

Model Answer

For

M. Sc. (Chemistry) (Second Semester) Examination, 2013

CHEMISTRY

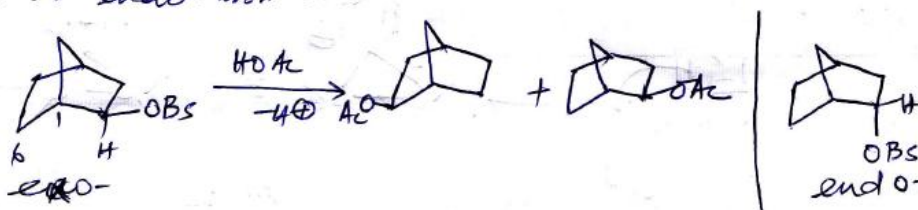
(ORGANIC CHEMISTRY – II)

AR-7129

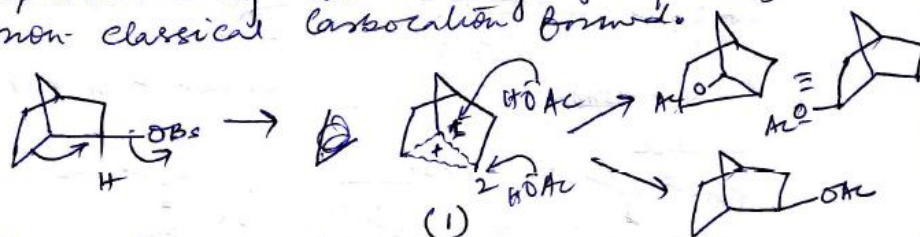
Section – A
(Short Answer Type Questions)

1. (i) Prove that the C-C single bond can participate in NGP.

- optically active exo-2-norbornyl brosylate gives racemic mixtures of two exo acetate, no endo-isomers were formed.
- exo-2-norbornyl brosylate solvolyzed 350 times faster than its endo-isomer.

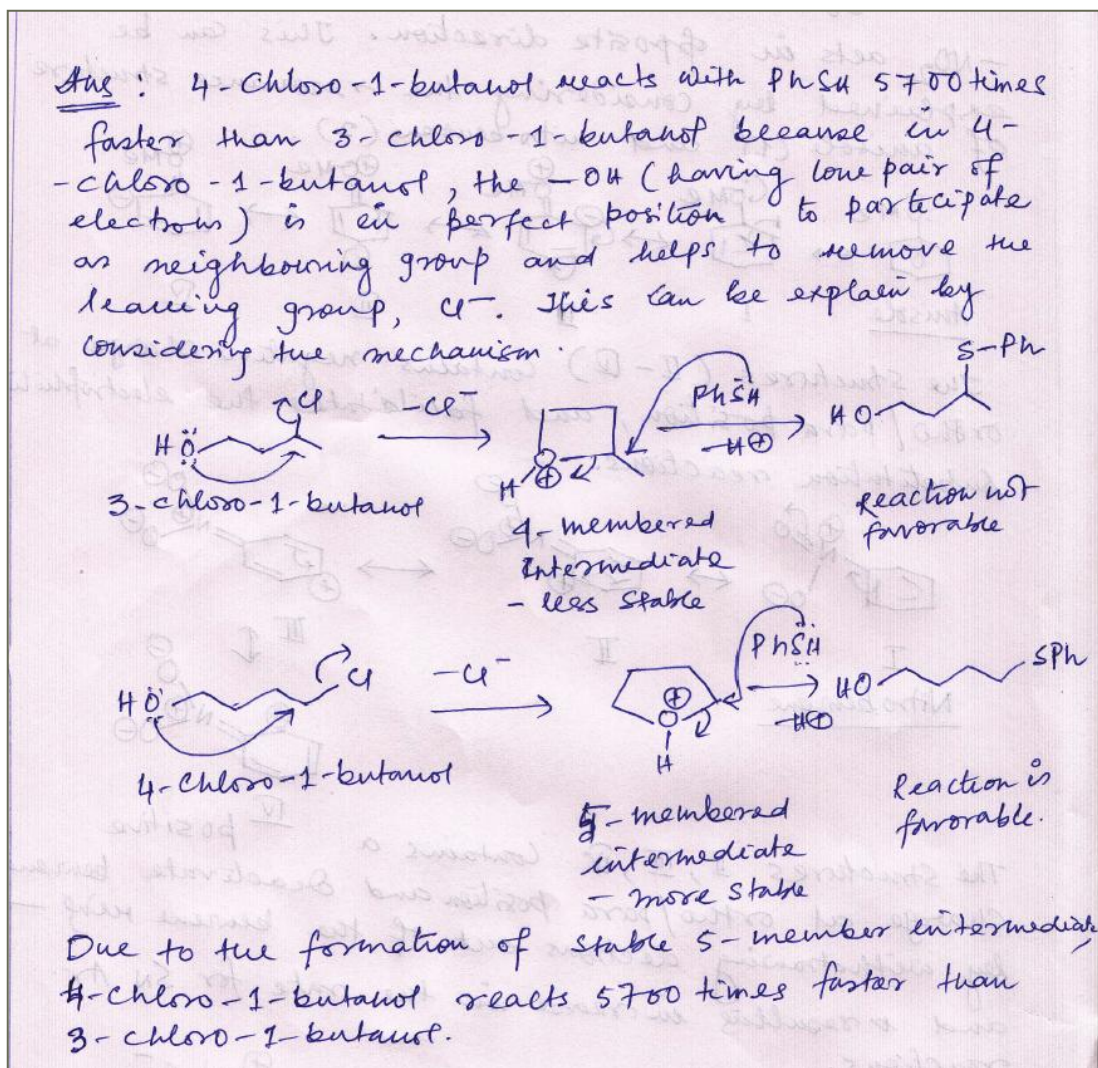


This phenomenon ~~can be~~ was explained by Winstein and Trifan as indicating that the 1,6-bond assists in the departure of the leaving group (OBs) and that a non-classical carbocation formed.

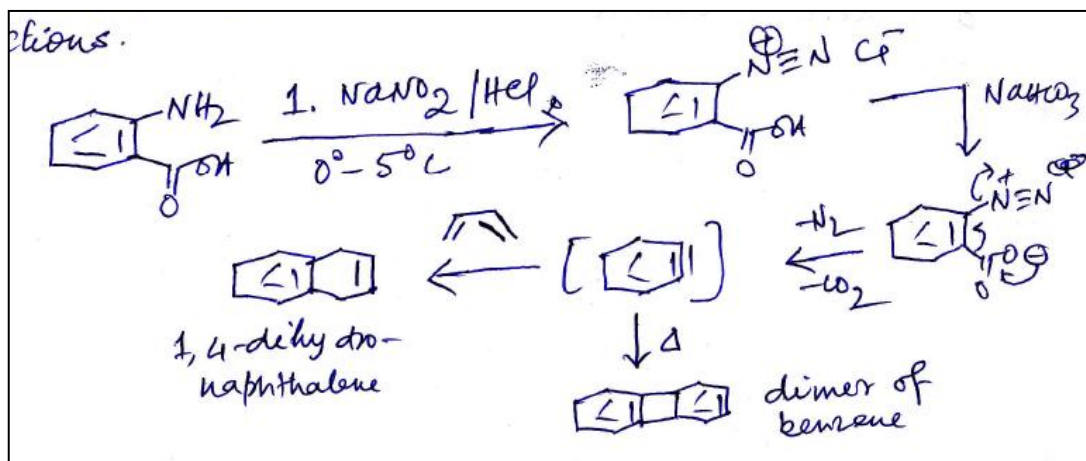


The solvolysis of endo isomer not assisted by 1,6-bond due to not favorable position for backside attack and rate of solvolysis is normal. Therefore much faster rate of solvolysis for exo-isomer must be caused by anchimeric assistance and the stereochemistry of the product is also explained by the intermediary (1), since the 1, and 2-positions are equivalent and would be attacked by nucleophile with equal facility, but only form the exo direction in either case. (1) is isolated at -150°C by Olah in $\text{SbF}_5\text{-SO}_2$ and $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ (by NMR, XPS).

1. (ii) 4-Chloro-1-butanol reacts with PhSH 5700 times faster than 3-chloro-1-butanol; Explain with mechanism.

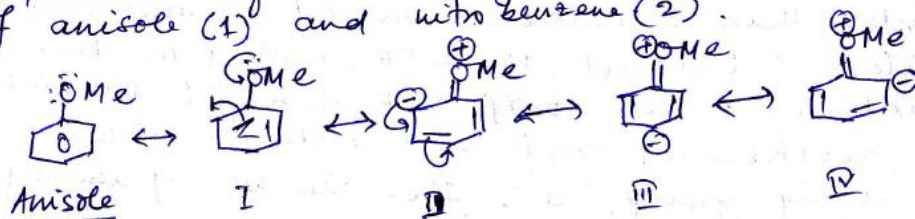


1. (iv) Complete the reactions:

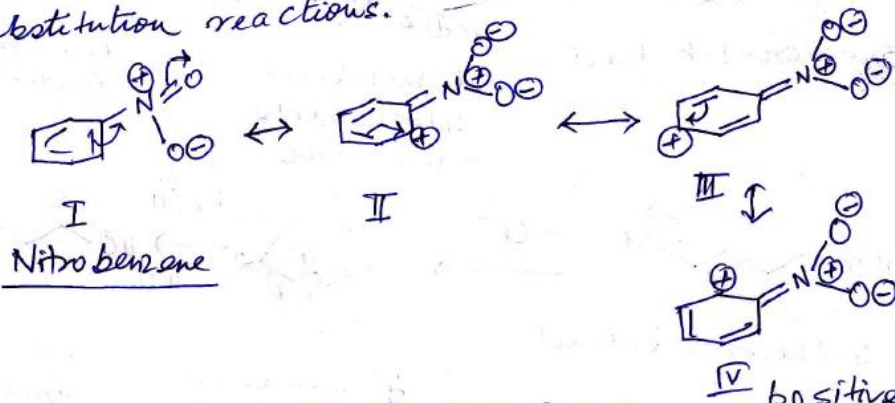


1. (iii) Presence of $-OMe$ group activate benzene ring towards electrophilic substitution reaction but deactivate benzene reaction for nucleophiles. On the other hand, $-NO_2$ acts in opposite direction. – Explain.

