

Efficient Synthesis of 5,6-Fused Ring Pyridazines for Advanced Organometallic Semiconductor Applications

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Abstract

Organometallic semiconductors have emerged as pivotal components driving technological innovations in recent years. With a rich history in chemistry, organometallic compounds have gained prominence for their semiconductive properties, leading to significant advancements in fields such as optoelectronics and materials science. This study focuses on streamlining the synthesis of 5,6-fused ring pyridazines, a critical organic building block for cutting-edge organometallic semiconductor technologies. Pyridazines, characterized by a six-membered aromatic ring with adjacent nitrogen atoms, exhibit remarkable stability and have diverse applications in optoelectronics and pharmaceuticals. The primary objective of this research is to develop a more efficient process for the synthesis of 5,6-fused ring pyridazines from 1,2-diphenyl fulvene and hydrazine, intended for use in organometallic semiconductor research. This endeavor seeks to optimize the production of this crucial building block, facilitating advancements in the field. The experimental design for this research project is organized in two phases: 1. Synthesis and Isolation. 2. Analysis. The synthesis of the 5,6-fused ring pyridazine was accomplished by reacting 1,2-diphenyl fulvene with excess hydrazine. The synthesized product was then separated and extracted using separatory funnel procedures with an associated magnesium sulfate (MgSO_4) drying agent. The product was then isolated using a simple distillation procedure followed by trituration. The product was then analyzed using several analytic techniques: percent yield, IR spectroscopy, and melting point analysis. The results and conclusions of this research project are yet to be determined as research is still in progress. There is also a possibility for an additional inorganic reaction to be conducted with the product and thallium to produce the desired organometallic semiconductor.

Introduction

Organometallic semiconductors have emerged as pivotal components driving technological innovations in recent years. With a rich history in chemistry, organometallic compounds have gained prominence for their semiconductive properties, leading to significant advancements in fields such as optoelectronics and materials science [1]. These advancements have led to the development of prominent new technologies such as OLED screens, nano spintronic communication devices, and various impactful pharmaceutical applications (anti-cancer therapy medications, antiparasitic drugs, and fungicide reagents) [2-7]. While producing newer and better semiconductors will always be an important field of study, a significant portion of the research in this field has been dedicated to finding more efficient ways of synthesizing the organic building blocks of the semiconductors currently in use. This study focuses on streamlining the synthesis of 5,6-fused ring pyridazines, a critical organic building block for cutting-edge organometallic semiconductor technologies. Pyridazines are a group of organic compounds composed of a six-membered, aromatic ring with two adjacent nitrogen atoms [8]. The resulting molecular formula for all pyridazines is $\text{C}_4\text{H}_4\text{N}_2$. Pyridazines are very stable compounds with the ability to attach a variety of R-groups to the 4 carbon positions in the ring. The stability and flexibility of pyridazine compounds are precisely the qualities that make them desirable organic foundations for organometallic semiconductors. The goal of this study is to demonstrate a new and more efficient process to synthesize 5,6-fused ring pyridazines from 1,2-diphenyl fulvene and hydrazine, intended for use in organometallic semiconductor research. This endeavor seeks to optimize the production of this crucial building block, facilitating advancements in the field.

