Stereochemistry of the Reaction of Oxygen Nucleophiles with a Phosphinous Chloride in the 7-Phosphanorbornene Series

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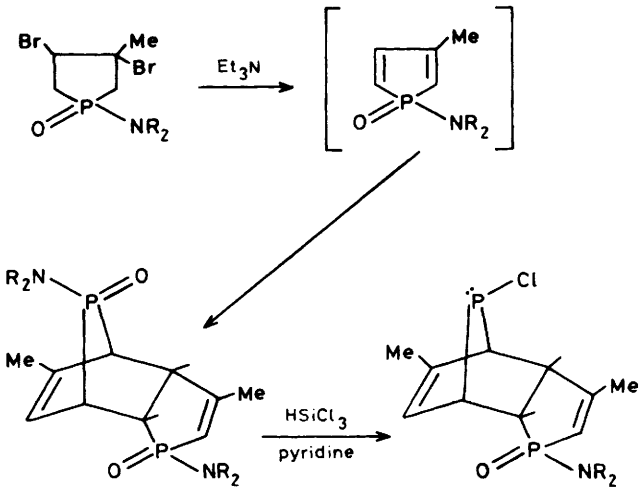
Dimers of 1-aminophosphole oxides react with trichlorosilane–pyridine at the 7-phosphanorbornene moiety to provide the *anti*-chloro derivative, useful for preparing other compounds. With sodium methoxide, chlorine displacement occurs smoothly to give exclusively the *anti*-phosphinite. This ester has been treated with benzyl and methyl halides to give tertiary phosphine oxides. The chloro compound reacts with methanol to give the same phosphinite, along with some of the secondary phosphine oxide from cleavage of the methyl group. The secondary phosphine oxide, with *anti*-oxygen, is the exclusive product of the hydrolysis of the chloride. The complete retention of configuration in these reactions, also observed previously in arylation with phenyl Grignard reagent and in a bromide-exchange reaction, is consistent with a mechanism involving a phosphoranide intermediate whose decay is governed by rules laid down for true trigonal bipyramidal intermediates.

The first phosphinous chlorides where the phosphorus atom is incorporated at the 7-position of the 7-phosphanorbornene (7-PNB) framework were recently prepared in this laboratory.[1,2] The method of synthesis requires the presence of a phosphinamide group in the 7-PNB framework, which is conveniently formed from the dimerisation of 1-aminophosphole oxides. The chlorides are formed on reaction with $HSiCl_3$–pyridine. The reaction appears to proceed through exchange of amino- and chloro-groups, followed by deoxygenation.

The *anti*-chloride is formed regardless of the configuration of the starting amide. Phosphinous chlorides are valuable precursors of other phosphorus functions, and we have already shown that the chlorines in (**1**) and (**2**) can be displaced by amines to form 7-PNB aminophosphines,[1] and by PhMgBr to form the tertiary phosphine group.[2] In these reactions, the presence of the second phosphinamide group in the fused 2-phospholene ring causes no complications, and thus valuable new types of diphosphorus compounds with mixed functionality can be produced.

In continuing our study of the chemistry of 7-PNB derivatives,[3] we have subjected the phosphinous chlorides to reaction with the oxygen nucleophiles MeO^-, MeOH, and H_2O, and have obtained new types of difunctional compounds with the phosphole dimer framework. Of particular interest in this study is the stereochemistry of the substitution reactions occurring at the 7-PNB position. The reaction with PhMgBr[2] had previously been found to give a product with complete retention of configuration, as did chlorine–bromine exchange,[2] and the reaction with amines gave products with retention predominating.[1] Since little is known about the stereochemistry of displacements of phosphinous chlorides, it became a goal of the present study to determine if displacements at 7-PNB phosphorus in general proceeded with retention. This study is greatly expedited by the fortunate result (also of stereochemical importance) that the initial synthesis of the 7-PNB phosphinous chlorides (**1**) and (**2**) gave exclusively a single (*anti*) isomer. Studies with other cyclic phosphinous chlorides [(**5**)[4,5] and (**6**)[6]] have had to employ *syn*, *anti* mixtures, which makes the interpretations more complicated. The 7-PNB system also offers the valuable feature of having *syn*, *anti* isomers with very different ^{31}P n.m.r. shifts and coupling constants to ^{1}H, ^{13}C, and even to ^{31}P, making product stereochemical analysis easy even when product isolation is not practical.

