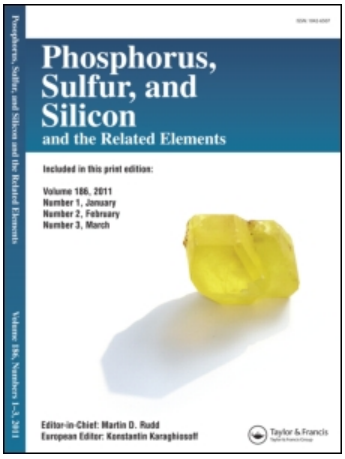

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REACTION OF GRIGNARD REAGENTS WITH PHOSPHINOUS CHLORIDES HAVING THE *ANTI*-7-PHOSPHANORBORNENE FRAMEWORK

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REACTION OF GRIGNARD REAGENTS WITH PHOSPHINOUS CHLORIDES HAVING THE *ANTI*-7-PHOSPHANORBORNENE FRAMEWORK

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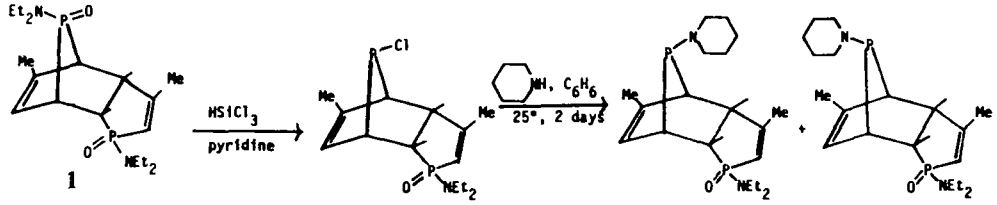
Trichlorosilane-pyridine converts the bridging phosphorus function in dimers of 1-aminophosphole derivatives to the phosphinous chloride with the *anti* configuration. The chlorine was replaced by phenyl with retention of configuration (as confirmed by stereospecific features in ^{31}P and ^{13}C NMR spectra) on attack of phenylmagnesium bromide in ether. Reactions with methylmagnesium bromide or *tert*-butylmagnesium chloride were not useful for producing tertiary phosphines. The *anti*-P-phenyl phosphine derivative was oxidized to the phosphine oxide which was readily isomerized by amines to the *syn*-compounds. In the mass spectra of these oxides, a peak for the P(II) species $[C_6H_5P{=}O]^+$ was present.

The first example of a compound (**2**) containing the phosphinous chloride functional group based on the 7-phosphanorbornene (7-PNB) system was recently prepared in this Laboratory[1] by treatment of the dimer of a 1-aminophosphole oxide with trichlorosilane-pyridine. This type of compound is potentially of synthetic utility in the generation of phosphole oxide dimer derivatives with mixed functionality at the two phosphorus atoms. Since a single isomer (chlorine *anti*) is formed, an opportunity is also presented for the study of the stereochemistry of nucleophilic substitution reactions. It has already been observed[1] that displacement of the chlorine from **2** with amines gives a high degree of stereochemical retention (Scheme 1). This contrasts with the action of amines on a monocyclic (phosphetane) phosphinous chloride, where substitution occurred with a preference for inversion[2,3] (sometimes followed by isomerization[3]). In the case of bridged ring systems with unlike faces, thermodynamic as well as kinetic effects may influence the stereochemical outcome, as has been recently seen for phosphinous chlorides in the 9-phosphabicyclo[4.2.1]nona-2,4,7-triene system.[4]



