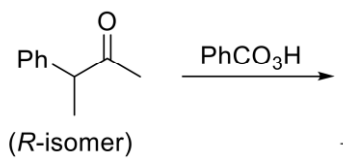


University of Calcutta Questions on Rearrangement Reactions in Organic Chemistry

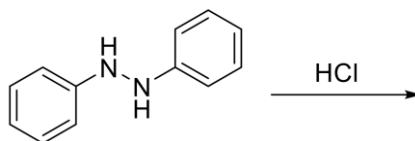
1. Predict the major product with plausible mechanism: (3) [Baeyer-Villiger]



[Variant: Predict the product and explain with mechanism: (3)

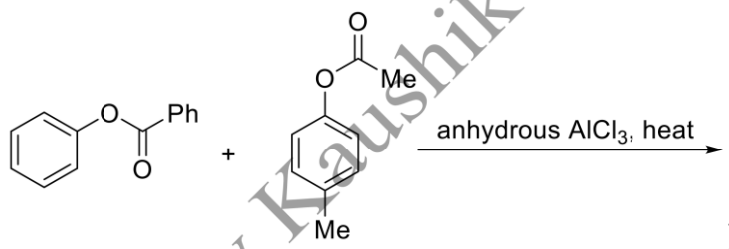


2. Predict the product of the following reaction with mechanism: (2) [Benzidine]

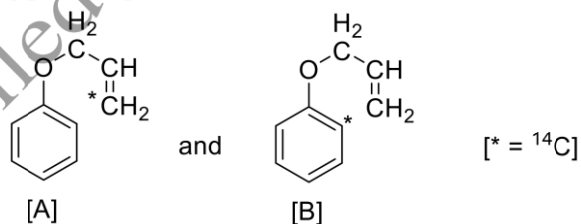


3. Write down the products when a mixture of phenyl acetate and α -naphthyl propanoate is heated with anhydrous AlCl_3 . Explain. (3) [Fries]

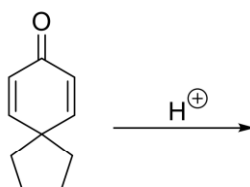
[Variant: Predict the products with mechanism: (3)



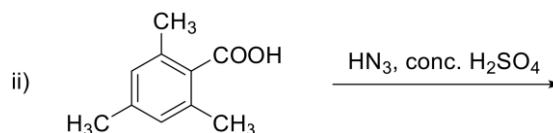
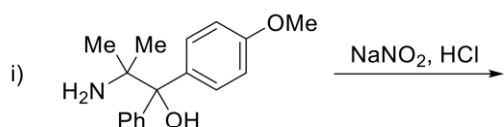
4. Write the structures of all possible products when a 1:1 mixture of [A] and [B] is heated together. Explain their formation. (3) [Claisen]



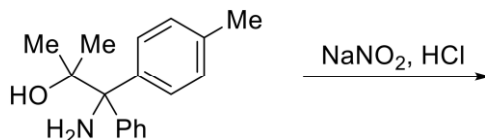
5. Predict the product of the following reaction with mechanism: (2) [Dienone-phenol]



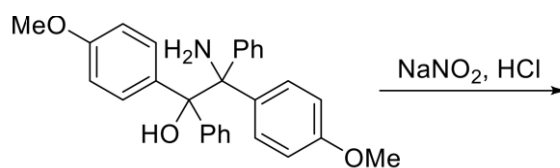
6. Predict the major product of the following reactions with plausible mechanism: (3) [Semipinacol, and Schmidt]



[Variant-1, of 6) i) Predict the product with plausible mechanism: (3)

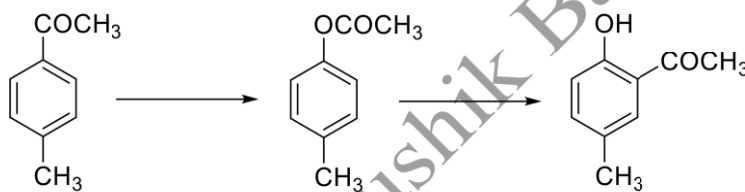


Variant-2, Same question, with



7. Provide the reagent and condition for the following sequence of reaction (mechanism not necessary).

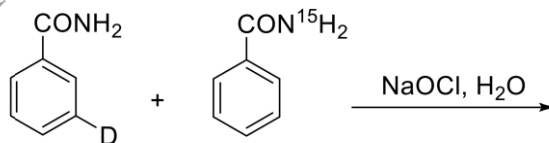
(2) [Baeyer-Villiger and Fries]



