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P/O Ligand Systems: Synthesis and Reactivity of Primary and Secondary *o*-Phosphinophenols

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ABSTRACT

Several organometallic reagents such as lithium 2-lithio 4-methylphenolate **1** *intermediates formed by orthometallation of o-bromoaryloxy-phosphorus(V)-* **2** *or -phosphorus(III)-derivatives* **3** *with magnesium and sodium, respectively, as well as O-methoxymethyl-protected o-lithio-4-methylphenol* **4** *were used to synthesize suitable precursors* **5,6,9,10** *of primary and secondary o-phosphinophenols. The P–C bond formation involved coupling with* $ClPR(NMe_2)$, $ClPR(O)(OEt)$ *or an intramolecular carbanionic O → C shift of the P-substituent. Reduction with* $LiAlH_4$, *in the cases of phosphonous or phosphinous acid amides after alcoholysis (to* **7,8,11***), produced primary and secondary o-phosphinophenols* **12**, *respectively, or O-protected derivatives* **13.** *o-Phosphinophenols* **12** *are easily protonated at the phosphorus atom, supported by a* P^+*-H. . .O hydrogen bridge. Metallation (***14***), acylation, and silylation (***16,17***) take place preferably at the hyxdroxy group and alkylation at the phosphorus atom. Alkylation of* **12** *and* **14** *was found to be slow, but C,O-dilithiated species* **15** *react to give P-secondary (***12b,d,e,***) or P-tertiary products (***20,21***). Cyclization of* **15a** *with* Me_2SiCl_2 *affords the 2,3-dihydro-1,3,2-benzoxaphosphasilol* **22,** *cyclocondensation of* **12c** *with* $RP(NMe_2)_2$ *or* $ClP(NMe_2)_2$ *furnishes 2,3-dihydro-1,2,3- benzodiphospholes* **23** *and* **24.** *A phosphinidenphosphoran* **25** *is detected in the reaction between* **12a** *and* $P(NMe_2)_3$. *© 1997 John Wiley & Sons, Inc. Heteroatom Chem* **8***: 383–396, 1997*

INTRODUCTION

Primary and secondary *o*-phosphinophenols are, like the related *o*-aminophenols, ambident binucleophilic reagents with a broad potential in the synthesis of hybrid or chelate ligands, complexes, or heterocycles. Surprisingly, there is not much known about these compounds. The synthesis of 2-phosphinophenol via a photoinduced Michaelis–Becker reaction of iodophenol with sodium diethyl phosphite and reduction of the resulting *o*-hydroxyphenylphosphonic acid ester was first reported by Issleib and Vollmer [1]. An alternative synthesis of 2-phosphinophenol and 2-phosphinocresol derivatives with organometallic reagents was used by us [2,3] in investigations on stable π-excess aromatic heterocycles with low-coordinated phosphorus [4]. Secondary 2-phosphinophenols have not been obtained in a pure state, although the formation of 2-(phenylphosphino)phenol and bis-(2-hydroxyphenyl)phosphine by sodium cleavage of a phenyl group from the corresponding *P*-tertiary derivatives has been described [5]. The reactivity of the title compounds has not yet been studied in more detail; the only known reac-

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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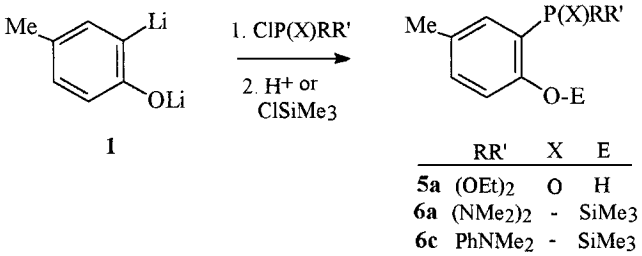
tions being the addition and ring closure reactions with imidoyl chlorides to give P=C–O heterocycles, the *O*-acylation allowing subsequent cyclodehydration, and a substitution reaction with $Me_2NCH(OMe)_2$ yielding bis(dimethylamino)-bis(*o*-hydroxyphenyl)-1,3-disphosphetane [6]. The aim of this work, following our recent investigations on tertiary hydroxyarylphosphines [7,8], is to explore in more detail the synthetic access, the properties, and the chemical behavior of primary and secondary 2-phosphinophenols. This includes a comparison of different P–C coupling reactions, *O*- and *P*-substitution reactions and applications in the synthesis of heterocycles. Descriptions of peculiarities caused by the presence of bulky substituents and phosphido bridging complexes of secondary *o*-phosphinophenols are being published separately [9,10].



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	RR'	X	E
5a	$(OEt)_2$	O	H
6a	$(NMe_2)_2$	-	$SiMe_3$
6c	$PhNMe_2$	-	$SiMe_3$

SCHEME 1

RESULTS AND DISCUSSION

Synthesis

The photoinduced reaction of a functionally substituted iodoarene with $NaP(O)(OEt)_2$ in liquid ammonia, reported in Ref. [1], is a laborious method to create a P–C bond. Furthermore, the ^{31}P chemical shift of the product (δ = 15) obtained with *o*-iododphenol is not in accordance with that of the assumed 2-hydroxyphenylphosphonic acid diethyl ester (δ = 22). Organometallic reagents allow a more convenient connection of phosphorus with phenols. The acidity of the hydroxyl group demands, however, the use of dimetallated **1** [procedure (a)] or an *O*-protected species. A particular case of the latter involves short-lived orthometallated phenoxyphosphorus intermediates, formed from **2** and **3,** which undergo an intramolecular substitution [procedure (b)]. *o*-Lithioarylmethoxymethyl ethers **4** are stable organometallic reagents that allow, after P–C-bond formation, an easy removal of the protective group [procedure (c)]. For the synthesis of the precursors of the title compounds, we applied all of these methods and provide here brief comparative descriptions.

a. C,O-Dilithio reagents **1,** produced from the respective *o*-bromophenols and two equivalents of butyllithium, react with one equivalent of $ClP(O)(OEt)_2$ or $ClPR(NMe_2)$, usually preferably at the carbon atom. The phosphonophenolate is neutralized with dilute sulfuric acid to give **5a,** the hydrolytically sensitive aminophosphine derivatives being treated with $ClSiMe_3$ to afford **6a,b** (Scheme 1). The selective C-phosphinylation of C,O-dilithio reagents may be used widely to synthesize hydroxy-substituted phosphines; however, limitations by side reactions have been observed, in the case of steric hindrance, e.g. in the synthesis of 1-phosphinonaphth-2-ols [8] or of 2-phosphino-4,6-di-*t*-butyl-phenols [9].

b. The second organometallic strategy to obtain 2-hydroxyarylphosphines involves the generation of orthometallated aryloxyphosphorus(III) or-(V) compounds. These are unstable, and presumably, an intramolecular attack of the carbanionic center of the organometallic moiety on the phosphoryl phosphorus atom with displacement of the phenolate moiety occurs (Scheme 2). Metallation with magnesium in ether is advantageous in the case of phosphoric or phosphonic *o*-bromoaryl esters. Compounds **2a** [3b] and **2b** afford high to reasonable yields of **5a** and **5b,** respectively. The analogous reactions of **3a,c,** seem to be hindered by the formation of insoluble products covering the surface of the metal. Even the use of the ultrasound technique did not alleviate this problem. However, this problem could be overcome by direct orthometallation of phosphoric acid aryl esters with LDA [11] or by metallation of the corresponding *o*-bromoaryloxy-dimethylaminophosphines **3a,c** with sodium. A competing reduction by sodium is suppressed by the presence of amino groups at P(III), allowing reasonable to high yields of **6a,c** to be formed. The latter are reacted with methanol to give *o*-hydroxyaryl phosphonous **7** or phosphinic acid esters **8.**

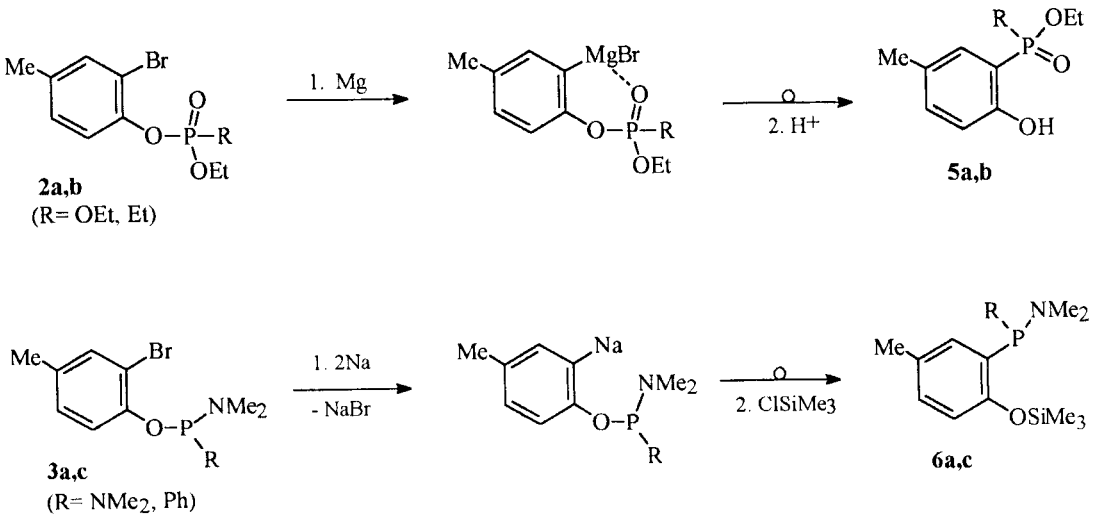
c. Grignard reagents of methyl- or isopropylphenyl ethers were used to prepare diphenyl- or di-*t*-butylphosphinophenols via coupling with Ph_2Cl or tBu_2PCl and subsequent ether cleavage with boiling concentrated hydrobromic acid [12,13]. However, attempts to effect an analogous ether cleavage with primary **o**-phosphinoanisoles caused P–C bond rupture to occur. The use of methoxymethyl phenyl ethers **4,** described for the synthesis of two tertiary derivatives $Ph_nP(C_6H_4OH)_{3-n}$ (n = 1,2) [14], overcame these problems. This approach allowed coupling of **4** with RP(O)(OEt)Cl or aminochlorophosphines to occur to give **9** or **10** and the subsequent alcoholysis of **10** without cleavage of the *O*-protection group that furnished **11** (Scheme 3). Advantages

of this method are the selective direct orthometallation supported by the intramolecular coordination of lithium and a lower probability of the occurrence of unfavorable side reactions.

