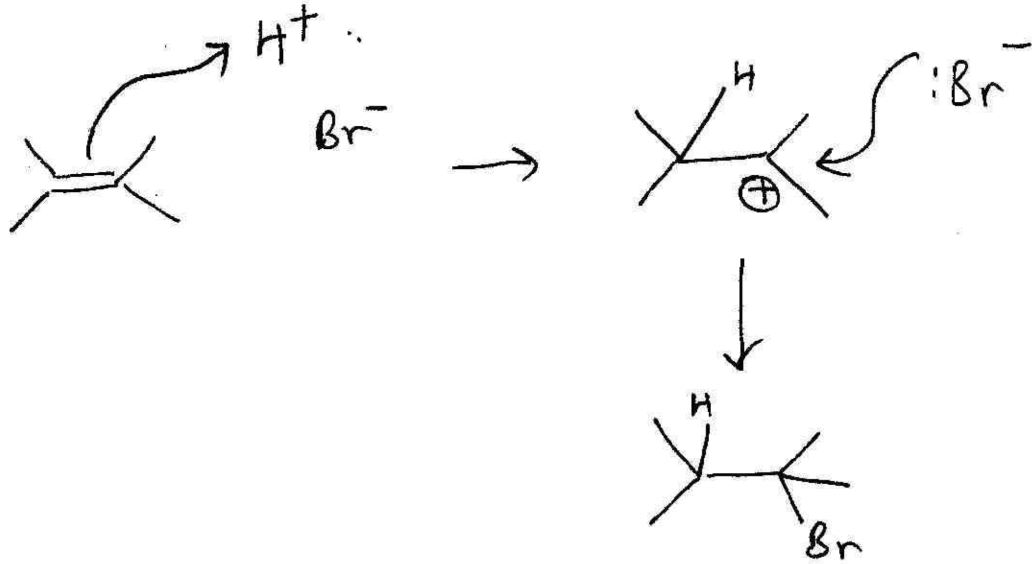
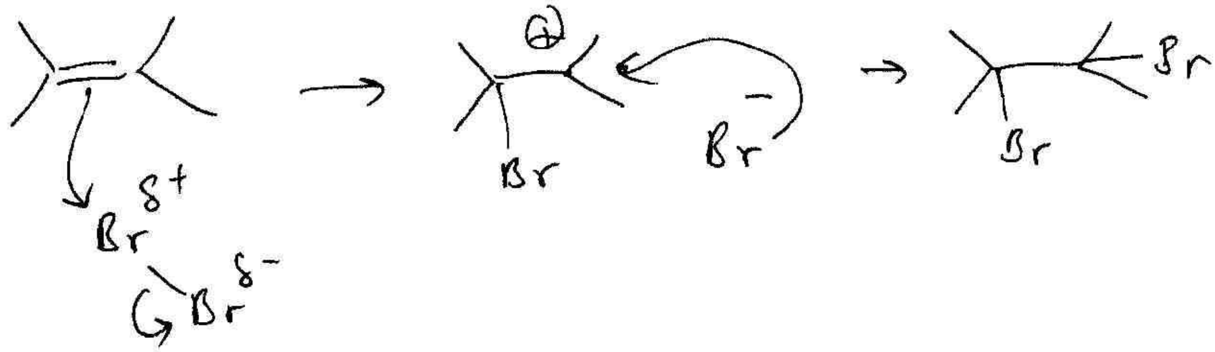
46. Electrophilic addition to the $>C=C<$.

1) Another important reaction which you will study in organic chemistry is electrophilic addition to the double bond.

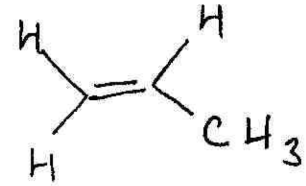


or another example:

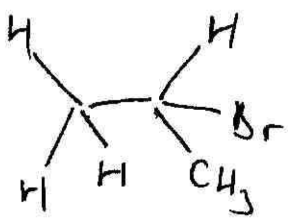
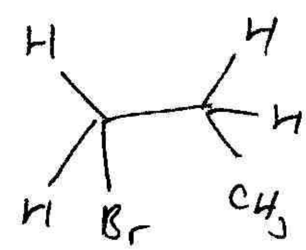
 + Br_2. We can think of Br_2 as Br^+ & Br^- or $Br^{\delta+} — Br^{\delta-}$



