

9-1-2020

Synthesis of 3-Vinylthiophene as a Precursor for Use in Solar-Cell Applications

Richard Hayenga
Winona State University

Robert Kopitzke
Winona State University

Follow this and additional works at: <https://openriver.winona.edu/studentgrants2021>

Recommended Citation

Hayenga, Richard and Kopitzke, Robert, "Synthesis of 3-Vinylthiophene as a Precursor for Use in Solar-Cell Applications" (2020). *Student Research and Creative Projects 2020-2021*. 8.
<https://openriver.winona.edu/studentgrants2021/8>

This Grant is brought to you for free and open access by the Grants & Sponsored Projects at OpenRiver. It has been accepted for inclusion in Student Research and Creative Projects 2020-2021 by an authorized administrator of OpenRiver. For more information, please contact klarson@winona.edu.

**WINONA STATE UNIVERSITY
UNDERGRADUATE STUDENT RESEARCH & CREATIVE PROJECTS
FINAL REPORT**

Submit this complete form and a copy of the project end product(s) no later than ten (10) days after the completion of the project. Submit items as email attachments to Grants & Sponsored Projects (grants@winona.edu).

For more information, go to the [Student Grants webpage](#).

Final Report Checklist

The final report **MUST** include this form and the end product (*check to verify inclusion of each component*):

- This final report fully completed
- A copy of the project end product. Indicate the format of your final product (*select all that apply*):
 - Research Report
 - Presentation
 - Poster
 - Other – Please describe:

Note: A copy of the project end product will be forwarded to Krueger Library for archival purposes.

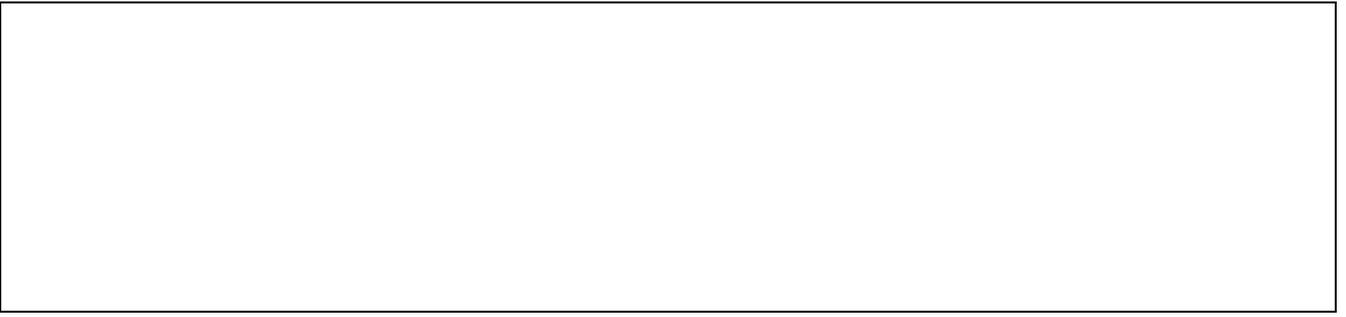
Project Information

Title of Project: Synthesis of 3-Vinylthiophene as a Precursor for Use in Solar-Cell Applications	
Student Name (PI): Richard Hayenga	Student Email: rhayenga15@winona.edu
Co-Investigators Names:	
Faculty Sponsor: Robert Kopitzke	Faculty Department: Chemistry
Was this a capstone, senior thesis, or other degree culminating project? No	

Project Abstract

What was the purpose of this research? What were the planned outcomes? What did you do to achieve them? What were the actual outcomes?