The primary and secondary 2-phosphinocresols **12a–c** were obtained from the above-mentioned phosphonous, phosphonic, or phosphinic acid esters **7, 8, 9,** and **11** by $LiAlH_4$ reduction and aqueous acid workup (Scheme 4). The pH had to be controlled and kept at 3–5 since substantial impurities of phosphonium chlorides, extracted by ether during workup with aqueous hydrochloric acid in the synthesis of **12,** caused slight decomposition during the distillation step and gave rise to contamination by *p*-cresol (P–C cleavage). The O-methoxymethylated secondary phosphines **13b,c** were accessible from **9** or **11** if the hydrolysis of excess hydride and of phosphide formed in the reduction was carried out with little water and under basic conditions. The methoxymethyl group is removed by mild acid-catalyzed hydrolysis without splitting off of the PHR substituent. The procedure via **13** allowed us to separate the aluminum hydroxide by filtration and avoided the unpleasant extraction from the aqueous phase of the air-sensitive phosphines.

PROTONATION AND DEPROTONATION

o-Phosphinophenols are amphoteric; they possess the weakly basic phosphino and the weakly acidic



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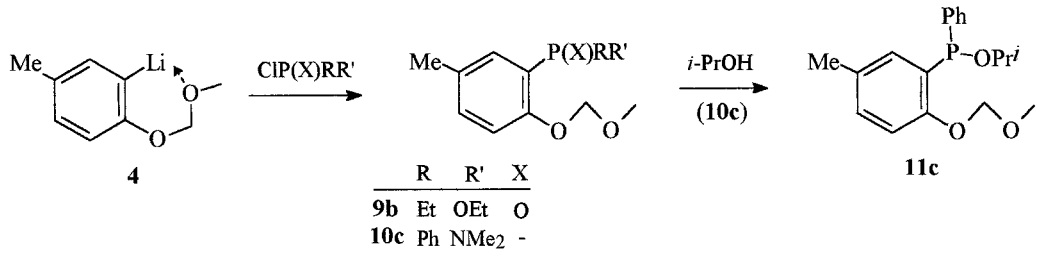

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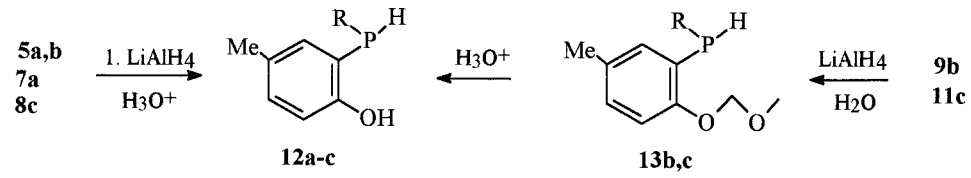


SCHEME 4

hydroxyl groups. The infrared spectra of **12a** and **12c** in dilute (0.5%) toluene solution exhibit strong OH-bands at 3543 and 3541 cm^{-1} that remain nearly unchanged (3540 and 3539 cm^{-1}) in a saturated solution and correspond to dimeric O..H–O associated species. A broad shoulder at ca. 3430 cm^{-1} in a conc. **12a** solution and at 3480 cm^{-1} in dilute as well as concentrated **12c** solutions indicate P..H–O interactions; however, these are much weaker than in *t*-butylphenylphosphinophenols (3360 cm^{-1} st) [8a]. The PH-bands are slightly broadened. Suspensions or dilute solutions of **12** in water–methanol show values of pH = 5–6. The solubility in water is usually quite low and decreases from primary to tertiary derivatives. The solubility increases considerably in strongly acidic or basic aqueous solutions. The protonation at phosphorus and deprotonation at hydroxyl and subsequently at PH groups were studied by ^{1}H and ^{31}P NMR spectra. Dilute solutions of **12** exhibit sharp proton NMR signals for PH and OH groups. At higher concentrations, the OH singlet is broadened. On addition of medium or strong acids, such as acetic, hydrochloric, or sulfuric acid, both signals become very broad, attributable to an extensive proton exchange between phosphorus and oxygen via a hydrogen bridging bond (Scheme 5). The protonation by HCl is tenacious. Even after distillation in vacuo, broad proton signals for PH- and OH were observed because the distillate was contaminated by its hydrochloride. The protonation of **12** by acetic acid is much less extensive, and complete removal of this acid was observed following distillation in vacuo.

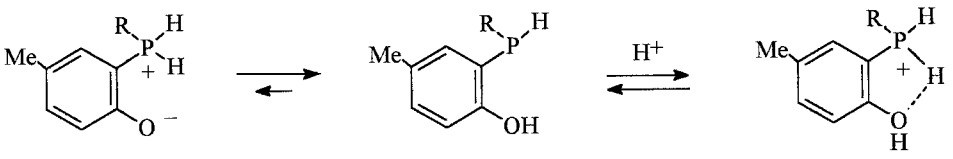
Compounds **12a–c** react with one equivalent of sodium in liquid ammonia to give colorless solutions of **14a–c.** The metallation of **12a–c** by butyllithium in ether proceeds similarly. The phosphinophenolate–phosphidophenol equilibrium strongly favors the former. By way of contrast, a 2-phosphinoalcohol exhibits a yellow-orange color. Here only on addition of a second equivalent of sodium or butyllithium does the solution turn to orange by formation of **15a–c** (Scheme 6).

Lithium- 2-phosphino-4-methylphenolate **14a** (M = Li), formed from **12a** ($\delta^{31}P = -152$) by the action of BuLi, reveals sharp ^{31}P ($\delta = -137$) and ^{7}Li NMR ($\delta = 1.21$) signals. The negligible influence of *O*-lithiation on the ^{1}J (PH) coupling constant of the PH_2 group indicates that there is no significant interaction between the phosphorus and lithium atoms. Addition of an excess of *n*-BuLi does not cause significant changes of the spectra until a molar ratio of about 1:1.5 is reached. We observed then, in the ^{31}P and ^{7}Li NMR spectra, a second broad signal (^{31}P: δ: = −147.8, −145; ^{7}Li: δ = 0.08, 1.78) at lower field that gains in relative intensity and is shifted slightly upfield on increasing lithiation. The effect is stronger in concentrated (Figure 1) than in dilute solution (Table 1). High field jumps appear at the ratio of 1:2 leading to $\delta^{31}P = -185$ and $\delta\ ^{7}Li = -1.76$. The ^{1}H NMR spectra reveal increasing broadening of the mixed PH_2/PH signal above a ratio of 1:1.5. At the stage of dilithiation (1:2), the PH signal cannot be distinguished from the noise.

SUBSTITUTION REACTIONS

Primary and secondary *o*-phosphinophenols **12** and their mono- or dimetallated species **14** and **15** can be attacked by electrophilic reagents at the phosphorus or oxygen atom. Silylation (**16a, 17**), phosphinylation (**18,19**), and acylation [6] take place primarily at the oxygen atom and proceed rapidly in the presence of an auxiliary base, after the stage of monolithiation or in the case of the use of P–N compounds (Scheme 7).

Reactions of alkyl bromides as well as of methyl iodide with **12a–c** or the respective sodium or lithium *o*-phosphinophenolates **14a–c** proceed very slowly. This behavior differs strongly from that of primary 2-phosphinoalcohols [15] and is attributed to the higher acidity of phenols and the much lower equilibrium concentration of phosphide. A reasonable conversion rate with selective attack at the phosphorus atom is achieved only after O,P-dimetaleation brought about with two equivalents of butyllithium in ether or with two equivalents of sodium in liquid ammonia (Scheme 8). But even the *o*-phosphidophenolates **15a–c** react at a considerably slower rate than is the case with ordinary aryl phosphides. Reaction times of two days are necessary to obtain yields of alkylation products of 50–70% with



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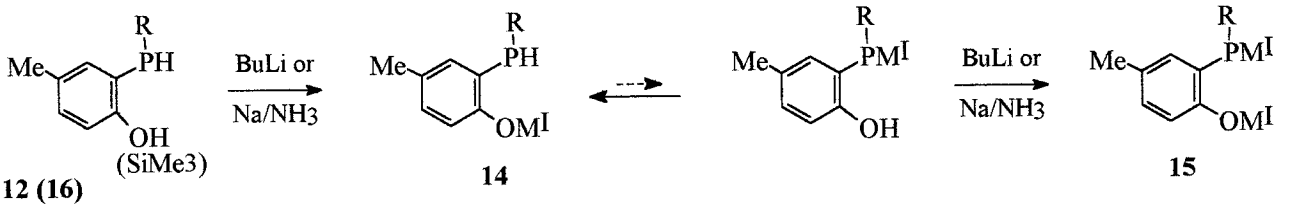

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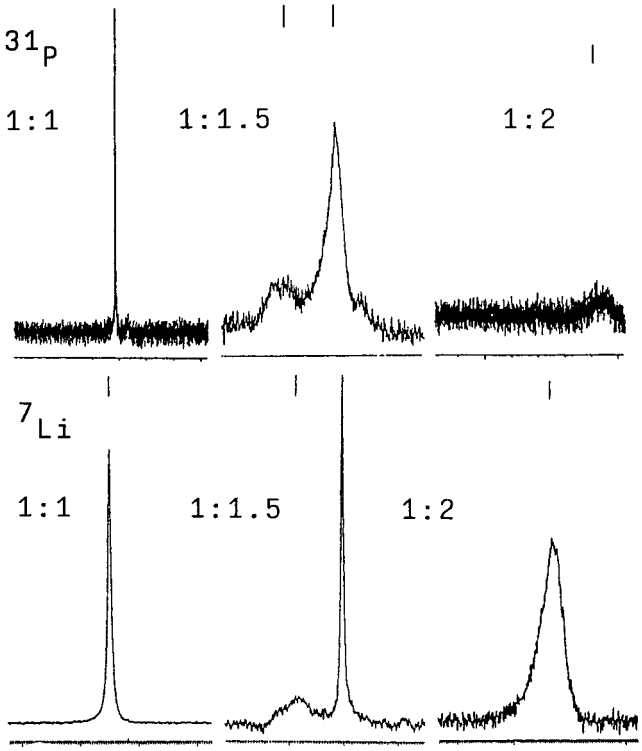


FIGURE 1 ^{31}P and ^{7}Li NMR spectra of mono-, 1.5-, and twofold lithiated **12a** (in THF-d_8).

