Synthesis of 2,5-diphenyl-3,4-di(phenylethenyl)cyclopentadienone, -pyrrole and -thiophene

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(Received on 14th April 2021, accepted in revised form 22nd November 2021)

Summary: 2,5-Diphenyl-3,4-di(phenylethenyl)cyclopentadienone (**2**), -pyrrole (**3**), and -thiophene (**4)** have been synthesized by bi-steps strategy. Step one involves the synthesis of cinnamil (**1**) by the condensation of 2,3-butanedione with benzaldehyde in the presence of Pyrrolidine as a catalyst. Step two involves the synthesis of 2,5-diphenyl-3,4-di(phenylethenyl)cyclopentadienone (**2**), -pyrrole (**3**), and -thiophene (**4**) by the condensation of cinnamil (**1**) with dibenzyl ketone, dibenzylamine, and dibenzyl sulfide, respectively in the presence of sodium hydride (base) and methylene chloride (solvent) while stirring. ^{1}HNMR, LC-MS, IR, UV-visible, and fluorescence spectroscopy were used to confirm these products **(2-4).** Our method facilitated the proficient installation of four various groups on the cyclopentadienone (**2**), pyrrole (**3**), and thiophene (**4**) rings in two steps with an extended conjugated framework.

Keywords: Cinnamil, Cyclopentadienones, Pyrrole, Thiophene, Electron absorption, Emission spectra.

Introduction

Cyclopentadienone, pyrrole, and thiophene are versatile ring systems possessing a variety of applications in pharmaceutics, natural products, nonlinear optics, and supramolecular chemistry [1]. Arylated cyclopentadienones have received much more attention from scientists for their use, as a photoluminescent probe due to their low HOMO-LUMO bandgap. Due to the extended conjugation upon oligomerization, they can be used as semiconductors in field-effect transistors (FET) and, as an emissive or absorbing material for LEDs or photovoltaics [2].

Particularly, pyrrole ring has been found in many compounds that occurred in nature such as heme, vitamin B12, and chlorophyll. Pyrrole is significantly privileged heterocycle moiety because of its occurrence in biomedical and pharmaceuticals. Certain antitumor agents, potassium-competitive acid blockers, the leading cholesterol-lowering drug Lipitor, and numerous natural products contain a pyrrole ring as a core structure. Additionally, pyrrole-based compounds have been reported as valuable building blocks for the synthesis of bioactive functionalized materials [3]. Therefore, several synthetic procedures for the synthesis of these systems have been cited in the literature [4].

The functionalized and polysubstituted thiophene-based conjugated polymers have gained attention in the current years as compared to other conjugated polymers. They can be structurally manipulated to obtain many novel polymers. Substituting thiophene imparts excellent electronical properties to be useful in designing liquid crystals, field-effect transistors, molecular wires, solar cells, semiconductors, photovoltaic material [5], non-linear optical material [6], and electroluminescent polymers in organic light-emitting diodes (OLEDs). They are easy to prepare and have efficient color tuning ability [7]. Other than electronic properties some thiophene derivatives are biologically active and can be used as anti-inflammatory [8, 9] analgesic, antioxidant, anti-cancer [10] and as raw material to produce herbicides/pesticides [11-14]. Thiophene based compounds have also been employed to treat Alzheimer's disease.

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The goal of this study is the synthesis of 2,5-diphenyl-3,4-di(phenylethenyl)cyclopentadienone (2), -pyrrole (3), and -thiophene (4) from cinnamil (1) by two steps strategy. Such systems have been prepared lastly from 1,3-dicarbonyl compounds. Classical methods, like Paal−Knorr, were trustworthy for the preparation of different thiophene ring-based moieties [15].

Tetraphenylcyclopentadienone (tetracyclone), was firstly reported by Dilthey and their group [16, 17]. Various methods have been designed in the literature for the synthesis of tetracyclone [18-20]. Scheme I involves the Knoevenagel condensation of benzil and dibenzyl ketone in basic media (*i.e.* potassium hydroxide in ethanol) to obtain a solid product (deep purple-color, M.P. 219−221°C).

