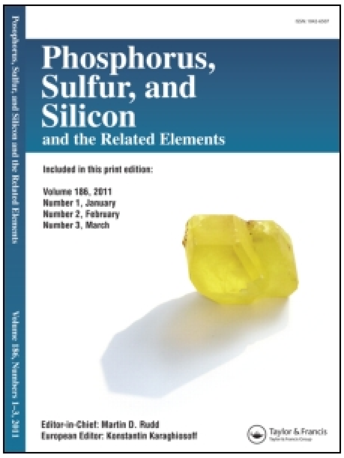

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Odorisio, Paul A. , Pastor, Stephen D. and Spivack, John D.(1984) 'REACTION OF SEVEN- AND EIGHT-MEMBERED CYCLIC PHOSPHOROCHLORIDITES WITH 3,5-DI-*tert*-BUTYL-4-HYDROXYBENZYL ALCOHOL: FACILE P-C BOND FORMATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 20: 3, 273 — 277

To link to this Article: DOI: 10.1080/03086648408077637

URL: http://dx.doi.org/10.1080/03086648408077637

Phosphorus and Sulfur, 1984, Vol. 20, pp. 273–277
0308-664X/84/2003-0273/$18.50/0

REACTION OF SEVEN- AND EIGHT-MEMBERED CYCLIC PHOSPHOROCHLORIDITES WITH 3,5-DI-*tert*-BUTYL-4-HYDROXY-BENZYL ALCOHOL: FACILE P—C BOND FORMATION

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(*Received April 6, 1984*)

The reaction of 2,4,8,10-tetra-*t*-butyl-6-chloro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin (**5**) or 2,4,8,10-tetra-*t*-butyl-6-chloro-dibenzo[d,f][1,3,2]dioxaphosphepin (**10**) with 3,5-di-*t*-butyl-4-hydroxybenzyl alcohol (**7**) gave the corresponding P-(4-hydroxybenzyl)phosphonates **9** and **12** rather than the expected phosphites **8** and **11**. IR and NMR spectral evidence for the phosphonate structure is discussed.

The uncatalyzed rearrangement of alkynyl and alkenyl phosphites to their corresponding phosphonates is well documented in the literature.[1] Less information is known about the thermal rearrangement of benzyl phosphites.[2] Ivanov and coworkers[3] have noted the interesting observation that the reaction of triethyl phosphite with **1** gave the phosphonate **3**. Both the mechanistic work of Ivanov and the recent reinvestigation by Chasar[4] support the intermediacy of **2** rather than the phosphite **4**. As part of our investigations on the chemistry of dibenzo[d,f][1,3,2]dioxaphosphepins and dibenzo[d,g][1,3,2]dioxaphosphocins[5], we describe herein the reaction of the corresponding seven- and eight-membered cyclic phosphorochloridites with 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol.

RESULTS AND DISCUSSION

Previously we had reported that the reaction of the chloridite **5** (prepared *in situ*) with benzyl alcohol using triethylamine as an acid acceptor gave the benzyl phosphite **6**.[5a] The ^{31}P NMR spectrum of **6** has a resonance at δ 128.7 which is consistent with a trivalent phosphorus ester.[6] In accord with this interpretation, a doublet was observed at δ 5.49 in the ^{1}H NMR of **6** which was assigned to the benzylic protons with $^{3}J_{HCOP} = 6$ Hz.

The reaction of **5** with the 4-hydroxybenzyl alcohol **7** using triethylamine as an acid acceptor, however, gave the phosphonate **9** (54% yield recrystallized) rather than the expected phosphite **8**.

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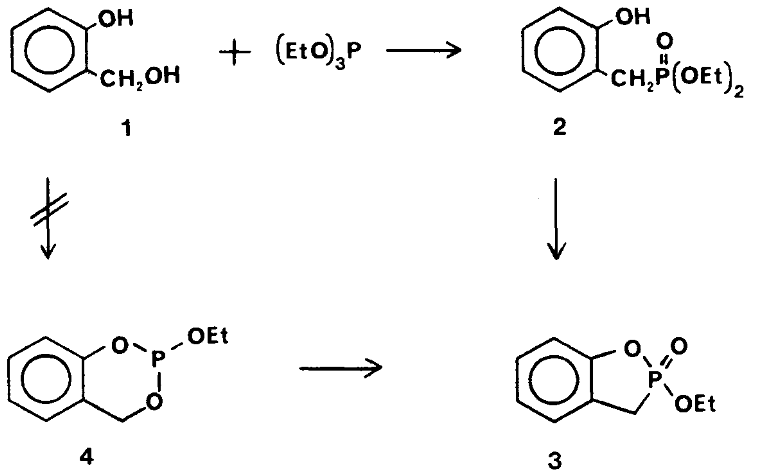

