Cationic Rearrangements in Pyrene Derivatives

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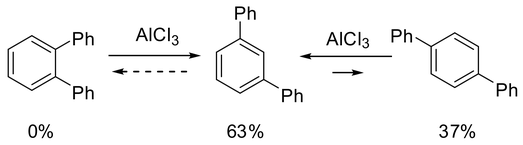
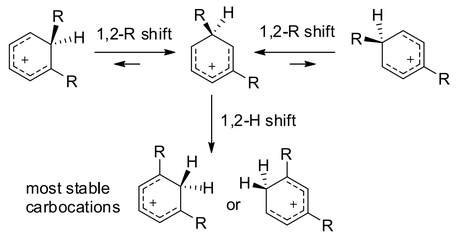
Introduction & History

After the discovery of the Friedel-Crafts alkylation, $AlCl_3$ catalyzed rearrangements were explored in the 1930's and 1940's due to the observation of *meta*-disubstituted products rather than the usual *ortho* + *para*.[1] Baddeley reported the first rearrangement of the *para* to *meta* isomer.[2] Allen and Pingert[3] studied the rearrangement of terphenyl isomers via Friedel-Crafts catalysis, and Olah and co-workers later reported the product distribution of the three isomers upon heating with $AlCl_3$, shown in **Scheme 1**.[4]



Scheme 1: Terphenyl rearrangement product distribution via Friedel-Crafts catalysis.[4]

In our group, the rearrangements of substituted arenes via Friedel-Crafts catalysis were studied, but inconsistent due to the hydroscopic nature of $AlCl_3$. To make the results more reliable, trifluormethanesulfonic acid (TfOH) in dichloromethane (DCE) was used as an alternative.[5] Mechanistic details of the terphenyl rearrangements were explained by Olah and co-workers, equating the preference for the *meta* isomer to the formation of the most stable carbocation, shown in **Scheme 2**.[6] This rearrangement occurs through an *ipso* arenium ion.[7]



Scheme 2: 1,2-R shifts and 1,2-H shifts of arenium ions.

Expected Results

In this project we explored the rearrangements of substituents on the highly conjugated pyrene. Electrophilic addition onto pyrene occurs most commonly on the 1 position, shown in **Scheme 3**. We wanted to show the rearrangement to the 2 position by acid catalysis.

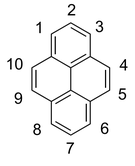
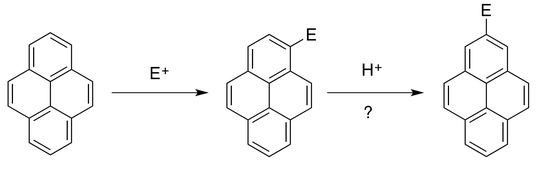


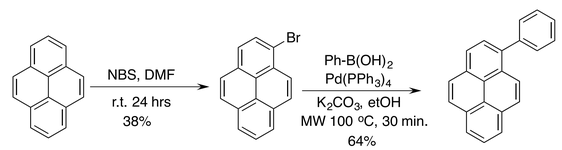
Figure 1: The numbering of pyrene.



Scheme 3: Electrophilic addiction to pyrene and expected acid-catalyzed rearrangement.

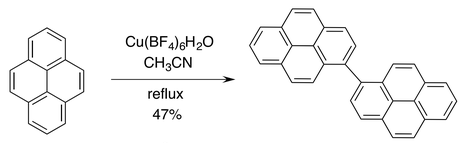
Synthesis

First, 1-bromopyrene was synthesized via electrophilic bromination. Once this was purified and characterized, Suzuki-Coupling was carried out using phenylboronic acid and a palladium (0) catalyst in the microwave reactor, shown in **Scheme 4**.



Scheme 4: Synthesis of 1-bromopyrene via electrophilic bromination and 1-phenylpyrene via Suzuki-coupling.[8]

1,1'-dipyrenyl was synthesized from copper (II) tetrafluoroborate in acetonitrile, then it was purified by refluxing in toluene, followed by a soxlet extraction in acetone. **Figure 2** shows the characterization of 1,1'-dipyrenyl. The yield was sufficient enough to move forward with rearrangement experiments at varying conditions.



