Developing New Sustainable C-C Bond Forming Reactions

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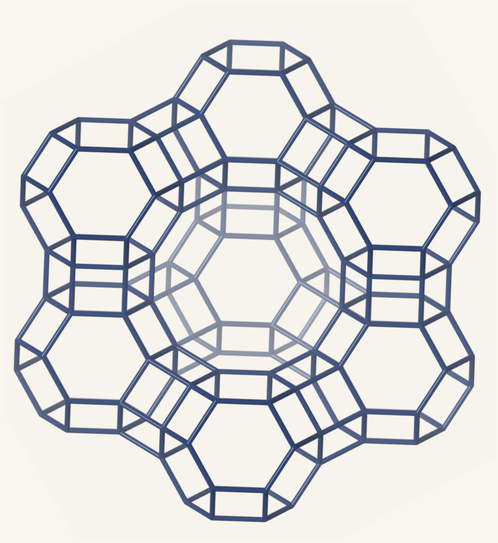
Background

The process of forming C-C bonds is vital in nearly all aspects of chemistry and make up the backbone of synthetic chemistry. A commonly practiced method to do this has been a class of reactions known as Freidel Crafts (FC) reactions. They, however, pose significant environmental concerns through their toxic and unsustainable reagents and catalysts. Finding alternative catalysts and reagents for such processes have become a very active area of research. One alternative is the Taylor group's[1] approach. This utilises a zeolite catalyst for a FC alkylation between mandelic acid and an aromatic reagent. These reagents are far less toxic and offer improved sustainability. The zeolite itself is far more sustainable, being composed of silicon, aluminium and oxygen – th most abundant elements on the planet!



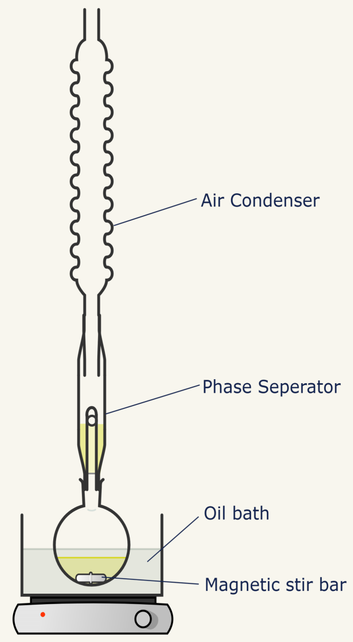
↑ The FAU zeolite used in the project [2].

Aims

- Determine the suitability of a FAU zeolite catalyst for the synthesis of diarylacetic acids from mandelic acid and a series of aromatic reagents
- Assess the suitability of the process developed by the Taylor group[1] for higher boiling point reagents
- Characterise the products produced in each of the reactions

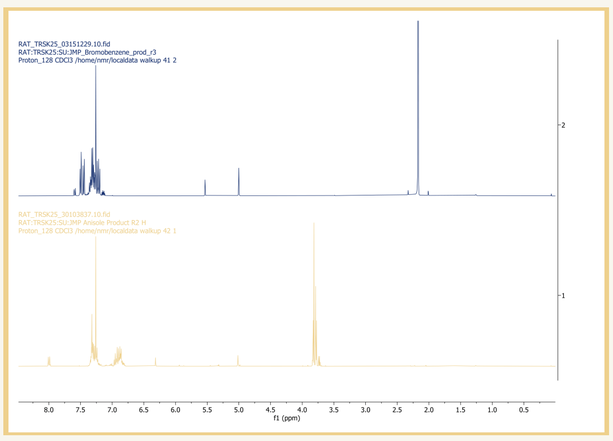
Methodology

- Mandelic acid, the aromatic reagent (in excess) and FAU zeolite were added to round bottom flask
- Phase condenser fitted to remove any water formed
- Mixture refluxed for ~22 hours and stirred throughout
- Resulting mixture was filtered and the voletile component removed on a rotary evaporator
- Samples for NMR spectroscopy were made up in CDCl3
- ^{1}H and ^{13}C NMR were performed and the results analysed



Results

Anisole + Bromobenzene



For both anisole and bromobenzene we found evidence that the desired diarylacetic acid products were formed!