MeI, EtBr, or *i*PrBr. The resulting alkylphosphinophenolates may be neutralized by the action of ammonium bromide to give **12b,d,e** or they may be treated with chlorotrimethylsilane to afford the respective *O*-trimethylsilylethers **16b,d,e.** Nevertheless, the alkylation of **12a** serves as a convenient alternative synthesis of secondary alkyl *o*-phosphinophenols. Alkylation of secondary derivatives allows one to obtain *P*-asymmetrically substituted tertiary phosphinophenols, such as the alkylene-bridged bis(*o*-phosphinophenol) derivative **20,** which was obtained, however, only in low yield. The bridged diphosphines were obtained more favorably by coupling of 1,3-dibromopropane with two equivalents of monolithiated **o**-phosphidophenyl methoxymethyl ethers, as shown by the synthesis of the hexadentate (2P,4O) ligand **21.**

The *o*-phosphinophenol derivatives were characterized by their ^{1}H, ^{31}P, and ^{13}C NMR spectra. Characteristic features are the downfield shift of $\delta^{31}P$ and increasing ^{1}J (PH) coupling constants with increasing alkyl substituents at phosphorus. The phosphorus chemical shifts of the respective *O*-trimethylsilyl ethers are downfield shifted by $\Delta\delta = 14$ to 18, slightly increasing with increasing steric demand of the *P*-alkyl group. The ^{1}J (PH) coupling constants of the silyl ethers **16** grow much slower with the size of the *P*-alkyl groups than those of **12** due to the large *o*-substituent (Table 2). Nevertheless, the steric hindrance is low. The two-bond P–C coupling constants, which depend on the dihedral angle toward the lone electron pair at the phosphorus atom [16], are similar for ^{2}J (PC1) and ^{2}J (PC3) and correspond to averaged conformations. The secondary *o*-phosphinophenols thus have a medium position between bulky substituted primary *o*-phosphinophenols with preferred *cis*- and tertiary *o*-phosphinophenols with preferred *trans*-orientation of the phenoxy group (Table 3). In ab initio calculations on unsubstituted *o*-phosphinophenol at the HF/3-21G(d) level of theory, the *cis*-conformation was found to be the lowest-energy conformer. The lowest barrier to rotation is 10.8 kJ/mol. The photoelectron spectra are consistent with a lack of π-interactions between the lone pair of phosphorus and the aryl π-system [17].

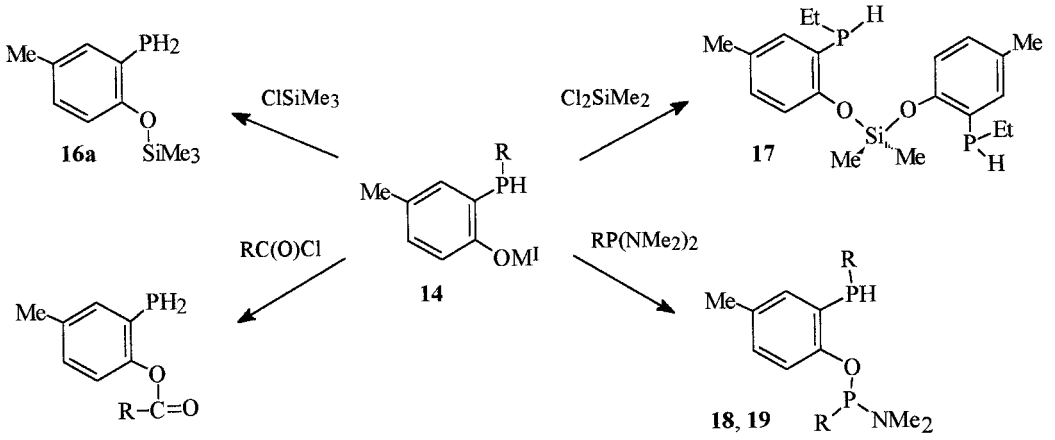
CYCLIZATION REACTIONS

Besides substitution at either the oxygen or the phosphorus atom, the bifunctional primary and secondary *o*-phosphinophenols can undergo substitution at both nucleophilic sites if they are reacted with bi- or multifunctional electrophiles. Heterocycles, oligomers, or polymers may be formed. Compound **15a** and one equivalent of dichlorodimethylsilane react stepwise to afford the 2,3-dihydro-1,3,2-benzoxaphosphasilol **22.** This heterocycle presents a thermally stable, reactive P–Si–O structural unit and exhibits the typical ^{31}P upfield shift of silyl phosphines ($\delta = -175$), a deshielded ^{29}Si nucleus ($\delta = 44$, $^{1}J_{PSi} = 18.3$ Hz), and two distinct Si-methyl groups, indicating the pyramidal configuration at phosphorus.

TABLE 1 ^{31}P and ^{1}H Chemical Shifts of 14a and 15a and Their Mixtures

THF-[d8]	*1:1*	*1:1.2*	*1:1.4*	*1:1.6*	*1:1.8*	*1:2*
$\delta^{31}P$	−139.9 rs	−138.4 rs	−138.0 rs	−139.8 br	−138.6 vbr −141.5 vbr	ca. −185 ebr
$\delta^{1}H$; $^{1}J_{PH}$ (Hz)	3.64 rs 197.5	3.63 rs 197.8	3.63 br 196.9	3.66 vbr ca. 196	3.63 vbr 196	ca. 3.6 ebr

rs = relatively sharp, br = broad, vbr = very broad, ebr = extremely broad, δ uncertain.



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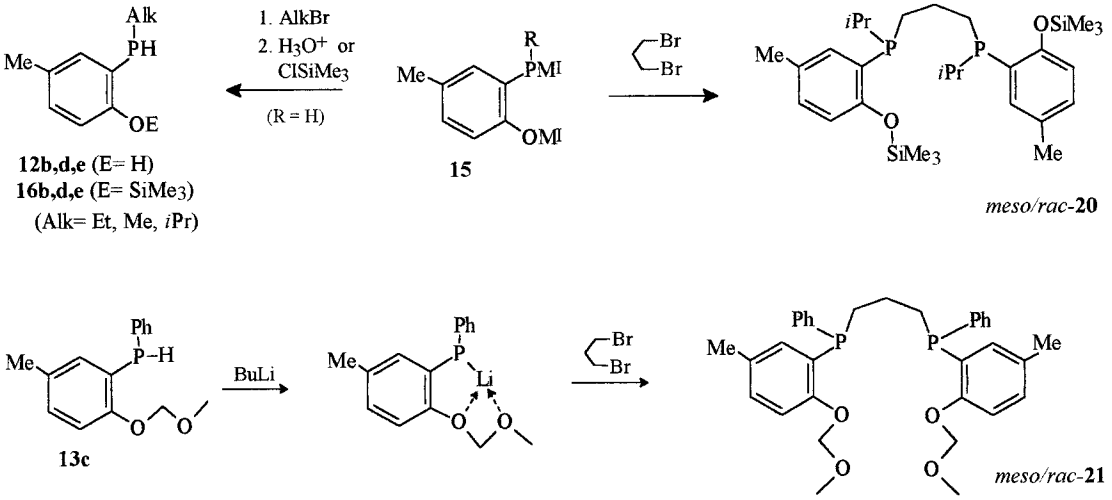


SCHEME 8

Attempts to use this method for the synthesis of other heterocycles by reaction of **15** with tBuPCl$_2$, Me$_2$N-PCl$_2$, Et$_2$SnCl$_2$, or zirconocene dichloride failed; ill-defined product mixtures were formed. Ring closure was achieved, however, by reaction of **12c** with diaminophosphines. The first amino group is selectively replaced by OR under mild conditions (**18** and **19,** see above), while the second reacts at the PH function on heating to give 2,3-dihydro-1,2,3-benzoxadiphospholes **23** and **24.** The uncommon substitution of an amino by a phosphino group is supported by ring formation. Another possibility, the reaction of **12c** with the aminochlorophosphine CIP (NMe$_2$)$_2$, makes use of the high driving force for formation of ammonium salts and allows a rapid and nearly quantitative synthesis of **23** (Scheme 9).

TABLE 2 ^{31}P Chemical Shift and ^{1}J (PH) Coupling Constants of 12 and 16.

R		δ ^{31}P	^{1}J (PH) (Hz)		$\delta^{31}P$	^{1}J (PH) (Hz)	$\Delta\delta$ (^{31}P)
H	**12a**	−151.70	205.9	**16a**	−137.45	204.2	14.25
Me	**12d**	−96.23	216.9	**16d**	−82.18	207.9	14.05
Et	**12b**	−70.63	218.9	**16b**	−54.63	212.4	16.0
i-Pr	**12e**	−54.51	220.5	**16e**	−35.96	210.5	18.55
Ph	**12c**	−64.67	226.1				

TABLE 3 ^{2}J (PC) Coupling Constants of Selected *o*-Phosphinophenols [Hz]

P-Subst.	*4,6-Subst.*	$^{2}J_{PC1}$	$^{2}J_{PC3}$
H_2[a]	tBu$_2$	2.5	40
H_2	MeH	5.1	21.2
H_2	H_2	6.0	20
PhH[a]	tBu$_2$	9	39
PhH	MeH	9.4	16.1
MeH	MeH	12.1	7.5
EtH	MeH	11.7	8.0
*i*PrH	MeH	12.9	6.0
AlkPhP[b]	MeH	20–22	0–1

[a][9].
[b][8a].

