Stereochemical Studies with Aminophosphines and Related Compounds Having the 7-Phosphanorbornene Structure

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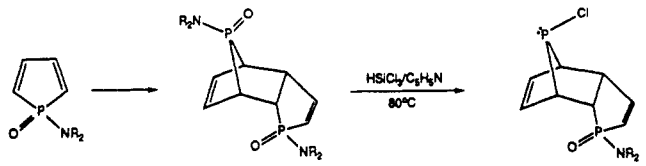
Amines react with phosphinous chlorides having the *anti*-7-phosphanorbornene structure to give a mixture of *syn,anti*-aminophosphines. Structure assignment is straightforward from stereospecific effects in their ^{31}P and ^{13}C NMR spectra. Spectra for an isomer pair enriched in ^{15}N also showed a structurally dependent $^{1}J_{PN}$ value. Oxides and sulfides were prepared from the aminophosphines and characterized spectrally. The ^{17}O NMR spectra for a syn,anti pair were profoundly different and were useful for structural analysis. Oxygen nucleophiles differ considerably in their reaction with such phosphinous chlorides and give only the product of retention. The different behavior of the amines is attributed to the lower apicophilicity of nitrogen in trigonal-bipyramidal intermediates that develop from an initially formed phosphoranide ion.

The dimerization of phosphole oxides constitutes a useful approach to compounds where a phosphorus atom is located at the 7-position of the norbornene framework. This structural feature has been shown in recent years to cause remarkable properties in some of the common functionalities of phosphorus chemistry,[1] presumably because of the sharply reduced C-P-C bond angle and the forced proximity of the phosphorus atom to the π-electrons of the double bond. These effects are responsible for some selective reactions of the bridging phosphorus. In the dimers of 1-aminophosphole oxides, whose stereochemistry has been established by X-ray analysis,[2] this selectivity in the reaction with trichlorosilane–pyridine has allowed the conversion of the bridging phosphinamide to the phosphinous chloride function,[3] which is of great value as a precursor of other groups. This reaction is also specific in forming exclusively the anti chloro isomer.



In previous papers,[4,5] we have described the substitution of the chlorine by a variety of nucleophilic species, including C_6H_5MgBr, NaOMe, HOMe, and H_2O. In every case the reactions proceeded with complete retention of the configuration at phosphorus, a new observation for a phosphinous chloride.[6] A mechanism that explains this result involves a phosphoranide intermediate,[7] where it is assumed that the usual principles for substitutions that proceed through a trigonal-bipyramidal intermediate are applicable. The preference for an equatorial lone pair orientation is an important feature of the stereochemical pathway. Other rules of importance are that the contracted C-P-C bond angle is best accommodated by apical–equatorial rather than diequatorial disposition and that attack and departure occur at the apical position (Scheme I). Now we describe the reaction with amines,[8] where it will be seen that the rigid control of the stereochemistry of substitution is relaxed, as manifested by the formation of considerable amounts of the inverted product. We also report on some chemical and spectral properties of the resulting *syn*- and *anti*-aminophosphines.

Reaction of Chlorophosphanorbornenes with Amines. The rate of displacement of the chlorine by attack of secondary amines on phosphinous chloride 1 was found to be strongly influenced by the size of the substituents on nitrogen. Thus, no displacement occurred when diethylamine was used in benzene solution at 25 °C for 5 days, but when piperidine was employed the displacement was complete under the same conditions. Dimethylamine was even more reactive, and complete displacement occurred even under very mild conditions (-20 °C in chloroform). Examination of the products by ^{31}P NMR spectroscopy (Table I, discussed in the next section) immediately revealed that isomers had been formed. Their identity and approximate relative amounts from the various substitutions are summarized in Scheme II. Solvent effects on the ratio were observed; thus, a chloroform medium provided more of the anti isomer than did benzene. This may be related to the fact that the amine hydrochloride byproduct precipitated from the latter but remained in solution in $CHCl_3$. This point will receive elaboration in the section on stereochemistry. The yields in the substitutions were virtually quantitative as judged by the spectral analysis, and no byproducts were detected. Since the products could not be crystallized and tended to decompose on handling, they were not isolated as pure substances. Solutions of the products that contained some of the starting amine were stable under a nitrogen atmosphere for several weeks, but syn to anti isomerization occurred in the absence of the amine. When the diethylamino analogue 8 of phosphinous chloride 1 was used in the reaction with amines, similar results were obtained.

Spectral Properties of the Aminophosphines. The ^{31}P NMR spectra (Table I) were greatly different for the two isomers and followed the shift and coupling patterns established for tertiary phosphines with the same structural framework. Thus, the isomers with *syn*-dialkylamino (**3**, **5**, **7**, and **10**) all had the ^{31}P shift for the bridging position far downfield (δ +155.2 to +163.0) of the expected position for an aminophosphine (e.g., +47.0 for 1-(di-

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(1) Quin, L. D.; Caster, K. C.; Kisalus, J. C. *Phosphorus Sulfur* **1983**, *18*, 105.
(2) Quin, L. D; Szewczyk, J.; Szewczyk, K.; McPhail, A. T. *J. Org. Chem.* **1986**, *51*, 3341.
(3) Quin, L. D.; Szewczyk, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1551.
(4) Keglevich, G.; Quin, L. D. *Phosphorus Sulfur* **1986**, *26*, 129.
(5) Quin, L. D.; Keglevich, G. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1029.
(6) (a) Corfield, J. R.; Oram, R. K.; Smith, D. J. H.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 713. (b) Nielsen, J.; Dahl, O. *J. Chem. Soc., Perkin Trans. 2* **1984**, 553.
(7) Holmes, R. R. *Pentacoordinated Phosphorus*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980; pp 163-166. The similarity to the 7-norbornene system, noted previously,[1] may suggest a neighboring group participation in these reactions. At this time we see no role for this effect, but will continue to consider it as we develop the chemistry of compounds like 1.
(8) Some preliminary results have been published in ref 3.

