

Synthesis of Fluorinated Rubrene

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Introduction

The use of organic semiconductors combines the values of plastic, it can be easily shaped, with that of semiconductors which are the basis of numerous electronics. Organic semiconductors can also be made smaller than current metal conductors, which can aid in the progressive shrinking of circuits within MP3 players, laptops and the like.

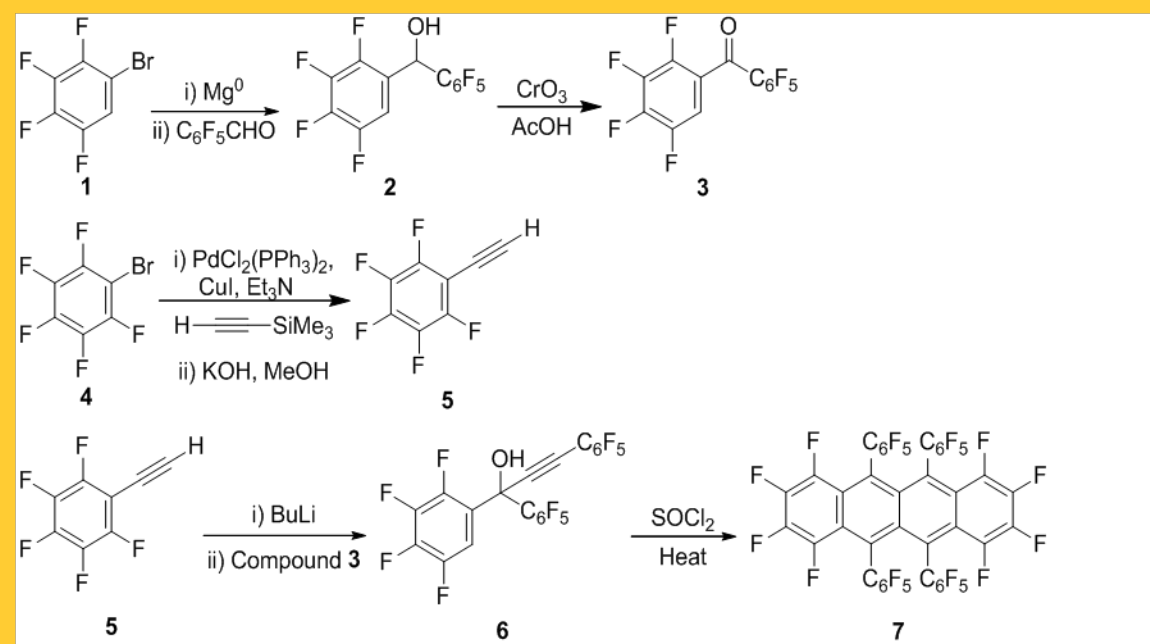
This research focused on the synthesis of a variation of the compound rubrene, which has been used as an organic semiconductor in organic light-emitting diodes (OLEDs). Ideally a semiconductor involving rubrene (a p-type compound) would have a companion molecule of similar shape to help carry the current (as in an n-type compound). It has been demonstrated previously that the replacement of the hydrogen atoms of a p-type organic semiconductor with fluorine atoms generates the corresponding n-type.¹ Due to the similarity in size of the fluorine and hydrogen atom, the two compounds are likely to form similar crystals as well, which would give us similar physical properties in the conductor sought after.

Methods

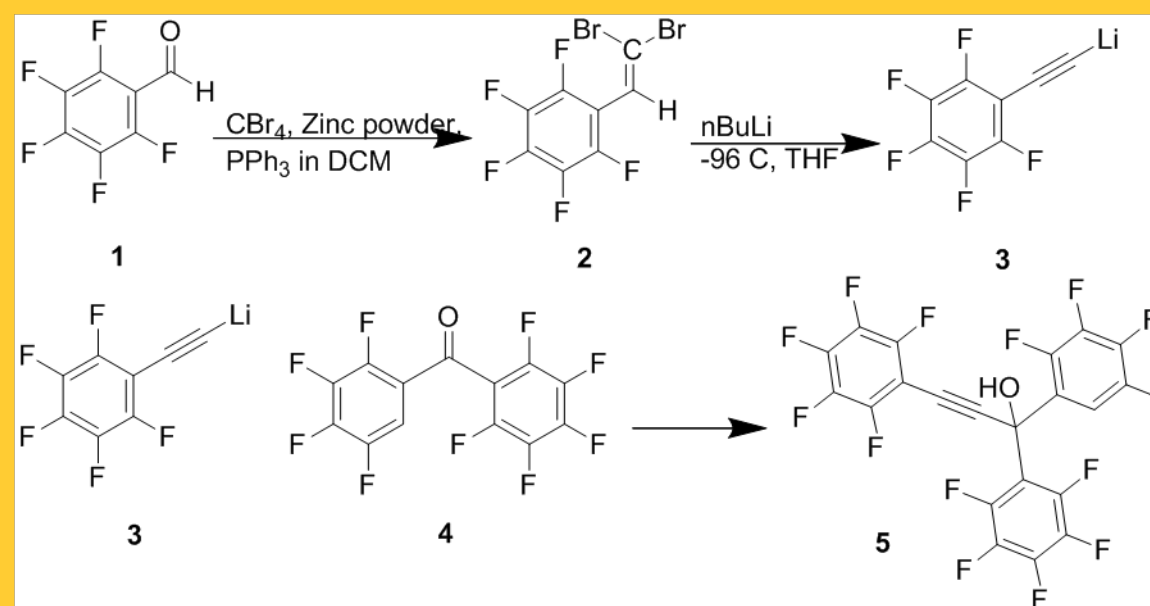
The initial scheme for synthesis of the desired compound was through a five step synthesis, beginning with pentafluorobromobenzene and 1-bromo-2,3,4,5-tetrafluorobenzene, compounds 1 and 4 in scheme 1. The first steps were performed as previously published, which include a Grignard reaction on the 1-bromo-2,3,4,5-tetrafluorobenzene² and a Sonogashira Coupling with the pentafluorobromobenzene³. Similar syntheses for the final steps (5→6, 6→7) had been reported and it was anticipated that the devised route would prove successful. Compounds 3 and 5 would be connected through a metalation with butyl-lithium followed by a carbonyl addition^{4,5}. A halogenation of the resulting alcohol with thionyl chloride followed by heating would result in the target molecule, compound 7.