FIGURE 1

The structure of **9** rests on the following observations. The ^{31}P NMR spectrum of **9** has a resonance at δ 11.2 which is in the region expected for a phosphonate.[7] In the ^{1}H NMR spectrum of **9**, a doublet was observed at δ 3.75 whose peak area integrated to two protons, which was assigned to the benzylic protons with $^{2}J_{HCP} = 20$ Hz. Both the observed chemical shift and the magnitude for the coupling of the benzylic protons to the phosphorus atom are supportive of a phosphonate rather than a phosphite structure. Further evidence for a phosphonate structure comes from the lack of an observable POC aliphatic stretch near 1000 cm^{-1} in the IR spectrum[8] of **9**, which was observed in the IR spectrum of **6**. A strong P=O absorption was observed at 1220 cm^{-1} in the IR spectrum of **9**.

Completely analogous chemistry was found for the reaction of the seven-membered phosphorochloridite **10** with **7**. The phosphonate **12** was isolated in 47% yield (recrystallized). The ^{31}P NMR spectrum of **12** had a resonance at δ 21.1. In the ^{1}H

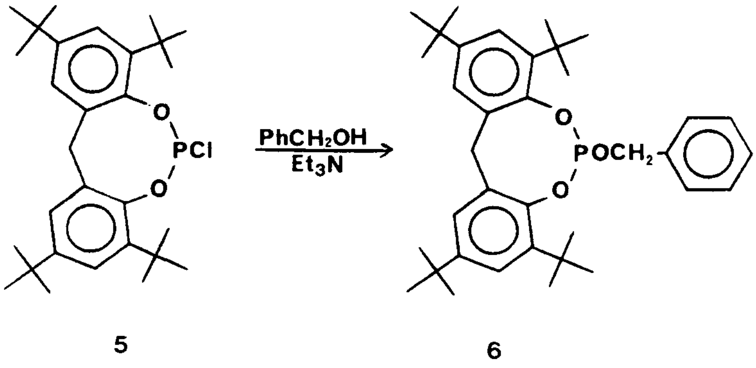

FIGURE 2

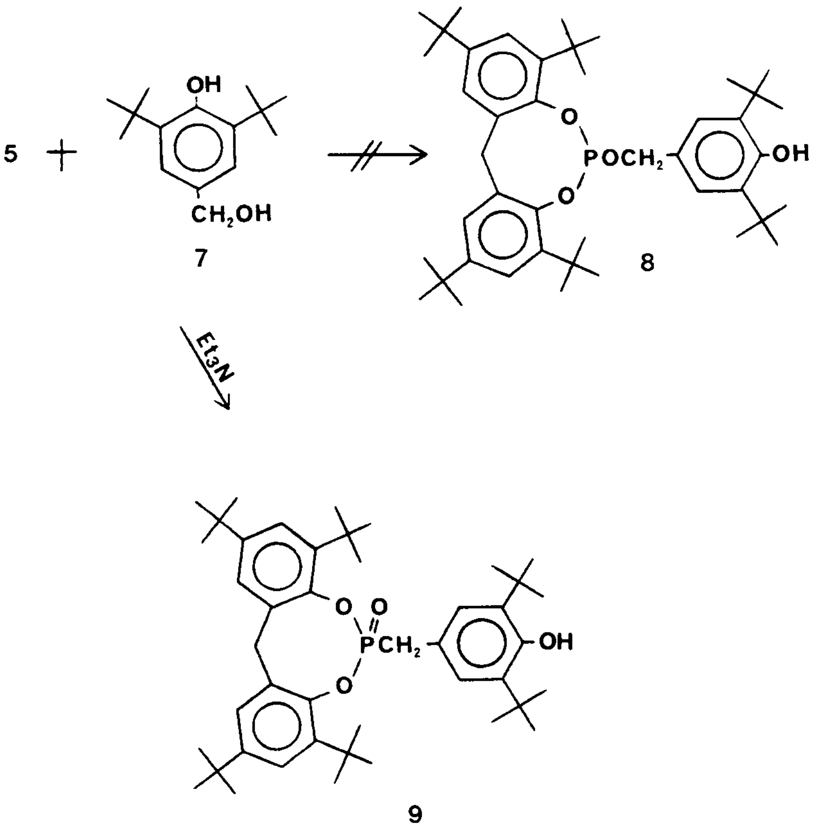

FIGURE 3

NMR spectrum of **12**, the benzylic protons were observed as a doublet at δ 3.31 with $^2J_{\mathrm{HCP}} = 20$ Hz. The P=O absorption was observed at 1230 cm^{-1} in the IR spectrum. These spectral results are fully in accord with a phosphonate structure.

The participation of the 4-hydroxy substituent of **7** in the reaction with the chloridites **5** and **10** to form the corresponding phosphonates **9** and **12** respectively is evident, since the reaction of **5** with benzyl alcohol leads to the unrearranged phosphite **6**. The participation of the hydroxyl group of **7** through the formation of a quinone methide intermediate is well documented in the literature,[9] although in the present case the intervention of a 4-hydroxy-stabilized benzyl cation intermediate[10] (formation catalyzed by the acidic triethylamine hydrochloride) must be considered. No evidence was seen by TLC or IR spectroscopy during the preparation of either **9** or **12** for the formation of the corresponding phosphites **8** and **11**, although their formation as transient intermediates followed by rapid rearrangement would probably have not been detected by these techniques. Quite possibly, the reaction mechanism does not involve intermediate phosphites at all, as suggested by the mechanistic work of Ivanov and Chasar. Further work is clearly needed to both delineate the mechanism of these reactions and to determine their potential synthetic utility for the formation of P—C bonds.