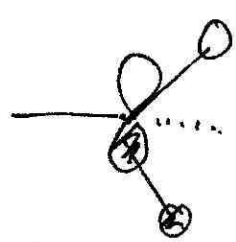
(2) Let's examine this reaction from an MO viewpoint & let's ask the question if one has

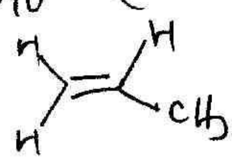
 + HBr

is the final product

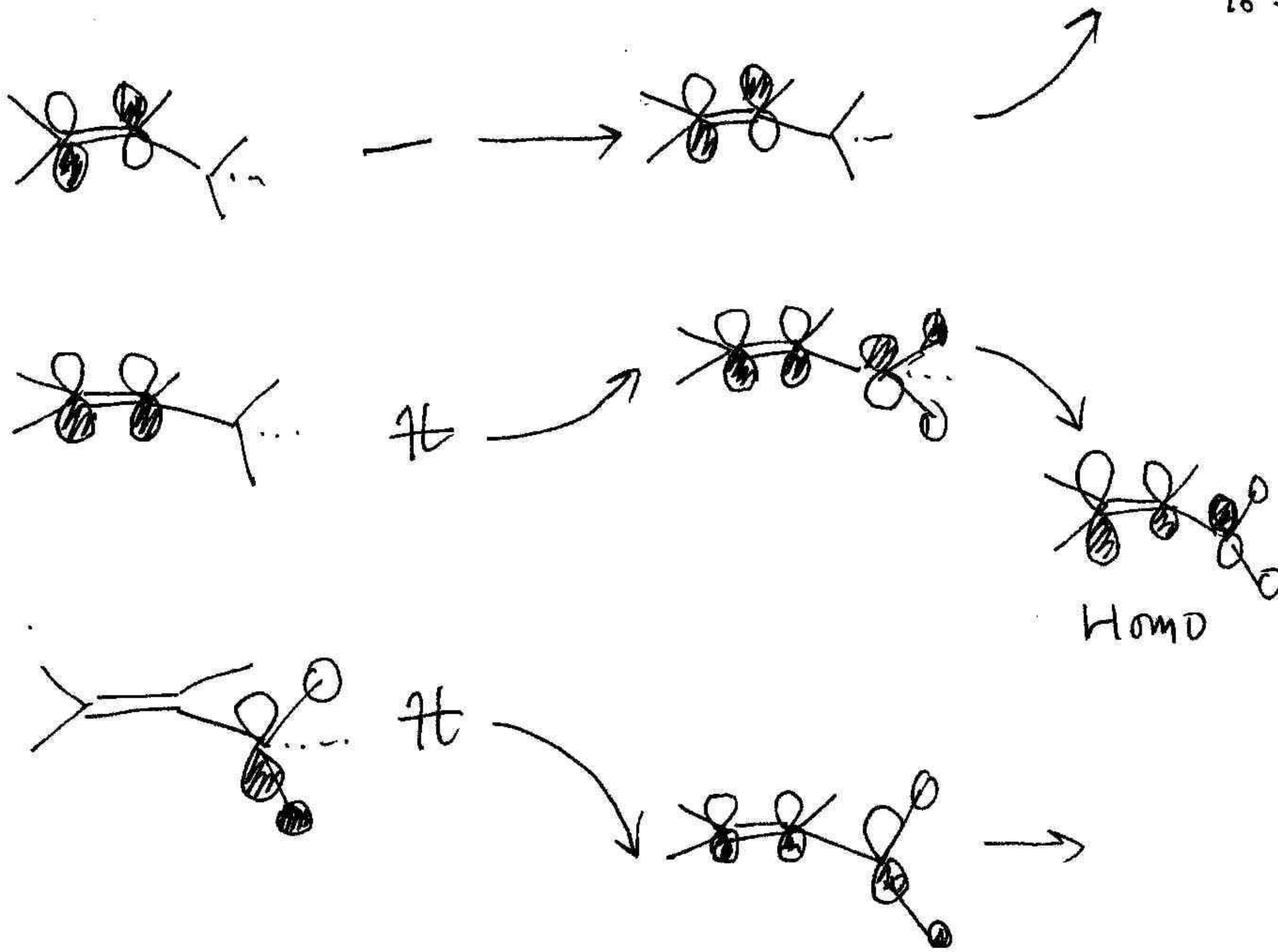
 or  ?