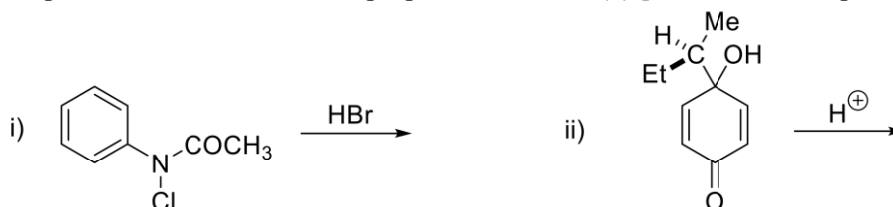
8. Both $\text{Ph}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}_2$ and $\text{Ph}(\text{Me})\text{C}(\text{OH})\text{C}(\text{OH})(\text{Me})\text{Ph}$ afford the same ketone when treated with 70% H_2SO_4 . Explain with mechanism. (3) [Pinacol-pinacolone]

[Variant: Elaborate with suitable reaction mechanism the major and the minor products obtained from the pinacol $(\text{CH}_3)_2\text{C}(\text{OH})-\text{C}(\text{OH})\text{Ph}_2$ on treatment with conc. H_2SO_4 . Give proper evidence in favour of your answer. (4)]

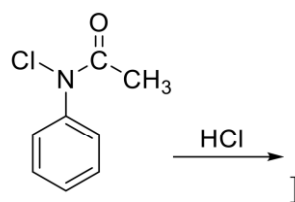
9. Predict the products of the following reaction and explain their formation. (2) [Hofmann]



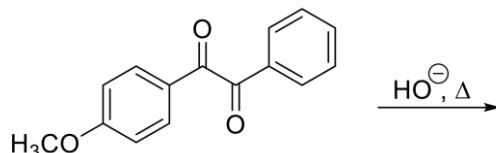
10. Identify the products in each case, with proper mechanism. (3) [Orton, Dienone-phenol]



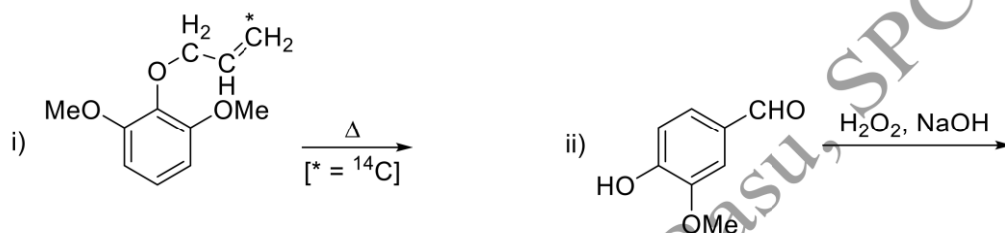
[Variant: Identify the product(s) with proper mechanism. (2) [Orton]



11. Predict the major product of the following reaction with plausible mechanism: (2) [Benzil-benzilic acid rearrangement]

