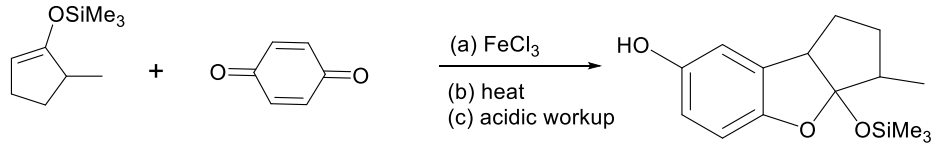
Birla Institute of Technology & Science, Pilani
CHEM G551: Advanced Organic Chemistry (Open Book)
December 21, 2022 (2.00 -5.00 pm) Max. Marks: 80 Time: 180 min.

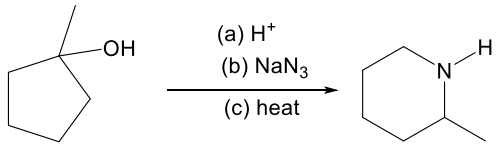
All questions are compulsory. Answer sub-parts of a question sequentially in the order given.

Q. No. 1. Propose a detailed mechanism for the following chemical transformations: [4x5=20]

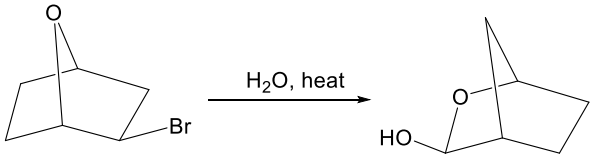
(i).



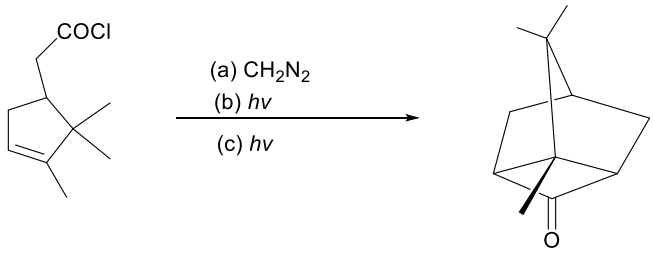
(ii).



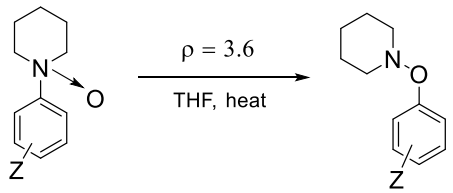
(iii).



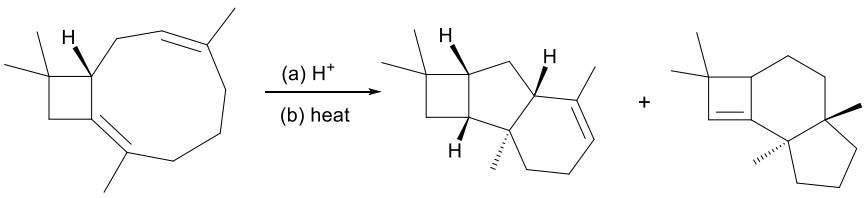
(iv).



Q. No. 2. (i). The reaction constant determined from the Hammett plot for the following chemical transformation is 3.6. Justifying this information, and predicting the structure of a possible intermediate, propose a detailed mechanism for this reaction. [5]

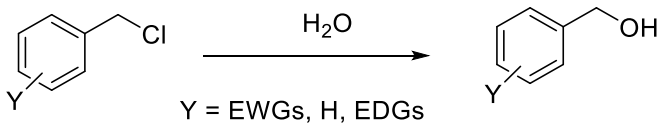


(ii). Acid-catalyzed reaction of substrate **B** gives a mixture of two products **C1** and **C2** *(structure shown below).* Predict detailed mechanism(s) for the formation of the two products. [5]

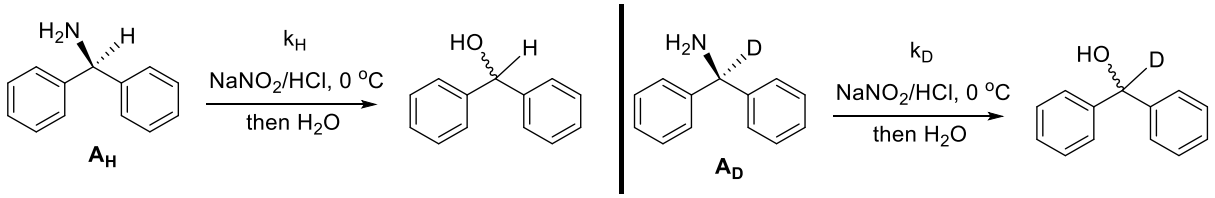


Substrate-B ***Product-C1*** ***Product-C2***

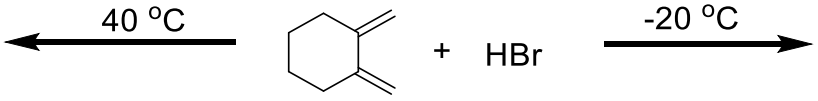
(iii). The reaction constant for hydrolysis of substituted benzyl chlorides is found to be -1.31 (experimentally determined from Hammett plot). How much faster *p*-chlorobenzyl chloride will hydrolyse than will *p*-cyanobenzyl chloride. Given that $\sigma_{p\text{-}Cl} = 0.23$; $\sigma_{p\text{-}CN} = 0.66$ [5]