(3) To answer this question we must decide whether $-CH_3$ is an electron donor or an electron withdrawer. As we discussed last time $-CH_3$ is an e^- donor & its "key" orbital is



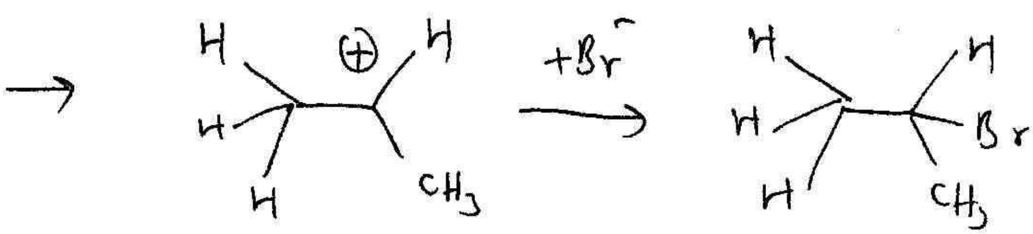
So let's see how this orbital changes the HOMO (note  is acting as nucleophile) of the  molecule.

③



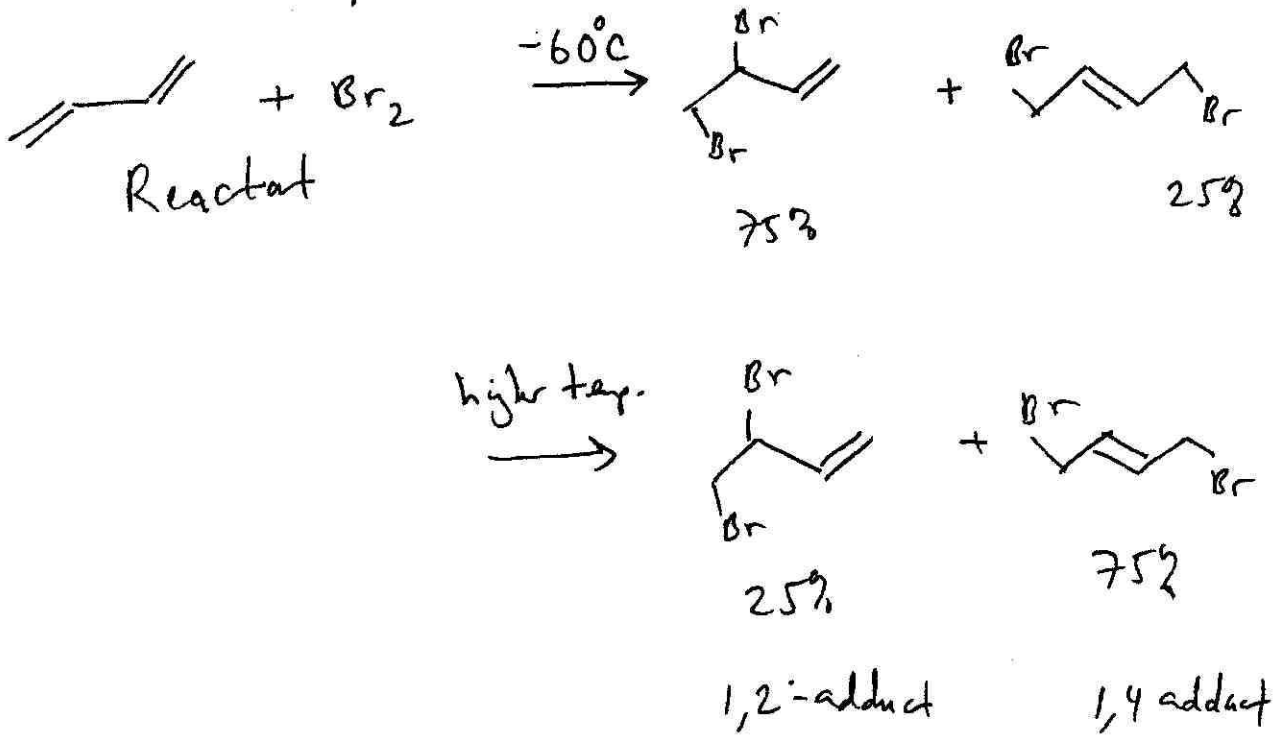