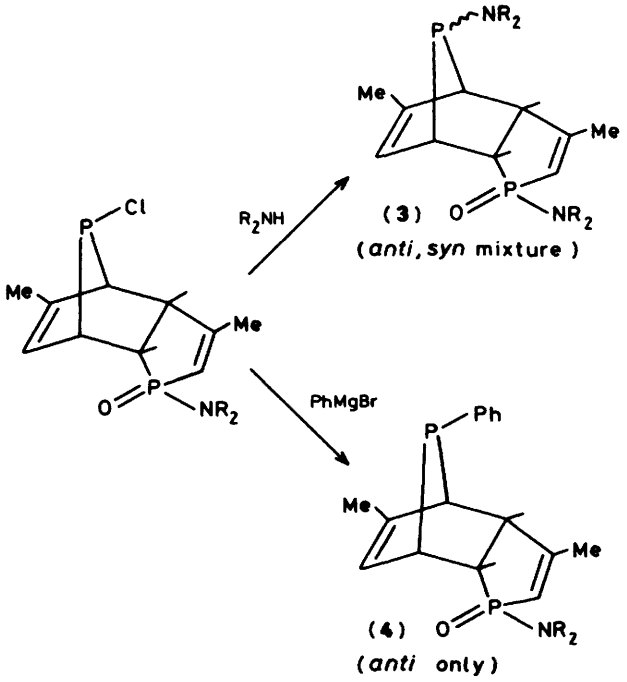
It was recognized at the outset that the establishment of the generality of product formation with retention (complete or predominant) in displacements of 7-PNB chlorides would be a new and perhaps surprising result relative to the literature on phosphinous chlorides. Thus, with the phosphetane system (**5**), inversion predominates,[4,5] although product isomerisation caused by the medium can then follow.[5] With the 9-phosphabicyclo[4.2.1]nona-2,4,7-triene system (**6**), quite variable results have been obtained.[6] For substitution at P^{III} in general, the picture seems to be developing that the actual substitution step may occur with inversion, but that medium-induced isomerisation processes either with the reactant or product may cause apparent losses of stereoselectivity.[5]

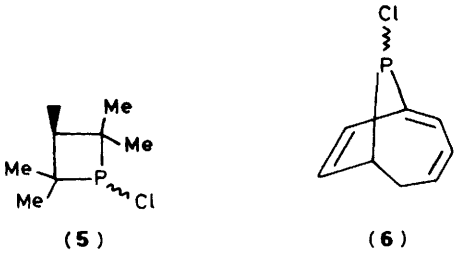


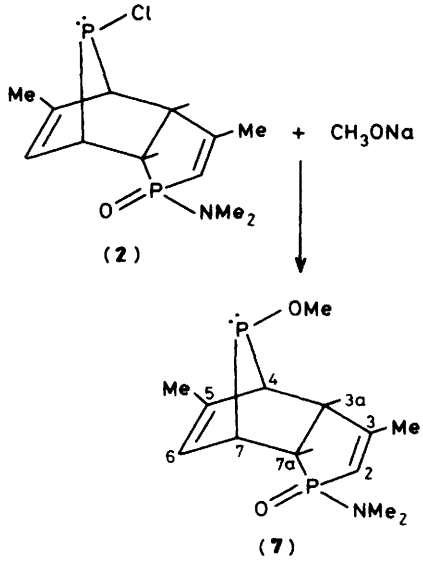
(**1**) R = Et[1]

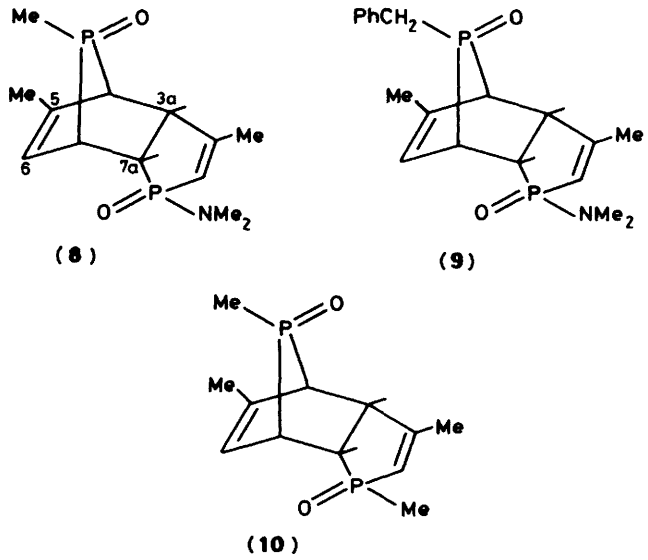
(**2**) R = Me[2]

Reaction with Sodium Methoxide.—Phosphinous chloride (**2**), which was used as the model 7-PNB chloride in all of these studies, reacted cleanly with sodium methoxide in ether–methanol at 25 °C to give a single phosphinite, as determined by ^{31}P n.m.r. analysis. The unaffected phosphinamide group had δ_P +60.9 and the phosphinite group had δ_P +108.1. Just as noted for the phosphinous chlorides (**1**) and (**2**), this value is somewhat upfield of that of a monocyclic phosphinite (*e.g.*, 1-ethoxy-3-methyl-3-phospholene,[7] δ_P +141.4). Of value for









stereochemical analysis is the $^3J_{PP}$ value in P^{III} derivatives with the phosphole dimer framework,[3] which is quite small or not observable with an *anti* substituent (lone pair remote) and quite large with a *syn* substituent (lone pair close). The product from (**2**) ($^3J_{PP}$ = 0) had $^3J_{PP}$ = 7.3 Hz and the *anti* structure (**7**) was indicated.

