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Synthesis and crystal structure of polyaryl substituted diene derivatives based on the reduction of diphenylacetylene with lithium naphthalenide

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Abstract

The reduction of diphenylacetylene with lithium naphthalenide produced two kinds of intermediates, **1** or **2**, depending on the ratio of diphenylacetylene to lithium naphthalenide. A series of polyaryl substituted ethylene/diene derivatives were synthesized by reaction of electrophiles with the corresponding intermediates produced in situ. All new compounds were fully characterized, and their single crystal structures were determined.

Keywords: Lithium naphthalenide; Reduction; Diphenylacetylene; Diene derivatives

The reduction of diphenylacetylene (DPA) or its derivatives with metallic reagents was an old and contemporary research, and much attention has been focused on the use of metal lithium as reductant [1–5]. On the other hand, lithium naphthalenide (LiNaph) is easily prepared by reaction of metallic lithium with naphthalene in THF and has been demonstrated to be an effective reductant in synthesis of 2,5-difunctional silole derivatives [6], π-conjugated ladder type molecules containing silicon- [7] or carbon- [8] bridge, with diethynylsilanes and (*o*-silylphenyl)-acetylene derivatives as starting materials, respectively. These reactions proceeded well under mild conditions and produced target molecules in moderate to good yields. However, only limit attention was paid on the reduction of unsubstituted DPA with LiNaph and the use of the reaction to synthesize siloles and other π-electron molecules [4,9,10].

Our interest in synthesis of ring-fused π-electron molecules by reduction of acetylene derivatives prompted us investigate the reaction of DPA with LiNaph. We found in a solution of THF, by tuning the ratio of DPA to LiNaph, two different reactive intermediates, 1,2-dilithio-1,2-diphenylethene (**1**) and 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**2**), were easily prepared in fair yields. We envisioned this reduction system may provide a convenient access to various polyaryl substituted ethylene and diene derivatives. In this paper, we would like to report synthesis of polyaryl substituted ethylene and diene derivatives by combination of the reduction reaction system with various electrophiles.

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1. Experimental

Melting points were measured on a melting point apparatus with a microscope, ^{1}H and ^{13}C NMR spectra were measured with a Bruker AVANCE 400 or Bruker AVANCE 600 spectrometer. Single crystal X-ray diffraction measurements were performed with Rigaku or Bruker single crystal diffractometer. Tetrahydrofuran (THF) and acetone were dried by normal procedures and distilled under an inert atmosphere before use, and all reactions were carried out under nitrogen atmosphere.

*Synthesis of (Z)-2,5-dimethyl-3,4-diphenylhex-3-ene-2,5-diol (**3a**)*: To the solution of lithium naphthalenide prepared from granular lithium (17.4 mg, 2.5 mmol) and naphthalene (320 mg, 2.5 mmol) in THF (10 mL) was added a solution of diphenylacetylene (178 mg, 1.0 mmol) in THF (3 mL) at room temperature. After stirring for 5 min, the new distilled acetone (0.18 mL, 2.4 mmol) was added to the reaction mixture at room temperature and stirred for 2 h. After normal work up, the mixture was passed through the silica gel column (petroleum ether/AcOEt) and re-crystallized from ethanol to give 92 mg (0.31 mmol) of **3a** in 31% yield as a colorless solid. Mp 189–190 °C, ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.95 (t, 4H, J = 7.2 Hz); 6.87 (t, 2H, J = 7.0 Hz); 6.80 (d, 4H, J = 7.5 Hz); 1.41 (s, 12H); 4.08 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.75, 143.24, 142.06, 129.96, 126.90, 126.81, 125.69, 125.10, 74.08, 32.45, 31.85; HRMS (SIMS): Calcd. for $C_{20}H_{24}O_2$: 296.1776. Found: 319.1667(M+Na).