So in

HBr + $H_2C=CH(CH_3)$ the H adds away from the CH_3 (the e^- donor).



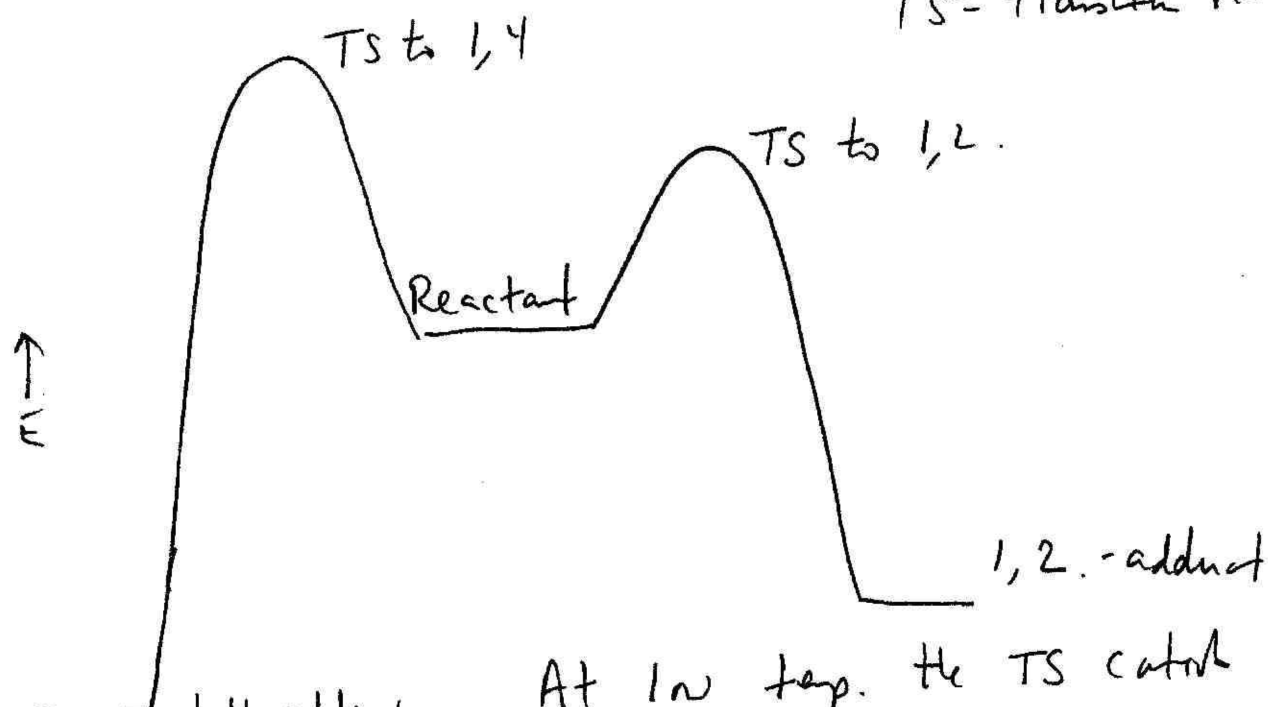
④ The halogen adds to the site with more CH_3 groups: This is Markownikov's rule.

(5) As another example consider



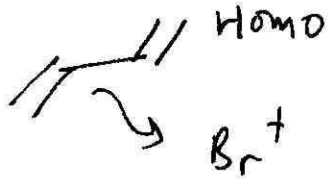
(6) Chemists generally guess what this data means: kinetic vs. thermodynamic control.