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Scheme I

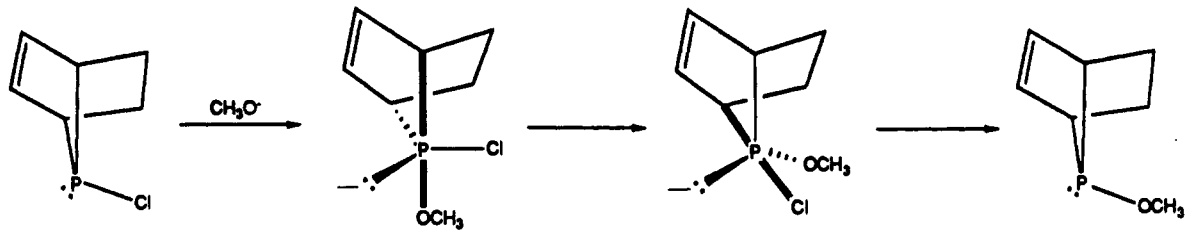
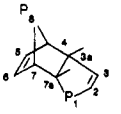


Table I. ^{31}P and ^{13}C NMR Spectral Data[a] for Aminophosphines[b] and Phosphinites[b]

	^{31}P NMR			partial ^{13}C NMR				
no.	δ(P-1)	δ(P-8)	$^3J_{PP}$	C-3a	C-4	C-5	C-6	C-7a
2	57.3	85.1	3.6					
3	64.5	155.2	47.6					
4	58.1	87.3	3.7					
5	64.2	158.6	48.2					
6	61.2	89.9	3.9	53.2 (19.8, 2.2)	48.9 (4.4, 17.6)	136.6 (0, 20.9)	123.6 (5.2, 19.4)	37.0 (90.1, 2.2)
7	65.0	163.0	48.8	47.8 (13.2, 36.2)	50.6 (0, 12.5)	135.0 (0, 3.3)	124.3 (4.4, 3.3)	33.2 (92.3, 31.9)
9	58.3	86.7	5.0	54.5 (19.8, 2.2)	49.8 (4.4, 17.6)	137.1 (0, 20.9)	125.3 (5.5, 19.8)	40.9 (90, 3.3)
10	65.6	159.0	48.9					
26	60.7	88.9	4.9	54.0 (17.6, ~1)	51.6 (4.4, 17.6)	136.4 (0, 23.1)	123.7 (5.5, 22.8)	38.1 (92.3, ~1)
28	63.1	104.8	6.4					

[a] $CDCl_3$ solutions. ^{31}P shifts downfield of 85% H_3PO_4 as reference; ^{13}C shifts downfield of $(CH_3)_4Si$ as reference. Values in parentheses are ^{31}P–^{13}C coupling constants in hertz for P_1 and P_8, respectively. [b] Numbering: 

ethylamino)-3,4-dimethyl-3-phospholene[9]) and had very large ^{31}P–^{31}P coupling constants (47.6 to 48.9 Hz). In the *anti*-dialkylamino series (**2**, **4**, **6**, **9**), the bridging phosphorus signal was much farther upfield (δ +85.1 to +89.9) although still showing the deshielding characteristic of the 7-phosphanorbornene system. The ^{31}P–^{31}P coupling constants were also much smaller for the anti compounds (3.6 to 5.0 Hz). This trend in coupling constants is empirically related to the orientation of the lone pair on phosphorus and has been observed for phosphines of the 7-phosphanorbornene system.[10] The constant is large when the lone pair is in close proximity to the coupled nucleus and is small when remote, just as is found for three-bond ^{31}P–^{13}C coupling in phosphines.[11]

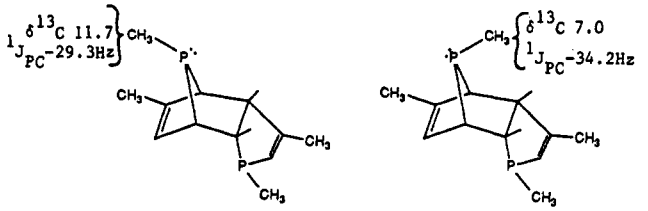
The ^{13}C NMR spectra (Table I) were also recorded for some of the isomer mixtures, and because of some pronounced stereocontrolled effects it was possible to assign the signals to the proper isomer. For the isomer pair **6**, **7**, these effects confirmed the major isomer to have the anti configuration **6** at the bridging phosphorus. The most notable differences arise in the value for $^2J_{PC}$, which are under the control of the lone pair orientation. Thus, as noted above for $^3J_{PP}$, the two-bond coupling in phosphole dimers is large when the lone pair is close to the carbon nucleus[10] and in the aminophosphines quite different values can also be expected for the framework carbons. In the syn isomer **7**, coupling to fusion carbons 3a and 7a was relatively large (32 to 36 Hz) and small to the olefinic carbons 5 and 6 (3 Hz), while in the anti isomer **6** the opposite is true (2 Hz to C-3a,7a; 19-21 Hz to C-5,6).

