Fisher Esterification Using Solar Irradiation

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Introduction

- Much research has been focused on developing new methods of synthesizing chemicals in a green, environmentally friendly manner. The majority of green synthesis research is centered on the development of methods to synthesize compounds safely in the environment.
- One aspect of a completely green synthesis that researchers are forgetting is the use of electricity as a heat source to drive the chemical reactions to completion.
- A solution to this problem has recently come about with the implement of solar ovens (simple parabolic reflectors) as heating sources.

Objective

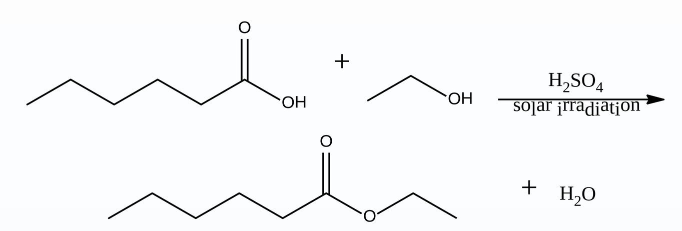
- This research focuses on the development of a solar heat source that can be used as the sole heat source for running reactions like Fisher esterification.
- This work served to find out whether or not it is practical to use solar irradiation to drive chemical reactions.

Methods & Materials

- A solar heat source has been designed through the repurposing of unused satellite dishes into reflective parabolic mirrors that are capable of attaining temperatures above 300°C. To attain the reflective properties needed to generate heat, satellite dishes are completely covered with Metalized Mylar® tape.

- Sunlight is reflected off of the dish as a single point of energy, which is concentrated onto the distillation flask painted black with high temperature paint. This energy heats the flask, just as electricity would heat the flask on a heating mantle.
- A condenser, filled with cold water was attached to the reaction flask. The flask was painted black with high-temperature automotive paint.
- Esterification reactions were run outside at a location of: N 36° 10.588 W 085° 30.283.

Results

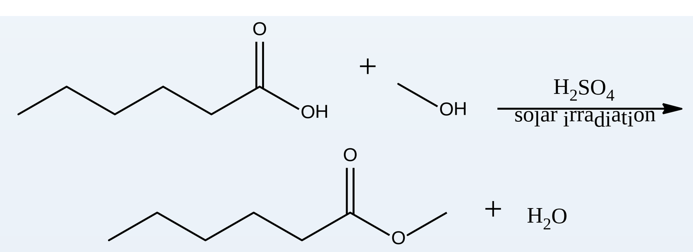


Ethyl Hexanoate Data

Hexanoic acid (5.855g, 50 mmol) and ethanol (2.788g, 50 mmol) were placed in a 14/20 100 mL round bottom flask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL). The flask was fitted with a condenser and placed on the satellite dish. It was irradiated for 70 minutes. Refluxing commenced immediately and the reaction mixture stayed at a gentle boil the whole time.

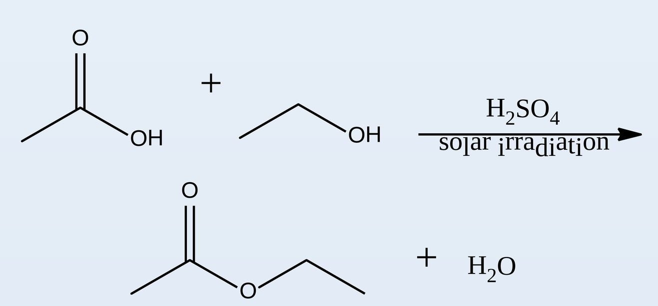
The reaction mixture was placed into a 100 mL separatory funnel and the lower layer drawn off. The organic phase as washed with 5% sodium carbonate solution, followed by water. The resulting crude product was dried over sodium sulfate and decanted into a labeled vial. The yield of crude product was 5.883 g, 82% (January 7, 2014 solar data).

