

Comparisons of Methods of Oxidation and Alkene Condensation In Advanced Synthesis Lab

Ngoc (Jade) Nguyen, Thy Le, Diana Cermak*, Knox College

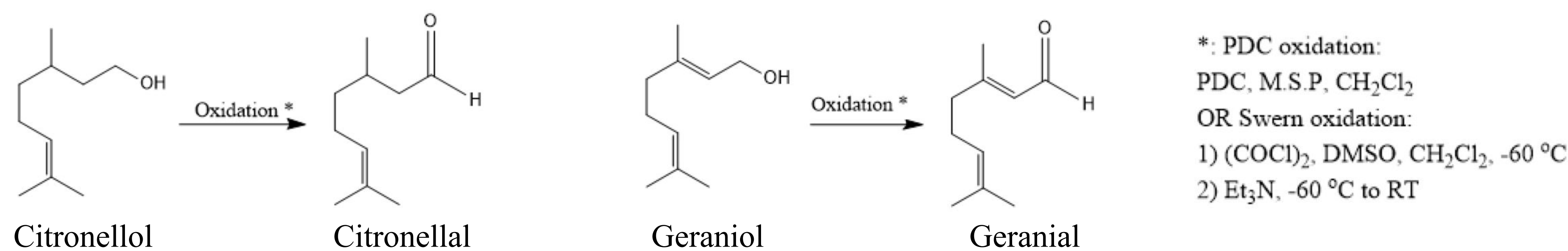
Introduction

Citronellol and Geraniol are both components of rose oils. Citronellol has a lemon-like smell whereas Geraniol has a rosy smell. The two compounds were chosen for the study because of their interesting structure. Geraniol is an allylic alcohol whereas Citronellol has a chiral center. In this study, different methods of mild oxidation were tested on the two compounds, followed by the trans-selective alkene synthesis. The effectiveness of each oxidation methods and alkene synthesis were analyzed.

Oxidation

PDC and Swern are mild oxidation method that can convert primary alcohol to aldehyde. PDC (Pyridinium Dichromate) is a Cr-based method whereas Swern oxidation is a Cr-free method which is more environmental-friendly. In this study, both methods were used to oxidize citronellol and geraniol, and the corresponding aldehydes were characterized using ^1H NMR spectroscopy.

Reaction Scheme



Results & Data Analysis

Experiment	Mass (g)	Yield (%)	trans : cis ratio
Citronellol – Cr based (PDC)	0.544	69.3	N/A
Geraniol – Cr based (PDC)	0.672	89.1	75 : 25
Geraniol – non-Cr based (Swern)	0.527	67.9	96 : 4

Table 1. Reaction yield and the ratio of 2 geometry isomers of the oxidation product. The trans:cis ratio was determined based on the integration of trans-aldehyde (more downfield) to that of cis-aldehyde (more upfield). The yield was calculated after the resulting aldehydes were purified.