In both syntheses, only one of the two pairs of diastereoisomers of the dihydrobenzoxadiphospholes is observed. We assume that the *E*-configuration of the two substituents at phosphorus is formed. The *ipso*-carbon atoms of the 2-phenyl and 3-phenyl groups exhibit large ^{2}J (PC) coupling constants that are consistent with small dihedral angles toward the lone electron pairs of the P atom in the β-position [16] (l*p*-P2-P3-*ipso*C and l*p*-P3-P2-*ipso*C). The ^{1}J (PP) coupling constants of about 230 Hz correspond to the typical range of P–P single bonds and are much lower than those of 2-diisopropylamino-1,1-diphenyl-1,2-dihydro-1,2,3-benzoxadiphospholium salts with ^{1}J (PP) = 382 Hz [18]. Abundant peaks for 1,2-dihydro-benzoxadiphospholium cations, the molecular and fragmentation ions, appear in the mass spectra of **23.** The intensive fragment peak at *m/e* = 168 (53%) is in accordance with a benzoxadiphosphole cation.

The reaction of primary **12a** with $P(NMe_2)_3$ was of interest since intramolecular elimination of a second Me_2NH could lead to a 1,2,3-benzoxadiphosphole. No evidence for the formation of this compound was obtained; we observed formation, however, besides a brown air-sensitive insoluble solid, of a phosphiniden-phosphorane **26** with characteristic chemical shifts $\delta(^{31}P)$ = −186.1 (P^{III}) and 131.2 (P^{V}) and a large coupling constant ^{1}J (PP) = 530 Hz [9,19]. It is probably formed via **25a** (R″ = Me), in a substitution reaction with $P(NMe_2)_3$ and decomposition of the resulting unstable aminosubstituted triphosphine as described in Ref. [9]. Compound **25** possesses a P(H)–P(O) structural unit and seems to be highly reactive. The derivative **25a** (R″ = Et) could be obtained as a crude product from reaction of **12a** with $ClP(NEt_2)_2$ and reveals a remarkable high-field chemical shift for a secondary diphosphine and a relatively low ^{1}J (PP) coupling constant [$\delta(^{31}P)$ = −94.0, 149.8; ^{1}J (PP) = 196 Hz] [20]. Decomposition takes place in attempts to distill **25b.**

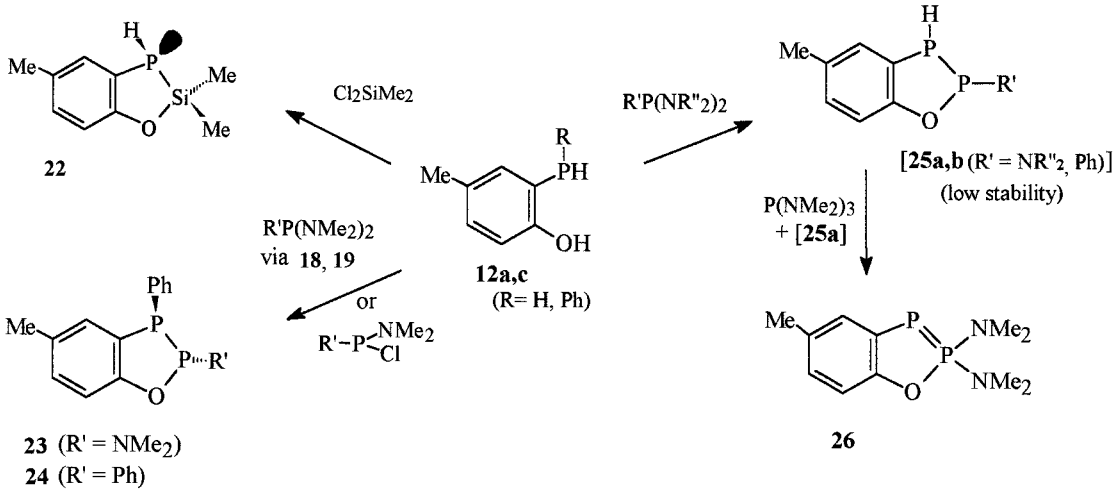
EXPERIMENTAL

Materials and Spectroscopy

All reactions were carried out under an argon atmosphere using the Schlenk technique and freshly distilled, dried solvents. Me_3SiCl was recondensed prior to use, and $ClP(NMe_2)_2$ [21a], $ClP(Ph)NMe_2$ [21b], and ClP(O)(Et)OEt [22] were prepared according to the literature. NMR data are recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), 59.6 (^{29}Si), and 121.5 MHz (^{31}P). References are TMS for ^{1}H, ^{13}C, and ^{29}Si and H_3PO_4 (85%) for ^{31}P. $CDCl_3$ is used as solvent unless otherwise indicated. Assignment numbers of atoms follow the nomenclature. Mass spectra (EI, 70 eV) were measured on a single-focusing sector-field mass spectrometer AMD40 (Intectra), IR spectra on a Model System 2000 of Varian.

a. P–C Bond Formation with C,O-Dilithium or C,O-Lithium-sodium Reagents: 5-Methyl-2-hydroxyphenylphosphonic Acid Diethyl Ester **5a**

A solution of 30.6 g (160 mmol) of 2-bromo-4-methylphenol in 500 mL of ether was reacted with 204 mL of 1.6 M BuLi (326 mmol) in hexane. A solution of 28.2 g (160 mmol) of $(EtO)_2P(O)Cl$ in ether (20 mL) was added dropwise at 0–5°C to the partly dissolved, partly suspended **1,** and the mixture was stirred for 2 days to complete the reaction. The mix-



SCHEME 9

ture was then hydrolyzed and acidified with 100 mL of 10% sulfuric acid, the ether extract dried with Na_2SO_4, and the solvent removed by distillation. Distillation of the residue at 90–100°C/0.01 Torr afforded a viscous oil that solidified and gave, after washing with hexane, 10 g (25%) of **5a,** mp 50–52°C. ^{31}P NMR: δ 23.1. ^{1}H NMR: δ 1.33 (t, J = 7.1 Hz, 6H, Me), 2.28 (s, 3H, 4-Me), 4.10 (m, 4H,CH_2), 6.86 (dd, $J_{HH/PH}$ = 8.4, 7.0 Hz, 6-H), 7.15 ($J_{HH/PH} \approx$ 2.1, 14.6 Hz, 3-H), 7.24 (J_{HH} = 8.4, 5-H). Anal. calcd for $C_{11}H_{17}O_3P$ (244.2): C, 54.10; H, 7.02%. Found: C, 54.05; H, 7.16%.

(5-Methyl-2-trimethylsiloxyphenyl)phenylphosphinous Acid Dimethylamide **6c.** A solution of 126 mL of 1.6 M BuLi in hexane (202 mmol) was added to a solution of 18.8 g (100 mmol) of 2-bromo-4-methylphenol in 200 mL of ether, the first half dropwise at −40°C and the second part rapidly without cooling. The suspension of **1** was stirred for 4 hours to complete the metal–halogen exchange, 18.8 g (100 mmol) ClP(Ph)NMe_2 then being added (−20°C), and, after 4 hours, 13 mL (103 mmol) of $ClSiMe_3$ was added. The suspension was filtered, the solvent removed from the filtrate, and the residue distilled at 130–135°C/0.2 Torr affording 20 g (60%) of **6c.** ^{31}P NMR: δ 56.7. For ^{1}H and ^{13}C NMR data, see Ref. [5]. In a synthesis with 200 mmol of the bromocresol, the yield dropped to 53%.

b. P–C Bond Formation on Metallation of Phosphorus or Phosphonic Acid o-Bromoaryl Ethers

A. Phosphorus or Phosphonic Acid o-Bromoaryl Ethers: Ethylphosphonic Acid 2-Brom-4-methylphenyl Ethyl Ester **2b.** Ethylphosphonic acid ethyl ester chloride (48.7 g, 0.31 mol) was added dropwise at 5°C with vigorous stirring to a solution of 2-bromo-4-methylphenol (60.0 g, 0.31 mol) in 50 mL of 25% aqueous NaOH solution. After the mixture had been stirred for a further 2 hours, 400 mL of toluene was added to extract the O-substituted product. The organic phase was washed with 80 mL of 10% NaOH solution, then with water, and finally dried over sodium sulfate. The toluene was evaporated and the residual oil distilled at a bp of 120°C/0.2 Torr to give 69.0 g (70% yield) of **2b.** ^{31}P NMR: δ 3.6.

B. Metallation Rearrangement: Ethyl-(2-hydroxy-4-methyl-phenyl)-phosphinic Acid Ethyl Ester **5b.** A mixture of 2 g of the total of 63.6 g (0.2 mol) of **2b** and a few drops of ether were added to 5.1 g (0.21 mol) of magnesium. After some minutes, if the reaction had started, a solution of the remaining 61.6 g of **2b** in a twofold volume of dry ether was added in such a manner that a slight reflux was maintained. The suspension was then refluxed for 2 hours and stirred overnight. Cold (10°C) 20% hydrochloric acid was added with stirring and cooling until the pH was about 2 to 3. The ether layer was separated, the aqueous phase extracted with ether, and the combined ether solution dried with sodium sulfate. The solvent was removed in vacuo, and the residue of 25.2 g (55% yield) of **5b** was distilled at a bp 145°C/0.1 Torr. ^{31}P NMR: δ 50.2.

c. P–C Bond Formation with O-Methoxymethyl Protected o-Lithiophenols

Ethyl-(2-methoxymethyloxy-5-methyl-phenyl)-phosphinic Acid Ethyl Ester **9b.** A solution of 20.0 g (0.13 mol) of *O*-(methoxymethyl)-4-methylphenyl

ether in dry ether (2 mL/mmol reagent) was cooled to −50°C, and 83 mL of 1.6 N *n*-BuLi was added dropwise. The mixture was stirred for 5 hours at 20°C and cooled again to −50°C with subsequent slow addition of ethylphosphonic acid ethyl ester chloride (20.4 g, 0.13 mol), dissolved in a twofold volume of ether. The suspension was stirred for 24 hours and filtered, the solvent evaporated from the filtrate and the residue distilled to yield 19.4 g (55%) of **9b,** bp 125°C/0.1 Torr. ^{31}P NMR: δ 45.4. Anal. calcd for $C_{13}H_{21}O_4P$ (272.24): P 11.35%. Found: P 11.52%.