(iv). For the following parallel reactions, the ratio of rate constants for the compounds $\mathbf{A_H}$ and $\mathbf{A_D}$ *(refer structure below)* is found to be 1.35. Determine the type of isotope effect & propose a detailed mechanism to justify the formation of a racemic product in both cases. [5]

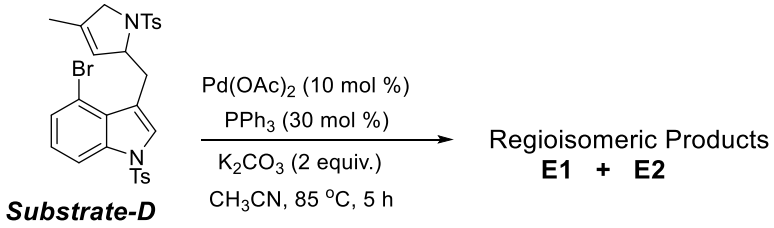


Q. No. 3. (i). Why a racemic product is obtained by the reaction of HBr with the given substrate at -20 °C, whereas a single product is obtained at 40 °C. Also, draw a labelled energy profile diagram depicting the formation of all the products for the two reaction conditions. [5]

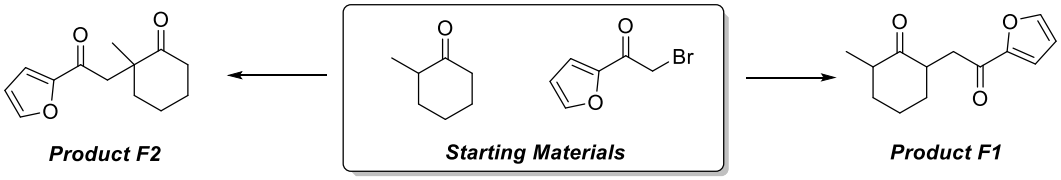


(ii). Propose a high yielding synthetic process for the preparation of but-3-en-2-one (CH_3–CO–CH=CH_2) from acetone (CH_3–CO–CH_3). [5]

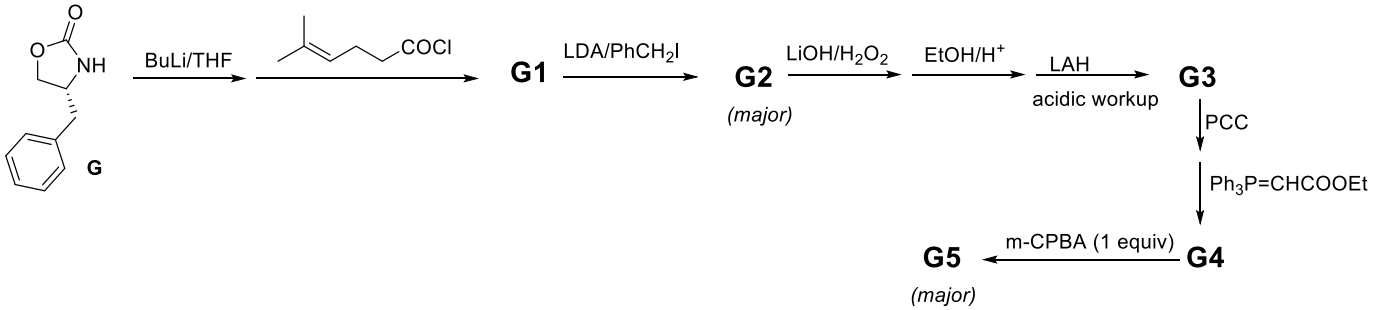
(iii). Two regioisomeric products are obtained for the following Pd-catalyzed cross-coupling reaction. Identify their structures (**E1** and **E2**), and sketch out a detailed mechanism for their formation. [5]



(iv). Using the given starting materials *(refer structures below)*, propose different synthetic schemes to prepare the following products (**F1** and **F2**). [5]



Q. No. 4. (i). Based on the information given in the below synthetic scheme, deduce the correct structures of the compounds, **G1** to **G5**. [5]



(ii). Identify the structures of final major products, **H-Q** for the following transformations? [10x1.5=15]

(a). 9-BBN → (i) *t*-Bu; (ii) CO, heat; (iii) $Li(OMe)_3AlH$; (iv) H_2O_2/OH^- → **H**

(b). → (i) C_6H_5Li; (ii) H_2O (work up) → **I**

(c). → (i) Me_3Si; THF; (ii) heat → **J**

(d). → $Pd(OAc)_2$ (10 mol%)); NaOEt (1 equiv); toluene, 100 °C, 12 h → **K**

(e). → heat → **L**

(f). → *hv*, Solvent → **M**

(g). → heat → **N**

(h). → heat → **O**

(i). → EtOOC; heat → **P**

(j). → heat → **Q**