Scheme 5: Synthesis of 1,1'-dipyrenyl.[9]

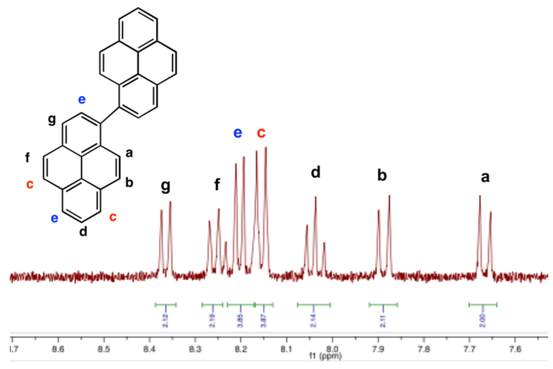


Figure 2: ^1H NMR of 1,1'-dipyrenyl.

Rearrangements

We carried out DFT computations (**Figure 3**), which suggested a high barrier that would require vigorous reaction conditions for the rearrangement of 1-phenylpyrene. Consequently, the first experiments using 1,1'-dipyrenyl were performed at 84 °C with 1.1 M TfOH. Unexpectedly, this gave predominantly pyrene. Milder reaction conditions appear to give the expected isomerization. Results are compiled in **Table 1**.

Table 1: 1,1'-dipyrenyl rearrangements at varying reaction conditions.

TfOH Conc.	Conditions	1,1'-dipyrenyl	1,2'-dipyrenyl	2,2'-dipyrenyl	pyrene
1.1 M	reflux 1 hr				100%
1.1 M	r.t. overnight	~50%			~50%
0.5 M	r.t. 2 hrs	~50%	~50%		
0.5 M	r.t. overnight	~70%		~30%	
0.5 M	r.t. ~60 hrs	minor		trace	major
0.5 M	reflux overnight			trace	major

Computational Studies

B3LYP/6-31G* computations support aryl migration followed by hydrogen atom migration to give a low energy carbocation. This supports the prediction of rearrangements in pyrene derivatives.

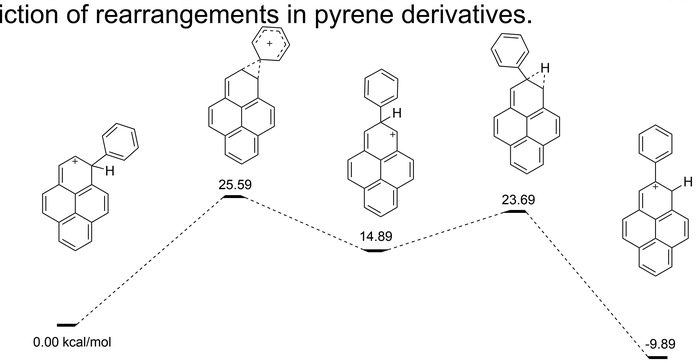
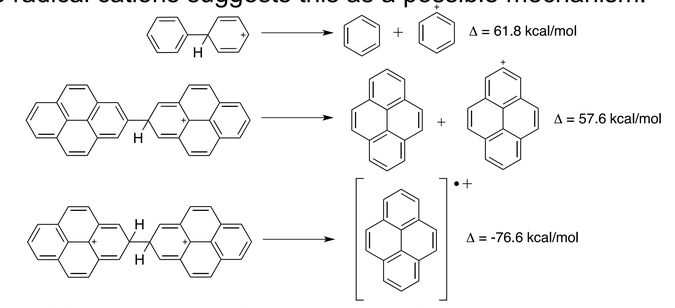


Figure 3: Energy diagram of 1-phenyl pyrene rearranging to 2-phenylpyrene using density functional theory, B3LYP/6-31G*.

To further understand why 2,2'-dipyrenyl would dissociate in acid catalysis, computations were carried out comparing the dissociation of the biphenyl cation, 2,2'-dipyrenyl cation, and 2,2'-dipyrenyl dication. The highly exothermic dissociation of the 2,2'-dipyrenyl dication to two pyrene radical cations suggests this as a possible mechanism.



Scheme 6: Biphenyl cation dissociation computation in comparison to 2,2'-dipyrenyl cation dissociation and 2,2'-dipyrenyl dication dissociation to the pyrene radical cation using density functional theory, B3LYP/6-31G*.

Conclusions

This work is still in progress. We have strong evidence for the expected rearrangements in bipyrene, but the products need to be isolated and completely characterized. Computations give a glimpse of reasoning into why 1,1'-dipyrenyl would dissociate into pyrene, but the results are still not definitive. Future work will include the rearrangement of 1-phenylpyrene and the isolation of 1,2'-dipyrenyl and 2,2'-dipyrenyl to confirm ^1H NMR results.

References

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Acknowledgements

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