Exploring the synthesis of maleanilic acids in bioderived, biodegradable solvents

Emily Fitzpatrick, Emily Rennells, and Dr. Eric Helms*
Dept. of Chemistry, SUNY Geneseo, Geneseo NY 14454

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Introduction

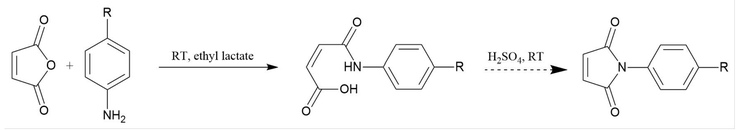

Figure 1: The general two-step reaction scheme for producing maleimides.

Objective: Our goal is to carry out a small-scale reaction using green solvents to achieve similar yields as established maleimide syntheses.

Maleimides have use industrially as building blocks of polymers. Many syntheses of maleimides from the literature use solvents like toluene, chlorobenzene, and DMF, which are not green solvents. In order to increase the greenness of our reactions, we try to replace our solvents with green solvents such as ethyl lactate and 2-methyl THF.

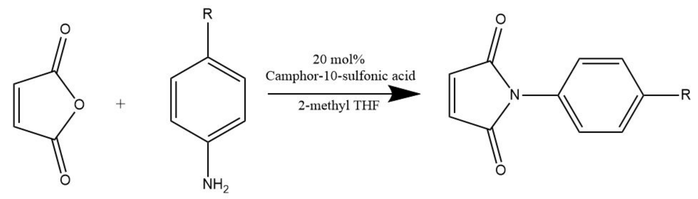

Figure 2: The one-step, catalyzed reaction mechanism used in this experiment.

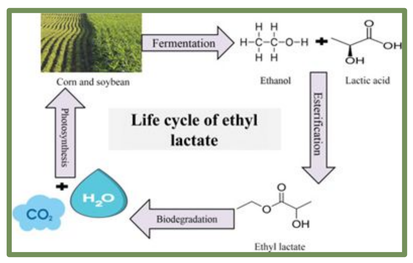

Figure 3. The life cycle of ethyl lactate, the green solvent used during the syntheses.

Experimental Procedure

1. 1 mmol of maleic anhydride and 1 mmol of substituted anilines were added to separate vials and dissolved in 1 mL of 2-methyl THF.
2. 20 mol% of camphor-10-sulfonic acid was dissolved in 1 mL of 2-methyl THF in a separate vial.
3. The maleic anhydride solution was pipetted into the aniline solution, then the catalyst was added.
4. The reaction was refluxed at 90 °C for 6 hours.
5. The product was purified using a trituration procedure that requires sodium bicarbonate.
6. The crude product was filtered and dried under vacuum.
7. NMR spectra were acquired in DMSO-d6 using a Varian MR-400.

IR Analysis

IR spectrum was analyzed for each of the maleamic acids versus the potential one-step reaction product. The one-step reaction maintained a carboxylic acid which is seen when comparing the acids IR spectrum. The heated reaction has the carboxylic acid present in the structure which means the heated reaction is not successful.

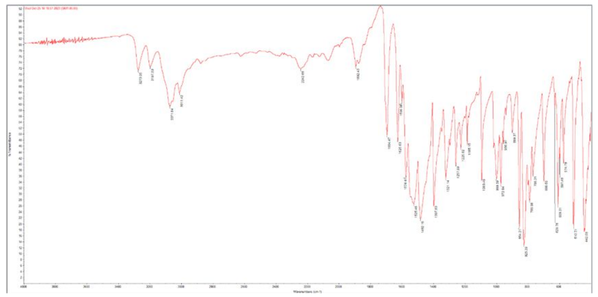

Figure 4. The IR spectrum for the intermediate made from 4-chloroaniline.

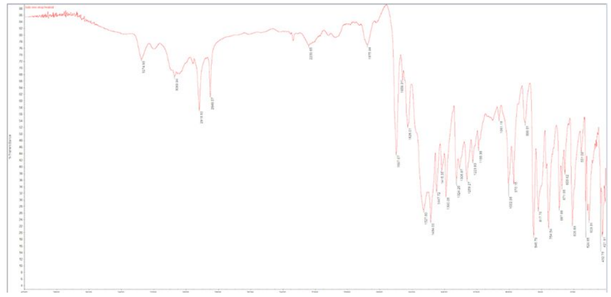

Figure 5. The IR spectrum for the intermediate acid made from 4-iodoaniline.

Computational Analysis

Table 1: Energy of the HOMO-LUMO gaps of some acids.

Para Substituent on Aniline Used	Chloro	Bromo	Methoxy	Iodo
E_{HOMO} (eV)	-8.79	-8.74	-7.72	-8.59
E_{LUMO} (eV)	-0.4	-0.41	-1.28	-0.41
$E_{HOMO-LUMO}$ (eV)	-8.39	-8.33	-6.44	-8.18

The calculations for the HOMO/LUMO gap were completed using Spartan Student. The bromo and methoxy compounds are similarly colored, but do not have similar HOMO/LUMO gap energies. This will require more complex computation to explain the reason behind the variety of colors observed.

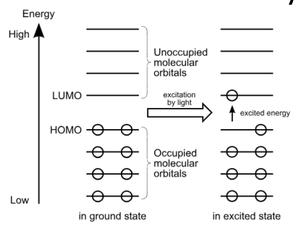

Figure 6: The size of the HOMO-LUMO gap can be used to predict the color that a compound would produce in solution.

Results and Discussion

Table 2: Percent yield and melting point data for acids

Aniline Used	Percent Yield (%)	Melting Point (SciFinder) (°C)	Melting Point (°C) Experimental
4-chloroaniline	86	199	188-190
4-bromoaniline	81.9	197-199	185-187
p -anisidine	89.6	212	181-182
4-ethynylaniline	N/A	no data	N/A
4-iodoaniline	76	"	178-183
4-methylsulfonyl anililine	67	"	174-180
4-trifluoromethyl aniline	57	"	170-175
4-fluoroaniline	67.5	216-218	206-209
meta-fluoroaniline	66.9	N/A	195-197.3

As shown in the table, many of the acids do not have reported melting points. Most melting points are below the literature value and have a wider range, suggesting impurities. The MelTemp will be recalibrated next semester and new data will be obtained.

Conclusions

NMR, IR, UV-Vis, melting point, and percent yields for the intermediates are have been collected. The two-step reaction successfully produced the intermediate acids. Our current work has been finding a procedure that completes the synthesis in one step. The procedure using the 2-methyl THF and trituration appears to be promising and the collection of the NMR and IR of these molecules will determine the future possibilities for this reaction.

Future Work

- Running NMR and MS for our molecules
- Determining the extinction coefficient for all products.
- New catalysts for the one-step reaction.
- Meta/ortho compounds.
- DFT Calculations to explain colorful products.

References

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