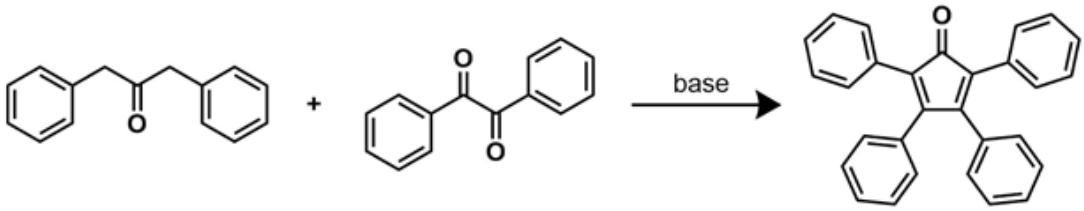
Cyclization of 1,4-diarylbutane-1,4-diones with suitable reagents lead to the formation of 2,5-diarylthiophenes and 2,5-diarylpyrroles. Lawesson's reagent (LR) were used for the synthesis of thiophenes via ring closure [21] whereas a pyrroles can be obtained by reacting 1,4-diketone with ammonia or primary amine [22] as shown in scheme II.

Result and Discussion

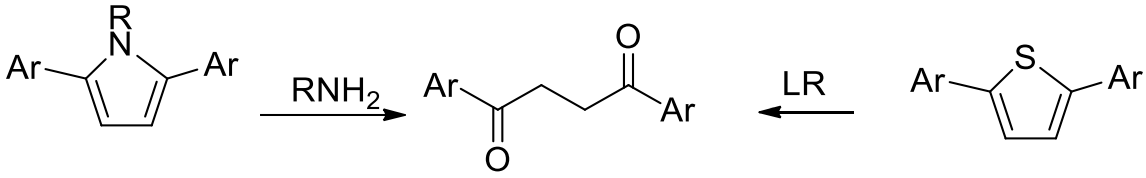
The synthesis of 2,5-diphenyl-3,4-di(phenylethenyl)cyclopenta-2,4-dien-1-one **(2),** -pyrrole **(3)** and -thiophene **(4)** were carried out by condensing the 1,6-diphenylhexa-l,6-diene-3,4-dione (cinnamil) (1) with dibenzyl ketone, dibenzylamine and dibenzyl sulfide respectively.

Synthesis of cinnamil was done with the excess of benzaldehyde with 2,3-Butanedione in the presence of pyrrolidine (Scheme III) [23].

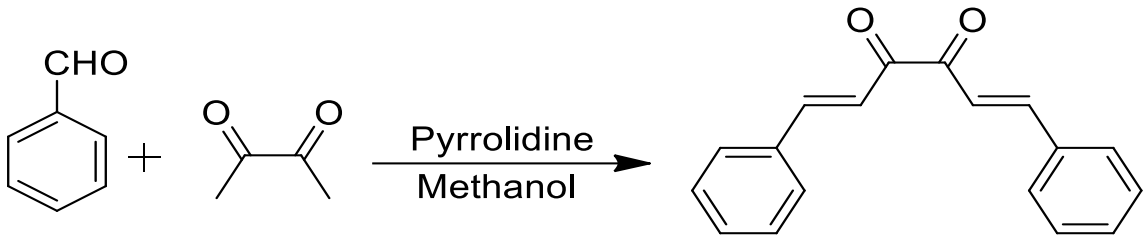
High yields of 2,5-Diphenyl-3,4-di(phenylethenyl)cyclopenta-2,4-dien-1-one (2), -pyrrole (3), and -thiophene (4) were obtained by condensing the cinnamil (1) with dibenzyl ketone (1,3-diphenylacetone), dibenzylamine, and dibenzyl sulfide, sodium hydride was used as a base and dry methylene chloride was used as a solvent (Scheme IV).