SCHEME 1

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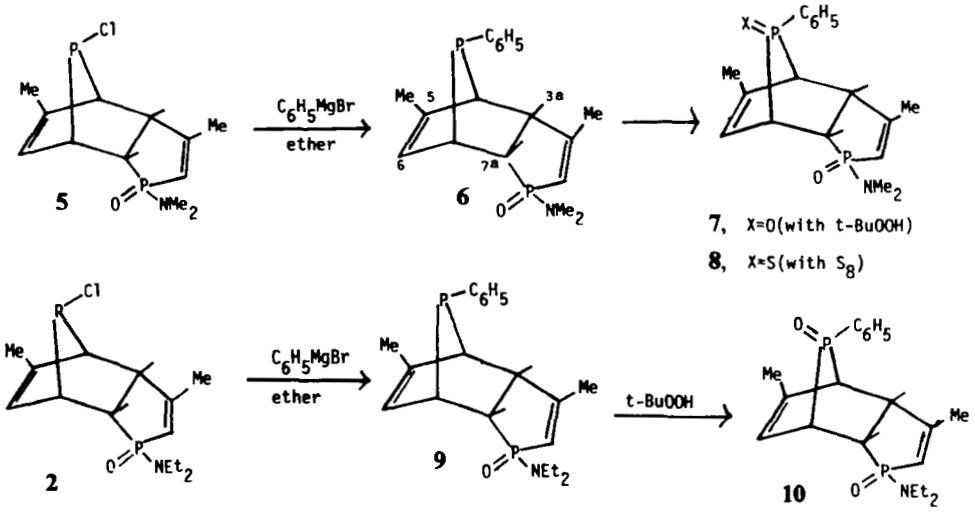
Other properties of 7-PNB derivative **2** were also unusual; the ^{31}P NMR shift, for example, of the P—Cl group was located in a region far upfield of that characteristic of this functionality. This is in sharp contrast to tertiary phosphines in the 7-PNB series, which experience abnormally large deshielding effects.[5]

Because of the novelty of the system, we have initiated a study of the behavior of phosphinous chlorides in the 7-PNB series towards nucleophilic reagents. We report here on the reaction with Grignard reagents; while this proved to be surprisingly complex, we were nevertheless able to confirm in one case that chlorine displacement occurred with complete retention of configuration. Some properties of the mixed tertiary phosphine-phosphinamide product are also described.

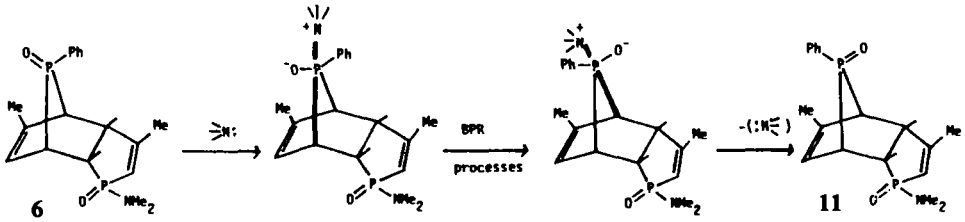
Phosphinous chlorides **2** and **5** were subjected to reaction with three typical Grignard reagents (phenyl, methyl, and *tert*-butyl) under a variety of conditions. The outcome of the reactions with these reagents varied considerably, and included (1) the desired displacement of chlorine, (2) fragmentation by loss of the bridging P function, and (3) exchange of halogen with the Grignard reagent. After the complexity of the process became obvious, we explored briefly the use of organolithium reagents, but no better results were obtained and are not discussed further.

Displacement of Chlorine. This process was only confirmed for the use of phenylmagnesium bromide in ether at 25°C (1.4 molar ratio relative to the chlorides); from chlorides **2** and **5**, the phosphine was formed in over 80% yield. Changes in these conditions led to more complex product mixtures, as noted below. The phosphine products **6** and **9** have only been obtained so far as non-crystallizing oils. They do, however, form crystalline phosphine oxides and sulfides which were employed for elemental analysis purposes. For phosphine **6**, the molecular formula was confirmed by high resolution mass spectrometry. The structure of the products and the stereochemistry at the phosphine function were determined from NMR properties. The ^{31}P NMR spectrum contained a signal ($\underline{\delta}$ +59.9) in the expected region[5] for an *anti*-substituted 7-PNB derivative, as well as for a phosphinamide function ($\underline{\delta}$ +66.5).