The goal of our proposed research is to develop a high-yielding single-step synthesis from 4-bromotrifluoromethylbenzene. A relatively low cost, high yielding synthetic route to 4-trifluoromethylstyrene is desired in this experiment. The palladium catalyzed coupling of 4-bromotrifluoromethylbenzene with vinyltrimethoxysilane is the synthetic method used. Synthetic precursors to 4-pentafluorosulfurylstyrene are quite expensive, therefore developing a high yielding single step route using cheaper precursors and catalysts are desirable. The main goal is to attempt and develop a successful single step synthetic route to 4-bromotrifluoromethylbenzene using these less expensive trifluoromethyl group precursors. The first steps of the project turned out to be successful, with high yields of the ligands, and then obtaining high yields of the precursor. The last experiment involved a 100% yield of 4-bromotrifluoromethylbenzene after several failed attempts.



One Step Synthesis of 4-Trifluoromethylstyrene by Palladium Catalyzed Coupling of Vinyltrimethoxysilane

Dylan Hayenga

Faculty Mentor: Dr. Robert Kopitzke

Abstract

The goal of our proposed research is to develop a high-yielding single-step synthesis from 4-bromotrifluoromethylbenzene. A relatively low cost, high yielding synthetic route to 4-trifluoromethylstyrene is desired in this experiment. The palladium catalyzed coupling of 4-bromotrifluoromethylbenzene with vinyltrimethoxysilane is the synthetic method used. Synthetic precursors to 4-pentafluorosulfonylstyrene are quite expensive, therefore developing a high yielding single step route using cheaper precursors and catalysts are desirable. The main goal is to attempt and develop a successful single step synthetic route to 4-bromotrifluoromethylbenzene using these less expensive trifluoromethyl group precursors. The first steps of the project turned out to be successful, with high yields of the ligands, and then obtaining high yields of the precursor. The last experiment involved a 100% yield of 4-bromotrifluoromethylbenzene after several failed attempts.

Introduction

Fluorinated and partially fluorinated polymers have been shown to display unique properties including; resistance to harsh chemical environments, thermal stability, excellent dielectric constants, and easy processing. Fluoropolymers are used among many applications today such as; medical devices with hoses and tubing, safety gear, textiles, aerospace industry, microelectronics, and coating applications for high acidic resistance. Fluorinated substituents are rather small but high in polarity, which provide excellent physical and chemical properties for polymeric materials

There's interest in CF_3 and SF_5 groups due to the possibility of synthetic routes from cheaper bromo and aldehyde functional group precursors. Polymers containing the SF_5 group show promise in properties and applications due to the bulky substituent being an improved CF_3 group. Polymers based on SF_5 groups are thus important to consider for further research exploration for new polymeric structures CF_3 groups have been studied and added to polymers, however pentafluorosulfonyl polystyrene polymers and copolymers based on the SF_5 group have not been studied.

Adding SF_5 groups directly on to organics requires expensive equipment and reactants that are not found in typical research laboratories. However, precursors containing the SF_5 group are available, specifically 3 and 4-bromo pentafluorosulfonyl benzene. These molecules can be converted into styrene in one or two small steps. The goal of our research was to develop a high-

yielding single step synthesis of 3 and 4-sulfonyl pentafluorostyrene for subsequent polymerization and copolymerization.

Due to the cost, we would like to develop these methods using less expensive precursors. We have chosen the trifluoromethyl precursor because it should exhibit similar reactivity. The resulting monomer can then be polymerized, and the materials can compare to the SF₅ analogs. After surveying our options, we decided to use palladium catalyzed coupling of vinyltrimethoxysilane with 4-bromobenzotrifluoride by using a reported ligand. The ligand was expensive but synthesized by using a cheaper method. This report specifically focuses on the synthesis of the ligand and its application toward the coupling first of 4-bromoacetophenone, which is a substrate used directly in the literature, and then of the precursor.

Experimental

Experiment #1) Coupling of 2,6-diisopropylaniline and glyoxal to synthesize (1E,2E)-1,2-Bis(2,6-Diisopropylphenylimino) ethane (DADs)

A solution 1,147ml glyoxal and 5ml methanol are prepared, along with a heated solution of 4.19ml 2,6-diisopropylaniline and 20 µL acetic acid was prepared in a round bottom flask. Solution was mixed under 50°C for one day. Heat was removed from the source, then crystals started to form in the solution. Solution was stirred for 10-hours under room temperature to form solid precipitate. Crystals were separated via vacuum filtration and dried over the course of three days.