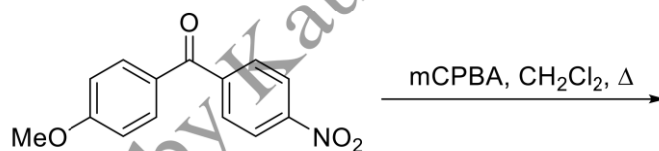


12. Predict the products of the following reactions with plausible mechanism. (3) [Claisen, Dakin]

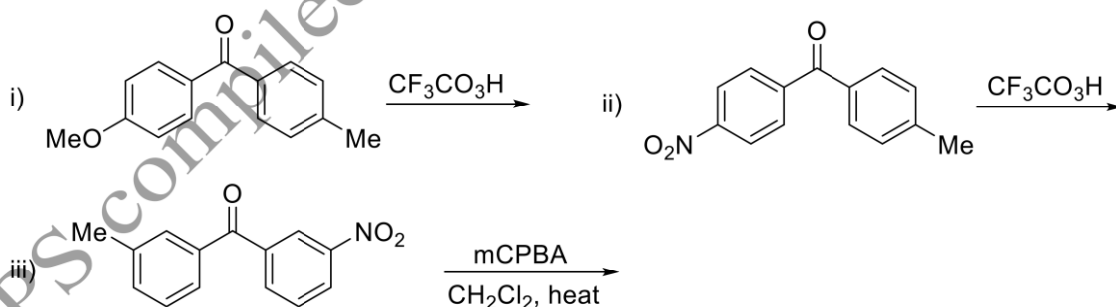


[Variant of 12. ii): What happens when vanillin is treated with alkaline hydrogen peroxide? Give mechanism. (1.5) [Dakin]]

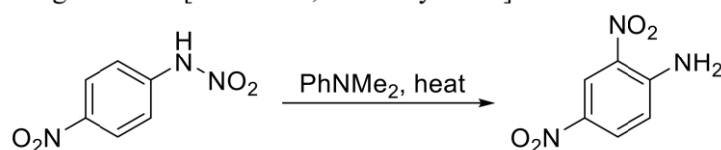
13. Explain the formation of the product in the following reaction with plausible mechanism. (2) [Baeyer-Villiger]



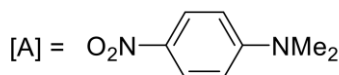
Variant-1: Same question, different structure. (3 each)



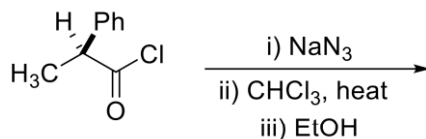
14. Explain the following reaction: [Nitramine, out-of-syllabus]



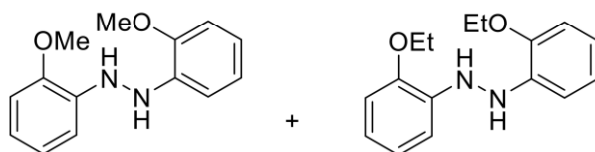
Why does [A] not form? (3)



15. Write the product obtained in the following reaction, with correct stereochemistry, and give the mechanism. (2) [Curtius]

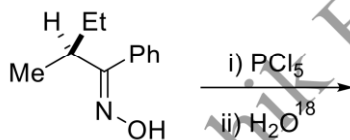


16. Predict the major products of the following reaction and explain with plausible mechanism. (3) [Benzidine]



[Variant: Benzidine rearrangement is intramolecular in nature. Justify the statement. (2)]

17. Complete the reaction indicating the stereochemistry of the product. (2) [Beckmann]

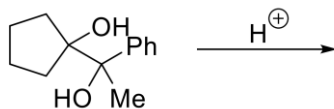


[Variant: Same question, but with a different migrating group:

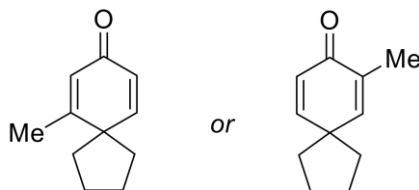


18. What happens when an acid chloride is treated with an excess of diazomethane and the product reacts with ethanol in the presence of Ag_2O catalyst? (3) [Arndt-Eistert]

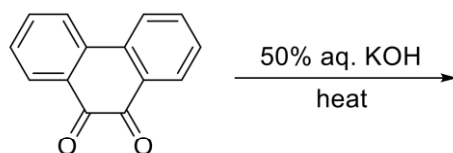
19. predict the major product of the following reaction and explain its formation mechanistically. (2) [Pinacol-pinacolone]



20. Which member of the following pair will undergo dienone-phenol rearrangement more rapidly and why? (3) [Dienone-phenol]



21. Predict the product and give mechanism of the following reaction. (2) [Benzil-benzilic acid]



22. Fries rearrangement is both intermolecular as well as intramolecular. Give supporting evidence in favour of this statement. (3) [Fries]

23. Predict the product and give plausible mechanism. (2) [Lossen]



24. How would you carry out the following transformation? (2) [Pinacol-pinacolone and Baeyer-Villiger]



[Variant: Propose a synthesis of *tert*-butyl acetate from 2,3-dimethylbutane-2,3-diol. (2)]