1 (iii) $-OMe$ group activate benzene ring towards $SEAr$ reaction but deactivate for $SNAr$, but $-NO_2$ acts in opposite direction. This can be explained by considering the resonance structure of anisole (1) and nitrobenzene (2).

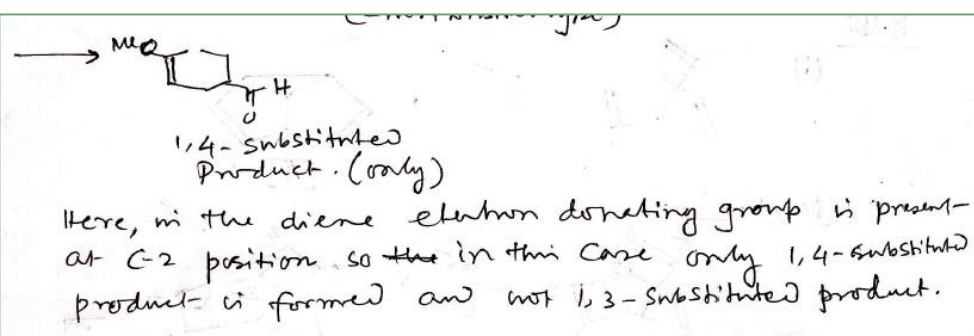
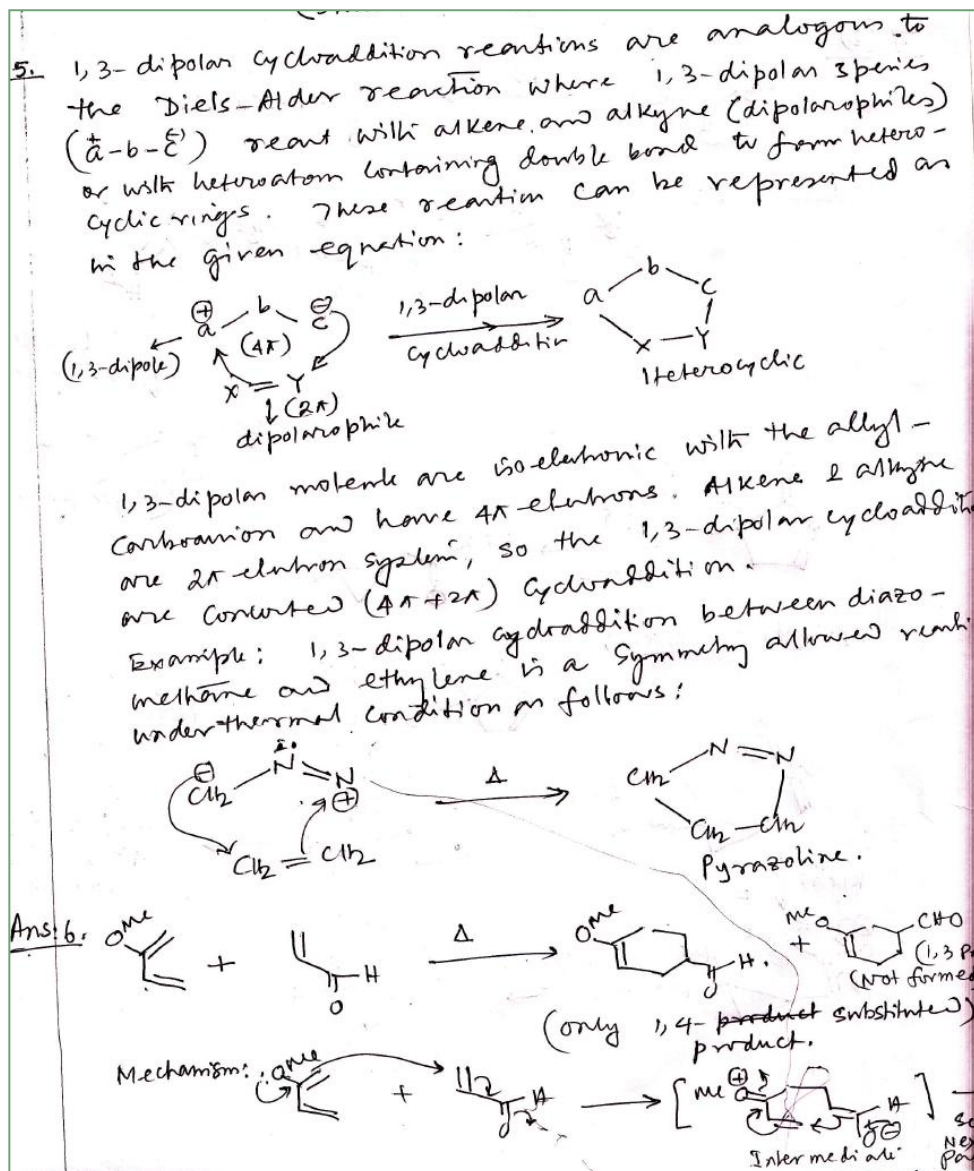


The structures (II-IV) contains negative charge at ortho/para position, and facilitates the electrophilic substitution reactions.

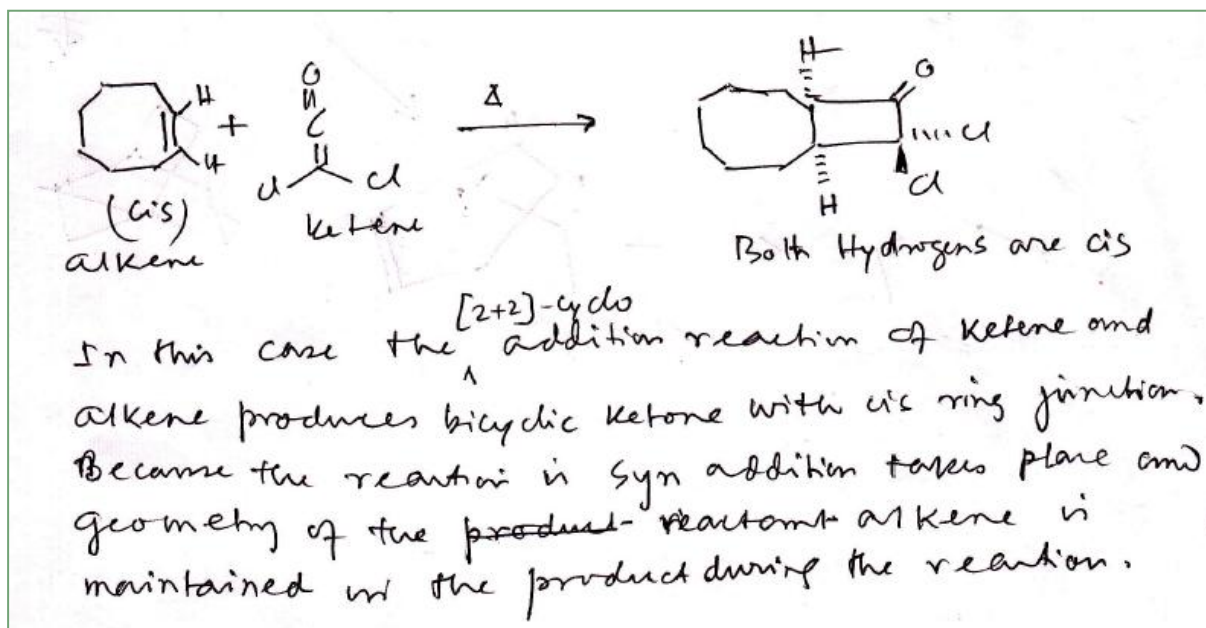


The structures II, III, IV contains a positive charge at ortho/para position and deactivate benzene ring by withdrawing electrons out of the benzene ring — deactivate for $SNAr$.