Some ^{15}N spectral data (Table II) of the (dimethylamino)phosphines **6** and **7** were obtained on samples (designated **6** and **7**) prepared from isotopically enriched dimethylamine. These measurements were made to explore the possibility that trends already established for $^1J_{PC}$ in tertiary phosphines in this series might be found also for $^1J_{PN}$. Thus, it is known[10] that the absolute one-bond ^{31}P–^{13}C coupling constant is larger in the anti isomer than in the syn. No sign determination has been made, but

Table II. ^{15}N and ^{17}O NMR Spectral Data[a]

		^{17}O NMR[c]			
no.	$^1J_{PN}$,[b] Hz	δ(O=P_1)	J_{OP1}, Hz	δ(O=P_8)	J_{OP8}, Hz
6′	47.6				
7′	74.5				
11	25.6	75.5	180	48.9	156
12	9.8	77.1	152	102.7	172
17	36.6				
18	22.5				

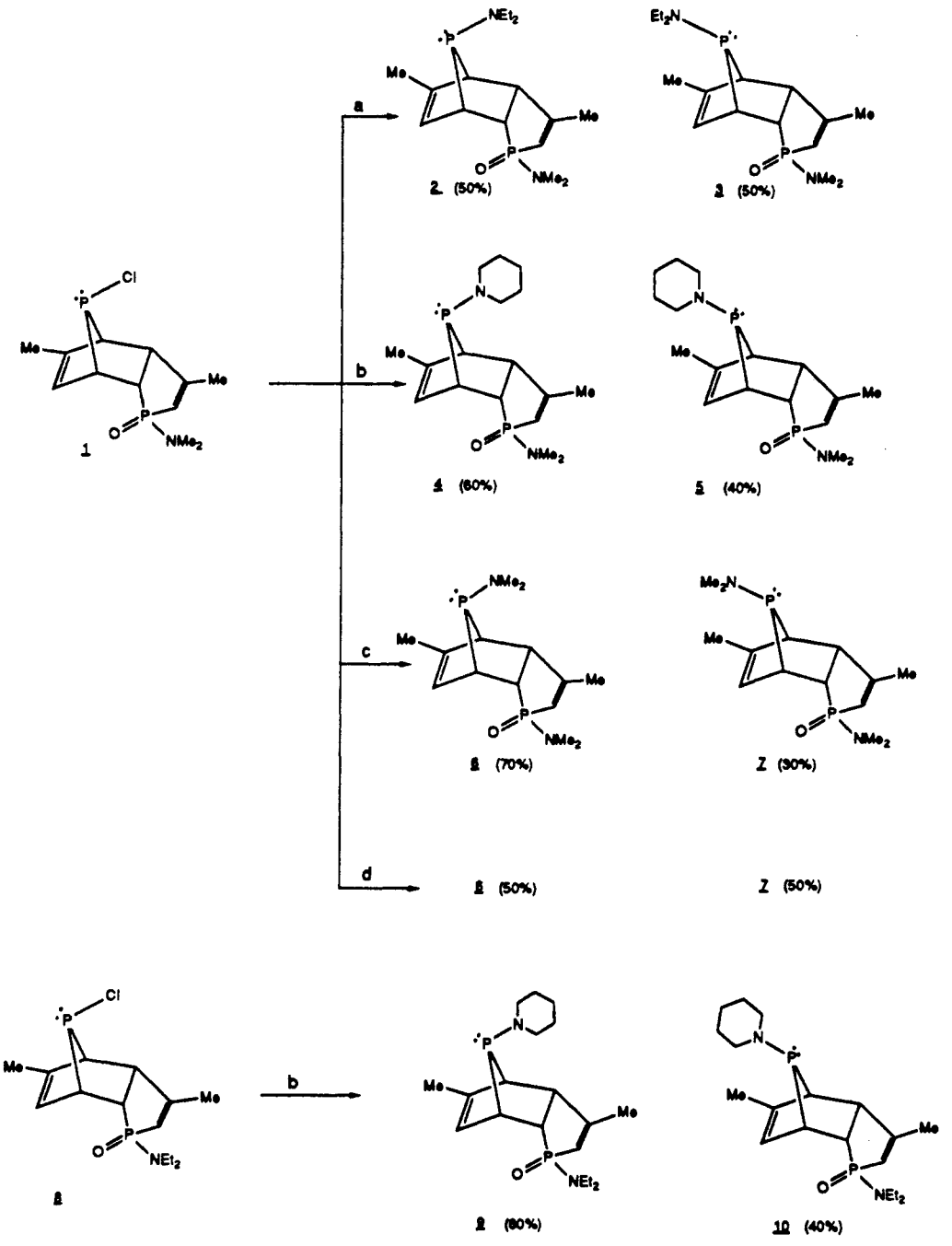
[a] Recorded with a Varian XL300 spectrometer. [b] From ^{31}P NMR spectrum in $CDCl_3$; ^{15}N signals not readily measurable except for **6′**, δ-360.8 (CH_3NO_2=O). [c] Chemical shifts downfield of H_2O as reference; CD_3CN solutions at 70 °C. Other parameters as described in ref 16. Coupling constants are ±10 Hz.



since tertiary phosphines are accepted to have negative $^1J_{PC}$ values,[12] it can be assumed that the coupling constant is more positive in the syn isomer. In *syn*-aminophosphine **7′**, the constant is 74.5 Hz, while for the anti isomer **6′** it is 47.6 Hz. Here the sign is taken to be positive,[13] and hence again the syn isomer is associated with the more

(9) Quin, L. D.; Szewczyk, J. *Phosphorus Sulfur* **1984**, *21*, 161.
(10) Quin, L. D.; Caster, K. C.; Kisalus, J. C.; Mesch, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 7021.
(11) Quin, L. D.; Gallagher, M. J.; Cunkle, G. T.; Chestnut, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 3136.
(12) Duangthai, S.; Webb, G. A. *Org. Magn. Reson.* **1983**, *21*, 125.
(13) Gray, G. A.; Albright, T. A. *J. Am. Chem. Soc.* **1976**, *98*, 3857. McFarlane, W.; Wrackmeyer, B. *J. Chem. Soc., Dalton Trans.* **1976**, 2351.

