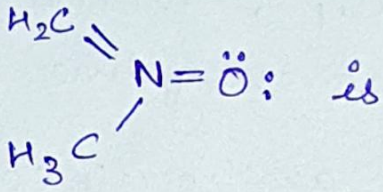
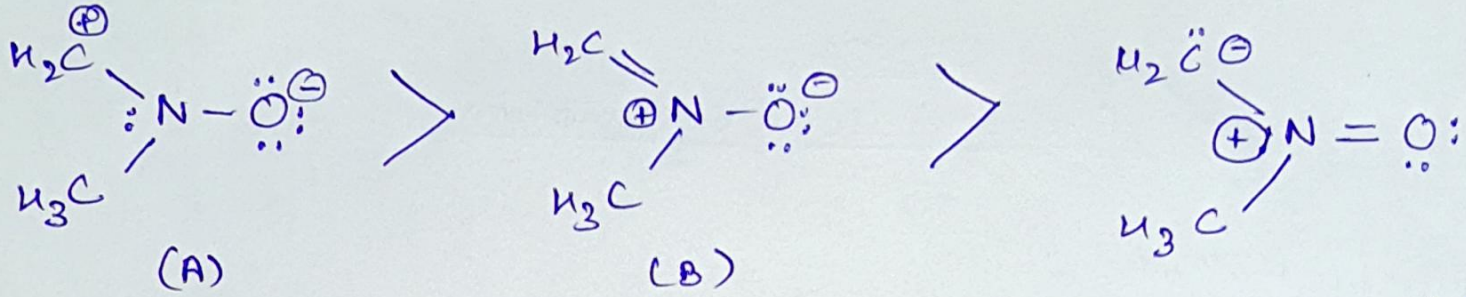
CH1101

End Semester Examination.

Name : Priyanshu Mahato

Roll No. : pm21ms002.

Q1. (a) I think structure C :  is not a permissible contributing structure, because in this structure, the N (nitrogen) atom makes a total of 5 (five) bonds with surrounding atoms which is not possible as extension of the octet rule is not possible with second ($2^{nd}$) period elements of the periodic table due to lack of any vacant d-orbitals to accomodate the extra electrons.

(b) 

(A) (B)

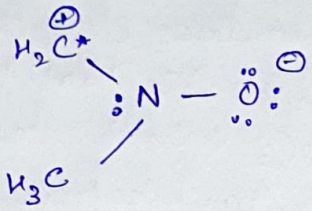
A should contribute maximum to the resonance hybrid because although carbon has only 6 electrons (<8), there is a negative charge on the more electronegative atom i.e., O.

After A, B comes in next, as though carbon has completed its octet, there is a positive charge on an electronegative atom i.e., N

D will contribute the least as N has the charge and carbon has negative charge (although N is more electronegative than carbon).

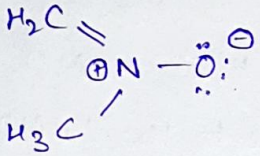
# Formal charges

(A)



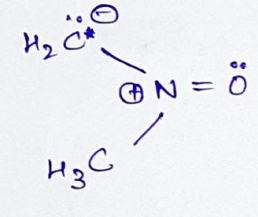
N : 0
O : -1
C* : +1 ; C : 0
H : 0

(B)



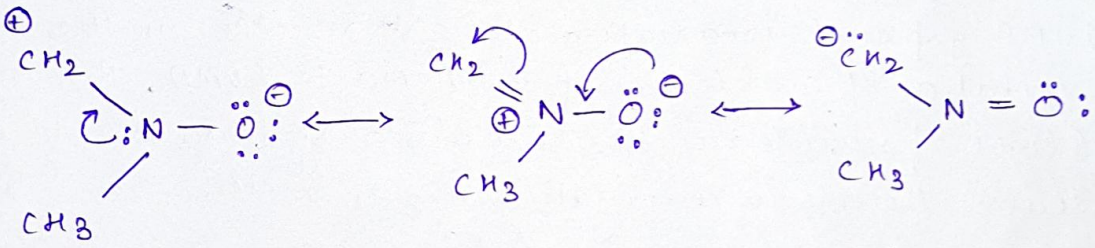
N ; +1
O : -1
C : 0
H : 0

(C)



