Comparison of Traditional and Alternative Wittig Reactions

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ABSTRACT

In this experiment, a synthesis reaction that is known as the Wittig reaction was conducted under traditional conditions. The purpose of this experiment is to compare the traditional and alternative methods to determine what effect the different methods have on product yield. After synthesis, extraction and purification methods were performed, followed by analysis using the melting point. It was determined that the melting point of the Wittig product was 151-154, which was exactly within the range of the true melting point and had a percent yield of 30%. The Alternative method could not be performed because there were issues with receiving supplies to conduct the experiment.

INTRODUCTION

The ability to synthesize carbon-carbon bonds is limited to a handful of mechanisms while creating new bonds is essential to drug design and development, polymer chemistry, and other synthetic processes. The general mechanism for these new bonds can be influenced by the reagents and reaction conditions, thus the location of the new bond can change from molecule to molecule. In a named organophosphorus reaction, the Wittig reaction, a carbon-carbon double bond is created, and its mechanism ensures that its location will always be the same. The Wittig reaction is a traditionally high-yield reaction, meaning it produces a lot of products compared to other reactions. This is due to the production of the thermodynamically favored side-product, Triphenylphosphine oxide (TPPO). This product is highly stable and drives the reaction in the forward direction compared to halting the reaction progress. As a result, using this mechanism to create new carbon-carbon bonds has a high product yield and is useful for production purposes as it forces more of the desired product to be created while limiting the amount of energy put into the system. One drawback is that the Wittig reaction uses solvents such as dichloromethane, which poses biological, chemical, and environmental hazards. Additionally, these solvents are expensive and costly to use and then dispose of. In literature, alternative methods and a green Wittig have been proposed and developed as possible replacements for the traditional Wittig reaction. The alternatives are either solventless or heatless reactions which reduce the associated cost, supplies, and potential safety risk associated with Wittig reactions. But a direct comparison of the yields from traditional vs alternatives has not been published for this mechanism.

METHODS

Traditional Synthesis – First, the ylid was prepared by weighing 1.00g of benzyl triphenyl phosphonium chloride and placed into a round bottom flask. Then 0.34g of trans-cinnamaldehyde was placed into the same flask with 5 mL of 50% NaOH. 5 mL of Dichloromethane was added to the reaction flask. The mixture was stirred with a magnetic stir bar for 15 minutes at room temperature. A separatory funnel was then prepared to extract the organic layer from the aqueous layer. After the organic layer was extracted, it was filtered through filter paper into a round bottom flask. The flask was then roto vaped to create a solid product. A silica gel column was prepared using hexane as a solvent to separate the products from any additional impurities that may have been present. 1 mL of DCM and excess hexane were placed into the reaction flask and then placed into the silica gel column. 25 samples were collected into 50 mL Erlenmeyer flasks. Spots from each sample were examined on silica gel plates and separated using hexane as a solvent. Samples that contained impurities were not collected while the rest of the samples were collected into a round bottom flask and roto vaped. NMR was attempted but failed due to instrument malfunction. Hexane was then used to dissolve the product and placed into an Erlenmeyer flask. The product was recrystallized by boiling it in excess hexane for several minutes until crystals formed. The product was then filtered via vacuum filtration to collect the solid crystals. The melting point and mass of the product were determined.

RESULTS

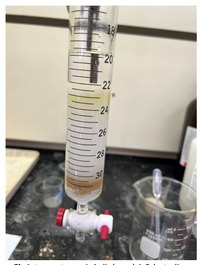


Fig1: trans, trans-1,4-diphenyl-1,3-butadiene was processed through a silica gel column using hexane as a solvent.

Fig2: 25 collected samples from the separatory funnel.

Fig3: trans, trans-1,4-diphenyl-1,3-butadiene before recrystallization.

Fig4: trans, trans-1,4-diphenyl-1,3-butadiene after recrystallization.

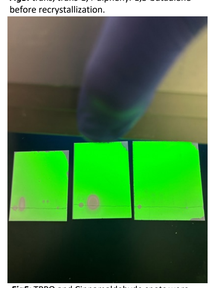


Fig5: TPPO and Cinnamaldehyde spots were compared to spots from products. Samples 1, 6, 11, 16, and 21 were spotted first. Then samples 16, 17, 18, 19, and 25 were spotted. Spots 21 and 25 seemed to have a contaminate.

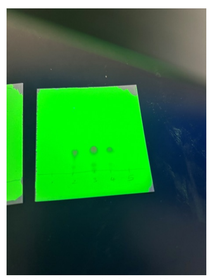


Fig6: Spots from samples 2, 3, 4, and 5. Product spots are present.

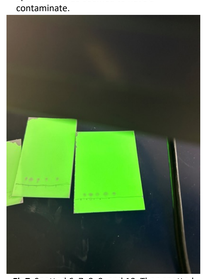
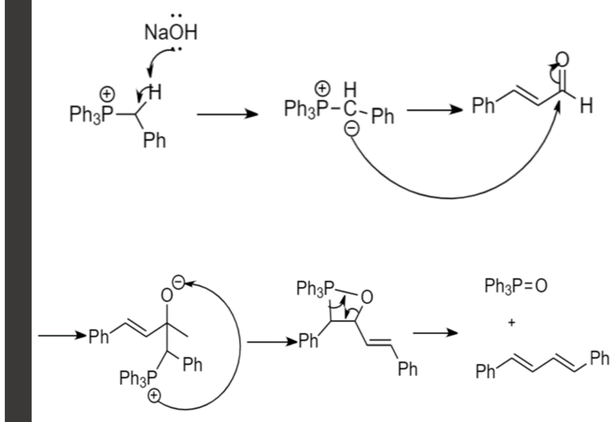


Fig7: Spotted 6, 7, 8, 9, and 10. Then spotted 11, 12, 13, 14, and 15. All spots revealed the Product.

Theoretical Yield: 0.531 grams
Actual Yield: 0.16 grams
Percent Yield: 30.1%

True Melting Point Rage: 151-154
Actual Melting Point Range: 151-154



DISCUSSION & CONCLUSION

Synthesis of trans, trans-1,4-Diphenyl-1,3-butadiene was achieved using the traditional method. The melting point of the purified product was 151-154, which was the true melting point of the product. This means that a pure product was synthesized because if it were to have melted outside the true melting point range, that would have implied that impurities were present.

The experiment resulted in a percent yield of 0.16 grams while the theoretical yield was 0.53 grams, which results in a percent yield of 30.1%. Some yield may have been lost during the extraction through the separatory funnel. Some yield was also lost from scraping the purified crystal onto the weighing paper because the product was still stuck on the walls of the Buchner funnel when the mass was recorded. The number one reason why the product was lost is that samples 21 through 25 were not collected due to a noticeable impurity on their TLC spots. Overall, the traditional reaction resulted in a purely synthesized product, with a decent percent yield.

The Green reaction was not completed due to issues regarding supply delivery.

References and Acknowledgements: Special thanks to Dr. Venki and Dr. Langston. Fallot, Lucas B. "'ON WATER' WITTIG REACTION LABORATORY EXPERIMENT AND THE DEVELOPMENT OF AN 'ON WATER' CATALYTIC WITTIG REACTION." San Diego State University, 1 Apr. 2014. Hubbard, Richard, director. *CHEM 2212L The Wittig Reaction*. *YouTube*, UGA Chemistry, 2 Apr. 2020, https://www.youtube.com/watch?v=22vNW7F7yVY. Accessed 16 Apr. 2022.