This assignment was confirmed by the ^{13}C n.m.r. spectrum (Table), employing first the stereospecificity in $^2J_{PC}$ for P^{III} functions. The orientation of the lone pair influences the magnitude of $^2J_{PC}$ in phosphole dimers,[3] causing the isomer with *anti*-substitution to have small values for the fusion carbons and large values for the sp^2 carbons. For (**7**), the *anti* structure must be present, since the fusion carbons had small coupling (C-3a, 5.0 Hz; C-7a, 2.2 Hz) and the sp^2 carbon had large values (C-5, 23.1 Hz; C-6, 20.9 Hz). A second ^{13}C n.m.r. effect in phosphole dimers with a P^{III} function is a similar influence on $^3J_{PC}$; the signal for C-3 would be expected to be of small size because of its remoteness to the lone pair,[3] and indeed it displayed no observable coupling.

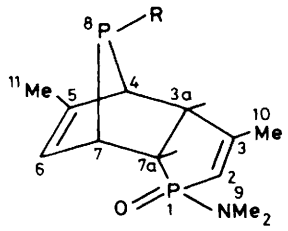
Phosphinite (**7**) was sensitive to oxygen and moisture, and it could not be isolated in a form suitable for elemental analysis. Instead, it was identified by high-resolution mass spectral analysis, which gave the correct *m/z* value for M^+.

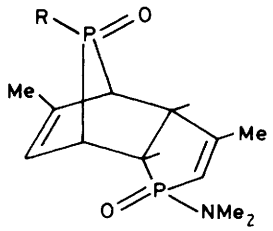
The phosphinite was further characterised by conversion into phosphine oxides in Arbusov reactions with methyl iodide and benzyl bromide at room temperature. The products [(**8**) and (**9**), respectively] were identified by high-resolution mass spectrometry, and in the case of (**8**) by elemental analysis. The ^{31}P n.m.r. spectra showed that a single isomer had been formed in each case, and since the initial step in the Arbusov reaction[8] is the nucleophilic displacement of halogen, structures (**8**) and (**9**) may be written with *syn* alkyl groups. ^{31}P N.m.r. spectra are not useful in the case of 7-PNB phosphine oxides for stereoisomer assignment; for both *syn* and *anti* isomers, there is significant deshielding of the 7-PNB phosphorus,[9] and the values for the phosphine oxide group in (**8**) (+88.4) and (**9**) (+90.2) display this effect. However, the ^{13}C n.m.r. spectra contain a feature which confirms the stereochemical assignment (and indirectly that of the starting phosphinite); the $^2J_{PC}$ value in 7-PNB derivatives is sensitive to the orientation of the P substituents.[9] The $^2J_{PC}$ values for (**8**) and (**9**) (shown in the Table) compare well with values for a phosphole oxide dimer of known structure [(**10**), J_{PC-3a} 12.3, J_{PC-7a} 11.1, J_{PC-5} 11.7, and J_{PC-6} 9.2 Hz].

The *anti* isomer of (**10**) has quite different values (*e.g.*, 20.1 Hz for C-3a; 4.4 Hz for C-5). An attempted Arbusov reaction of ethyl bromide was without effect on phosphinite (**7**); on refluxing (**7**) with isopropyl iodide, Arbusov rearrangement to (**8**) was the major path followed.

The thermal stability of (**7**) was examined by heating a sample in toluene at 110 °C for 5 days. The ^{31}P n.m.r. spectrum showed that only a few percent of a new species (**12**) was

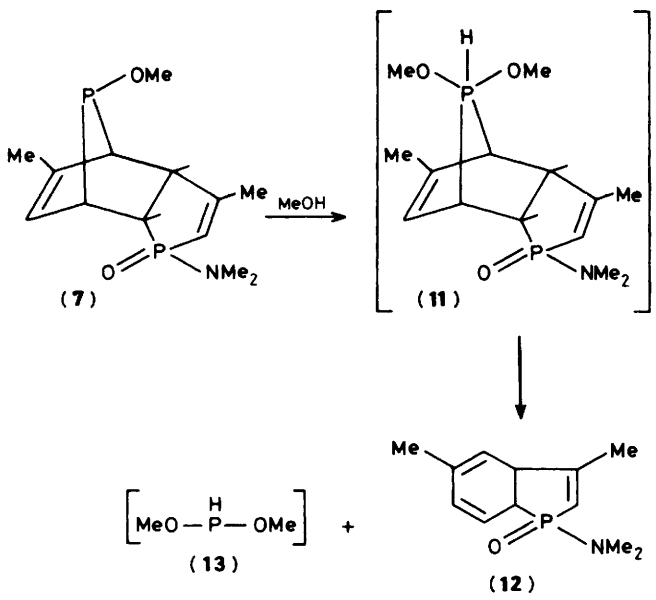
Table. ^{13}C N.m.r. spectral data[a]

