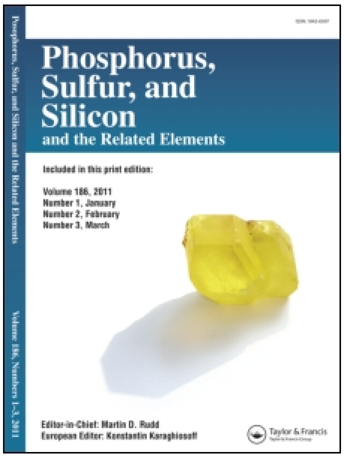

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6H-DIBENZ[c,e][1,2]OXAPHOSPHORINS: SYNTHESIS AND CHEMISTRY

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The reaction of 1-phenylphenol with phosphorus trichloride at elevated temperature using zinc chloride as a catalyst gave the 6H-dibenz[c,e][1,2]oxaphosphorin **1**. The reaction of **1** with the phenols **3a–e** gave the corresponding 6-phenoxy derivatives **4a–e**. In the case of the sterically hindered phenol **3e**, an improved procedure involved the reaction of the sodium phenolate of **3e** with **1**. The reaction of the benzenethiols **5a–b** with **1** using triethylamine as an acid acceptor gave the corresponding derivatives **6a–b**.

The synthesis of both the 6-oxide and 6-sulfide derivatives of the 6H-dibenz[c,e][1,2]oxaphosphorin ring system (Figure 1) has been reported in the literature.[1] Despite widespread reports in the patent literature,[2] the preparation and characterization of the 6H-dibenz[c,e][1,2]oxaphosphorin ring system containing trivalent phosphorus has received scant mention in the literature. In particular, Cherynshev and coworkers have reported the synthesis of the 6-chloro derivative **1** by the reaction of 2-phenylphenol with phosphorus trichloride followed by cyclization using aluminum trichloride as a catalyst.[3]

We report herein details of the synthesis of **1** and its subsequent reactions with both phenols and benzenethiols.

RESULTS AND DISCUSSION

Cherynshev *et al.* reported that although attempted pyrolytic cyclization of **2** at 550 to 600°C failed, cyclization of **2** to **1** was achieved in organic solvents using aluminum trichloride as a catalyst.[3] These results suggested that pyrolytic cyclization of **2** could be achieved in the absence of solvent using a Lewis acid catalyst. Indeed, the reaction of 2-phenylphenol with phosphorus trichloride gave the presumed intermediate **2** which upon heating to 194°C in the presence of zinc chloride gave **1** in high yield (79% distilled).

The structure of **1** rests on the following observations. In the ^{31}P NMR spectrum of **1**, a single phosphorus resonance was observed at δ 132.2 which is in the region expected for the proposed structure.[4–5] In the ^{1}H NMR spectrum the expected complex multiplet was observed in the aromatic region. The MS of **1** displayed a molecular ion at m/z 234. Both the spectral and elemental analyses were fully in accord with structure **1**.

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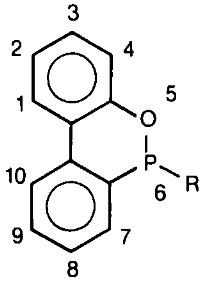


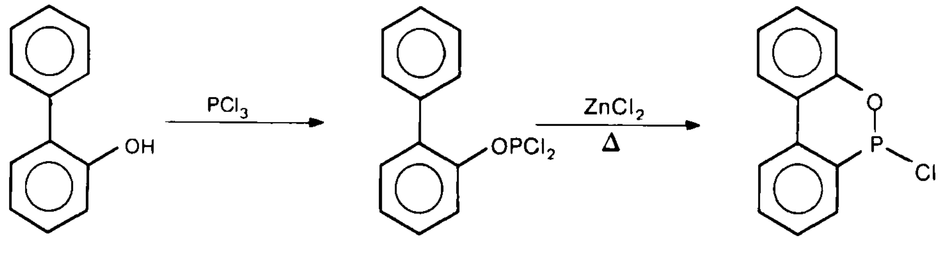
FIGURE 1

The phenoxy-substituted derivative **4a** was prepared by the reaction of **1** with **3a** at elevated temperature (94% distilled). Since phenolic phosphonites do not readily undergo the Michaelis–Arbusov reaction,[6] the use of an acid acceptor was not necessary.[7]

