

Prabhat Kumar College, Contai
M.Sc., Semester-III
Chemistry (Organic Special), Paper- CEM 302
2021
Full marks: 40

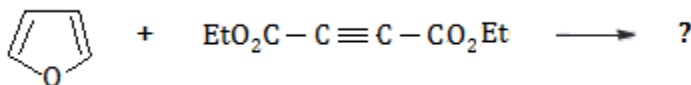
Answer any four questions

1. a) Draw the correlation diagram for the following conversion in the thermal and photochemical condition. [4 + 4]



Indicate symmetry allowed path for each condition.

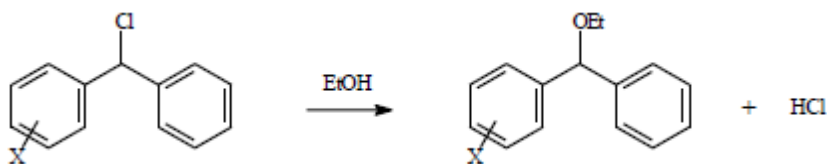
- b) Predict the product/s of the following reaction indicating F.O.I. 2



2. a) Define alternant and non-alternant hydrocarbon with examples. [2 + 2]
 b) Write down the unique properties of alternant systems. 3
 c) Why the Hammett equation is called a linear free energy relationship? 3
3. a) The pKa values of m- and p-monosubstituted benzoic acids in 50% aqueous ethanol correlate with σ , and have a ρ value of 1.60. The pKa of benzoic acid in this system is 5.71. The pKa values of some 4-X-3,5-dimethylbenzoic acids in this solvent system are given below. Use these results to examine and comment on the applicability of additivity of σ values. [6]

X	N(CH ₃) ₂	NH ₂	Cl	Br	CN	COOCH ₃	NO ₂
pK _a	6.23	6.88	5.59	5.55	4.90	5.44	4.91

- b) The solvolysis of substituted diphenylcarbinyl chlorides was studied in ethanol at 25°C. A plot of log *k* versus σ^+ was linear with a slope of -5.1. Suggest a mechanism consistent with this observation and provide an explanation of the ρ value in terms of the *Hammond postulate*. [4]



4. Answer each of the following with reference to the corresponding substituent constants considering both inductive and resonance electronic contributions (σ_I and σ_R). Illustrate your answer showing resonance structures for substituted benzoic acids, where appropriate.
- a) The σ_{meta} and σ_{para} values for the $-\text{CO}_2\text{CH}_3$ group are both positive with $\sigma_{\text{para}} > \sigma_{\text{meta}}$. [4]
- b) The values of σ_{meta} for the methoxy substituent ($-\text{OCH}_3$) is positive, whereas the values for σ_{para} is negative. [3]
- c) The picryl (2,4,6-trinitrophenyl) substituent, $-\text{C}_6\text{H}_2(\text{NO}_2)_3$ is relatively large with the ortho nitro groups sterically interfering with atoms in the ortho positions on an adjacent aromatic ring. Predict the sign and relative magnitude of σ_{meta} and σ_{para} for the picryl substituent. [3]
5. Write down the rules of nucleophilic addition to organometallic complexes with examples and explanation [10]
6. Applying aromatic transition state theory predict the selectivity of thermal [4 + 2] cycloaddition reaction and electrocyclic reaction of $[4n + 2]$ pi electron system in thermal and photochemical condition. [5 + 5]
7. a) What are the currently accepted theories for regiocontrol observed in the nucleophilic displacement of hydride in arenechromium-carbonyl complexes? 3
 b) What is the reason behind the enhanced acidity of the benzylic proton in the arenechromiumtricarbonyl complex in comparison to the uncomplexed arene? 3
 c) Account for the enhancement in the rate of solvolysis of chromiumtricarbonyl complex of benzyl chloride in comparison to the uncomplexed compound? 4
8. a) Explain the conceptual basis of Yukawa Tsuno equation. 5
 b) Why does acid catalysed esterification of substituted benzoic acid give a Hammett plot with a negligible slope? 5