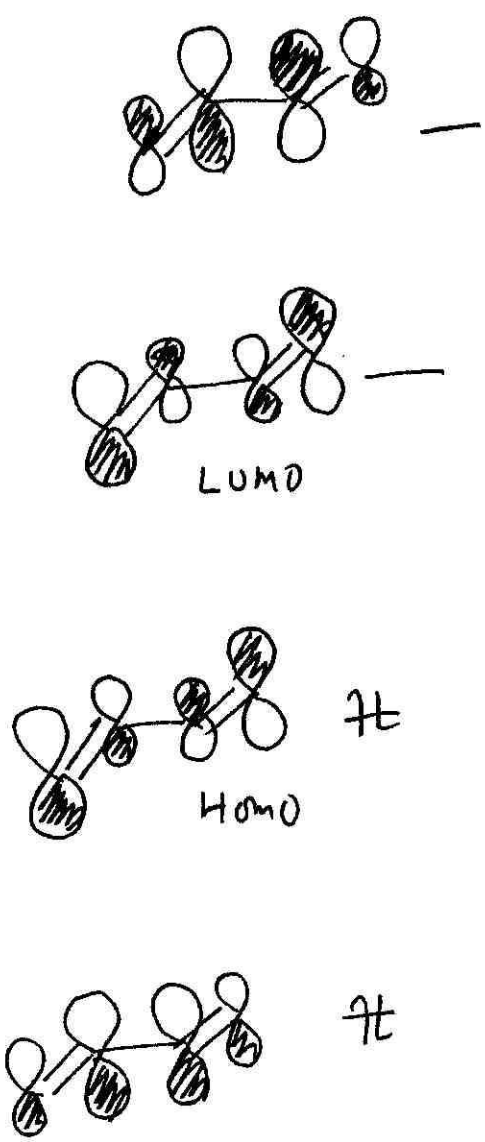
TS = transition state



At low temp. the TS controls which product
At high temp, equilibrium is achieved
& the energy of 1,2 vs 1,4 is controlling factor

(9) In MO theory we will study what the kinetic product is. So let's follow the course of the reaction.

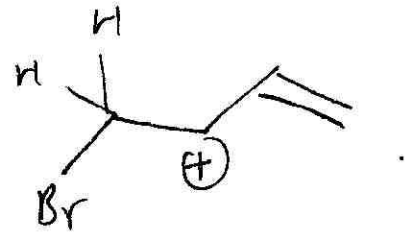




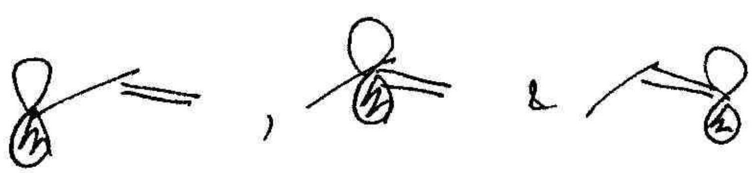
∴ 1st Br addition is to outer C.

(8)

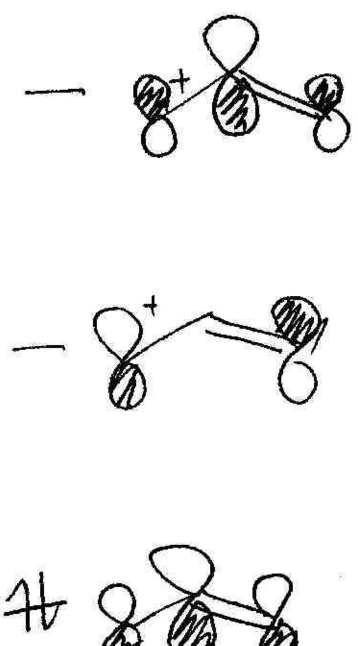
Now we have the molecule



What does the MO diagram of this molecule look like? First let's draw the MO diagram of  & then we will consider the action of CH_2Br— (which we will assume is an e^- donating group)

