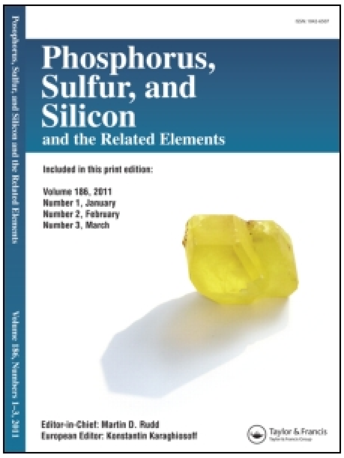

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2,4,8,10-TETRASUBSTITUTED DIBENZO[d,f][1,3,2]DIOXAPHOSPHEPINS

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2,4,8,10-TETRASUBSTITUTED DIBENZO[d,f][1,3,2]DIOXAPHOSPHEPINS

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The synthesis of the dibenzo[d,f][1,3,2]dioxaphosphepin ring system from substituted biphenyl-2,2′-diols and alkylphosphonous dichlorides is described. The NMR spectral data are consistent with either rapidly interconverting ring conformers or a static non-planar ring conformation.

Recently, we have described the synthesis of the eight-membered 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring system, whose NMR spectral data suggested a boat-like non-fluxional ring conformation.[1] In this paper, we report an extension of this work to the synthesis of the seven-membered dibenzo[d,f][1,3,2]dioxaphosphepin ring system.

Previous workers have reported the synthesis of the unsubstituted dioxaphosphepin ring system from dibenzo[d,f][1,3,2]dioxasilepins and arylphosphonous dichlorides, and by reaction of biphenyl-2,2′-diol with phosphorus trichloride.[2] Although substituted dibenzo[d,f][1,3,2]dioxaphosphepins have been advocated in the patent literature as stabilizers to prevent polymer degradation,[3–6] neither a detailed account of their preparation nor characterization has been given. Prior synthetic procedures reported in the patent literature utilized the reaction of biphenyl-2,2′-diols with (aryl) alkylphosphorous dichlorides,[3] and phosphorous trichloride followed by reaction with alcohols, sec-amines, or thiols.[4–6]

RESULTS AND DISCUSSION

The reaction of the *t*-pentyl substituted biphenyl-2,2′-diol **1a** with *t*-butyl-phosphonous dichloride utilizing triethylamine as an acid acceptor gave **2a** in 85% recrystallized yield. Similarly, the phosphonites **2b–4b** were prepared by the reaction of the appropriately substituted biphenyl-2,2′-diol with the corresponding alkyl or arylphosphonous dichloride in 53–91% recrystallized yield.

The phosphonites **2a–4a** were stable to routine laboratory manipulations suggesting that the bulky substituents in the 4 and 8 positions (*ortho* to oxygen) sterically hinders the reaction of the phosphonite with atmospheric moisture and oxygen. The steric retardation of phosphonite and phosphite hydrolysis with atmospheric moisture has been reported.[7]

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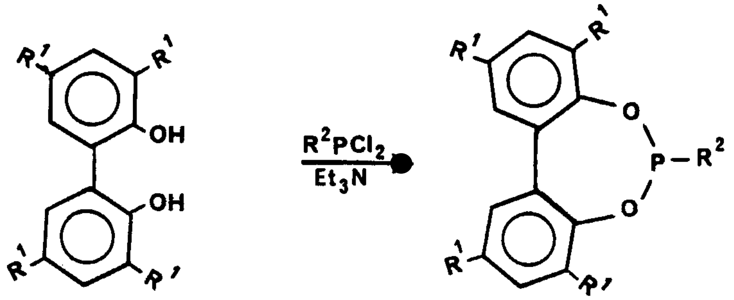

1
a. R^1 = 1,1-dimethylpropyl
b. R^1 = 1,1,3,3-tetramethylbutyl
c. R^1 = 1,1-dimethylethyl

2 R^1 = 1,1-dimethylpropyl
a. R^2 = 1,1-dimethylethyl
b. R^2 = methyl
c. R^2 = phenyl
3 R^1 = 1,1,3,3-tetramethylbutyl
a. R^2 = methyl
b. R^2 = ethyl
4 R^1 = 1,1-dimethylethyl
a. R^2 = phenyl
b. R^2 = methyl

SCHEME 1

In contrast, **4b** was readily oxidized upon exposure to atmospheric oxygen to the corresponding phosphonate **4c**. A mixture of **4b** and **4c** was obtained as evidenced by molecular ions at m/e 454 and m/e 470 in the mass spectrum. The ^{1}H NMR spectrum and elemental analysis were consistent with this interpretation.

In the ^{1}H NMR spectrum of **2a**, only one signal was observed for each pair of equivalent *tert*-butyl hydrogens on either side of the phosphorus atom. Similarly, in the ^{13}C NMR spectrum of **2a**, the two pairs of equivalent non-substituted aromatic carbons appeared as singlets at δ 129.2 and δ 126.5. A single resonance was observed in the ^{31}P NMR spectrum.