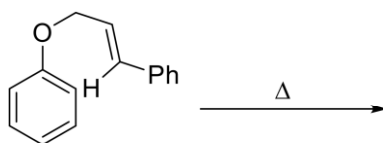
25. How will you prepare phenol from benzene via cumene? Give the mechanism of the reactions involved. (3) [Cumene-phenol]

[Variant-1: Suggest the reagents and propose the mechanism of the key step for the following transformation. (2)]

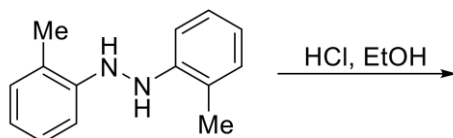


Variant-2: How will you prepare phenol and acetone commercially in a single chemical process?]

26. Write the product of the following reaction. (1.5) [Claisen]

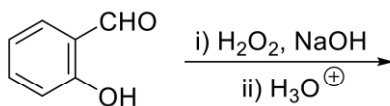


27. Predict the product and explain the mechanism involved. (2) [Benzidine]



[Variant: Same substrate, reagent is H^+ , marks allotted 1.5]

28. Predict the product of the following reaction with plausible mechanism: (2) [Dakin]

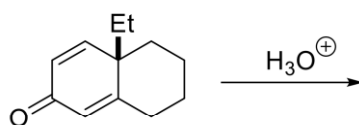


[Variant: Carry out the following conversion: (2)

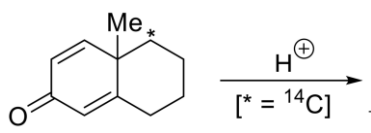


29. What happens when diazoaminobenzene is treated with dil. HCl? Explain mechanistically. (2) [C-azo to N-azo]

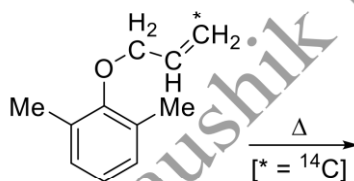
30. Predict the products of the following reaction with mechanism. (1.5) [Dienone-phenol]



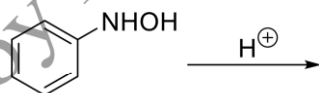
[Variant: Give the product(s) of the following reaction with plausible mechanism. (2)



31. Identify the product of the following reaction with mechanism: (3) [Claisen]



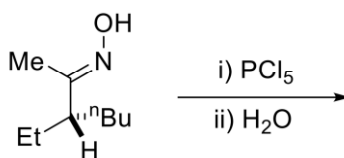
32. Predict the product and suggest mechanism. (2) [Bamberger]



[Variant: same question, only 1 mark allotted; also, reaction arrow is reversible.]

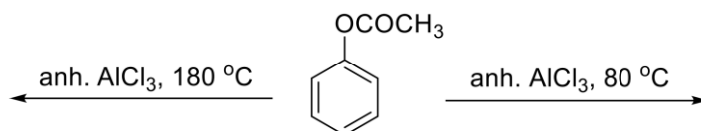
33. What happens when $PhCH_2COCl$ is treated with CH_2N_2 and the resultant product is allowed to react with Ag_2O in water? Give the mechanism of the second step. (3) [Arndt-Eistert]

34. Predict the mechanism of the following reaction and give mechanism. (2) [Beckmann]



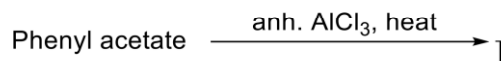
35. $RCONHMe$ does not undergo Hofmann amine formation reaction. Offer an explanation. (2) [Hofmann]

36. Provide the product(s) of the following reaction along with plausible mechanisms. [Fries]

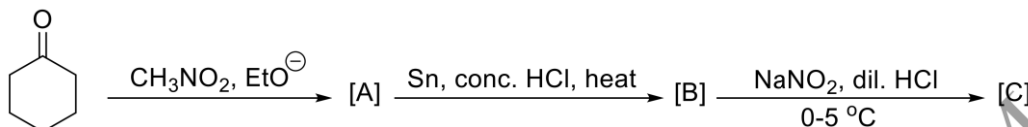


How do you justify the formation of different products with the change in reaction temperature? (3)

[Variant: Predict the product and explain. (2)]

