Eight-Membered Heterocycles. 12*H*-Dibenzo[*d*,*g*][1,3,2]dioxaphosphocin and 12*H*-Dibenzo[*d*,*g*][1,3,2]dioxaborocin Derivatives

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The synthesis of phosphonite and thiophosphite derivatives of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system is described. The ^{1}H nmr shows evidence for long-range coupling of the C-12 methine proton to phosphorus. The ^{1}H nmr of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocin ring system is compared to that of the phosphorus analog. The nmr spectral data suggest that the phosphorus and boron containing ring systems have similar ring conformations.

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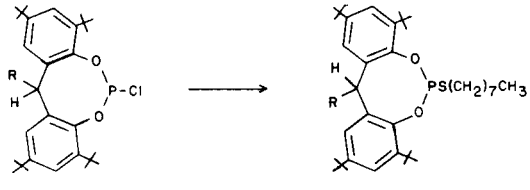
Although derivatives of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system have been extensively reported in the literature as stabilizers for polymeric substrates, neither a detailed account of the synthesis nor spectral characterization has been given [1-7]. Recently we have reported a facile synthesis of the 2,4,8,10-tetra-*t*-butyl-6-alkoxy-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system and have shown evidence for a long-range coupling of phosphorus to one C-12 (bridging methylene carbon) methylene proton in the ^{1}H nmr spectrum [8]. The non-equivalence of the C-12 protons suggested a tub-like non-inverting ring conformation, similar to that reported for the dibenzo[*d*,*g*][1,3,2]diazaphosphocine ring system [9].

In this paper we report the synthesis of phosphonite and thiophosphite derivatives of the dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system and the synthesis of the analogous dibenzo[*d*,*g*][1,3,2]dioxaborocin ring system.

Scheme I



1a, R = H
1b, R = Methyl
1c, R = Propyl

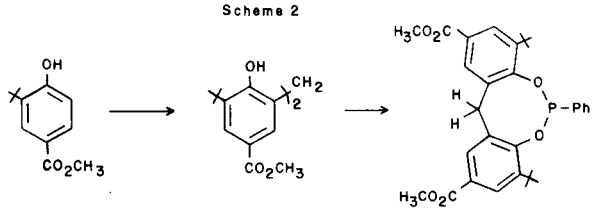
2a, R = H
2b, R = Methyl
2c, R = Propyl

Results and Discussion.

The reaction of an alkyl mercaptan and a phosphorochloridite in the presence of a tertiary amine is a general method for the preparation of thiophosphites [10-12]. However, the reaction of the chloridite **1a** and *n*-octylmercaptan in the presence of triethylamine failed to give the desired thiophosphite.

The reaction of **1a** with potassium *n*-octylmercaptide in toluene using *N,N,N,N*-tetra-*n*-butylammonium bromide as a phase transfer catalyst [13] gave **2a**. Similarly, **2b** and **2c** were prepared from the corresponding chloridites **1b** and **1c** (prepared *in situ*) in recrystallized yields of 20 to 50 percent. Examination of molecular models suggest that the unreactive nature of **1** under normal base catalyzed conditions is attributable to steric hindrance of nucleophilic attack at phosphorus.

Scheme 2



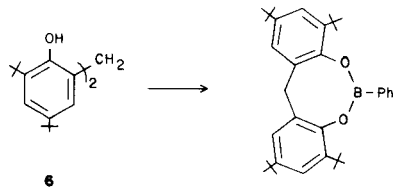
3 **4** **5**

The ^{1}H nmr spectra of **2a-c** are similar to the previously reported phosphite derivatives. The C-12 methylene protons of **2a** were observed to be non-equivalent, appearing as two doublets. The downfield doublet was further split into a doublet of doublets by phosphorus with a $^5J_{HP}$ = 3 Hz. A similar proton coupling pattern was observed in the spectra of **2b** and **2c**. Examination of the reaction mixture prior to workup by tlc shows no evidence for the formation of other isomers.

The reaction of the bisphenol **4** and phenylphosphonous dichloride utilizing triethylamine as an acid scavanger gave the phosphonite **5** as a white crystalline solid in 73% recrystallized yield. However, the synthesis of the starting bisphenol **4** deserves comment. The condensation of the phenol **3** [14] with formaldehyde under the usual acid [15-17] or base [18-19] catalyzed reaction conditions was unsuccessful. Patrick *et al.* [20] have condensed 4-substituted phenols with paraformaldehyde using the high-boiling solvent tetralin and potassium *t*-butoxide to prepare calixarenes [21-22]. The condensation of **3** with paraformaldehyde under these conditions gave the desired bisphenol **4** in 44% recrystallized yield. The difficulty encountered in the condensation of **3** is presumably due to the electron withdrawing nature of the carbomethoxy substituent. The ^{1}H nmr spectrum observed for **5** showed the same

coupling behavior to phosphorus as **2a-c** with a $^5J_{HP}$ = 2 Hz.