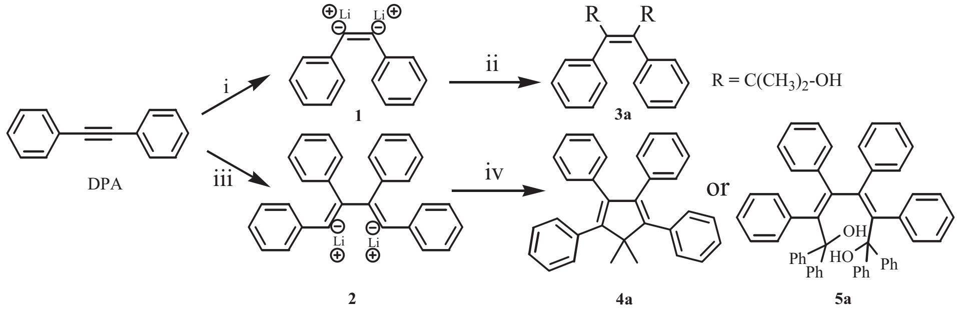
*Synthesis of (5,5-dimethylcyclopenta-1,3-diene-1,2,3,4-tetrayl) tetrabenzene (**4a**)*: The compound **4a** was prepared in the similar manner as described for **3a** in 20% yield as a colorless solid with the molar ratio of LiNaph to DPA was 1.2. Mp 192–194 °C, ^{1}H NMR (600 MHz, CDCl$_3$): δ 6.90–7.33 (m, 20H); 1.38(s, 6H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 152.34, 140.16, 137.49, 135.78, 130.17, 127.95, 127.27, 126.55, 126.03, 56.19, 22.19; HRMS (EI): Calcd. for $C_{31}H_{26}$: 398.2035. Found: 398.2039.

*Synthesis of (2Z,4Z)-1,1,2,3,4,5,6,6-octaphenylhexa-2,4-diene-1,6-diol (**5a**)*: The compound **5a** was prepared in the similar manner as described for **3a** in 39% yield as a colorless solid with the molar ratio of LiNaph to DPA was 1.2 and benzophenone as an electrophile. Mp 234–236 °C, ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.54–6.86 (m, 20H); 7.07–7.17 (m, 12H), 7.28 (s, 8H), 5.16 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 146.95, 144.62, 143.95, 142.70, 142.36, 141.53, 131.80, 128.95, 127.41, 127.15, 127.06, 126.79, 126.61, 126.26, 125.69, 125.42, 85.40; HRMS (SIMS): Calcd. for $C_{54}H_{42}O_2$: 722.3185. Found: 745.3052 (M+Na).

2. Results and discussion

The reductant, LiNaph, was prepared in situ by reaction of equal molar amount of lithium and naphthalene in THF at room temperature. The followed reaction of DPA with LiNaph was carried out by addition of a THF solution of DPA to the as prepared LiNaph/THF mixture under N_2 atmosphere. The reaction proceed very fast at room temperature, accompanied by disappearance of dark green color, the characteristics of LiNaph, within 5 min after addition of DPA (see Scheme 1).

Upon change in the ratio of DPA to LiNaph, two different dilithium adducts can be formed as major in reactive intermediates. Thus, when the molar ratio of LiNaph to DPA is 2 or more, the dominative reactive intermediate is dilithium adduct **1**, which was confirmed by isolation of (Z)-diphenylethylene in 42% yield when the reaction mixture



Scheme 1. The reaction mechanism based on the reduction of DPA with LiNaph. (i) LiNaph, the molar ratio of LiNaph to DPA is about 2.5. (ii) Electrophile (acetone). (iii) LiNaph, the molar ratio of LiNaph to DPA is about 1.2. (iv) Electrophiles (acetone or benzophenone).

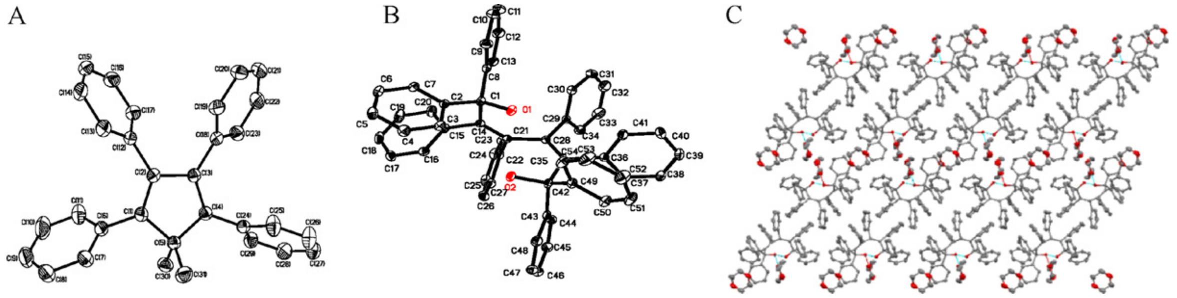


Fig. 1. ORTEP drawings of the compounds (A) **4a** and (B) **5a** and crystal packing of **5a** (C) along *b* axis in 1,4-dioxane (50% probability for thermal ellipsoids, hydrogen atoms are omitted for clarity).

