Towards Greener Fragrances Esterification Reactions With Ionic Liquids.

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Summary

Aliphatic esters with favourable fragrances have been produced using a green chemistry pathway involving a protic ionic liquid. An acidic ionic liquid has been successfully synthesised and used favourably as an alternative to mineral acids in esterification reactions. The ionic liquid can combine the roles of a catalyst and solvent. The ester product forms a separate phase from the ionic liquid which can easily be separated using a separating funnel and used for further reaction cycles promoting sustainability. The ionic liquid can be rejuvenated and used propitiously for further cycles.

Research Aims

- To synthesise Brønsted acidic ionic liquids from tertiary alkyl amines and sulfuric acid.
- Evaluate the effect of multiple cycles of esterification using the same ionic liquid catalyst.
- To investigate methods to recycle the ionic liquid catalyst.

Introduction

The esterification reaction traditionally was catalysed with an acidic catalyst such as sulfuric acid, due to its low price. However, difficulties with product separation, purification, miscibility with the reaction medium, a long reaction time and difficult reaction conditions demanded a greener alternative. Acids are also corrosive and generate large amounts of waste during the purification process. Brønsted acidic ionic liquids have been explored as an alternative to mineral acids in esterification reactions. Ionic liquids can be used as acidic catalysts and combine the roles of a catalyst and a solvent. Ionic liquids are also thermally stable and the product ester is immiscible with the ionic liquid and can easily be separated.

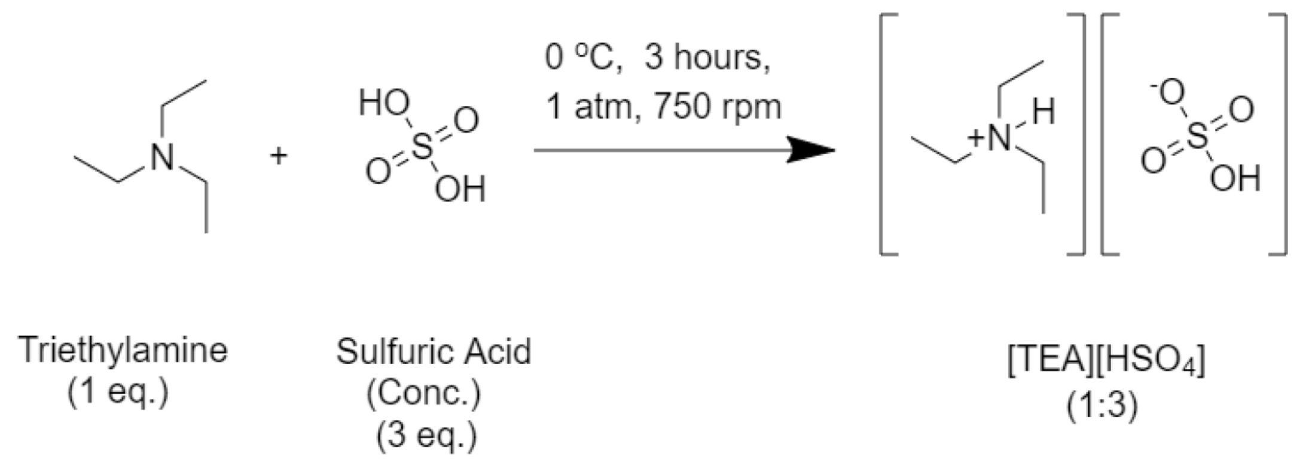
Esters are chemicals that can be used for the production of fuel additives, solvents, fragrances, and pharmaceuticals. They have a low toxicity and pleasant smell, making them very attractive for use as fragrances.

Experimental Method

Experimental Method For Production Of Protic Ionic Liquid

The ionic liquids were synthesised according to the literature[1] procedure. 1 mole equivalent of tertiary amine (triethylamine) was weighed into a 250ml round bottomed flask equipped with a stirring bar. The flask was placed in an ice bath and stirred at 1000 rpm. Concentrated sulfuric acid was added slowly dropwise with a dropping pipette. The required amount of sulfuric acid (1, 2, or 3 mol equivalents) was added slowly to the stirred amine. The mixture was left to stir and react (750 rpm, 3 hours, 25 °C, 1 atm). Figure 1. The apparatus was set up in a fume cupboard. The ionic liquid was distilled at 105 °C after 7 cycles to remove water impurity.