Scheme 3



6 **7**

It was of interest to compare the ^{1}H nmr spectra of the prevously prepared dioxaphosphocins with a similarly substituted ring system with boron substituted for phosphorus. The condensation of phenylboronic acid [23] with the 2,2'-methylenebisphenol **6** [24] gave the phenyl substituted 12*H*-dibenzo[*d,g*][1,3,2]dioxaborocin **7** [25]. The C-12 methylene protons of **7** are observed in the ^{1}H nmr spectrum as two sharp doublets with no further coupling. The observed non-equivalence of the C-12 protons in **7** suggest a ring conformation similar to the analogous phosphorus ring system.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra (1% solution - potassium bromide cells) were recorded on a Perkin-Elmer 710 spectrophotometer. The ^{1}H nmr spectra were taken on Varian model XL-100, FT-80 and CFT-20 spectrophotometers. All chemical shifts are reported in ppm relative to tetramethylsilane. The ^{31}P nmr spectra were run on a Varian model FT-80 spectrometer and chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Unless noted otherwise, reagents were purchased from Aldrich Chemical Company. All reactions were carried out in flame-dried apparatus under a dry nitrogen atmosphere.

2,4,8,10-Tetra-*t*-butyl-6-(*n*-octylthio)-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin (**2a**).

To a stirred suspension of 4.89 g (10 mmoles) of **1a** and 1.84 g (10 mmoles) of potassium *n*- octylmercaptide [27] in 50 ml of dry toluene was added 0.32 g (1 mmole) of *N,N,N,N*-tetrabutylammonium bromide. The reaction mixture was stirred overnight and the resultant potassium chloride suspension was removed by filtration. The solvent was removed *in vacuo*. The residue was purified by flash chromatography [26] and it was recrystallized from acetonitrile to give 1.70 g (20%) of white crystals, mp 115-118°; ^{1}H nmr (deuteriochloroform): δ 0.85 (t, -CH_3, 3H), 1.25-2.07 (m, -CH_2-, 12H), 1.34 and 1.48 (2s, -$C(CH_3)_3$, 18H each), 3.22 (m, SCH_2-, 2H), 3.42 (d, $^2J_{HCH}$ = 13 Hz, 1H), 4.35 (d of d, $^2J_{HCH}$ = 13 Hz, $^5J_{HP}$ = 3 Hz), 7.04-7.40 (m, 4H); ^{31}P nmr (deuteriochloroform): δ 170.21.

Anal. Calcd. for $C_{37}H_{59}O_2PS$: C, 74.2; H, 9.9. Found: C, 73.8; H, 9.9.

2,4,8,10-Tetra-*t*-butyl-12-methyl-6-(*n*-octylthio)-12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin (**2b**).

A solution of 13.75 g (0.10 mole) of phosphorus trichloride and 20.24 g (0.20 mole) of triethylamine in 200 ml toluene at 10° was treated with a solution of 43.87 g (0.10 mole) of 2,2'-ethylidenebis(4,6-di-*t*-butylphenol) in 175 ml of toluene [24]. The reaction mixture was stirred at room temperature until disappearance of the phenolic OH absorption in the ir spectrum (approximately five hours). The reaction mixture was cooled to 10° and it was treated with 3.2 g (0.01 mole) of *N,N,N,N*-tetra-*n*-butylammonium bromide and 18.44 g (0.10 mole) of potassium *n*-octylmercaptide. The reaction mixture was stirred 13 hours at room temperature and the resultant suspension was filtered. The solvent was removed *in vacuo* and the residue was recrystallized from 2-propanol-toluene to give 34.40 g (56%) of a white solid, mp 135-138°; ^{1}H nmr (benzene-d_6): δ 0.77-2.03 (m, 18H), 1.27 and 1.54 (2s, -$C(CH_3)_3$, 18H each), 3.25 (d of t, -SCH_2-, $^3J_{HCCH}$ = 7.0 Hz, $^3J_{HCSP}$ = 4.6 Hz), 5.30 (d of q, $^3J_{HCCH}$ = 7.7 Hz, $^5J_{HP}$ = 2.6 Hz), 7.35-7.61 (m, 4H); ^{31}P nmr (benzene-d_6): δ 169.2.

Anal. Calcd. for $C_{38}H_{61}O_2PS$: C, 74.5; H, 10.0. Found: C, 74.7; H, 9.8.

2,4,8,10-Tetra-*t*-butyl-6-(*n*-octylthio)-12-propyl-12*H*-dibenzophosphocin (**2c**).

