

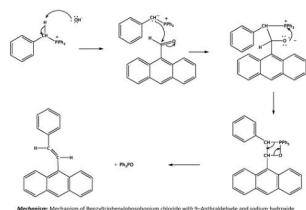
Comparison of Traditional and Alternative Wittig Reactions

ABSTRACT

In this experiment, a named organic synthesis reaction, The Wittig Reaction, was performed under traditional conditions and green conditions. The purpose of the experiment is to determine what effect the conditions have on the yield of the reaction. After synthesis, extraction and purification were performed, followed by analysis via NMR and melting point. It was observed that the green synthesis resulted in a smaller yield compared to the traditional synthesis.

INTRODUCTION

The Wittig reaction between an aldehyde or ketone with a phosphorous containing compound known as a Ylide. This reaction produces an alkene and a byproduct salt known as triphenylphosphine oxide (TPPO). Synthesis of the two product requires little energy such as heat due to the stable nature of the TPPO that drives the cyclic reaction intermediate to decompose. Traditional Wittig reactions are run in organic solvents such as THF and dichloromethane, which are expensive and hazardous and pose health effects to the users. The reaction also requires hazardous and strong bases such as 50% NaOH (19M) and n-butyllithium. A safer alternative green reaction has been proposed that eliminates the need for hazardous bases and solvents and more cost effective in industry and education. Current literature mentions the green technique but does not mention the associated yields or effectiveness. This research is focused on comparing the two classifications of Wittig reactions.



Mechanism: Mechanism of Benzyltriphenylphosphonium chloride with 9-Anthraldehyde and sodium hydroxide

METHODS

Traditional Synthesis – DCM, benzyltriphenylphosphonium chloride, 50% NaOH, 9-Anthraldehyde (CHO) combined in a 50mL round bottom (rb) flask with a stir bar. The mixture was stirred at room temperature for 45min-1hr. TLC plate was run in hexane to check reaction with spots of the TPPO/ethanol, CHO/ethanol, Ylide/ethanol, and the rxn mixture. If the TLC showed high amounts of the product, 9-styrylanthracene(alkene), compares to the CHO; then the mixture was extracted several times with water and DCM. The organic layers were collected and dried, Na₂SO₄ was filtered off and the mixture was rotovap to remove all DCM. Column was run.

Green Synthesis – Anhydrous NaOH, CHO, and the ylide were added together in a clean mortar and ground together for several hours. And left to sit and react over night followed by more crushing. A TLC of the mixture and the reagents was run like in the traditional method. The contents were filtered via vacuum filtration with ethanol and the filtrate was kept, ethanol was left to evaporate. Column was run. **Column** – A slurry of 37g dry silica gel/hexane was added to the closed column and allowed to settle to a height of 2-4inches The column was run in pure hexane.

Analysis – Record mass of each product and calculate percent yield. Determine the melting point of the solid and perform H-NMR.

RESULTS



Fig2: Reaction of Benzyltriphenylphosphonium chloride and NaOH (aq) after 4 minutes.

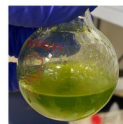


Fig3: Reaction of deprotonated ylide and 9-Anthraldehyde (aq) after 4 minutes.

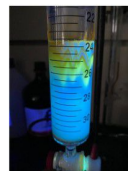


Fig4: Column exposed to UV light after running for some time, showing product (orange band), Anthraldehyde (green yellow), and other impurities (from UV source itself).

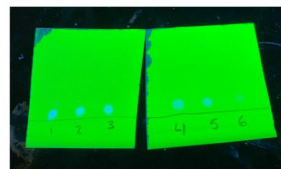


Fig5: TLC plates run in hexane of spots from every three fractions. All three show a single spot, all fluoresce blue under UV.



Fig6: Round bottom flask filled with fractions from flash column under UV lamp.



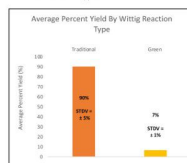
Fig7: Round bottom flask filled with fractions from flash column under UV lamp during solvent evaporation.



Fig8: Reaction of Benzyltriphenylphosphonium chloride and NaOH (aq) after 15 hours.



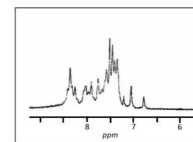
Fig9: Reaction deprotonated ylide and 9-Anthraldehyde. Vacuum filtered with water to remove inorganic salts. Organic solid remains.



Chem2: Average % Yield by Wittig Reaction Type

Sample	Mp Range	Units	Accepted
Tp1	128-130 °C	128-131	
Tp2	128-130 °C	128-131	
G1	129-131 °C	128-131	
G2	129-130 °C	128-131	

Chem2: Experimental Melting Points



Chem3: The 1H-NMR of the traditional product

DISCUSSION & CONCLUSION

Synthesis of trans-9-styrylanthracene was achieved using the green and traditional methods. Both reactions yielded the fluorescent product which was confirmed by NMR and melting point analysis. Comparison of the reaction time and percent yield of the green vs traditional method shows a remarkable difference. The green reaction is tedious as grinding the base and the Wittig reagent takes very long and the product yield was very low, additionally, changes in grinding can change the depth of reaction progress. The traditional method takes less time and is easy to carry out in a lab period. Since students in an undergraduate lab setting have limited time the traditional Wittig reaction would work better. The biggest hurdle in purifying the product was the presence of TPPO. The TPPO “sticks” to solvents and is hard to remove by regular means of recrystallization and filtration. The addition of ZnCl₂/ethanol solution to the reaction mixture, formed a ZnCl₂(TPPO)₂ complex which the complex is insoluble and could be filtered out of the mixture. After filtration, the TPPO was still present in small amounts, and alternative purification methods were needed. A flash column using hexane and a small amount of DCM as the solvent, was performed separating the alkene product from the TPPO based on polarities. This method achieved better levels of separation compared to the ZnCl₂ method.