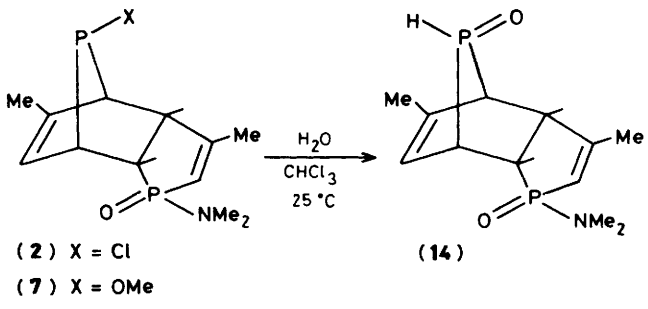




	(7) R = O^{12}Me			(8) R = ^{12}Me			(9) R = $^{12}CH_2Ph$[b]			(14) R = H		
Carbon	δ	J_{C-P_1}	J_{C-P_8}	δ	J_{C-P_1}	J_{C-P_8}	δ	J_{C-P_1}	J_{C-P_8}	δ	J_{C-P_1}	J_{C-P_8}
2	120.4	115.4	*c*	122.8	118.7	4.4	121.9	118.7	4.4	122.8	115.9	8.2
3	161.4	27.5	*c*	160.4	27.5	9.9	159.7	27.5	8.8	160.1	26.4	9.9
3a	51.2	17.0	5.0	50.6	16.5	12.1	49.8	16.5	12.1	50.4	16.5	14.3
4	53.4	*c*	17.6	48.1	*c*	63.7	46.1	*c*	60.4	47.8	2.2	61.5
5	135.2	*c*	23.1	135.9	*c*	12.1	134.7	*c*	12.1	134.0	*c*	15.4
6	123.3	5.5	20.9	124.7	4.4	8.8	123.8	4.4	8.8	122.4	5.5	12.1
7	43.8	4.4	17.6	42.5	2.2	60.4	40.7	*c*	57.1	41.9	*c*	57.1
7a	37.4	89.0	2.2	35.8	91.2	9.9	34.7	90.1	9.9	35.3	89.0	12.1
9	34.9	3.3	*c*	35.0	3.3	*c*	34.1	3.3	*c*	35.2	3.3	*c*
10	18.8[d]			19.2	18.7	*c*	18.4	18.7		19.4	17.6	*c*
11	18.8[d]			19.1	*c*	3.3	18.3	*c*	3.3	19.5		2.2
12	54.4	*c*	19.8	6.4	*c*	63.7	27.9	*c*	56.0			

[a] $CDCl_3$ solutions; J_{PC} given in Hz. [b] *ipso*-C, 131.6 (8.8 Hz); *ortho*-C, 127.8 (11.0 Hz); *meta*-C, 127.7 (3.3 Hz); *para*-C, 125.7 (3.3 Hz). [c] No coupling observed. [d] Signals overlapped.



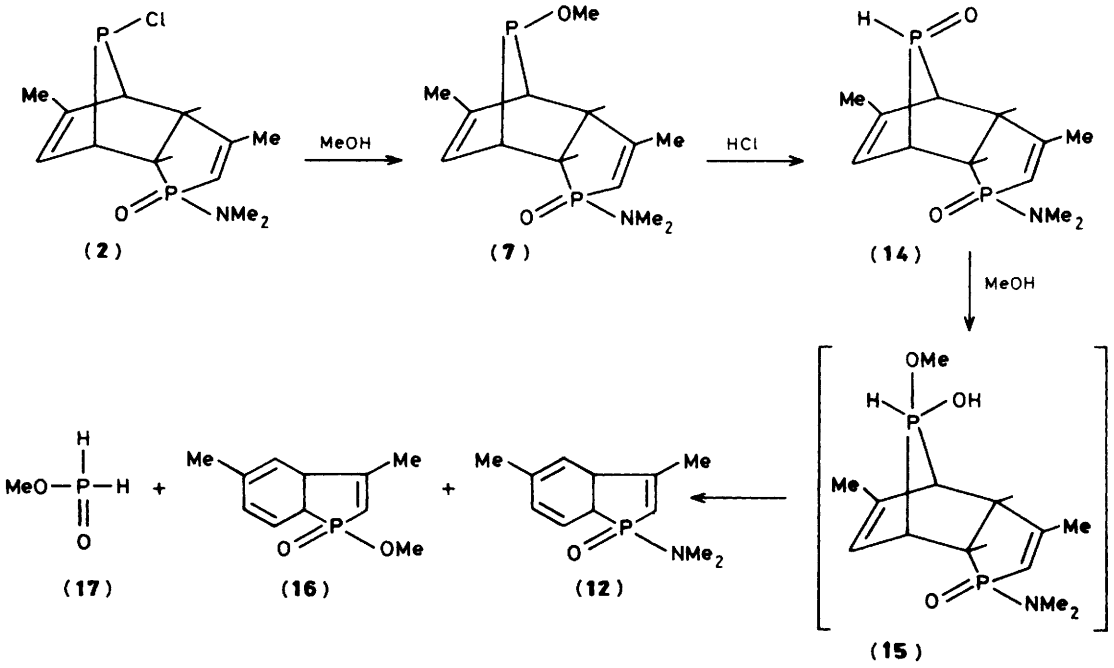


formed. This product (δ_P +68.1) resulted from the elimination of the P bridge. The possibility that the decomposition could be provoked by forming a P^V adduct with 3,4-dimethylbutadiene, as has been found for 7-PNB phosphines,[10] was explored, but there was no observable effect at 110 °C. At 160 °C in mesitylene, however, extensive (91%) decomposition to the dihydrophosphindole (**12**) took place after 3 days. Phosphinite (**7**) was quite unstable when heated in methanol; after 1 day, complete loss of the P bridge occurred. An intermediate (**11**) such as that proposed for the related reaction occurring between tertiary 7-PNB phosphines and methanol[11,12] may be involved. The identity of the ejected fragment [shown as (**13**)] has not been confirmed, however.