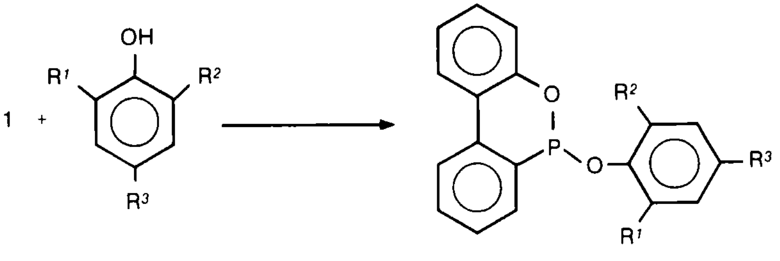
A more convenient procedure for the preparation of the 6-phenoxy derivatives was the reaction of **1** with the appropriate phenol using triethylamine as an acid acceptor. The reaction of **1** with **3b–d** utilizing triethylamine as an acid acceptor gave **4b–d**. The yield of product, however, decreased dramatically from 54% to 19% in the homologous series **4b** through **4d**, respectively. A reasonable explanation of these observations is that the rate of nucleophilic displacement of chloride ion at phosphorus is slowed due to the increased steric demand brought about by the increasing *ortho* substitution of the phenol.

Consistent with this suggestion, the reaction of **1** with the sterically-hindered phenol **3e** required extended reaction times at elevated temperature using triethylamine as the reaction medium. Similar observations were made in a previous study during the preparation of sterically-hindered acyclic phosphonites.[8] An improved procedure for the preparation of **4e** was found to be the reaction of the sodium phenolate of **3e** with **1** in tetrahydrofuran (THF). The increased nucleophilicity of the phenolate anion allowed the reaction to be carried out at room temperature.

The reaction of thiols with phosphorus halides is well known in the literature.[8,9] The reaction of **1** with the benzenethiols **5a–b** gave the expected derivatives **6a–b**.



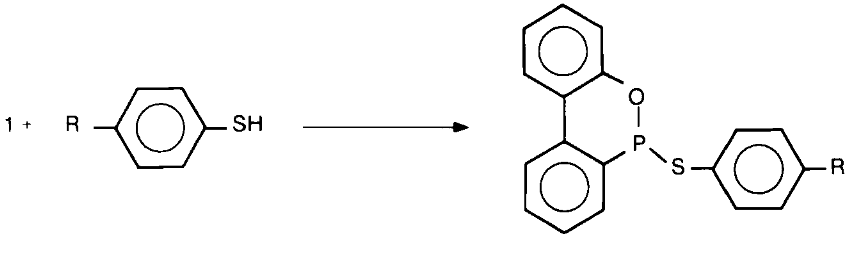
SCHEME 1



3.
a. $R^1 = R^2 = R^3 = H$
b. $R^1 = R^2 = H$; R^3 = t-Butyl
c. $R^1 = H$; $R^2 = R^3$ = t-Butyl
d. $R^1 = R^2 = R^3$ = Methyl
e. $R^1 = R^2$ = t-Butyl; R^3 = Methyl

4.
a. $R^1 = R^2 = R^3 = H$
b. $R^1 = R^2 = H$; R^3 = t-Butyl
c. $R^1 = H$; $R^2 = R^3$ = t-Butyl
d. $R^1 = R^2 = R^3$ = Methyl
e. $R^1 = R^2$ = t-Butyl; R^3 = Methyl

SCHEME 2



5.
a. R = H
b. R = Methyl

6.
a. R = H
b. R = Methyl

SCHEME 3

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas–Hoover melting point apparatus and are uncorrected. Infrared spectra (1% solution in potassium bromide cells) were recorded on a Perkin–Elmer Model 710 or 1300 spectrometer. ^1H NMR spectra were taken on either a Varian Model XL-100 or CFT-20 spectrometer. ^{31}P NMR spectra were taken on a Varian Model XL-200 spectrometer. All ^1H chemicals shifts are reported in ppm relative to tetramethylsilane. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{31}P NMR spectra were acquired by using a 35° flip angle, a 1.4-s repetition rate with 0.6-s pulse delay with full proton decoupling. Mass spectra were obtained on a Finnegan Model 8200 mass spectrometer. All solvents were dried prior to use.

