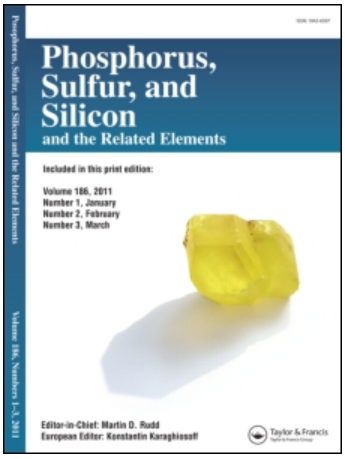

Phosphorus, Sulfur, and Silicon and the Related Elements

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BRIDGED HETEROCYCLES: The Reaction of Seven- and Eight-Membered Cyclic Phosphorochloridites with Polyols

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The syntheses of novel bridged dibenzo[d,f][1,3,2]dioxaphosphepin and dibenzo[d,g][1,3,2]dioxaphosphocin ring systems are described. The ^{1}H NMR spectral data of the eight-membered bridged dioxaphosphocins suggest the observation of a single conformational isomer. The ^{1}H NMR spectrum of the dibenzo[d,g][1,3,2]dioxaborocin **5** requires that either a single nonplanar conformation is being observed or that ring inversion is slow on the NMR time scale. A lower limit of $\Delta G^{\ddagger}$ for ring inversion of **5** has been calculated to be 14.4 Kcal/mole. The ^{1}H NMR of the C-12 methyl substituted dioxaphosphocins **4h–i** showed the presence of a *cis–trans* isomer mixture.

Recently we have reported the facile synthesis of 6-alkoxy, 6-alkylthio, and 6-alkylamino derivatives of the dibenzo[d,f][1,3,2]dioxaphosphepin and 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring system from the corresponding seven- and eight-membered cyclic phosphorochloridites.[1-4] The ^{1}H NMR spectra of the 12H-dibenzo[d,g][1,3,2]dioxaphosphocin derivatives have shown evidence for long-range coupling of one H-12 (bridging methylene carbon) methylene proton to phosphorus. The significant non-equivalence of the H-12 protons in the ^{1}H NMR suggested the observation of a single nonplanar ring conformation, similar in structure to that reported for the 12H-dibenzo[d,g][1,3,2]diazaphosphocine or dibenzo[b,g]phosphocin ring system.[5]

Although alkanediyldioxy-bridged heterocycles derived from cyclic phosphorochloridites and polyols have been extensively reported in the patent literature as stabilizers for polymeric substrates,[6] neither a detailed account of their synthesis nor spectral characterization has been given. We describe in this paper the reaction of seven- and eight-membered cyclic phosphorochloridites with polyols.

RESULTS AND DISCUSSION

The eight-membered cyclic phosphorochloridite **2a** was prepared by the reaction of **1a** with phosphorus trichloride using triethylamine as an acid scavenger as reported

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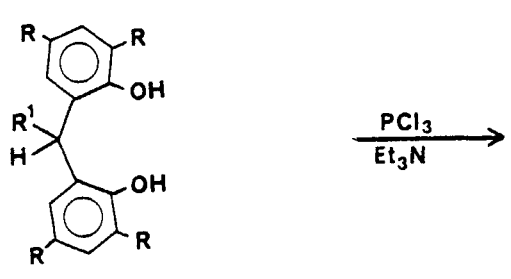
previously.[4] The phosphorochloridites **2b–e** were prepared in an analogous manner from the corresponding bisphenols **1b–e** and phosphorus trichloride.



1

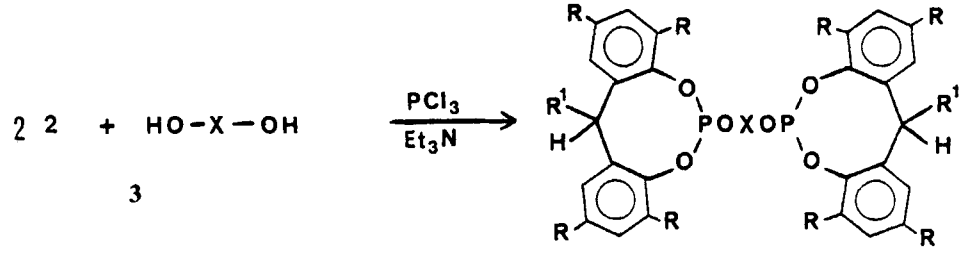
a. R = t-Bu; R^1 = H
b. R = t-Bu; R^1 = Me
c. R = t-Bu; R^1 = n-Propyl
d. R = 1,1-Dimethylpropyl; R^1 = n-Propyl
e. R = 1,1-Dimethylpropyl; R^1 = Me

