

**Birla Institute of Technology & Science, Pilani**  
**Pilani Campus, Rajasthan - 333 031**

II Semester 2017-2018, Comprehensive examination

Course: CHEM F415

Part A: **Closed Book**

Time: 90 min.

Course Title: Frontiers in Organic Chemistry

Max. Marks: 40

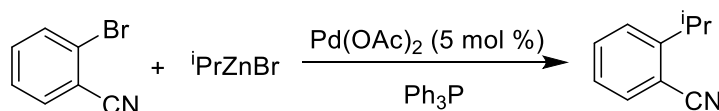
Instruction to students: Answer all questions and answer all parts of a question together

**Q. 1 a)** Of the three enolate equivalents, which one is most similar to naked enolate? Provide order of reactivity of the three enolate equivalents. **2**

**b)** In cyclic ketones, enamines show preference for less substituted double bond, why? **2**

**c)** Benzylation of ethyl propionate in the presence of sodium ethoxide generally leads to undesired product. Write structure of the undesired product obtained in this reaction. Mention an appropriate condition to overcome this problem. **4**

**d)** In order for catalysis to proceed in the below reaction, the palladium precatalyst must be reduced from Pd(II) to Pd(0). How might this happen in the reaction shown? **4**



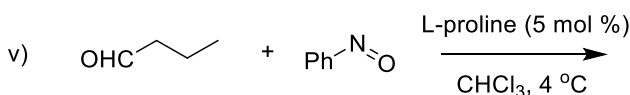
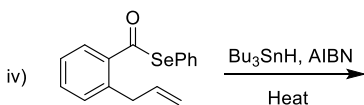
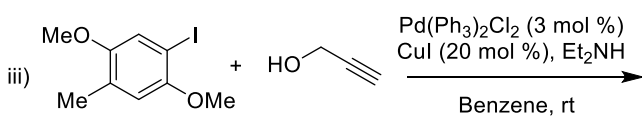
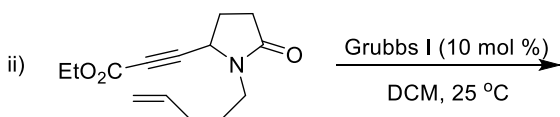
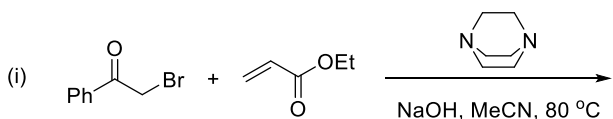
**Q. 2 a)** Provide an example for intermolecular Rh-catalyzed [2 + 2 + 2] carbocyclization reaction of 1,6-eneyne with symmetrical alkyne and write its mechanism. **5**

**b)** Why do we not see hydroalkoxylation as often as hydroamination? **3**

**Q. 3 a)** Draw molecular orbital diagrams (with appropriate labelling) to explain the fact that the radicals are stabilized by electron-withdrawing as well as electron-donating groups. **6**

**b)** Write one reactions each where radical behaves as nucleophilic and electrophile, respectively. **4**

**Q. 4** Write most appropriate product(s) of the following transformations. **10**



**-End of the examination-**

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Part B: **Open Book**

Time: 90 min.

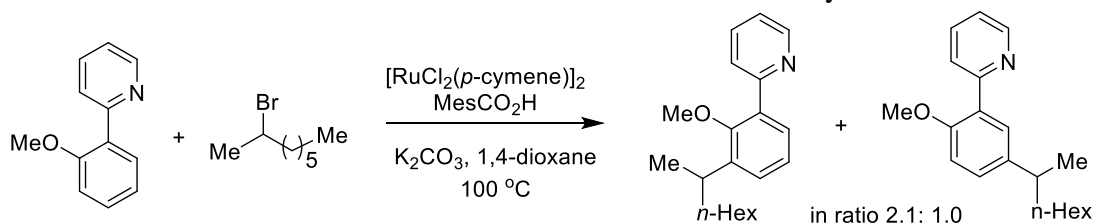
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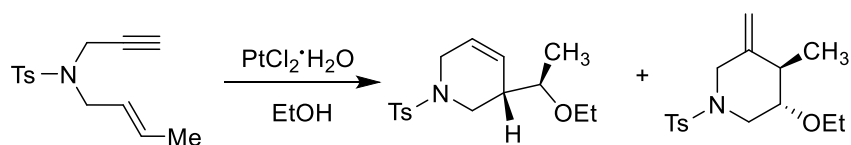
Instruction to students: Answer all questions and answer all parts of a question together