Dihydrophosphindole derivatives are common products in degradations of structures with the phosphole dimer framework, and the structure of (**12**) was easily established by mass and n.m.r. spectral techniques.

Phosphinite (**7**) was readily hydrolysed by water, giving the secondary phosphine oxide (**14**) as the main product. This compound was also formed by the hydrolysis of chloride (**2**), and its characterisation is described in the next section. The hydrolysis reaction of (**7**) is of stereochemical significance, since just as in the displacement of Cl by OMe, the displacement of OMe by attack of water occurs with complete retention.

Reaction of Phosphinous Chloride (**2**) *with Water.*—Phosphinous chloride (**2**) underwent hydrolysis on exposure to a water–chloroform medium for 10 h at room temperature. The secondary phosphine oxide (**14**) was the only product detected by ^{31}P n.m.r. analysis, and was isolated in 71% yield. Its exact mass value and ^{31}P n.m.r. spectrum confirmed its structure. The ^{31}P n.m.r. spectrum consisted of two doublets (δ +62.2 and +57.42, $^3J_{PP}$ 39.1 Hz). When run with ^1H-coupling, the spectrum showed the upfield signal as a doublet of doublets with $^1J_{PH}$ 510 Hz. The stereochemistry at the bridging phosphorus was determined from the magnitude of the values of two-bond ^{13}C–^{31}P couplings associated with P-8, which were consistent with



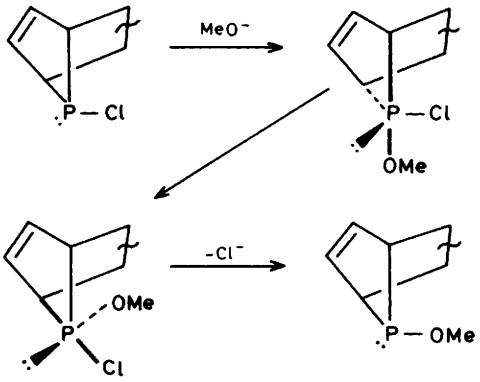
those for tertiary phosphine oxides with an *anti* oxygen (see Table).

As noted above, the same secondary phosphine oxide was formed as the single product on hydrolysis of phosphinite (**7**) under similar conditions. Both displacement reactions therefore occur to give a product with complete retention of configuration.

Reaction with Methanol.—The displacement of chlorine from phosphinous chloride (**1**) at room temperature by methanol, in the absence of base, provided (**7**) as the only phosphinite. There was also formed some of the secondary phosphine oxide (**14**) from the attack on the ester by the hydrogen chloride released in the reaction. When the reaction was conducted in refluxing methanol, however, loss of the bridging phosphorus was extensive and dihydrophosphindole oxides (**12**) and (**16**) (from methanolysis of the remaining phosphinamide group) were the major products. Also, a ^{31}P n.m.r. signal at δ +18.5 was present in the reaction product, and from the appearance of the signal on proton-coupling, it was assigned to methyl hypophosphite (**17**). Thus, the chemical shift matched that reported by Gallagher and Honegger;[13] the presence of two P–H bonds was evident from the splitting of the signal to a triplet with the expected large $^{1}J_{PH}$ value (570 Hz). The substance accounts for the phosphorus that is ejected in the formation of the dihydrophosphindole oxide, and suggests that the loss of the fragment probably occurs by attack of methanol on the secondary phosphine oxide (**14**) to form the P^{V} adduct (**15**) which undergoes retrocycloaddition.

In one experiment, the methanolysis reaction was interrupted after only about 25% of (**2**) had reacted (1.5 h). The only phosphinite present was (**7**) (20% of ^{31}P n.m.r. signals), accompanied by a small amount (5%) of secondary phosphine oxide (**14**). None of the *syn* phosphinite was present, a result that suggests that the displacement occurs directly with retention of configuration. The point is considered further in the next section.

Stereochemistry of Chloride Displacement from Phosphinous Chloride (**2**).—The mechanism of nucleophilic substitution on P^{III} compounds has not been extensively studied in the past but



Scheme.

