Dibenzophosphole Synthesis from 4-4'-ditertbutyl-1,1'-biphenyl by Double C-P Bond Formation

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INTRODUCTION

Organic light-emitting diode (OLED) displays are a type of LED that uses organic compounds to emit light.[1] These screens are gaining prevalence due to their improved image quality and efficiency.[2]

Figure 1. The Apple Watch (left), and the color contrast between OLED and LCD displays.[3,4]

Because of their pi-conjugated, light-emitting systems, phosphole research has been shown to be useful in the development of OLED displays.[2] Due to their high degree of conjugation, there is interest in dibenzophospole research and their application to OLED technology.[2]

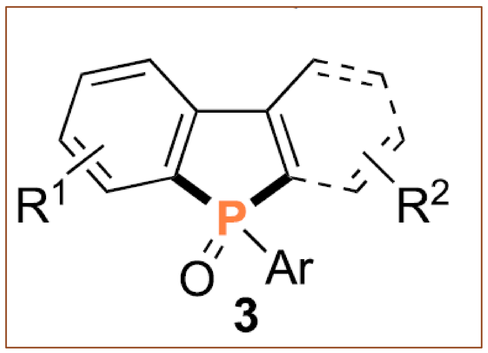
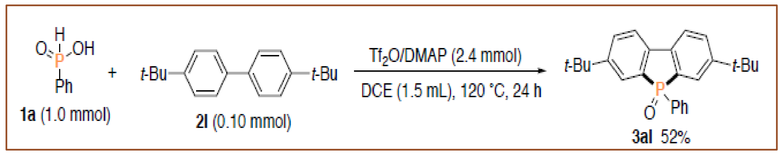


Figure 2. Dibenzophosphole structure indicating locations for potential attachment sites. (R^1 & R^2).[5]

Traditional dibenzopohspole synthesis is often costly and time-consuming.[5] Recently, Nishimura et al developed a simplified method for the direct preparation of dibenzophospholes. The focus of our research is to replicate aspects of Nishimura et al's research and apply this method to generate novel compounds.



Scheme 1. Scheme used by Nishimura et al. 1a = phosphinic acid.; 2l = 4,4'-di-*tert*-butyl-1,1'-biphenyl; *3al = the dibenzophosphole product,* 3,7-di-*tert*-butyl-5-phenylbenzo[*b*]phosphindole 5-oxide.[5]

RESULTS

The reaction is air-sensitive, so it was carried out under nitrogen conditions in a pressure tube which was placed behind a blast shield.

Figure 3. Reaction setup with the pressure tubes in an oil bath at 120°C behind a blast shield due to the reaction's pressure.

Trial 1: The reaction mixture was heated at 120°C for 24 hours. Following a thin-layer chromatography (TLC) test, there was only faint evidence of product and significant unreacted starting material as shown by the large spots under the top line in figure 4 (left).

Trial 2: The reaction was heated for 96 hours. TLC showed emissive blue spots as the likely dibenzophosphole product, but there were still significant unreacted starting materials.

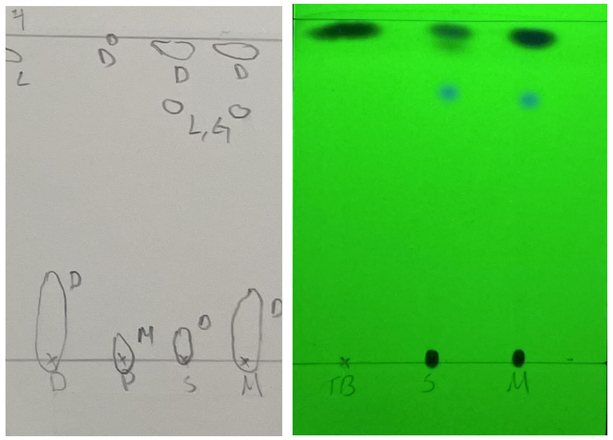


Figure 4. Trial 1 TLC (left) comparing starting materials with the product (S) and a mix of all (M). Spot descriptions: D = dark; L = light; G = glows; M = medium. Trial 2 TLC (right) with emissive blue spots showing likely product.

CONCLUSION AND FUTURE WORK

Replicating Nishimura et al's method would open the door to further study and utilize dibenzophospholes. Establishing a reproducible protocol is one of the goals of our research. The next steps are to isolate the product through column chromatography, and to raise the heat throughout the 96-hour reaction period to increase product yield.

REFERENCES

1. JOLED. (2021). *Characteristics of OLED Display OLEDIO™*. Retrieved April 8, 2021, from https://www.j-oled.com/eng/technology/

2. Duffy, M. P., Delaunay, W., Bouit, P., & Hissler, M. (2016). π-conjugated phospholes and their incorporation into devices: Components with a great deal of potential. *Chemical Society Reviews*, *45*(19), 5296-5310.

3. Nast, C. (2019, September 18). *Apple watch series 5 review: Always on time*. Wired. https://www.wired.com/review/apple-watch-series-5/

4. Purdy, K. (2021, April 9). *Our tested LCDs are a budget option for iPhone X, XS, and XS Max screens*. iFixit. https://fr.ifixit.com/News/35826/our-tested-lcds-are-a-budget-option-for-iphone-x-xs-and-xs-max-screens

5. K. Nishimura, K. Hirano, M. Miura, Org. Lett. 2020, 22, 3185– 3189