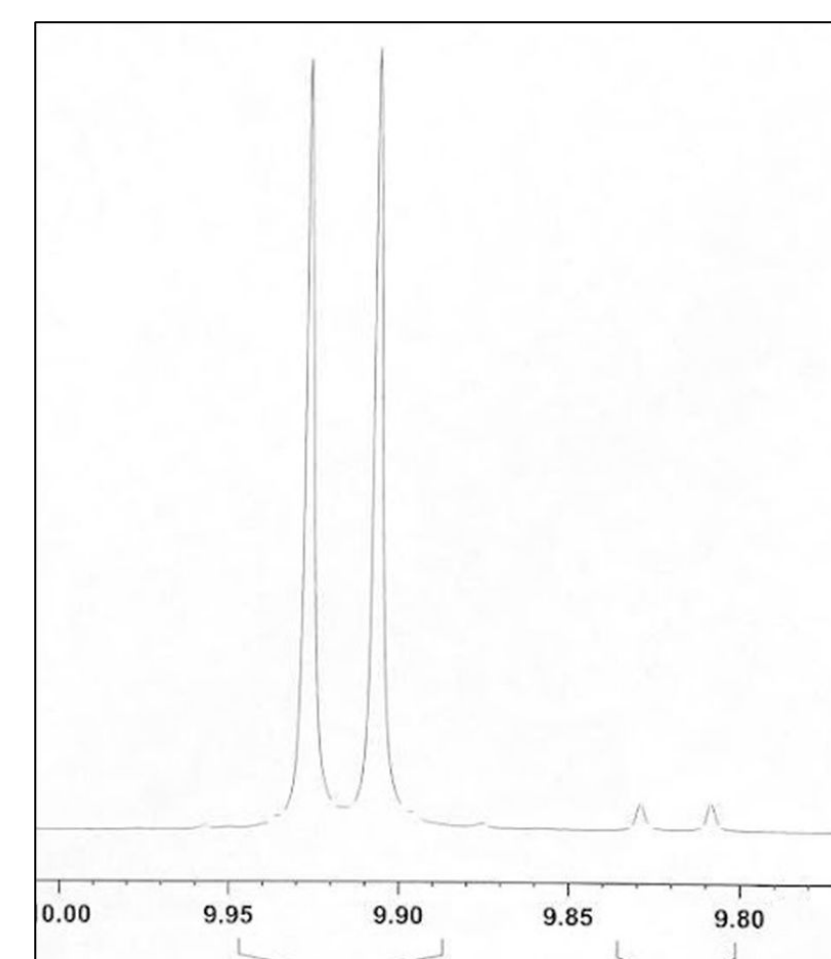


Figure 1. The ^1H NMR spectrum of geranial, an aldehyde resulting from oxidizing geraniol using Swern oxidation.

Conclusion

Oxidizing geraniol using PDC method resulted in a mixture of cis-trans isomers due to the double bond in the structure. Since the citronellol does not have a double bond, oxidizing it using either Swern or PDC yielded the same aldehyde.

Swern oxidation can reduce the formation the cis-aldehyde to produce a final product with a higher purity. The trans:cis ratio after oxidizing Geraniol was 75:25 with PDC and was improved to 96:4 with Swern oxidation.

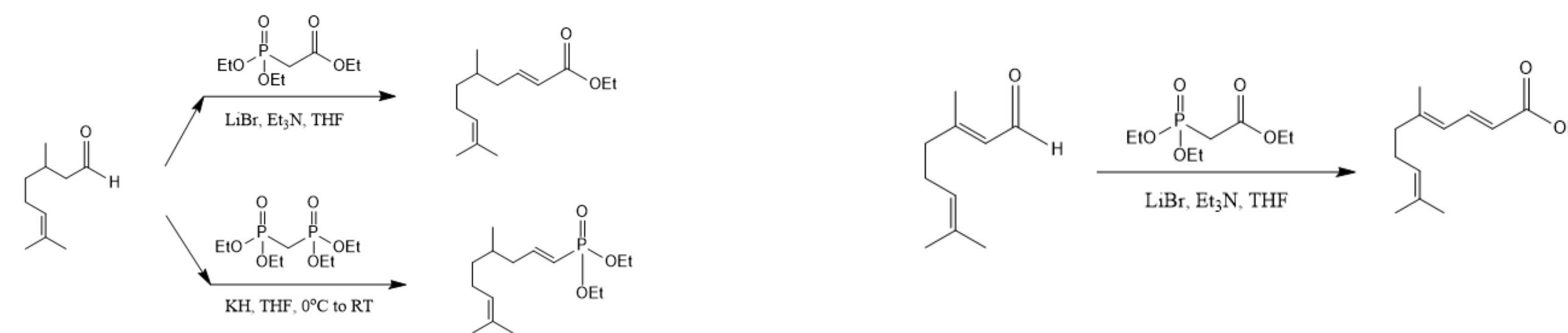
Acknowledgement

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Alkene Condensation

To synthesize alkenes from citronellal and geranial, the Horner-Wadsworth-Emmons (HWE) condensation method was applied. Compared to the Wittig reaction, a conventional condensation method, HWE uses an aldehyde and phosphonate reagent. Two modifications of HWE method used in this study involve either a weak base (Et_3N) or a strong base (KH) and are both trans-selective, which could be confirmed by ^1H NMR spectroscopy.

