Synthesis and Cationic Rearrangement of Polynaphthyls

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Introduction

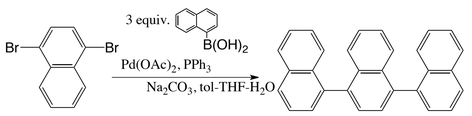
Our research group is studying the superacid-catalyzed rearrangement of arenes.[1] Both group migrations and skeletal rearrangements have been observed. 1,1-binaphthyl rearranges rapidly to 2,2-binaphthyl in the presence of catalytic trifluoromethane sulfonic acid (TfOH; pKa = ~-15).[2]

Goals of the Research

The goal of this thesis was to discover the products that would result from an acid catalyzed rearrangement of ternaphthalene and tetranaphthalene, which are a homologue of binaphthyl.

Results and Discussion - Synthesis of the polynaphthalenes

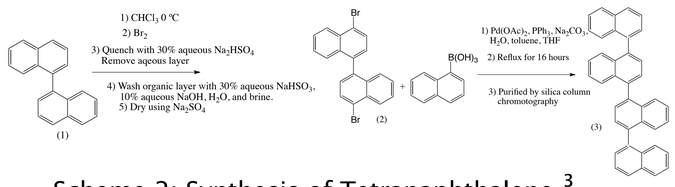
Ternaphthalene - The synthesis of ternaphthalene was preformed via Suzuki coupling using 1,4-dibromonaphthalene.



Scheme 1: Synthesis of Ternaphthalene [3]

- Yield 0.858 grams (85.2 %)
- Melting point 189-191 ºC

Tetranaphthalene - This was synthesised through the dibromination of 1,1-binaphthyl and Suzuki coupling of 4,4-dibromo-1,1-binaphthyl.



Scheme 2: Synthesis of Tetranaphthalene [3]

- Total yield 0.400 grams
- Melting point 174-177 ºC

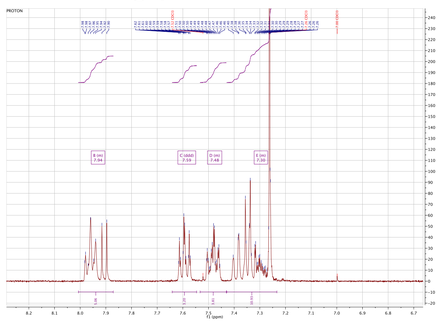


Figure 1. NMR spectrum of ternaphthalene ^{H} NMR (400 MHz, CDCl3) ς = 7.94 (m, 4H), 7.59 (m, 12H), 7.48 (m, 2H), 7,30(m, 2H).

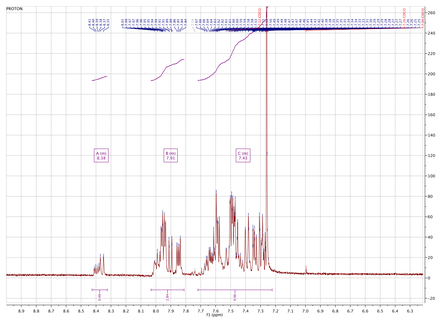
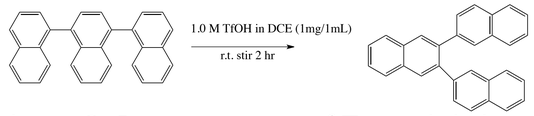


Figure 2. NMR spectrum of tetranaphthalene ^{H} NMR (400 MHz, CDCl3) ς = 8.38 (m, 4H), 7.91 (m, 16H), 7.43 (m, 6H).

Results and Discussion - Acid-Catalzed Rearrangement

All rearrangements were done using 1.0 M trifluoromethanesulfonic acid (TfOH) in dichloromethane at a 1 mg /1 mL concentration.