2

a. R = t-Bu; R^1 = H
b. R = t-Bu; R^1 = Me
c. R = t-Bu; R^1 = n-Propyl
d. R = 1,1-Dimethylpropyl; R^1 = H
e. R = 1,1-Dimethylpropyl; R^1 = Me

The reaction of two molar equivalents of **2a** (prepared *in situ*) with an equivalent of the diol **3a** gave the bridged dioxaphosphocin **4a**. Similarly, **4b–i** were prepared by the reaction of the appropriate phosphorochloridite **2a–e** with the corresponding diol **3a–c**. Either pyridine or triethylamine were utilized as an acid acceptor.

The ^{1}H NMR spectrum of **4g** showed significant non-equivalence of the H-12 methylene protons, which were observed at δ 3.41 and δ 4.39. In addition to the



3

a. X = $-(CH_2)_6-$
b. X = $-CH_2C(CH_3)_2CH_2-$
c. X = $-CH_2CH_2SCH_2CH_2-$

4

a. R = t-Bu; R^1 = H; X = $-(CH_2)_6-$
b. R = t-Bu; R^1 = n-Propyl; X = $-(CH_2)_6-$
c. R = 1,1-Dimethylpropyl; R^1 = H; X = $-(CH_2)_6-$
d. R = t-Bu; R^1 = H; X = $-CH_2C(CH_3)_2CH_2-$
e. R = t-Bu; R^1 = Me; X = $-CH_2C(CH_3)_2CH_2-$
f. R = t-Bu; R^1 = n-Propyl; X = $-CH_2C(CH_3)_2CH_2-$
g. R = t-Bu; R^1 = H; X = $-CH_2CH_2SCH_2CH_2-$
h. R = t-Bu; R^1 = Me; X = $-CH_2CH_2SCH_2CH_2-$
i. R = 1,1-Dimethylpropyl; R^1 = Me; X = $-CH_2CH_2SCH_2CH_2-$

expected geminal coupling, the down-field proton showed long-range coupling to phosphorus with $^5J_{HP}$ = 3.0 Hz. The ^{1}H NMR spectrum of **4g** at 26°C appears to be that of a single conformational isomer. The presence of two distinct (or interconverting slowly on the NMR time scale) conformational isomers is unlikely by the fact that the only evidence for it would be the methylene proton signals, as no other signal is split into two separate regions.

An alternate explanation that the methylene protons of **4g** are *inherently* non-equivalent (even if conformational interchange is rapid on the NMR time scale) as a result of molecular asymmetry at phosphorus seems unlikely since the source of the asymmetry is well removed from the prochiral methylene protons in question. At such distances the non-equivalence of the methylene protons would be expected to be slight.[7] Rapidly inverting ring conformations which bring the prochiral methylene protons into close proximity to the chiral phosphorus atom cannot be rigorously excluded. However, the explanation of a single conformational isomer is supported by a previous study on the analogous 12H-dibenzo[d,g][1,3,2]dioxaborocin derivative **5**, whose H-12 methylene protons displayed significant non-equivalence (δ 3.51 and δ 4.27 respectively).[1] Since trivalent boron has a trigonal planar geometry,[8] rapid ring inversion of **5** would be expected to render the methylene protons magnetically equivalent. This would be the case as rapid ring inversion in **5** would generate a molecular symmetry plane (σ plane) bisecting the HCH angle in the planar transition state for inversion.