Figure 1

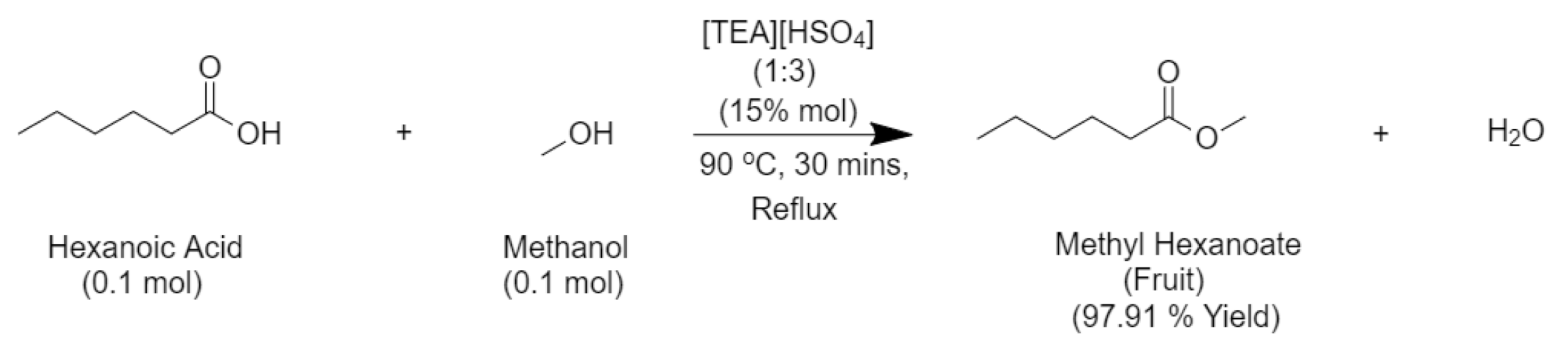


Experimental Method For Esterification

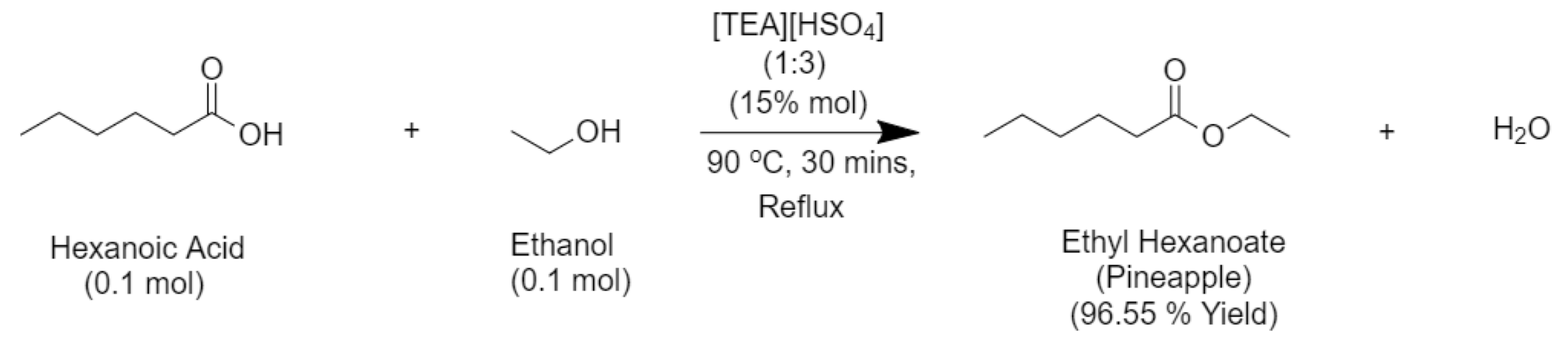
In a typical procedure, carboxylic acid (0.1 mol), ionic liquid (15% mol, 1:3) and alcohol (0.1 mol) were placed in a 100ml round bottomed flask, equipped with a magnetic stirring bar and reflux condenser. The flask was lowered into an oil bath and the mixture was refluxed and stirred vigorously (750 rpm, 30 mins reflux, at 90 °C). Figure 2. A biphasic system was formed, and the upper layer containing ester and excess of alcohol was decanted and analysed by IR and 1H NMR spectroscopy.