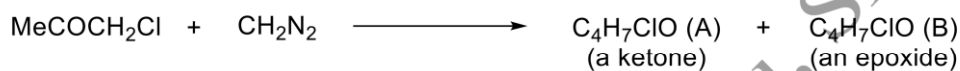


37. Suggest structures of A, B and C. Also suggest a mechanism of conversion from B to C. (3)
[Semipinacol]

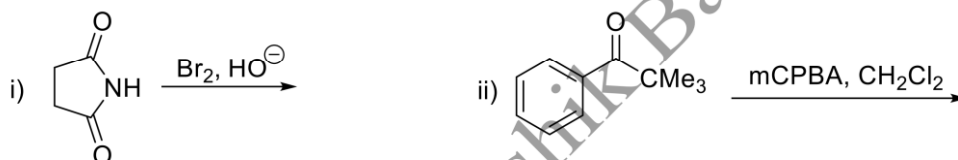


38. Benzaldehyde fails to undergo Dakin's reaction. Account for this observation. (2) [Dakin]

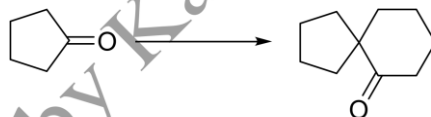
39. Suggest structures for (A) and (B) and give mechanism for their formation: (3) [Semipinacol]



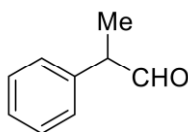
40. Predict the product with mechanism: (2 each) [Hofmann, Baeyer-Villiger]



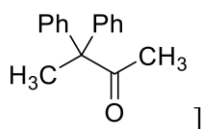
41. Carry out the following transformation: (2) [Pinacol-pinacolone]



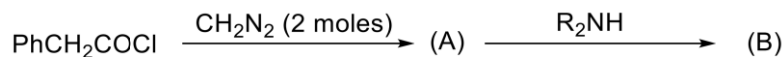
42. Using the retrosynthetic approach, outline an efficient synthesis of the following compound involving the pinacol-pinacolone rearrangement as one of the steps: (3) [Pinacol-pinacolone]



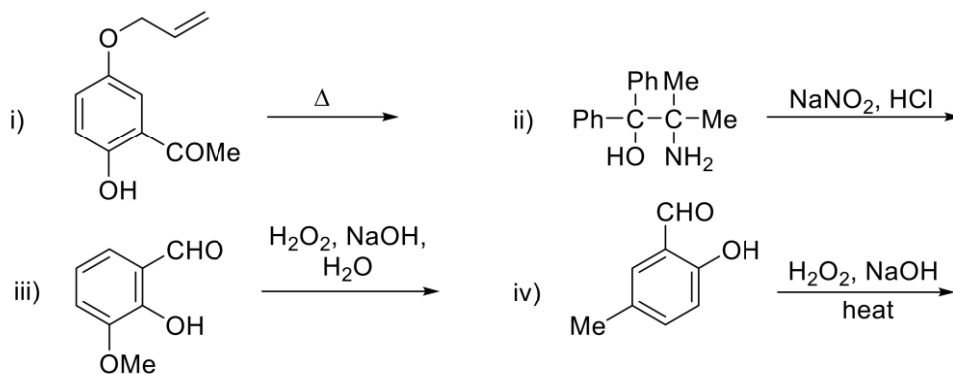
[Variant: Work backwards to identify the starting material which on pinacol-pinacolone rearrangement would provide: (3)]



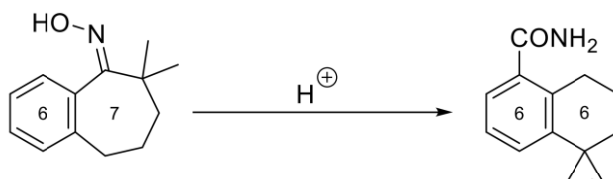
43. Identify (A) and (B) in the following sequence and explain why 2 equivalents of diazomethane are required for the first step of the sequence. (2) [Arndt-Eistert]



