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The synthesis and characterization of a 2,10-bis(alkoxycarbonyl)-substituted 6-oxo-12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin, **6**, is described. The lack of an observable  $^5\text{J}_{\text{HP}}$  coupling of phosphorus to the downfield C-12 methylene proton and the observation of a  $^3\text{J}_{\text{MCH}}$  geminal coupling constant of 14 Hz suggest that the conformation of **6** in solution is not solely a boat-chair conformation, but may involve a rapid equilibrium of the boat-chair with either a boat or twist-boat conformation.

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The chemistry of phosphites is extensively documented in the literature [1,2]. Quite recently, we reported the synthesis of sterically hindered derivatives of both silicon [3] and phosphorus [4], which in certain cases showed unusual spectral properties attributed to restricted conformational freedom within the molecule [5]. In the patent literature *O,O*-bis[4-(alkoxycarbonyl)phenyl] phosphonates, commonly termed *sec*-phosphites, are claimed as light stabilizers for poly(vinyl chloride) [6]. Despite this interest, the synthesis and spectral characterization of these molecules and the corresponding eight-membered 6-oxo-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin derivative is unreported in the chemical literature.

### Results and Discussion.

*sec*-Phosphites are known to be formed by the hydrolysis of a phosphorochloridite in the presence of an amine acid acceptor [7]. We have previously used this methodology to prepare sterically hindered *O*-aryl-phenylphosphinates [4].

The phosphorochloridite **2a** was prepared *in situ* by the

reaction of the 3,5-di-*tert*-butyl-4-hydroxybenzoate ester **1a** with phosphorus(III) chloride in the presence of a mixture of triethylamine and pyridine as acid acceptors. The reaction was complete after heating for three hours at 50° as determined by the disappearance of the hindered phenolic OH absorption at 3620  $\text{cm}^{-1}$  in the ir spectrum. The hydrolysis of the chloridite **2a** with one equivalent of water at room temperature gave the phosphonate **3a**. In a similar manner **3b,c** were prepared by the hydrolysis of the corresponding chloridites **2b,c** obtained by the reaction of phosphorus(III) chloride with **1b,c**, respectively.

The structure of **3a** rests on the following observations. In the ir spectrum of **3a**, a P-H absorption was observed at 2450  $\text{cm}^{-1}$  [8]. In the  $^1\text{H}$  nmr spectrum of **3a**, a doublet resonance was observed at  $\delta$  7.25 that was assigned to the proton bonded to phosphorus. The magnitude of the one-bond phosphorus-proton coupling ( $^1\text{J}_{\text{HP}} = 726$  Hz) observed is that expected for the phosphonate structure [2b].

Our interest in both conformational and synthetic aspects of the 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin

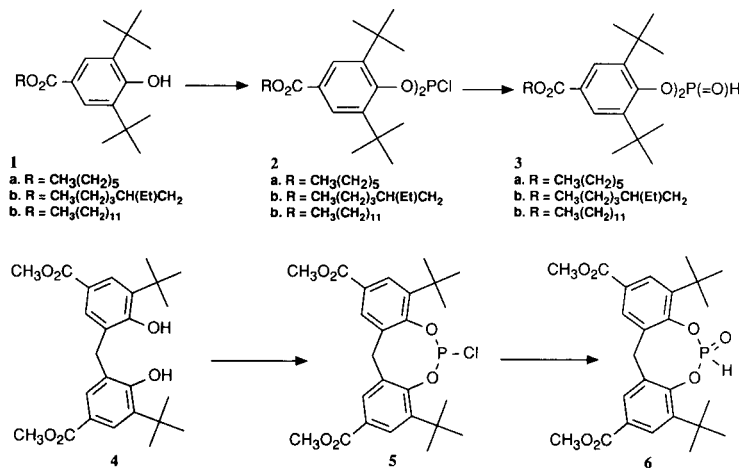


Figure 1

ring system prompted efforts to extend this methodology to synthesize the corresponding 6-oxo-substituted heterocycle **6** [9,10]. Related eight-membered ring systems were previously prepared by transesterification of the corresponding bisphenol with diphenyl phosphite [11]. Our previous efforts in preparing the corresponding 1,3,6,2-dioxaphosphocin by hydrolysis of the corresponding chloridite were unsuccessful [9g].

