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### Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

# Synthesis and Characterization of a New Chiral Pentacyclic Phosphine

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To cite this article: Souad Moussa, Faouzi Aloui & Béchir Ben Hassine (2013): Synthesis and Characterization of a New Chiral Pentacyclic Phosphine, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 43:2, 268-276

To link to this article: <u>http://dx.doi.org/10.1080/00397911.2011.596986</u>

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*Synthetic Communications*<sup>®</sup>, 43: 268–276, 2013 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911.2011.596986

## SYNTHESIS AND CHARACTERIZATION OF A NEW CHIRAL PENTACYCLIC PHOSPHINE

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#### **GRAPHICAL ABSTRACT**



**Abstract** A new helically chiral pentacyclic phosphine, containing one thiophene ring, was prepared in good yield and purity via a five-step sequence involving a Wittig reaction, a palladium-catalyzed Mizoroki–Heck coupling, and classical oxidative photocyclization reactions. The investigation using ultraviolet–visible spectroscopy shows that the helicene precursor of the target helical phosphine as well as its phosphine oxide have interesting behaviors.

Keywords Heck reaction; helicene; phosphine; photocyclization; Wittig reaction

#### INTRODUCTION

Helicenes are an extremely attractive class of conjugated molecules consisting of *ortho*-fused aromatic rings.<sup>[1–5]</sup> They combine the electronic properties afforded by their extensive conjugated  $\pi$  system with the chiroptical properties<sup>[6,7]</sup> afforded by their peculiar helixlike structure. However, interest in heterohelicenes has been not merely speculative but also applicative because these molecules have a nicely delocalized  $\pi$ -electron system and exhibit interesting opto- and photoelectronic

Received May 23, 2011.

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properties.<sup>[8,10]</sup> Recently, some potential applications of these helical compounds have been discovered.<sup>[11]</sup> The preparation of helicenes has become an increasingly important subject. Helicenes, especially heterohelicenes, are promising candidates as chiral auxiliaries and ligands for various asymmetric reactions because of their stable polyconjugated helical framework and the presence of heteroatoms, such as sulfur, nitrogen, and oxygen. The heteropentahelicenes are the smallest group in the helical family and exhibit intriguing electrical and optical properties.<sup>[12,13]</sup> Beside carbohelicenes, many heterohelicenes have been investigated for various properties and applications such as circularly polarized luminescence<sup>[14]</sup> and nonlinear optics. Not only the main skeleton frameworks but also the substituted groups can determine the properties of these compounds. In recent years, the preparation of heterohelicenes has been studied extensively to exploit the unique properties of these molecules. However, thiahelicenes bearing phosphoryl groups were not sufficiently elaborated despite their possible applications in various branches of chemistry.

The present work reports the synthesis of a new helically chiral pentacyclic system 1, containing one thiophene unit and bearing a bromine atom. The synthetic route involves a Wittig reaction and Mizoroki–Heck coupling followed by oxidative photocyclizations. The resulting bromothiahelicene was then converted into the corresponding helical phosphine 2 through lithiation–phosphination. The new helicene derivatives have been characterized by the usual <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopic techniques. Their optical properties have also been investigated and show interesting behaviors.

#### **RESULTS AND DISCUSSION**

The synthetic route to pentahelicene derivative 1 started from the synthesis of the substituted alkenes 5 [(E, Z) isomers], which are obtained through Wittig reaction between the phosphonium salt 3 and 2-thiophene carbaldehyde 4. The photocyclization of diarylethenes 5 affords the phenanthrene-like system 6 in 85% yield (Scheme 1).

This last one was reacted with an excess amount of 4-bromostyrene according to the following conditions:<sup>[15]</sup> 1% of Hermann's palladacycle [*trans*-di( $\mu$ -acetato)-bis[o-(di-o-tolylphosphino)benzyl]dipalladium] as the catalyst, sodium acetate as the base, and *N*,*N*-dimethylacetamide (DMA) as the solvent. The mixture was heated at 140°C for about 48 h to give the desired diarylethene 7 in 76% yield (Scheme 2). The resulting alkene 7 was subjected to photocyclization in toluene, on a 200-mg scale per run, for about 3 h. The photolysis was carried out in the presence of a stoichiometric amount



Scheme 1. Synthetic route toward the phenanthrene-like derivative 6.



Scheme 2. Synthetic strategy for the synthesis of the helically chiral phosphine 2.

of iodine as an oxidizing agent and an excess of propylene oxide<sup>[16]</sup> to give the expected bromothiapentahelicene 1 in 64% yield, after purification by column chromatography.