Time	Air Temperature	Solar Irradiation
12:34 pm	11.5° C	543 W/m²
12:44 pm	11.7° C	536 W/m²
12:54 pm	12.4° C	522 W/m²
1:04 pm	12.2° C	512 W/m²
1:14 pm	13.0° C	499 W/m²
1:24 pm	12.6° C	480 W/m²
1:34 pm	13.7° C	466 W/m²
1:44 pm	13.7° C	448 W/m²



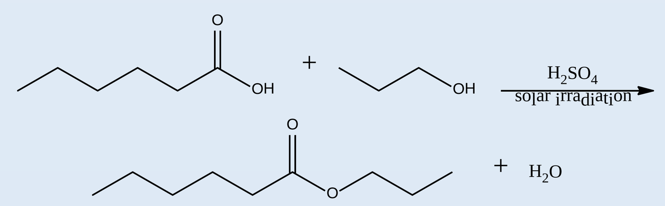
Methyl Hexanoate Data

Hexanoic acid (50 mmol) and methanol (50 mmol) were placed in a 14/20 100 mL round bottom flask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction was run as previously described. The yield of crude product was 3.585 g, 55%.



Ethyl Acetate Data

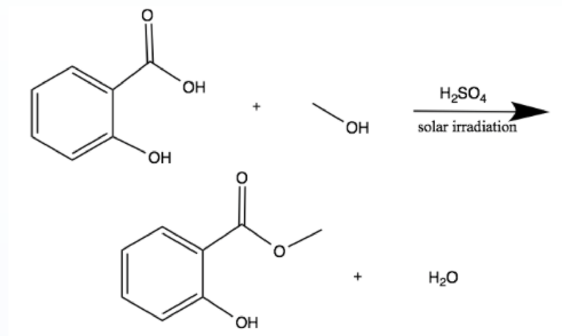
Acetic acid (50 mmol) and ethanol (50 mmol) were placed in a 14/20 100 mL round bottom flask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction run as previously described. The yield of crude product was 2.238 g, 51%.



Propyl Hexanoate Data

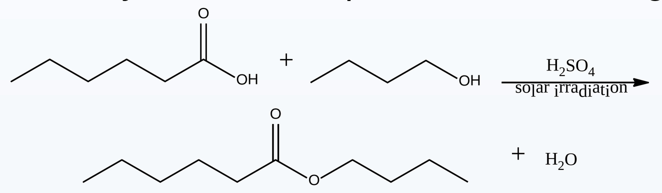
Hexanoic acid (50 mmol) and propanol (50 mmol) were placed in a 14/20 100 mL round bottom flask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction was run as previously described. The yield of crude product was 6.781 g, 86%.

Results



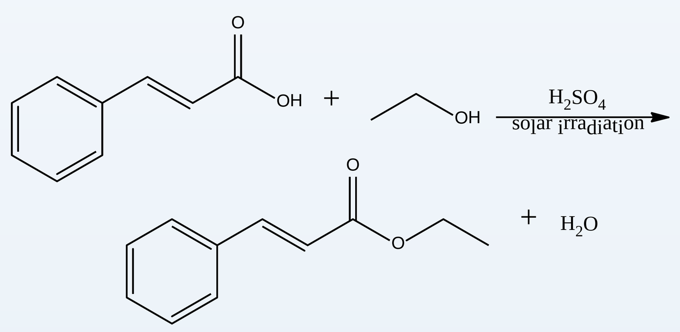
Methyl Salicylate Data

Salicylic acid (50 mmol) and methanol (50 mmol) were placed in a 14/20 100 mL round bottom flask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (10.0 mL) and the reaction was run as previously described. Product formed after the fourth run with these specific chemicals. The yield of crude product was 2.611 g, 34%.



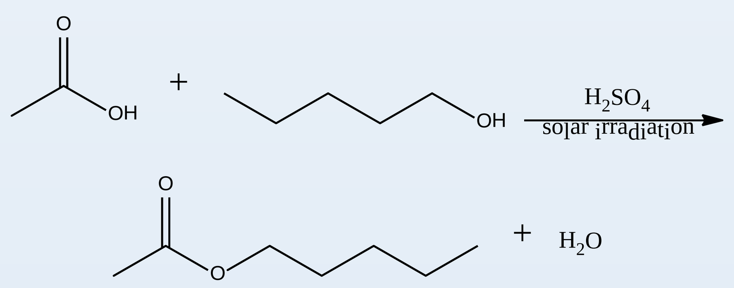
Butyl Hexanoate Data

Hexanoic acid (50 mmol) and propanol (50 mmol) were placed in a 14/20 100 mL round bottom flask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction was run as previously described. The yield of crude product was 6.828 g, 79%.



