ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

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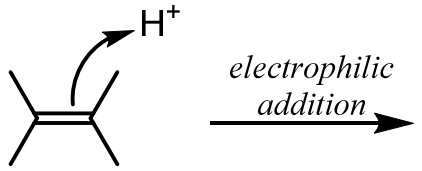
Lesson IV.7. Electrophilic Aromatic Substitution I: Friedel-Crafts Alkylation and Acylation

A powerful electrophile is needed to react with benzene

We have seen that C=C bonds can undergo electrophilic addition with electrophiles to form a carbocation:



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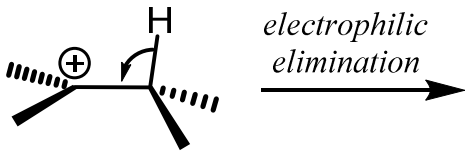
We have also seen electrophilic elimination of a proton from a carbocation to form a C=C bond:



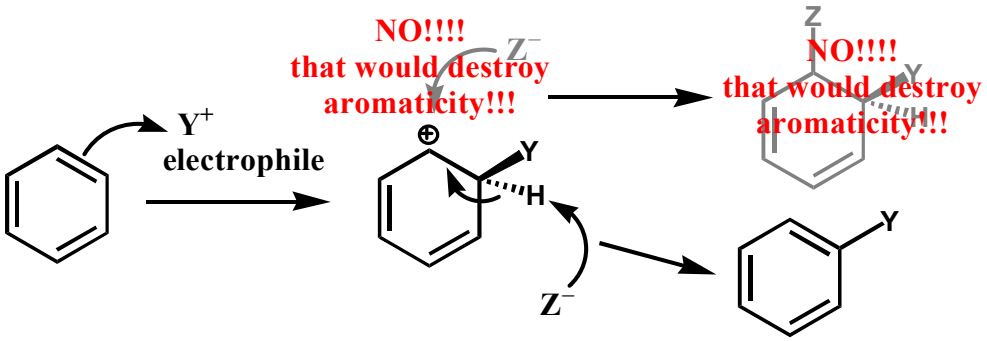
B

Notes

Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

Reactivity of C=C bonds in benzene

For C=C bonds in an arene, a better electrophile is needed than those that do electrophilic addition to isolated C=C bonds. Arenes also do not readily undergo addition reactions like isolated alkenes because this would break the aromaticity:



Instead, arenes undergo **electrophilic aromatic substitution (EAS):**

A

Notes

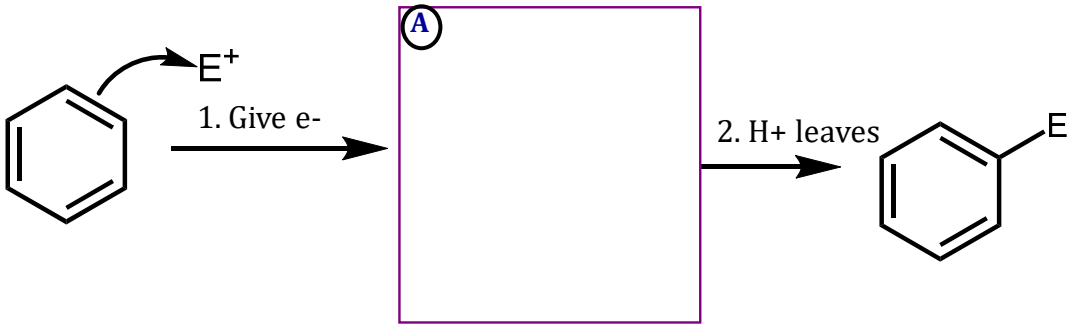
Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

Electrophilic Aromatic Substitution

You will learn many electrophilic aromatic substitution reactions;

They all use the same mechanism!

1. Electrophilic addition of the electrophile to the arene (makes a carbocation)
2. Electrophilic elimination of H^+ (yields the aromatic compound with the electrophile on it):



The following pages show specific examples. The only really unique thing is that a different **ELECTROPHILE** is involved in each case, and the reactants you use lead to formation of these electrophiles in different ways…

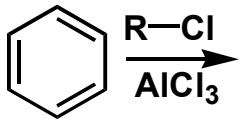
Notes

Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

Friedel-Crafts Alkylation

The first reaction is called **Friedel-Crafts Alkylation**:

I. The reaction



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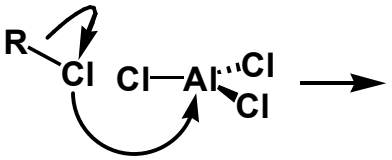
II. How is the electrophile generated?