Good analytical data were obtained for the helically chiral compound 1, which is a white solid. Characteristic spectroscopic data of this compound consisted of a doublet <sup>1</sup>H NMR resonance at 8.85 ppm for H-13 (J=1.5 Hz) in CDCl<sub>3</sub> at room temperature (Fig. 1).

No other isomer was isolated from the reaction mixture, indicating that the ring closure of alkene 7 had occurred from the opposite side of the tricyclic system. Especially, the anthracene-like derivative 8 (Fig. 2) has not been formed through the cyclization step, because this kind of regioisomer should display characteristic singles in <sup>1</sup>H NMR for both H-6 and H-13 at low field.<sup>[17,18]</sup>



Figure 1. <sup>1</sup>H NMR spectra of the thiapentahelicene 1, recorded in CDCl<sub>3</sub>.



Figure 2. Chemical structure of the anthracene-like derivative 8.

The last step of the synthetic sequence is formation of the phosphine, which can be achieved through lithiation-phosphinylation of the bromohelicene **1**. Thus, the metallation of **1** proceeded well via metal-halogen exchange using *n*-butyllithium at -78 °C. Subsequent treatment of the resulting lithiated species with chlorodiphenylphosphine yielded the desired phosphinohelicene **2** in 78% yield and in 25% overall yield over five steps, starting from the readily available 2-thiophene carbaldehyde **4** (Scheme 2). This resulting helically chiral trivalent phosphine was a slightly airsensitive solid. It is better handled and stored under an inert atmosphere or treated with a 35% hydrogen peroxide solution to give the corresponding phosphine oxide **9** in excellent yield. Compound **9** is more stable than phosphine **2** and could be resolved, by high-performance liquid chromatography (HPLC), using a column packed with cellulose-tris(3,5-dimethylphenyl-carbamate) and *n*-heptane/2-propanol (80:20) mixture as the mobile phase.<sup>[19]</sup>

#### **Optical Properties**

The optical properties of the pentahelicene derivatives 1 and 9 were investigated using the UV-vis absorption for dilute chloroform solutions (Fig. 3).<sup>[20]</sup>



Figure 3. Absorption spectrum of compounds 1 and 9 obtained for  $CHCl_3$  solutions. (Figure is provided in color online.)

 Table 1. Physical proprieties of the helically chiral pentahelicenes 1 and 9

Compound	$\lambda_{\max}^{Abs}$ (nm)	$E^{Opt}$ (eV)
1	257	3.43
9	288	3.32

The results summarized in Table 1 show an absorption maxima at 257 nm for 1 and 288 nm for 9, respectively.

The UV absorption results show that the optical band gap of these new helicene derivatives was lower than 3.5 eV. This result can be originated from the formation of aggregation to  $\pi - \pi^*$  stacking or intermolecular interaction caused by their nonplanar structures. Moreover, the incorporation of a (POPh<sub>2</sub>) group instead of the bromine atom in helicene 1 resulted in decreasing the gap energy of the corresponding derivative. The thiapentahelicenes 1 and 9 show greater optical band gap than the functionalized thiaheptahelicene derivatives, which have been developed by Bossi et al., indicating that the optical properties are not significantly affected by the electron delocalization but are affected by the functional groups linked to the helicene backbone.<sup>[21]</sup>

#### CONCLUSION

In this work, we have developed a straightforward method for the preparation of a new helical chiral phosphine starting from readily available and inexpensive materials. We completed the synthesis of the framework of 2 in five steps, with an overall yield of 25%, under mild conditions following an easy purification. The new chiral phosphine could serve as a metal-chelating agent leading to helical metallated complexes capable of catalyzing asymmetric reactions.

#### **EXPERIMENTAL**

All reactions were performed under an argon atmosphere and were monitored by thin-layer chromatography (TLC) Merck 60 F-254 silica-gel plates (layer thickness 0.25 mm). Column chromatography was performed on silica gel (70-230 mesh) using ethyl acetate and cyclohexane mixture as eluents. Melting temperatures were determined on an Electrothermal 9002 apparatus and were reported uncorrected. NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 MHz (<sup>1</sup>H), 121.5 MHz (<sup>31</sup>P), and 75 MHz (<sup>13</sup>C). All chemical shifts were reported as  $\delta$  values (ppm) relative to internal tetramethylsilane. Toluene, methanol, tetrahydrofuran, and dichloromethane were distilled prior to use. Photocyclizations were carried out in a 1.5-L water-cooled quartz photoreactor equipped with a high-pressure mercury immersion lamp [Heraeus TQ 500]. Mass spectra (MS) were recorded on a Hewlett-Packard HP 5989 instrument. High-resolution mass spectra (HRMS) were recorded on a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) Perspective Biosystems Voyager DE-STR instrument.