The NMR spectral data of **2a** does not differentiate between either rapidly interconverting ring conformations or a symmetrical non-fluxional ring conformation (Figure 1).

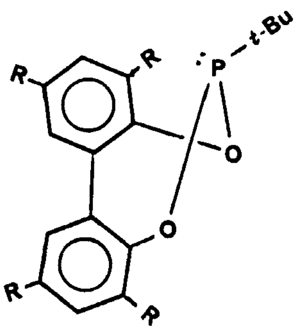

FIGURE 1

Molecular models suggest, however, that conformational freedom is restricted by the benzo ring fusions.[8] For comparison, the unsubstituted cycloheptatriene ring system exists as rapidly equilibrating non-planar conformers with an activation energy of approximately 6 Kcal/mole,[9-10] whereas Tochterman *et al.* have reported activation energies as high as 16 Kcal/mole for substituted dibenzocycloheptatrienes.[11-12] Analogous steric restraints imposed by benzo groups have been reported in the dibenzodioxaphosphocin,[1] dibenzodiazaphosphocine,[13] and dibenzophosphonin ring systems.[14]

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H, ^{31}P and ^{13}C NMR spectra were taken on a Varian model FT-80 spectrometer equipped with a broad band probe. All ^{1}H and ^{13}C chemical 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 using a 45° slip angle, a 1-*s* repetition rate with no pulse delay and with full proton decoupling. Mass spectra were determined on an AEI (KRATOS) MS 902. Alkylphosphonous dichlorides were purchased from Strem Chemical and used without purification. All other reagents were purchased from Aldrich Chemical Company. Reactions were carried out in flame-dried apparatus under a dry nitrogen atmosphere. All compounds were prepared by the procedure used for compound **2a**. Analytical data are collected in Table I. Elemental analyses were carried out in Analytical Research Services, CIBA-GEIGY Corporation.

TABLE I

Analytical data and spectral data

Compound	^{31}P$^{(1)}$	mp (°C)	Recryallization Solvent	Percent Yield	Calcd. C	Calcd. H	Found C	Found H
2a	δ 162.2	117.5–118	Acetonitrile	85%	78.2	10.4	77.9	10.2
2b	δ 153.6	64–65	Heptane	91%	77.6	10.1	77.4	9.8
2c	—	97–100	Acetonitrile: Benzene	73%	79.7	9.3	79.6	9.5
3a	—	102–105	Acetonitrile	53%	79.6	11.1	79.4	10.8
3b	—	97–99	Acetonitrile: Toluene	91%	79.7	11.2	79.6	11.1
4a	—	166–168	Acetonitrile: Ethyl Acetate	74%	79.0	8.8	79.2	8.8
4b$^{(2)}$	—	—	Acetonitrile	—	75.3	9.4	75.4	9.4

Compound	^{1}H NMR$^{(3)}$	MS (relative intensity)
4b$^{(4)}$	1.32 (s, —C(CH$_3$)$_3$, 18 H), 1.42 (s, —C(CH$_3$)$_3$, 18 H), 7.11–7.46 (c, Ar—H, 4 H)	m/z 454 (M$^+$, 60), 439 (M-15, 100), 424 (65)
4c$^{(4)}$	1.32 (s, —C(CH$_3$)$_3$, 18 H), 1.48 (s, —C(CH$_3$)$_3$, 18 H) 7.15–7.46 (c, ArH, 4 H).	m/z 470 (M$^+$, 95), 455 (M-15, 100), 440 (40)

(1) The solvent is benzene-d$_6$. (2) 50 : 50 mixture of phosphonite and phosphonate. (3) The solvent is deuteriochloroform. (4) The P-methyl group was partially obscured by tert-butyl groups but integration was correct.

2,4,8,10-Tetrakis(1,1-dimethylpropyl)-6-(1,1-dimethylethyl)-dibenzo[d,f][1,3,2]dioxaphosphepin **2a**. A solution of 8.00 g (17.1 mmol) of 3,3′,5,5′-tetrakis(1,1-dimethylpropyl)-biphenyl-2,2′-diol[15] and 3.47 g (34.7 mmol) of triethylamine in 40 mL of toluene was slowly treated with a solution of 2.73 g (17.1 mmol) of *tert*-butylphosphonous dichloride in 6 mL of toluene. The reaction mixture was heated to 65°C for 15 hours. The reaction mixture was cooled and the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 6.80 g (85%) of a white crystalline solid, mp 117.5–118°C; ^{1}H NMR (benzene-d_6): δ 0.77 (overlapping triplets, CH_3, 12 H), 1.20 (d,—$C(CH_3)_3$,$^3J_{HCCP}$ = 11.4 Hz, 9 H), 1.23 (s, CH_3, 12 H), 1.48 (s, CH_3, 12 H), 1.80 (overlapping quartets,—CH_2—, 8 H), 7.07–7.40 (m, aromatic, 4 H).

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