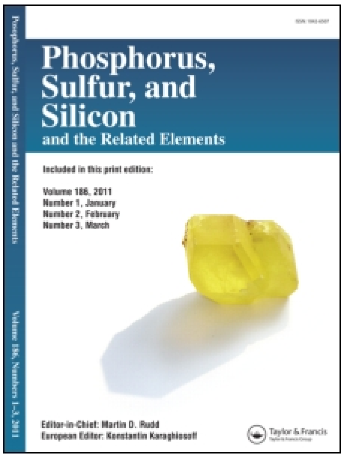

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THERMAL DEGRADATION OF DIMERS OF PHOSPHOLES

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THERMAL DEGRADATION OF DIMERS OF PHOSPHOLES[1]

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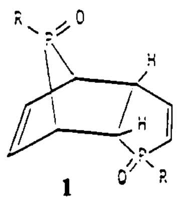
The pathway followed by dimers of P-methylphospholes in their thermal degradation in solution is strongly dependent on the concentration. At low concentrations (around 0.04 M) in *n*-decane or toluene as solvent, decomposition is extensive after 17 h in the range 120–130°C. The major product is the P-methylphosphole from de-dimerization. At concentrations above 1.0 M, decomposition is faster and intermolecular interactions are more important. These interactions dominate over de-dimerization and lead to the loss of the bridging *P* in the 7-phosphanorbornene moiety to yield the *cis*-3a,7a-dihydrophosphindole system. From the dimer of 1,3-dimethylphosphole, isomeric dihydrophosphindoles are formed, which differ in location of the methyl group on the 6-membered ring and in configuration at phosphorus. These seem to result from attack by a phosphine group as a nucleophile on the bridging P, followed by bond rearrangements in the resulting phosphoranide ion. Decomposition was faster in the presence of tri-*n*-butylphosphine, which apparently acted as a catalyst through a similar mechanism. By using appropriate conditions each dihydrophosphindole isomer (1,3,5- or 1,3,7-trimethyl) could be made to predominate and this allowed their isolation. Characterization of the isomers and of some derivatives by ^{31}P, ^{1}H, and ^{13}C NMR techniques was performed. Most of the thermolysis products were highly complex mixtures and many minor products remain unidentified. The dimer of 1-phenyl-3-methyl-phosphole did not decompose to the phosphole, but the product composition was dependent on concentration.

After developing techniques[2] for the deoxygenation of dimers of phosphole oxides (**1**), we initiated a study of the chemistry of the resulting diphosphines (**2**). Among their novel properties is the attack by dienes[3] at a bridging P—CH_3 group in the 7-phosphanorbornene moiety of **2**; this results in the formation of a transient species with pentacoordinate phosphorus, decomposing by retro-cycloaddition. The final products are a 3a,7a-dihydrophosphindole (**3**) and a 3-phospholene (**4**). In the present study, we have examined the thermal stability and pathways for decomposition of the phosphole dimers. Contrary to our expectations, we have not obtained any evidence to support a decomposition pathway involving unimolecular ejection of the bridging P as a phosphinidene (R-P̈:). The decomposition pathway for P-methyl derivatives of **2** is highly dependent on the concentration; in dilute solution, de-dimerization to the phosphole is favored, but in concentrated solution, remarkable intermolecular interactions take place that lead to loss of the bridging unit with and without rearrangement of the molecular framework. The rearrangement that we will describe appears to be without precedent in cyclic phosphine chemistry.



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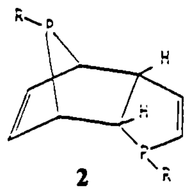

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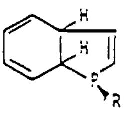

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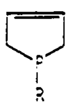

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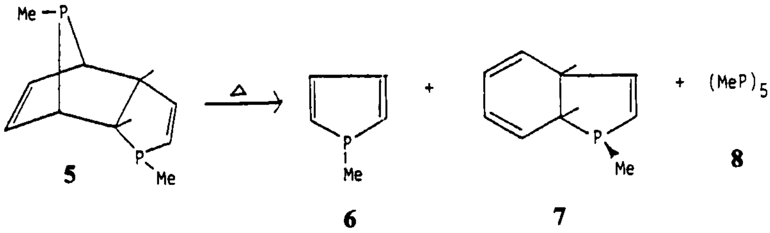
*Author to whom all correspondence should be addressed.

Results of thermal decompositions. 1-methylphosphole dimer. The products of the thermal decomposition of **5** depend heavily on the concentration of the solution. In a very dilute solution (e.g., 0.07 M in *n*-decane), the major product after 17 h at 126 ± 4°C was 1-methylphosphole (**6**), which accounted for 39% of the total recorded ^{31}P NMR signals.[4] While this is the first instance where de-dimerization of a phosphole dimer in solution has been effected, the process is nearly quantitative in the gas phase[5] at about 400°C. The secondary product was dihydrophosphindole **7** (20%), with about 38% of unchanged dimer (**5**). The fate of the ejected P in forming **7** was not revealed. In toluene under the same conditions, the decomposition was less extensive; the product consisted of 76% unchanged **5**, 8% **6**, and 16% **7**. The high volatility of the phosphole relative to other members of the complex mixture allowed its selective removal by the bulb-to-bulb technique on a vacuum line. Its identity was revealed not only by its characteristic ^{31}P NMR shift but also by its behavior on oxidation, which gave as the final product the dimer of the phosphole oxide.