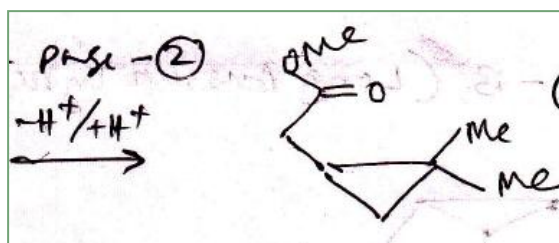
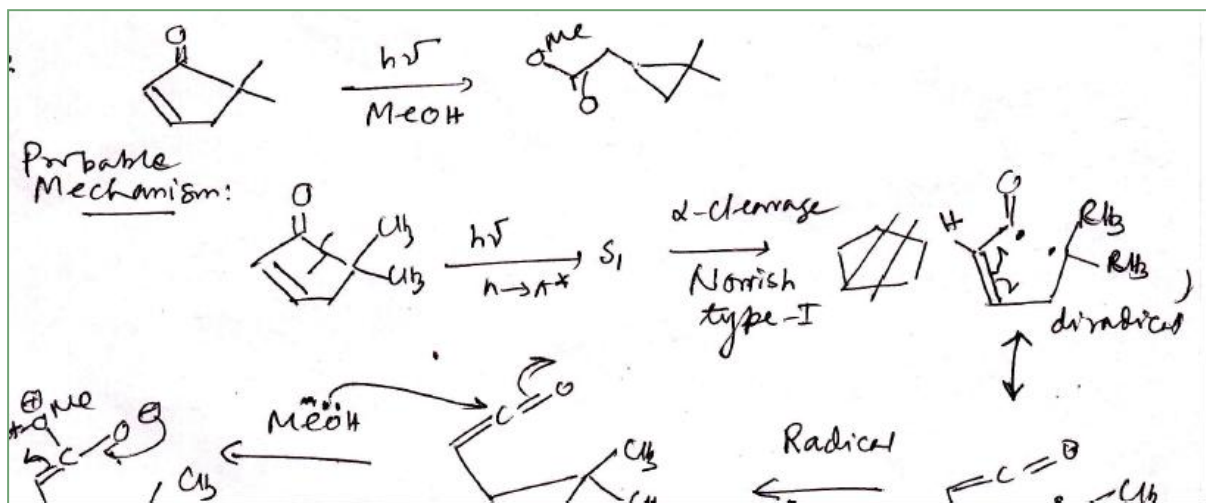
1. (v)



1. (vii)

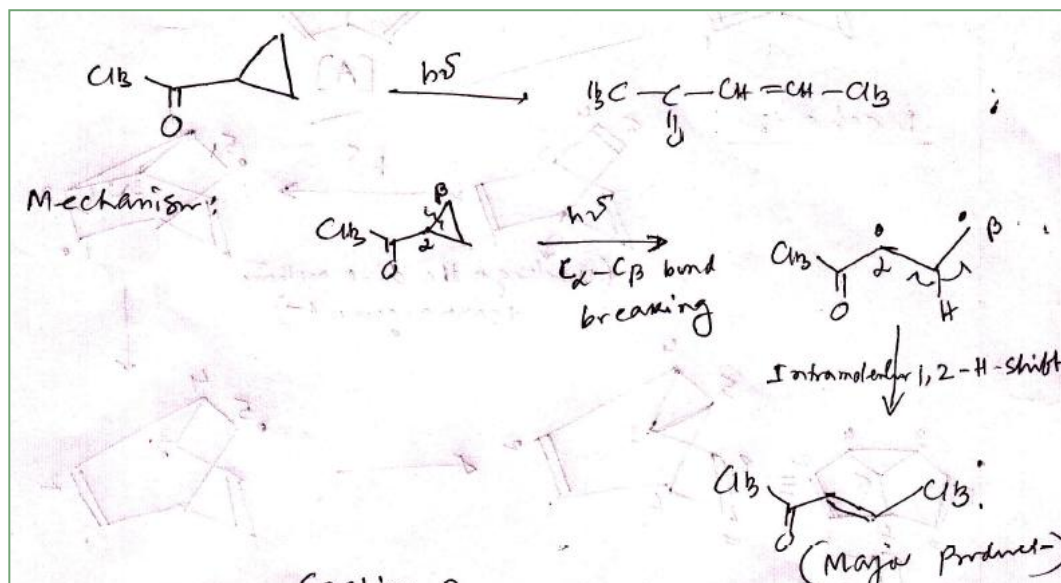


1. (ix) Give probable mechanism for the following photochemical reaction

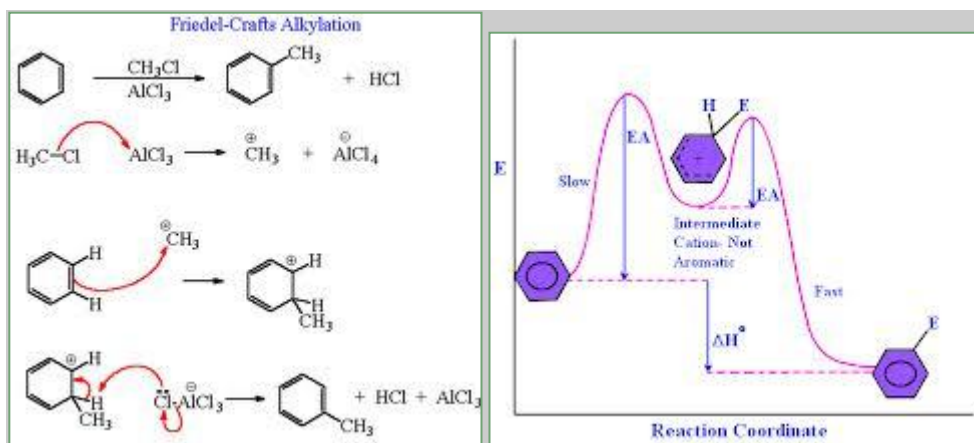


Model Answer for M.Sc. (Chemistry) Second Semester Examination, 2013
Organic Chemistry – II (CMT – 203)

1. (x) Suggest mechanism for the following photo reaction

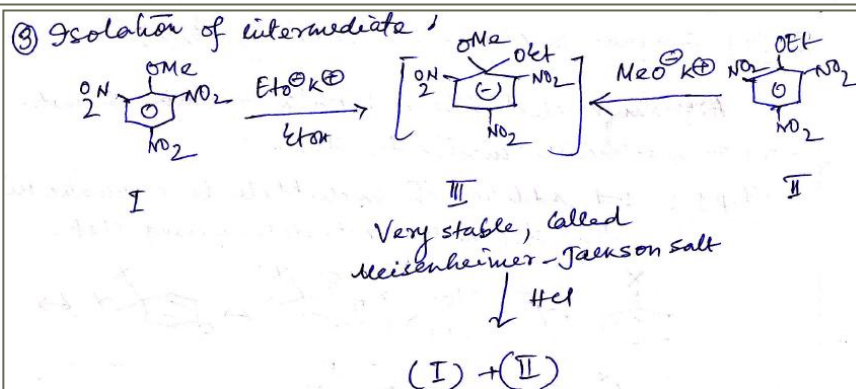
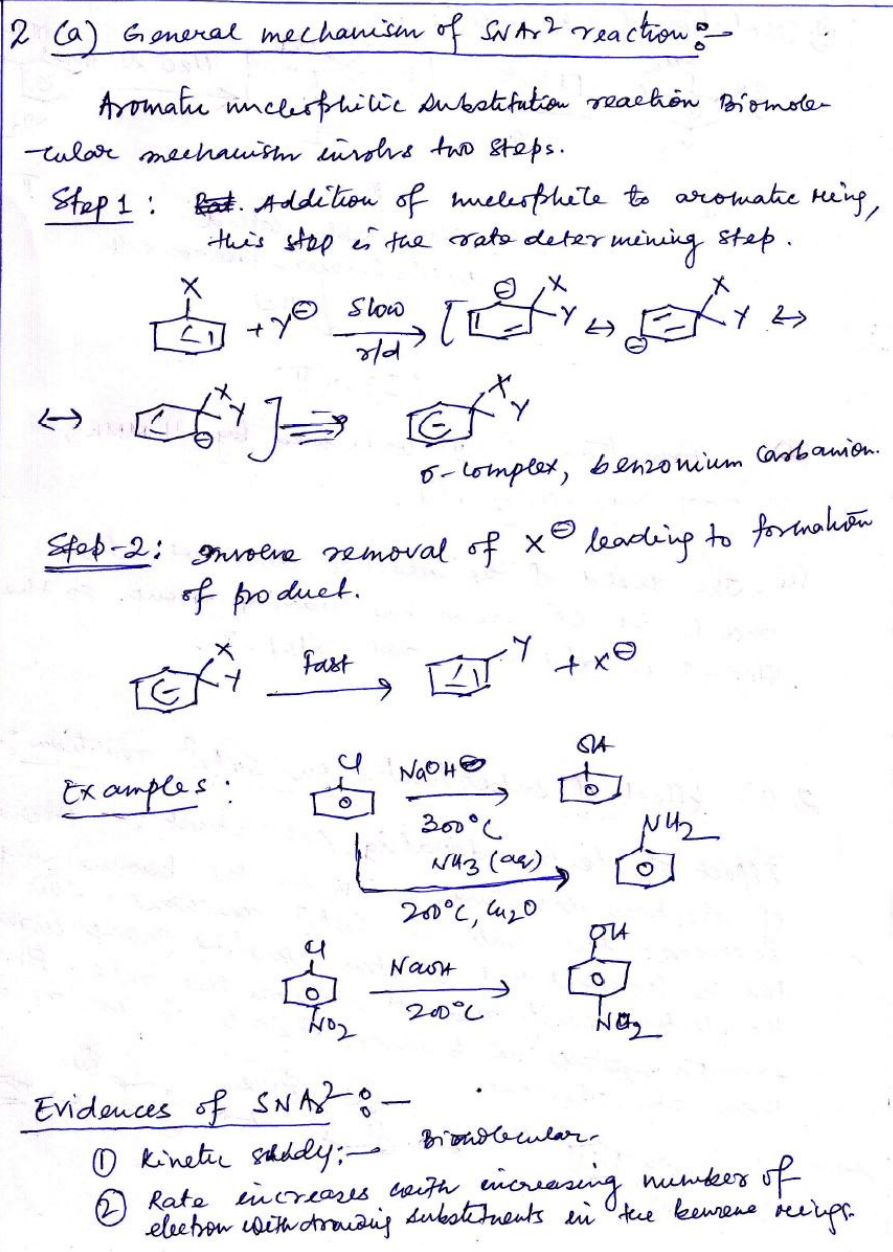


1. (vii) General mechanism and Energy profile diagram of Friedel-Craft reaction.