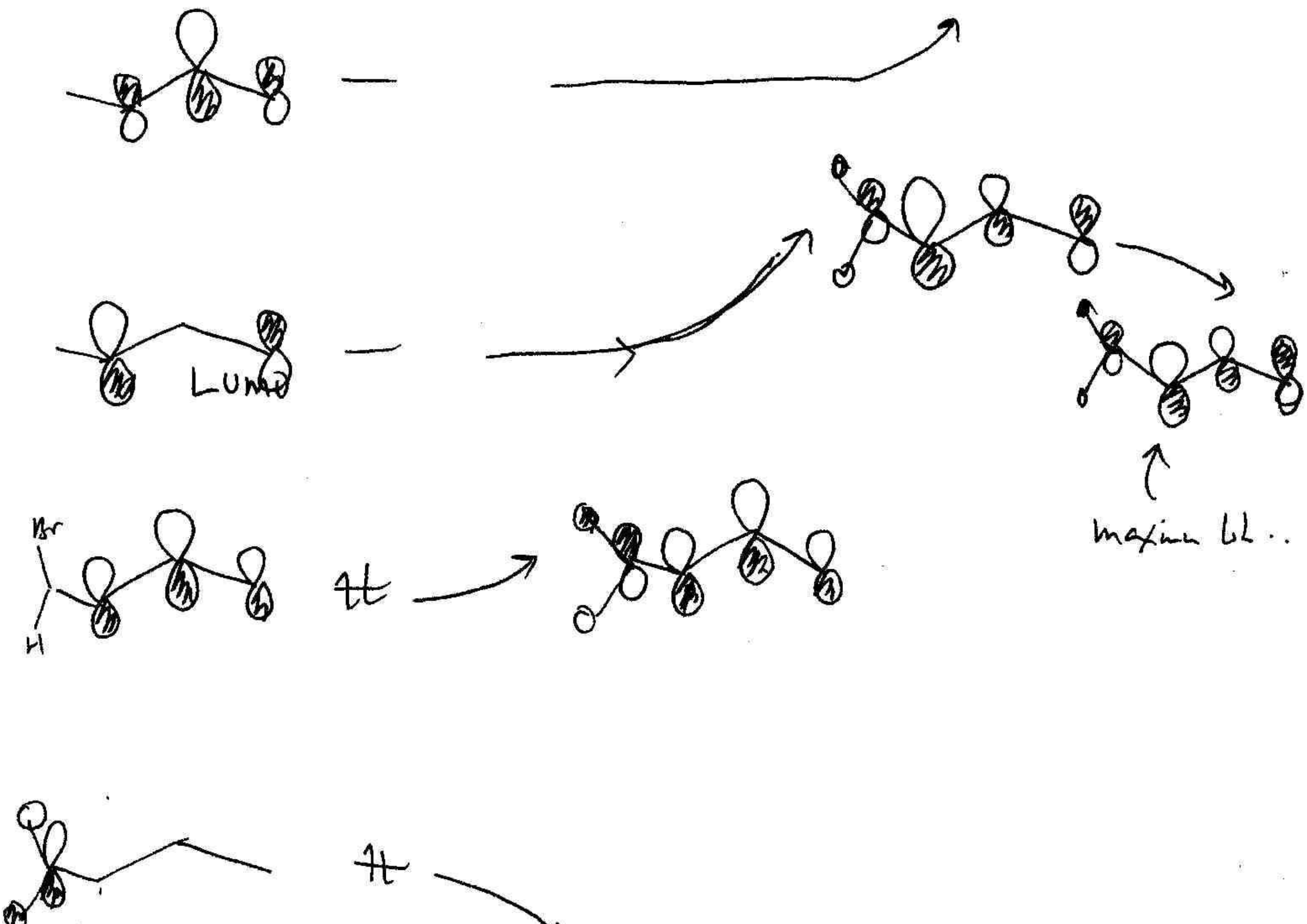
(9)  comes from 

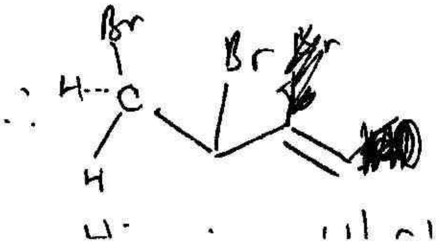
MO diagram



⑩ As we are interested in

the organic piece is acting as the electrophile & we need to look at the LUMO.





will be the kinetic product.

[illegible] observed.

