**Introduction & History**

After the discovery of the Friedel-Crafts alkylation, AlCl₃ 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. Baddeley reported the first rearrangement of the para to meta isomer. Allen and Pingert 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 AlCl₃, shown in **Scheme 1**.

In our group, the rearrangements of substituted arenes via Friedel-Crafts catalysis were studied, but inconsistent due to the hydroscopic nature of AlCl₃. To make the results more reliable, trifluoromethanesulfonic acid (TfOH) in dichloromethane (DCE) was used as an alternative. 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**.

This rearrangement occurs through an ipso arenium ion.

**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.

**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’-dipryenyl 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**.

**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**.

**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.

**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’-dipryenyl 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'-dipryenyl and 2,2'-dipryenyl to confirm 1H NMR results.

**References**


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