Scheme II



a: Et_2NH in C_6H_6, 70°C, 3 days.

b: $(CH_2)_5NH$ in C_6H_6, 25°C, 5 days.

c: Me_2NH in $CHCl_3$, -20°C(30min), 25°C(2h).

d: Me_2NH in C_6H_6, 25°C, 6-12 h.

positive coupling constant. The correlation may be accidental, however, since bonding differences are strong between otherwise comparable P–C and P–N derivatives. The hybridization of nitrogen has been reported to influence the P–N coupling constant,[14] with the larger values taken to indicate more sp^2 character at N. The extremes are 50 Hz for sp^3 N and 91 Hz for sp^2 N, and on this basis it could be suggested that *syn*-aminophosphine **7** has more sp^2 character than *anti*-aminophosphine **6**. However, hybridization differences at P and the nature of its lone pair also can control the magnitude of $^1J_{PN}$, and until structural parameters are obtained for an isomer pair, conclusions on the origin of the $^1J_{PN}$ difference observed for **6** and **7** seem premature.

Reactions of the Aminophosphines. The addition of sulfur[15] occurred smoothly with the aminophosphines and

(14) Gousenard, J. P.; Dorie, J. *J. Mol. Struct.* **1980**, *67*, 297. Gousenard, J. P.; Dorie, J.; Martin, G. J. *Can. J. Chem.* **1980**, *58*, 1295.

(15) These reactions on P(III) occur with complete retention. See: Horner, L.; Winkler, H. *Tetrahedron Lett.* **1964**, 175.

Scheme III

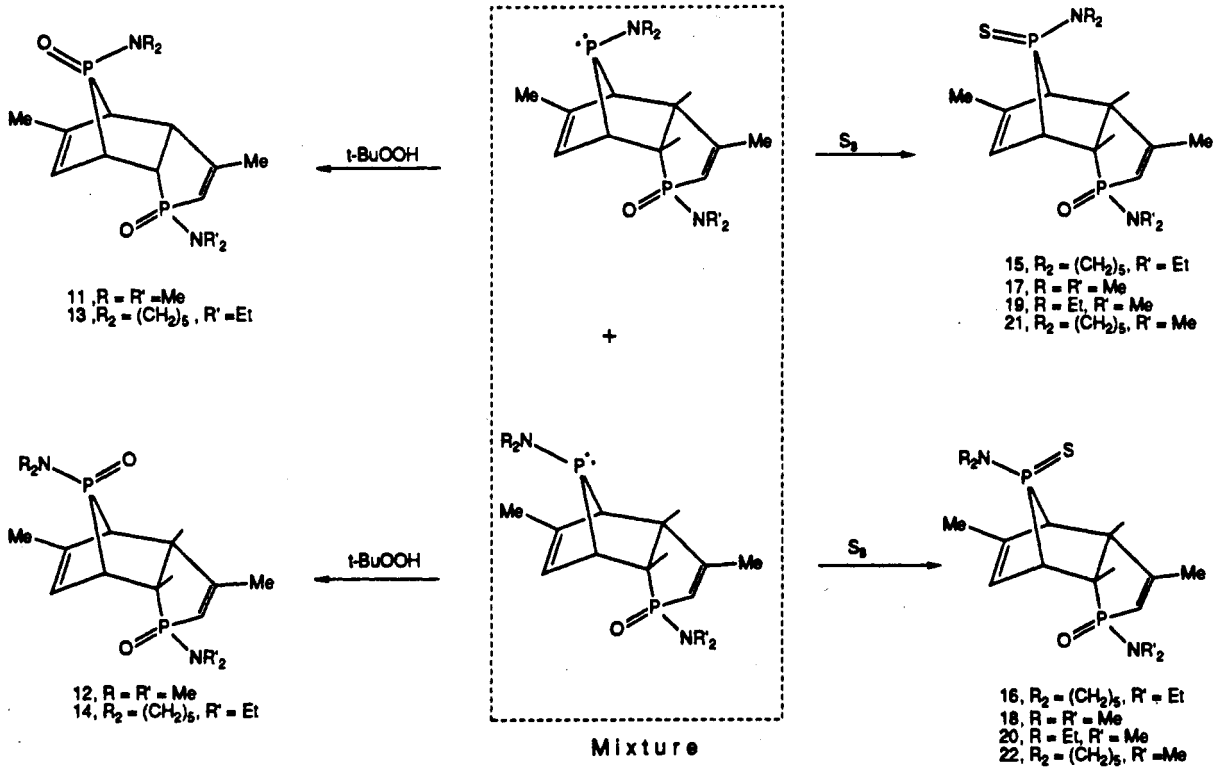


Table III. Data for Phosphinamides and Thiophosphinamides Prepared from Aminophosphines

			^{31}P NMR[a]			analysis					
						C		H		P	
no.	yield, %	mp, °C	$\delta(P_1)$	$\delta(P_8)$	$^3J_{PP}$	calcd	found	calcd	found	calcd	found
11	51	123–125	64.5	83.0	36.6	53.50	53.63	7.64	7.89	19.75	19.58
12[b]	13	134–136	64.8	83.0	41.5						
13	45	85–88	62.1	80.5	36.6	59.68	59.76	8.38	8.63	16.23	15.99
14[c]	18	93–96	61.2	79.7	41.5						
15	45	161–163 dec	60.2	121.0	35.5	57.29	56.99	8.04	7.98	15.58	15.36
16	21	165–167 dec	61.7	130.5	46.4	57.29	57.03	8.04	8.17	15.58	15.73
17	54	94–95	62.5	125.0	34.2	50.91	50.93	7.27	7.24	18.79	18.72
18	17	162–166 dec	63.6	133.5	43.9	50.91	51.07	7.27	7.38	18.79	19.07
19	23	145–146	62.7	122.8	34.2	53.63	53.33	7.82	8.05		
20	18	115–116	63.9	131.1	43.9	53.63	53.89	7.82	7.49	17.32	17.32
21	46	160–162	62.4	120.8	34.2	55.14	55.45	7.57	7.66	16.76	16.90
22	22	177–179	63.8	131.3	43.9	55.14	54.93	7.57	7.81	16.76	16.53