SCHEME 2

In the ^{13}C NMR spectrum (Table I), the stereospecificity of the three-bond $^{31}P—^{31}P$ coupling for a P(III) function was especially useful in confirming the stereochemical assignment. Thus, it is known[5] for other phosphines with the phosphole dimer framework that when the lone pair of a phosphine in the bridging position is in the *syn*-position relative to the phosphorus in the 2-phospholene moiety, coupling will be of very small size or not detectable, but in the *anti* position the $^3J_{PP}$ value is sizeable (about 25 Hz for diphosphines). The effect is also present in phosphinous chlorides **2** and **5** which fail to show P—P coupling.[1] Since neither of the Grignard reaction products **6** and **9** showed coupling between the phosphine and phosphinamide ^{31}P nuclei, the stereochemistry depicted in Scheme 2 was indicated. A second stereospecific coupling effect confirmed the assignments; two-bond $^{31}P—^{13}C$ coupling in P(III) derivatives is large when the lone pair is close to the coupled carbon, and small or absent when remote, as has been shown for phosphole dimers.[5] Pertinent $^2J_{PC}$ values for **6** were: C-3a, 3.3 Hz; C-7a, 3.8 Hz; C-5, 26.4 Hz. Further confirmation of the assignment made use of the stereospecificity in the two-bond $^{31}P—^{13}C$ coupling in P-oxides of the 7-PNB system.[6] The dimers of 3-methyl-1-phenylphosphole oxide (Table II) serve as models, and show that $^2J_{PC}$ is larger in the isomer where oxygen is directed away from the coupled carbon. Conversion of phosphine **6** to its oxide **7** with *tert*-butylhydroperoxide then gave a product with $^2J_{PC}$ parameters matching those of the phosphole oxide dimer with the *anti*-substituent. Furthermore, it was found that oxide **7** could be isomerized readily with amines to form the *syn*-phenyl isomer (**11**) whose $^2J_{PC}$ values matched the phosphole oxide dimer with *syn*-phenyl structure (Table II). A typical isomerization process involved exposure of **7** to 2.5 equivalents of diethylamine for 2 days at 25°C; the inversion at the bridging P was complete. Benzylamine and triethylamine also effected the isomerization, but at slower rates. Water is known to effect *anti* to *syn* inversion in other 7-PNB oxides,[7] but neither water nor methanol under similar conditions had this effect on **7**. However, some isomerization (24%) did occur when a chloroform solution of **7** was allowed to stand for 3 weeks, and in a similar period, neat **10** developed signals (16%) for the isomer. The inversion with amines probably proceeds through a P(V) intermediate (where apical groups are shown with heavy lines) which undergoes isomerizations (BPR) and then collapses to a more stable oxide.



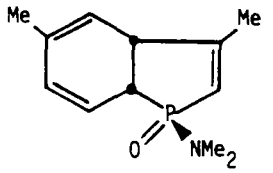
6 **11**

Noteworthy is the failure of an examination of the crude Grignard reaction mixtures by ^{31}P NMR to reveal any of the *syn* isomer. The displacement therefore proceeds with nearly 100% retention.

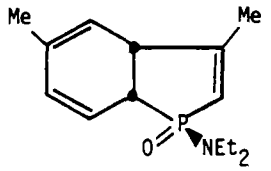
When the solvent in the Grignard reaction was changed to tetrahydrofuran (THF), only a small amount of the phosphine was detected, and debridging and

halogen-exchange (see below) were the major result. The reaction with methylmagnesium bromide in THF or in ether gave only debridging and halogen-exchange products. *Tert*-butylmagnesium chloride, which was quite slow in its reaction with **5** (about 90%[8] unreacted after 8 days at 25°C in ether, or after 2 days in refluxing THF) also failed to perform the desired chlorine displacement.

Loss of P Bridge. A common experience in working with 7-PNB derivatives is the loss of the P-bridge in a retro-cycloaddition process[5,9]. This process usually occurs when a P(V) intermediate develops in a reaction; loss of a P(III) molecule occurs in a process resembling the reverse of the McCormack cycloaddition with dienes. The tendency is strong to form the P(V) structure since it offers a bond angle (apical-equatorial, 90°) more compatible with that at the bridging P (82.3° in dimer **1**[10]). In the present research, the debridging resulted in the formation of dihydrophosphindole derivatives **12** and **13**, readily detected by their ^{31}P NMR signals.



12, $\delta^{31}P = +68.4$



13, $\delta^{31}P = +65.7$

This was the major result of reactions with methylmagnesium bromide (e.g., with **5**, 100% in ether or 75% in THF, 1.7 molar ratio, 2 days at 25°C), but small amounts of debridged products were formed under all other Grignard reaction conditions studied. Since both the starting chloride and the phosphine products are stable at