THF was distilled immediately prior to use from a deep blue solution of sodium ketyl (sodium/benzophenone). Reagents were purchased from commercial laboratory supply houses. Reactions were carried out in flame-dried apparatus under a dry-nitrogen atmosphere. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation.

6-Chloro-6H-dibenz[c,e][1,2]*oxaphosphorin,* (**1**)

A mixture of 204 g (1.2 mol) of 2-phenylphenol and 206 g (1.5 mol) of phosphorus trichloride was heated slowly to 148°C over a 5 h period. The removal of evolved hydrogen chloride was facilitated by a slow sweep of nitrogen. To the reaction mixture was added 1.2 g (9 mmol) of anhydrous zinc chloride. The reaction mixture was heated to 194°C over a 75 m period. The reaction mixture was cooled and the residue was distilled to give 236 g (79%) of a colorless liquid which solidified on standing: bp 170–175°C (0.3 mm); mp 79–82°C; ^{31}P NMR (d_6-benzene) δ 132.2; ^{1}H NMR ($CDCl_3$) δ 6.83–7.65 (complex m); MS m/z 234 (M^+). Anal. Calcd. for $C_{12}H_8ClOP$: C, 61.4; H, 3.4. Found: C, 61.2; H, 3.6.

6-Phenoxy-6H-dibenz[c,e][1,2]*oxaphosphorin,* (**4a**)

A mixture of 47.0 g (0.20 mol) of **1** and 24.3 g (0.26 mol) of **3a** was heated at 210°C for 4 h. The excess phenol was removed by distillation (Kugelröhr) and the residue was distilled to give 55.0 g (94%) of a colorless liquid: bp 173–174°C (0.001 mm); ^{1}H NMR ($CDCl_3$) δ 6.69–7.94 (complex m). Anal. Calcd. for $C_{18}H_{13}O_2P$: C, 74.0; H, 4.5. Found: C, 73.8; H, 4.8.

6-(4-tert-Butylphenoxy)-6H-Dibenz[c,e][1,2]*oxaphosphorin,* (**4b**)

To a solution of 10.5 g (70 mmol) of **3b** and 7.07 g (70 mmol) of triethylamine in 80 mL of toluene cooled with an ice bath was added dropwise a solution of 16.4 g (70 mmol) of **1**. The reaction mixture was allowed to warm to rt and then it was heated at 65 to 70°C for 3 h. The cooled reaction mixture was filtered to remove triethylamine hydrochloride and the solvent was removed *in vacuo*. The residue was recrystallized from 2-propanol to give 12.8 g (53%) of a white solid: mp 87–89°C; ^{31}P NMR (d_6-benzene) δ 124.4; ^{1}H NMR ($CDCl_3$) δ 1.33 (s,$(CH_3)_3C$, 9 H), 6.95–7.90 (complex m, 12 H). Anal. Calcd. for $C_{22}H_{21}O_2P$: C, 75.8; H, 6.1. Found: C, 75.7; H, 6.5.

6-(2,4-Di-tert-butylphenoxy)-6H-Dibenz[c,e][1,2]*oxaphosphorin,* (**4c**)

Following the procedure used to prepare **4b**, compound **4c** was prepared from 16.4 g (70 mmol) of **1**, 14.4 g (70 mmol) of **3c** and 7.07 g (70 mmol) of triethylamine.[10a] The residue was recrystallized from 2-propanol to give 7.6 g (31%) of a white solid: mp 80–83°C; ^{1}H NMR (d_6-benzene) δ 1.20 (s, 9 H), 1.30 (s, 9 H), 6.90–7.80 (complex m, 11 H). Anal. Calcd. for $C_{26}H_{21}O_2P$: C, 77.2; H, 7.2. Found: 76.9; H, 7.5.

6-(2,4,6-Trimethylphenoxy)-6H-Dibenz[c,e][1,2]*oxaphosphorin,* (**4d**)

Following the procedure used to prepare **4b**, compound **4d** was prepared from 18.8 g (80 mmol) of **1**, 10.82 g (80 mmol) of **3d** and 8.08 g (80 mmol) of triethylamine.[10b] The residue was recrystallized from acetonitrile to give 5.2 g (19%) of a white solid: mp 77–79°C; ^{31}P NMR (d_6-benzene) δ 129.8; ^{1}H NMR (d_6-benzene) δ 2.77 (s, 3 H), 2.90 (s, 6 H), 7.14–8.58 (complex m, 10 H). Anal. Calcd. for $C_{21}H_{19}O_2P$: C, 75.4; H, 5.7. Found: C, 75.6; H, 5.9.