The art of chemistry often involves many trials and failures prior to success, so it was likely that variations to the proposed scheme would need to be prepared. These failures led to the developments of scheme 2 and 3, which include Corey-Fuch reactions.

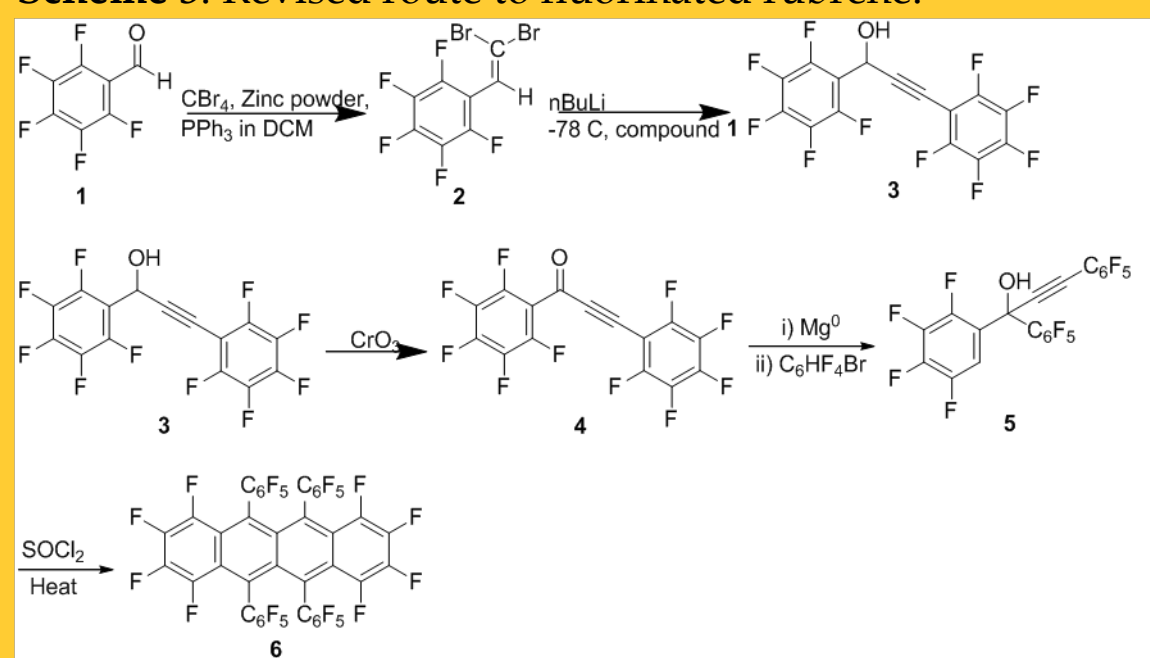
Scheme 1. Initial reaction route to fluorinated rubrene.



Scheme 2. Revised route to fluorinated rubrene.



Scheme 3. Revised route to fluorinated rubrene.



Results

The initial reaction scheme was successful for the creation of compound 2 with a 93% yield and then compound 3 with a 95% yield, appearing as clear, needle-like crystals. Compound 5 was also synthesized as proved by nuclear magnetic spectroscopy, however it could not be isolated in large enough amounts for the subsequent step.

After the development of scheme 2, the synthesis of the dibromoolefin, compound 2, was accomplished with a 75% yield as pure crystals. Compound 3 was formed in situ as proved by thin layer chromatography, however the nucleophilic attack of compound 3 into the ketone proved to be unattainable. It was determined that the large diphenyl-ketone was simply too hindered to allow attack by the phenyl-containing electrophile.

With the development of scheme 3, compound 2 from scheme 2 was used to synthesis a smaller electrophile. The coupling by n-butyl lithium gave compound 3 with a 45% yield as a clear liquid. Unfortunately preliminary efforts to oxidize the alcohol of compound 3 did not give the desired compound. Attempts with a variety of other oxidizing agents are underway, including IBX and magnesium oxide.

Conclusion

While a complete route to the total synthesis of fluorinated rubrene remains elusive, there is much hope with the new reaction scheme. It is likely that following the oxidation of the diphenyl ketone, the next steps will proceed without failure. Considering the growing use of organic semiconductors in the electronic world today, the continued effort applied to this synthesis is definitely worthwhile.

References

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