONS SEPARATE THE "BRIDGEHEAD" CARBONS

4 CARBON PATH BETWEEN BRIDGEHEADS



BICYCLO[4,4,0] DECANE

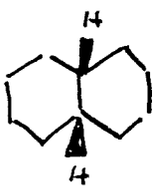
DECALIN, A FUSED RING



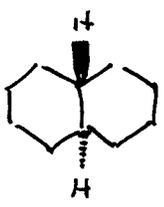
BICYCLO[2,2,1] HEPTANE

NORBORNANE, A BRIDGED BICYCLIC

3 PATHS BETWEEN BRIDGEHEADS 2, 2 AND 1 CARBON



CIS DECALIN



TRANS DECALIN

CHAPTER 3

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