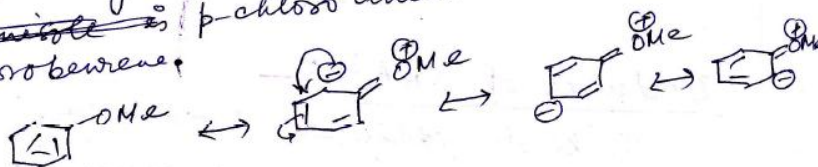
Section – A
(Short Answer Type Questions)

2. (a) Write the general mechanism, evidences and effect of substituent's on S_NAr^2 reaction.

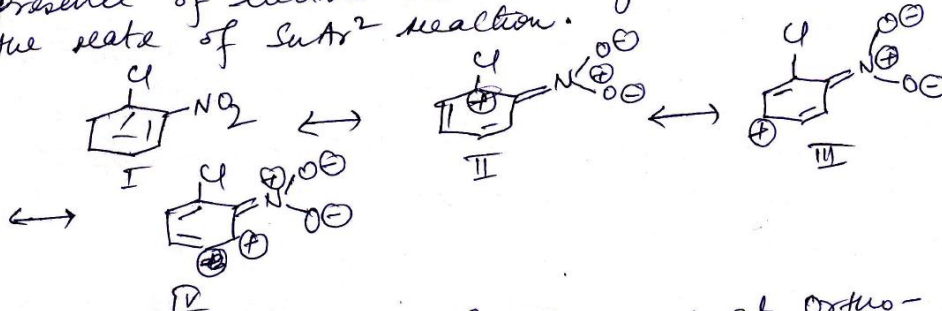


2 (b) Effect of substituents on S_NAr^2 reaction:—

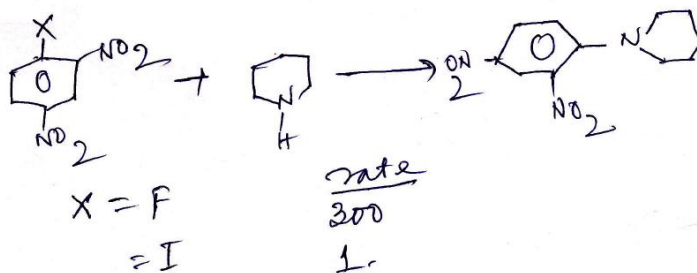
Effect of electron donating substituent:— Presence of electron donating group in the benzene ring decrease the rate of S_NAr^2 reactions. This is due to the fact that electron donating group increase the electron density and ~~not~~ decrease the rate. For example ~~anisole~~ is p-chloro anisole is less reactive than chlorobenzene.



Presence of electron withdrawing substituents increase the rate of S_NAr^2 reaction.

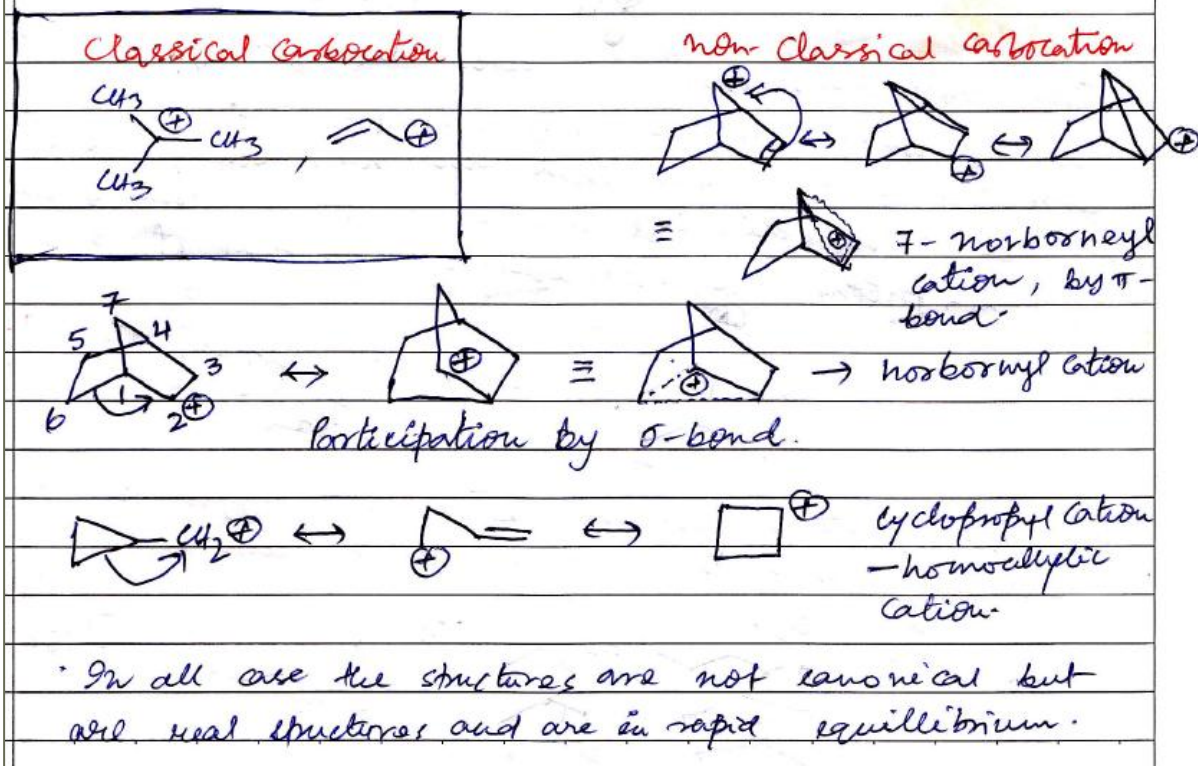


Due to the presence of nitro group at ortho-position a positive charge is generated at carbon atom which is attached to chlorine atom (C-Cl). The attack by incoming nucleophile facilitates and rate increases. With increasing number of electron-withdrawing substituents at o/p-position amount of positive is also increases, and thus rate of S_NAr^2 increases. For similar reason, fluoro benzene is more reactive than chlorobenzene and iodobenzene.



2. (b) Discuss the NGP by sigma and Pi-bond

The C=C π bonds, C-C σ bond and C-H σ bonds can act as NGP and the intermediates involved in such cases are called non-classical (or bridged) carbocation. In classical carbocation the positive charge is localized on one carbon-atom or delocalized by resonance involving an unshared pair of electrons or a double or triple bond in the allylic position. In a non-classical carbocation, the positive charge is delocalized by a single bond, double bond or a triple bond that is not in allylic position.



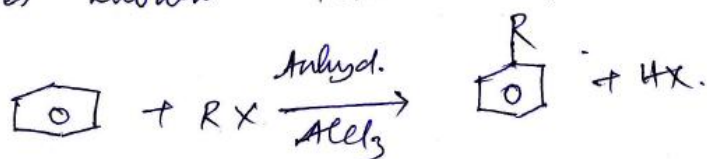
Discuss details with suitable examples.

3 (a) Friedel-Craft reaction:

3 (a) Friedel-Craft Reaction :-

General Statement :-

When benzene reacts with alkyl halide in presence of anhydrous $AlCl_3$ to form alkyl benzene. This rxn is known as Friedel-Craft alkylation.



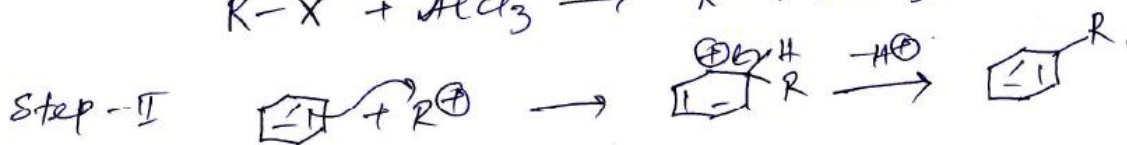
R = alkyl group
X = Cl, Br, I etc.

Give examples. —

Ethylene, alcohols can be used as alkylating agent and for the conc. H_2SO_4 is used as catalyst.

Mechanism :-

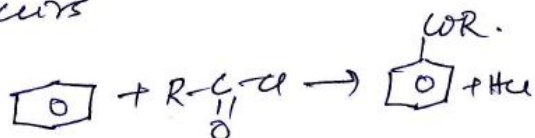
Step-I: Formation of alkyl carbonium ion.



Give limitations :- (discuss in details).

