# **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.

· officilly active exo-2-norbornyl brosylate gives racemile mintures of the exo acetate, no endoisomers were formed. exo-2-norkornyl brogglate solvo byred 350 times forster than its endo-isomer. nBc end oepo-This phenomenan and the was explain by winstein and Trifan as indicating that the 1,6 -bond assists in the deparature of the baning group (OBS) and that a non- classical lassocation formed. De to Ac > mo The solvolysis of endo esomes not assisted by 1,6-bond due to not fororable position for back side altack and sate of solvolysis is nor mal. Therefore much justar nate of solvolysis for exo-isomer must be caused ley auchimeric assistance and the stereschemistry of the product is also explained by the intermedicary (1), since the 1, and 2-positions are equivalent and would be alfamed by nucleoptice with equal facility, but only form the exo direction in either case. O les isolated at -150°C by Olate in SF5-SO, and FSO3H-SbF5-SO, (by MUR, XPS)

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

stroate direction. Jus a Aus: 4-Chloro-1-butanol reacts with PhSH 5700 times faster than 3- chloro - 1- kutanot because in 4-- chloro - 1 - butanot, the - OH ( having love pair of electrons) is in perfect position to participate as neighbouring group and helps to remove the learning more the leauing group, ct-. This can be explain by Considering fue mechanism s-Ph Phin HOL Reaction ust 3-chloso-1-butanof 9-membered forvorable Intermediate - less stable PhSH SPh 40 H Reaction is favorable. 4- Chloso -1 5-membered intermediate more state Due to the formation of stable 5-member intermediat 4-chloro-1-butanol reacts 5700 times faster than 3- chloro-1-butanot.

1. (iv) Complete the reactions:

ctions. DEN CF 1. Navo2/Her 0°-5°C 1, 4 - dely drodimer o naphthalene

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

1 (11) - OME group acterate bemene ning todoords SEAr meaction but deacturate for SNAr, But -NO2 acts in opposite direction. Ities can be explained by considering the resonance structure of anisole (1) and with benzene (2). + EI + GEI + THO I Anisole Т The structures (I-I2) contains negative charge at or the / para position, and facilitates the electrophilic substitution reactions. I T Nitro benzane The Structures I, II, De Contains a IV positive Chaorge at ortho/para possition and Deaeterrate benzene bey with strong electrons out of the benzene neig-

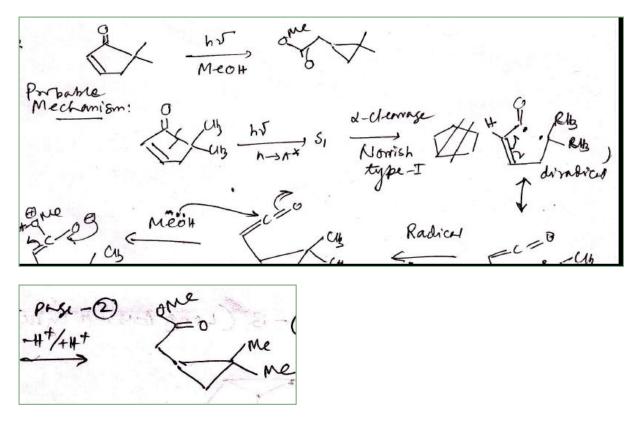
1. (v)

1, 3- dipolar cycloaddition reactions are analogous to the Diels-Alder reaction where 1,3-dipolar spenies 5. (à-b-E) reart with atkene and alkyne (dipolarophiles) or with heteroatom containing double bond to form heterocyclic rings. These reaction can be represented as in the given equation: 1/3-dipolan a Cycluaddrkin 16 8 Heteroychic 1,3-dipolar motente are iso-elationic with the ally 1-(21) Corboarrion and have 4x electrons. Alkene 2 allight ore 2r elaborn system, so the 1,3-dipolar cycloaddith are contented (Ar +2A) Gydwarddition. Example: 1,3-dipolar cydraddition between diazomethome and ethylene is a Symmetry allowed renti under thermal condition on follows ; Cin Clb=1 clb Pyrazoline Ans 6. 0 (1,38 (Not form cubstitute vduct Inter me di alu 1,4- substituted Product . (only) Here, in the diene electron donating group is presentat C-2 position so the in this Case only 1, 4- substituted product is formed and not 1,3-substituted product.