(2-Methoxymethyloxy-5-methyl-phenyl)-phenyl-phosphinous Acid Dimethylamide **10c.** A 63 mL amount of 1.6 N *n*-BuLi was added dropwise to a cold (−30°C) solution of 15.3 g (0.1 mol) of *O*-(methoxymethyl)-4-methylphenyl ether in ether (150 mL), and the mixture was stirred for 1 day at 20°C. The suspension of **4** was cooled at −20°C, 18 g (0.1 mol) of $ClP(Ph)NMe_2$ was added dropwise, and, after 8 hours, the precipitate was filtered off. The solvent was removed from the filtrate, and 19.8 g (65%) of **10c** was distilled at 120–130°C/0.1 Torr. ^{31} P NMR: δ 56.5. ^{1}H NMR: δ 2.32 (s, Me), 2.67 (d, J_{PH} = 9.3 Hz, NMe_2), 3.26 (s, OMe), 5.02 (dd, $J_{HAHB/PH}$ = 6.8, 6 Hz, O_2CH_A), 4.99 (d, J_{HAHB} = 6.8 Hz, O_2CH_B), 7.01 (m, 1H, 3-H), 7.13 (m, 2H, 4,6-H), 7.2–7.5 (m, 5H, Ph). Anal. calcd for $C_{17}H_{22}NO_2P$ (303.34): P 10.21%. Found: P 9.85%.

Alcoholysis of Phosphonous or Phosphinous Acid Amides and Reduction with $LiAlH_4$

(2-Hydroxy-5-methyl-phenyl)phenylphosphinous Acid **8c.** A 7.1 g (21.4 mmol) amount of **6c** was refluxed for 3 hours in 20 mL of methanol (not dried), and 4.5 g (91% yield) of **8c** crystallized in spectroscopically pure form on cooling, mp 138–141°C ($EtOH/C_6H_6$). ^{31}P NMR: δ 21.4. ^{13}C NMR: δ(J_{PC} in Hz) 20.3 (Me), 112.8 (d, 103.4, C-1), 117.0 (d, 7.1, C-3), 128.8 (d, 12.9, C-*m*), 128.8 (d, 12.9, C-5), 130.6 (d, 11.8, C-*o*), 131.0 (d, 9.1, C-6), 131.2 (d, 103, C-*i*), 132.6 (d, 2.3, C-*p* or C-4), 135.4 (d, 1.9, C-4 or C-*p*), 158.9 (d, 4.3, C-2). ^{1}H NMR: δ 2.19 (s, 5-Me), 6.84 (dd, $J_{HH/PH}$ = 1.8, 16.2 Hz, 6-H), 6.88 (dd, $J_{HH/PH}$ = 8.4, 5.3 Hz, 3-H), 7.49 (m, $J_{HH} \approx$ 8.4, 4-H), 7.5–7.7 (m, 3H, Ph), 7.73–7.80 (m, 2H, Ph), 8.23 (d, $^1J_{PH}$ = 492.5, PH).

(2-Methoxymethyloxy-5-methyl-phenyl)phenyl-phosphinous Acid Isopropyl Ester **11c** *and (2-Methoxymethyloxy-5-methyl-phenyl)phenylphos-phine* **13c.** A 5 mL (3.9 g, 65 mmol) amount of *i*PrOH was added to 19.7 g (65 mmol) of **10c,** the mixture heated 24 hours at 60°C, and volatile products removed in vacuo to give crude **11c,** δ^{31}P 96.6 (ca. 70%), with impurities exhibiting resonances at 15.3 and 30.5. This crude material was dissolved in a small amount of ether and dropped at ca. 10°C into a suspension of $LiAlH_4$ (2.5 g) in 300 mL of ether. After having been refluxed (2 h) and stirred overnight to complete the reduction, the mixture was cautiously hydrolyzed at 10°C by addition of degassed water until the $Al(OH)_3$ precipitation had formed particles and the evolution of hydrogen had ceased. The mixture was filtered, the filtrate dried with sodium sulfate, the ether removed, and the residue distilled at 137–143°C/0.1 Torr to yield 7.5 g (60%) **13c.** ^{31}P NMR: δ −54.0. ^{13}C NMR: δ(J_{PC} in Hz) 20.4 (5-Me), 113.7 (C-3), 124.1 (d, 11.6, C-1), 128.3 (C-*p*), 128.24 (d, 6.5, C-*m*), 131.3 (d, 3.3, C_q-5), 130.7 (C-4), 134.3 (d, 17.4, C-*o*), 134.1 (d, 10.6, C-*i*), 135.5 (d, 8.9, C-6), 156.1 (d, 10.4, C-2). ^{1}H NMR: δ 2.26 (s, 5-Me), 3.37 (s, OMe), 5.12 and 5.16 (2m, $J_{HAHB/PH}$ = 6.8, 1–2 Hz, $O_2CH_AH_B$), 5.22 (d, J_{PH} = 223 Hz, PH), 6.99 (dd, $J_{HH/PH}$ = 8.2, 3.6 Hz, 3-H), 7.10 (dd, J_{HH} = 8.2, 2 Hz, 4-H), 7.32 (dd, $J_{HH/PH}$ = 2, 6.5 Hz, 6-H), 7.2–7.3 and 7.5–7.6 (m, 5H, Ph). Anal. calcd for $C_{15}H_{17}O_2P$ (260.25): P 11.90%. Found: P, 12.0%.

4-Methyl-2-phenylphosphino-phenol **12c.** A 10 mL amount of methanol was added to 35.4 g (107 mmol) of **6c,** and the mixture was slowly heated to 70°C until the evolution of Me_2NH ceased. $MeOSiMe_3$ and excess MeOH were evaporated at 60°C (bath)/0.01 Torr. The residue was dissolved in ether (100 mL) and added dropwise to 3.0 g (79 mmol) of $LiAlH_4$ in 400 mL of ether. The mixture was stirred overnight to complete the reduction and then hydrolyzed at 0–10°C by addition of ca. 100 mL of 10% sulfuric acid. The ether phase was combined with benzene extracts of the acidic aqueous phase, dried first with Na_2SO_4 and then azeotropically by distilling off some benzene. The residual solvent was removed in vacuum and 15.5 g (67%) of **12c** was collected by distillation at 106–107°C/0.001 Torr. ^{31}P NMR: δ −65.3. ^{13}C NMR: δ (J_{PC} in Hz) 20.3 (Me), 115.4 (d, 1.7, C-6), 118.2 (d, 9.4, C-2), 128.4 (C-*p*), 128.7 (d, 5.9, C-*m*), 130.1 (d, 6.3, C-4), 132.2 (C-5), 133.0 (d, 16.1, C-*o*), 133.2 (d, 8.2, C-*i*), 137.0 (d, 16.1, C-3), 155.8 (d, 9.4, C1). ^{1}H NMR: δ 2.23 (s, 4-Me), 5.14 (d, J_{PH} = 226 Hz, PH), 5.6 (s, OH), 6.76 (dd, $J_{HH/PH}$ = 8.2, 3.5 Hz, 6-H), 7.07 (m, J_{HH} = 8.2, 2.1, 0.6 Hz, 5-H), 7.21 (dd, $J_{HH/PH}$ = 2.1, 8.5 Hz, 3-H), 7.25–7.30 and 7.4–7.5 (m, 5H, Ph). Anal. calcd for $C_{13}H_{13}OP$ (216.2): C, 72.22; H, 6.06%. Found: C, 71.30; H, 5.64%. MS (70 ev): m/z = 216 (vs, M^+), 138 (vs), 110, 109, 108 (vs), 92 (vs).

A 19.7 g amount of **10c** (65 mmol) was heated with 5 mL of abs. *i*PrOH (24 h at 60°C), affording crude **11c** (see above). This was dissolved in ether (300 mL), reduced with 3.0 g $LiAlH_4$ as for **13c,** but worked up with 10% sulfuric acid as described above to give 10.9 g (65%) of **12c,** $\delta(^{31}P)$ −64.7.

Primary and Secondary o-Phosphinophenols from Phosphonic and Phosphinic Acid Esters 2-Phosphinophenol **12.** For preparation, see Refs. [3,6]. Selected NMR data: ^{31}P NMR: δ −151.6. ^{13}C NMR: $\delta(J_{PC}$ in Hz) 113.7 (d, 9.5, C-2), 115.4 (d, 1.9, C-6), 121.1 (d, 1.6, C-4), 129.7 (d, 1.6, C5), 137.0 (d, 20, C3), 157.3 (d, 6.0, C1). ^1H NMR: δ 3.74 (d, J_{PH} = 207 Hz, PH_2), 5.9 (OH).