The chloridite **5** was prepared by the reaction of 2,2'-methylenebis(6-*tert*-butyl-4-methoxycarbonylphenol) [9a] with phosphorus(III) chloride in the presence of triethylamine. The hydrolysis of **5** with water using triethylamine as an acid acceptor gave the desired heterocyclic phosphonate **6** (40% recrystallized). In the ir spectrum of **6**, a P-H absorption was observed at 2475 cm<sup>-1</sup>. In the <sup>1</sup>H nmr spectrum of **6**, a doublet resonance was observed at δ 7.53 that was assigned to the proton bonded to phosphorus. The magnitude of the observed one-bond phosphorus-proton coupling constant (<sup>1</sup>J<sub>HP</sub> = 754 Hz) is consistent with a proton bonding to a tetracoordinate pentavalent phosphorus atom [2d].

The conformation of the dibenzo[*d,g*][1,3,2]dioxaphosphocin ring system has received renewed importance in light of recent reports of their derivatives as being superior ligands in transition-metal-mediated hydroformylation reactions [12]. As pointed out in a recent paper by Arshinova and *et al.* [13], there is a considerable difference between various authors in the use of terms that describe the various possible conformations of the dibenzo[*d,g*][1,3,2]dioxaphosphocin ring system. In this paper the commonly accepted nomenclature advocated by Anet [14] and Fraser [15] is used, which was adopted in the excellent review of Moore and Anet of eight-membered heterocycles [16], namely, the boat-chair (C<sub>s</sub> symmetry), boat-boat (C<sub>s</sub> symmetry), boat (C<sub>1</sub> symmetry), twist-boat (C<sub>1</sub> symmetry) and the twist (C<sub>2</sub> symmetry), for which the abbreviations BC, BB, B, TB, and T, respectively, will be used (Figure 2).

As observed in previous studies [9], the C-12 (bridging-methylene) protons of **6** are nonequivalent (AB quartet)

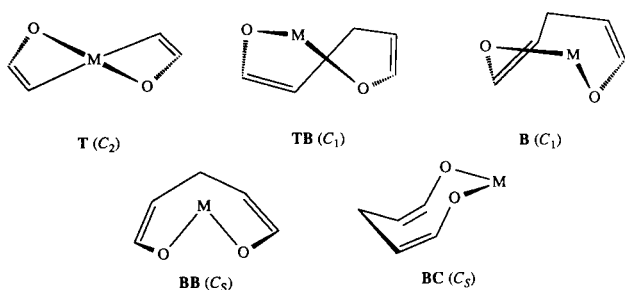


Figure 2. Conformations of the 12H-dibenzo[*d,g*][1,3,2]dioxaphosphocin ring system [M=P(III) or P(IV)] viewed without the annulated benzo groups. The TB conformation illustrated represents only one of a family of flexible TB forms.

and are observed as two doublet resonances at δ 3.88 and δ 4.60. The observation of both two equivalent *tert*-butyl and methoxycarbonyl substituents in the <sup>1</sup>H nmr spectrum of **6** requires that a σ plane of symmetry pass through the C-12 methylene carbon and the phosphorus atom as, for example, in the BC conformation. This must be the case in order to explain both the nonequivalence of the C-12 methylene protons along with the observation of two equivalent *tert*-butyl and methoxycarbonyl substituents. The presence of twisted nonplanar conformations that rapidly pass through structures possessing the required symmetry plane, as either a transition state or intermediate cannot be excluded. Five-bond <sup>5</sup>J<sub>HP</sub> coupling of the downfield proton to phosphorus is not observed. Furthermore, the magnitude of two-bond geminal coupling constant (<sup>2</sup>J<sub>HCH</sub> = 14 Hz) is larger than that observed for the previously reported trivalent phosphorus compounds for which the BC conformation has been established [2] [9a] [13]. The lack of an observable <sup>5</sup>J<sub>HP</sub> coupling and the earlier established relationship of the geminal coupling constant to the conformation of eight-membered rings [13] [17] suggest that the conformation of **6** in solution is not solely a BC conformation, but rather a rapid equilibrium involving the BC with additional contributions from either a B or TB conformation [18]. Five-bond <sup>5</sup>J<sub>HP</sub> coupling would not be expected in a BC conformation with the phosphoryl oxygen in an pseudoequatorial position based upon the through-space mechanism for transmission of coupling information involving the lone-pair of electrons of the endocyclic oxygen atoms proposed by Goddard *et al.* [19].

## EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer Model 710 spectrophotometer, and reported peak absorptions are estimated to be accurate to ± 10 cm<sup>-1</sup>. The <sup>1</sup>H nmr spectra were taken on a Varian Model CFT-20 or Varian Model XL-100 spectrometer. All <sup>1</sup>H chemical shifts are reported in ppm relative to tetramethylsilane where a positive sign is downfield from the standard. The abbreviations used for peak multiplicity are: s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad.

Whatmann DSC-1F silica gel was used for all dry-column chromatography [20]. Merck pre-coated (0.25 mm) silica gel 60 F-254 plates were used for tlc. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry, inert atmosphere of either nitrogen or argon. Elemental analyses were performed by Analytical Research Services, CIBA-GEIBY Corp.

### 2-Ethylhexyl 3,5-Di-*tert*-butyl-4-hydroxybenzoate (**1b**).

In a flask equipped with a Dean-Stark trap, a mixture of 100.1 g (0.4 mole) of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid, 78.1 g (0.6 mole) of 2-ethylhexanol, and 7.6 g (40 mmoles) of *para*-toluenesul-

fonic acid monohydrate was heated at 155-160° until 7.2 ml of water was collected in the Dean-Stark trap. Excess 2-ethylhexanol was removed *in vacuo* (90°, 0.5 torr). The residue was recrystallized from ethanol to give 85.1 g (58%) of light-yellow crystalline solid, mp 50-52°; ir (carbon tetrachloride):  $\nu$  3650 (OH), 1710 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  0.85 (overlapping t, 6 H), 1.25 (overlapping m, 9 H), 1.45 (s,  $(\text{CH}_3)_3\text{C}$ , 18 H), 4.24 (d, 2 H), 5.72 (exchangeable s, OH, 1 H), 7.92 (s, 2 H).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{38}\text{O}_3$ : C, 76.20; H, 10.56. Found: C, 76.18; H, 10.82.

*O,O*-[2,6-Di-*tert*-butyl-4-(hexyloxycarbonyl)phenyl] Phosphonate (**3a**).

To a cooled solution of 10.10 g (100 mmoles) of triethylamine and 3.96 g (50 mmoles) of pyridine in 20 ml of toluene was added 7.00 g (51 mmoles) of phosphorus(III) chloride. To the resultant mixture at 28-30° was added dropwise over 30 minutes a solution of 33.40 g (100 mmoles) of **1a** in 80 ml of toluene. The reaction mixture was stirred at room temperature for 48 hours and then was heated at 50° for 5 hours. The resultant reaction mixture was cooled with an ice-water bath and 0.90 g (50 mmoles) of water was added. The reaction mixture was stirred overnight. To the reaction mixture was added 25 ml of water and the resultant mixture was stirred for 3 hours at room temperature. The resultant phases were separated and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized from hexane to give 23.42 g (66%) of a white crystalline solid, mp 124-126°; ir (carbon tetrachloride):  $\nu$  2450 (PH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  0.85 (t, 6 H), 1.40 (overlapping m, 16 H), 1.58 (s,  $(\text{CH}_3)_3\text{C}$ , 36 H); 4.32 (m, 4 H), 7.25 (d, PH;  $^1J_{\text{HP}} = 726$  Hz, 1H), 8.02 (s, 4 H).

*Anal.* Calcd. for  $\text{C}_{42}\text{H}_{67}\text{O}_7\text{P}$ : C, 70.55; H, 9.44; P, 4.34. Found: C, 70.83; H, 9.24; P, 4.28.

