Tutorial for Health Sciences and Pharmacy Students. Week 4-5

In these weeks we studied: Alkenes, double bond equivalents, rotation around a double bond, conjugation, *cis-trans* isomersation, *E-Z* isomers, reactivity of alkenes, nucleophiles, electrophiles, addition reaction, carbocation, stability of carbocations, Markovnikov, addition of HX, stereochemistry of addition reaction, addition of H_2O, addition of X_2, stereochemistry of X_2 addition, hydrogenation of alkenes, halohydration, radical addition, anti-Markovnikov, alkynes, electron structure, addition of HX, X_2, X_2 + H_2O etc., alkylation, addition of water using mercuric ion catalysis, enol-keto tautomerism, reduction, *cis- trans* selectivity, Lindlar, Li/NH_3(l), alkyl halides, substitution vs. elimination reactions, nucleophilic substitution, transition state, stereochemistry of substitution reactions, kinetics, reaction rate, S_N2, reactivity of alkyl halides, leaving group, reactivity: good *vs.* poor leaving group, elimination reactions, E2, Zaitsev's rule, stereochemistry of E2, S_N1, stereochemistry of S_N1, E1, structure of benzene, stability and structure of benzene, resonance stability, aromaticity, electrophilic aromatic substitution reactions, halogenation, nitration, phenol, activation, deactivation, substituent effects, *orto, meta* and *para*, resonance stability in phenols, nucleophilicity of phenol, some of these will be addressed in the questions below.

Question 1. Draw the *cis* or the *trans* forms of the following:

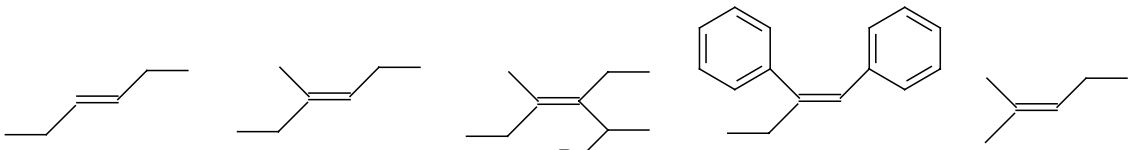
(a) *cis*-CH_3-CH=CH-CH_3 (b) *trans*-CH_3-CH=CH-CH_3
(c) *cis*-CH_3-CH_2-CH=CH-CH_3 (d) *trans*-CH_3-CH_2-CH=CH-CH_3
(c) *cis*-CH_3-CH_2-CH=CH-CH_3 (d) *trans*-CH_3-CH_2-CH=CH-CH_3
(e) *cis*-Ph-CH_2-CH=CH-CH_3 (f) *trans*-Ph-CH_2-CH=CH-CH_3

Question 2. Draw the *E* or the *Z* forms of the following:

(a) *E*-CH_3-CH=CH-CH_3 (b) *Z*-CH_3-CH=CH-CH_3
(c) *Z*-CH_3-CH_2-CH=CH-CH_3 (d) *E*-CH_3-CH_2-CH=CH-CH_3
(c) *E*-CH_3-CH_2-CH=CH-CH_3 (d) *Z*-CH_3-CH_2-CH=CH-CH_3
(e) *Z*-Ph-CH_2-CH=CH-CH_3 (f) *E*-Ph-CH_2-CH=CH-CH_3

Question 3. Why is it not always easy to go between *cis* and *trans*? What methods can sometimes be used to achieve such isomersation?

Question 4. Assign the stereochemistry as either *E* or Z of the following:



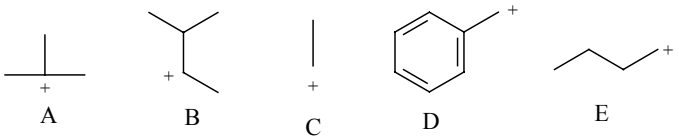
Question 5. Why are alkenes usually considered as nucleophiles?