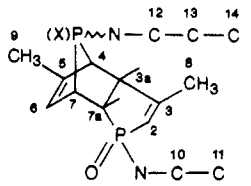
[a] Chemical shifts are downfield of 85% H_3PO_4 as reference; $CDCl_3$ solutions. [b] Reported in ref 2. [c] Satisfactory analysis not obtained.

is of note because the resulting crystalline thiophosphinamides proved to be readily separable by column chromatography on silica gel into the syn and anti isomers. The aminophosphines were also oxidized with *tert*-butyl hydroperoxide,[15] and again the isomeric phosphinamides were separable by column chromatography or by fractional crystallization. Products prepared are summarized in Scheme III and were characterized by elemental analysis (Table III), ^{31}P NMR (Table III), and ^{13}C NMR spectroscopy (Table IV).

The ^{31}P NMR data for the various isomeric pairs of thiophosphinamides show that two consistent effects are present that are controlled by the configuration at the bridging phosphorus. When the amino group is in the anti position, the ^{31}P signal is shifted upfield by 8–10 ppm, and the $^3J_{PP}$ value is 9–11 Hz smaller than that for the syn isomer. These effects, which are not observed in the corresponding phosphinamides nor in dimers of phosphole oxides, can be useful for structure assignment purposes.

The ^{13}C NMR spectra of the thiophosphinamides also show some consistent effects that are related to the configuration at the bridging phosphorus. The most significant is the coupling through two bonds; the data are clear in showing that when sulfur is positioned over the coupled carbon, the $^2J_{PC}$ value is considerably larger (50–100%) than when it is remote. This effect is useful in this series of compounds to establish stereochemistry. The effect is absent in the phosphinamides, although for phosphine oxides with the phosphole dimer framework, the opposite relation is routinely observed. A three-bond effect is found at the alkyl substituent on the bridging group in both the thiophosphinamide and the phosphinamide; the $^3J_{PC}$ value for the β-carbon of the substituent is nearly twice as large when the amino substituent is anti than when it is syn. However, a three-bond effect at ring carbon C-3 is just the opposite; for the thiophosphinamides (but not the phosphinamides), $^3J_{PC}$ is about one-third larger when the substituent is in the syn position. While no explanation can be offered for these coupling effects, they are pointed out as being useful in an empirical way for stereochemical analysis of derivatives of the phosphole dimer framework. Chemical shifts in this series are less indicative of stere-

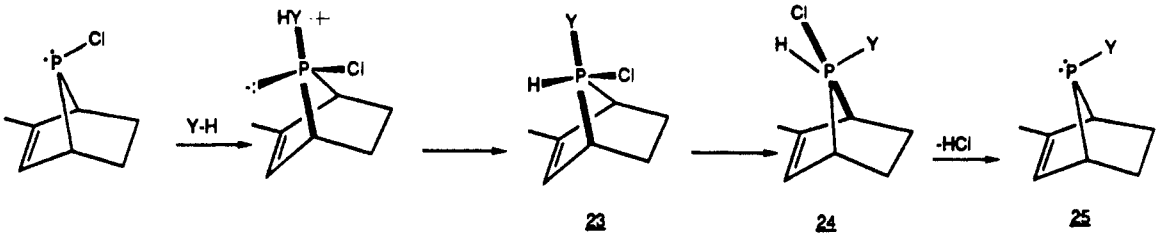
Table IV. Partial ^{13}C NMR Spectral Data[a] for Phosphinamides and Thiophosphinamides



no.	C-3	C-3a	C-5	C-6	C-7a	C-13
11	160.4 (28.6, 9.9)	49.5 (16.5,[b] 14.3[b])	137.0 (0, 8.8)	125.3 (5.5, 4.4)	35.9 (91.2, 13.2)	
12	160.7 (28.6, 9.9)	50.8 (15.4, 15.4)	134.8 (0, 9.9)	124.6 (6.6, 5.5)	36.1 (91.2, 13.2)	
13	160.2 (28.5, 9.9)	50.3 (15.0, 15.0)	137.0 (0, 7.7)	125.5 (5.5, 5.5)	38.8 (92.3, 13.2)	26.2 (0, 7.7)
14	159.9 (27.5, 9.9)	50.6 (15.5, 15.5)	131.1 (0, 11)	124.3 (7.6, 4.4)	38.2 (91.2, 13.2)	25.2 (0, 3.3)
15	159.7 (27.5, 8.8)	50.7 (14.3, 14.3)	137.8 (0, 11.0)	125.7 (4.4, 8.8)	39.3 (90.1, 11.0)	25.6 (0, 9.9)
16	160.6 (27.5, 11.5)	51.4 (15.4, 20.9)	135.7 (0, 6.6)	125.6 (4.4, 4.4)	38.8 (91.6, 17.6)	25.8 (0, 5.5)
17	159.9 (27.5, 8.8)	50.0 (14.3, 14.3)	137.5 (0, 11.0)	125.3 (4.4, 8.7)	36.4 (90.1, 9.4)	
18	160.4 (27.5, 11.0)	51.1 (14.1, 20.8)	135.8 (0, 6.6)	125.0 (4.4, 4.4)	36.3 (92.3, 18.7)	
19	160.3 (28.0, 8.2)	50.7 (14.3, 14.3)	138.2 (0, 11.0)	125.9 (4.4, 8.8)	36.8 (90.1, 11.0)	13.4 (0, 5.5)
20	161.0 (28.2, 12.1)	51.1 (14.8, 20.5)	135.5 (0, 6.6)	125.0 (4.0, 4.0)	35.9 (90.0, 17.5)	13.7 (0, 2.7)
21	160.2 (26.8, 8.0)	50.9 (14.8, 14.8)	138.1 (0, 10.8)	125.8 (5.4, 9.4)	36.9 (91.3, 9.4)	25.8 (0, 9.4)
22	161.3 (27.5, 12.1)	51.5 (15.4, 20.9)	136.0 (0, 6.6)	125.4 (4.4, 4.4)	36.5 (91.2, 17.6)	25.8 (0, 5.5)

[a] $CDCl_3$ solutions, with chemical shifts referenced to $(CH_3)_4Si$. Values in parentheses are J_{CP-1} and J_{CP-8}, respectively, in hertz. [b] Not assigned.