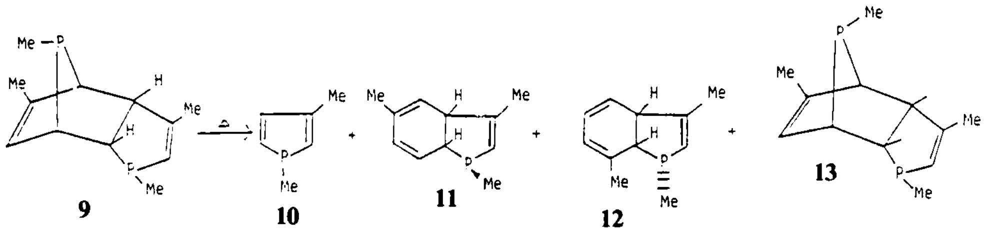


In more concentrated solutions, the product mixtures were much more complicated and degradation of the dimer was more extensive. In 0.3 M *n*-decane (126 ± 4°C, 17 h), no dimer remained; phosphole **6** (13%) and dihydrophosphindole **7** (10%) were minor products relative to $(MeP)_5$ (17%) and an assortment of some 16 other compounds (60% of ^{31}P signals). Similar results were obtained in toluene (5% **5**, 11% **6**, 19% **7**, 17% **8**, and 14 others, 48%).

The de-dimerization of **5** to the phosphole must occur by a retro-[4 + 2] cycloaddition; it is a major pathway for decomposition of **5** in dilute solutions, as well as in the gas phase,[5] because competitive intermolecular interactions are minimized under these conditions. As the concentration is increased, the probability of intermolecular interactions increases, leading to great product complexity.

Another unimolecular decomposition pathway for **5**, retro-cycloaddition to eject methylphosphinidene (CH_3P), does not seem to be followed. In the gas phase the only unimolecular process was de-dimerization. In dilute solution, a small amount of dihydrophosphindole (**7**) does form, but it is more likely (but not confirmed) to be the result of the intermolecular interactions, the nature of which will be discussed subsequently.

1,3-dimethylphosphole dimer. Unimolecular de-dimerization was again favored in dilute solution for dimer (**9**); in 0.04 M *n*-decane (126 ± 1°C, 17 h), a relatively simple mixture consisting of 47% unreacted **9**, 20% of phosphole **10** (isolated as for **6**) and 13% of dihydrophosphindole **11**. In addition, some inversion at the bridging P of **9** occurred, since the mixture also contained 20% of *anti*-isomer **13**. In the gas phase,[5] de-dimerization of **9** was the only process occurring and as for **5** was virtually complete.



Very different results were obtained in concentrated solutions. In 1.2 M *n*-decane, decomposition of **9** was again nearly complete but the major product (36%) was a dihydrophosphindole (**12**) of isomeric structure relative to **11** (11%). The phosphole content was small (4%); $(MeP)_5$ was present (12%) and at least 11 other compounds were produced (36% total). Similar products were obtained in toluene but the amount of **12** was greater (28% of P). The relative amounts of the dihydrophosphindole isomers could be manipulated by the proper choice of reaction conditions so that either could be formed as the major product and then isolated by distillation. For **11**, this was accomplished in 0.2 M xylene at 126 ± 5°C; distillation gave **11** as the main product in 67% crude yield from dimer **9**. Isomer **12** was the major product when the dimer was heated without solvent at the same temperature. The yield after distillation was 54%.

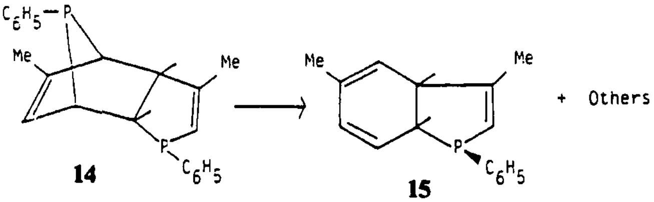
The nature of the intermolecular reactions leading to dihydrophosphindole formation was revealed through the observation that a simple trialkylphosphine (n-Bu_3P) catalyzed the process. When 15 mole % of n-Bu_3P relative to dimer **9** was present, decomposition was complete in a 0.08 M *n*-decane solution at 122 ± 4°C (17 h) whereas the mixture contained 32% of unreacted **9** in the absence of the added phosphine. The major product in the phosphine-catalyzed process was dihydrophosphindole (**11**) (29%, with 7% of phosphole **10** and many other compounds). The complexity of the product mixtures was reduced somewhat when a 7–8 fold excess of n-Bu_3P was present but the unidentified compounds (seven) amounted to 63% of the total.

