

Inclusion property and Diels-Alder reaction of bis (diphenylphosphine oxide)butadiyne

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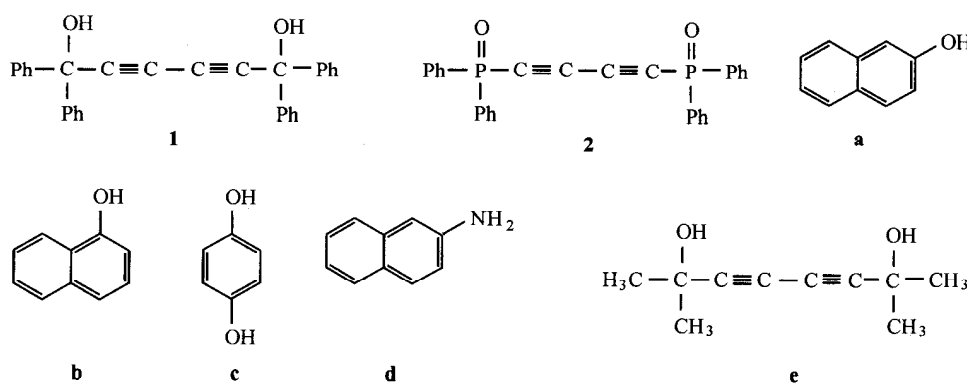
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The host molecule, bis (diphenylphosphine oxide) butadiyne (2), includes a variety of guests to form five complexes (2a—2e). In addition, the Diels-Alder reaction between 2 and anthracene gives 9, 9', 10, 10'-tetrahydro-9, 9', 10, 10'-biethenoanthracene-11, 11'-bis (diphenylphosphine oxide) (3) which is a potential di- π -methane reactant and can undergo photorearrangement.

Keyword Inclusion, Diels-Alder reaction, phosphine oxide, solid-state reaction

Introduction

1, 1, 6, 6-Tetraphenylhexa-2, 4-diyne-1, 6-diol (1)



Compound 2: host; Compounds a—e: guest

Our model compound bis (diphenylphosphine oxide)butadiyne (2) has both characters of 1 and TPPO, and can be easily modified into P-chiral molecule.

has the property of including a variety of organic compounds to form crystalline complexes¹ and has been widely used as separating and resolving reagent, which provide a new route to extract active components from traditional Chinese medicine.² Its inclusion property is mainly related to its rigid structure of diacetylene linkage and its bulky shape.

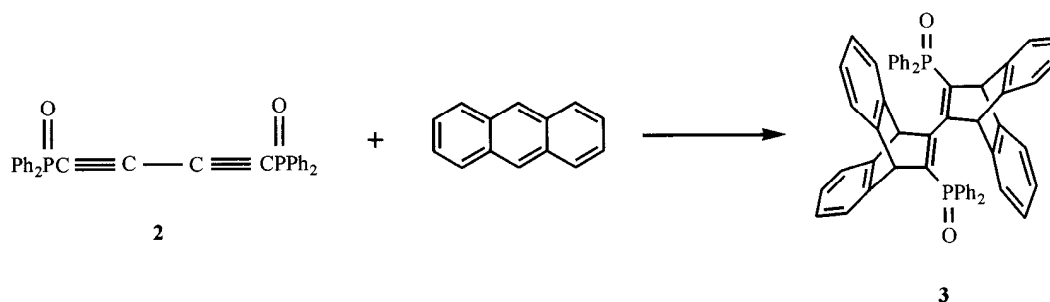
Triphenylphosphine oxide (TPPO) is a good proton acceptor, and has been known to form complexes in solution with a variety of organic molecules.³⁻⁵ These complexes are stabilized by the strong hydrogen bonds between the phosphoryl oxygen and the proton donors of the substrates.⁶

Moreover, compound 2 undergoes Diels-Alder reaction with anthracene to give a new compound 9, 9', 10, 10'-tetrahydro-9, 9', 10, 10'-biethenoanthracene-11, 11'-bis-

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Scheme 2



In IR spectrum, the $\nu(\text{C}\equiv\text{C})$ characteristic absorption (2096 cm^{-1} , strong) of **2** disappeared in **3**. The ^1H NMR spectrum showed the expected bridge H. The molecular ion (m/z 806) of **3** was observed under EI conditions and further characteristic fragments were formed by loss of reasonable fragments from this ion. The elemental analysis showed the expected results. Compound **3** gave well-formed crystals, and X-ray structure determination is in progress.

Experimental

Melting points were determined with microscope melting point apparatus and uncorrected. ^1H NMR spectra were recorded on a Jeol FX-90 Q or Bruker AC-P 200 in CDCl_3 . Elemental analysis was carried out by YANACO CHN CORDER MT-3 apparatus. IR spectra were recorded on a PYE UNICAN SP-300 and mass spectra on a VG-70 spectrometer. Solvents were dried and distilled before use. Tetrahydrofuran (THF) was dried over sodium benzophenone. Ph_2PCl was purchased from Aldrich.