TABLE 15-3
Principal Metal Toxins

	Arsenic	Lead	Mercury	Thallium
Clinical tip-off	Red hands and burning feet with hyperhidrosis	Peripheral neuropathy that may appear to be a single nerve involvement (such as a wristdrop or footdrop)	Severe spontaneous arm and leg pain	Alopecia
Exposure	Homicide attempts; insecticides; medicinal arsenic; Paris green; accidental contamination; Fowler's solution (potassium arsenite)	Industrial ingestion; tetraethyl gasoline; lead paint; burning lead batteries; eating from pewter or dishware with a glaze containing lead; melting for purposes of molding	Ingestion of methyl mercury (Minamata disease), especially from fish in polluted areas; industrial exposure; antifungal treatment of grain	Homicide; insecticide; rodent poison
Clinical syndrome	"Stocking-glove," mainly sensory neuropathy; severe pain and paresthesias, especially of feet; "burning feet and hands," red hands with hyperhidrosis and subsequent motor neuropathy involving distal muscles of hands and feet	Primarily a motor neuropathy that frequently may appear as though single nerves are involved, such as the radial nerve (wristdrop), the median nerve (thenar atrophy), or the peroneal nerve (footdrop); painful joints; cerebral edema in children	Dementia with primary motor neuropathy; occasional sensory stocking-glove neuropathy; acrodynia (pink disease) in infants and young children	Distal sensorimotor neuropathy of stocking-glove type with alopecia
Diagnosis	24-hour urine analysis; hair analysis; blood arsenic level	Blood lead level; 24-hr urine analysis	24-hr urine analysis	24-hr urine analysis
Treatment	Penicillamine 250 mg 4 times a day (may also use BAL or EDTA)	Penicillamine 250 mg 4 times a day (may also use BAL or EDTA)	Penicillamine 250 mg 4 times a day (may also use BAL or EDTA)	Diphenylthio-carbazone or sodium dicarbamate

	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8	8B 9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	
[redacted]																	[redacted]
3 Li Lithium 6.941	4 Be Beryllium 9.01218											[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
11 Na Sodium 22.98977	12 Mg Magnesium 24.305											13 Al Aluminum 26.98154	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.9559	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.9380	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.9059	40 Zr Zirconium 91.224	41 Nb Niobium 92.9064	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.82	50 Sn Tin 118.710	[redacted]	[redacted]	[redacted]	[redacted]
55 Cs Cesium 132.9054	56 Ba Barium 137.327	57 *La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.2	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.9804	[redacted]	[redacted]	[redacted]
87 Fr Francium (223)	88 Ra Radium 226.0254	89 †Ac Actinium 227.0278	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (268)	110 (269)	111 (272)	112 (277)						

*Lanthanide Series	58 Ce Cerium 140.115	59 Pr Praseodymium 140.9077	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.9254	66 Dy Dysprosium 162.50	67 Ho Holmium 164.9303	68 Er Erbium 167.26	69 Tm Thulium 168.9342	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
† Actinide Series	90 Th Thorium 232.0381	91 Pa Protactinium 231.0359	92 U Uranium 238.0289	93 Np Neptunium 237.048	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)

Price/gram most expensive elements

21 Sc $131	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.9380	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	
39 Y Yttrium 88.9059	40 Zr Zirconium 91.224	41 Nb Niobium 92.9064	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru $2.50	45 Rh $71	46 Pd $7	47 Ag $0.25	48 Cd Cadmium 112.411	49 In Indium 114.82	50 Sn Tin 118.710
57 *La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re $12	76 Os $95	77 Ir $6	78 Pt $31	79 Au $15	80 Hg $0.02	81 Tl Thallium 204.3833	82 Pb Lead 207.2

Sources: http://www.minerals.usgc.gov/minerals
http://metalsplace.com/metalsboard (Os)

1: J Agric Food Chem. 2000 Oct;48(10):4830-4.

Related Articles, Links

ACS PUBLICATIONS HIGH QUALITY HIGH IMPACT

Organoleptic impact of 2-methoxy-3-isobutylpyrazine on red bordeaux and loire wines. Effect of environmental conditions on concentrations in grapes during ripening.

Roujou de Boubee D, Van Leeuwen C, Dubourdieu D.