Scheme IV



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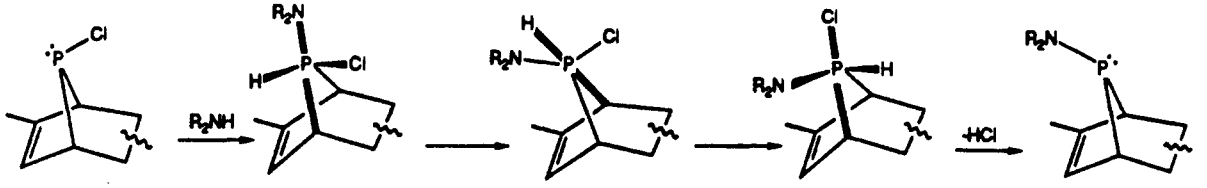
Scheme V



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ochemistry, although a consistent shielding effect of 2–3 ppm is observed at ring carbon 5 when the amino substituent is positioned over it in the syn series.

The ^{15}N-enriched aminophosphines **6′** and **7′** were also converted to the phosphinamides and thiophosphinamides. The ^{31}P–^{15}N coupling constants were obtained from the ^{31}P NMR spectra, since the ^{15}N NMR signals were not clearly distinguished from the noise. Data are given in Table II. Again signs are proposed from relations in the literature, and it is seen that the syn isomers are significantly more positive than the anti. It has been established by X-ray analysis[2] that the phosphinamide with the *syn*-dimethylamino group has a nearly planar structure at nitrogen, but since no data are available for an anti isomer it cannot be assumed that the larger negative value for the anti isomer implies a different (nonplanar) geometry. Increases in one-bond coupling can also be attributed to increased s character, which could arise at the bridging position from the contraction of the ring C–P–C angle and an increase in p character.

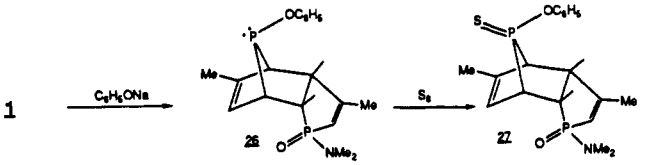
We have also recorded the ^{17}O NMR spectra at the natural abundance level for the pair of syn,anti isomers **11** and **12**. This measurement was prompted by the observation[16] of remarkable chemical shift differences for a pair of isomers with the phosphole oxide dimer framework; the syn isomer for the dimer of 1,3-dimethylphosphole oxide had a chemical shift of δ 100.8 (H_2O = 0 ppm) and the anti δ 42.1. We observed exactly the same effect with phosphinamides **11** and **12**; the syn isomer had δ 102.7, while the anti isomer was far upfield at δ 49.0. The $^1J_{PO}$ values were rather similar for the isomer pair, again an effect seen for the phosphine oxides.[16] To our knowledge, these are the first ^{17}O measurements on a phosphinamide and indicate the potential value of the technique in structural investigations.

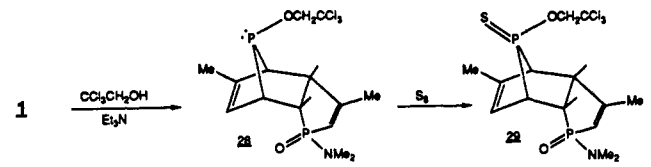
Stereochemistry of Formation and Reactions of Aminophosphines. As noted in the introduction, all substituents of 7-PNB phosphinous chlorides, except by amines, proceed with complete retention of configuration. Retention is readily explained by a phosphoranide ion intermediate as shown in Scheme I. However, if a proton is present on the attacking nucleophile, it likely is transferred to phosphorus to form a true pentacovalent species

(16) Quin, L. D.; Szewczyk, J.; Linehan, K.; Harris, D. L. *Magn. Reson. Chem.*, in press.

(23) as in Scheme IV. Polytopal isomerization may follow to give species 24, which possesses apical Cl and thus may collapse to the tricovalent form with retained configuration. However, if Y is a group of low apicophilicity relative to H, a species with H-apical, Y-equatorial will be of lower energy than 23 and can be achieved by another isomerization. When this species isomerizes again to place chlorine apical for departure, the final product has the inverted configuration. Amino is just such a group[7,17] and is used in the illustration of these events in Scheme V. Unlike nitrogen, oxygen is an atom of high apicophilicity;[7] in reactions with water or alcohols, there would be little tendency for isomerization to a species like 25, and thus no inverted product would be expected.