- ① Isomerization/rearrangement of carbocation (C^+)
- ② Poly alkylation occurs

Friedel-Craft acylation :-

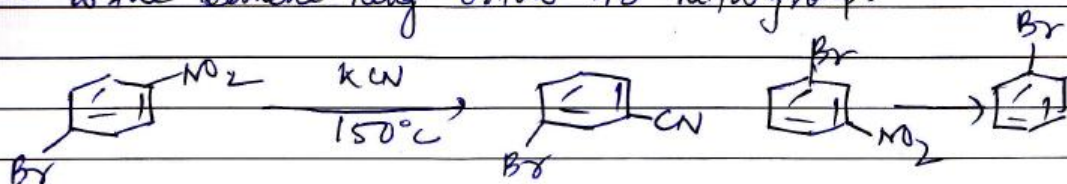


Need Give mechanism :-

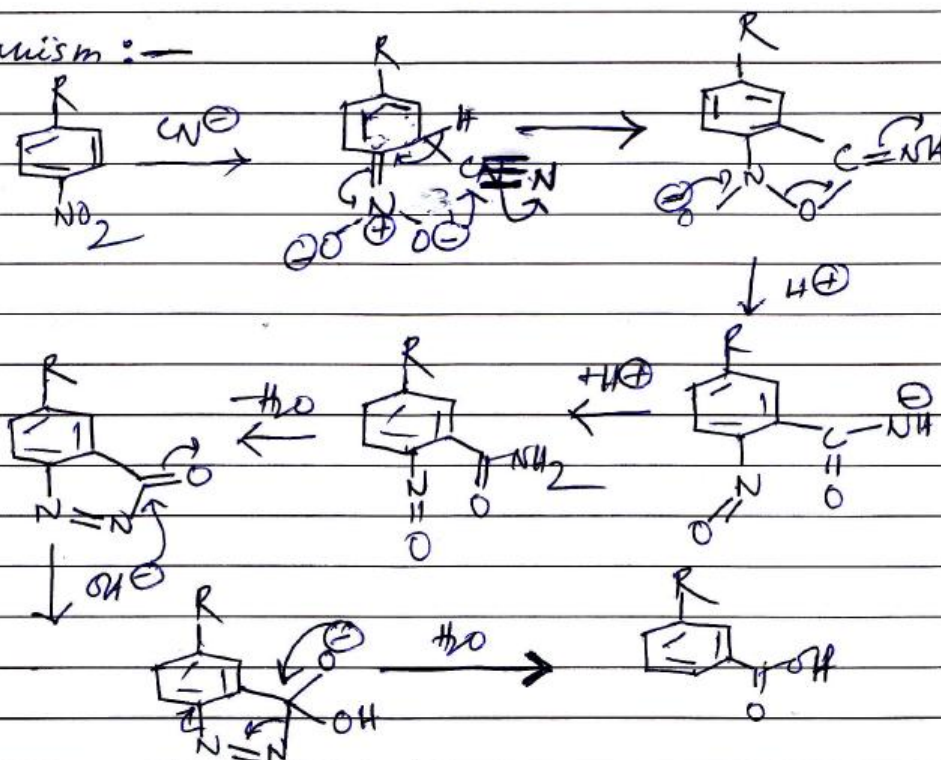
Need Give applications of Friedel-Craft alkylation/acylation

3 (b) von-Richter Reaction

When aromatic halonitrobenzene is heated with KCN at 150°C, the -NO₂ group is expelled and a cyano group enters to the benzene ring ortho to nitro group.

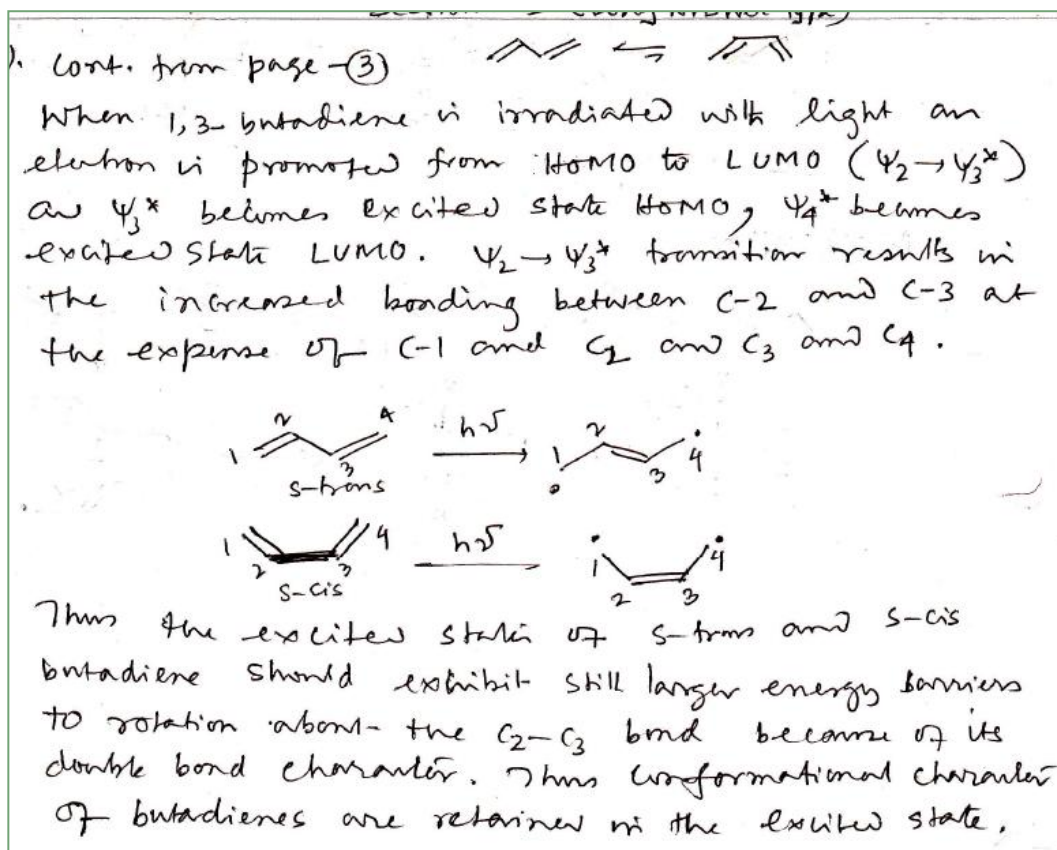
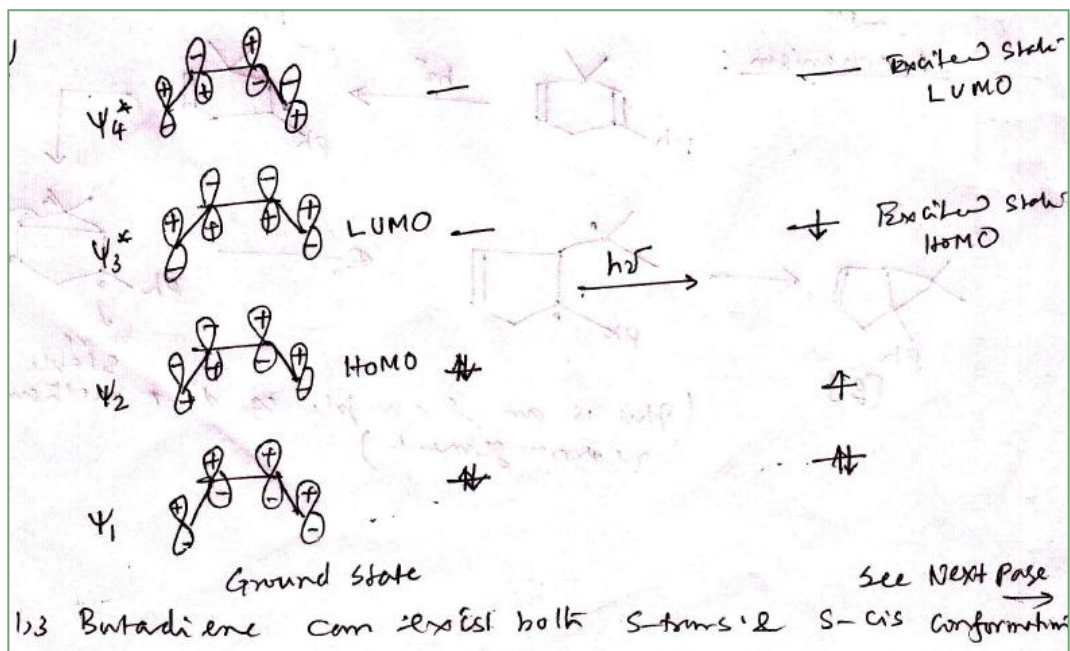