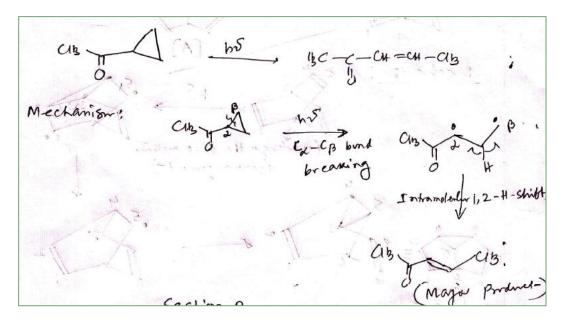
1. (vii)

0 mu H u's) alkene Both Hydrogens are cis In this case the addition reachin of Ketene and Keter alkene produces bicyclic ketone with us ring junction. Became the reaction is Syn addition takes place and geometry of the product reactant askene is maintained in the product during the reaction.

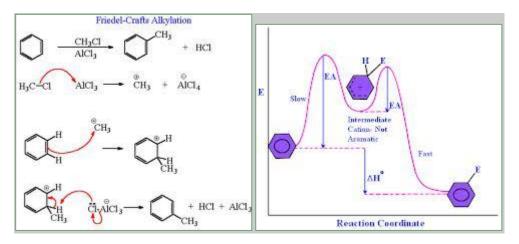
1. (ix) Give probable mechanism for the following photochemical reaction



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  $S_{N}Ar^{2}\,\text{reaction}.$ 

2 (b) Effect of substituent's on surtr2 reaction:-Effect of electron donating substituent: - Preserve of electron donating group in the berrene ring decrease the rate of SNAr2 meactions. Juis decrease the rate of SNAr2 meactions. due to the fact that electron donating group inverse the election density and that decrease the sate. For example aniste is p-chloso anicole is less reactive STO bewerere, B. SME BUNE EN ELE SME EN ELE EN ELE SME than chlorobenrene. presence of election with drawling substituents encrease the seate of Sutra mealton. He seate of Sutra mealton. INO2 () INO I DING Due to the presence of hitro group at Orthoposition a positive charge is generated at Carbon atom which is attach to chlorine atom (E-cl). The altack by encoming unclespliche face litates and recte increases. With increasing number of electron-- with drawing substituents at 0/p- position amont f positive is also increases, and turns rate of nen eucreases. For similar reason, fluoro beurene is more reactive than chlorokenne and iodokennene. nte X = F300 FI 1-

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

C= C TT bonds, L-C 6 band and C-H & bands The Can det an NG and the intermediates enrolled in bridged) of corres called non- Classifal or Carbocertion. the positive In @ Cassial Carbola is Idalized on 2 doculized one Carbou 08 Charge' enolvedia bair uns bon of an resonan double or doctor 20 bosition. In a Confortion hon- Classical is Delotatized Bositive charge ky bond or a bond, double bible bond that in not allific bosi tion capocation non classical agesical Carborat CHS @ cutz Ð Usa E 7-norborney lation, by T bond. hostornyl ation  $\leftrightarrow$ Porticipation By 0-bond ation Cyclobs -homoallylic Cation. " In all are the structures are not canonical but yeal spuctures and are in rapid equillibrium. are

Discuss details with suitable examples.

