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Synthesis of Dihydrocarvide

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ABSTRACT

Sustainable polymers are a topic of interest due to their environmental benefits. Dihydrocarvide is a monomer for ring-opening polymerization, derived from citrus peels. This monomer can be obtained by the Bayer-Villiger oxidation of dihydrocarvone with oxone, a green oxidant, and sodium bicarbonate in methanol/water. Although this reaction has been investigated in prior studies, it has been complicated by epoxidation of the double bond. The approach for this study in organic methodology was to run multiple trials while varying conditions such as mode of reagent addition, stirring time, and the presence of co-oxidants. Progress was monitored via ¹H NMR spectroscopy. A single addition of reagents followed by a 4-hour stir provided the most promising result. An observed ratio of 2:1 alkene:oxymethine integration in the ¹H NMR indicated the Baeyer-Villiger oxidation without epoxidation. The result remained consistent through a scale-up of the reaction. The monomer will be used in ring-opening polymerizations leading to numerous possible application directions illustrating the advantages of green chemistry.

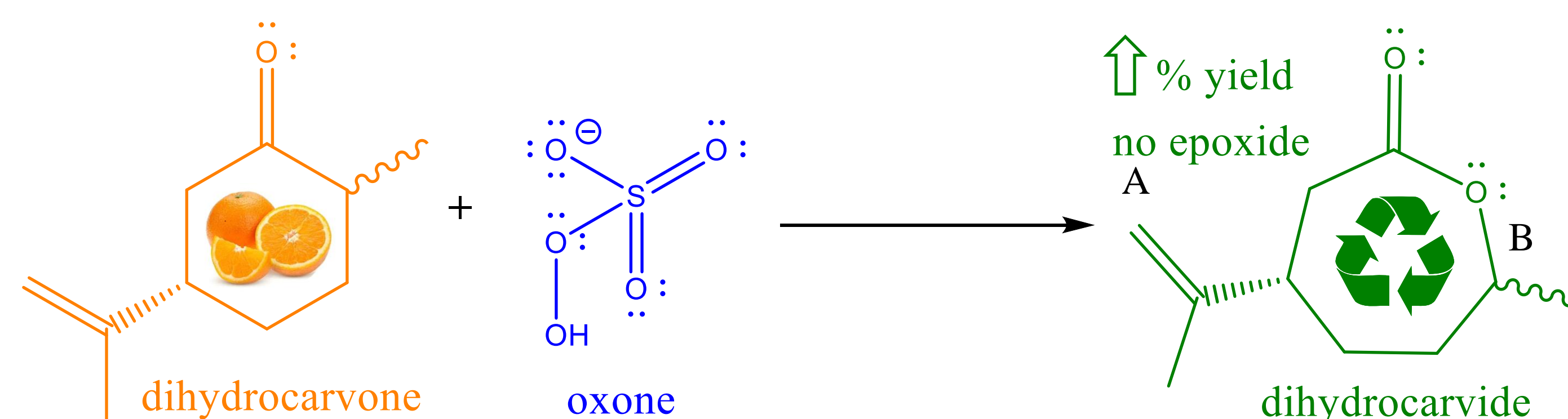
BACKGROUND

Green chemistry is a rising concern for researchers due to its benefits for human health, the environment, and the economy.¹ The synthesis of green monomers is of interest due to the competitive performance and low cost of these materials, which are derived from renewable resources, and allow easy and safe recycling or decomposition.² Past studies have been conducted on related topics. One group had examined the synthesis of monomer menthene in which the starting material was derived from mint.² Using this compound, the group was able to develop a class of sustainable triblock polymers to make elastomeric materials.² Another group found interest in a new approach for the synthesis of lactone involving the use of oxone as the oxidant as well as solvents containing ionic liquids.³ Our interest in this research is to find an alternative synthesis of the monomer dihydrocarvide by utilizing a Bayer-Villiger oxidation reaction. Previous researchers in this lab have run numerous reactions looking at presence of promoters such as co-oxidants to improve yield of the product. The focus of this study was to examine the method of reagent addition and reaction time.

REACTION TRIALS

Reaction	Additive Technique	Stir Time	Peak Ratio at 4.7:4.4 ppm	Scale
A	All at once	7 days	1:1	0.11 mL
B	All at once	4 days	2:1	0.22 mL
C	All at once	1 day	2:1	0.22 mL
D	All at once	4 hours	2:1	11 mL