Inversion would also result from an isomerization that placed the ring carbons in diequatorial positions, as has been proposed[6a] for 1-chlorophosphetanes, but the severe angle constraint in the 7-PNB framework speaks against this possibility. This explanation does have one attractive feature: the substituting group can reside on the less crowded (olefinic) face of the 7-PNB framework in the TBP from which chloride departs. A test of this possibility was performed by using two oxygen nucleophiles (C_6H_5ONa and CCl_3CH_2OH with Et_3N) of larger size than previously used; any significant contribution of a TBP equivalent to 25 would give some inverted product. However, the products were exclusively those with the retained configuration. The ^{31}P and ^{13}C NMR spectra of these compounds (Table I) were decisive, as they were for the aminophosphines, in proving their structure. Thus, the very far downfield shifts and small $^3J_{PP}$ leave no doubt that they have the anti structure (26 and 28). They were

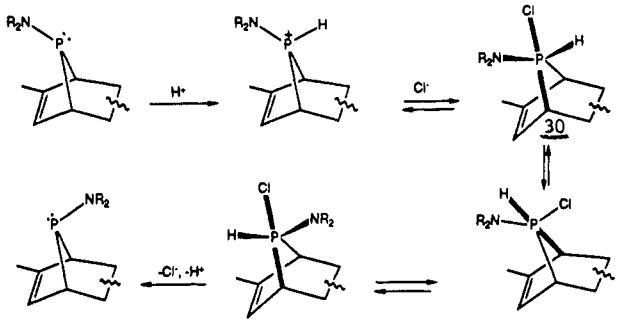




conveniently analyzed as their sulfur addition products. These results again emphasize the novelty of the amine reaction in giving some inverted product. An attempt to employ an amine anion as the nucleophile, to determine if this caused any change in stereochemistry, was not successful; degradation of the phosphinous chloride (1) was extensive with $(C_2H_5)_2N^-$, and no simple substitution products could be recognized.

Another explanation for an inverted product is that a direct, concerted displacement of chlorine in an S_N2 process has occurred. This cannot be the exclusive mechanism for the chlorine displacements, however, since it does not account for the high degree of retention. Nevertheless, it cannot be ruled out completely as a process which occurs simultaneously with that involving TBP intermediates. There would be no logical explanation for such a concerted process occurring only for amines, and for no other nucleophiles, however.

Scheme VI

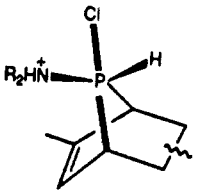


Finally, the possibility needs to be considered that in *all* of these substitutions the initial product has the syn structure and that rapid isomerization by pyramidal inversion occurs under the reaction conditions to give the anti product. Again the aminolysis reaction would be unique in not giving complete isomerization. However, the availability of both isomers of an aminophosphine offers an opportunity for answering the question, since the stability of the syn isomer toward pyramidal inversion can be tested. *syn*-Aminophosphine 7, in mixtures with different amounts of the corresponding anti isomer 6, was in fact quite stable at 25 °C and showed no approach to an equilibrium mixture. Even at 70 °C, the syn to anti rearrangement is not fast; in the presence of excess amine, 7 required 3–5 days for inversion. Finding that the anti isomer is more stable than the syn is not a new observation; tertiary phosphines with the 7-PNB structure have the same property.[10] However, it was noted that syn to anti isomerization was more rapid if 1 equiv of the corresponding amine hydrochloride was added to the aminophosphine in a good solvent ($CHCl_3$) for all participants. Thus, a mixture of *syn*-7 (30%)–*anti*-6 (70%) isomers was completely converted to the anti form after 5 h at 25 °C. When a 5-fold excess of the amine was present in such an experiment, the isomerization was retarded and required 3 days at 65 °C for completion. We interpret this result to indicate a role for HCl in the isomerization, since the process does not occur if excess base is present to compete with the aminophosphine for the HCl. The stereochemistry of the isomerization process can be expressed as in Scheme VI. Under the conditions used, the HCl addition product 30 is given sufficient opportunity to isomerize among the various TBP forms (others are also possible); collapse to the more stable aminophosphine ensues. This process is not fast enough, however, under conditions used in the original syntheses of the aminophosphines to account for the formation of the anti isomers as a step subsequent to the formation of the syn isomers (as from an S_N2 process).

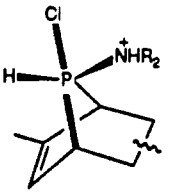
Another explanation for the isomerizing action of an amine salt might be that amine exchange occurs. This possibility was easily disposed of by employing ^{15}N-enriched $Me_2NH_2^+Cl^-$ in the reaction with 7. Inversion to the anti isomer was complete after 15 h at 25 °C, but the product contained *no* ^{15}N since the ^{31}P NMR signal showed no splitting. Only after 3 days at 65–70 °C was a small amount (10%) of ^{15}N-incorporation noted. No exchange was noted after ^{15}N-enriched Me_2NH and aminophosphine 6 were allowed to stand at 25 °C for several days.

(17) Van der Knaap, T. A.; Bickelhaupt, F. *Phosphorus Sulfur* **1984**, *21*, 227.

In a concluding experiment, we considered the stereochemical consequences in the 7-PNB system of the cleavage of aminophosphines by excess anhydrous HCl. Starting with a mixture of syn (5) and anti (4) isomers of the piperidinophosphines, the reaction led exclusively under a variety of conditions (25 °C in benzene, $CHCl_3$, or ether–benzene; −10 °C in THF) to the *anti*-chloro product 1. This result may be explained by the formation of pentacoordinate adducts (e.g., 31 and 32, respectively)



31



32

which may isomerize before collapse to the more stable *anti*-phosphinous chloride. The special character of the 7-phosphanorbornene system is again evident in this reaction; when an acyclic optically active aminophosphine ($EtPhPNEt_2$) was reacted with dry HCl in ether at 0 °C, the phosphinous chloride product was racemic.[18]

Experimental Section

General. Proton NMR spectra were obtained on an IBM NR-80 spectrometer at 80 MHz, using tetramethylsilane (Me_4Si) 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 Me_4Si as an internal standard. Broadband proton noise-decoupling was employed on all carbon-13 and phosphorus-31 NMR spectra. Nitrogen-15 and oxygen-17 spectra were obtained with a Varian XL-300 spectrometer. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Combustion analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of Phosphinous Chlorides with Amines. A solution of 0.020 mol of the amine in 50 mL of benzene was added to a solution of 0.005 mol of phosphinous chloride 1 in 50 mL of benzene. Reaction conditions are stated in Scheme II. The precipitated amine salt was filtered off, and excess amine and solvent were stripped with a rotary evaporator. The crude products were characterized by NMR spectroscopy (Table I), and because of their sensitivity were used directly without further purification. Isomer ratios (Scheme II) were determined from ^{31}P NMR spectra. Phosphinous chloride 8 was reacted with piperidine in the same manner as for 1, providing aminophosphines 9 and 10.