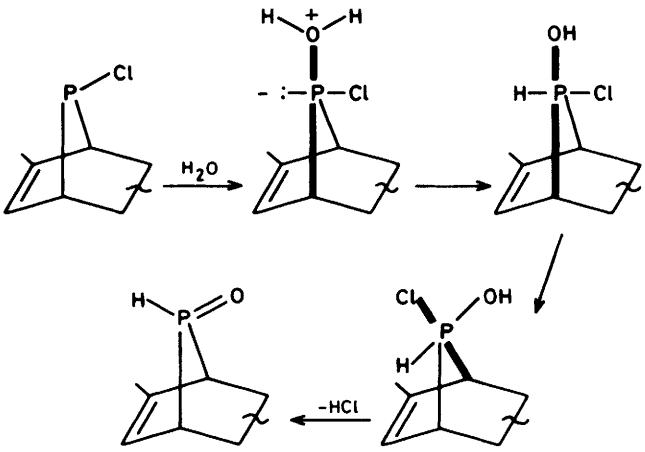
it has recently become a subject of interest.[5,14] It is convenient to picture such reactions as proceeding through an intermediate that can be described as a pseudo-pentaco-ordinated phosphoranide ion,[15] with the lone electron pair occupying an equatorial position of the trigonal bipyramid (TBP) to minimize electronic repulsions. In a study on substitutions of trimethyl phosphite in the gas phase, stable phosphoranide species were indeed observed.[14] If the other principles[15] concerning TBP of true P^{V} species are applicable to phosphoranide ions, then angle-constrained rings would occupy apical-equatorial positions, and the attacking nucleophile would adopt an apical position. These requirements place the potential leaving group in an equatorial position; for it to appear in the apical position required for departure, a polytopal isomerisation (Berry pseudorotation or Turnstile Rotation) is necessary, and this then would result in a final P^{III} product with retention of the original configuration of phosphorus.[15] This is precisely the result we have obtained in all of the nucleophilic substitutions with phosphinous chloride (**2**); in reaction with NaOMe, MeOH, H_2O, PhMgBr, and Br^-, the *anti*-chlorine was displaced with complete *retention*, while secondary amines gave predominantly retention.[1] The hydrolysis of *anti*-phosphinite (**7**) also was stereospecific and gave the *anti*-secondary

phosphine oxide (**14**). A stereochemical sequence such as that shown in the Scheme for methoxide attack on (**2**) could account for these results.

However, another strained cyclic phosphinous chloride, 1-chloro-2,2,3,4,4-pentamethylphosphetane as a mixture of diastereoisomers, has been shown[4] to react with NaOMe and amines with *inversion*, and this was confirmed in a later study.[5] This result has been explained by assuming that the ring adopts the diequatorial disposition in the phosphoranide intermediate.[4] The angle between diequatorial substituents is probably smaller (perhaps 100—105 °C) in a phosphoranide than in a true P^V form,[16] and the barrier to a ring assuming these positions is not as large. It may be that the rigidity of the 7-phosphanorbornene system is so great that it does not allow the angle expansion required for diequatorial positioning; consequently this reaction pathway is disfavoured relative to the retention pathway. However, another explanation for the divergent results needs consideration; the 7-PNB chloride may react with inversion but the *syn* product undergoes isomerisation to *anti* in the reaction medium. However, it seems most unlikely that the isomerisation would be complete, and leave no detectable trace of the *syn* isomer. This is particularly unlikely for the tertiary phosphine resulting from attack of the phenyl Grignard reagent on phosphinous chloride (**2**), since *syn* phosphines in the 7-PNB system are well known and configurationally stable. Thus, phosphole dimers with *syn*-phenyl substitution are quite stable at room temperature in the presence of substances such as benzene, pyridine, dioxane, and alcohols. Only on heating for several h in alcohols or aqueous dioxane does *syn* to *anti* isomerisation take place.[11,12] There is no reason to expect the *syn* isomer corresponding to phosphine (**4**), if formed initially, to have such greatly increased tendencies towards isomerisation that this process can proceed to completion during the reaction. In the case of methanol attack, an experiment was specifically performed to search for the *syn* isomer; the reaction was stopped when only 25% complete, and the mixture examined immediately by ^{31}P n.m.r. Not a trace of *syn* product could be detected. Retention is complete also in the hydrolysis reaction of phosphinous chloride (**2**), but this reaction requires consideration of another type. Here the final product is a P^{IV} compound, the secondary phosphine oxide (**14**). It is this structure which would have to undergo *syn* to *anti* isomerisation, and while a possible mechanism may exist for this (formation and collapse of a P^V intermediate), again it is doubtful if this process would leave no trace of a *syn* compound, especially since it is known[2] that some tertiary phosphine oxides in the 7-PNB series actually rearrange in the opposite way (*anti* to *syn*). The hydrolysis of phosphinous chloride (**2**) is of interest in another sense; the initially formed phosphoranide ion is probably quenched by a proton transfer, giving a true P^V form which is responsible for the establishment of the stereochemistry of the product.

Similar events should occur in aminolysis reactions; here some inverted product develops, suggesting that, as proposed for the chlorophosphetane, other isomerisation processes may be involved. This point is to be considered further in studies on aminolysis reactions now in progress (with J. Szewczyk).

The tentative conclusion is reached, therefore, that the *anti*-7-chloro-7-phosphanorbornene derivative (**2**) reacts with nucleophiles according to the predictions for a phosphoranide ion intermediate that obeys the rules so well established for true P^V intermediates. It is the only phosphinous chloride that gives stereochemical retention on nucleophilic attack, and this is attributed to adherence to the rule that a strained ring prefers the apical-equatorial disposition in a trigonal bipyramid. The *anti*-7-PNB system may well serve as a useful model in other studies of stereochemistry and mechanism for P^{III} derivatives. Regrettably, we have had no success so far in attempts to prepare the *syn* chloro isomer of (**2**), so as to explore the stereochemical consequences of this structure and the stability of species such as the *syn* isomer of phosphinite (**7**).