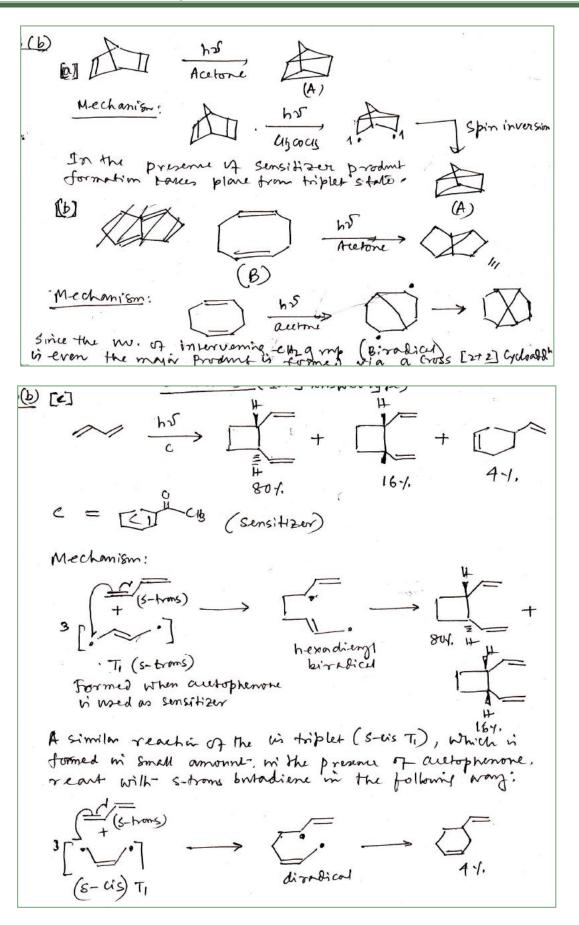
3 (a) Friedel-Craft reaction:

#### 3 (b) von-Ritcher Reaction

When aromatic halonitobernene is heated with KUN at 15°C, the - No, group is expelled and a cyanogrou enters to the bornene reing or two to hitrogroup. Br Br Br Br ISO°C Br Br JEL
at 15° c, the - No, group is expelled and a cyano grou
enters to the bemere keing ortho to hipograp.
0 Br
CIM2 KW FEI FEI STAT
ISD°C FOR LELMON LELMON LEL
Br Br
R L
$\frac{\text{Mechanism}:-}{N^{2}} \xrightarrow{K} \xrightarrow{K} \xrightarrow{K} \xrightarrow{K} \xrightarrow{K} \xrightarrow{K} \xrightarrow{K} $
THE CENT
NO2 DE DE
R HA
the Fit the Letter
NENT 10 0
0
NOR R
1 8 the Fline
N=N OHO N N=N OHO N N=N OHO N N=N OHO N N=N OHO N N N N N N N N N N N N N N N N N
If the new is carried out in aquerous ethanof.
the second secon

Q. 4 (a)

- Exciten Stehr LUMO Revailed Stoke UMO HOMO HOMO A Ground State See Next Pase 13 Butadiene com ilsotsi bolt Stoms il S-cis conformation cond with the little 11 · Cont. from page -(3) When 1, 3- but adiene is irradiated with light an elubon is promoted from Homo to LUMO (42-143\*) an 4/2 becomes excited state Homo, 4/4 becomes excited State LUMO. 42-, 43\* transition results in the increased bonding between C-2 and C-3 at the expense of (-1 and (2 and (3 and (4. s-trons has 12 3 4 14 hrs in 14 Thus the excited station of s-trues and s-cis butadiene should exhibit still larger energy barniers to rotation about the c2-c3 boud became of its double bond character. This conformational character of butadienes are retarined in the esciled state.