Figure 2

Methyl Hexanoate



Ethyl Hexanoate



References

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3. H. Zhang, F. Xu, X. Zhou, G. Zhang, C. Wang, A Brønsted acidic ionic liquid as an efficient and reusable catalyst system for esterification, Green Chem. 9 (2007) 1208–1211.
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Results

Ester	Cycle	% Yield of Ester
MH	1	98.27
MH	2	96.39
MH	3	86.16
MH	4	79.36
MH	5	76.16
MH	6	70.91
MH	7	67.28
MH	1A	80.86

Ester	Cycle	% Yield of Ester
EH	1	98.62
EH	2	95.45
EH	3	91.80
EH	4	78.34
EH	5	76.03
EH	6	74.16
EH	7	65.18
EH	1A	78.87

Figure 3

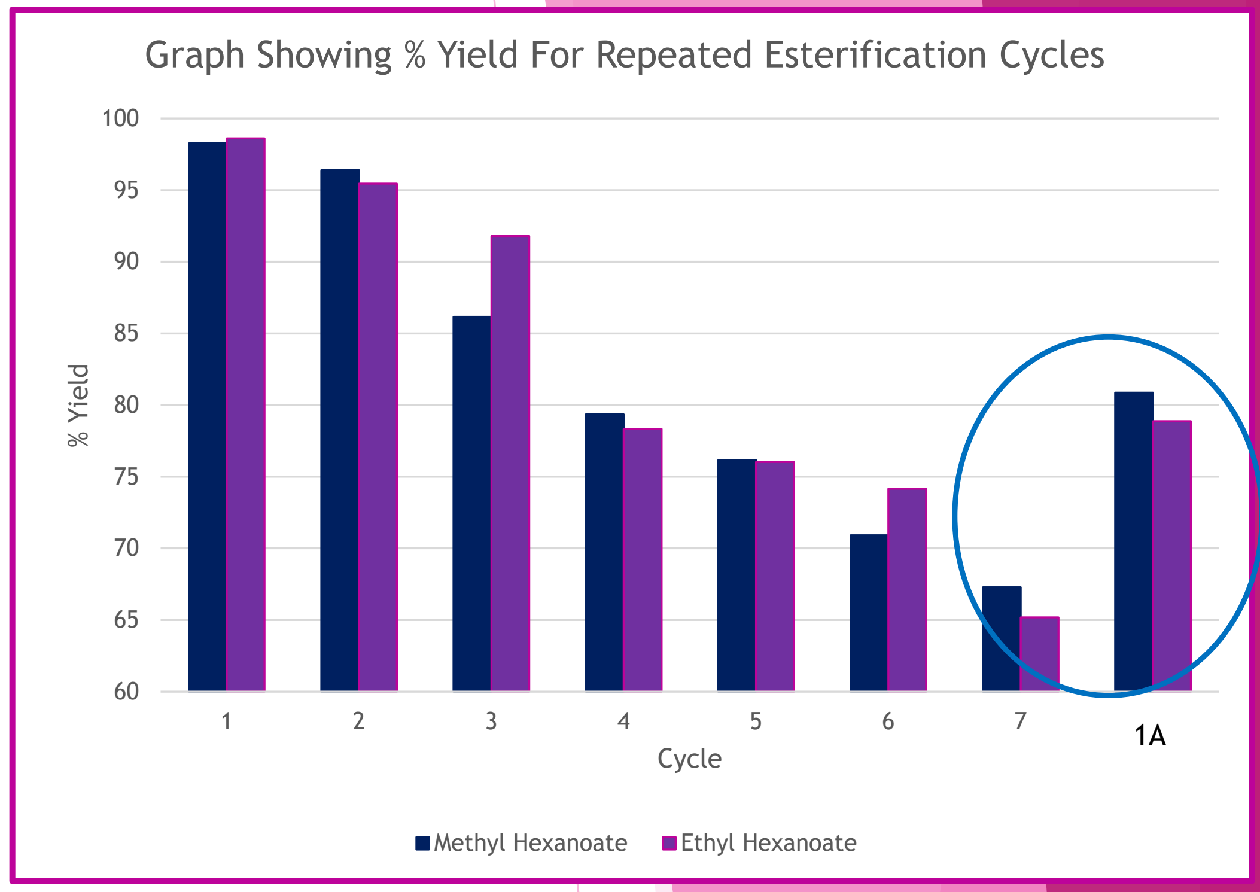


Figure 4a
Methyl hexanoate 1H NMR cycle 1A:

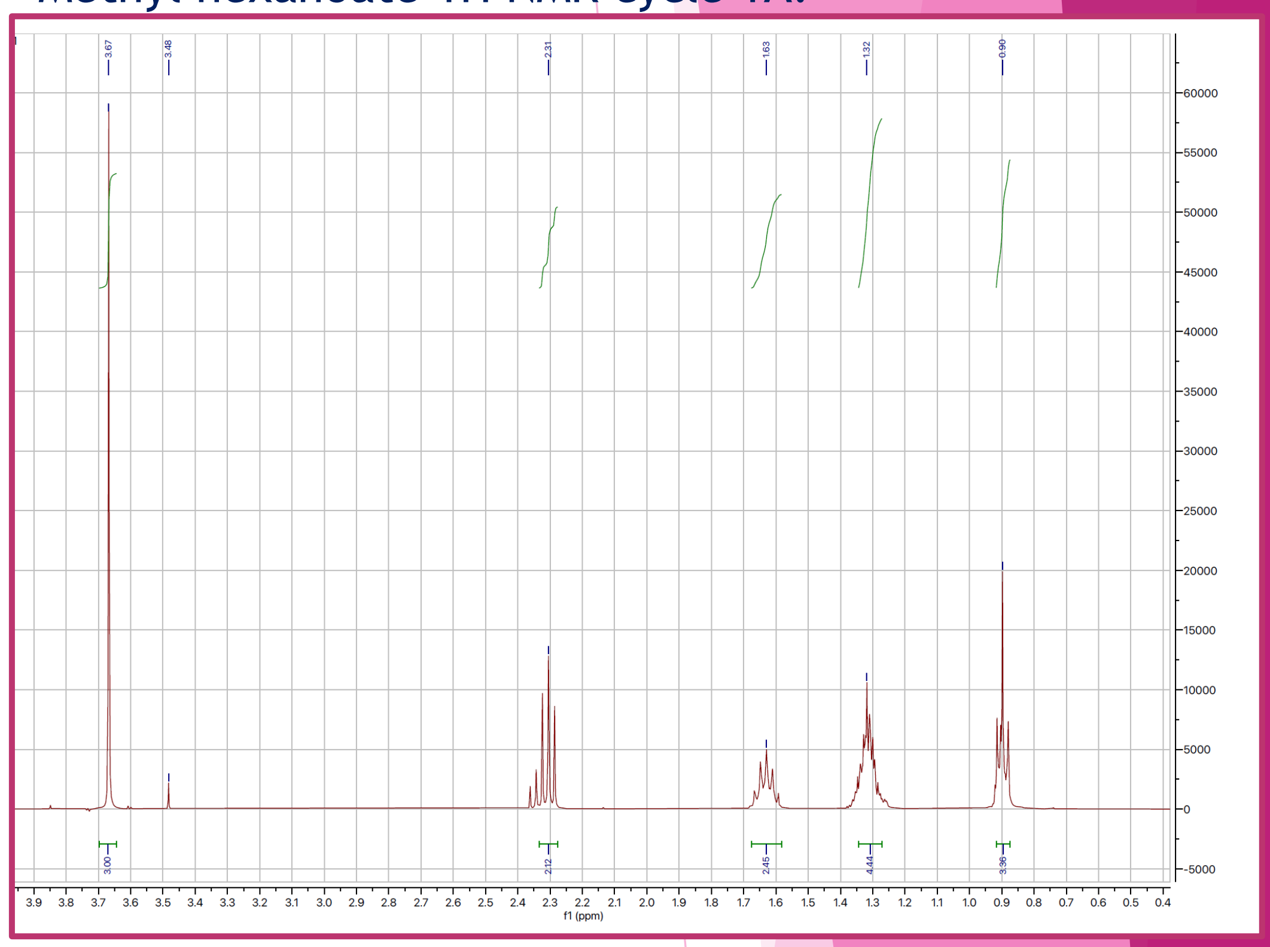


Figure 4b
Ethyl hexanoate 1H NMR cycle 1A:

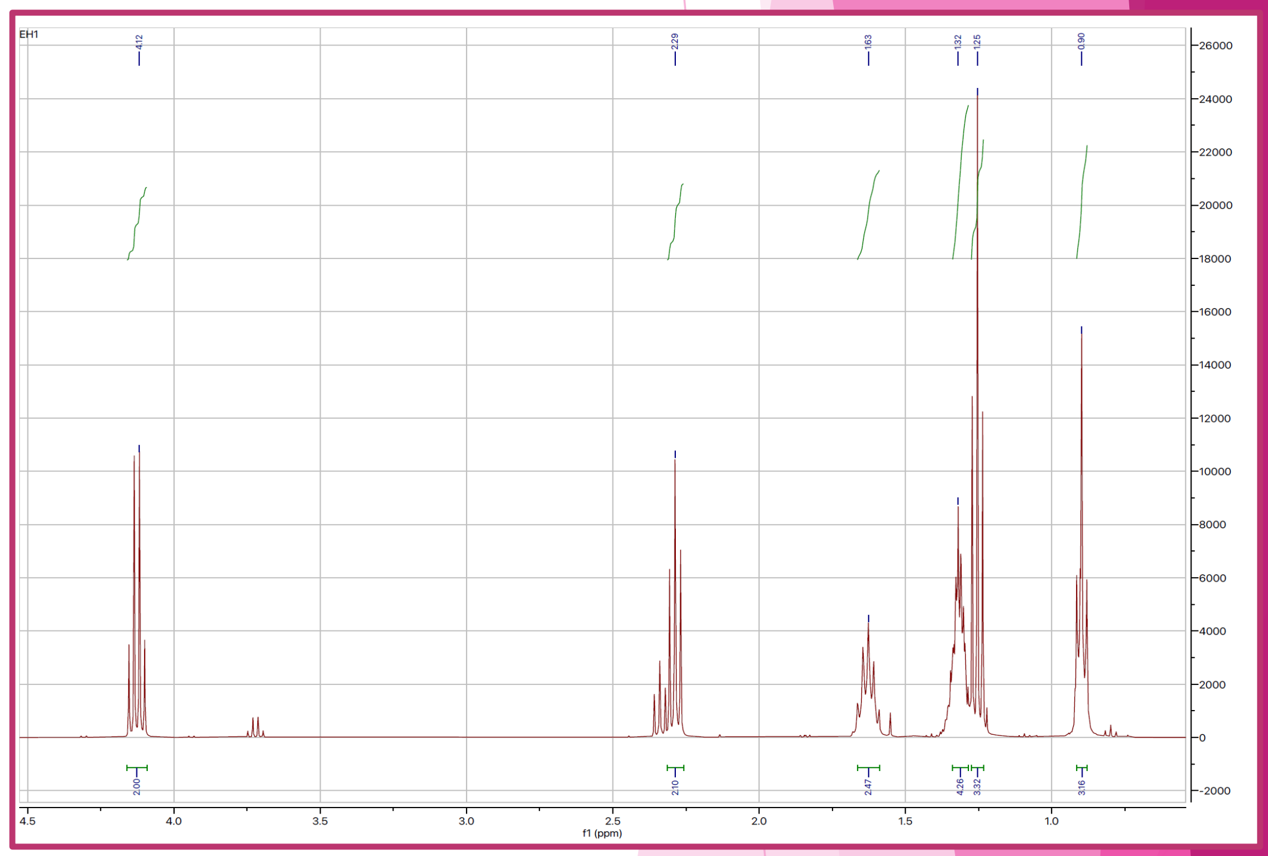
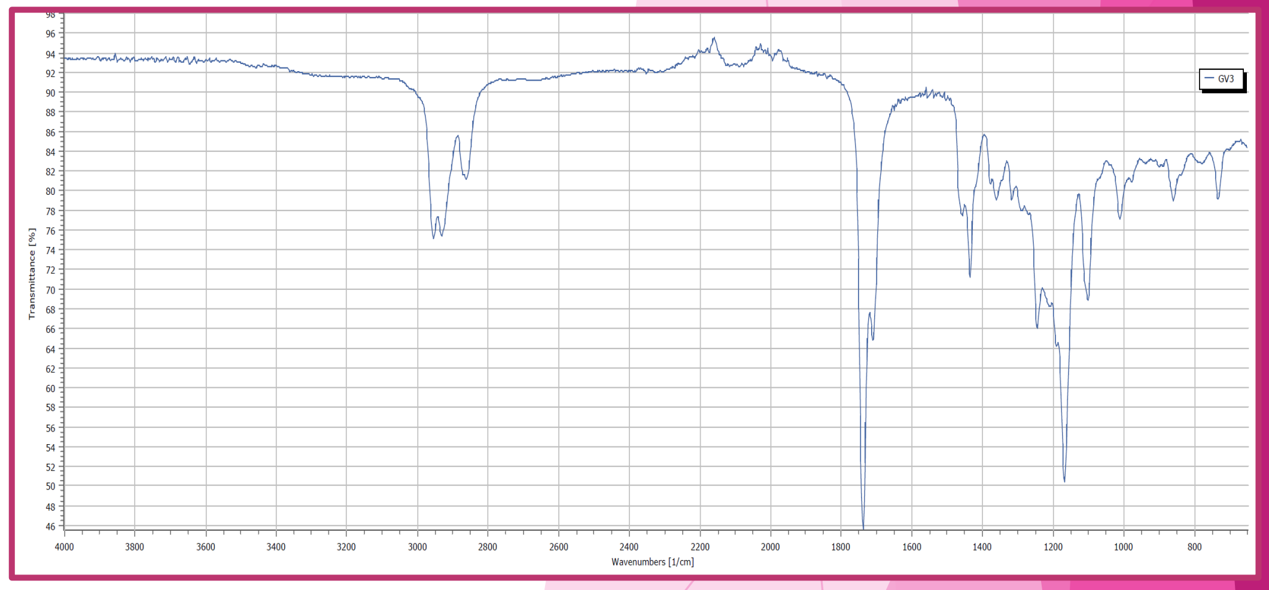