Experimental

General.—Proton n.m.r. spectra were obtained on an IBM NR-80 spectrometer at 80 MHz, using $SiMe_4$ (TMS) as internal standard. Phosphorus-31 spectra (FT) were obtained on a JEOL FX-90Q spectrometer at 36.2 MHz, using H_3PO_4 as external standard, with internal deuterium lock. Positive shifts are downfield of the reference. Carbon-13 spectra (FT) were obtained on a JEOL FX-90Q spectrometer at 22.5 MHz, using TMS as internal standard. Broad-band proton-noise-decoupling was employed on all carbon-13 as phosphorus-31 n.m.r. spectra. M.p.s. were taken on a Mel-Temp apparatus and are corrected. Combustion analysis were performed by MHW Laboratories, Phoenix.

Reaction of Phosphinous Chloride (**2**) *with Sodium Methoxide.*—The mixture (under nitrogen) from the addition of sodium methoxide (0.182 g, 3.37 mmol) in dry methanol (10 ml) to phosphinous chloride (**2**) (0.80 g, 2.76 mmol) in dry ether (120 ml) was stirred at room temperature for 5 h. Solids were removed by filtration, and the liquid was evaporated under reduced pressure to give a partly crystalline residue (0.8 g). By ^{31}P n.m.r. analysis, the product (**7**) was of 98% purity. Its sensitivity to water and oxygen required its use in other reactions without delay; δ_P +60.9 and +108.1 ($^3J_{PP}$ 7.3 Hz); ^{13}C n.m.r., Table [Found: *m/z*, 285.1047 (M^+). $C_{13}H_{21}NO_2P_2$ requires *M*, 285.1048]; δ_H 1.7 and 1.93 (both s, C-Me), 2.61 (d, J_{PH} 8 Hz, 6 H), 2.87 (m, 4 H partly overlapped), 3.49 (d, J_{PH} 10 Hz, OMe), 5.4 (d, J_{PH} 20 Hz, olef. H), and 5.82 (s, olef. H).

Reaction of Phosphinous Chloride (**2**) *with Water.*—A solution of 0.30 g (1.04 mmol) of (**2**) (0.30 g, 1.04 mmol) in chloroform (20 ml) was stirred with water (20 ml) for 10 h under nitrogen. The organic layer was dried ($MgSO_4$) and evaporated to give a semi-solid residue (0.2 g, 71%), which by ^{31}P n.m.r. analysis consisted solely of the secondary phosphine oxide (**14**). Attempts to purify the product on a silica gel column (chloroform–methanol, 97:3) failed to give a crystalline sample, although it showed no impurities by n.m.r. analyses; δ_P +57.4 and +62.2 ($^3J_{PP}$ 39.1 Hz, $^1J_{PH}$ 510 Hz); δ_H 1.79 and 1.99 (s, Me), 3.2 (m, 4 H), 5.78 (m, 2 H, olef. H), and 6.14 (d, $^1J_{PH}$ 508 Hz, PH); ^{13}C n.m.r., Table [Found: *m/z*, 271.0894 (M^+). $C_{12}H_{13}NO_2P_2$ requires *M*, 271.0892].

Reaction of Phosphinous Chloride (**2**) *with Methanol.*—A solution of phosphinous chloride (**2**) (0.05 g, 0.173 mmol) in 1:1 methanol–chloroform (2 ml) was sealed in an n.m.r. tube under nitrogen. After 30 h at room temperature, ^{31}P n.m.r. analysis showed that all of (**2**) had reacted, and the product consisted of 80% of phosphinite (**7**) and 20% of secondary phosphine oxide (**14**). In a similar experiment, the ^{31}P n.m.r. analysis was performed after only 1.5 h, showing 75% of unchanged (**7**), 20% of phosphinite (**7**), and 5% of phosphine oxide (**14**). No *syn* isomers were detected.

The reaction was also conducted in methanol [40 ml, containing 0.7 g of (**2**)] at reflux for 3 days. By ^{31}P n.m.r. analysis of a concentrated sample, it was found that no (**2**) remained, and that the products were phosphinite (**7**) and dihydrophosphindole derivatives (**12**) and (**16**) (ratio 9:27:64). The fragmentation product methyl hypophosphite (**17**) was also present.

The major product (**16**) (0.15 g, 90%) was isolated by chromatography on silica gel (chloroform–methanol, 97:3); δ_P +74.1; δ_C 19.2 (*J* 19.8 Hz, 3-Me), 21.3 (5-Me), 38.0 (*J* 85.7, C-7a), 43.8 (*J* 13.2, C-3a), 52.1 (*J* 6.6, OMe), 116.3 (*J* 3.3, C-7), 117.5 (*J* 125.3, C-2), 120.0 (*J* 12.1, C-4 or C-6), 126.5 (*J* 11.0, C-4 or C-6), 129.6 (*J* 4.4, C-5), and 165.7 (*J* 37.4, C-3); δ_H 1.76 and 2.06 (s, C-Me), 3.7 (d, $^3J_{PH}$ 11 Hz, OMe), and 5.7 (m, 4 H, olef. H) (Found: *m/z M*, 210.0797 (M^+). $C_{11}H_{15}O_2P$ requires 210.0810).