5. (i)

exo-2-norkoonyl brogglate kolio typed 350 times forster than its endo-isomer. end oero-This phenomenan and was explain by winst and Trifan as indicating that the 1,6 bound assists in the deparature of the being group (OBs) and that a non- classical Carbocation for HOA (1)

5. (ii)

Cyclopsopyl methyl chloride soliolyzed aburmally Aus. aster rates and the products often inchi ly clopropy methy but also cyclopatyl and homolle compou Etor /11/20 4

5 (iii)

Cyclobulize substates also solvolyze abnorma ridly and give the similar products thorough mon but similar interemediate like cy cation. The CHSE TI-Jowte. K-m 5-route Ð 120 OH OH 40 Teacher's Signature :

6 (a)

6. (a) Enc reaction involves the thermal reaction of an alkene (called ene) having an ally his hydrogen with a compound having multiple bond  $(X=Y \ , X=Y)$ , called enophile. The general reaction can be written as follows: + 115 A TT T enophile (Adduct) During The reaction, transfer of allytic hydrogen (1,5-migration of hydrogen), shift of allytic double bond and See Next Page

6(a) cont. from page-(5) bonding between two unsaturated termini take place to form 1:1 adduct as Shown above. In this reaction twis of a 7 bond and goin of two or bonds takes place in a concerted manner A representative example of one reaction is provided below. H- LOOUB CHZE 230°C COOUL enophile 12C The above reaching involved six elabor cydonddition, where four elabors are & etahons but two elabors are oelectrons, Thus, activation energy of this nearties is greater and required high temperature to proceed. (6) Dissolution BGhS "Cib (2E, 4Z)-2,4 hexadiene. troms - 3, 4- dimethon cyclobutene 4 rsystem) Δ Dissolator 5, 6- trons-dimettint-22,42,6至) -2.4.6-1,3- Cydoheradiene octativere major

7 (a)

(a)only. 1, 4-substituted 1,3-Subshituter product Product Not formed formed Mechani dienophile Here, both diene and dienophile are unsymmetrically substituted, the Diels-Alder produit - i formed as single somer rash- 1.4- substituted. them mix here. The single homer is formed because (Only pordu in the diene etubion doneting group is present at 62 position and in dremsphile etuhon wilt drawing group i present, which preferably give 114-disubstituted produl and not 1,3-disubstituted product- as shown above mechanistically. ome ome one 12-Substitute 1,3-Swoshim produl (formed) Product Here, elabor donching group is present colles Cnot formed at et c-1, of diene, sand elation withdrawing group presul- in the dienophile. So imaginary flow of elution to this case shown mechanistically below and mechanish'

Ka) Cont. from Pase () Section-B (Long Answer Type)	
Port 2 ! only 1, 2-disubstitutes product is formed gra	the
than 1,3-disnostituted product.	
	*
-F.C. A his a life of the	
-7.6) -7.6) 	
Mechanismi 2 hos in i)	
Mechanismi 15 2 hos hos 13 y and 14 hos	
O breaking Ht	
Inframaten 1,2-H-Shi	le la
1 12-H-SM	15-
is y als	2
Mayor produ	5
1 ho means 1	-9
Meot Meot	
	. 1
Probable Mechanism: City host SI d-cleavage City host SI Norrish Type -I	
Cib n=x* Norrish Type	
V V	
The Recombination of City	z
( free . for the for t	」 内
Meolf . #	20 2
on the	
02 me me -++/+++ T me	
Filme	
a second and a second	
$\lambda$	

8. (a)

Tso Acetolysis of compound - 2 Question :-10" times faster than comp-1. (1) Explain : This can be explain by NGP by TI bond. In compand -2 the double bond is geometrically fined and in perfect position for the back side altack on the Carbon bearing learing group (OTS) and hence large rate of the reaction. enhancement in Acor > Tso obstitul involved in the T - participation as Bollows. LUMO: suppy 5\* orbital of C-0 bond Homo: filled I to orbital of Ts The men also proceeds wife sectention of configuration The evidance for the formation of non classical Carboration (3) cames from an nimer study of relatively Stuble norbordienerge Cation (4). The spectrum shows that 2,3 protons are not equivalent to that of 5, 6-protons. [42 -0- (0Ts)]

8. (b)