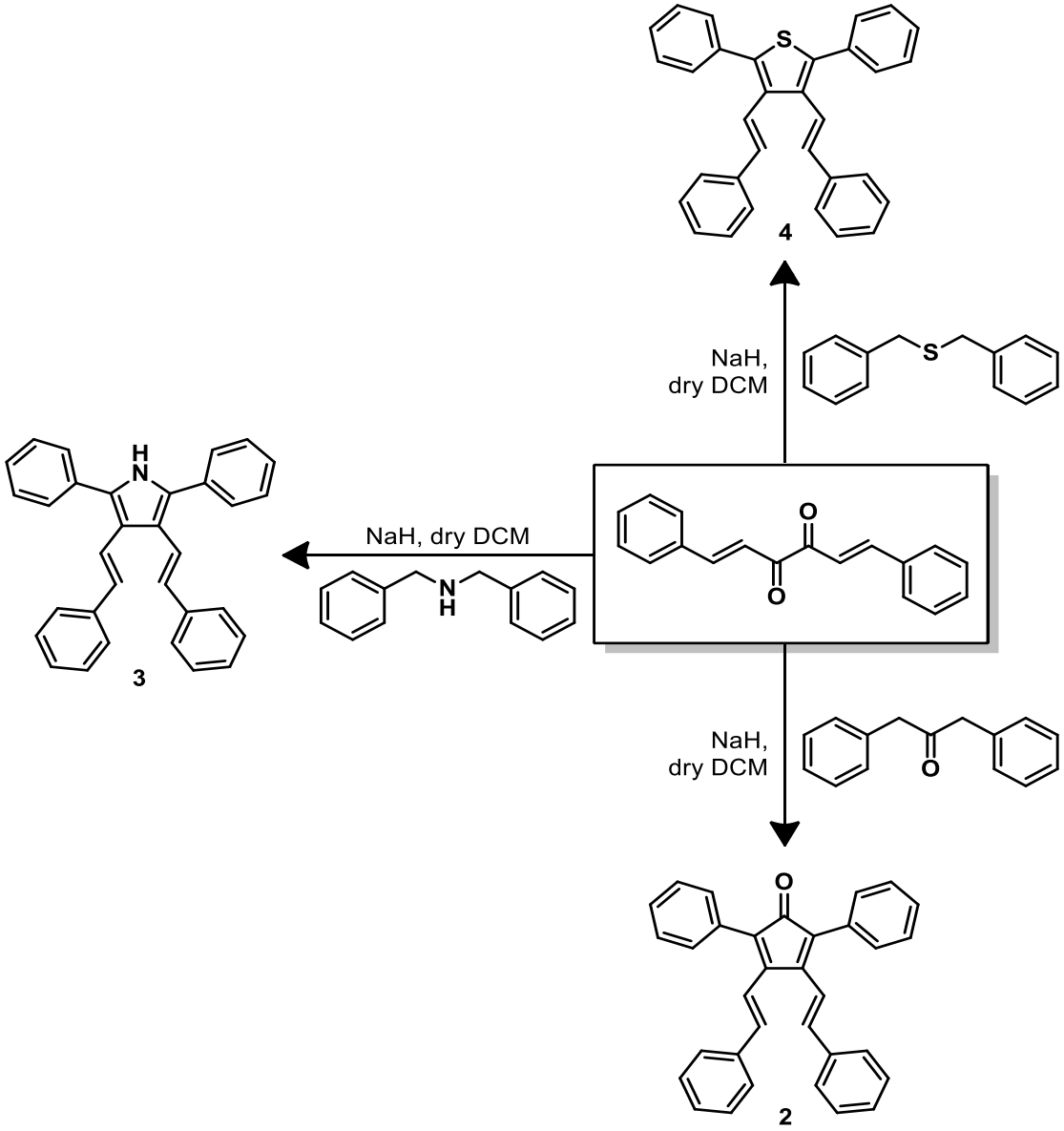
Scheme-I: Synthesis of Tetracyclone.