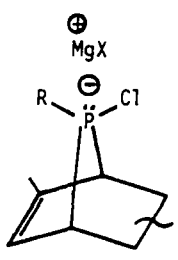
TABLE I

^{13}C NMR spectral data for non-aromatic carbons

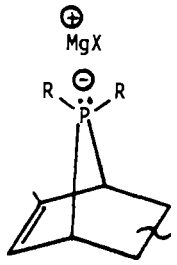
Compound	$\delta^{13}C$										
	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	3-CH_3	5-CH_3	N-CH_3
6	117.6	166.3	55.1	49.0	141.7	—[a]	41.7	38.9	20.0	18.8	35.7
$J_{C,P-1}$	120.9	28.6	20.9	4.4	—		3.9	95.0	19.8	—	4.4
$J_{C,P-8}$	—	—	3.3	14.3	26.4		14.8	3.8	—	—	—
7	123.2	159.6	47.9	46.4	135.1	124.6	40.9	34.4	19.3	19.3	34.8
$J_{C,P-1}$	118.1	28.6	13.2	—	—	2.2	2.2	91.2	18.7	—	3.3
$J_{C,P-8}$	6.1	9.9	20.9	67.0	4.4	2.2	62.6	16.5	—	3.3	—
8	123.4	157.5	50.2	51.7	137.9	125.9	46.1	36.7	19.4	20.1	35.2
$J_{C,P-1}$	117.8	27.5	17.7	—	—	5.5	2.5	90.3	13.4	—	3.7
$J_{C,P-8}$	6.1	8.8	14.0	51.3	7.9	5.5	47.0	14.0	—	1.8	—
10	124.9	159.4	48.4	46.9	136.2	125.0	41.2	37.1	19.5	19.6	37.9[c]
$J_{C,P-1}$	116.5	28.6	20.9	—	—	2.2[b]	2.2	91.2	18.7	—	4.4
$J_{C,P-8}$	6.6	9.9	13.2	68.1	4.4	4.3[b]	62.6	16.5	—	3.3	—
11	122.9	160.2	50.8	47.1	135.2	124.8	41.6	35.9	19.1	19.0	34.9
$J_{C,P-1}$	118.7	26.9	15.4	1.1	—	4.4	2.2	90.7	18.7	—	4.4
$J_{C,P-8}$	4.4	9.3	13.2	65.9	12.1	4.4	60.4	10.4	—	4.4	—

[a] Overlapped with C_6H_5 signals.
[b] Could be reversed.
[c] For N—CH_2; CH_3 δ 14.2 (s).

room temperature in ether or THF solutions, the de-bridging appears to arise from a reaction intermediate, possibly **14**.



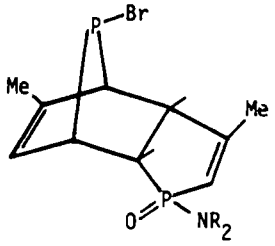
14



15

Species **14** is a phosphoranide ion, a type involved in the interaction of certain tertiary phosphines with phenyllithium,[11] and a postulated intermediate in other nucleophilic displacements on phosphinous chlorides.[2,3] The possibility was also considered that some of the debridging occurred after the formation of the tertiary phosphine, through a related phosphoranide ion (**15**), and indeed phosphine **6** was observed to undergo extensive (57%) debridging after 20 hours of stirring in ether with a 3-fold excess of phenylmagnesium bromide. Since a large excess of Grignard reagent is avoided in the reactions of **5**, it is more likely that the debridging occurs through the intermediate (**14**) formed from the chloride.

Halogen Exchange. In many of the reactions with methyl- and phenylmagnesium bromides in THF (but not in ether), there was significant replacement of chlorine on phosphorus by bromine. As much as 65–74% of the total ^{31}P NMR signal intensity could be attributed to such a product (**17**) when methylmagnesium bromide reacted with chloride **2** in THF. A smaller amount of exchange occurred with chloride **5** under comparable conditions (forming **16**, 17%), and from both **2** and **5** on reaction with phenylmagnesium bromide there was formed about 35% of the bromo product.

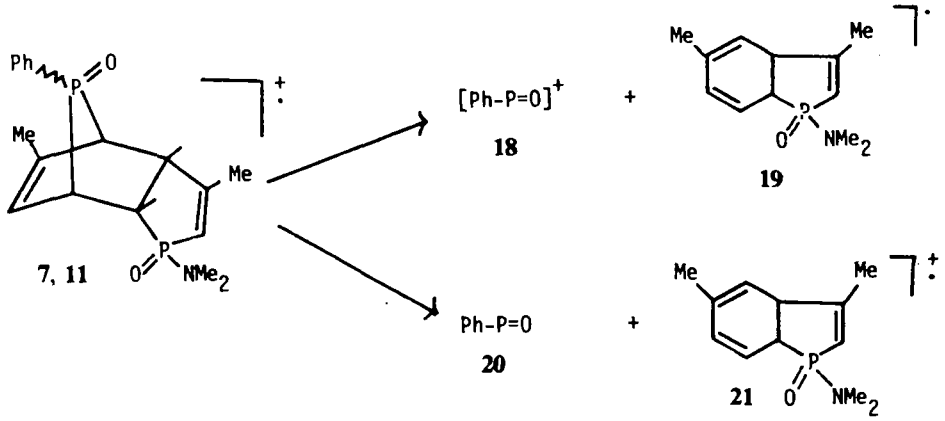


16, R=Me ($\delta\ ^{31}P$ = +65.0, +37.5)