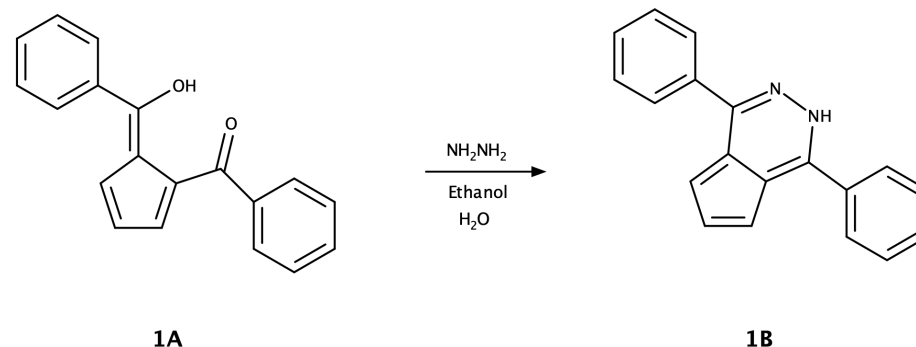
Methods

Synthesis and Isolation of 5,6-Fused Ring Pyridazines

- The synthesis and isolation of 5,6-fused ring pyridazines were carried out using a 100 mL, round-bottom flask containing 50 mL of ethanol ($\text{C}_2\text{H}_5\text{OH}$) and approximately 0.941 mmol (0.258 g) of 1,2-diphenyl fulvene. A heating mantle with a stir bar was used to stir the mixture, to which an excess of 1 mL of hydrazine (N_2H_4) was added. The solution was stirred and left to react for 24 hours.
- After this reaction period, 25 mL of water was added to the reaction solution. The solution was then transferred to a separatory funnel to complete an extraction procedure. The extraction was achieved using dichloromethane (CH_2Cl_2) as the organic phase. The initial extraction consisted of 15 mL of dichloromethane followed by two additional extractions, each using 15 mL of dichloromethane (CH_2Cl_2).
- The extracted product was then subjected to distillation using a water bath and a simple distillation apparatus. During distillation, condensation inside the round-bottom flask was observed at a temperature of 33°C . The first drop of distillate fell at 3.2 seconds into the distillation process. After 25 minutes of distillation, the condensation thermometer read 41°C with significant amounts of condensation. At the 50-minute mark, the amount of condensation began to significantly decrease with drops occurring at a rate of 1-2 per minute and condensation thermometer reading as high as 60°C . It was determined by the research team that more distillation needed to occur to successfully separate the pyridazine product from the dichloromethane solvent. The simple distillation apparatus was then hooked up and subjected to vacuum for the next 30 minutes. The rate of distillation was significantly higher under vacuum until at the 90-minute mark the rate slowed, and the condensation temperature rose to 73°C . This prompted the cessation of distillation at 91 minutes.
- After distillation, the solution was left overnight in the fume hood. Upon observation the next day, an orange-brownish residue was noted. To produce the needed homogeneous pyridazine product, a trituration procedure was completed. The trituration was completed using an ice bath, pentane (C_5H_{12}), and a glass rod (C_5H_8) was added to the solid product, 2 mL per round, and placed in the ice bath. The solution was then stirred and scraped to promote agitation of the product in the pentane with a glass rod to remove contaminants. Subsequently, the mixture was poured into a vacuum-sealed Buchner funnel lined with filter paper. This process was repeated multiple times until all gatherable precipitate was obtained. The solid obtained from this filtration process was left to dry overnight. The following day, the solid was scraped to ensure its crystalline nature and then stored in a vial for further analysis and use in subsequent experiments.

Analysis of 5,6-Fused Ring Pyridazine Product

- The solid product was weighed to calculate the percent yield of the reaction.
- The solid was then observed using melting point and IR spectroscopy techniques to analyze the purity and accuracy of the reaction procedure.



Scheme 1. Synthesis of the desired 5,6-fused ring pyridazine. (1A) 1,2-diphenylfulvene, (1B) 1,2- $\text{C}_5\text{H}_3(\text{CC}_6\text{H}_5\text{NH})(\text{CC}_6\text{H}_5\text{N})$ 5,6-fused ring pyridazine product.