Reaction Scheme



Results & Data Analysis

Experiment	J-value (Hz)	trans : cis ratio
citronellal - weak base (Et_3N)	16	100 : 0
citronellal - strong base (KH)	20	100 : 0
geranial - weak base (Et_3N)	12	100 : 0

Table 2. Isomeric ratio of products of trans-selective HWE reaction. The data was collected after the product was purified by column chromatography.

The coupling constant, J-value, is calculated based on the peaks of the alkene. These two hydrogen will split each other, and the distance between peaks is measured. Given that J-value for trans alkene ranges is at 12-20 Hz, while for cis alkene is 8-12 Hz, all products are characterized as trans alkenes.

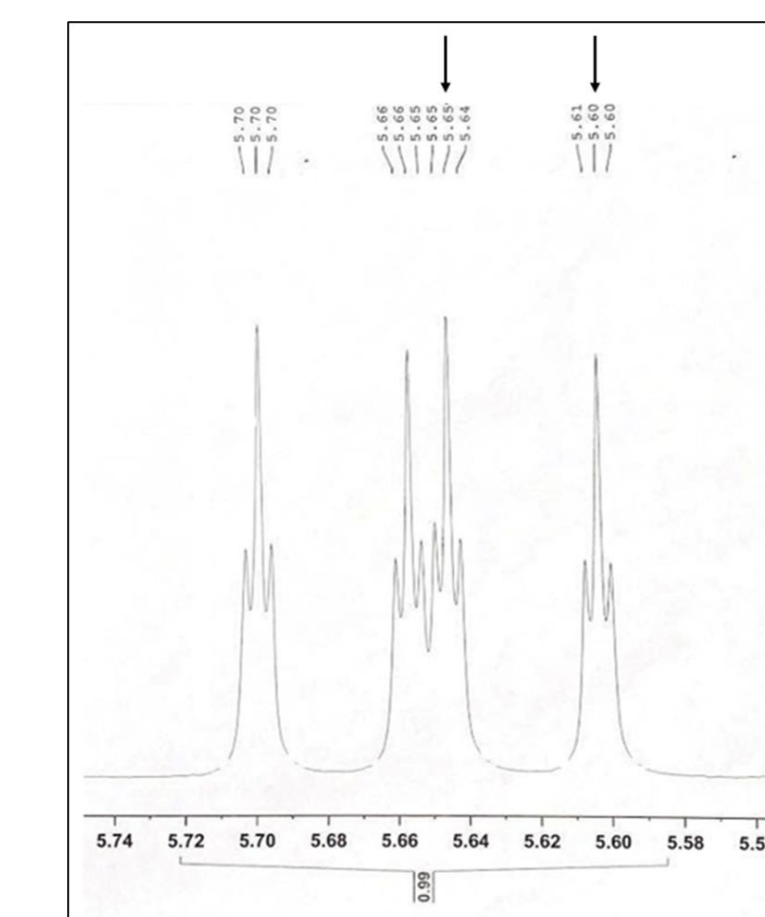


Figure 2. The ^1H NMR spectrum of the purified phosphonate product synthesized from citronellal, potassium hydride (KH) and bisphosphonate. The arrow indicated the chemical shift used for J-value calculation.

Conclusion

Both modifications of HWE reaction used in this study are trans-selective. The trans : cis ratio of 100:0 observed in all 3 reactions shown in Table 2 confirmed this trans isomer selectivity.

Reference

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