was quenched with water. However, the reaction of DPA with LiNaph in 1:1 molar ratio yields dilithium adduct **2** as main intermediate species, and (*Z*)-1,2,3,4-tetraphenyl-1,3-butadiene was obtained in 60% yield after protonation of the reaction mixture with H_2O. Dilithium adduct **2** as well as other 1,4-dilithio-1,3-butadienes with various substituents on the butadienyl skeleton have recently drawn intensive attention in construction of various new compounds, such as silole derivatives and partially fluorinated π-conjugated compounds [4,9–11]. This work provides a convenient approach to design such molecules.

We examined the reaction of intermediates **1** and **2** with several electrophiles, and found polyaryl substituted ethylene/diene derivatives were easily achieved by combination of appropriate electrophile and corresponding intermediate.

The reaction of intermediate **1** with acetone was first investigated. Thus, the reaction of an excess amount of acetone with intermediate **1** generated in situ from equimolar ratio of LiNaph and DPA produced (*Z*)-2,5-dimethyl-3,4-diphenylhex-3-ene-2,5-diol (**3a**) as a colorless crystal. The structure of **3a** was well confirmed by NMR, HRMS, and single-crystal X-ray analysis [12]. No E-isomer of the compound **3a** was obtained, suggesting the electrophile addition of acetone to dilithio intermediate **1** prefers to form *Z*-isomer.

However, the replacement of acetone with benzophenone failed to afford expected 1,1,2,3,4,4-hexaphenylbut-2-ene-1,4-diol, the analogue of **3a**. This may be attributed to synergistic steric hindrance caused by phenyl group of ketone and short distance between the two C-Li moieties of intermediate **1**.

The reactions between intermediate **2** and acetone, benzophenone were also examined, respectively. Cyclopentadiene derivative **4a**, (5,5-dimethulcyclopenta-1,3-diene-1,2,3,4-tetrayl) tetrabenzene, was the only isolated compound when **2** reacted with acetone. The structure of **4a** is similar to that of 1,1-dimethyl-2,3,4,5-tetraphenyl-1*H*-silole. **4a** also showed the phenomenon of aggregation induced emission that commonly existed for silole derivatives. However, the use of benzophenone resulted in formation of uncyclized diene **5a**, (2*Z*,4*Z*)-1,1,2,3,4,5,6,6-octaphenylhexa-2,4-diene-1,6-diol, and no corresponding cyclopentadiene derivative was obtained. These results suggest that benzophenone is different from acetone as an electrophile because of phenyl ring's electronic structure and hindrance effect.

Single crystals of **4a** and **5a** suitable for X-ray diffraction were obtained from ethanol and THF solution, respectively. Their molecular structure was shown in Fig. 1. **4a** crystallized in the monoclinic space group *P21/n*, and four phenyl groups were distributed around cyclopentadiene ring like propeller. Compound **5a** crystallized in the triclinic space group *P-1*. In crystal structure, the molecule of **5a** adopt a *cis*-conformation and the two hydroxyl groups stick out like antennae to capture disorder solvent molecules THF through hydroxyl bond interaction. Interestingly, single crystal of compound **5a** obtained from 1,4-dioxane adopts monoclinic space group *P21/c*, and Fig. 1c shows the crystal packing along *b* axis. There also exists hydroxyl interaction between the molecules of **5a** and 1,4-dioxane.

3. Conclusion

Upon changing the molar ratio of LiNaph to DPA, two dilithio intermediates, 1,2-dilithio-1,2-diphenylethene (**1**) and 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**2**) can be prepared. By choice of intermediates and electrophiles, various polyaryl substituted diene derivatives were achieved. The reaction system may provide a new approach to construct π-electron molecules.

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