Figure 5
IR Spectra
Methyl hexanoate IR cycle 1A:



Analysis & Conclusions

The esters produced had favourable aromas and were liquids at room temperature. They could be used as diffusers in the fragrance industry with their fresh fruity smells.

Methyl hexanaote had a general fruity smell. Ethyl hexanaote had a more specific smell of pineapple. The esters were straightforward to synthesise, separate and analyse as all reagents and products were in the liquid phase. The product ester was in the upper organic layer with excess alcohol and the water produced went into the lower ionic liquid layer. The lower ionic liquid layer was run off using a separating funnel and used for several cycles with new portions of alcohol and acid. The yield of ester decreased with increased cycles, due to the water accumulating from the esterification reaction at each stage. After the water and excess alcohol was distilled from the ionic liquid the esterification yield increased. Figure 3.

A 1:1 ratio of ionic liquid was not used because it was a sticky solid at room temperature, this made experiment progress difficult. A 1:2 ratio of ionic liquid produced a lower initial yield compared to the 1:3 ratio of ionic liquid. Previous research which we built upon, used 1:3 ratio, this meant we could compare our data for reliability.

The NMR and IR spectra were relatively clean, hexanoic acid impurities increased as ester yield decreased. Figure 4. The IR spectra showed clear C-O, C=O and C-H peaks, Figure 5.

Future Work

1. Continue cycles after distillation to analyse changes in yield of ester.
2. To investigate 1:4 or 1:5 ratios of sulfuric acid in the protic ionic liquid.
3. To try and remove water from the ionic liquid using a less energy intensive option. This could be done using molecular sieves and/or drying agents e.g. calcium chloride.