

Organic Electronic Materials

Exercise 5

1. In the reaction mechanism (catalytic cycle) of the Suzuki-Miyaura coupling, the base plays a crucial role in the activation of the boronic acid/ester. Explain briefly the reason of its reactivity with the boron derivatives.
2. How is the degree of polymerization related to the stoichiometric ratio r and the functional group conversion x_p ? Describe with the help of a graph the implications and the consequences involved in a polymerization process. Besides these parameters, what other factors do you need to take care of in order to obtain high molecular weight conjugated polymers?
3. Why is it possible to polymerize thiophenes but not benzenes electrochemically? Describe the mechanism of the electrochemical polymerization of thiophene, and draw all the different defect structures resulting from this process! Which of these defects would not be expected in the electropolymerization of 3,4-ethylenedioxythiophene (EDOT)?
4. Describe the mechanism of the Kumada coupling using $\text{Ni}(\text{bipy})\text{Cl}_2$ as the catalyst! How is the catalyst initially activated? What is formed as a side product of the activation reaction? Describe the synthesis of α,ω -dihexyl-sexithiophene from two different bithiophene derivatives as the starting materials via the Kumada coupling (just give the two starting materials, no mechanism required)!
5. Describe the synthesis of α,ω -dihexyl-quaterthiophene from one bithiophene derivative via the Yamamoto protocol (net reaction, no mechanism required)! Why do you need stoichiometric amounts of the Ni reagent in this case?
6. Describe the synthesis of α,ω -dibutyl-quinquethiophene from two different (oligo)thiophene derivatives via the Stille protocol (net reaction, no mechanism required)! Why would you avoid this route?

Reading suggestions:

Organic Chemistry, Clayden, Greeves & Warren 2012 – Chapter 48 – Organometallic Chemistry

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Exercise 6

1. Draw the complete catalytic cycle of the Mizoroki-Heck cross-coupling. This cross-coupling is another example where a base plays a crucial role in the catalytic cycle. Describe the differences between the function of the base in the Suzuki-Miyaura and in the Mizoroki-Heck cross-coupling reactions.
2. In the case of the McCullough route, the employed Kumada polycondensation has two particularities. Firstly, what is the result (in terms of the product structure) of the activation of the catalyst? Secondly, what are the consequences of the formation of the so-called *associated pair*? How would you imagine that this allows you to control (meaning: tailor) the molecular weight of the resulting P3HT?
3. Describe the synthesis of pentacene and bis(ethynyl)pentacene, showing the starting materials and key intermediates (no mechanism). What is the advantage of introducing the ethynyl groups?
4. Polycyclic aromatic hydrocarbons (PAHs) such as rubrene and hexabenzocoronene are commonly synthesized using Diels-Alder pericyclic cycloaddition. Which two types of functionalities react in a Diels-Alder cycloaddition? Explain, with the help of molecular orbitals, how these species interact with each other to form the desired final product.
5. Perylene anhydride has two distinctive functionalization sites. What is the effect of the functionalization of these two sites? What are the reactions commonly performed for their functionalization?
6. Although porphyrin and phthalocyanine are both tetrapyrroles, their synthesis differs significantly. Why is a metal center necessary in the synthesis of the phthalocyanines but not the porphyrins?
7. The functionalization of fullerene with the Wudl route typically leads to two PCBM isomers. What is the reason for the formation of these two isomers? What is the structural difference between the two products? What type of chemical species actually reacts with the fullerene? Draw the synthetic scheme for the preparation of this species.

Reading suggestions:

Organic Chemistry, Clayden, Greeves & Warren 2012