44. Predict the products and offer explanation. (2 each) [Claisen, semipinacol, last two both Dakin]



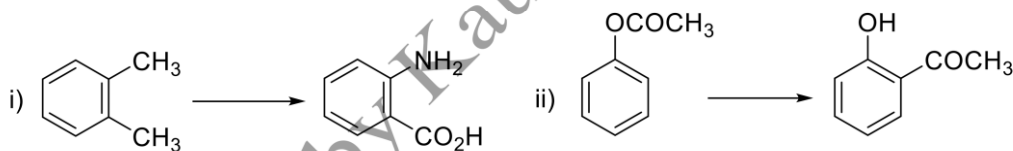
45. Mechanistically account for the following transformation. (2) [Beckmann-related]



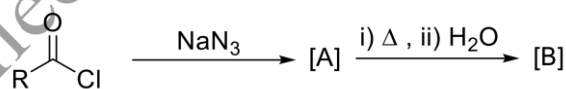
46. In Arndt-Eistert synthesis, two equivalents of diazomethane is used. Why? What happens if only one equivalent is used? (2+1) [Arndt-Eistert]

47. An organic compound (A) [C₈H₉ON] on treatment with H₂SO₄ isomerizes to (B) which on hydrolysis furnishes aniline and acetic acid. What are (A) and (B)? Explain the above facts and show mechanism for the isomerization step only. (3) [Beckmann]

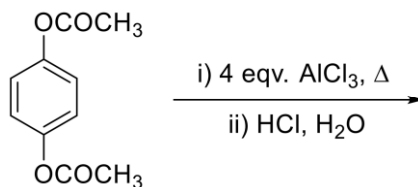
48. Carry out the following conversions: (2 each) [Hofmann, Fries]



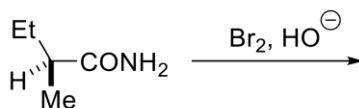
49. Identify (A) and (B). Provide mechanism. (3) [Curtius]



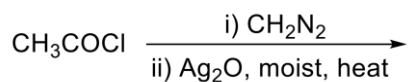
50. Predict the product and explain. (3) [Fries]



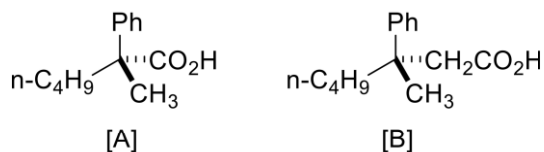
51. Predict the product and explain with mechanism. (3) [Hofmann]



53. Predict the product and explain with mechanism. (3) [Arndt-Eistert]

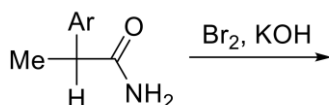


54. Convert [A] to [B] and vice versa. (4) [Arndt-Eistert]

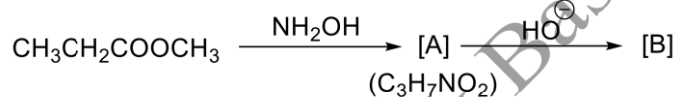


55. What happens when *p*-methylphenyl acetate is heated with anhydrous AlCl_3 ? Give the mechanism of the reaction. (2) [Fries]

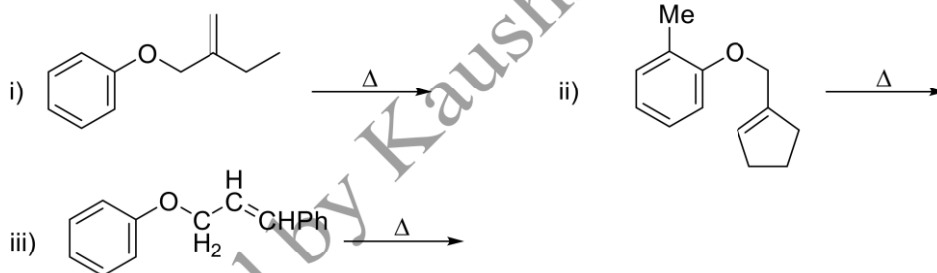
56. Predict the product and explain with mechanism. (2) [Hofmann]



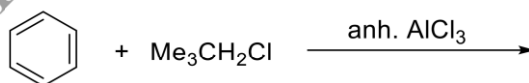
57. Identify [A] and [B]. Show the mechanism of conversion from [A] to [B]. (3) [Lossen]