By the procedure used to prepare compound **2b**, compound **2c** was prepared from 14.00 g (0.03 mole) of 2,2'-butylidenebis(4,6-di-*t*-butylphenol), 4.12 g (0.03 mole) of phosphorus trichloride, 5.53 g (0.03 mole) of potassium *n*-ocytlmercaptide, 6.07 g (0.06 mole) triethylamine, and 0.97 g (0.003 mole) of *N,N,N,N*-tetra-*n*-butylammonium bromide [28]. The residue was recrystallized from 2-propanol to give 8.09 g (42%) of a white solid, mp 124-127°; ^{1}H nmr (benzene-d_6): δ 0.90 (m, -CH_3, 6H), 1.01-1.98 (m, 16H), 1.28 and 1.54 (2s, -$C(CH_3)_3$, 18H each), 3.27 (d of t, -SCH_2-, $^3J_{HCCH}$ = 7.1 Hz, $^3J_{HCSP}$ = 4.2 Hz), 5.14 (d of t, $^5J_{HP}$ = 2.7 Hz, 1H); 7.13-7.62 (m, 4H); ^{31}P nmr (benzene-d_6): δ 169.6.

Anal. Calcd. for $C_{40}H_{65}O_2PS$: C, 75.0; H, 10.2. Found: C, 75.1; H, 10.0.

2,2'-Methylenebis(6-*t*-butyl-4-carbomethoxyphenol) (**4**).

In a flask equipped with a Dean-Stark trap, a mixture of 20.8 g (0.1 mole) of **3**, 4.5 g (0.15 mole) of paraformaldehyde, 11.2 g (0.1 mole) of potassium *t*-butoxide, and 200 ml of tetralin was slowly heated to 170°. The reaction temperature was held at 170° for three hours. The reaction mixture was cooled and the presence or absence of starting phenol **3** was determined ty tlc. If unreacted **3** was present, additional paraformaldehyde was added and the reaction mixture was reheated. This procedure was repeated until **3** was no longer present. The precipitate was filtered, washed with toluene and it was dried in a vacuum oven. The solid was triturated with 60 ml hot glacial acetic acid and it was allowed to stand overnight. The crystals were filtered and washed with cold acetic acid and water. The crystals were dried and then were recrystallized from a cyclohexane:toluene mixture to give 9.53 g (44%) of a white solid, mp 197°; ir (chloroform): δ 3595 cm^{-1}, 3425 cm^{-1} (OH), 1740 cm^{-1} (ester); ^{1}H nmr (deuteriochloroform): δ 1.41 (s, -$C(CH_3)_3$, 18H), 3.86 (s, -CH_3, 6H), 3.99 (s, -CH_2-, 2H), 5.57 (br s, OH, 2H), 7.91 (m, 4H).

Anal. Calcd. for $C_{25}H_{32}O_6$: C, 70.1; H, 7.5. Found: C, 70.2; H, 7.6.

4,8-Di-*t*-butyl-2,10-bis(carbomethoxy)-6-phenyl-12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin (**5**).

A solution of 7.00 g (16.3 mmoles) of **4** and 3.63 (35.9 mmoles) of triethylamine in 200 ml of dry toluene at 5° was treated dropwise with a solution of 2.92 g (16.3 mmoles) of phenylphosphonous dichloride in 50 ml dry toluene. The reaction mixture was stirred overnight at room temperature and the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane and it was extracted three times with water. The organic phase was dried with anhydrous sodium sulfate and the solvent was removed *in vacuo*. The residue was recrystallized from toluene to give 6.33 g (73%) of a white solid, mp 279-281°; ir (choroform): 1720 cm^{-1} (ester); ^{1}H nmr (deuteriochloroform): δ 1.30 (s, -$C(CH_3)_3$, 18H), 3.62 (d, $^2J_{HCH}$ = 12 Hz, 1H), 3.90 (s, CH_3, 6H), 4.55 (d of d, $^2J_{HCH}$ = 12 Hz, $^5J_{HP}$ = 2 Hz, 1H), 7.5-8.2 (m, 9H); ^{31}P nmr (deuteriochloroform): δ 166.8.

Anal. Calcd. for $C_{31}H_{35}O_6P$: C, 69.7; H, 6.6. Found: C, 70.1; H, 6.7.

2,4,8,10-Tetra-*t*-butyl-6-phenyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaborocin (**7**).

In a flask equipped with a Dean-stark trap, a solution of 31.85 g (0.075 mole) of **6**, 9.14 g (0.075 mole) of phenylboronic acid, and 0.71 g (3.75 mmoles) of *p*-toluenesulfonic acid monohydrate in 250 ml of toluene was refluxed until no more water was collected. The ir spectra showed complete disappearance of the phenolic OH absorption. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 23.45 g (61%) of a white solid, mp 184-186°; ^{1}H nmr (deuteriochloroform): δ 1.29 and 1.41 (2s, -$C(CH_3)_3$, 18H each), 3.51 (d, $^2J_{HCH}$ = 14 Hz, 1H), 4.27 (d, $^2J_{HCH}$ = 14 Hz, 1H), 7.10-8.16 (m, 9H).

Anal. Calcd. for $C_{35}H_{47}BO_2$: C, 82.3; H, 9.3. Found: C, 82.6; H, 9.1.

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