Faculte d'OEnologie, Universite Victor Segalen Bordeaux II, 351 Cours de la Liberation, 33405 Talence Cedex, France. droujou@u-bordeaux2.fr

The 2-methoxy-3-isobutylpyrazine content in grapes and red wines was assayed by stable isotope dilution gas chromatography-mass spectrometry, following vapor extraction and purification on a cation resin microcolumn. The threshold beyond which the green bell pepper character is marked in wines has been determined. From a comparison of the 2-methoxy-3-isobutylpyrazine concentrations of 50 red Bordeaux and Loire wines from different vintages and grape varieties (Cabernet Sauvignon, Cabernet franc, and Merlot) with the intensity of the green bell pepper character as perceived on tasting, the threshold value was estimated to be 15 ng/L. Statistical analysis of the 2-methoxy-3-isobutylpyrazine concentrations of 89 red Bordeaux wines showed that Cabernet wines were more commonly affected by this vegetative character. Changes in the 2-methoxy-3-isobutylpyrazine concentration as the grapes ripen are affected by the environmental and cultural conditions (soil, climate, training system, etc.). A very good correlation was shown between the breakdown of malic acid and 2-methoxy-3-isobutylpyrazine as the grapes ripened, irrespective of grape variety, type of soil, or weather conditions.

PMID: 11052741 [PubMed - indexed for MEDLINE]

Leffingwell & Associates

Odor Properties & Molecular Visualization

Pyrazines

DETECTION THRESHOLDS & Molecular Structures

2-Methylpyrazine ...$C_5H_6N_2$
Odor Detection Threshold (in water) = 60,000 ppb
Green, nutty, cocoa, musty, potato, fishy-ammoniacal notes

2-Ethylpyrazine...$C_6H_8N_2$
Odor Detection Threshold (in water) = 6,000 ppb
Musty, nutty, buttery, peanut odor; chocolate-peanut taste

2,3-Dimethylpyrazine...$C_6H_8N_2$
Odor Detection Threshold (in water) = 2,500 ppb
Green, nutty, potato, cocoa, coffee, caramel, meaty notes

2,5-Dimethylpyrazine...$C_6H_8N_2$
Odor Detection Threshold (in water) = 800 ppb
Chocolate, roasted nuts, earthy; chocolate taste

2,6-Dimethylpyrazine...$C_6H_8N_2$
Odor Detection Threshold (in water) = 200 ppb
Chocolate, roasted nuts, fried potato odor

2,3,5-Trimethylpyrazine...$C_7H_{10}N_2$
Odor Detection Threshold (in water) = 400 ppb
Nutty, baked potato, roasted peanut, cocoa, burnt notes

2,3,5,6-Tetramethylpyrazine...$C_8H_{12}N_2$
Odor Detection Threshold (in water) = 1000 ppb
Weak, nutty, musty, chocolate odor; chocolate taste

2-Ethyl-3-methylpyrazine...$C_7H_{10}N_2$
Flavor Detection Threshold (in water) = 0.4 ppb
Potato, burnt nutty, roasted, cereal, earthy

2-Ethyl-5-methylpyrazine...$C_7H_{10}N_2$
Odor Detection Threshold (in water) = 100 ppb
Nutty, roasted, somewhat "grassy"

2-Ethyl-3,5-dimethylpyrazine...$C_8H_{12}N_2$

A European breed of paprika

Used plant part

Berry fruits. Removal of seeds and veins results in a less pungent and more brightly coloured product.

Plant family

Solanaceae (nightshade family).

Sensory quality

Sweet and aromatic. Some qualities show no pungency at all, others are fairly hot.

Main constituents

The pungent principle, capsaicin, is contained only in small amounts, as low as 0.001 to 0.005% in ?mild? and 0.1% in ?hot? cultivars (see chiles for details on capsaicin).

Apart from capsaicin, the taste of paprika is mostly due to essential oil (<1%; with long–chain aliphatic hydrocarbons, fatty acids and their methyl esters); paprika scent is mostly do to a range of alkylmethoxypyrazines (e.g., 3–isobutyl 2–methoxy pyrazine, ?earthy? flavour). Ripe paprika contain up to 6% sugar.