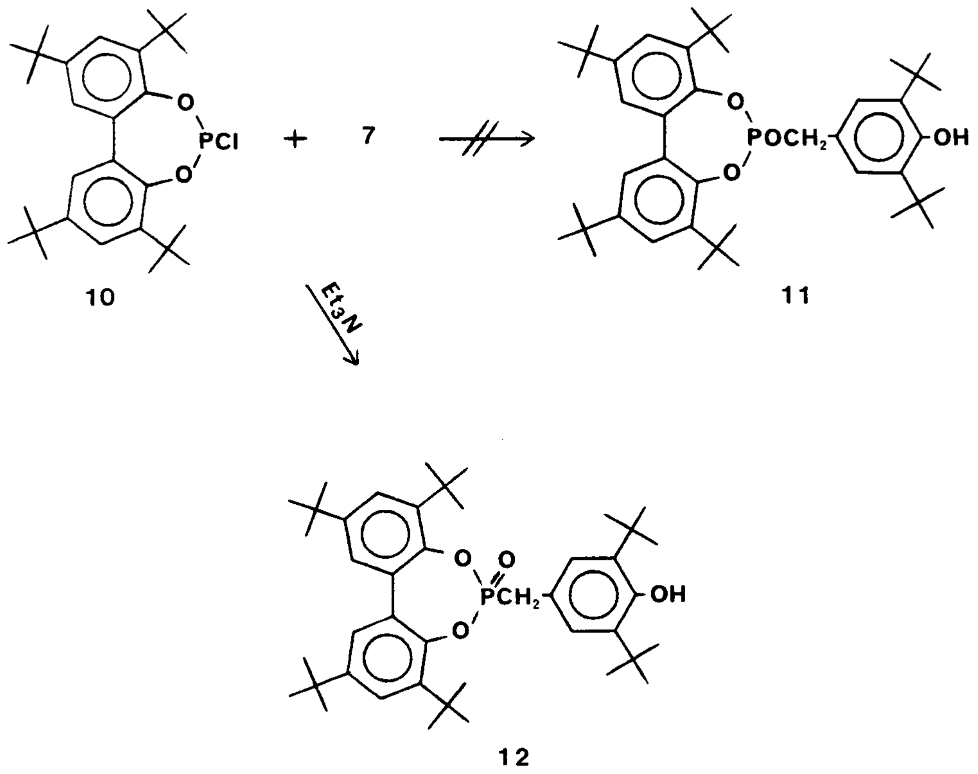

FIGURE 4

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas–Hoover melting point apparatus and are uncorrected. IR spectra (1% solution in carbon tetrachloride, KBr cells) were recorded on a Perkin–Elmer model 710 spectrometer. ^1H NMR spectra were taken on a Varian model CFT-20 spectrometer. All ^1H chemical shifts are reported in ppm relative to internal tetramethylsilane. ^{31}P NMR spectra were taken on a Varian XL-200 spectrometer. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external). Positive chemical shifts indicate resonances downfield from the standard. ^{31}P NMR spectra were acquired using a 35° flip angle, a 1.4 s repetition rate with a 0.6 s pulse delay and with full proton decoupling. Unless otherwise indicated, all reagents were purchased from Aldrich Chemical Company. All solvents were dried prior to use when necessary. Reactions were carried out in flame-dried apparatus under a dry-nitrogen atmosphere. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation.

2,4,8,10-Tetra-tert-butyl-6-(3,5-di-tert-butyl-4-hydroxybenzyl)-6-oxo-12H-dibenzo[d,g][1,3,2]dioxaphosphocin, (**9**). To a stirred solution of 13.4 g (98 mmol) of phosphorus trichloride in 150 mL of toluene was added dropwise at 5 to 10 °C a solution of 41.6 g (98 mmol) of 2,2′-methylenebis(2,4-di-*tert*-butylphenol)[5e,1] and 19.8 g (196 mmol) of triethylamine in 200 mL of toluene. The reaction was then stirred at room temperature until disappearance of the phenolic OH absorption in the IR spectrum (approximately five hours). To the reaction mixture was added dropwise a solution of 23.2 g (98 mmol) of **7** and 9.9 g (98 mmol) of triethylamine in 100 mL of toluene. The reaction mixture was stirred overnight and the suspension of triethylamine hydrochloride was removed by