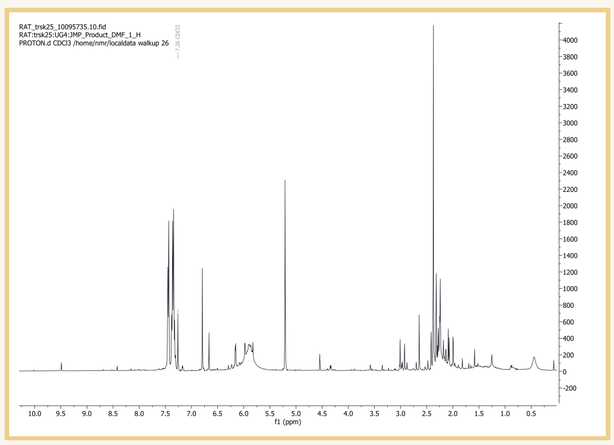
In both cases, there was a mixture of the ortho, meta and para isomers formed. Further work is required to determine the selectivity of the reaction.

In each case there was also some uncertainty in the product composition, expanded on in the report, so further separation would be useful to confirm these findings.

2,5-Dimethyl Furan

2,5-dimethyl furan unexpectedly did not react with the mandelic acid, rather it underwent a ring opening reaction to form 3-hexene-2,5-dione.

We believe that this went on to react with itself and the reagent to form a complex mixture of oligomers. Further separation would be required to identify the makeup of the product mixture, as a result of the very "busy" ^{1}H NMR.⟶



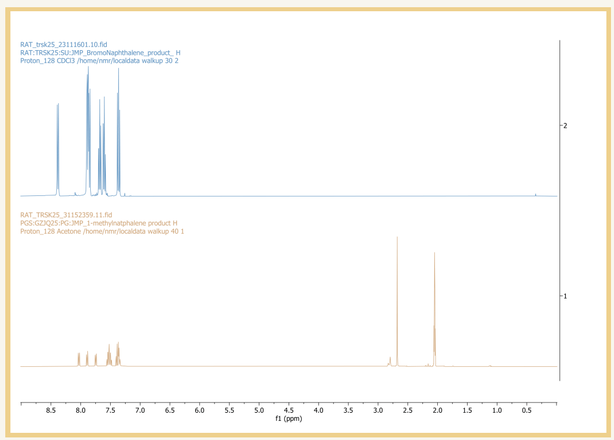
+ O_2 ⟶ ⟵ The observed reaction of 2,5-dimethyl furan to form 3-hexene-2,5-dione

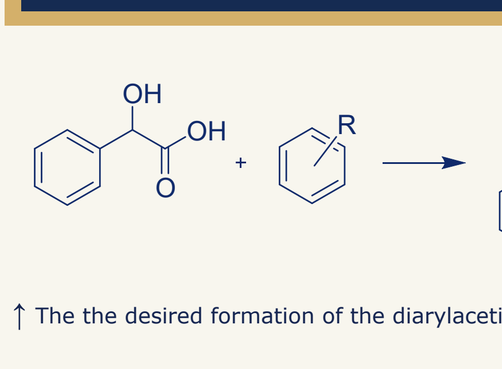
1-Bromonaphthalene + 1-Methylnaphthalene

We found the current procedure unsuitable for either of the high boiling point naphthalene reagents.

This is a result of:
- The inability to heat to reflux
- Difficulty in removing the solvent

Both of these problems made identifying any products produced unachievable with the current experimental procedure.