58. Predict the product and explain with mechanism. (3 each) [Claisen]

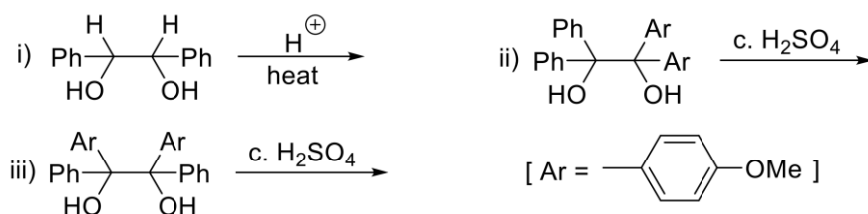


59. Predict the product and explain with mechanism. (2) [Wagner-Meerwein]

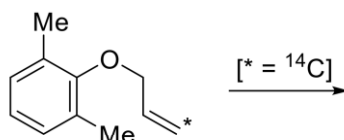


60. Lossen and Curtius rearrangements are mechanistically similar. Justify. (3) [Lossen and Curtius]

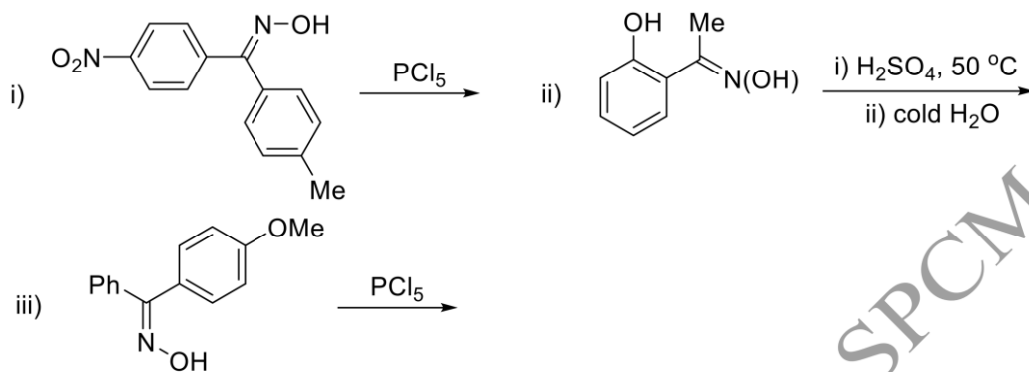
61. Predict the product and explain with mechanism. (2) [Pinacol-pinacolone]



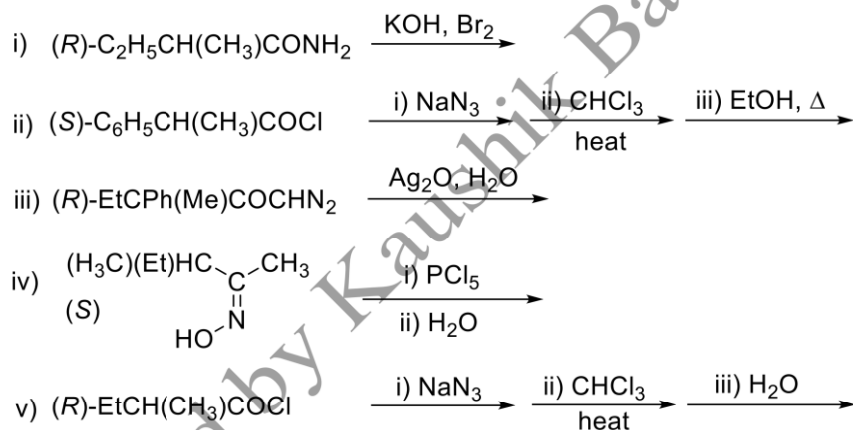
62. Predict the product and explain with mechanism. (3) [Claisen]



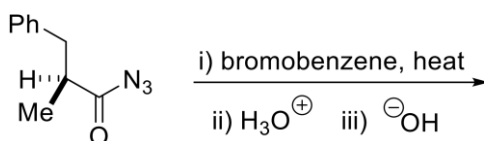
63. Predict the product and explain with mechanism. (3+2) [Beckmann]