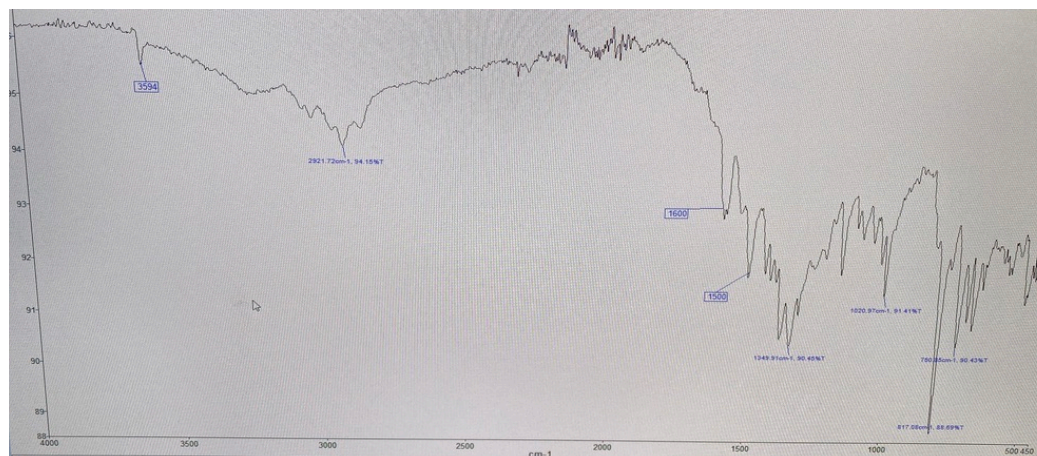


Figure 1. IR spectroscopy of the synthesized 1,2- $\text{C}_5\text{H}_3(\text{CC}_6\text{H}_5\text{NH})(\text{CC}_6\text{H}_5\text{N})$ 5,6-fused ring pyridazine product. The peak at 3594 cm^{-1} is indicative of the N-H secondary amine bond found in the central ring of the desired pyridazine product. The peak at 2922 cm^{-1} corresponds with the aromatic rings found in the pyridazine. The peak at 1349 cm^{-1} is indicative of C-N bonds located in an aromatic ring, also found in the central ring of the pyridazine product.

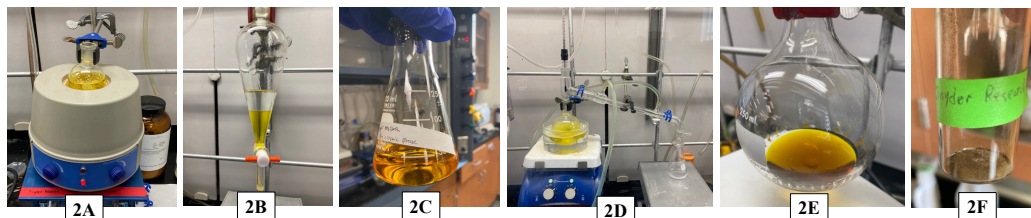


Figure 2. Reaction procedure for the synthesis, extraction, isolation, and purification of the desired 1,2- $\text{C}_5\text{H}_3(\text{CC}_6\text{H}_5\text{NH})(\text{CC}_6\text{H}_5\text{N})$ 5,6-fused ring pyridazine product.

Results and/or Conclusion

- The reaction procedure, extraction, distillation, and trituration procedures were successful in synthesizing and isolating the desired pyridazine product. The physical appearance of the brownish-black crystalline powder produced in this project is consistent with the desired pyridazine product [SOURCE].
- The final pyridazine product was weighed to be 0.070g. This gave us a percent yield of 27.6%. The low percent yield can be attributed to a variety of factors, but mainly from transferring our product to multiple different vessels during the trituration procedure. There was a notable amount of product that was left behind in each of these vessels due to the sticky nature of the pyridazine powder when in contact with pentane (C_5H_{12}). To limit product loss in future reactions, the number of vessel transfers during the trituration procedure should be kept to a minimum.
- The melting point range was tested and found to be $152.8^\circ\text{C} - 153.2^\circ\text{C}$. This very tight melting point range is indicative of a pure pyridazine product.
- The pyridazine product was analyzed using IR spectroscopy and was determined to be representative of the desired pyridazine product. The critical peak at 3594 cm^{-1} was indicative of the N-H bond present in the desired product. Another critical peak located at 1349 cm^{-1} was indicative of the aromatic N-C bonds found in the desired pyridazine product.

Future Work

- Continuing the synthesis of the organometallic semiconductor by reacting the 5,6-fused ring pyridazine product with thallium salt to create a semiconductive transitional metal complex
- Additional testing and work with the transitional metal complex to determine its semiconductive properties and efficacy as a practical semiconductor.

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