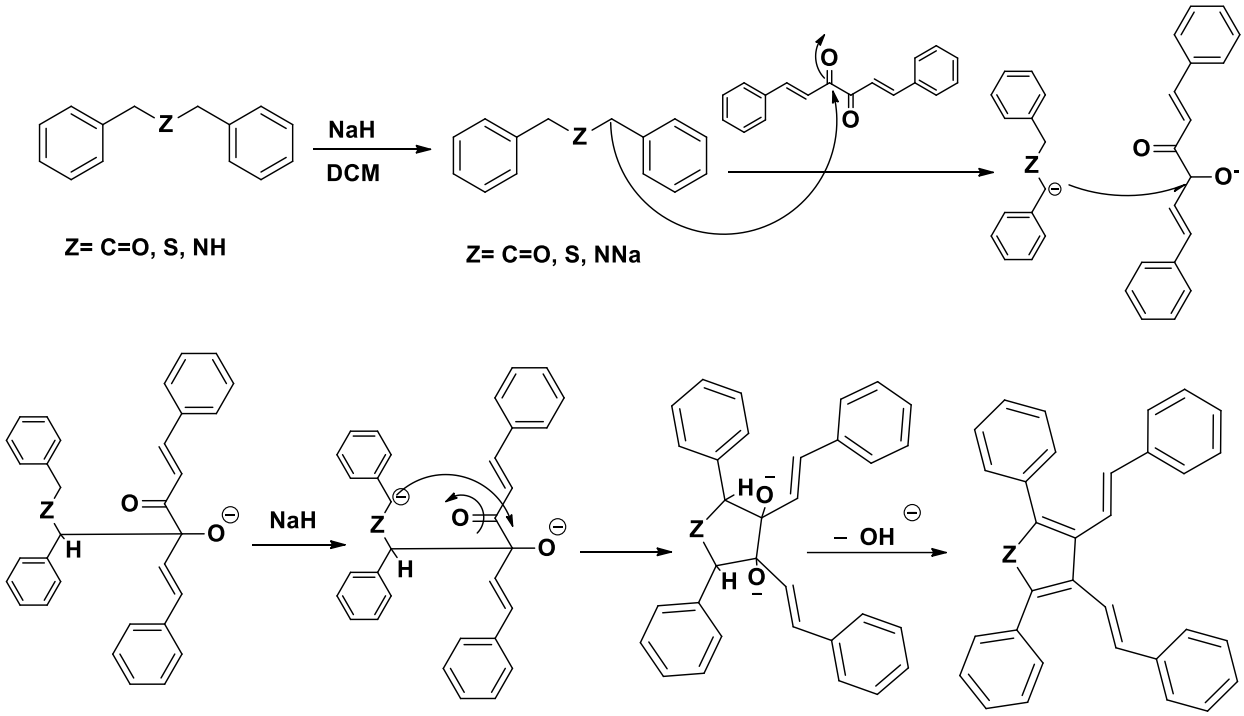
Scheme-II: Cyclization reactions of 1,4-diketone.



Scheme-III: Synthesis of 1,6-di(phenyl)hexa-1,5-diene-3,4-dione [Cinnamil] **(1).**



Scheme-IV: Synthesis of 2,5-diphenyl-3,4-diphenylethenylcyclopentadienone(2),), -pyrrole (3) and -thiophene **(4).**



Scheme-V: Mechanism Involved for the formation of 2, 5-Diphenyl-3,4-di(phenylethenyl)cyclopenta-2,4-dien-1-one (2), -pyrrole (3) and -thiophene (4)

Characterization of all the products was done by ^{1}H-NMR, LC-MS, IR, and UV-visible spectroscopy. The particular signals (aromatic and olefinic proton) are prominent as a multiplet (δ7.50-7.79) in the ^{1}H-NMR spectra. The functional groups present in the cinnamil (1) are seen at 3073 cm^{-1}(C=C-H), 1670 cm^{-1} (C=O), 1590cm^{-1} (C=C) in the infrared spectra. LC-MS spectra were recorded in the methylene dichloride (ES^{+1} and ES^{-1}). Absorbance and emission wavelengths were recorded and compared in UV-visible and fluorescence spectra. The proposed mechanism for the synthesis of products **2,3** and **4** is given in scheme V.