O : 0
N ; +1
C* : -1 ; C : 0
H : 0

(C)



(A) (B) (D)

Q2. The intermediate structure 'A' is more probable because when a nucleophile attacks butadiene, it does it either from the $C_1$ or the $C_4$ side. From $\psi_2$ it is visible that there will be an in-phase overlap between $C_2$ & $C_3$ which would increase electron density at $C_2$ & $C_3$. It has electron density because $\pi$ MO in butadiene are delocalised. Thus, when a nucleophile approaches a butadiene, it will approach from either $C_1$ or $C_4$ side. Here, HOMO of nucleophile will transfer two electrons to the LUMO of $C_1$ & $C_4$ that is $\pi^*$. When 2 electrons will be transferred from HOMO→LUMO it will result in Bond Order = 0. Therefore, bond will break and an intermediate similar to (A) is formed.

Q5. As taught in the lectures, an increase in the no. of double bonds in conjugation leads to decrease in HOMO-LUMO gap and irradiation of light results in the excitation of an electron from HOMO to LUMO. The color (light of visible range) originates only when the no. of double bonds in conjugation is 8 or more.

∴, since HOMO-LUMO are closer in case of β-carotene, it absorbs blue color for the $e^{\ominus}$ transition and gives off an orange colour.

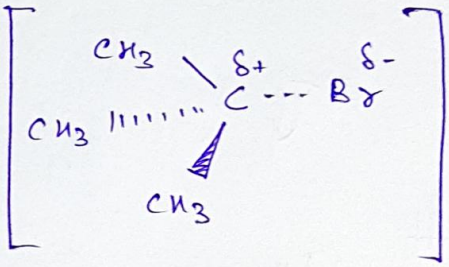
whereas in case of Butadiene, the HOMO-LUMO gap is more and the resultant radiation falls in the UV range and hence, invisible to the human eyes.

Q3. The structure (b) of the isomeric carbocations is most stable because it has the most no. of C–H σ bonds with the neighbouring carbon atoms which interact with the vacant p-orbitals of the carbocation. This brings extra stabilisation as the two σ-electrons in the C–H bond become lower in energy. In this specific structure, there are 7 C–H σ bonds and so 7 hyperconjugation structures are possible and hence, most stable.

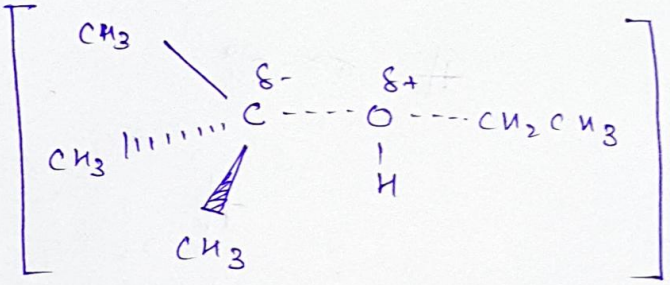
Q4. The transformation 'B' will most probably occur:

$(CH_3)_3CBr + CH_3CH_2OH \longrightarrow$ Pdts.

I →

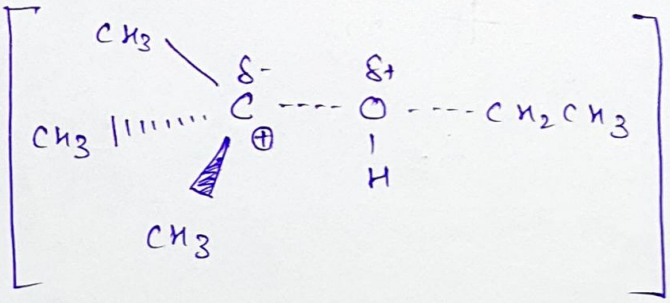


J →

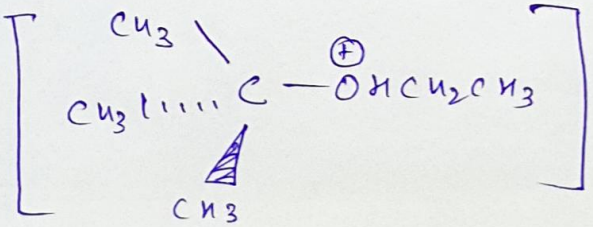


(planar)