Experiment #2) Synthesis of ligand: 1,3-Bis(2,6-diisopropylphenyl) imidazolium chloride (IPr-HCl) from (1E,2E)-1,2-Bis(2,6-Diisopropylphenylimino) ethane

A solution of 45ml purified ethyl acetate, 0.635ml trimethylsilyl chloride, and 1.86g of DADs were prepared in a bottom flask, then placed in an oil bath. Stirring occurred for 2-hours at 70°C. Then, the solution was cooled in an ice bath and continually mixed for an hour. Once a dark brown viscous precipitate appeared, small amounts of ethyl acetate and methyl tert-butyl ether were added while under vacuum filtration. This step helps filter out the solid. Solution was dried for several days with white powder remaining.

Experiment #3) Coupling of 4-Bromoacetophenone with Vinyltrimethoxysilane to synthesize 4-VinylAcetophenone

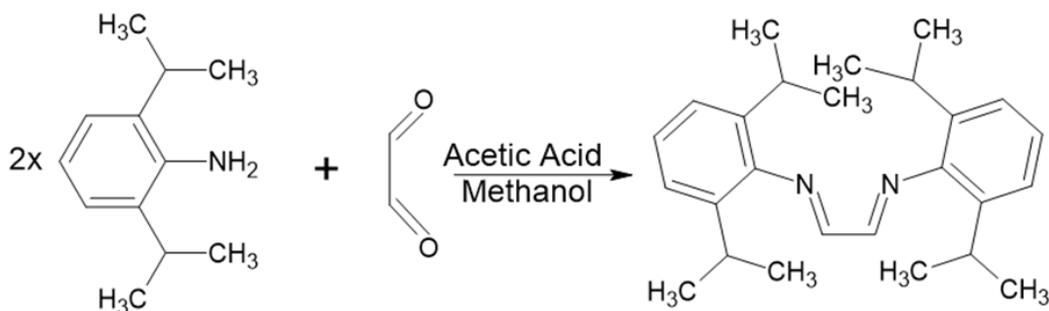
In a round bottom flask; 13mg ligand, 6.7mg palladium acetate, 3ml 1,4-dioxane, 0.2g 4-bromoacetophenone, 0.380ml vinyltrimethoxysilane, and 2ml TBAF/THF were added and stirred in an oil bath at 80°C for 4-hours. After cooling the mixture, the solution was then quenched with 40ml water, then extracted three times with dichloro-methane. It was then dried over with MgSO₄ then separated and dried via vacuum filtration. Solution was then concentrated in the roto evaporator, which evaporated ~98% of solution, all solvent. \

Experiment #4) Coupling of 4-Trifluoromethylstyrene with Vinyltrimethoxysilane to synthesize 4-Trifluoromethylstyrene

Synthetic route was same as experiment #3, however, 0.28ml of 4-bromobenzotrifluoride was used instead of 4-bromoacetophenone.

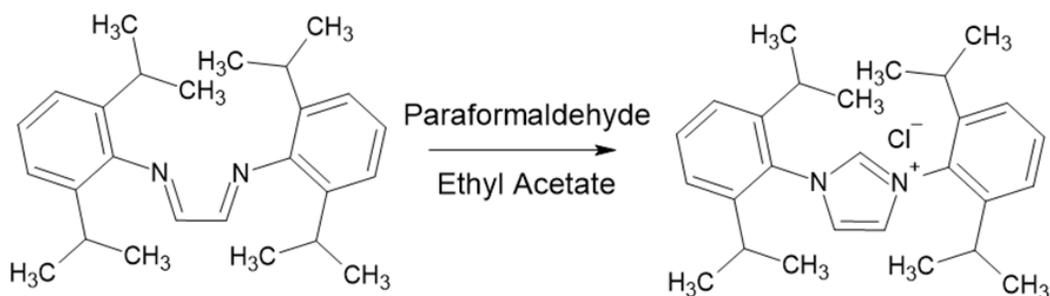
Results

Experiment #1) Synthesis of DADs: (1E,2E)-1,2-Bis(2,6-Diisopropylphenylimino)ethane