#### **Diarylethenes (5)**

A sodium methoxide solution ( $120 \mu$ L, 1 M in methanol) was added over 0.5 h under Ar to a solution of the triphenylphosphonium salt **3** (1 g, 1.95 mmol) and 2-thiophene carbaldehyde (0.14 mL, 1.5 mmol) in dry methanol (25 mL). Stirring was continued for 3 h. The reaction mixture was concentrated under vaccum to half its volume. Water was added, and the solution was extracted three times with a large volume of CH<sub>2</sub>Cl<sub>2</sub>. After drying and solvent evacuation, the residue was chromatographed on silica gel using cyclohexane / ethyl acetate (98: 02) as the eluent to yield 290 mg (80%) of compounds **5** [(*E*, *Z*) isomers]; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 6.60 (d, *J*=12 Hz, 2H), 6.91 (m, 1H), 6.94 (d, *J*=16 Hz, 2H), 7.01–7.12 (m, 2H), 7.20–7.48 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 121.31, 121.55, 122.53, 124.04, 124.81, 125.84, 126.59, 126.67, 127.02, 127.57, 127.76, 127.80, 128.48, 130.63, 131.76. 131.86, 135.97, 136.25, 139.39, 142.53.

#### Procedure a for the Photocyclization Reactions A

Iodine (1.1 equiv.) was added to a solution of the olefin in toluene. The solution was degassed for 15–30 min, and propylene oxide (50 equiv.) was added. Irradiation was performed using a falling-film photoreactor and a high-pressure Hg-vapor lamp (500 W, Heraeus). The argon flow was maintained throughout the irradiation. The reaction was monitored by TLC. Then the reaction mixture was concentrated in vacuum, and the crude product was purified by column chromatography on silica gel.

#### Phenanthrene-Like System (6)

Compound **6** was obtained from alkenes **5**, in 85% yield, according to the procedure **A**. It was purified by column chromatography using cyclohexane as the eluent and resulted as a white solid; mp = 142–144 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 7.61 (m, 2H), 7.7 (d, J = 9 Hz, 1H), 7.8 (d, J = 8.7 Hz, 1H), 7.9 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 5.1 Hz, 1H), 8.46 (d, J = 1.5 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 124.62, 124.79, 126.19, 126.44, 127.77, 128.61, 129.44, 130.18, 130.47, 131.85, 134.97, 138.25; ESI-MS: m/z = 263.1 [M<sup>+</sup>].

#### **Diarylethene (7)**

A solution of the thiophene-like system **6** (1 g, 3.80 mmol) and dry sodium acetate (342 mg, 4.18 mmol) in *N*,*N*-dimethylacetamide (8 mL) was placed in a double-necked flask fitted with a septum, repeatedly degassed, and purged with argon. To this was then added 0.7 mL of 4-bromostyrene (5.32 mmol), and the mixture was heated to 100 °C. When this temperature was reached, a solution of the Herrmann's catalyst (35 mg, 1%) in *N*,*N*-dimethylacetamide (3 mL) was added, and the reaction mixture was heated to 140 °C. Heating was maintained for about 48 h. The reaction was quenched by an addition of 5% HCl solution, stirred for 30 min at room temperature, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined layers were dried over MgSO<sub>4</sub> and evaporated to dryness. After column chromatography with cyclohexane / ethyl acetate 90:10 as the eluent, the final product **7** was obtained in

76% yield (1.05 g) as a light yellow solid; mp = 177–149 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 7.22 (d, J = 16.5 Hz, 1H, H<sub>vinyl</sub>), 7.35 (d, J = 16.5 Hz, 1H, H<sub>vinyl</sub>), 7.44–7.55 (m, 4H), 7.63 (d, J = 5.4 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.77 (dd, J = 8.4 Hz, and J = 1.8 Hz, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 8.04 (d, J = 5.4 Hz, 1H), 8.35 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 121.21, 121.84, 122.31, 123.04, 123.14, 125.15, 126.48, 128.31, 128.43, 129.38, 129.92, 129.98, 131,02, 132.25, 135,37, 136.30, 136.66, 138.27.