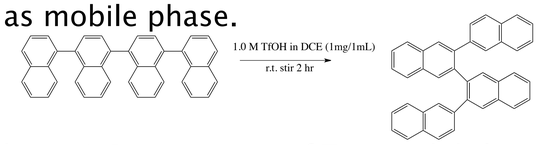
Ternaphthalene - This reaction was completed on both a 30 mg and 10 mg scale resulting in similar results for both syntheses. The product was purified using the Colmbiflash with hexanes as mobile phase.



Scheme 3: Rearrangement of Ternaphthyl

- Yield from the 30 mg synthesis was approximately 20 mg
- Yield from 10 mg synthesis was approximately the same

Tetranaphthalene - This reaction was done on a 10 mg scale. The product was purified on the Colmbiflash with hexanes as mobile phase.



Scheme 4: Rearrangment of Tetranaphthyl

- Yield from 10 mg synthesis was approximately the same amount as the starting 10 mg

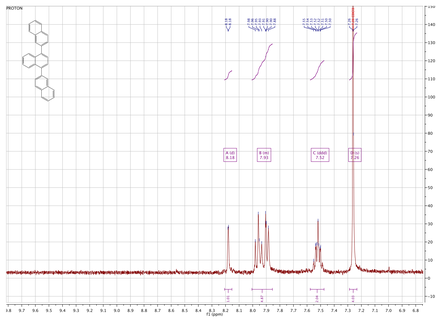


Figure 3. NMR spectrum of ternaphthalene rearrangement ^{H} NMR (400 MHz, CDCl3) ς = 8.18 (d), 7.93 (m), 7.52 (ddd).

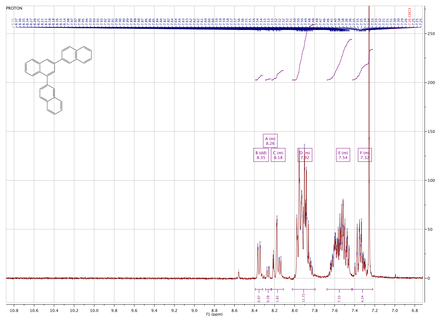


Figure 4. NMR spectrum of ternaphthalene rearrangement ^{H} NMR (400 MHz, CDCl3) ς = 8.35 (dd), 8.26 (m), 8.18 (m), 7.92 (m), 7.54 (m), 7.32 (m).

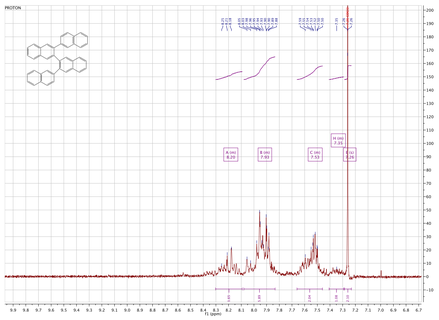


Figure 5. NMR spectrum of tetranaphthalene rearrangement ^{H} NMR (400 MHz, CDCl3) ς = 8.20 (m), 7.93 (m), 7.53 (m), 7.35 (m).

Future Work

For future work I would like to run tetranaphthalene rearrangement again as well as both the rearrangements under different conditions. I would like to run the rearrangements under reflux as well as in the microwave using the same amounts of starting materials and the same concentration of acid to see if any other products would be formed.

Conclusions

Ternaphthalene and Tetranaphthalene both undergo acid catalyzed rearrangement. These products are likely the results of 1,2-shifts based on spectral calculations but more work will be required to prove the structures.

References

(1)Ajaz, A.; McLaughlin, E.; Skraba, S. L.; Thamatam, R.; Johnson, R. P.; *J. Org. Chem.* **2012,** 77, 9487-9495.

(2)Skraba, S.; McLaughin, E.; Ajaz, A.; Johnson, R. *Scholl Reactions of Aryl Naphthalenes: Rearrangement Precedes Cyclization*, Not yet published.

(3)Guo, W.; Faggi, E.; Sebastian, R.; Pleixats, R.; Vallribera, A.; Shafir, A. *J. Org. Chem.* **2013**, 78, 8169-8175.

Acknowledgments

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