New variants of the Friedel-Crafts/Bradsher cyclisation reaction in the synthesis of (hetero)acenes

Emilia Kowalska

Supervisor: Prof. dr hab. Piotr Bałczewski

Co-supervisor: dr Joanna Skalik

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Chemistry, Laboratory of Synthesis of Functional Materials, Sienkiewicza 112, 90-363 Łódź

Abstract:

The aim of research in my doctoral dissertation is to develop and improve three, new variants of the Friedel-Crafts/Bradsher cyclization reaction. The incentive to undertake the research on these modifications was the cyclization reaction of *ortho*-acetalodiarylomethyl ethers, carried out under acidic conditions (1M HCl/MeOH/rt to reflux), to give acenes and heteroacenes of potential application in optoelectronics. This reaction was developed in our laboratory several years ago under the name of "oxygen version". Current modifications include:

I Application of unconventional energy source, such as ultrasounds and 6.8 M HCl_{aq}/CH_3CN/r.t. in the **modified Friedel-Crafts/Bradsher** cyclization reaction of *ortho*-acetaldiarylmethyl ethers to (hetero)acenes containing OR substituents at the newly formed benzene ring, as one of the first uses of ultrasounds in the aromatic, electrophilic cylisation reactions of type S_EAr. The use of ultrasounds allowed not only to receive cyclic products in good to excellent yields as well as to decrease long reaction times from minutes to a few seconds at room temperature.

II Application of ultrasounds/6.5 M HCl_{aq}/acetone/rt in the **original Bradsher** cyclisation reaction of *ortho*-formyl diarylmethane to give (hetero)acenes without substituents at the newly formed benzene ring. The original Bradsher cyclization reaction requires drastic reaction conditions, such as extremely high temperatures, high concentrations of inorganic acids and use of sealed tubes. The proposed modification allowed using much milder reaction conditions i.e. room temperature and water as a reaction medium.

III Thio-modification of the Friedel-Craft/Bradsher cyclization reaction of *ortho*-dithioacetaldiarylmethyl thioethers ($FeCl_3$/KI/EtOH/reflux) to (hetero)acenes containing SR substituents at the newly formed benzene ring and subsequent **oxidation of sulfur atom** in obtained sulfenylated acenes to the corresponding sulfoxides and sulfones.

The obtained acenes and heteroacenes constitute valuable compounds which may be regarded as organic optoelectronic materials that can not be synthesized by known literature methods.

Keyword: Friedel-Crafts reaction, Bradsher reaction, optoelectronics, (hetero)acenes, ultrasounds