6-(2,6-Di-tert-butyl-4-methylphenoxy)-6H-dibenz[c,e][1,2]*oxaphosphorin,* (**4e**)

METHOD A Triethylamine Reaction Medium

A solution of 16.4 g (70 mmol) of **1**, 15.4 g (70 mmol) of **3e** and 7.07 g (70 mmol) of triethylamine in 100 mL of toluene was heated at reflux for 7 h. From the reaction mixture, 70 mL of solvent was removed by distillation. To the resultant reaction mixture was added 70 mL of triethylamine and the resultant mixture was heated at 85 to 90°C until disappearance of the phenolic OH absorption in the IR spectrum of a reaction sample (approximately 35 h). The volatiles were removed *in vacuo* and the residue was triturated with 100 mL of benzene and the suspension of triethylamine hydrochloride was removed by filtration. The residue remaining after evaporation of the benzene was triturated with acetonitrile and the resultant solid was recrystallized from a mixture of hexane and toluene to give 21 g (72%) of white crystalline solid: mp 133–135°C; ^{31}P NMR (d_6-benzene) δ 135.6; ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 18 H), 2.30 (s, 3 H), 7.04 (s, 2 H), 7.20–8.15 (complex m, 8 H); Anal. Calcd. for $C_{27}H_{31}O_2P$: C, 77.5; H, 7.5. Found: C, 77.5; H, 7.9.

METHOD B Reaction of Phenolate with **1**

To a suspension of 0.28 (20 mmol) of sodium hydride in 25 mL of dry THF was added dropwise a solution of 4.41 g (20 mmol) of **3e** in 25 mL of THF. After phenolate formation was complete as evidenced by the disappearance of the sodium hydride, a solution of 4.69 g (20 mmol) of **1** in 25 mL of THF was added dropwise to the reaction mixture cooled with an ice bath. The reaction mixture was allowed to warm to rt and it was stirred for 8 h. The reaction mixture was diluted with toluene and the suspension of sodium chloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 3.34 g (40%) of a white solid identical in every respect to that prepared by Method A.

6-(Phenylthio)-6H-Dibenz[c,e][1,2]*oxaphosphorin,* (**6a**)

Following the procedure used to prepare **4b**, compound **6a** was prepared from 4.69 g (20 mmol) of **1**, 2.20 g (20 mmol) of **5a**, and 2.02 g (20 mmol) of triethylamine.[10c] The residue was recrystallized from acetonitrile to give 3.39 g (55%) of a white solid: mp 99.5–100.5; ^{31}P NMR (d_6-benzene) δ 109.7; ^{1}H NMR

(d_6-benzene) δ 6.85–8.05 (Complex m). Anal. Calcd. for $C_{18}H_{13}OPS$: C, 70.1; H, 4.3. Found: C, 70.4; H, 4.3.

6-(4-Methylphenylthio)-6H-Dibenz[c,e][1,2]*oxaphosphorin*, (**6b**)

Following the procedure used to prepare **4b**, compound **6b** was prepared from 18.8 g (80 mmol) of **1**, 10.08 g (80 mmol) of **5b**, and 8.08 g (80 mmol) of triethylamine.[10d] The residue was triturated with hot petroleum ether and the resultant solid was recrystallized from acetonitrile to give 17.0 g (66%) of a white solid: mp 72–74°C; ^{1}H NMR (d_6-benzene) δ 2.02 (s, 3 H), 6.80–7.80 (complex m, 12 H). Anal. Calcd. for $C_{19}H_{15}OPS$: C, 70.8; H, 4.7. Found: C, 70.6; H, 4.6.

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10. (a) The reaction mixture was heated at 75 to 80°C for 5.5 h. (b) The reaction mixture was heated at 75 to 80°C for 6 h. (c) The reaction mixture was stirred 72 h at rt. (d) The reaction mixture was heated at 75 to 80°C for 8 h.