The photophysical data for the absorption and emission wavelengths for 2, 5-diphenyl-3,4-di(phenylethenyl)cyclopenta-2,4-dien-1-one **(2),** pyrrole **(3)** and, thiophene **(4)** were recorded in methylene chloride. Bathochromic shifts (λmax) were observed for all the products **(2-4)**. The maximum shift (680 nm) was recorded for the 2,5-diphenyl-3,4-di(2-phenylethenyl)thiophene **(4).** The electronic excitation in the near UV-region from 230-330 nm to strong emission 500 -690 nm, has proven a significant π-interaction of the extended conjugated system to consider them as light-harvesting species.

Experimental

All reagents and solvents were get from commercial sources. Benzaldehyde, 2,3-butanedione, Pyrrolidine, dibenzyl ketone, dibenzyl sulfide, dibenzyl amine were obtained from Merck. Methylene di chloride (CH_2Cl_2) was dried over CaH_2 and freshly distilled before to use. Methanol was dried with MgI2, distilled, and kept over molecular sieves. Nitrogen was purged through the distilled solvents and reagents to deoxygenate.^{1}HNMRs were recorded on 500 MHz, on a Bruker DRX 500 NMR spectrometer. All NMR spectra were measured at 25°C in the indicated deuterated solvents. Proton chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The resonance multiplicity in the ^{1}H-NMR spectra is" described as "s" (singlet), "d" (doublet), "t" (triplet), and "m" (multiplet), and broad resonances are indicated by "br". The residual protic solvent of $CDCl_3$ (^{1}H, δ 7.27 ppm; ^{13}C, δ 77.2 ppm (central resonance of the triplet)) and tetramethylsilane (TMS) were used as the internal reference in the ^{1}H-NMR spectra. The progress of the reaction was tracked by thin-layer chromatography using silica gel pre-coated plates. Compounds were envisioned by 254 nm light and with iodine. The purity of the products was determined by a combination of thin-layer chromatography (TLC) with HPLC. The

analysis of the samples was performed on a Perkin-Elmer Series 10 high-performance liquid chromatograph equipped with an LC-100 column oven (40 °C), a Nelson Analytical 900 Series integration data station, a Shimadzu RID-10A refractive index (RI) detector, and two gel columns (PL gel 10 μm 500 Å column). THF (Fisher, HPLC grade) was used as eluent at a flow rate of 1 mL/min. accurate mass measurements were performed on LC-MS (Mass Spectrometry Facility, University of Pennsylvania). Either protonated molecular ions $[M+H]^+$ or $[M-H]^+$ or sodium adducts $[M+Na]^+$ were used for empirical formula confirmation.

Synthesis of 1,6-diphenylhexa-1,5-diene-3,4-dione [Cinnamil] **(1)**

Pyrrolidine (0.01 mol) was added to a stirred solution of benzaldehyde (0.05 mol) and 2,3-butanedione (0.01 mol) dissolved in methanol (20 mL). The reaction mixture was refluxed for 5 minutes, concentrated and kept at 0 °C overnight. The crystals were filtered, washed with cold methanol, and dried under vacuum to get the solid orange product.

M.P. = 166 ºC (lit.169ºC) [23]
^{1}H-NMR (500 MHz, $CDCl_3$) δ_H: 7.39-7.46 (6H, m, *3H,3`H,4H, 4`H, 5H, 5`H),* 7.47(2H, d, *J*=16.0Hz, *αH, α`H*) 7.65-7.67(4H, dd, *J* =7.5Hz,1.5Hz, *2H,2`H,6 H, 6`H*) 7.87(2H, d, *J* =16Hz, *βH, β`H*)

IR (neat, cm^{-1}): 3072(C=C-H), 1669(C=O), 1592(C=C), 1158, 1033,754, 689
UV-VIS; λ_{max} (CH_2Cl_2/nm) = 235, 260, 330 nm
LC-MS $_{ES+}$ (m/z): $[M+H]^+$ 263.20