Question 6. In an addition reaction (when two reactants add together to form a new single bond) of alkenes, the first intermediate is a carbocation, why?

Question 7. Show every mechanistic step and transition state structure for the addition of HCl to ethylene. Identify which reactants are acting as 'nucleophiles' and which are 'electrophiles' in this reaction.

Question 8. What is meant by 'stability of carbocation'?

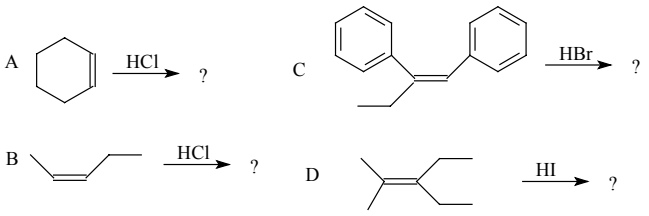
Question 9. Arrange these carbocations in order of decreasing stability:



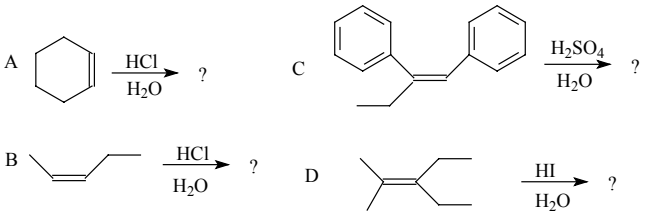
Question 10. Reaction of HBr with 2-methylpropane gives what product(s)?

Question 11. Reaction of HCl with 2-pentene gives what product(s)?

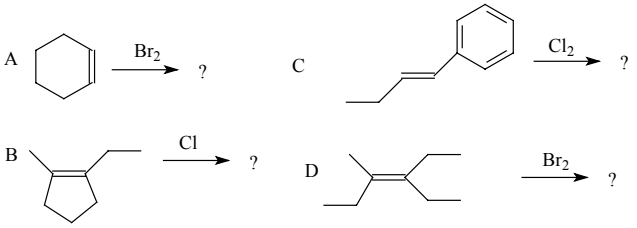
Question 12. Show the mechanism and the product(s) for the following reactions:



Question 13. Show the mechanism and the product(s) for the following reactions:

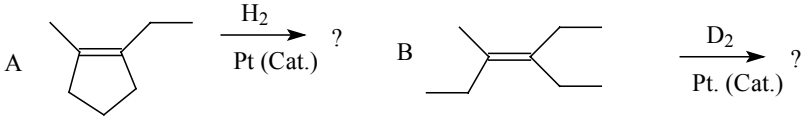


Question 14. Show the mechanism and the product(s) for the following reactions:



Question 15. How would you write a reaction energy diagram for the first step in the reaction of ethylene with HCl (look at Prof. Corish notes)? Then draw a reaction diagram for a fast reaction that has low E_{act}, and is highly exothermic?

Question 16. What is/are the product(s) of the following reactions:



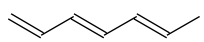
Question 17. What is/are the product(s) of the following reactions:

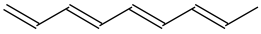
A $CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{(Syn addition)}]{H_2.Ni_2B(P\text{-}2)}$

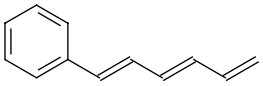
B $CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow{H_2.Pd/CaCO_3}$

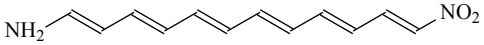
C $CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[NH_4Cl]{Li,\ C_2H_5NH_2}$

Question 18. Write the resonance structures of the following compounds:

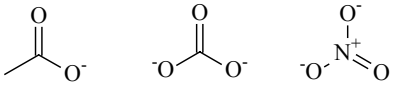
A 

C 

B 

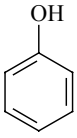
D 

Question 19. Write the resonance structures of the following compounds:



A B C

D



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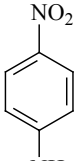

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Question 20. What is/are the product(s) of the following reactions?