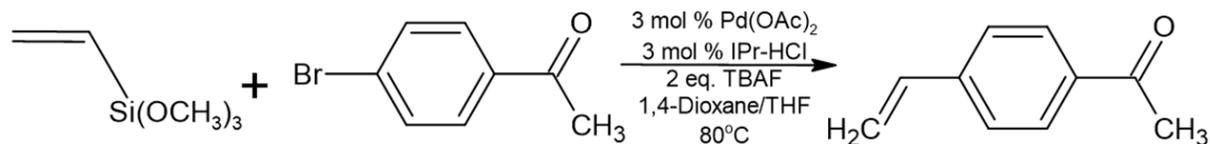
Yellow powder precipitate formed, and NMR analysis concluded that an 89.7% conversion rate was achieved.

Experiment #2) Synthesis of IPr-HCl Ligand: 1,3-Bis(2,6-diisopropylphenyl) imidazolium chloride



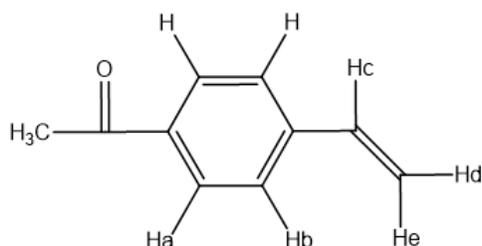
According to NMR analysis, a ~95% yield was obtained of pure product.

Experiment #3) Synthesis of 4-VinylAcetophenone

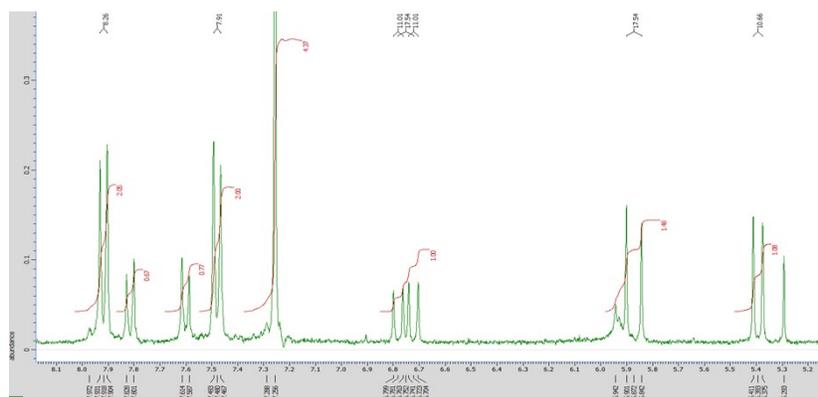


Product was characterized by NMR to conclude a 72% yield.

Proton Assignments for 4-VinylAcetophenone product



NMR Spectra of 4-VinylAcetophenone from experiment

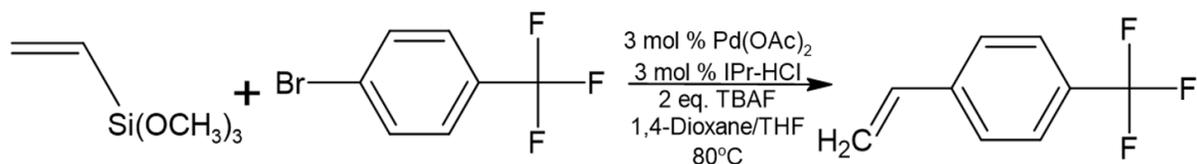


Integration: % Conversion = $2.00/2.77 \times 100\% = 72\%$

Table 1: Proton Assignments with chemical shifts, splitting, and coupling

Assignment	Chemical Shifts	Splitting	Coupling Constants
Ha	7.972 - 7.904	d	8.3
Hb	7.587 - 7.614	d	7.9
Hc	6.704 - 6.799	dd	11.0, 17.5
Hd	5.375 - 5.411	d	10.7
He	5.842 - 5.942	d	17.5