2-Phosphino-4-methylphenol **12a.** A solution of **5a** (63.7 g, 0.26 mol) in 50 mL of ether was added dropwise at 0°C to 10 g (0.26 mol) of $LiAlH_4$ in 500 mL of ether. The suspension was stirred overnight, refluxed for 1 hour, and cautiously hydrolyzed at 0–5°C by addition of degassed water. When the hydrogen evolution ceased, hydrochloric (10%) was added until the pH was about 3. The combined ether extracts were dried with Na_2SO_4, the ether was evaporated, toluene (50 mL) was added, and residual water was removed azeotropically. The residual liquid was distilled through a spinning band column to give 23.0 g (63% yield) of **12a,** bp 72°C/0.1 Torr. ^{31}P NMR: δ −152.0. ^{13}C NMR: $\delta(J_{PC}$ in Hz) 20.4 (4-Me), 112.8 (d, 9.3, C-2), 114.9 (d, 1.5, C-6), 130.1 (d, 7.7, C-4), 131.6 (C-5), 137.5 (d, 21.2, C-3), 155.3 (d, 5.1, C-1). ^1H NMR: δ 2.26 (s, 4-Me), 3.74 (d, J_{PH} = 205 Hz, PH_2), 5.29 (brs., OH), 6.75 (dd, J = 8.2, 2.5 Hz, H6), 7.05 (dd, J = 8.2, <1 Hz, H5), 7.28 (dd, $J_{HH/PH}$ = 2.5, 7.7 Hz, H3). Anal. calcd for C_7H_9OP (140.12): P 22.11%. Found: P 21.5%.

2-Ethylphosphino-4-methylphenyl Methoxymethyl Ether **13b.** A solution of 12.0 g (0.044 mol) of **9b** in 15 mL of ether was added dropwise at 10–15°C to a suspension of 2.0 g (50 mmol) of $LiAlH_4$, and the mixture was stirred overnight, refluxed for 2 hours to complete the reduction, and worked up as described for **13c.** A 5.1 g (55%) amount of **13b** was obtained, bp 110°C/0.1 Torr. ^{31}P NMR: δ −54.4. ^{13}C NMR: $\delta(J_{PC}$ in Hz), 13.1 (d, 6.3), and 14.4 (d, 10.1) (PEt), 20.3 (4-Me), 55.8 (OMe), 94.5 ($O\underline{C}H_2O$), 113.9 (C6), 128.3 (C2), 130.0 (C5), 130.8 (d, 2.1, C4), 135.1 (d, 6.9, C3), 156.2 (d, 9.4, C1). ^1H NMR: δ = 1.14 (dt, $J_{HH/PH}$ = 7, 12.9 Hz, $PCCH_3$), 1.78 and 1.89 (dd, J = 34.5, 7 Hz and J = 34.5, 7.7 Hz, PCH_AH_B), 2.29 (s, 4-Me), 3.48 (s, OMe), 4.05 (ddd, $J_{PH/HH}$ = 212.7, 6.5, 1.5 Hz, PH), 5.19 (s, OCH_2O), 6.98 (m, H6), 7.04 (m, H5), 7.23 (dd, J = 6.7, 1.4 Hz, H3).

2-Ethylphosphino-4-methylphenol **12b.** A. A solution of 9.8 g (43 mmol) of **5b** in 50 mL of ether was reduced with 2.0 g $LiAlH_4$ in 300 mL of ether. Acidic workup with 10% sulfuric acid, as described above for **12c,** furnished 3.6 g (50%) of **12b,** bp 90°C/0.1 Torr. ^{31}P NMR: $\delta(J_{PC}$ in Hz) 12.7 (d, 8.3, C*Me*), 14.8 (d, 7.2, *C*Me), 20.3 (4-Me), 115.2 (C-6), 119.4 (d, 9.5, C-2), 129.6 (d, 3.7, C-4), 131.4 (C-5), 136.0 (d, 8.0, C-3), 155.9 (d, 11.7, C-1). ^1H NMR: δ 1.08 (dt, $J_{HH/PH}$ = 7.5, 10.6 Hz, $PCCH_3$), 1.78 (m, 2H, PCH_2), 2.22 (s, 4-Me), 3.99 (dt, $J_{PH/HH}$ = 218.9, 6.3 Hz, PH), 5.90 (s, OH), 6.75 (dd, J = 8.2, 4.2 Hz, H6), 6.95 (dd, J = 8.2, 2.0 Hz, H5), 7.17 (dd, $J_{HH/PH}$ = 2.0, 6.4 Hz, H3). Anal. calcd for $C_9H_{13}OP$ (168.17): P 18.42%. Found: P 18.2%.

B. A solution of 9.8 g (36 mmol) of **9b** in 50 mL of ether was reduced with 2.0 g $LiAlH_4$ and worked up as above with dilute sulfuric acid to give 3.5 g (58%) of **12b,** with identical NMR data.

C. **12b** *by O-Deprotection of* **13b.** A 6.3 g (30 mmol) amount of **13b** was heated to reflux (1/2 h) with 100 mL of a mixture of methanol and 10% hydrochloric acid. The product was extracted with ether, dried with sodium sulfate, and the solvent evaporated. Then toluene was added, residual water removed azeotropically, and the residue distilled at bp 90°C/0.1 Torr to yield 4.0 g (80%) of **12b.** NMR data as above.

O-Silylation Reactions

2-Phosphino-4-methylphenyl Trimethylsilyl Ether **16a.** A. A 2.9 g (21 mmol) amount of **12a,** dissolved in 40 mL of ether, was lithiated with one equivalent of 1.6 N BuLi in hexane (13.2 mL) at −20°C, and, after 2 hours, the mixture was treated with $ClSiMe_3$ (2.3 g, 21 mmol). The suspension that resulted was filtered, the solvent removed from the filtrate, and the residue distilled yielding 4.0 g (90%) of **16a,** bp 55°C/0.1 Torr. B. Metalation with 21 mmol of NaH in toluene (40°C, 3 h) in place of BuLi and subsequent reaction with $ClSiMe_3$, as in (A), afforded 2.9 g (65%) of **16a.** ^{31}P NMR: δ −134.2. ^1H NMR: δ 0.40 (s, $SiMe_3$), 2.26 (s, 4-Me), 3.70 (d, J_{PH} = 204.2 Hz, PH), 6.75 (dd, J = 8.2, 2.5 Hz, H6), 7.05 (dd, J = 8.2, 2 Hz, H5), 7.28 (dd, J = 7.6, 2.0 Hz, H3). Anal. calcd for $C_{10}H_{17}OPSi$ (212.29): C 55.65, H 7.87%. Found: C 55.89, H 8.07%.

Bis(2-ethylphosphino-4-methylphenyl) Dimethylsilyl Ether **17.** Fifteen milliliters of 1.6 N BuLi (24 mmol) in hexane was added dropwise to a solution of 3.9 g (23 mmol) of **12b** in ether (50 mL) at −30°C.

Then, a solution of 1.4 mL (1.5 g, 12 mmol) of Cl_2SiMe_2 in 5 mL of ether was slowly added, the suspension filtered (after 1 d), the solvent evaporated from the filtrate, and the residue distilled at 170–175°C/0.1 Torr to give 3.0 g (65%) of **17.** NMR spectra show two pairs of diastereoisomers (A): (B) ca. 70:30% (*meso, rac* designations could not be assigned) with hindered rotation at 30°C of the *o*-phosphinoaryl groups about the Si–O and O–C bond. ^{31}P NMR: (A) δ −54.93 (s), −55.21 (s), (B) δ −55.01 (d), −55.06 (d, J_{PP} = 6.1 Hz). ^{29}Si NMR: (A) δ 5.44 (s), (B) δ 5.56 (d, J_{PSi} = 1.8 Hz). ^{13}C NMR [(A)/(B), partly superimposed]: δ (J_{PC} in Hz) = −2.41, −2.33/−0.61, −0.49 ($SiMe_AMe_B$), 13.19/9.73 (d, 6.0/12.8, PC*Me*), 14.31/17.34 (d, 10.6/11.3, P*C*Me), 20.29, 20.36/20.59 (4-Me), 118.1/119.1 (C-6), 130.1/129.9 (C-5), 131.1/130.8 (d, C-4), 135.15/135.15 (d, C3), 126.05/126.05 (d, C-2), 153.55/153.60 (2d, C-1). The ^{1}H NMR signals were superimposed; the most intensive set (without coupling constants, assigned by CH-COSY): δ = 0.43/0.39 ($SiMe_AMe_B$), 1.15, (PCMe), 1.76/1.88 (PCH_AH_B), 2.29 (4-Me), 4.02 (J_{PH} = 212 Hz, PH), 6.86, 6.98, 7.23 (3-H, 5-H, 6-H). Anal. calcd for $C_{20}H_{30}O_2P_2Si$ (392.49): P 15.78%. Found: P 16.0%.

P-Alkylation Reactions

A. Alkylation after Dimetallation by n-BuLi in Ether. A 5.0 g (36 mmol) amount of **12a** was dissolved in 150 mL of ether, and 44 mL of 1.6 N BuLi (70 mmol) in hexane was added dropwise (30 min, −30°C). Stirring was continued for 4 hours at room temperature, then 35 mmol of the corresponding alkyl halide (MeI, EtBr, *i*PrBr) was added to the yellow suspension. The mixture was allowed to stir for 2 days (20°C) to complete the reaction. The crude phosphinophenolate was treated with a degassed 15% aqueous solution of NH_4Br, the ether extract predried with Na_2SO_4, solvents removed, the crude product dried azeotropically with toluene, and distilled through a spinning band column.

B. Alkylation on Dimetallation by Sodium or Potassium in Liquid Ammonia. Dry ammonia (250 mL) was condensed on 1.6 g (70 mmol) of sodium at −55°C, and a solution of 4.9 g (35 mmol) of **12a** in 10 mL of ether was added with stirring. When the color turned from blue to orange-yellow, indicating the reaction to be complete, a solution of 35 mmol of the corresponding alkyl halide (MeI, EtBr, *i*PrBr) in ether (10 mL) was added. The mixture was stirred overnight, and the ammonia was allowed to evaporate. After addition of ether (100 mL), the resulting phosphinophenolate was hydrolyzed by addition of a degassed solution of NH_4Cl (15%) in water, and the mixture was worked up as described in procedure A.

2-Ethylphosphino-4-methyl-phenol **12b.** Yield:(A) 3.9 g (65%) and (B) 3.0 g (51%), bp 90°C/0.1 Torr. NMR data are identical with those given above.