Bis(diphenylphosphine)butadiyne (4)

The apparatus for preparing bis(diphenylphosphine)butadiyne consisted of a decomposition flask (A) and a reactor flask (B). The diacetylene was generated by adding 1,4-dichloro-2-butyne (5.07 g, 0.042 mol), potassium hydroxide (5.55 g, 0.10 mol), water (45 mL) and dioxane (4.5 mL) to flask A and the mixture was stirred vigorously under reflux. The diacetylene was then led into a previously prepared solution of ethylmagnesium bromide (magnesium 0.066 mol; EtBr, 0.066 mol; THF, 60 mL) at -5°C in flask B. The solution was cooled to -10°C and to which Ph_2PCl (14.56 g,

0.066 mol) in 100 mL THF was added dropwise. The mixture was stirred at room temperature for 2 h, hydrolyzed with a saturated solution of NH_4Cl and extracted with pentane ($3 \times 100\text{ mL}$). The pentane layer was dried over anhydrous magnesium sulfate and evaporated to give a greenish residue.¹² The residue was washed with boiling MeOH to give **4** as pale beige powder, yield 50% (Lit.¹² 42%, Lit.¹¹ 26%), mp 105°C .

Bis(diphenylphosphine-oxide)butadiyne (2)

H_2O_2 in acetone (3%, 12 mL) was dropped into a solution of **4** (1.5 g, 3.6 mmol) in acetone (13 mL), and was refluxed for half an hour, then the solvent was removed to leave a solid, which was recrystallized from MeOH to give **2**, as colorless crystals, 1.3 g, yield 80%. mp 192°C (Lit.¹⁵ 191°C). ν_{max} : $2096(\text{C}\equiv\text{C})$, 1598, 1210, 1180, 1120, 1100 cm^{-1} , δ_{H} : 7.2–7.8 (m, ArH), m/z (%): 450(M^+); 373($\text{M}^+ - \text{Ph}_2\text{P}=\text{O}$); 225($\text{M}^+/2$), 201($\text{Ph}_2\text{P}=\text{O}^+$). Anal. $\text{C}_{28}\text{H}_{20}\text{P}_2\text{O}_2$. Calcd: C, 74.66; H, 4.48. Found: C, 74.51; H, 4.59.

Complexes of 2

Complexes of **2** were prepared by dissolving 0.1 mmol of guests (**a–f**) and 0.05 mmol of **2** together in solution in the ratio listed in Table 1, then allowing the solution to evaporate slowly at room temperature.

2a ν_{max} : 3120(OH) (**a**, 3300), 2100($\text{C}\equiv\text{C}$), 1652, 1559, 1440, 1398, 1250, 1220, 1100, 1080 cm^{-1} . δ_{H} : 7.2–7.8 (m, 34H, ArH) 6.5 (s, 2H, OH). Anal. Calcd: C, 78.04; H, 4.91. Found: C, 77.82; H, 4.97.

2b ν_{\max} : 3170—3020(OH) (**b**, 3300), 2100 (C≡C), 1573, 1435, 1380, 1365, 1278, 1210, 1195, 1160, 1120, 1100, 1080 cm^{-1} . δ_{H} : 7.2—7.8 (m, 27H, ArH); 6.8—6.9 (dd, 1H, OH). Anal. Calcd: C, 78.04; H, 4.91. Found: C, 77.94; H, 5.37.

2c ν_{\max} : 3200(OH) (**c**, 3220), 2100(C≡C), 1590, 1510, 1470, 1440, 1250, 1220, 1180, 1120, 1000, 830 cm^{-1} . δ_{H} : 7.2—7.8 (m, 48H, ArH); 2.7—5.0 (m, 4H, OH). Anal. Calcd: C, 71.64; H, 4.81. Found: C, 71.58, H, 4.62.

2d ν_{\max} : 3447, 3315(NH) (**d**, 3415, 3325), 2100(C≡C), 1640, 1505, 1435, 1290, 1210, 1298, 1115, 1098 cm^{-1} . δ_{H} : 7.2—7.8 (m, 48H, ArH); 6.8 (s, 2H, NH). Anal. Calcd: C, 78.25; H, 5.20; N, 3.80. Found: C, 78.30; H, 5.16; N, 4.06.

2e ν_{\max} : 3260—3200(OH) (**e**, 3350—3230), 2980, 2940, 2100(C≡C), 1440, 1210, 1170, 1120, 1100, 945 cm^{-1} . δ_{H} : 7.2—7.8 (m, 20H, ArH); 1.2—1.5 (m, 12H, CH). Anal. Calcd: C, 74.02; H, 5.56. Found: C, 73.92; H, 5.82.

9,9',10,10'-Tetrahydro-9,9',10,10'-biethenoanthracene-11,11'-bis(diphenylphosphine oxide) (**3**)

Compound **3** was prepared by heating the powder mixture of **2** (0.2678 g, 0.59 mmol) and anthracene (0.3152 g, 1.77 mmol) up to 220°C and the melted mixture was kept at 200°C for about 30 min until it solidified again. The excessive anthracene was sublimed after reaction. Recrystallized from CH_2Cl_2 /petroleum ether, **3-CH₂Cl₂** was obtained as colorless crystals, yield 94%, mp > 300°C. ν_{\max} : 3390 (OH), 3052

(CH), 2960, 1630, 1590, 1460, 1437, 1262, 1250, 1205, 1160, 1120, 1100, 1160 cm^{-1} , δ_{H} : 7.2—7.8 (m, 36H, ArH); 4.76—4.98 (m, 4H, bridgehead H). m/z (%): 806(M^+ , 0.12); 605($\text{M}^+ - \text{Ph}_2\text{P}=\text{O}$, 8.29); 201($\text{O} = \text{PPh}_2^+$, 13.57); 178($\text{C}_{14}\text{H}_{10}^+$, 100). Anal. $\text{C}_{56}\text{H}_{40}\text{P}_2\text{O}_2/\text{CH}_2\text{Cl}_2$: Calcd: C, 76.77; H, 4.75. Found: C, 77.09; H, 4.88.

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