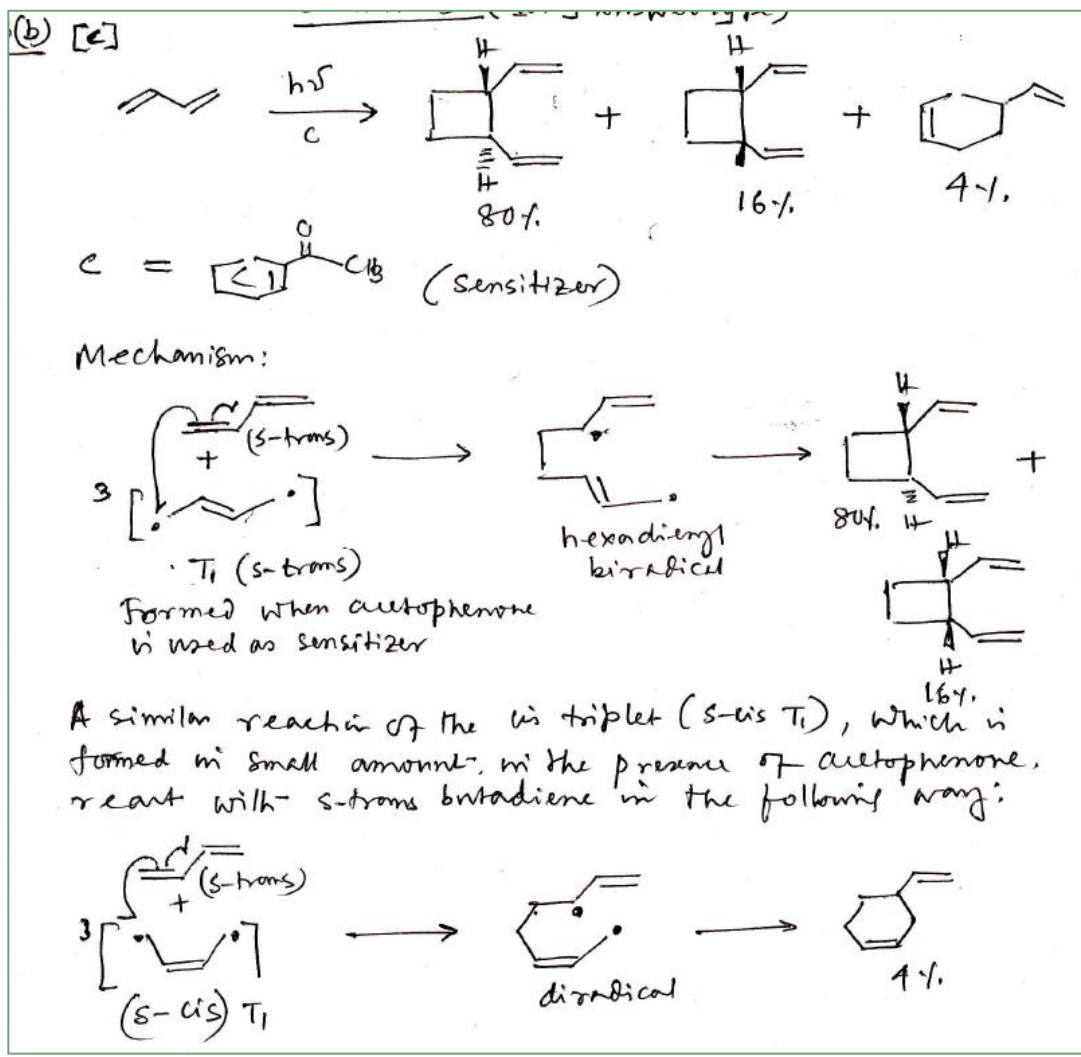
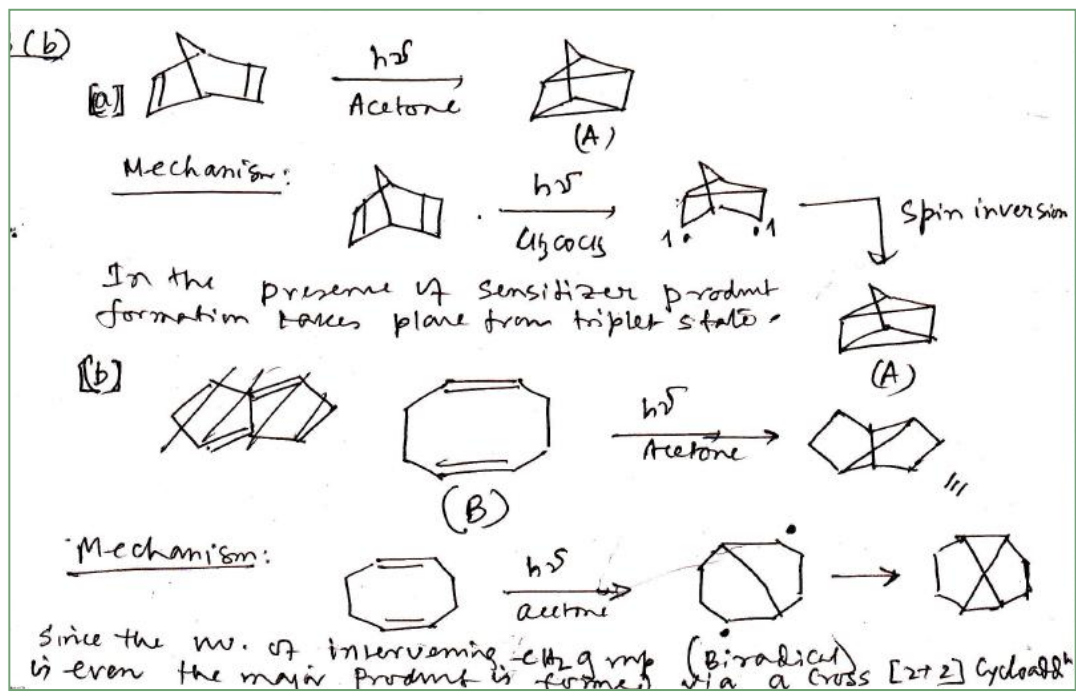
Mechanism:—



If the rxn is carried out in aqueous ethanol.

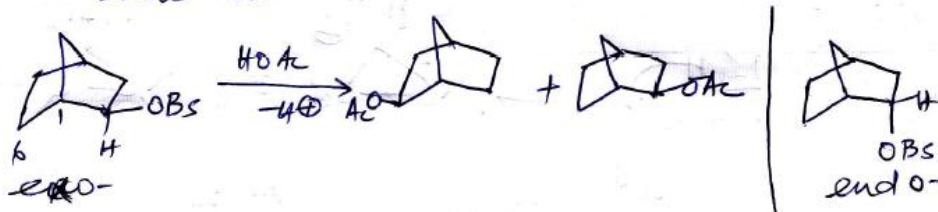
Q. 4 (a)



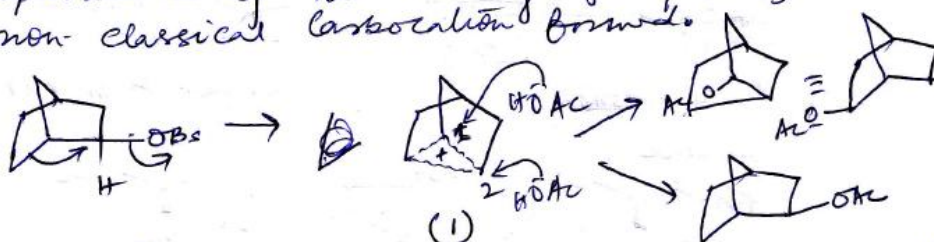


5. (i)

- exo-2-norbornyl brosylate solvolyzed 350 times faster than its endo-isomer.

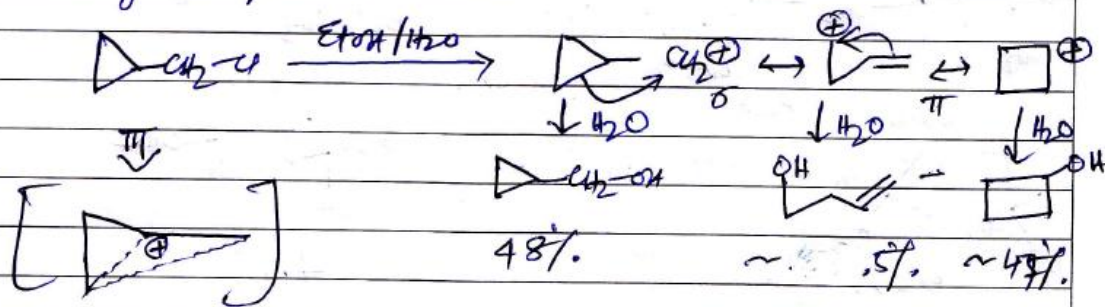


This phenomenon can be explained by Winstein and Trifan as indicating that the 1,6-bond assists in the departure of the leaving group (OBs) and that a non-classical carbocation is formed.