Samples of aminophosphines 6 and 7 enriched in ^{15}N were prepared exactly as above by employing dimethylamine with 95% ^{15}N as the reactant.

Oxidation of Aminophosphines with *tert*-Butyl Hydroperoxide. The bis(dimethylamino) derivatives 6 and 7 in admixture, prepared as above from 1, were dissolved in 150 mL of chloroform and treated at −10 °C with a solution of 0.0075 mol of *tert*-butyl hydroperoxide in 50 mL of chloroform. The mixture was stirred for 2 h at 0 °C and then overnight at 25 °C. Solvent was then stripped from the mixture, and the residue was subjected to silica gel column chromatography with elution by 3% methanol in chloroform (v/v). This provided a crystalline mixture of the *syn,anti* bis(phosphinamide) isomers, which was then separated by fractional crystallization from ethyl acetate–hexane; the syn isomer (12) crystallized, leaving the anti (11) isomer in solution from which it was recovered by evaporation. Products were recrystallized from ethyl acetate–hexane. The syn isomer (13% yield, mp 134–136 °C) is a known compound;[2] the anti isomer (51% yield) had mp 123–125 °C. Analytical and spectral data are given in Tables III and IV. Similarly, the isomer mixture 9,10 was oxidized and the product was chromatographed to provide isomer 13 (45%, mp 85–88 °C). Spectral data are recorded in Tables III and IV. The syn isomer 14 (18%) was not obtained in analytical purity.

Reaction of Aminophosphines with Sulfur. The aminophosphine (0.0005 mol) in 50 mL of benzene was treated with a solution of 0.0015 mol of sulfur in 20 mL of benzene. The mixture was stirred overnight, and then solvent was removed on a rotary evaporator. The residue was extracted with benzene to remove sulfur and then chromatographed on silica gel with elution by ethyl acetate. The syn isomer was eluted first; both isomers were recrystallized from ethyl acetate–hexane. The yields and analytical and spectral data for the thiophosphinamides synthesized are given in Tables III and IV.

Reaction of Phosphinous Chloride 1 with Sodium Phenoxide. The solution of phosphinous chloride 1, obtained by the $HSiCl_3$ reduction[3] of 0.005 mol (1.57 g) of aminophosphole oxide dimer 12, in 20 mL of benzene was added to a suspension of 0.006 mol of sodium phenoxide in 50 mL of benzene containing 20 mg of 18-crown-6. The reaction temperature was moderated with an ice bath. The mixture was stirred overnight and then filtered. Benzene was removed by rotary evaporation. The ^{31}P and ^{13}C NMR spectra were recorded on the residue (Table I) and showed that the only product was the *anti*-phenoxy phosphinite 26. The product was reacted with sulfur by the procedure used to prepare phosphinamides. The single thiophosphinate 27 that resulted was recrystallized from ethyl acetate–hexane, yield 68%: mp 167–169 °C; ^{31}P NMR ($CDCl_3$) δ 62.6 (P-1) and 117.3 (P-8), $^3J_{PP}$ = 38.0.

Anal. Calcd for $C_{18}H_{23}NO_2P_2S$: C, 56.99; H, 6.07; P, 16.36. Found: C, 56.98; H, 6.14; P, 16.33.

Reaction of Phosphinous Chloride 1 with Trichloroethanol. A solution of phosphinous chloride 1, obtained by the silane reduction of 0.005 mL (1.57 g) of dimer 12, in 20 mL of benzene was added to a mixture of 0.97 g (0.006 mol) of trichloroethanol and 0.7 g (0.007 mol) of triethylamine in benzene. The mixture was refluxed for 3 days, and salt that precipitated on cooling was filtered off. Solvent and volatile materials were removed by rotary evaporation, and the residue was subjected to high vacuum evaporation. The product was found by ^{31}P and ^{13}C NMR analysis (Table I) to consist of a single compound, phosphinite 28, with the *anti*-trichloroethoxy group. Addition of sulfur as described for the aminophosphines gave thiophosphinate 29, 56%, recrystallized from ethyl acetate–hexane: mp 154–156 °C; ^{31}P NMR ($CDCl_3$) δ 65.2 (P-1) and 122.0 (P-8), $^3J_{PP}$ = 39.0 Hz.

Anal. Calcd for $C_{14}H_{20}Cl_3NO_2P_2S$: C, 38.67; H, 4.60; P, 14.27. Found: C, 38.89; H, 4.60; P, 14.51.

Reaction of Aminophosphines with Hydrogen Chloride. Dry hydrogen chloride was passed through a solution prepared from 0.001 mol of a 60:40 mixture of aminophosphines 4 and 5. Solvent and temperature were benzene, 25 °C; chloroform, 25 °C; ether–benzene (1:1), 25 °C; tetrahydrofuran, −10 °C. The reactions were monitored by ^{31}P NMR. The only product in every case was phosphinous chloride 1.

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(18) Horner, L.; Jordan, M. *Phosphorus Sulfur* **1980**, *8*, 235.