*O,O*-[2,6-Di-*tert*-butyl-4-(2-ethylhexyloxycarbonyl)phenyl] Phosphonate (**3b**).

Following the procedure used to prepare **3a**, compound **3b** was prepared from 6.87 g (50 mmoles) of phosphorus(III) chloride, 10.10 g (100 mmoles) of triethylamine, 3.96 g (50 mmoles) of pyridine, 36.30 g (100 mmoles) of **1b**, 0.90 g (50 mmoles) of water, and 100 ml of toluene. The residue was purified by dry-column chromatography (4:1 toluene:chloroform eluent) to give 23.07 g (60%) of a viscous liquid; ir (carbon tetrachloride):  $\nu$  2450 (PH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform)  $\delta$  0.95 (overlapping t, 12 H), 1.40 (overlapping m, 18 H), 1.55 (s,  $(\text{CH}_3)_3\text{C}$ , 36 H), 4.22 (m,  $\text{OCH}_2$ , 4 H), 7.25 (d,  $^1J_{\text{HP}} = 726$  Hz, 1 H), 8.02 (s, 4 H).

*Anal.* Calcd. for  $\text{C}_{46}\text{H}_{75}\text{O}_7\text{P}$ : C, 71.65; H, 9.80; P, 4.02. Found: C, 71.66; H, 9.61; P, 4.00.

*O,O*-[2,6-Di-*tert*-butyl-4-(1-dodecyloxycarbonyl)phenyl] Phosphonate (**3c**).

Following the procedure used to prepare **3a**, compound **3c** was prepared from 7.00 g (51 mmoles) of phosphorus trichloride, 10.10 g (100 mmoles) of triethylamine, 3.96 g (50 mmoles) of pyridine, 41.80 g (100 mmoles) of **1c**, 0.90 g (50 mmoles) of water, and 140 ml of toluene. The residue was recrystallized three times from hexane to give 27.93 g (63%) of fine white needles, mp 115-116°; ir (carbon tetrachloride):  $\nu$  2450 (PH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  0.85 (t, 6 H), 1.25 (complex m, 40 H), 1.48 (s,  $(\text{CH}_3)_3\text{C}$ , 36 H), 4.28 (t,  $\text{OCH}_2$ , 4 H), 7.20 (d, PH,  $^1J_{\text{HP}} = 720$  Hz,

1 H), 7.98 (s, 4 H).

*Anal.* Calcd. for  $\text{C}_{54}\text{H}_{91}\text{O}_7\text{P}$ : C, 73.42; H, 10.39; P, 3.51. Found: C, 73.13; H, 10.31; P, 3.71.

4,8-Di-*tert*-butyl-2,10-bis(methoxycarbonyl)-6-oxo-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin (**6**).

To a cooled solution of 0.70 g (5 mmoles) of phosphorus(III) chloride in 20 ml of toluene was added 1.52 g (15 mmoles) of triethylamine. To the resultant solution was added dropwise over a 1 hour period a solution of 2.14 g (5 mmoles) of **4** in 30 ml of toluene (warmed to effect solution). The reaction mixture was allowed to warm to room temperature and was stirred overnight. To the reaction mixture at 25° was added 0.10 g (5.5 mmoles) of water whereupon the temperature of the reaction mixture rose to 27°. After stirring the reaction mixture for 72 hours, the precipitate of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized twice from a 1:1 cyclohexane:toluene mixture to give 0.46 g (19%) of a white crystalline solid, mp 176-180°; ir (carbon tetrachloride):  $\nu$  2475 (PH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.45 (s,  $(\text{CH}_3)_3\text{C}$ , 18 H), 3.88 (d,  $^2J_{\text{HCH}} = 14$  Hz, 1 H), 3.92 (s,  $\text{OCH}_3$ , 6 H), 4.60 (d,  $^2J_{\text{HCH}} = 14$  Hz, 1 H), 7.53 (d, PH,  $^1J_{\text{HP}} = 754$  Hz, 1 H), 7.94 (m, 4 H).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{31}\text{PO}_7$ : C, 63.28; H, 6.59. Found: C, 63.40; H, 6.40.

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