2-Methylphosphino-4-methyl-phenol **12d.** Yield: (A) 3.1 g (55%) and (B) 2.4 g (45%), bp 60°C/0.1 Torr. ^{31}P NMR: δ −96.2. ^{13}C NMR: δ(J_{PC} in Hz) 4.8 (d, 9.1, PMe), 20.3 (4-Me), 114.9 (C6), 120.6 (d, 8.3, C2), 131.1 (C5), 131.5 (d, 6.7, C4), 134.9 (d, 7.5, C3), 155.4 (d, 12.1, C1). ^{1}H NMR: δ1.35 (dd, J = 7.2, 2.0 Hz, PMe), 2.24 (s, 4-Me), 4.12 (dq, $J_{PH/HH}$ = 216.9, 7.2 Hz, PH), 6.0 (br. s, OH), 6.70 (m, 1H, H6), 6.97 (m, 1H, H5), 7.20 (d, J = 6.3 Hz, 1H, H3). Anal. calcd for $C_8H_{11}OP$ (154.13): P 20.1%. Found: P 20.0%.

2-Isopropylphosphino-4-methylphenol **12e.** Yield: (A) 4.6g (70%) and (B) 3.5g (55%), bp 98°C / 0.1 Torr. ^{31}P NMR: δ-54.5. ^{13}C NMR: δ(J_{PC} in Hz) 20.9 (d, 17.3, Me), 21.9 (d, 10.6, Me), 23.3 (d, 3.6, P*C*H), 20.3 (4-Me), 115.0 (d, 2.1, C6), 118.1 (d, 9.4, C2), 129.7 (d, 3.2), and 131.8 (d, 3.0) (C4 and C5), 137.1 (d, 6.0, C3), 156.4 (d, 12.9, C1). ^{1}H NMR: δ = 1.06 (dd, $J_{PH/HH}$ = 16.5, 7.2 Hz, PCH*Me*$_A$), 1.16 (dd, $J_{PH/HH}$ = 14.1, 6.9 Hz, PCH*Me*$_B$), 2.23 (m, 1H, PCH), 2.27 (s, 4-Me), 3.90 (dd, $J_{PH/HH}$ = 220.5, 5.3 Hz, PH), 5.70 (br. s, OH), 7.03 (dd, J = 8.2, 4.1 Hz, H6), 7.06 (dd, J = 8.2, 2.2 Hz, H5), 7.23 (dd, J = 6.0, 2.2 Hz, H3). Anal. calcd for $C_{10}H_{15}OP$ (182.19): P 17.1%. Found: P 17.0%.

1,3-Propylen-bis-P[(4-methyl-2-phenylphosphino)phenol Methoxymethyl Ether] **21.** A solution of 2.6 g (12 mmol) of **12c** in 30 mL of ether was monolithiated at −30° with 7.6 mL of 1.6 N BuLi (12.2 mmol) in hexane, and 0.6 mL 1,3-dibromopropane in 2 mL ether was added dropwise. After the mixture had been stirred for 2 days, the precipitate was filtered off and washed, the solvent removed from the filtrate, and the solid residue crystallized from methanol/methylene chloride to afford 1.6 g (47%) of two pairs of diastereoisomers of **21.** ^{31}P NMR: δ −25.6, −25.3, (A):(B) ca. 85:15%. ^{13}C NMR: δ (J_{PC} in Hz) 20.64 / 20.49 (Me-4), 22.65 / si (t, 19.5, C_2CH_2) 28.27 / 28.28 (2dd, si, PCH_2), 55.80 / 55.73 (OCH_3), 94.21 / 94.17 (O_2CH_2), 113.70 / si (C-6), 127.30 / 127.10 (dd, 6/6, C-2), 128.25 / 128.07 (d/d, 5.1/7.6, C-*m*), 130.33 / 130.27 (C-5), 131.0 / 131.02 (C-4), 132.36 / 132.28 (d/d, 5.8 / 5.5, C-3), 132.83 / 132.72 (d/d, 8.2 / 8.2, C-*o*), 138.55 / 138.52 (d/d, 12.9 / 12.9, C-*i*), 156.73 / 156.57 (d/d, 6.6 / 6.4, C-1) [si = superimposed]. ^{1}H NMR ([d6]aceton): δ 0.86 (m, 2H, C_2CH_2), 1.41 (m, 4H, PCH_2, 3.13 / 3.15 [s/s, 3/3H(A/

B), OMe], 4.95 / 4.99 [m/m, 2/2H(A/B), O_2CH_2], 6.91–7.01 (m, 6H, aryl), 7.3–7.6 ppm (m, 10H, Ph). Anal. calcd for $C_{33}H_{38}O_4P_2$ (560.61): P 11.05%. Found: P 11.0%.

P-Alkylation and O-Silylation. The first step, the alkylation, followed procedure (A) or (B) of the above description; the subsequent silylation was somewhat different for both procedures because of the reaction of the chlorosilanes with ammonia.

A. A 4.6 mL (36 mmol) amount of $ClSiMe_3$ was added at 20°C to the crude phosphinophenolate of the above (A). It was stirred for 3 hours, filtered, the solvent removed from the filtrate, and the residue distilled through a spinning band column.

B. The suspension of the crude phosphinophenolate (procedure B) in ether was refluxed in a slight stream of argon to remove ammonia. To complete this process, about 50% of the solvent was distilled off before 5 mL of $ClSiMe_3$ was added. Further workup was the same as in procedure (A).

2-Ethylphosphino-4-methyl-phenol Trimethylsilyl Ether **16b.** Yield: (A) 5.8 g (67%) and (B) 5.1 g (61%), bp 84°C / 0.1 Torr. ^{31}P NMR: δ −54.6. ^{13}C NMR: $\delta(J_{PC}$ in Hz) 0.3 ($SiMe_3$), 13.4 (d, 9.3, PCH_2), 14.4 (d, 15.2, PC*C*H_3), 20.5 (4-Me), 118.0 (C6,), 126.5 (d, 9.0, C2), 130.6 (C5), 130.7 (d, 8.2, C4), 135.2 (d, 7.5, C3), 154.7 (d, 7.5, C1). ^{1}H NMR: δ 0.31 (s, $^2J_{SiH\text{-}sat.}$ = 6.7 Hz, $SiMe_3$), 1.15 (dt, J = 12.7, 7.5, Hz, CCH_3), 1.78 (m, 2H, PCH_2), 2.22 (s, 4-Me), 3.99 (dt, $J_{PH/HH}$ = 218.9, 6.3 Hz, PH), 5.9 (br. s, OH), 6.75 (dd, H6), 6.95 (dd, J = 8.2, 2.0 Hz, H5), 7.17 (dd, J = 6.2, 2.0 Hz, H3). Anal. calcd for $C_{12}H_{21}OPSi$ (240.34): P 12.9%. Found: P 12.7%.

2-Methylphosphino-4-methylphenol Trimethylsilyl Ether **16d.** Yield: (A) 4.9 g (60%) and (B) 4.4 g (56%), bp 57°C / 0.1 Torr. ^{31}P NMR: δ −82.2. ^{13}C NMR: $\delta(J_{PC}$ in Hz) 0.4 ($SiMe_3$), 4.4 (d, 15.1, PMe), 20.4 (4-Me), 117.8 (C6), 120.5 (d, 13.6, C2), 129.8 (C5), 130.7 (d, 8.2, C4), 133.7 (d, 8.3, C3), 154.6 (d, 15.1, C1). ^{1}H NMR: δ 0.40 (s, $SiMe_3$), 1.34 (dd, J = 7, 2 Hz, PMe), 2.26 (s, 4-Me), 4.14 (dq, $J_{PH/HH}$ = 209, 7 Hz, PH), 6.66 (dd, J = 8.0, 3.6 Hz, H6), 6.97 (dd, J = 7.4, 2.1 Hz, H5), 7.15 (dd, J = 8.1, 2.1 Hz, H3). Anal. calcd for $C_{11}H_{19}OPSi$ (226.32): P 13.7%. Found: P 13.5%.

2-Isopropylphosphino-4-methylphenol Trimethylsilyl Ether **16e.** Yield: (A) 4.6 g (65%) and (B) 3.5 g (60%), bp 92°C / 0.1 Torr. ^{31}P NMR: δ −36.0. ^{13}C NMR: $\delta(J_{PC}$ in Hz) 0.4 (d, 0.9, $^1J_{SiC}$ = 59.3 Hz, $SiMe_3$), 20.4 (4-Me), 21.5 (d, 18.8, Me_A), 22.6 (d, 7.7, PCH), 23.0 (d, 3.2, Me_B), 117.9 (d, 1.2, C6), 126.2 (d, 13.3, C2), 130.2 (C5), 130.3 (d, 4.7, C4), 136.3 (d, 9.1, C3), 154.8 (d, 9.6, C1). ^{1}H NMR: δ 0.34 (s, $SiMe_3$), 1.11 (dd, $J_{PH/HH}$ = 3.4, 7.0 Hz, PCH*Me*$_A$), 1.18 (dd, $J_{PH/HH}$ = 10.2, 7.0 Hz, PCH*Me*$_B$), 2.24 (dm, $J \approx$ 1–2, 7 Hz, PCH), 2.30 (s, 4-Me), 3.68 (dd, $J_{PH/HH}$ = 210.4, Hz, PH), 6.73 (dd, J = 8.1, 3.1 Hz, H6), 7.03 (dd, J = 8.1, 2 Hz, H5), 7.25 (dd, J = 6, 2 Hz, H3). Anal. calcd for $C_{13}H_{23}OPSi$ (254.379): P 12.2%. Found: P 12.2%.