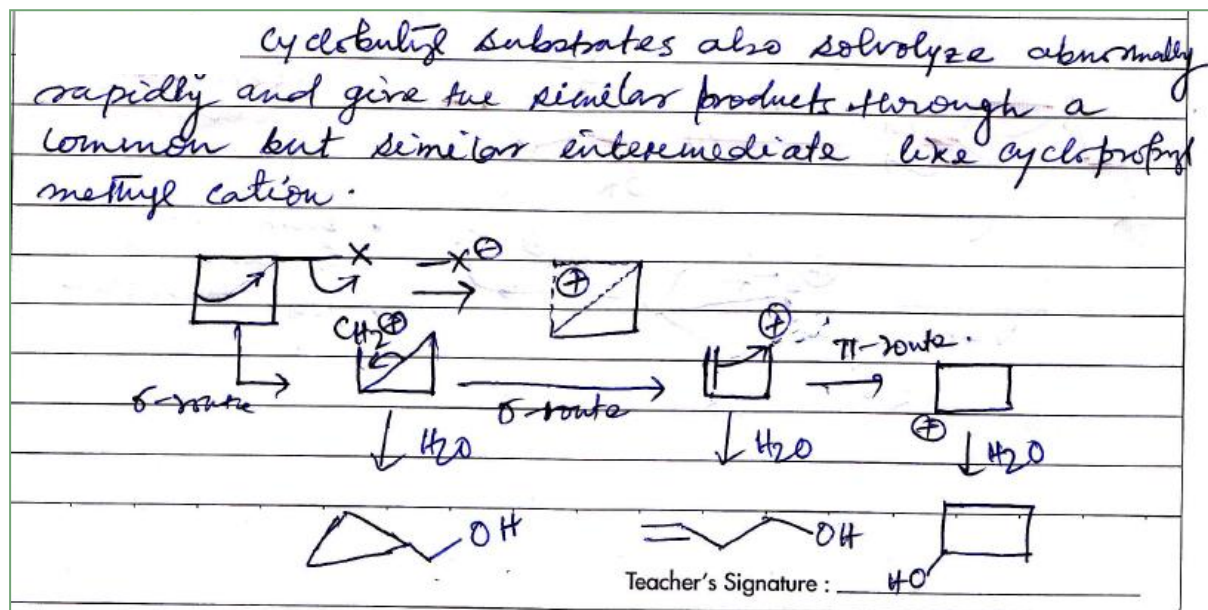


5. (ii)

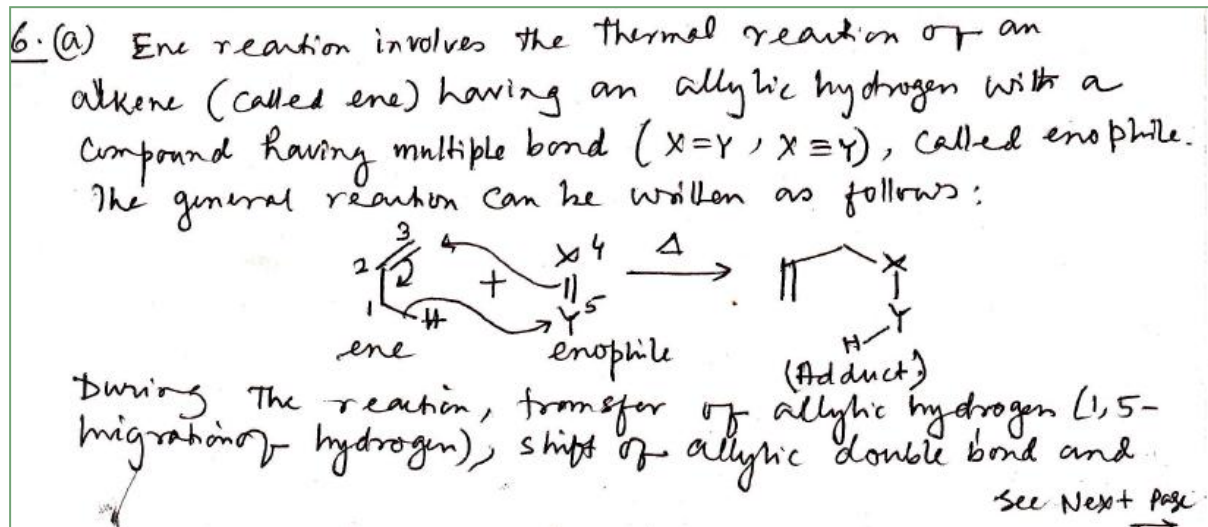
Aus. Cyclopropyl methyl chloride solvolyzed abnormally faster rates and the products often include not only cyclopropyl methyl but also cyclobutyl and homallyl compounds.



5 (iii)

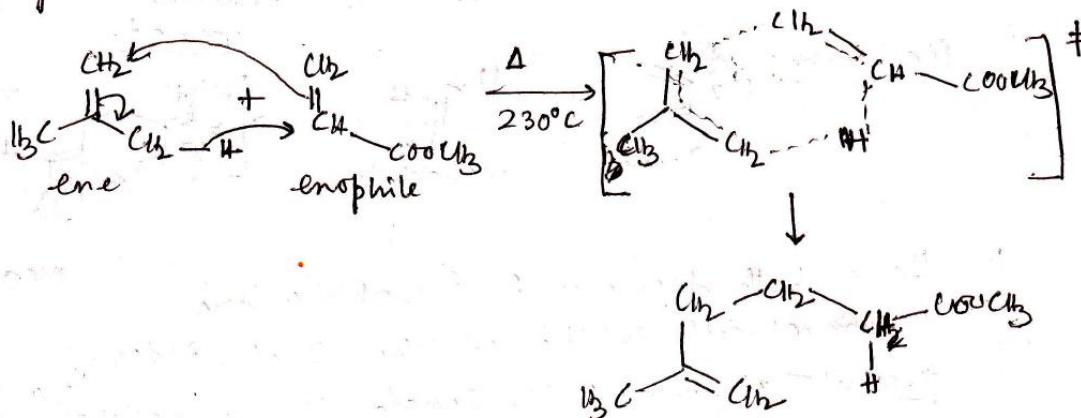


6 (a)



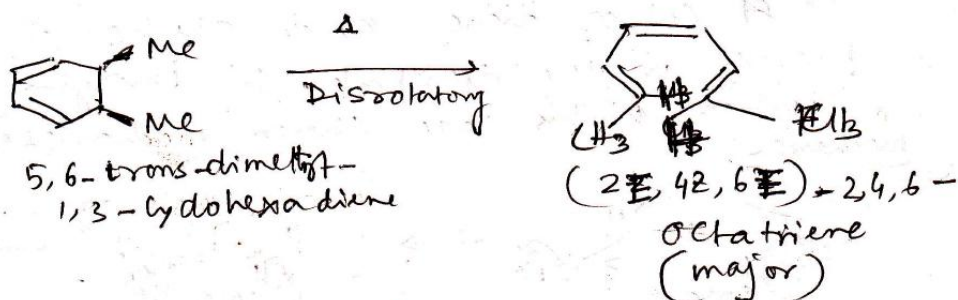
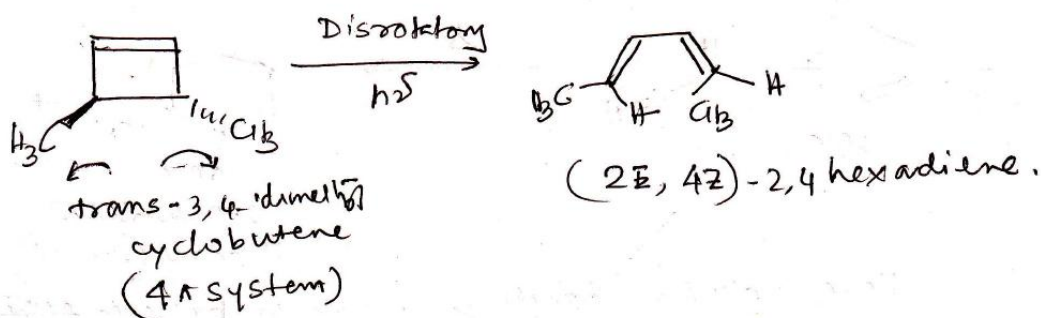
6(a) Cont. from page - (5)

bonding between two unsaturated termini take place to form 1:1 adduct as shown above. In this reaction loss of a π bond and gain of two σ bonds takes place in a concerted manner. A representative example of ene reaction is provided below.