The examination of a molecular model of **5** suggests a nonplanar conformation such as that illustrated, which possesses a σ plane of symmetry through the boron and C-12 carbon atom. This must be the case in order to explain both the observation of non-equivalent methylene protons along with the observation of two equivalent pairs of *tert*-butyl groups in the ^{1}H NMR spectrum of **5**. The presence of twisted conformers (to minimize steric interactions) of **5** which rapidly pass through the required symmetry plane as either a transition state or intermediate cannot be excluded. The lower limit for the $\Delta G^{\ddagger}$ of ring inversion calculated using Eqs. (1) and (2) is 14.4 kcal/mole.[9] The non-equivalence of H-12 methylene protons has also been observed in the ^{1}H NMR spectrum of an analogously substituted dibenzo[d,g][1,3,2]dioxasilocin possessing a molecular symmetry plane bisecting the HCH angle in the transition state for ring inversion, for which the coalescence temperature has been observed ($\Delta G^{\ddagger}$ = 13.9 kcal/mole).[10]

$$k_c = \pi|\delta\nu|/\sqrt{2} \tag{1}$$

$$\Delta G^{\ddagger} = 4.57\, T_c[10.32 + \log(T_c/k_c)] \tag{2}$$

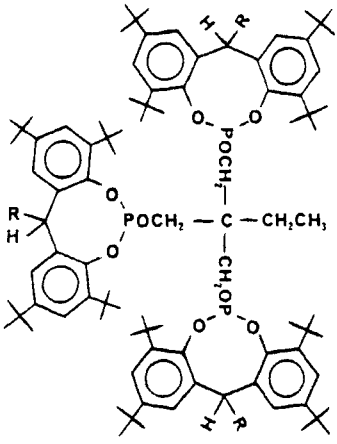
Interestingly the ^{1}H NMR spectrum of **4h** showed two doublets at δ 1.62 and δ 1.84, which were assignable to the protons of two non-equivalent C-12 methyl groups. Similarly, two multiplets were observed at δ 4.20 and δ 4.90, which were assigned to two non-equivalent H-12 methine protons. In a decoupling experiment, irradiation of the methine protons led to the collapse of both methyl doublets. These observations can be reasonably explained by the presence of a mixture of *cis* and *trans* isomers i.e. the C-12 methyl groups being either *cis* or *trans* to the non-bonding electron pair on phosphorus.

Although assignment of the individual spectral resonances to either isomer was not possible, integration of the methyl proton resonances indicated an isomer ratio of 3 : 2. This appears to be the first reported observation of configurational isomerism in the 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring system.

Similar observations were made in the ^{1}H NMR spectrum of **4i**. In this case, the ^{1}H NMR spectrum also showed two resonances at δ 1.38 and δ 1.40, which were assigned to the gem-dimethyl protons of one pair of *tert*-pentyl groups in the *cis* and *trans* isomers respectively (the other pair being accidently equivalent). In accord with this interpretation, two doublets were observed in the ^{1}H NMR spectrum of **4i** at δ 1.59 and δ 1.61, which were assignable to the protons of two non-equivalent C-12 methyl substituents. On heating the NMR probe to 120°C (d_5-nitrobenzene), no change was observed in the ^{1}H NMR spectrum of **4i**. Although the alternate explanation of the observation of two ring conformations (or interconverting slowly on the NMR time scale) cannot be excluded, the chemical shift difference of either the non-equivalent gem-dimethyl or H-12 methyl protons allows one to calculate that the $\Delta G^{\ddagger}$ for interconversion must be greater than 22 kcal/mole.

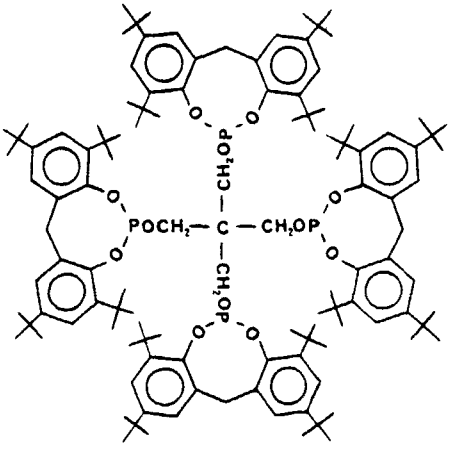
The ^{1}H NMR spectrum of the neopentyl bridged **4e** does not show evidence for *cis-trans* isomerism. It is likely that the increased steric demand of the neopentyl bridging group leads to the formation of a single configurational isomer.

The reaction of three equivalents of either **2a** or **2b** with one equivalent of 2-ethyl-2-hydroxymethyl-1,3-propanediol gave the tris(dioxaphosphocin-6-yl) derivatives **6a** and **6b**, respectively. The reaction of four equivalents of **2a** with an equivalent of pentaerythritol gave the novel structure **7**.