#### Bromohelicene (1)

The photocyclization of 200 mg (0.41 mmol) of compound 7 in 1 L of toluene yielded 127 mg of compound 1 (64%) as a white solid, after column chromatography on silica gel (eluent: cyclohexane / ethyl acetate 98:02); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 7.5 (d, J = 5.4 Hz, 1H), 7.67 (dd, J = 8.7 Hz and J = 1.5 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.90–7.82 (m, 5H), 7.96 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.85 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 119.15, 122.15, 124.56, 125.37, 125.97, 126.01, 126.28, 126.85, 127.26, 127.48, 128.79, 129.66, 129.69, 131.52, 131.66, 131.78, 131.88, 132.59, 136.11, 140.00. Anal. calcd. for C<sub>20</sub>H<sub>11</sub>BrS: C, 66.13; H, 3.05. Found: C, 66.07; H, 3.03.

#### Diphenylphosphinohelicene (2)

To a solution of the bromothiapentahelicene 1 (0.2 g, 0.55 mmol) in anhydrous THF (5 mL) was added 300 µL of *n*-BuLi (2 M in hexane), under argon. The mixture was stirred at -78 °C for 1 h. Then a solution of chlorodiphenylphosphine (110  $\mu$ L, 0.60 mmol) in THF (3 mL) was added dropwise at -78 °C. The resulting mixture was stirred overnight at room temperature. The solution was then cooled at 0°C, and a 30% aqueous NaOH solution was added dropwise. The organic phase was extracted with ether under argon, dried over MgSO<sub>4</sub>, and filtered through a short silica-gel column with cyclohexane / ethyl acetate (90:10) as the eluent to afford 2 as a white solid in 78% yield; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 7.08–7.15 (m, 1H), 7.19–7.31 (m, 8H), 7.36–7.41 (m, 2H), 7.67–79 (m, 9H), 8.52 (d, J = 8.4 Hz1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm): 120.03, 123.65, 124.50, 124.59, 124.94, 125.13, 125.31, 125.72, 126.54 (d, *Jcp* = 2.4 Hz, CH), 126.69, 126.93, 127.33, 127.42, 127.45, 127.492, 127.51, 127.54, 128.01 (d, *Jcp* = 1.95 Hz, CH), 128.93, 130.29, 130.80, 131.72, 132.09, 132.12, 132.37 (d,  $J_{cp} = 2.32$  Hz, CH), 134.49, 134.82, 135,80 (d, Jcp = 7.57 Hz, C), 135.92, 135.96, 136.04 (d, Jcp = 8.6 Hz, C),136.18 (d, Jcp = 12.6 Hz, C), 142.32; <sup>31</sup>P NMR (121.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): -16.22 (s); ESI-MS:  $m/z = 468.1 \, [M^+]$ .

#### Diphnenylphosphine Oxide 9

A 35% hydrogen peroxide solution (15 mL) was added at room temperature to a solution of phosphine 2 (50 mg, 0.106 mmol) in 15 mL of dichloromethane. The resultant mixture was stirred vigorously at room temperature until the reaction was completed (30 min, monitored by TLC). The organic layer was separated, and the aqueous phase was extracted three times with dichloromethane. The organic layers were combined and dried over MgSO<sub>4</sub>, and the solvent was evaporated to give 84 mg (94%) of pure

diphenylphosphine oxide **9**; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 7.10–7.90 (m, 1H), 7.34–7.42 (m, 6H), 7.36–7.41 (m, 2H), 7.47 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.52–7.59 (m, 2H), 7.65–7.75 (m, 4H), 7.79–7.98 (m, 6H), 8.43 (d, J = 8.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 121.56, 125.24, 126.58, 126.79, 126.85, 127.72, 127.95, 128.14, 128.37, 128.78 (d, *J*cp = 3.37 Hz), 129.07, 130.17, 131.89, (d, *J*cp = 3.22 Hz), 132.09, 132.14, 132.25 (d, *J*cp = 3.30 Hz, C), 132.27, 132.63, 133.16, 136.68, 136.83; <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 24.50 (s), ESI-MS: *m*/*z* = 484.1 [M<sup>+</sup>]. HRMS (MALDI-TOF) calcd. for C<sub>32</sub>H<sub>21</sub>OPS [M<sup>+</sup>]: 484.10486. Found: 848.10507.

#### ACKNOWLEDGMENT

The authors are grateful to Direction Générale de la Recherche Scientifique of the Tunisian Ministry of Higher Education and Scientific Research for financial support.

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