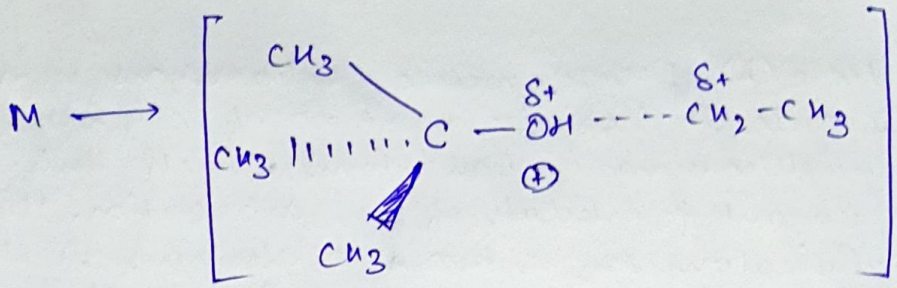
K →

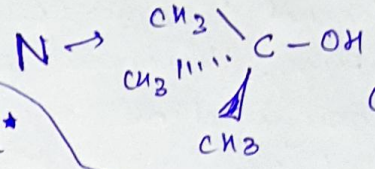


L →

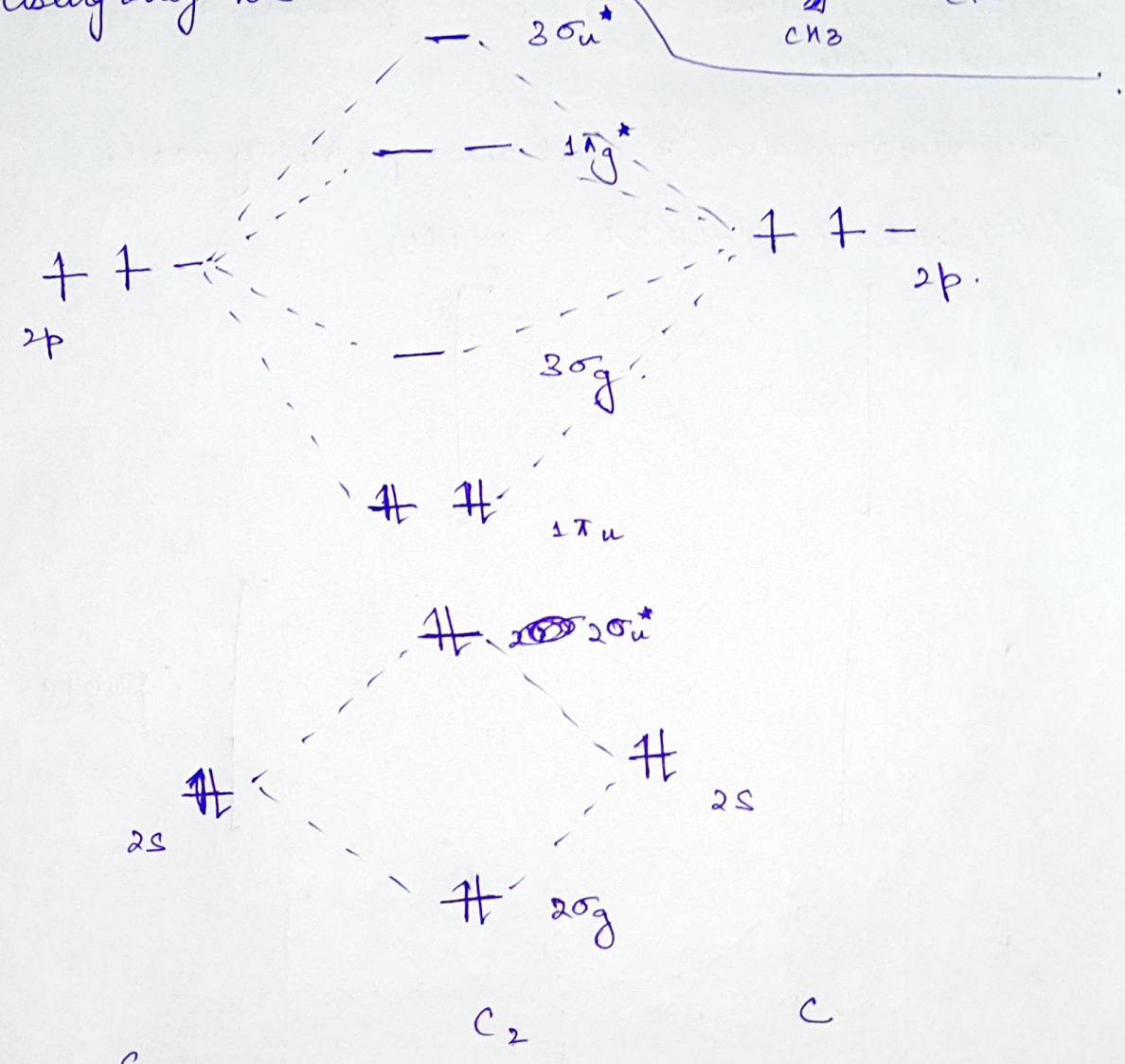


(tetrahedral)