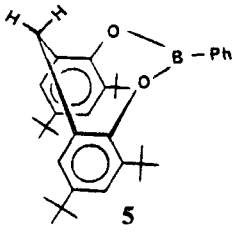
6

a. R = H
b. R = Methyl



7

Completely analogous chemistry was found for the seven-membered dibenzo[d,f][1,3,2]dioxaphosphepin ring system. The reaction of the phosphorochloridite **8** with the appropriate stoichiometric amount of **3c** using triethylamine as an acid acceptor gave the bridged dioxaphosphepin **9**. Similarly the reaction of four equivalents of **8** with one equivalent of pentaerythritol gave **10** (73% recrystallized).



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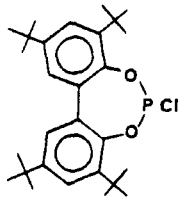

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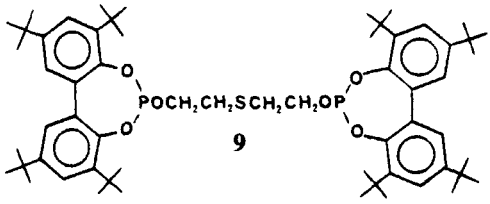

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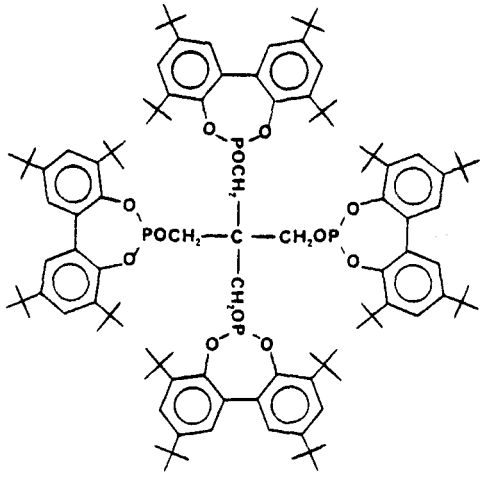

10

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra (1% solution in carbon tetrachloride; potassium bromide liquid cells) were recorded on a Perkin-Elmer 710 spectrophotometer. ^{1}H NMR spectra were taken on a Varian model XL-100 or CFT-20 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane. MERCK 9385 Silica gel-60 (230–400 mesh) was used for flash chromatography.[11] All solvents were dried prior to use when necessary. Reactions were carried out in flame-dried apparatus under a dry-nitrogen atmosphere. In general, the derivatives prepared held onto solvent tenaciously and they required heating at 100–120°C (0.1 mmHg) for approximately 10 hours for complete removal of solvents in order to obtain the correct elemental analysis. All spectral data were obtained on analytical samples. Elemental analysis were performed by Analytical Research Services, CIBA-GEIGY Corporation. The preparation of compounds **1a, 1c, 1e, 4g, 6a,** 7, and **10** are illustrative of the methods employed for compound preparation. Analytical and spectral data are collected in Tables I and II.

2,2'-Methylenebis(4,6-di-tert-butylphenol), (**1a**). To a mixture of 103.2 g (0.5 mole) of 2,4-di-*tert*-butylphenol, and 7.9 g (0.25 mole) of 95% assayed paraformaldehyde in 125 mL of heptane at 5°C was

