# Birla Institute of Technology and Science, Pilani 

Mid-semester Examination, $1{ }^{\text {st }}$ Semester, 2016-2017
Course Name: Organic Chemistry-1
Course No. CHEM F212
Note for students: Attempt all questions. Attempt all parts of a question together at one place only.
Q. 1 Based on the information provided for the reactions given below, predict type of isotope effect, reaction mechanism and provide reasonable explanation for your answer in each case.
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a) $\mathrm{PhCH}_{2} \mathrm{CH}_{2}\left(\mathrm{D}_{2}\right) \mathrm{CH}_{2} \mathrm{Br} \xrightarrow[\text { EtOH }]{\mathrm{NaOEt}} \quad \mathrm{PhCH}_{2} \mathrm{CH}(\mathrm{D})=\mathrm{CH}_{2} \quad \mathrm{~K}_{\mathrm{H}} / \mathrm{K}_{\mathrm{D}}=6.7$
b) $\quad \mathrm{PhCH}_{2} \mathrm{CH}_{2}\left(\mathrm{D}_{2}\right) \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{Br} \xrightarrow[\text { EtOH }]{\mathrm{NaOEt}} \quad \mathrm{PhCH}_{2} \mathrm{CH}(\mathrm{D})=\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2} \quad \mathrm{~K}_{\mathrm{H}} / \mathrm{K}_{\mathrm{D}}=1.4$
Q. 2. As you know the reaction constant $\rho$ in Hammett equation is dependent upon the nature of reaction. Mention for which of the following reactions $\rho$ will be positive and for which it will be negative. Also provide the decreasing order of $\rho$ for these four reaction.
a) $\mathrm{ArCOOH}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{ArCOO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
b) $\mathrm{ArCH}_{2} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{ArCH}_{2} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
c) trans $-\mathrm{ArCH}=\mathrm{CHCOOH}+\mathrm{H}_{2} \mathrm{O} \longrightarrow$ trans- $\mathrm{ArCH}=\mathrm{CHCOO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
d) $\mathrm{ArCOOEt}+\mathrm{H}_{2} \mathrm{O} \xrightarrow[\text { aq. } \mathrm{EtOH}]{\mathrm{H}^{+}} \mathrm{ArCOOH}+\mathrm{EtOH}$
Q. 3 In 1944 Woodward and Baer found that a mixture of two isomers was obtained which they labelled as the $\alpha$-adduct and $\beta$-adduct, respectively, from Diels-Alder addition between 6,6-pentamethylenefulvene and maleic anhydride (J. Am. Chem. Soc., 1944, 66, 645-649). These two isomers were found to have quite distinctive physical and chemical properties and their formation to be preferentially favored or disfavored by certain changes in the reaction conditions. They reported that
........allowed to react in benzene solution, at room temperature, an $\alpha$-adduct, $C_{15} H_{16} O_{3}$, m.p. $132^{\circ}$, is obtained. If, however, the mother liquor from the recovery of this product is allowed to stand for several weeks, very large beautiful crystals of a new, $\beta$-adduct, $C_{15} H_{16} O_{3}$, m.p. $93^{\circ}$, gradually separate. Further, as the initial condensation is carried out at higher temperatures, the formation of the $\beta$-adduct takes place more rapidly, and less of the $\alpha$-adduct is obtained.

Based on these observations predict the kinetic and thermodynamic controlled product of the above mentioned reaction.
Q. 4 Write structure of the product obtained by Moses on treating triphenylmethyl chloride with silver metal.
Q. 5 Explain, why bromination of pentane with NBS results in poor yields of 1-bromopentane, while cyclopentane can be readily brominated under similar conditions to yield bromocyclopentane.
Q. 6 Write plausible arrow-pushing mechanism for the following reactions.
a)

b)

Q. 7 Write product(s) of the following reactions with appropriate stereochemistry, if any.
a)

b)

c)


d)


Q. 8 Provide synthetic sequence with appropriate reagents/conditions for the following transformation.

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Q. 9 Which of the following reaction will generate racemic acetate? Provide a suitable explanation for your answer.
2.5
a)

b)

Q. 10 Hydrolysis of (chloromethyl)cyclopropane (reaction given below) results in the formation of three alcohols. Write the structure of the three alcohols obtained and explain their formation.