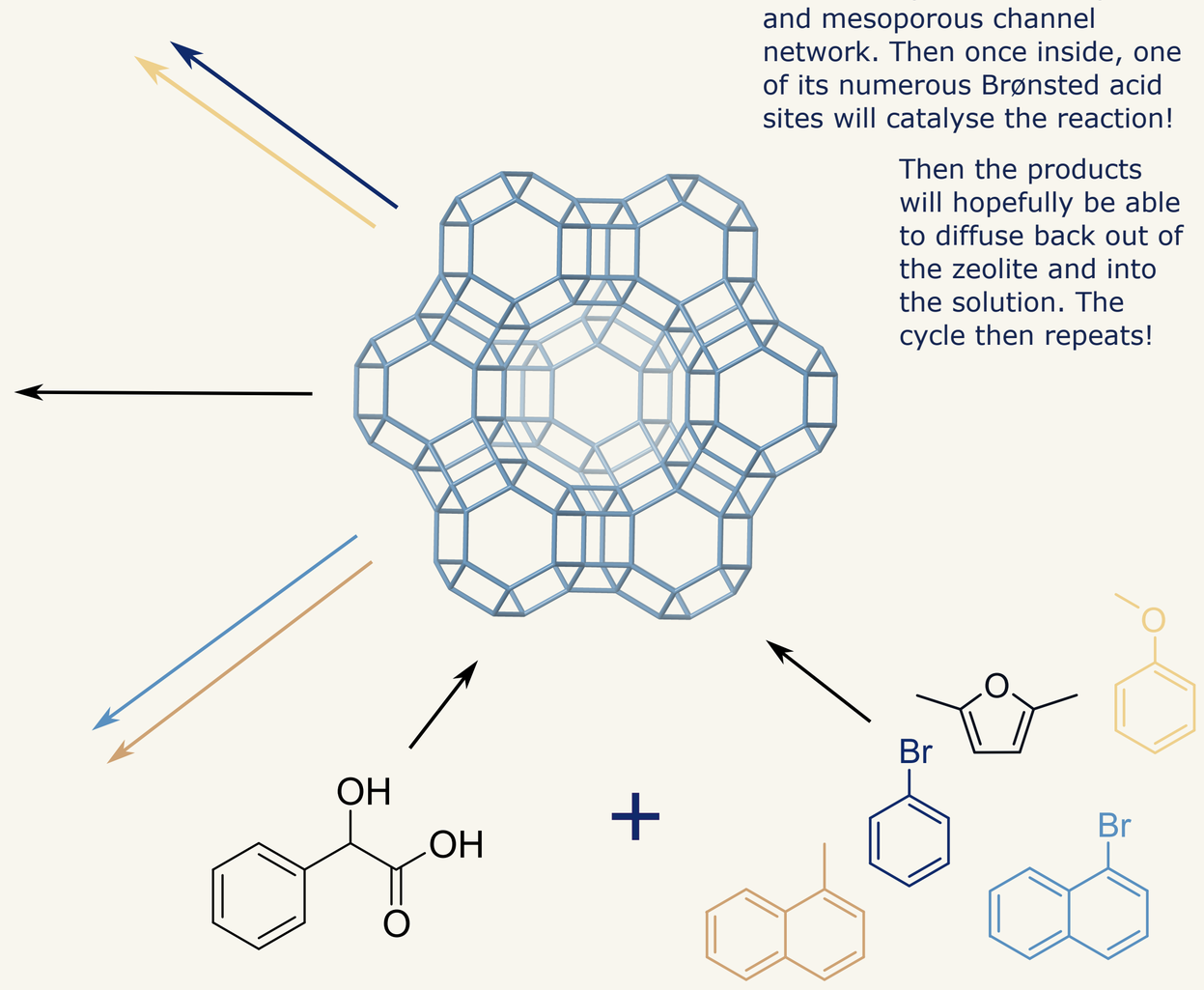


↑ The the desired formation of the diarylacetic acid product

Info!

Here the FAU zeolite will hopefully catalyses the reaction between the mandelic acid and the aromatic reagent. The reagents diffues into the zeolite's expansive microporous and mesoporous channel network. Then once inside, one of its numerous Brønsted acid sites will catalyse the reaction!

Then the products will hopefully be able to diffuse back out of the zeolite and into the solution. The cycle then repeats!



Future Work

Future work should focus on further separation and characterisation of the product mixture. Adaptation of the procedure for those higher boiling point compounds would also be beneficial, as we observed some product formation, suggesting that the larger naphthalene rings may be able to enter the zeolite pores. Finally, it would be interesting to probe the mechanism for the ring opening of the DMF to see if it is similar to previously reported mechanisms for ring openings outside a zeolite.

Full Paper!
References!

Acknowledgements

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