TABLE I

Analytical data

Compound	mp (°C)	Percent yield[a]	Recrystallization solvent	Calcd. C	Calcd. H	Found C	Found H
1a	147–149.5	81%	Heptane	82.0	10.4	81.9	10.4
1c	110–12	45%	Petroleum Ether	82.4	10.8	82.0	10.6
1d	54–57	32%	Methanol/Water[f]	82.4	10.9	82.4	11.1
1e	116–117	27%	Heptane	82.5	11.0	82.5	11.1
4a	263–267	66%	Acetone/Toluene	75.1	9.5	75.2	9.5
4b	270–276	50%	[b]	75.9	9.8	76.2	9.8
4c	175–178	60%	Acetonitrile/Toluene[c]	76.1	9.9	76.2	10.0
4d	253–256	83%	Heptane	75.0	9.4	75.2	9.5
4e	297–308	20%	2-Butanone	75.3	9.5	75.4	9.8
4f	254–258	26%	Heptane	75.8	9.8	75.8	9.6
4g	236–243	51%	Heptane	72.5	9.0	72.4	9.0
4h	257–275	20%	2-Butanone/Toluene[d]	72.9	9.2	72.9	8.9
4i	157–165	56%	2-Butanone	74.1	9.7	73.9	9.9
6a	176–182	67%	Heptane	74.9	9.3	74.9	9.4
6b	285–295	29%	Acetonitrile[e]	75.2	9.4	75.2	9.2
7	187–195	27%	2-Butanone	74.7	9.1	74.5	9.1
9	219–225	52%	2-Butanone	72.1	8.9	72.1	9.0
10	208–218	73%	Acetonitrile/Toluene	74.3	9.0	74.4	8.6

[a]Analytically-pure isolated yields.
[b]Flash chromatography; toluene eluent.
[c]Subsequent flash chromatography; toluene eluent.
[d]Prior flash chromatographic separation; 1 : 1 toluene : chloroform eluent.
[e]Subsequently triturated with 2-butanone.
[f]Prior flash chromatographic separation; heptane : ethyl acetate eluent.

TABLE II

Spectral data

Compound	IR (cm^{-1})	^1H NMR (deuteriochloroform)
1a	3600, 3480 (OH)	δ 1.25 (s, $(CH_3)_3C$, 18 H), 1.38 (s, $(CH_3)_3C$, 18 H), 3.93 (s, CH_2, 2 H), 5.81 (s, OH, 2 H) 7.13 (m, ArH, 4 H)
1c	3600, 3480 (OH)	δ 1.00 (t, CH_3, 3 H), 1.31 (s, $(CH_3)_3C$, 18 H), 1.38 (s, $(CH_3)_3C$, 18 H), 1.38–2.25 (c, $(CH_2)_2$, 4 H), 4.31 (t, methine H, 1 H), 5.69 (s, OH, 2 H), 7.19 (m, ArH, 4 H)
1d	3600, 3500 (OH)	δ 0.60 (t, CH_3, 6 H), 0.63 (t, CH_3, 6 H), 1.24 (s, CH_3, 12 H), 1.36 (s, CH_3, 12 H) 1.56 (q, CH_2, 4 H), 1.80 (q, CH_2, 4 H), 3.92 (s, CH_2, 2 H), 5.46 (s, OH, 2 H), 7.02 (c, ArH, 4 H)
1e	3600, 3480 (OH)	δ 0.50 (t, CH_3, 6 H), 0.62 (t, CH_3, 6 H), 1.26 (s, CH_3, 12 H), 1.31 (s, CH_3, 12 H), 1.58 (q, CH_2, 4 H), 1.67 (q, CH_2, 4 H), 1.67 (d, $CH\overline{CH_3}$, 3 H), 4.33 (q, methine H, 1 H), 5.16 (s, OH, 2 H), 7.08 (c, ArH, 4 H)

TABLE II (*Continued*)