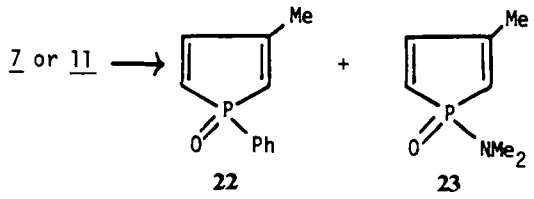
17, R=Et ($\delta\ ^{31}P$ = +60.3, +38.9)

These products were recognized by their characteristic ^{31}P NMR signals; since no $^{31}P—^{31}P$ coupling was observed the *anti* configuration is again suggested, and the process occurs with complete retention. It was not possible to isolate these bromides, but in one case (**16**) confirmation of the structure was obtained by mass spectrometry on a crude sample, which gave the expected m/z values for M^+ containing the two Br isotopes. Halogen exchange is not unknown when P-chlorides react with Grignard bromides; reaction of 2-norbornyl magnesium bromide with PCl_3 gave 32% of the isomeric bromo-chloro derivative,[12] and 16% of the expected phosphine.

Mass Spectral Fragmentation of 7-Phosphanorbornene Derivatives. As encountered in this and previous work,[5] phosphorus is sometimes ejected from the 7-PNB system in reactions when intermediates with P(V) structure are formed. This process appears to be a retro-cycloaddition which releases a P(III) species and a diene unit. Subjecting 7-PNB oxides **7** and **11** to mass spectral conditions would allow the consideration of the possibility that a P(II) species could be generated by a similar retrocycloaddition process. Such an event would be detectable from the formation of ions **18** or **21** (or their radicals) in the mass spectrum.



Oxides **7** and **11** gave mass spectra of great complexity and several fragmentation pathways seem to be followed. By exact mass measurements the composition of all major species was determined (Table III, which includes postulated origins of the peaks). For each the base peak was M^+—$PONMe_2$, and there was no difference in the identity of the other major ions formed. There were, however, differences in the relative abundances (RA) of the ions, the most significant being in that for the ion of phosphole oxide **22** (a reverse Diels-Alder product) and its protonated species.

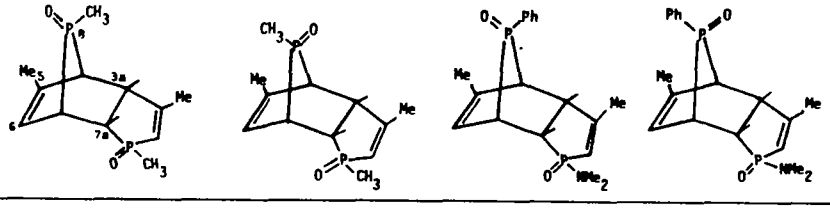


The RA for $[22]^+$ from oxide **7** was 8.3%, and from oxide **11**, 0.9%. The protonated forms were more prominent (37.4 and 6.2%, respectively). No ion based on **23** was detected.

Unequivocal evidence for the retro-cycloaddition with ejection of a P(II) species resulted from the exact mass measurements. The species $[C_6H_5P{=}O]$ was a significant peak in the spectra of both oxides **7** (20.4% RA) and **10** (13.7% RA). The ion (**21**) of the diene unit from the retro-cycloaddition was even more prominent (52.8 and 46.1% RA, respectively). These are the first observations of the formation of the

TABLE II

Comparison of $^2J_{PC}$ values in phosphine oxides



Coupling (Hz)				
$P_8—C_{3a}$	20.1	12.3	20.9	13.2
$P_8—C_{7a}$	18.3	11.1	16.5	10.4
$P_8—C_5$	4.4	11.7	4.4	12.1
$P_8—C_6$	1.2	9.2	2.2	4.4