1,3-Propylen-bis-P[(4-methyl-2-isopropylphosphino)phenol Trimethylsilyl Ether] **20.** A 2.9 g (16 mmol) amount of **12e** in 30 mL of ether was dilithiated with BuLi (20 mL 1.6N, 32 mmol), and 0.8 mL (1.6 g, 8 mmol) of 1,3-dibromopropane was added (20°C) and allowed to react for 2 days. A 1.7 g (16 mmol) amount of $ClSiMe_3$ was added, the mixture filtered (after 2 h), the solvents evaporated, and the residue distilled at 185–195°C / 0.01 Torr to give 0.9 g (20%) of viscous **20,** consisting of two pairs of diastereoisomers in a ratio of 1:1. The ^{31}P NMR: δ −15.24, −15.74. ^{1}H and ^{13}C signals of the diastereomers were partly superimposed (= si). ^{13}C NMR: $\delta(J_{PC}$ in Hz) 0.51 / si ($SiMe_3$), 19.18 / 20.0 (d/d, 14.7 / 16.4, CH*Me*$_2$), 20.53 / 20.57 (2s, 4-Me), 23.56 / si ("t", 15.8, C*C*H_2C), 24.82 / 24.95 (d/d, 4.6 / 4.8, CH), 25.22 / 25.41 (2dd, 7.4, 11.4 / 8.0, 10.8, P*C*H_2), 117.80 / 117.84 (d/d, 1.6 / 2, C-6), 127.39 / 127.63 (d/d, 8.2 / 8.2, C-2), 129.90 / 129.91 (d/d, 2.4 / 2, C-4), 130.0 / si (C-5), 133.86 / 134.02 (d/d, 10.0 / 10.9, C-3), 156.04 / si (d, 11.8, C-1). ^{1}H NMR: δ 0.34 / 0.35 (2s, $SiMe_3$), 1.05 (m, C*Me*$_2$), 1.51, 184 (m, PC*H*$_2$), 2.08 (m, C*H*Me_2), 2.29 / 2.33 (2s, 4-Me), 6.65, 6.90 (2m, 5,6-H), 7.07 / 7.11 (2dd, $J_{HH/PH}$ = 2.2, 5.7 / 5.9 Hz, 3-H). Anal. calcd for $C_{29}H_{50}O_2P_2Si_2$ (548.83): P 11.3%. Found: P 11.29%.

Heterocycles

2,2,5-Trimethyl-2,3-dihydro-1,3,2-benzoxaphosphasilole **22.** A 2.9 g (21 mmol) amount of **12a,** dissolved in 60 mL of ether, was dilithiated with 26.5 mL of BuLi (1.6 N in hexane, 42.4 mmol) at −40°C, and the mixture was stirred 2 hours at 20°C. A 2.5 mL (2.7 g, 21 mmol) amount of Cl_2SiMe_2 was added dropwise at −20°C. After 8 hours, the precipitate was filtered off, the solvent removed, and the residue distilled to give 1.6 g (40%) **22** of bp 70°C / 0.1 Torr. ^{31}P NMR: δ −175.0 ^{29}Si NMR: δ 44.1 (d, J_{PSi} = 18.3 Hz). ^{13}C NMR: $\delta(J_{PC}$ in Hz) 1.5 (d, 24.7, $SiMe_A$), 2.6 (d, 3.5, $SiMe_B$), 20.4 (5-Me), 115.0 (C-7), 118.9 (d, 18.9, C-3a), 130.1 (d, 7.5, C-5), 130.9 (C-6), 135.9 (d, 24.1, C-4), 159.6 ppm (s, C-7a). ^{1}H NMR: δ 0.53 (d, J_{PH} = 5.8 Hz, $SiMe_A$), 0.69 (d, J_{PH} = 1.1 Hz, $SiMe_B$),

2.27 (s, 5-Me), 3.05 (d, J_{PH} = 184 Hz, PH), 6.89 (d, J_{HH} = 8.2 Hz, 7-H), 7.03 (dm, J_{HH} = 8.2, 1.3, $J_{PH} \approx$ 0.7 Hz, 6-H), 7.35 ppm (ddd, J_{HH} = 1.3, 0.8, $J_{PH} \approx$ 7.2 Hz, 4-H). Anal. calcd for $C_9H_{13}OPSi$ (196.26): P 15.78%. Found: P 15.7%.

Phosphorous Acid Bis(dimethyl)amide [4-Methyl-2-(phenylphosphino)phenyl] Ester **18** *and 2-Dimethylamino-5-methyl-3-phenyl-2,3-dihydro-1,2,3-benzoxadiphosphole* **23**

A solution of 1.6 g (5.6 mmol) of **12c** and 1.0 g (6.1 mmol) of $P(NMe_2)_3$ in 5 mL of toluene was heated at 60–70°C until the evolution of gaseous Me_2NH ceased (ca. 1 h). A 0.2 mL sample of the solution formed on evaporation of the toluene in vacuo consisted of a viscous oil that was identified by NMR as nearly pure **18.** The main solution was refluxed for 6 hours, the solvent removed, and the residue distilled at 150–155°C / 5 × 10^{-4} Torr to give 1.0 g (62%) of viscous oily **23,** which eventually solidified and formed needles, mp 75–77°C (hexane). **18:** ^{31}P NMR: δ −55.3 (s), 132.5 (s). ^{1}H NMR: δ 2.19 (s, 4-Me), 2.55 (d, J_{PH} = 9.5 Hz, 3H, NMe_A), 2.60 (d, J_{PH} = 9.6 Hz, 3H, NMe_B), 5.21 (d, J_{PH} = 221 Hz, PH), 6.8–7.5 ppm (m, 8H, aryl). **23:** ^{1}H NMR: δ = 2.32 (s, 5-Me), 2.72 (dd, $^3J_{PH}$ = 9.6, $^3J_{PH}$ = 1.0 Hz, NMe_2), 7.02 (d, J_{HH} = 8.3 Hz, 7-H), 7.09–7.25 (m, 6H, Ph and 6-H), 7.45 (m, $^3J_{PH/HH}$ = 6.2, 2.1, <0.4 Hz, 4-H). ^{13}C NMR: δ 20.6 (Me-5), 42.3 (dd, $^{2/3}J$ = 13.5, 9.4 Hz, NMe_2), 113.8 (C-7), 121.8 (dd, $^{1/2}J$ = 19.3, 4.4 Hz, C-3a), 128.4 (d, J = 2.8 Hz, C-*p*), 128.6 (dd, $^{3/4}J$ = 6.9, 1.6 Hz, C-*m*), 131.3 (d, J = 7.5 Hz, C-5), 132.1 (dd, $^{2/3}J$ = 23.8, 6.1 Hz, C-*o*), 132.2 (C-6), 133.0 (dd, ^2J = 23.3, ^3J = 1.7 Hz, C-4), 134.3 ("t", $^1J + {}^2J$ = 38.6, C-*i*), 163.4 (d, ^2J = 14.1, C-7a). ^{31}P NMR: δ −25.9 (d, P-3), 166.2 (d, J_{PP} = 232.5 Hz, P-2). Anal. calcd for $C_{15}H_{17}NOP_2$ (289.25): C 62.27; H 5.93%. Found: C 60.94; H 6.25%. MS (70eV): *m/z* = 289 (100%, M^+), 246 (85%, M^+-$NMeCH_2$), 168 (53%, $MeC_6H_3OP{=}P^+$), 121 (38%, $MeC_6H_3P^+$).

Phenylphosphonous Acid Dimethylamide [4-Methyl-2-(phenylphosphino)phenyl] Ester **19** *and 2,3-Diphenyl-5-methyl-2,3-dihydro-1,2,3-benzoxadiphosphole* **24**

A solution of 2.2 g (10.2 mmol) of **12c** and 2.0 g (10.2 mmol) of $PhP(NMe_2)_2$ in 10 mL of toluene was heated at 60°C (Me_2NH evolution) for 2 hours. ^{31}P and ^{1}H NMR control spectra gave evidence of a nearly quantitative formation of two diastereoisomers of **19.** The solution was then refluxed; after 10 hours ca. 75% of **19** had cyclized to **24.** The solvent was removed, and the residue distilled at 172–175°C / 0.01 Torr to give 1.95 g (59%) of viscous oily **24,** which slowly forms crystals, mp 63–64°C. **19:** ^{31}P NMR: δ = −55.15, −55.62, [di]pp = $5H_Z$ (C_2PH); 131.68, 131.99, [di]pp = $5H_Z$ (C_2PN). **24:** ^{31}P NMR: δ −9.43 and 137.90 (d, J_{PP} = 233 Hz, P3 and P2). ^{13}C NMR: δ = 20.6 (Me-5), 115.2 (d, J = 0.8 Hz, C-7), 122.0 (dd, $^{1/2}J$ = 22.5, 4.8 Hz, C-3a), 128.36 (dd, $^{3/4}J$ = 5.0, 1.1 Hz, Ph2-*m*), 128.67 (dd, $^{3/4}J$ = 6.6, 1.3 Hz, Ph3-*m*), 128.68 (d, J = 2.8 Hz, Ph-*p*), 128.88 (d, J = 2.2 Hz, Ph-*p*), 129.0 (dd, $^{2/3}J$ = 18.1, 7.4 Hz, Ph2-*o*), 132.44 (d, J = 7.8 Hz, C-5), 132.07 (dd, $^{2/3}J$ = 18.5, 5.2 Hz, Ph3-*o*), 132.23 (C-6), 133.7 (dd, $^{2/3}J$ = 24.4, 1.4 Hz, C-4), 135.9 (dd, $^{1/2}J$ = 9.3, 23.7, Ph3-*i*), 139.7 (dd, $^{1/2}J$ = 9.7, 37.1, Ph2-*i*), 162.9 (d, ^2J = 14.1, C-7a). ^{1}H NMR: δ 2.28 (s, 4-Me), 7.13–7.42 (m, aryl). Anal. calcd for $C_{19}H_{16}OP_2$ (322.28): C, 70.81; H, 5.00%. Found: C, 70.58; H, 5.08.

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[20] **12a** and $ClP(NEt_2)_2$ react to give also $MeC_6H_3(2\text{-}PH_2)\text{-}OP(NEt_2)_2$ ($\delta^{31}P = -137.9$, 128.3) and $[MeC_6H_3(2\text{-}PH_2)\text{-}O]_2PNEt_2$ ($\delta^{31}P = -137.95$, 165.4) besides **25a(R**^{11} = NEt_2). J. Heinicke, E. Moussina, G. N. Nikonov, unpublished results.
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