BAEYER-VILLIGER OXIDATION

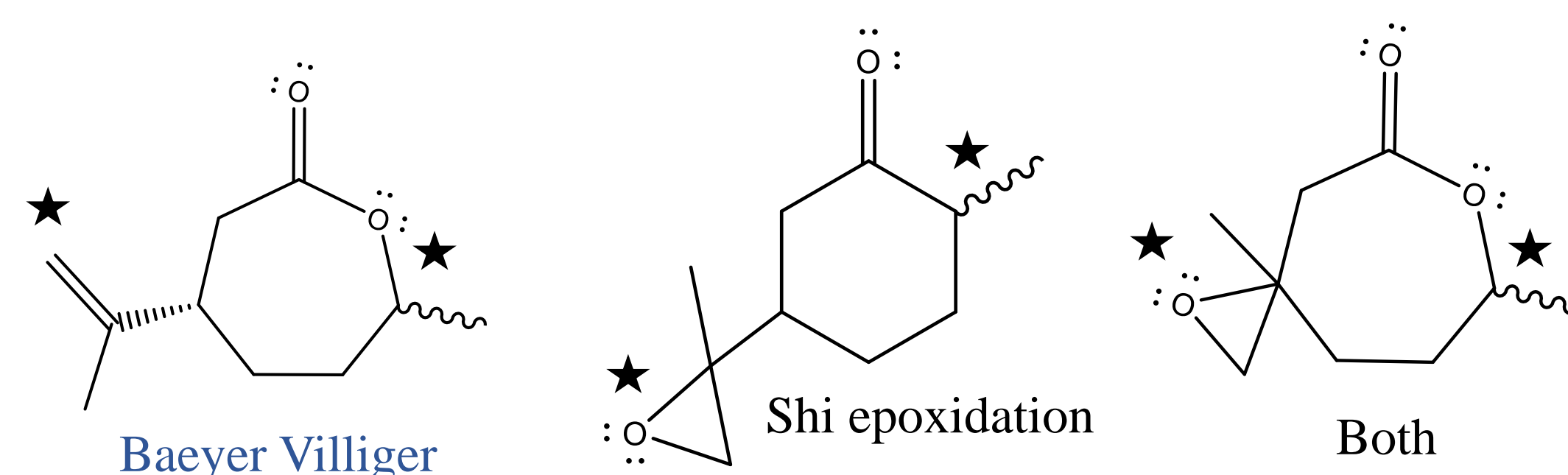


Why are we looking for a 2:1 ratio between ¹H NMR peaks shifted at 4.4 ppm and 4.7 ppm?

That is a good indication of whether the ester is the sole product or if an epoxide has also been synthesized.

With this reaction, there are 3 possible products (with 3 possible alkene H: oxymethine H ratios):

- Baeyer Villiger (2H:1H)
- Shi epoxidation (0H:1H)
- Both (0H:1H)

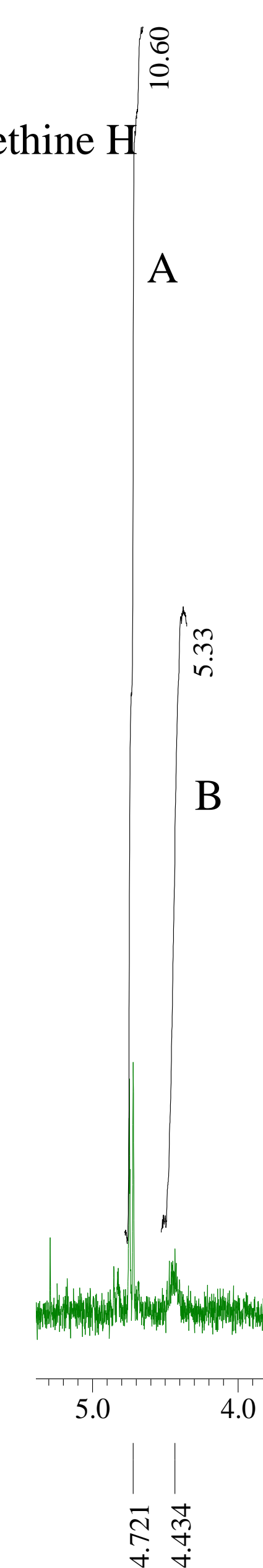


Each reaction contains a variation of the following:

- Dihydrocarvone (substrate)
- Solvents
 - deionized water, methanol
- Oxidant
 - Oxone (stoichiometric)
 - Sodium bicarbonate (pH control)

Each reaction is worked up uniformly in the following steps:

1. Rotary evaporated methanol
2. Liquid-liquid extraction with ethyl acetate
3. Washed with sodium bisulfite
4. Washed with DI water
5. Washed with brine
6. Dried with MgSO₄
7. Filtered
8. Rotary evaporated ethyl acetate
9. Characterization (¹H NMR)



We want to see a 2H:1H ratio between peaks labeled A and B

DISCUSSION

Our interest in this research is to find an alternative synthesis of the monomer dihydrocarvide by utilizing a Bayer-Villiger oxidation reaction.⁴ When implementing the application of green reagents, as well as aqueous conditions, sustainable chemistry techniques are displayed.³ Numerous reactions have been run varying stir times, method of addition and presence of promoters.⁵ In the most promising reaction thus far, all the starting materials were added together at once and left to stir for four hours. The key ¹H NMR spectral features show a pair of alkene hydrogens near 4.7 ppm and a methine hydrogen adjacent to oxygen near 4.4 ppm in the desired ester. An epoxide would lack the alkene hydrogen, whereas a ketone would lack the H-C-O methine

FUTURE WORK

Once dihydrocarvide can be synthesized in high yield on gram scales, the monomer will be used in ring-opening polymerization reactions. It is hoped that post-polymerization modification through addition to the side-chain alkene will lead to a range of applications.

CONCLUSION

Oxidizing the starting material dihydrocarvone with oxone in methanol and water using a Baeyer-Villiger oxidation reaction, leads to the synthesis of 3 major products. Within these three products there is only one without an epoxide. In this study, we worked on synthesizing the non-epoxide product, the monomer dihydrocarvide.

The most promising conditions include a single addition of reagents, with a 4-hour reaction time at room temperature. Using this procedure, the reaction was scaled up to 100 times the original quantity. The use of recrystallization may help to separate the two products differing in chirality. During characterization, ¹H NMR spectra were utilized. By monitoring peaks around 4.4 and 4.7 ppm. Having a 2:1 ratio between these shifts indicated the ester formation without epoxidation. NMR also suggests the presence of a minor diastereomer in the reaction.

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