TABLE III

Selected high resolution mass spectral data for **7** and **11**

7		**11**				
m/z	*RA*	*m/z*	*RA*	Formula	Calc *m/z*	Origin
347.1203	22.33	347.1198	32.19	$C_{18}H_{23}NO_2P_2$	347.1206	M^+
303.0712	4.22	303.0695	8.07	$C_{16}H_{17}O_2P_2$	303.0705	$M^+—Me_2N$
270.0814	2.80	270.0815	2.16	$C_{12}H_{18}NO_2P_2$	270.0814	$M^+—C_6H_5$
256.0048	100	256.0048	100	$C_{16}H_{17}OP$[a]	256.1018	$M^+—Me_2NPO$
223.1120	52.80	223.1118	46.05	$C_{12}H_{18}NOP$	223.1127	$M^+—PhPO$
222.1029	57.14	222.1034	42.58	$C_{12}H_{17}NOP$	222.1049	$[M^+—PhPO]—H$
191.0628	6.28	191.0627	37.42	$C_{11}H_{12}OP$	191.0627	[M⁺-**23**] + H
190.0568	0.87	190.0546	8.30	$C_{11}H_{11}OP$	190.0548	M⁺-**23**
179.0637	15.12	179.0624	9.89	$C_{10}H_{12}OP$	179.0627	$[M^+—PhPO]—Me_2N$
177.0469	39.00	177.0470	24.59	$C_{10}H_{10}OP$	179.0470	*m/z* 179-H_2
132.0937	16.51	132.0936	12.66	$C_{10}H_{12}$	132.0940	*m/z* 256[b]-PhPO
130.0772	7.28	130.0773	4.88	$C_{10}H_{10}$	130.0783	*m/z* 132[c]-H_2
129.0701	12.90	129.0700	10.96	$C_{10}H_9$	129.0705	*m/z* 130-H
125.0155	20.79	125.0156	14.64	C_6H_6OP	125.0157	$PhPOH^+$
124.0064	20.41	124.0031	13.66	C_6H_5OP	124.0079	$PhP{=}O^+$
115.0548	30.90	115.0548	21.97	C_9H_7	115.0548	$C_9H_7^+$
91.0550	65.96	91.0549	47.26	C_7H_7	91.0548	$C_7H_7^+$
91.0189	50.36	91.0189	32.46	C_2H_6NOP	91.0188	$Me_2NP{=}O^+$
77.0405	39.61	77.0405	27.95	C_6H_5	77.0392	$C_6H_5^+$

[a] Formulas providing better match are impossible.
[b] Or *m/z*-PO
[c] Or *m/z* 177-PO

species $C_6H_5P{=}O$ in a mass spectral fragmentation of a 7-PNB oxide; in a thermal degradation, the species $C_6H_5P{=}S$ has been released and trapped chemically.[13]

EXPERIMENTAL

General. Proton NMR spectra were obtained on an IBM NR-80 spectrometer at 80 MHz, using tetramethylsilane (TMS) as an internal standard. Phosphorus-31 spectra (FT) were obtained on a JEOL-FX 90Q spectrometer at 36.2 MHz, using 85% H_3PO_4 as an external standard with an internal

deuterium lock. Negative shifts are upfield and positive shifts downfield of the reference. Carbon-13 spectra (FT) were obtained on a JEOL FX-90Q spectrometer at 22.5 MHz, using TMS as an internal standard. Broad band proton noise-decoupling was employed on all carbon-13 and phosphorus-31 NMR spectra. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Combustion analyses were performed by MHW Laboratories, Phoenix, AZ.

Preparation of Phosphinous Chlorides. Compound **5** was prepared by the reported procedure for **2**.[1] A mixture of 4.0 g (12.7 mmol) of the dimer of 1-dimethylamino-3-methyl-phosphole oxide, 1.3 ml (12.7 mmol) of trichlorosilane and 3.1 ml (38.2 mmol) of pyridine in 120 ml of benzene was refluxed for 3 h. The mixture was filtered, and the filtrate evaporated to dryness. The residue was purified by column chromatography (alumina; ethyl acetate) to give 2.4 g (65%) of **5** as white crystals; ^{31}P NMR ($CDCl_3$) +43.8 (P-8), +58.9 (P-1), $^3J_{PP} \sim 0$.

