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Oxidation of Secondary Aromatic Alcohols

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Oxidation of Secondary Cyclic Alcohols

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Abstract

Secondary alcohols are oxidized to corresponding ketones. This poster will compare traditional and microwave methods of the oxidation of aromatic secondary alcohols. The oxidizing agent of choice for this study is chromium trioxide resin. 9-Hydroxyfluorene, Benzhydrol, and other alcohols are being investigated. Educational as well as research applications are being explored.

BACKGROUND INFORMATION

Microwave Assisted Organic Synthesis:

•Reduce reaction time by directly transferring heat to the interior of the microwave vessel while providing control over reaction conditions [4,5].
•Reaction conditions are kept the same throughout each synthesis [2,4].

Optimization of Microwave Assisted Organic Synthesis:

•The optimization of the microwave is still being investigated for a variety of different organic reactions [1,6].
-Diels- Alder Reactions
-Esterifications
-Oxidations
-Williamson Ether Synthesis

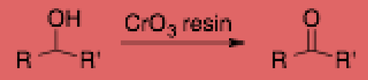
Microwave-Enhanced Ketone Synthesis:

•Carbonyl Compounds:
-Intermediates in both manufacturing and research
-Reagents and Solvents
-Found in flavorings, plastics, fabrics, pharmaceuticals
-Naturally occurring in carbohydrates, proteins, nucleic acids
•Conventional means of ketone synthesis are time-consuming.[6].
•A decrease in reaction time and increase in yield will demonstrate the importance of microwave assisted reactions
•Use of polymer supported chromium trioxide resin is a environmentally friendly agent.

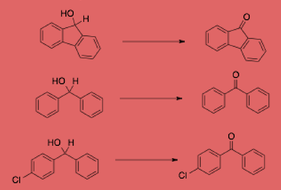
Research Goals:

•Synthesis of aromatic ketones: 9-fluorenol, benzophenone, 4-chlorobenzophenone.
•Synthesis of aliphatic ketones: cyclopentanone, and cyclooctanone.
•Alcohols are oxidized only through the use of polymer supported chromium trioxide.

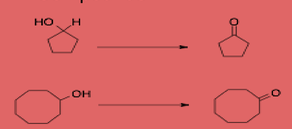
Results



Aromatic Compounds



Aliphatic Compounds

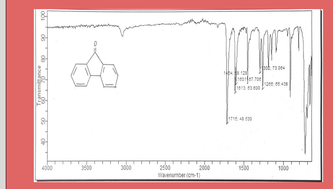


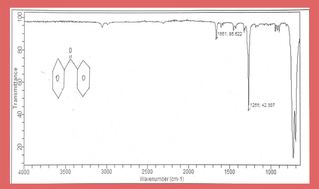
Aromatic

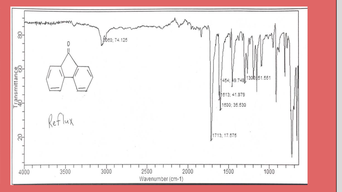
Product	Wattage	Time (Min)	℃	Yield
4-Chlorobenzophenone	1200	15	120	85%
9-Fluorenone	1200	15	120	89%
9-Fluorenone (Reflux)	Reflux	60	120	78%
Benzophenone	1200	15	120	88%

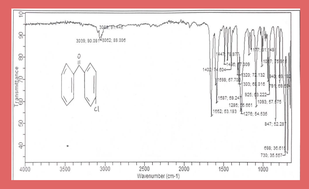
Aliphatic

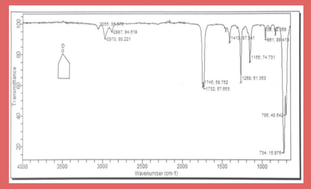
Cyclooctanone	1200	15	120	73%
Cyclopentanone	1200	15	120	68%

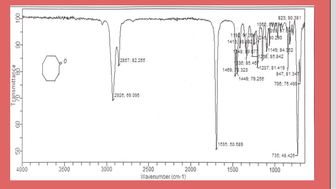












Experimental Section

General Procedure A: Reactions were run in a 25 mL quartz closed-pressurized vessel equipped with a magnetic stir bar and Welfon rod. The reaction vessel was charged with 5.49 x 10^{-4} moles of the secondary alcohol and dissolved in 16 mL of dichloromethane, followed with 750 mg of polymer-supported chromic acid. The reaction was irradiated in the microwave. The resulting mixture was vacuum filtrated into a 25-mL round-bottom flask, ultimately leaving the resin behind. Dichloromethane was evaporated using the rotary evaporator. Aromatic products were purified via column chromatography. Aliphatic products were purified by distillation. Purity was determined by FT-IR or thin layer chromatography.
General Procedure B: All oxidation reactions were run in 25-mL round-bottom flask equipped with a magnetic stir bar and Welfon rod. The reaction vessel was charged with 5.49 x 10^{-4} moles of the secondary alcohol and dissolved in 16 mL of dichloromethane, followed with 750 mg of polymer-supported chromic acid. The reaction was refluxed for 60 minutes which was monitored by TLC's taken every 10 minutes. A constant temperature was maintained using a thermometer. The resulting mixture was purified via column chromatography.

Discussion

Synthesis:

•Each ketone was synthesized from a secondary alcohol either aromatic (9-fluorenol. Benzophenone, 4-chlorobenzophenone or a cyclic hydrocarbon (cyclopentanol, cyclooctanol). The alcohols were oxidized using a polymer supported chromium trioxide resin and were heated by microwave irradiation

.•*Reaction Conditions and Isolation;*

•All microwave reactions were run at 1200 W for 15 minutes. The purified 9-fluorenone produced a 88.9% yield in the microwave compared to the 77.6% via the traditional reflux technique.

•All reactions were monitored by TLC or FT-IR. Ketones were isolated and purified by column chromatography or distillation.

Conclusion & Future Work

• The utilization of the microwave enhances the percent yield of ketones and reduces reaction time when used in organic reactions.

•Several more secondary alcohols are going to be synthesized in the future.

References

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