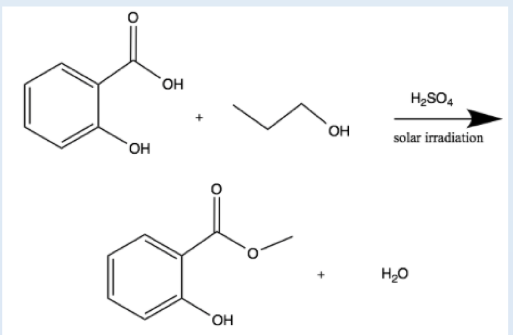
Ethyl Cinnamate Data

Cinnamic acid (50 mmol) and Ethyl Alcohol (50 mmol) were placed in a 14/20 100 mL round bottom lask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction run as previously described. The yield of crude product was 3.321 g, 41%.



Pentyl Acetate Data

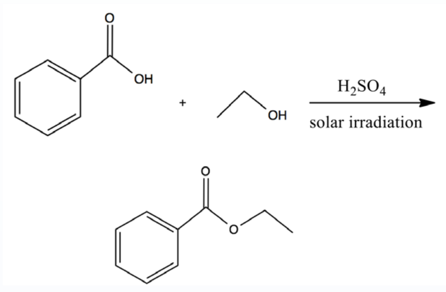
Acetic acid (50 mmol) and pentanol (50 mmol) were placed in a 14/20 100 mL round bottom lask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction run as previously described. The yield of crude product was 4.171 g, 56%. Product originally appeared green do to an impurity however, once distilled product color changes to clear.



Propyl Salicylate Data

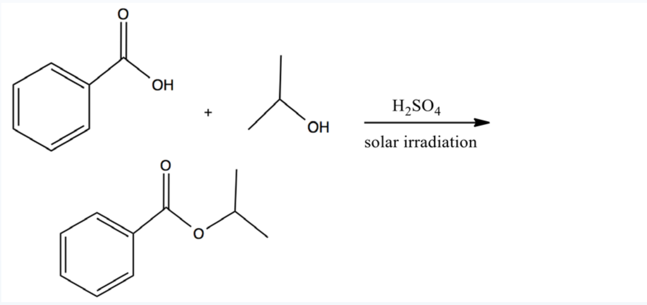
Salicylic acid (50 mmol) and 1- Propanol (50 mmol) were placed in a 14/20 100 mL round bottom lask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (20.0 mL) and the reaction run as previously described. The yield of crude product was 13.886 g, 75%.

Results



Ethyl Benzoate Data

Benzoic acid (50 mmol) and ethanol (50 mmol) were placed in a 14/20 100 mL round bottom lask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction run as previously described. The yield of crude product was 1.711 g, 68%.



Isopropyl Benzoate Data

Benzoic acid (50 mmol) and isopropanol (50 mmol) were placed in a 14/20 100 mL round bottom lask with the lower 2/3 painted black. To the resulting mixture was added sulfuric acid (1.0 mL) and the reaction run as previously described. The yield of crude product was 1.391 g, 54%.

Conclusion

- Seasonal periods of the year do not appear to affect the heat source. Reactions are feasible as long as the solar irradiation is at 400 W/m² or greater.
- Because the reactions are run outdoors under windy conditions, a portion of the more volatile alcohols might be lost up the condenser. Adding excess methanol or ethanol might increase the yield of ester.

Future Work

- We plan to produce a series of Fisher esterification products using both aliphatic and aromatic acids.
- The products produced will be purified by distillation using solar energy.

Selected References

1. Agee, Brian; Mullins, Gene; Swartling, Daniel. Friedel-Crafts Acylation Using Solar Irradiation. ACS Sustainable Chem. Eng., 2013, 1(12). 1580-1583.
2. All weather data is taken from the Millard Oakley STEM Center weather station, Tennessee Tech University: http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KTNCOOKE16

Acknowledgements

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