**Q. 1 a)** In 2001, Fu reported Suzuki cross-coupling of an alkyl bromide that contains  $\beta$ -hydrogens (1-bromododecane) with an arylborane (*B*-*n*-octyl-9-BBN) using  $\text{Pd}(\text{OAc})_2/\text{PCy}_3$  in the presence of  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ . It was found that no coupling occurs when anhydrous  $\text{K}_3\text{PO}_4$ , rather than  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ , is employed. By adding 1 equiv. of water to reactions with anhydrous  $\text{K}_3\text{PO}_4$ , similar results were obtained as with  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ . Based on these experimental evidences, write appropriate mechanism of the reaction. **4**

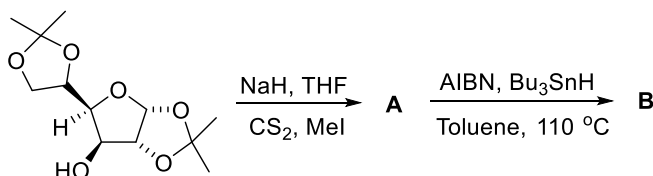
**b)** Ackermann group reported *meta*-selective alkylation of 2-arylpyridines using ruthenium(II) carboxylate catalyst,  $[\text{RuCl}_2(p\text{-cymene})]_2$  and  $\text{Me}_3\text{CO}_2\text{H}$  (Scheme given below). Provide a suitable mechanism for this transformation and comment on observed selectivity. **5**



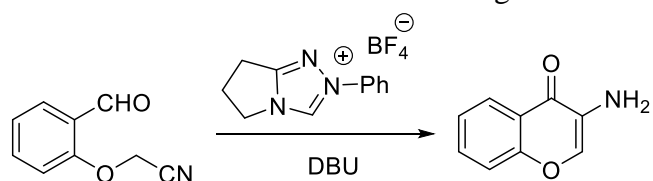
**Q. 2 a)** For the following carbocyclization identify intermediates that can explain formation of the two observed products. Also mention type of the cyclization (based on Baldwin rules) happening for these intermediates. **6**



**b)** Write structure of product **A** and **B** in the following transformations and propose mechanism for conversion of **A** to **B**. **6**

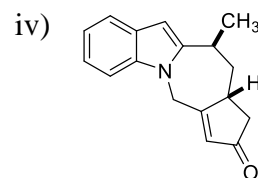
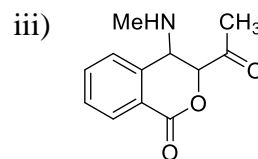
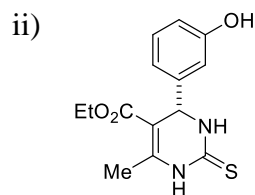
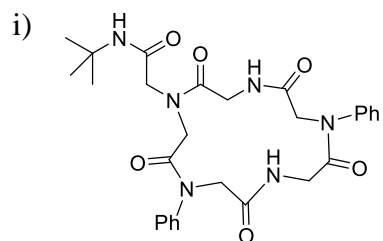


**Q. 3 a)** Write appropriate reaction mechanism for the following transformation. **4**

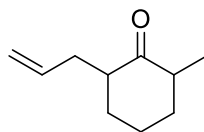


**b)** Based on the L-proline catalysis, propose mechanism for the L-proline catalyzed transamidation of acetamide with benzylamine. **5**

**Q. 4 a)** Write all the substrates for the synthesis of following compounds using multicomponent (Ugi, Bignelli, Mannich, or Pauson–Khand) reactions. [4 + 1 + 1 + 1]



**b)** Write reagents in sequence order to prepare given compound **X** from 2-methylcyclohexanone and diallyl carbonate. 3



**X**

*-End of the examination-*