filtration with subsequent washing of the filter cake with hot toluene. The solvent was removed *in vacuo* and the residue was recrystallized from both acetonitrile and acetone to give 36.6 g (54%) of a white solid, mp 245–247 °C; IR: ν 3640 cm^{-1} (OH), 1220 (P=O); ^{31}P NMR (benzene-d_6): δ 11.2; ^1H NMR ($CDCl_3$): δ 1.31 (s, $(CH_3)_3C$, 18 H), 1.54 (overlapping s, $(CH_3)_3C$, 36 H), 3.53 (d, C12—H, 1 H), 3.75 (d, PCH_2, $^2J_{HCP} = 20$ Hz, 2 H), 4.22 (d of d, C12—H, 1 H), 5.19 (exchangeable s, OH, 1 H), 7.31 (c, ArH, 6 H). Anal. Calcd. for $C_{44}H_{65}O_4P$: C, 76.7; H, 9.5; P, 4.5. Found: C, 76.6; H, 9.3; P, 4.5.

2,4,8,10-Tetra-tert-butyl-6-(3,5-di-tert-butyl-4-hydroxybenzyl)-6-oxo-dibenzo[d,f][1,3,2]dioxaphosphepin, (**12**). By the procedure used to prepare compound **8**, compound **12** was prepared from 13.4 g (98 mmol) of phosphorus trichloride, 40.0 g (98 mmol) of 3,3′,5,5′-tetra-*tert*-butyl-biphenyl-2,2′-diol[12], 23.2 g (98 mmol) of **7**, and 29.7 g (294 mmol) of triethylamine. After removal of the suspension of triethylamine hydrochloride by filtration, the filtrate was concentrated to approximately one-half its volume and the resultant cooled suspension was filtered to give 34 g (47%) of a white solid, mp 250–252°C; IR: ν 3640 cm^{-1} (OH), 1230 (P=O); ^{31}P NMR (benzene-d_6): δ 21.1; ^1H NMR ($CDCl_3$): δ 1.28 (s, $(CH_3)_3C$, 18 H), 1.34 (s, $(CH_3)_3C$, 18 H), 1.38 (s, $(CH_3)_3C$, 18 H), 3.31 (d, PCH_2, $^2J_{HCP}$ = 20 Hz, 2 H), 5.10(s, OH, 1 H), 7.16–7.47 (c, ArH, 6 H). Anal. Calcd. for $C_{43}H_{63}O_4P$: C, 76.5; H, 9.4. Found: C, 76.3; H, 9.4.

ACKNOWLEDGMENT

We thank CIBA-GEIGY Corporation for support and permission to publish this work. The author wishes to thank Nancy Lovallo for preparation of the manuscript.

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