A $CH_3CH_2CH_2C{\equiv}CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} ?$

B $CH_3CH_2C{\equiv}CCH_3 + H_2O \xrightarrow[HgSO_4]{H_2SO_4} ?$

C $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2C{\equiv}CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} ?$

Question 21. What is/are the product(s) of the following reactions?

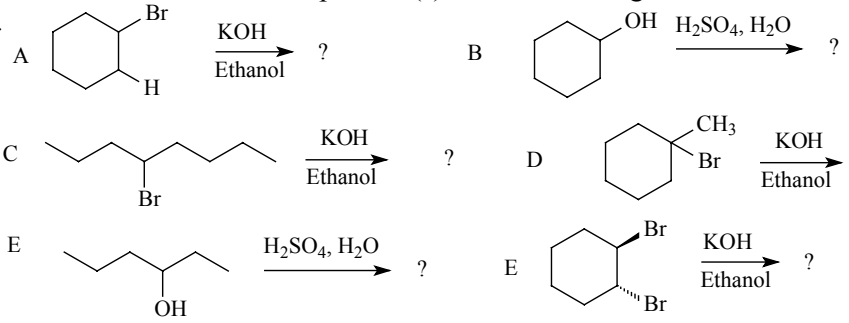
A $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{NaNH_2} ? \xrightarrow{CH_3CH_2Br} ?$

B $CH_3CH_2C{\equiv}CH \xrightarrow{NaNH_2} ? \xrightarrow{CH_3CH_2CH_2Br} ?$

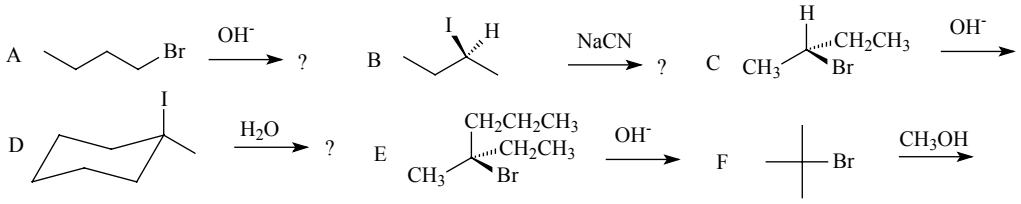
C $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2C{\equiv}CH \xrightarrow{LDA} ? \xrightarrow{PhCH_2Br} ?$

Question 22. Why is it necessary to carry out the reactions in question 21 in two steps?

Question 23. What is/are the product(s) of the following reactions? Identify them as either E1 or E2.



Question 24. What is/are the product(s) of the following reactions? Identify them as the products of either S_N1 or S_N2 reactions?

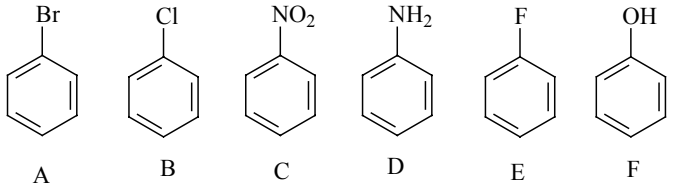


Question 25. Assign the stereochemistry as either *R* or *S*, for those products formed in question 24 that have stereogenic centres.

Question 26. How does the solvent affect: (a) S_N1 and S_N2 and (b) E1 and E2 reaction rates?

Question 27. How does the nature of the leaving group affect S_N1 and S_N2 reaction rates?

Question 28. Show how you would make the following molecules from benzene:



Question 29. Write the mechanism and resonance stabilisation forms (the stabilisation of the carbocation!) for the formation of the above compounds. Then write all the resonance forms for the above compounds

Question 30. Show how you would make the following molecules from the substituted benzene precursors (NB, it is very important to investigate the order of which you introduce the substituents!!!):