Experiment: #4) Synthesis of 4-TrifluoromethylStyrene



Several trials of this experiment occurred; however, a 23% yield was the highest yield achieved. Experiments varied in amounts of catalyst used, temperature, reaction time, and other parameters. Recently, another reaction of this exact sequence was run with 100% yield, with NMR analysis confirmation.

Discussion

IR analysis confirms the structure of a product in comparison to literature. The DADs precursor was synthesized from 2,6-diisopropylaniline and glyoxal. The reagents were purchased from Sigma-Aldrich. Reaction proceeds easily and after the work up, the DADs product is of high enough purity to continue with the next step directly. Produced a high yield of >89%.

The IPr-HCl ligand is formed as shown in equation 2 with a great yield of ~95%. ¹H NMR and FTIR was used to ensure that the ligand synthesized was in comparison to literature, and pure enough for use as a catalyst the synthesis of the polymer precursors.

4-Vinylacetophenone was formed as shown and produced a 72% yield. ¹H NMR analysis confirmed the proper result of the product. Integration of the ¹H NMR Spectra is shown on the right, with assignments for each proton.

4-Trifluoromethylstyrene is formed as shown but with only a produced yield of 26% yield, with confirmation with ¹H NMR analysis. Reaction conditions with future work will be optimized to improve upon higher yielding one-step syntheses.

Conclusion

¹H NMR and FTIR data confirms that the anticipated chemical structure of the DADs precursor was achieved with a high yield of 89%. ¹H NMR and FTIR characterizations data confirms that the anticipated chemical structure of the IPr-HCl ligand was achieved, thus able to be used as the precursor catalyst. Characterization by ¹H and ¹³C NMR confirms that the anticipated precursor of 4-vinylacetophenone was achieved in high-yield from the single-step synthesis after several reaction modifications, producing a 72% yield.

Experimenting in the synthesis of 4-trifluoromethylstyrene included varying different amounts of reagents and reaction conditions in the experiments. The highest producing yield displayed a 23% conversion rate. Future work includes optimizing the reaction conditions, synthetic methods, and improving variables to improve the reaction and increase the yield of the precursor.

Polymerization of the precursor and improving the synthetic method to achieve 4-pentafluorosulfonyl polystyrene are recommendations for future work. Comparing this polymeric structure and its properties to other similar polymer and copolymer structures may be conducted

by characterization and other test methods. Improving the synthetic methods, increasing yields, and maximizing polymer properties in future work will benefit this research.

A special thanks to Dr. Robert Kopitzke for his support, insight, and confidence on the project, as well as his extensive on the subject matter. Another special thanks to Winona State University for its facilities and student grant funding.

References

1. Expedient Syntheses of the N-Heterocyclic Carbene Precursor Imidazolium Salts Ipr·HCl, Imes·HCl and Ixy·HCl. *Organic Chemistry* 2011, 229–238.
2. Lee, H. M.; Nolan, S. P. ChemInform Abstract: Efficient Cross-Coupling Reactions of Aryl Chlorides and Bromides with Phenyl- or Vinyltrimethoxysilane Mediated by a Palladium/Imidazolium Chloride System. *ChemInform* 2000, 31 (45).
3. Alacid, E.; Najera, C. Aqueous Sodium Hydroxide Promoted Cross-Coupling Reactions of Alkenyltrialkoxysilanes under Ligand-Free Conditions. *JOC Article* 2007, 2315–2322.
4. TWPinternationalpol. <https://www.ipolymer.com/blog/6-acid-resistant-materials-that-can-be-used-effectively-in-a-lab/> (accessed Apr 12, 2021).