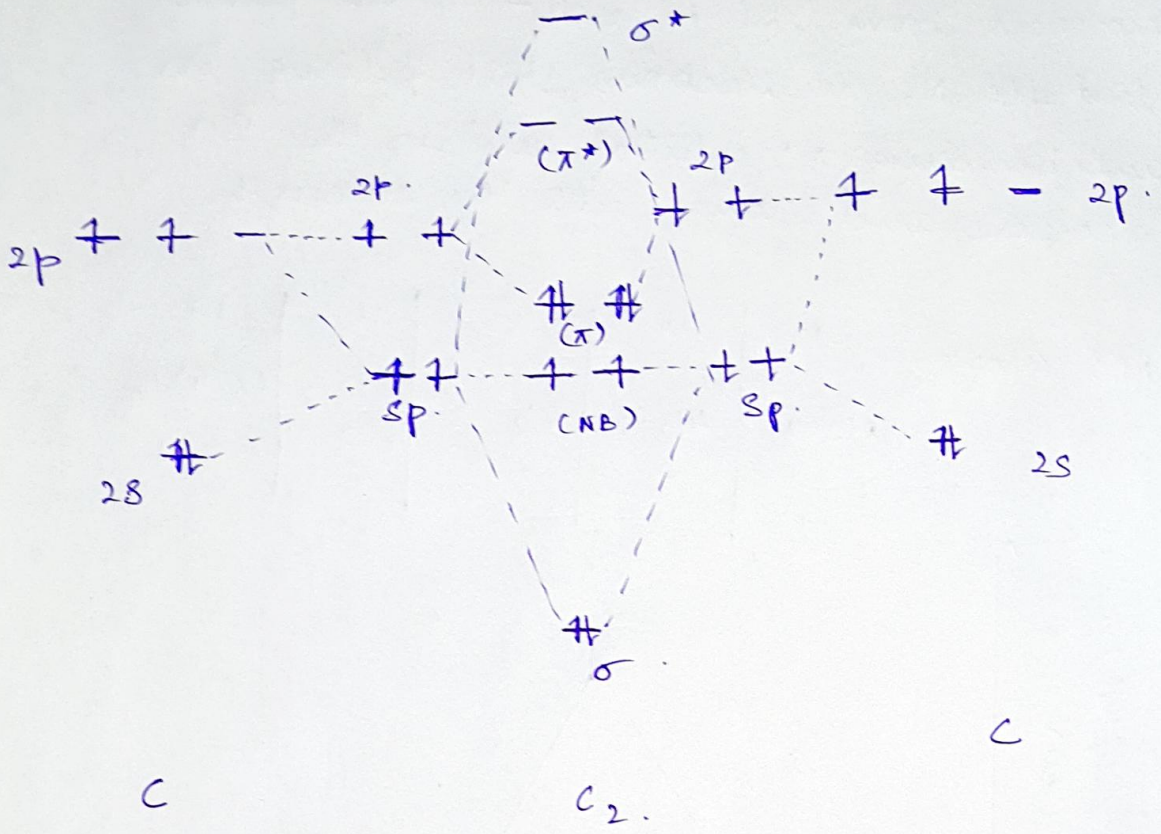



Q6. Using only AO's :-



Using sp - hybrid orbitals :-

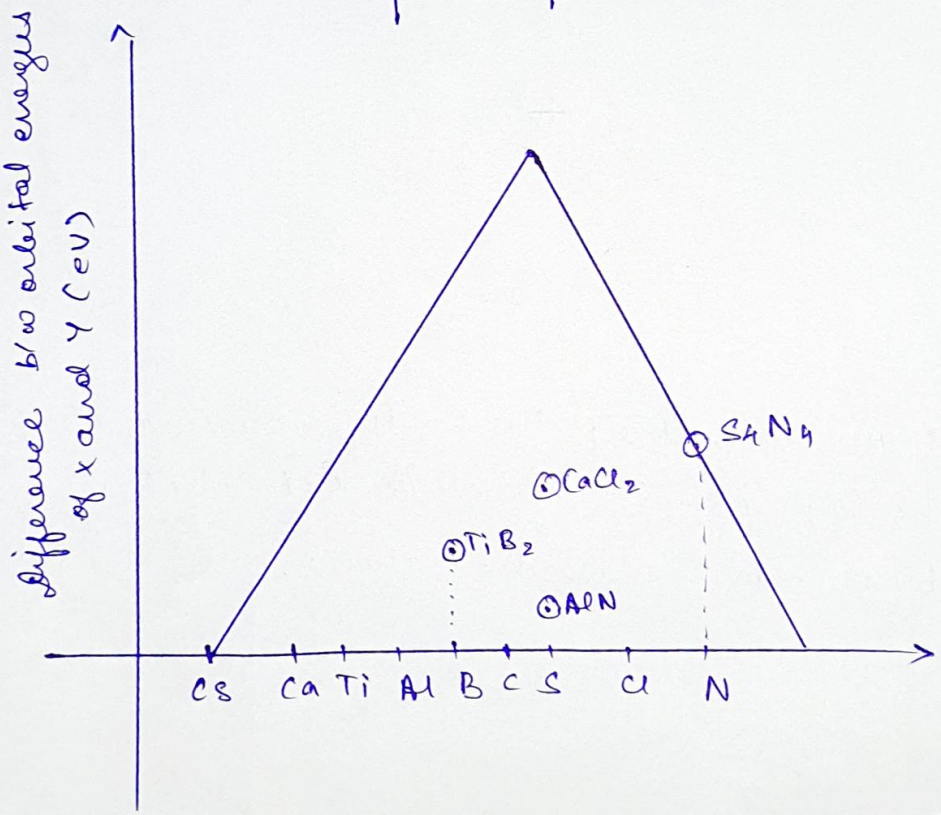



The hybrid MO portrays the Lewis Structure better because the lone pair on the Lewis Dot Structure are justified by the non-bonded electrons.

Q7. From $B_2$ to $N_2$ the electrons are filled into Bonding Orbitals and so the BO and Bond strength increases from left to right in and period but after $N_2$ the electrons start filling in antibonding $\pi^*$ orbital and so the BO decreases and same with the strength.

| BO: Group. | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|
| | 2/2 = 1 | 4/2 = 2 | 6/2 = 3 | (6-2)/2 = 2 | (6-4)/2 = 1 |

Q8.




(minus) avg orbital energy of X & Y (eV)

Q7. (continued). The Bond strength of $O_2$ is weaker than $C_2$ even though the BO is same because in $O_2$ the $e^{\ominus}$'s have entered Anti Bonding Orbitals making the bond weaker.