Preparation of Phosphine **6** *from Phosphinous Chloride* **5**. A solution of 1.2 g (4.15 mmol) of phosphinous chloride **5** in 120 ml of dry ether was placed in a flame-dried, nitrogen-filled flask, which was then closed with a rubber septum. A solution of phenylmagnesium bromide (1.93 ml of 3 M concentration, 5.81 mmol) was slowly added from a syringe inserted through the septum. The reaction was quite slow and not exothermic. After 15 h of stirring at room temperature, excess Grignard reagent was destroyed with 5 ml of methylene chloride. Volatiles were evaporated with a rotary evaporator, and the residue was taken up in chloroform. The filtrate was again evaporated. ^{31}P NMR analysis of typical crude products showed the presence of about 80–95% of phosphine **6** and 10–15% of the dihydrophosphindole derivative **12** ($\underline{\delta}$ +68.4; high resolution M.S., M^+ calcd for $C_{12}H_{18}NOP$ 223.1126, found *m/z* 223.1128) from loss of the P bridge. Further purification of phosphine **6** was hindered by its sensitivity but sample of this purity were useful for NMR characterization; ^{31}P NMR $\underline{\delta}$ +59.9 and +66.5 ($^3J_{PP} \sim 0$); ^{13}C NMR, Table I; ^{1}H NMR, $\underline{\delta}$ 1.8 (s, CH_3), 1.93 (s, CH_3), 2.61 (d, J = 10 Hz, N($C\underline{H}_3$)$_2$), 5.56 (m, 2 H, olefinic H), 7.25 (m, 5 H, Ar$\underline{H}$), other signals not resolved; high resolution M.S. calcd. for $C_{18}H_{23}NOP_2$, M^+ 331.1256; found *m/z* 331.1253. The phosphine was further characterized by conversion to its oxide (**7**) and sulfide (**8**). (See below).

Preparation of the Oxide (**7**) *of Phosphine* **6**. A solution of 0.77 ml (5.62 mmol) of *tert*-butyl hydroperoxide in 5 ml of chloroform was added dropwise at 0°C to a solution of 1.55 g (5.3 mmol) of crude phosphine **6** in 150 ml of chloroform. After 5 min of stirring, there was added 100 ml of saturated $FeSO_4$ solution to destroy unreacted peroxide. The organic layer was dried over $MgSO_4$ and evaporated to give 1.5 g of crude **7** as an oil. A sample (0.35 g, 19%) was obtained for analysis by chromatographing it twice on silica gel (elution with chloroform-methanol, 95 : 5) and after three recrystallizations from n-pentane-chloroform (95 : 5) had m.p. 230–234°C following decomposition at 220°C. ^{13}C NMR spectral data are given in Table I; ^{1}H NMR $\underline{\delta}$ 1.95 (m, 6 H, CH_3), 2.43 (d, J = 10 Hz, N—$C\underline{H}_3$), 3.26 (m, 4 H), 6.1 (m, 2 H, olefinic H), 7.5 (m, 5 H, ArH), other signals not resolved; M.S. calcd. for $C_{15}H_{13}NO_2P_2$, M^+ 347.1206, found *m/z* 347.1203. $C_{18}H_{23}NO_2P_2 \cdot 1/2H_2O$; Calcd.: C, 60.66; H, 6.80; P, 17.38. Found: C, 60.56; H, 6.67; P, 17.43.

Preparation of the Sulfide **8** *of Phosphine* **6**. Powdered sulfur (0.29 g, 8.97 mmol) was added to a solution of 2.0 g (6.9 mmol) of crude phosphine **6** in 100 ml of dry benzene under nitrogen. The precipitated sulfide (**8**) was purified by column chromatography (three passages through silica gel with benzene-acetone, 1 : 1) and recrystallization from n-pentane-chloroform (95 : 5), yielding 0.40 g (12%) of white crystals, m.p. 215–216°C. ^{13}C NMR spectral data are given in Table I; ^{1}H NRM, $\underline{\delta}$ 1.85 (m, 6H, CH_3), 2.32 (d, J = 9 Hz, N—$(CH_3)_2$), 3.32 (m, 4 H), 5.5 (m, 1 H, olefinic H), 6.15 (m, 1 H, olefinic H), 7.3 (m, 5 H, ArH), other signals not resolved. $C_{18}H_{23}NOP_2S$: Calcd.: C, 59.48; H, 6.39; P, 17.04. Found: C, 59.37; H, 6.13; P, 16.75

Preparation of Phosphine **9** *from Phosphinous Chloride* **2**. Phenylmagnesium bromide was reacted with phosphinous chloride **2** in the same manner as for **5**, but with a reaction time of 6 h. The crude product consisted of 75% of phosphine **9** and 25% of dihydrophosphindole **13**;[10] ^{31}P NMR for **9**, $\underline{\delta}$ ($CDCl_3$) +62.7 (P-1), +57.9 (P-8), $^3J_P \sim 0$; for **13**,[10] +65.7. The oxide (**10**), prepared in the same way as **7**, was an oily material that could not be analyzed. ^{13}C NMR spectral data are given in Table I.