B

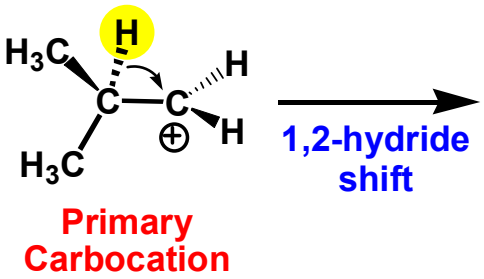
III. The Mechanism:

Notes

Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

Carbocation rearrangement

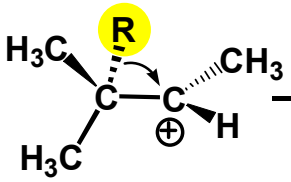
When looking at any reaction in which a carbocation intermediate is involved, you must be wary of carbocation rearrangement:



Primary Carbocation

1,2-hydride shift

A



Secondary Carbocation

1,2-alkyl shift

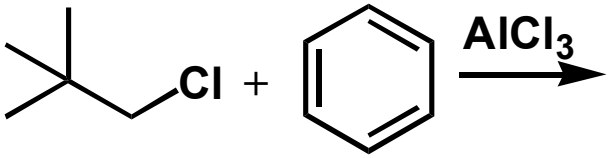
B

Notes

Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

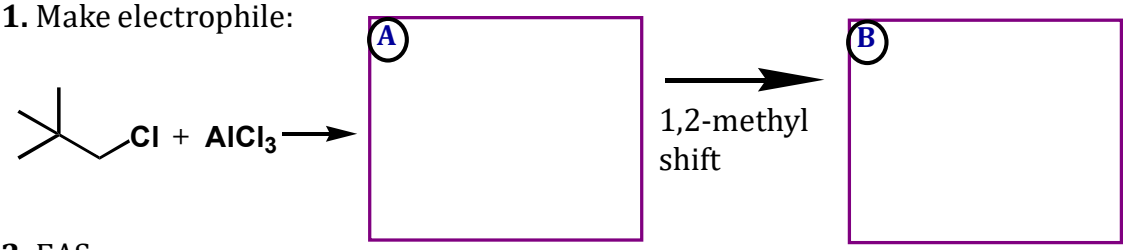
Friedel-Crafts Alkylation

Give the major product of the following reaction:



To solve, go through the mechanism:

1. Make electrophile:



2. EAS:

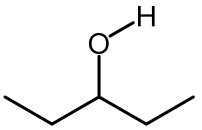
Notes

Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

Carbocation generation – three ways

The carbocation for use as the electrophile in the Friedel-Crafts alkylation can also be generated by one of the other ways that we already know:

1) Alcohol in the presence of acid



H_2SO_4 →

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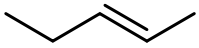
2) Alkene in the presence of acid



H_2SO_4 →

B

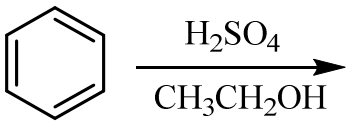
Notes

Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

Friedel-Crafts Alkylation

So, all three of these reactions are examples of Friedel-Crafts alkylation, just using different ways to make the carbocation needed as the electrophile:

1) Carbocation is from an Alcohol in the presence of Sulfuric Acid



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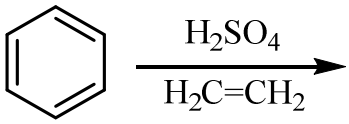
2) Carbocation is from an Alkene in the presence of Acid



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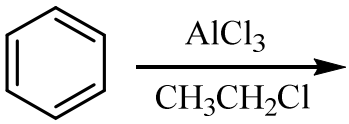
3) Carbocation is from Alkyl chloride in the presence of $AlCl_3$



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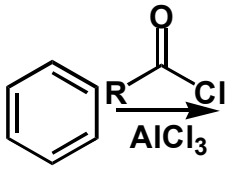
Notes

Lesson IV.7. EAS I: Friedel-Crafts Alkylation and Acylation

Friedel-Crafts Acylation

Friedel-Crafts acylation is another example of EAS. An acyl cation cannot rearrange, so the process is simpler than when a carbocation is involved:

I. The reaction



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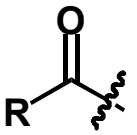

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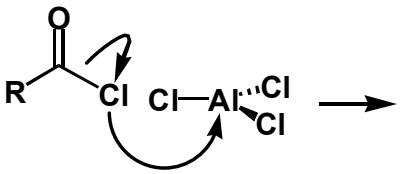
II. How is the electrophile generated?



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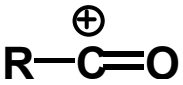

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III. The Mechanism:

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