**Structure-Reactivity Relationship: Hydrocarbon Reactivity – ANSWER KEY (40 Marks)**

Together, you and your TA are comparing the reactivity of an assortment of hydrocarbons with bromine. Watch the required videos of the experiment when noted. These will help you to determine what you will see when performing the reaction. Experimental details will be provided where necessary. Please use ChemDraw for all of your figures and schemes.

Today, you will be reacting the following hydrocarbons with bromine. Complete the following questions.

1. Why is hydrocarbon reactivity with bromine important? Eg. Why would we want to brominate a hydrocarbon? **(1 marks)**

* Halogens are good leaving groups and can help with the installation of new functional groups on molecules
* Halogenation reactions are important in the pharmaceutical industry for selective reactivity
* Halogenated rings are common in cross-coupling reactions

\*\*Anything along these lines is acceptable\*\*

1. Research how bromine reacts with the three different functional groups that are present in the following table. For each functional group name the reaction type and draw a general reaction mechanism. For those involving a catalyst, draw the reaction scheme only. Ensure that you indicate if a catalyst, light, heat, or otherwise is required for the reaction.
2. Radical Substitution: Alkanes **(3 marks)**

* Should show the homolytic cleavage of bromine
* Radical abstraction of H from the alkane (most stable position) to form a radical and HBr
* Should show the re-combination of a bromine radical with the alkane radical

1. Electrophillic Addition: Alkenes **(3 marks)**

* Should show the attack of the alkene to the bromine atom and formation of Br-
* Should show the bronium ion intermediate with proper charges
* Should show attack of the Br- to form the di-halogenated product

1. Electrophillic Aromatic Substitution: Aromatic Rings **(3 marks)**

* Should show the need for heat and a catalyst
* Catalyst should be defined (FeBr3) is one that works
* Should show the halogenated product as well as the HBr formed from the reaction

1. Complete the following table **(9 marks)**

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **Structure** | **Functional Groups** | **Reaction Type** |
| Cyclohexane | 0.5 for each structure  0.5 for each functional group filled out  0.5 for each reaction type | * Alkane | Radical Substitution |
| Cyclohexene |  | * Alkane * Alkene | Electrophillic Addition |
| Toluene |  | * Alkane * Aromatic | Radical Substitution |
| Ethylbenzene |  | * Alkane * Aromatic | Radical Substitution |
| Isopropylbenzene |  | * Alkane * Aromatic | Radical Substitution |
| *t*-Butylbenzene |  | * Alkane * Aromatic | Radical Substitution |

1. Using the following information, determine the products of the reaction and show the calculation of the limiting reagent for the reaction of bromine with cyclohexane.



Product of the reaction **(2 marks)**

Calculation for the limiting reagent **(2 marks)**

|  |  |  |
| --- | --- | --- |
| **MW (g/mol)** | 84.16 |  |
| **Amount** | 0.5 mL | 1.0 mL |
| **Conc.** | / | 0.5 M |
| **Density (g/mL)** | 0.779 |  |
| **mmol** | 4.63 | 0.5 |

Limiting Reagent: ­­­­­­­\_\_\_\_\_\_Bromine \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

1. Why do we limit this specific reagent in the reaction? What does is tell us about what we should SEE during the reaction? **(2 marks)**

* Bromine is dark red
* Upon consumption of all bromine, the reaction will change from red to clear, allowing for rate comparisons.

Time for the lab to commence! You have 6 unknown sample vials. You know that the contents of each of the vials corresponds to one of hydrocarbons you outlined above. Assess the following reactions to help you determine which unknown number belongs to which hydrocarbon!

1. A bromine water mixture can be used to help determine whether a compound contains an alkene functional group. A bromine/water mixture is added to the hydrocarbon and shaken. There is NO UV light used for this reaction. Watch the following video and assess your in-lab data from the table below to help you determine which hydrocarbon belongs to each unknown number.

<https://www.youtube.com/watch?v=vBMGNzRYngk>

|  |  |
| --- | --- |
| **Unknown Number** | **Observations** |
| 1 | Colour remained yellow |
| 2 | Colour remained yellow |
| 3 | Colour remained yellow |
| 4 | Colour slowly changed to clear upon shaking |
| 5 | Colour remained yellow |
| 6 | Colour remained yellow |

1. Why does the reaction described above not require UV light to react?

* UV light is not required because bromine does not have to undergo homolysis to form a bromine radical in order for the reaction to proceed **(1 mark)**

1. To each of your unknown samples (0.5 mL) is added 1.0 mL of liquid bromine in the fumehood. The samples are gently shaken and then exposed to UV-light for a period of time. Watch the following video and assess your in-lab data from the table below to help you determine which hydrocarbon belongs to each unknown number.

<https://www.youtube.com/watch?v=-UZxyJX0gHo>

|  |  |  |
| --- | --- | --- |
| **Unknown Number** | **Observations** | **Time to React (seconds)** |
| 1 | Red colour rapidly changed to clear | 725 |
| 2 | Red colour became slightly lighter, but never became clear | 1310 |
| 3 | Red colour immediately became clear | 1 |
| 4 | Red colour immediately became clear | 1 |
| 5 | Red colour did not change | 1800 |
| 6 | Red colour rapidly changed to clear | 320 |

1. Why does this reaction require exposure to UV-light?

* This reaction required UV light because bromine must first undergo homolysis to form a bromine radical in order for the reaction to proceed, eg. initiation **(1 mark)**

1. Complete the following table assigning each hydrocarbon to an unknown number **(3 marks)**

|  |  |
| --- | --- |
| **Unknown Number** | **Hydrocarbon** |
| 1 | Toluene |
| 2 | Cyclohexane |
| 3 | Isopropylbenzene |
| 4 | Cyclohexene |
| 5 | *t*-Butylbenzene |
| 6 | Ethylbenzene |

1. Describe how you assigned each hydrocarbon to an unknown number. Take into consideration the reaction type, the reaction intermediates, what controls the rate of each reaction, and factors affect the stability of various intermediates. A well-rounded discussion will make it clear *chemically* why a reaction order or type is expected for each of the hydrocarbons. **(10 marks)**

* 4 must be cyclohexene because it was the only compound to react with the bromine/water test
* Cyclohexane undergoes electrophilic addition with bromine and therefore its reaction rate cannot be compared to the other compounds
* All other compounds should undergo radical substitution reactions on the alkane branches as no catalyst was used for the reaction (meaning no electrophilic aromatic substitution)
* Radical stability is affected by two major factors: resonance and hyperconjugation
* The stability of the alkane radical will affect the rate of the reaction. The more stable the radical, the faster the reaction will proceed.
* Isopropylbenzene, ethylbenzene, and toluene can stabilize a radical at the benzylic position via resonance through the benzene ring
* Cyclohexane and t-butylbenzene cannot be stabilized by resonance
* Reactivity order for the resonance stabilized compounds should be isopropylbenzene (3°) > ethylbenzene (2°) > toluene (1°)
* Reactivity order for the hyperconjugation ONLY stabilized complexes should be cyclohexane (2°) > t-butylbenzene (1°)
* Looking at the reaction times, 3 is the fastest to react so it must be isopropylbenzene, 6 is next to react therefor is ethylbenzene, 1 is next to react (toluene). The colour of both remaining unknowns does not completely disappear, but cyclohexane should react more than t-butylbenzene so 2 must be cyclohexane and 5 t-butylbenzene.