Compound	IR (cm^{-1})	^1H NMR (deuteriochloroform)
4a	1010 (POC aliphatic stretch)	δ 1.20–1.94 (c, CH_2, 8 H), 1.28 (s, $(CH_3)_3C$, 36 H), 1.40 (s, $(CH_3)_3C$, 36 H), 3.40 (d, H-12, $^2J_{HCH}$ = 13 Hz, 2 H), 4.25–4.59 (c, OCH_2 and H-12, 6 H), 7.28 (c, ArH, 8 H)
4c	1010 (POC aliphatic stretch)	δ 0.67 (t, CH_3, 12 H), 0.68 (t, CH_3, 12 H), 1.28 (s, $C(CH_3)_2$, 24 H), 1.40 (s, $C(CH_3)_2$, 24 H), 1.40–1.74 (c, CH_2, 8 H), 1.62 (q, CH_2, 8 H), 1.84 (q, CH_2, 8 H), 3.40 (d, H-12, $^2J_{HCH}$ = 12.8 Hz, 2 H), 4.35 (d of d, H-12, $^2J_{HCH}$ = 12.8 Hz, $^5J_{HP}$ = 3.0 Hz, 2 H), 4.45 (d of t, OCH_2, $^3J_{HCCH} = {}^3J_{HCOP}$ = 6 Hz, 4 H), 7.08 (d, ArH, 4 H), 7.19 (d, ArH, 4 H)
4d	1020 (POC aliphatic stretch)	δ 1.28 (s, $C(CH_3)_2$, 6 H), 1.31 (s, $(CH_3)_3C$, 36 H, 1.44 (s, $(CH_3)_3C$, 36 H), 3.44 (d, H-12, 2 H), 4.40 (d, OCH_2, $^3J_{HCOP}$ = 6 Hz, 4 H), 4.44 (d of d, C12-H, 2 H), 7.31 (c, ArH, 8 H)
4e	1020 (POC aliphatic stretch)	δ 1.30 (s, $C(CH_3)_2$, 6 H), 1.33 (s, $(CH_3)_3C$, 36 H), 1.46 (s, $(CH_3)_3C$, 36 H), 1.65 (d, $C\underline{H}_3$—C-12, $^3J_{HCCH}$ = 7.5, 6 H), 4.43 (d, OCH_2, $^3J_{HCOP}$ = 4.5 Hz, 4 H), 4.99 (d of q, $^3J_{HCCH}$ = 7.5 Hz, $^5J_{HP}$ = 2.2 Hz, 2 H), 7.24 (d, ArH, 4 H), 7.43 (d, ArH, 4 H)
4g	1000 (POC aliphatic stretch)	δ 1.38 (s, $(CH_3)_3C$, 36 H), 1.43 (s, $(CH_3)_3C$, 36 H), 3.15 (t, SCH_2, $^3J_{HCCH}$ = 7 H, 4 H), 3.41 (d, H-12, $^2J_{HCH}$ = 12.5 Hz), 4.39 (d of d, H-12, $^2J_{HCH}$ = 12.5 Hz, $^5J_{HP}$ = 3.0 Hz, 2 H), 4.69 (d of t, $^3J_{HCCH} = {}^3J_{HCOP}$ = 7.0 Hz, 4 H), 7.26 (c, ArH, 8 H)
4h	1000 (POC aliphatic stretch)	Major Isomer: δ 1.32 (s, $(CH_3)_3C$, 36 H), 1.46 (s, $(CH_3)_3C$, 36 H), 1.62 (d, C$\underline{H}$-C-12, 6 H), 3.08 (c, SCH_2, 4 H), 4.63 (c, OCH_2, 6 H), 4.90 (c, H-12, 2 H), 7.19 (m, ArH, 8 H). Minor Isomer: δ 1.32 (s, $(CH_3)_3C$, 36 H), 1.46 (s, $(CH_3)_3C$, 36 H), 1.84 (d, $C\underline{H}_3$-C-12, 6 H), 3.08 (c, SCH_2, 4 H), 4.20 (c, H-12, 2 H), 4.63 (c, OCH_2, 4 H), 7.19 (d, ArH, 4 H), 7.41 (d, ArH, 4 H)
4i	1000 (POC aliphatic stretch)	Major Isomer: δ 0.66 (br t, CH_3, 24 H), 1.16–2.18 (c, CH_2, 16 H), 1.26 (s, $C(CH_3)_2$, 24 H), 1.38 (s, $C(CH_3)_2$, 24 H), 1.59 (d, $C\underline{H}_3$-C-12, $^3J_{HCCH}$ = 7.5 Hz, 6 H), 3.09 (t, SCH_2, $^3J_{HCCH}$ = 7 Hz, 4 H), 4.63 (d of t, OCH_2, $^3J_{HCOP} = {}^3J_{HCCH}$ = 7 Hz, 4 H), 4.88 (c, C12-H, 2 H), 7.25 (c, ArH, 8 H) Minor Isomer: δ 0.66 (br t, CH_3, 24 H), 1.16–2.18 (c, CH_2, 16 H), 1.26 (s, $C(CH_3)_2$, 24 H), 1.40 (s, $C(CH_3)_2$, 24 H), 1.61 (d, $C\underline{H}_3$-C-12, $^3J_{HCCH}$ = 7.5 Hz, 6 H), 3.09 (t, SCH_2, $^3J_{HCCH}$ = 7 Hz, 4 H), 4.63 (d of t OCH_2, $^3J_{HCCH} = {}^3J_{HCOP}$ = 7 Hz, 4 H), 4.88 (c, H-12, 2 H), 7.25 (c, ArH, 8 H)
5	1330 (B-O stretch)	δ 1.29 (s, $C(CH_3)_3$, 18 H), 1.41 (s, $C(CH_3)_3$, 18 H), 3.51 (d, H-12, $^2J_{HCH}$ = 13 Hz, 1 H), 4.27 (d, H-12, $^2J_{HCH}$ = 13 Hz, 1 H), 7.10–8.16 (c, ArH, 9 H)