Methyl hypophosphite was identified in the reaction mixture by ^{31}P n.m.r.: δ_P +18.5 split to a triplet ($^1J_{PH}$ 570.1 Hz) of quartets ($^3J_{PH}$ 12.2 Hz) (lit.,[13] δ_P +19.2, $^1J_{PH}$ 569 Hz, $^3J_{PH}$ 13 Hz). Characterisation of dihydrophosphindole (**12**) is presented in the section on the methanolysis of (**7**) (*vide infra*).

Hydrolysis of Phosphinite (**7**).—A solution of phosphinite (**7**) (0.13 g, 0.46 mmol) in degassed chloroform (5 ml) was mixed with water (0.5 ml) at 0 °C in a nitrogen atmosphere. The mixture was then stirred for 10 h at room temperature. Vacuum evaporation left a residue which consisted only of phosphine oxide (**14**) by ^{31}P n.m.r. analysis.

Reaction of Phosphinite (**7**) *with Methyl Iodide.*—A solution of phosphinite (**7**) (0.8 g, 2.81 mmol) in dry, degassed benzene (20 ml) was treated with methyl iodide (4 ml, 64.2 mmol), and stirred at room temperature under nitrogen for 24 h. Vacuum evaporation of liquids left a semi-solid mass which was purified by chromatography on silica gel (chloroform–methanol, 97:3) to give phosphine oxide (**8**) (0.3 g, 37%) as a white crystalline solid. After two recrystallisations from pentane–chloroform (95:5), the m.p. was 159—160 °C; δ_P +63.2 and +88.4, $^3J_{PP}$ 36.6 Hz; ^{13}C n.m.r., Table; δ_H 1.52 (d, $^2J_{PH}$ 12 Hz, P–Me), 1.73 and 1.92 (both s, C–Me), 2.57 (d, $^3J_{PH}$ 10 Hz, NMe_2), 2.89 (m, 4 H), and 5.7 (m, 2 H, olef. H) [Found: C, 53.1; H, 7.6. $C_{13}H_{21}NO_2P_2 \cdot 0.5H_2O$ requires C, 53.09; H, 7.48%. Found: *m/z*, 285.1049 (M^+), $C_{13}H_{21}NO_2P_2$ requires *M*, 285.1048].

Reaction of Phosphinite (**7**) *with Benzyl Bromide.*—Phosphinite (**7**) (0.27 g, 0.95 mmol) was treated with benzyl bromide (1.63 ml, 2.21 mmol) in benzene (7 ml) for 4 days at room temperature. The product (**9**) was isolated and purified as performed for (**8**), yielding the phosphine oxide (**9**) (0.2 g, 58%), m.p. 96—97 °C; δ_P +62.9 and +90.2, $^3J_{PP}$ 36.6 Hz; ^{13}C n.m.r., Table; δ_H 1.78 and 1.95 (both s, C–Me), 2.58 (d, $^3J_{PH}$ 11 Hz, NMe_2), 3.33 (6 H, m with doublet of $^2J_{PH}$ 13 Hz for PhCH_2 at δ 3.25), 5.82 (m, 2 H, olef. H), and 7.28 (s, ArH) (Found: *m/z*, 361.1367 (M^+); $C_{19}H_{25}NO_2P_2$ requires *M*, 361.1363).

Reaction of Phosphinite (**7**) *with Isopropyl Iodide.*—Refluxing a sample of phosphinite (**7**) with a large excess of isopropyl iodide for 2 days gave as the major product the Arbusov rearrangement product phosphine oxide (**8**) (80%), isolated by column chromatography. The ^{31}P n.m.r. spectrum also contained signals probably attributable to the desired *P*-isopropyl phosphine oxide (20%, δ_P +63.7 and +99.2, $^3J_{PP}$ 36.6 Hz), but this was not isolated or further studied.

Decomposition of Phosphinite (**7**) *with Methanol.*—A solution of phosphinite (**7**) (1.1 g, 3.86 mmol) in methanol (120 ml) was unchanged after one day at room temperature. After 1 day at reflux, no (**7**) remained, and ^{31}P n.m.r. analysis (δ_P +68.1; lit.,[2] δ_P +68.4) showed that the major product was the dihydrophosphindole derivative (**12**). This was isolated (0.5 g, 58%) by silica gel chromatography with chloroform–methanol, 96:4; δ_H 1.76 and 2.05 (both s, C–Me), 2.62 (d, $^3J_{PH}$ 10 Hz, NMe_2), 3.03 (m, 2 H), 5.66 (m, 4 H, olef. H) (Found: *m/z*, 223.1128 (M^+); $C_{12}H_{18}NOP$ requires *M*, 223.1126).

That the decomposition was promoted by methanol was established by testing the thermal stability of (**7**) in other media. In toluene at 110 °C, only slight decomposition was detected after 3 days. The presence of 2,3-dimethylbutadiene in this solution had no effect. However, in mesitylene at 160 °C, about 91% of phosphinite (**7**) was converted into the dihydrophosphindole derivative (**12**) as determined by ^{31}P n.m.r. analysis.

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