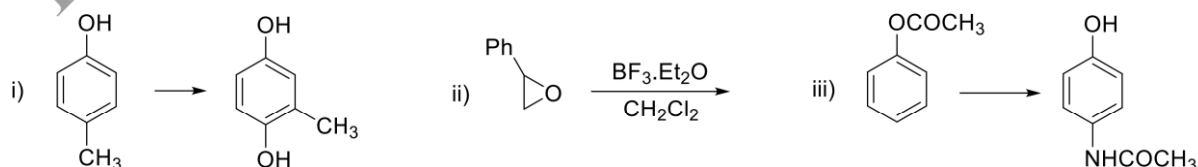
64. Predict the products in each case and indicate the features common to both the reactions: (3+3) [Hofmann, Curtius, Arndt-Eistert (Wolff), Beckmann, Curtius]



65. Predict the product and explain with mechanism. (2) [Curtius]



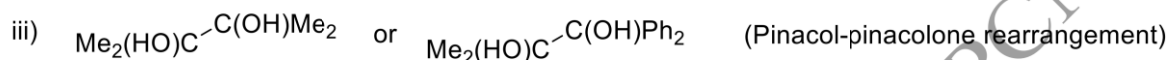
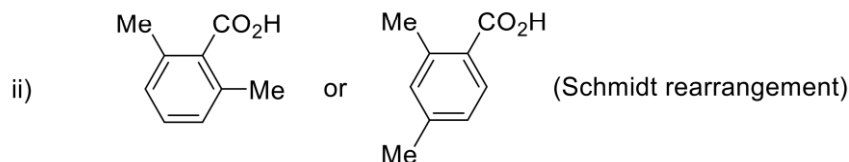
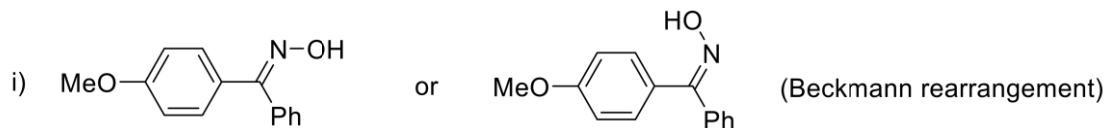
66. How to carry out the following conversion: [Dienone-phenol, pinacol-pinacolone-type, Fries combined with Beckmann]



[For 66. i), Variant-1; Convert *p*-cresol to 1,4-dihydroxymethylbenzene, (3)

Variant-2: Predict the product with mechanism. (2)

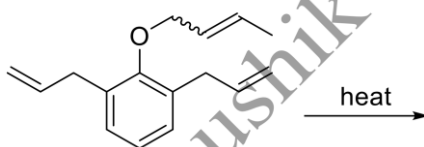
78. Which compound, in each of the following pairs will undergo the indicated rearrangement more readily? Justify with mechanism and give the product in each case. (4 each) [Beckmann, Schmidt, pinacol-pinacolone]



79. What happens when *N*-methylphthalimide reacts with bromine in aqueous NaOH at 0-5 °C. Would *N*-methylphthalimide react analogously? Give reasons for your answer. (4) [Hofmann]

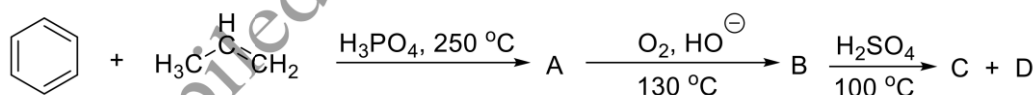
80. The benzil-benzilic acid rearrangement and the Cannizzaro reaction are both base-catalysed reactions, give mechanism for both and point out similarities, if any. (2) [Benzil-benzilic acid.]

81. Give the product(s) of the following reaction: (1) [Claisen]

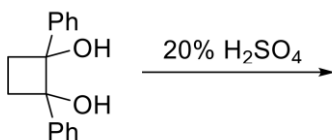


82. Write down the structures of the products when RCOOH and R₂C=O are separately subjected to the Schmidt reaction. (1)

83. Give the structures of A-D in the following scheme. Suggest mechanism for the conversion of B to C and D. [Cumene-phenol] (3)



84. The following reaction gives a single product. Give the structure of that product and explain mechanistically why the isomeric product does not form. (3) [Pinacol-pinacolone]



85. Explain the formation of A and B mechanistically. (3) [Pinacol-pinacolone]