TABLE II (*Continued*)

Compound	IR (cm^{-1})	^1H NMR (deuteriochloroform)
6a	1020 (POC aliphatic stretch)	δ 1.28–1.71 (c, $(CH_3)_3C$ and CH_3CH_2, 113 H) 3.42 (d, H-12, $^2J_{HCH}$ = 13.0 Hz, 3 H), 4.42 (d of d, H-12, $^2J_{HCH}$ = 13.0 Hz, $^5J_{HP}$ = 2.8 Hz, 3 H), 4.72 (d, OCH_2, $^3J_{HCOP}$ = 4.5 Hz, 6 H), 7.22 (C, ArH, 12 H)
7	1010 (POC aliphatic stretch)	δ 1.28 (s, $(CH_3)_3C$, 72 H), 1.40 (s, $(CH_3)_3C$, 72 H), 3.69 (d, H-12, 4 H), 4.46 (d of d, H-12, 4 H), 4.92 (d, OCH_2, $^3J_{HCOP}$ = 8 Hz), 7.13 (c, ArH, 16 H)
9	990 (POC aliphatic stretch)	δ 1.36 (s, $(CH_3)_3C$, 36 H), 1.48 (s, $(CH_3)_3C$, 36 H), 2.59 (t, SCH_2, $^3J_{HCCH}$ = 7 Hz, 4 H), 3.80 (d of t, OCH_2, $^3J_{HCOP} = {}^3J_{HCCH}$ = 7 Hz), 7.17 (d, ArH, 4 H), 7.43 (d, ArH, 4 H)
10[a]	1010 (POC aliphatic stretch)	δ 1.31 (s, $(CH_3)_3C$, 72 H), 1.47 (s, $(CH_3)_3C$, 72 H), 4.22 (d, OCH_2, $^3J_{HCOP}$ = 6 Hz, 8 H), 7.31 (d, ArH, 8 H), 7.50 (d, ArH, 8 H)

[a] ^1H NMR solvent is d_6-benzene.

added 0.37 g (3.75 mole) of conc. sulfuric acid. The reaction mixture was stirred at room temperature for 5 hours and subsequently it was heated to 60°C. The reaction mixture was stirred at 50°C overnight and then it was heated to reflux, removing the water of reaction azeotropically with a Dean-Stark trap. The reaction mixture was filtered hot and it was cooled overnight. The resultant precipitate was filtered to give 86 g (81%) of a white solid, **1a**.

2,2'-Butylidenebis(4,6-di-tert-butylphenol), (**1c**). To a stirred mixture of 206.3 g (1 mole) of 2,4,-di-*tert*-butylphenol, 36.1 g (0.5 mole) of butyraldehyde, and 50 g of anhydrous calcium chloride at 60°C was added dropwise 40 mL of conc. hydrochloric acid. The reaction mixture was stirred at 55–60°C for 15 hours. The resultant pasty solid was twice stirred with water and the aqueous layer was decanted. The solid was dried on a porous plate and then it was recrystallized from petroleum ether to give 105.4 g (45%) of a white crystalline solid, **1c**.

2,2'-Ethylidenebis[4,6-bis(1,1-dimethylpropyl)phenol], (**1e**). To a stirred mixture of 468.8 (2 mole) of 2,4-bis(1,1-dimethylpropyl)phenol and 44.1 g (1 mole) of acetaldehyde in a flask equipped with an acetone/dry ice cooled Dewar Condenser was added dropwise 16 mL of concentrated hydrochloric acid. The reaction mixture was stirred at 55–60°C for two hours. To the reaction mixture was added 600 mL of heptane and then it was heated to reflux removing the water of reaction using a Dean-Stark trap. The reaction mixture was cooled and the resultant solid was filtered to give 132 g (27%) of a white solid, **1e**.