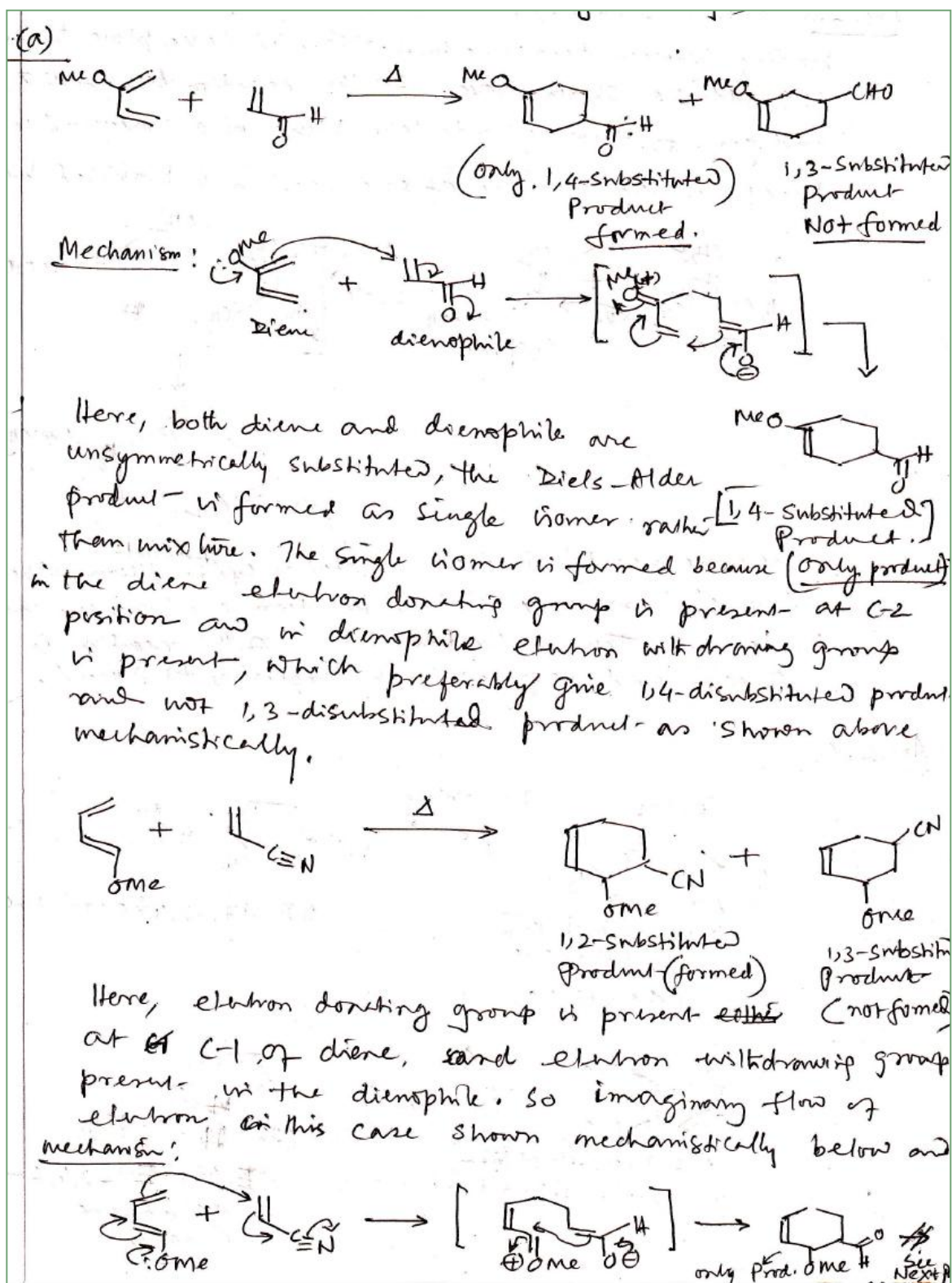


The above reaction involved six electron cycloaddition, where four electrons are π electrons but two electrons are σ -electrons. Thus, activation energy of this reaction is greater and requires high temperature to proceed.

(b)



7(a)



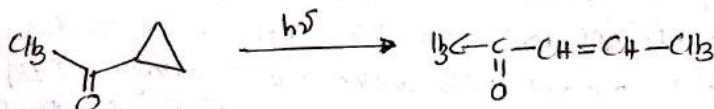
7(a)

Cont. from page 7

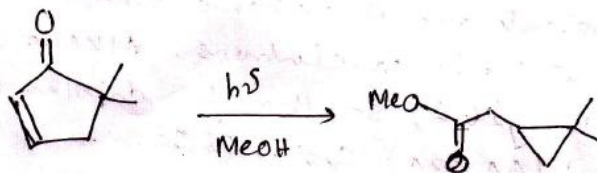
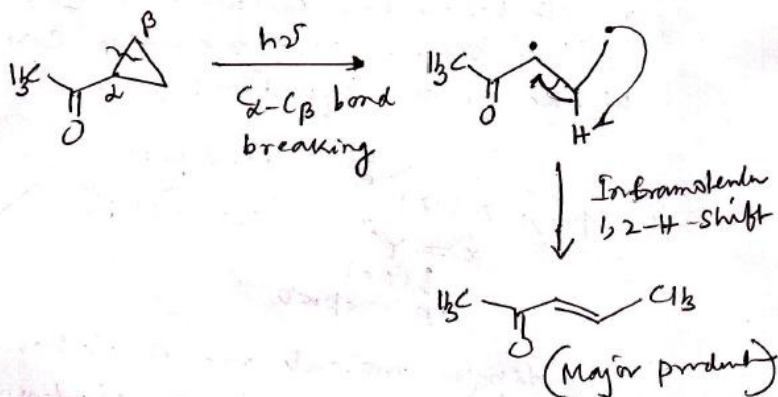
Section-B (Long Answer Type)

Part 2: only 1,2-disubstituted product is formed rather than 1,3-disubstituted product.

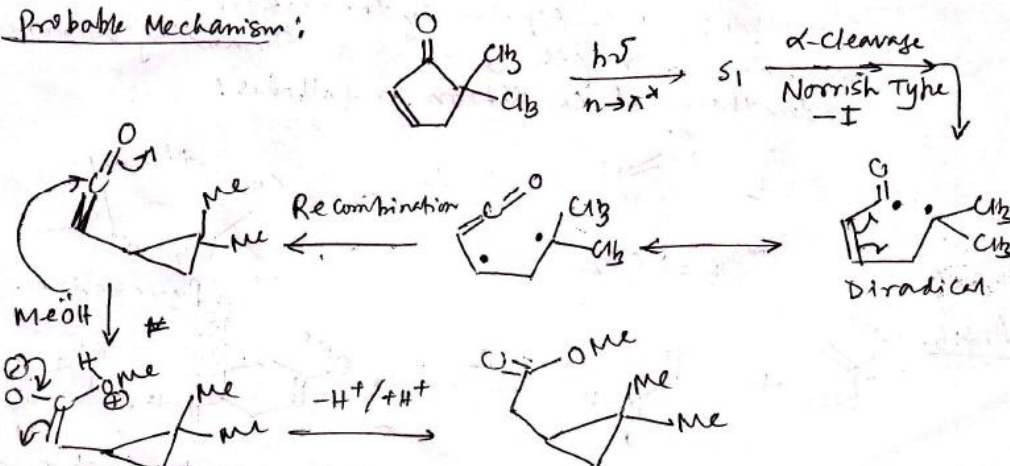
7(b)



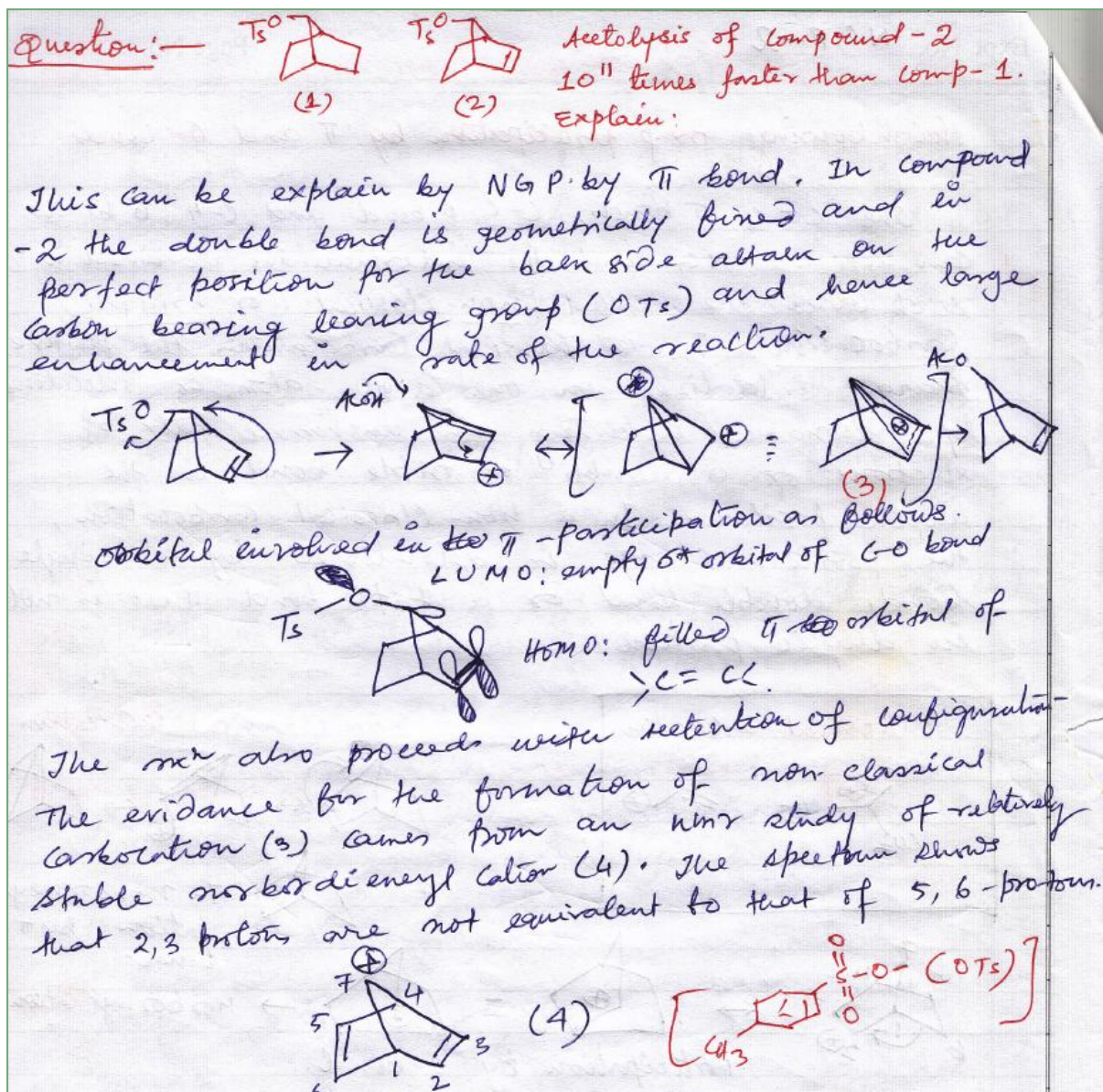
Mechanism:



Probable Mechanism:



8. (a)



8. (b)