Synthesis of 2, 5-diphenyl-3,4-di(phenylethenyl)cyclopenta-2,4-dien-1-one **(2)**

1,3-Diphenyl-2-propanone[dibenzyl ketone] (0.01 mol) was added to a solution of 1,6-dipheylhexa-1,5-diene-3,4-dione (0.01 mol) in dry methylene chloride (100 mL). Sodium hydride (60%, 0.02 mol) was added with stirring. The reaction mixture was heated at 35 ºC for 24 hours. TLC and ^{1}HNMR were used to monitor the progress of the reaction. After completion, the reaction contents were diluted with dry dichloromethane (50 mL) and washed with a saturated solution of NH_4Cl. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and evaporated. To purify the compounds silica gel column chromatography was done [EtOAc: hexanes (3:1)]. After drying under a high vacuum, the solid compound was obtained [24].

- A yellow solid M.P. = 180ºC, Yield 90%;
- ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H: 6.62–7.39 (m, 24H)
- ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 126.41, 127.48, 128.04, 128.34, 128.54, 129.35, 130.54 130.66, 131.12, 140.63, 140.66, 143.03
- IR (neat, cm^{-1}) 3027, 1715, 1462, 762
- UV-VIS; λ_{max} (CH_2Cl_2/nm)
- λ(absorption) = 230, 260 nm
- λ(Emission) = 520, 570 nm
- LC-MS_{ES-} (m/z): $[M-H]^+$ 435.21

Synthesis of 2,5-diphenyl-3,4-di(2-phenylethenyl)-1H-pyrrole **(3)**

Dibenzylamine (0.01 mol) was added to a solution of 1,6-dipheylhexa-1,5-diene-3,4-dione (0.01 mol) in dry methylene chloride (100 mL). Sodium hydride (60%, 0.04 mol) was added with stirring. The reaction mixture was heated at 35 ºC for 24 hours. TLC and 1HNMR were used to monitor the progress of the reaction. After completion, the reaction contents were diluted with dry dichloromethane (50 mL) and washed with a saturated solution of NH_4Cl. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and evaporated. To purify the compounds silica gel column chromatography was done [EtOAc: hexanes (3:1)]. After drying under a high vacuum, the solid compound was obtained.

- A brown solid M.P. = 160ºC, Yield 87%
- ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H: 7.30 –7.89 (m, 24H), 10.02 (s,1H, NH);
- IR (neat, cm^{-1}) 3026, 1606, 1452, 760
- UV-VIS; λ_{max} (CH_2Cl_2/nm)
- λ(absorption) = 225, 260 nm
- λ (Emission) = 520, 570, 620, 680 nm
- LC-MS $_{ES+}$ (m/z): $[M+H]^+$ 424.24

Synthesis of 2,5-Diphenyl-3,4-di(2-phenylethenyl)thiophene **(4)**

Dibenzyl sulfide (0.01 mol) was added to a solution of 1,6-dipheylhexa-1,5-diene-3,4-dione (0.01 mol) in dry methylene chloride (100 mL). Sodium hydride (60%, 0.02 mol) was added with stirring. The reaction mixture was heated at 35 ºC for 24 hours. TLC and ^{1}HNMR were used to monitor the progress of the reaction. After completion, the reaction contents were diluted with dry dichloromethane (50 mL) and washed with a saturated solution of NH_4Cl. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and evaporated. To purify the compounds silica gel column chromatography was

done [EtOAc: hexanes (3:1)]. After drying under high vacuum, the solid compound was obtained

- A brown solid M.P. = 200ºC, Yield 85%
- ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H: 6.70–8.36 (m, 24H);
- IR (neat, cm^{-1}) 3029, 1654, 1560, 696
- UV-VIS; λ_{max} (CH_2Cl_2/nm)
- λ(absorption) = 235, 270 nm
- λ (Emission) =523, 570, 620 nm
- LC-MS $_{ES+}$ (m/z): $[M+H]^+$ 441.16

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