6,6'-[Hexane-6,6'-diyldioxy]bis[2,4,8,10-tetrakis(1,1-dimethylethyl)-12H-dibenzo[d,g][1,3,2]dioxaphosphocin], (**4a**). To a solution of 18.75 g (137 mmol) of phosphorus trichloride in 200 mL of toluene at 10°C was added dropwise a solution of 58 g (137 mmol) of 2,2'-methylenebis(4,6,-di-*tert*-butylphenol) and 27.64 g (274 mmol) of triethylamine in 250 mL of toluene. 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°C and then a mixture of 8.07 g (68 mmol) of 1,6-hexanediol and 13.82 g (137 mmol) of triethylamine was added. The reaction mixture was stirred for 13 hours at room temperature. The resultant suspension of triethylamine was removed by filtration and the filter cake was washed with hot toluene. The solvent was removed *in vacuo* and the residue was recrystallized from a 3 : 1 acetone : toluene mixture to give 46.1 g (66%) of a white solid, **4a**.

6,6'-[[2-ethyl-2-[[[2,4,8,10-tetrakis(1,1-dimethylethyl)-12H-dibenzo[d,g][1,3,2]dioxaphosphocin-6-yl]-oxy]methyl]-1,3-propanediyl] bis (oxy) bis[2,4,8,10-tetrakis(1,1-dimethylethyl-12H-dibenzo[d,g]-[1,3,2]dioxaphosphocin], (**6a**). To a solution of 13.73 g (0.1 mole) of phosphorus trichloride in 200 mL of toluene at 10°C was added dropwise a solution of 42.47 g (0.1 mole) of 2,2'-methylenebis(4,6-di-*tert*-butylphenol) and 20.24 g (0.2 mole) of triethylamine in 175 mL of toluene. The reaction mixture was stirred at room temperature until disappearance of the phenolic OH in the IR spectrum. The reaction

mixture was cooled to 10°C and 7.91 g (0.1 mole) of pyridine and 4.47 g (0.033 mole) of 2-ethyl-2-hydroxymethyl-1,3-propanediol was added. The reaction was stirred at 65°C for 15 hours and the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from heptane to give 33.03 g (67%) of a white solid, **6a**.

6,6'-[[2,2-bis[[[2,4,8,10-tetrakis(1,1-dimethylethyl)-12H-dibenzo[d,g][1,3,2] dioxaphosphocin-6-yl]oxy]-methyl]-1,3-propanediyl]bis(oxy)]bis[2,4,8,10-tetrakis(1,1-dimethylethyl)-12H-dibenzo[d,g][1,3,2]dioxaphosphocin], (**7**). To a solution of 10.99 g (80 mmole) of phosphorus trichloride in 150 mL of toluene at 10°C was added dropwise a solution of 33.97 (80 mmole) of 2,2'-methylenebis(4,6-di-*tert*-butylphenol) and 24.29 g (240 mmole) of triethylamine in 100 mL of toluene. The reaction mixture was stirred at room temperature until disappearance of the phenolic OH absorption in the IR spectrum. The reaction mixture was cooled to 10°C and then to it was added (2.72 g (20 mmole) of pentaerythritol. The reaction was stirred at 70°C for 15 hours and the resultant suspension of triethylamine was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized twice (2-butanone) to give 10.7 g (27%) of a white solid, **7**.

6,6'-[[2,2-bis[[[2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[d,f][1,3,2]dioxaphosphepin-6-yl]oxy]-methyl]-1,3-propanediyl]bis(oxy)]bis[2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[d,f][1,3,2]dioxaphosphepin], (**10**). By the procedure used to prepare compound **7**, compound **10** was prepared from 41.07 g (0.1 mole) of 3,3'5,5'tetra-*tert*-butyl-biphenyl-2,2'-diol, 13.73 g (0.1 mole) of phosphorus trichloride, 3.40 g (0.025 mole) of pentaerythritol, and 30.36 g (0.3 mole) of triethylamine. The residue was recrystallized from an acetonitrile : toluene mixture to give 34.62 g (73%) of a white solid, **10**. ^{31}P NMR ($CDCl_3$): δ 138.4.

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