Isomerization of Phosphine Oxide **7** *at P-8.* A solution of 0.5 g (1.44 mmol of oxide **7**) and 36 mmol of diethylamine in 5 ml of chloroform was allowed to stand at room temperature for 2 days. Analysis by ^{31}P NMR showed the complete disappearance of oxide **7** and the formation of an isomer. The solution was evaporated to dryness and the residue was recrystallized from *n*-pentane-chloroform (95 : 5), yielding 0.4 g (80%) of **11**, m.p. 190–192°C. ^{13}C NMR spectral data are given in Table I; ^{1}H NMR ($CDCl_3$ $\underline{\delta}$ 1.58 (s, CH_3), 1.97 (s, CH_3), 2.58 (d, J = 10 Hz, N—$(CH_3)_2$), 3.94 (m, 4 H), 5.8 (m, 2 H, olefinic H), 7.36 (m,

5 H, ArH); ^{31}P NMR ($CDCl_3$) $\underline{\delta}$ +62.8 and +81.8 ($^3J_{PP}$ = 36.6 Hz); $C_{18}H_{23}NO_2P_2 \cdot 1/2\ H_2O$: Calcd: C, 60.66; H, 6.80; P, 17.38. Found: C, 60.79; H, 6.70; P, 17.25. High resolution M.S., M^+ calcd for $C_{18}H_{23}NO_2P_2$ 347.1206, found m/z 347.1198).

Isomerization was also complete after exposure for 4 days to benzylamine, or for 21 days to triethylamine, under conditions where diethylamine gave complete isomerization after 2 h.

Reaction of Phosphinous Chlorides **2** *and* **5** *with Phenylmagnesium Bromide in THF.* A mixture of 0.25 g (0.86 mmol) of **5** in 50 ml of dry THF and 0.29 ml (0.87 mmol) of a 3 M solution of phenylmagnesium bromide was stirred for 2 days under nitrogen at room temperature. Unreacted Grignard reagent was then destroyed with 3 ml of chloroform and the mixture filtered. Evaporation provided a solid residue which by ^{31}P NMR analysis contained 43% of unreacted **5**, 35% of phosphinous bromide **16** [$\underline{\delta}$ ^{31}P NMR +65.0, +37.5 ($^3J_{PP}$ ~ 0)], 17% of dihydrophosphindole **12** and 5% of phosphine **6**. The mixture was subjected to mass spectral analysis; the presence of **16** was indicated by peaks of m/z 333 ($C_{12}H_{18}{}^{79}BrNOP_2$) and 335 ($C_{12}H_{18}{}^{81}BrNOP_2$).

In a similar manner, phosphinous chloride **2** was reacted with phenylmagnesium bromide; the product mixture contained ^{31}P NMR signals for **17** (35%) at $\underline{\delta}$ +60.3 and +38.9 (J_{PP} ~ 0).

Reaction of Phosphinous Chlorides with Methylmagnesium Bromide. The reaction of **5** (0.1 g, 0.35 mmol) with 0.59 mmol of Grignard reagent in 25 ml of ether for 2 days gave only dihydrophosphindole **12**,[10] $\underline{\delta}$ ^{31}P +68.4. This material (0.05 g, 65%) was recovered by column chromatography on silica gel (chloroform-methanol, 97 : 3). In THF, a mixture comprising 8% unreacted **5**, 75% **12**, and 17% of phosphinous bromide **16**, as determined by ^{31}P NMR measurements, was formed. With **2** in THF, phosphinous bromide **17** comprised 74% of the reaction mixture (with 14% **2**, 12% **13**).

Reaction of Phosphinous Chloride **5** *with tert-Butylmagnesium Chloride.* A typical result for reaction in THF was the formation of a mixture consisting of 39% of dihydrophosphindole **12** and 61% of unreacted **5** after 2 days at room temperature; in ether, very little reaction occurred (90% recovery of **5**).

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