When the n-Bu_3P catalysis of the reaction was performed at a lower temperature (83 ± 1°C) where dimer **9** has been found to be relatively stable (only 6% decomposition), a new result was obtained; most of **9** was converted to its *anti*-isomer (**13**), (69%, with 14% **9**, 13% **11**, 4% others).

At the completion of these processes, the ^{31}P NMR signal for n-Bu_3P was always very strong; that no new signals were observed indicated that the n-Bu_3P acted only as a catalyst and was not converted to other products.

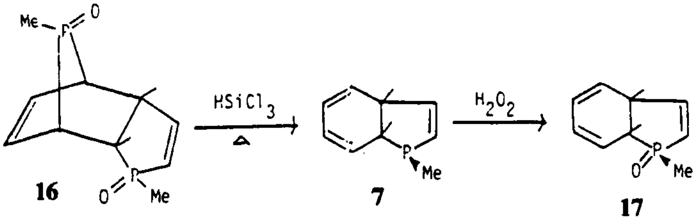
1-Phenyl-3-methylphosphole dimer. P-Phenylphosphole dimers have not been emphasized in this work. In an earlier study,[6] the thermal decomposition of neat 1-phenylphosphole dimer was reported to provide 1-phenyl-3a,7a-dihydrophosphindole on a preparative scale in 50% yield. We have now subjected 1-phenyl-3-methylphosphole dimer (**14**) to solution decomposition studies, and found that it too gives a product distribution that is quite dependent on concentration. Thus, in 0.04 M toluene (126 ± 3°C, 17 h), the major product was the dihydrophosphindole **15** (27%); very little phosphole (2%) was formed in contrast to the behavior of the P-methyl compound,[7] and significant amounts of $(C_6H_5P)_4$ (9%) and $(C_6H_5P)_5$ (6%)

were produced, along with 13 others (47%). In 0.9 M solution, the dihydrophosphindole (**15**) only accounted for 11% of the products, and there was a definite increase in unidentified substances (78%). Two of these were of similar concentration to **15**, and were close to it in ^{31}P NMR shift (δ + 28.3, 13%; δ + 26.5, 11%; cf. **15**, δ + 25.6); it is probable that one is the 7-methyl isomer of **15**, but no evidence bears on this point since the mixture was too complicated to separate. In another departure from the pattern established for the P-methyl compounds, the rate of the decomposition of dimer **14** was not greatly different at the two concentrations. The possibility exists that unimolecular C_6H_5P ejection may occur in the dilute solutions, and this may be the source of the $(C_6H_5P)_{4-5}$ species. The decomposition process was considered too complicated to warrant further consideration of this possibility.



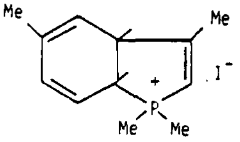
14 **15**

Identification of dihydrophosphindoles. 1-Methyl-*cis*-3a,7a-dihydrophosphindole (**7**) had been previously isolated from the reaction of 1-methylphosphole oxide dimer (**16**) with $HSiCl_3$.[2] The reported ^{13}C and ^{31}P NMR spectra were reproduced for this product when formed by decomposition of **5**. These data are included in Table I for comparison purposes.



16 **7** **17**

The ^{13}C and ^{31}P NMR data[2] for 1,3,5-trimethyl-*cis*-3a,7a-dihydrophosphindole (**11**) are also given in Table I. The former spectrum has now been obtained at two magnetic fields and with the aid of the INEPT technique to insure correct recognition of doublets and of carbon types. Spectral data for the methiodide (**18**)[2] agreed with published values.[2] From oxide **19** was obtained the aromatized derivative **20** on dehydrogenation with Pd-C in cumene.



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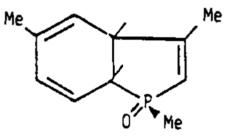

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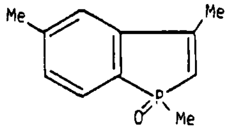

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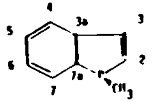
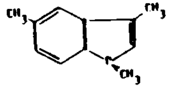
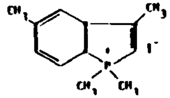
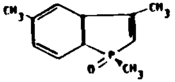
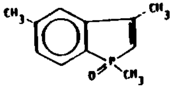
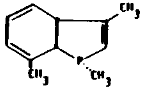
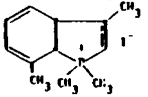
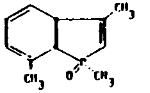
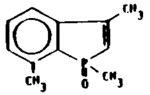
TABLE I

^{31}P and ^{13}C NMR data for phosphindole derivatives

Compound		^{31}P NMR[b]	^{13}C NMR[c]											
			C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	C-3 CH_3	C-5 CH_3	C-7 CH_3	P-CH_3
	(7)[d,e]	+11.7	132.5 (18.6)	141.2 (4.9)	45.0 (2.0)	124.6 (4.9)	122.3 (2.9)	121.1 (11.7)	128.0 (17.6)	42.3 (5.9)				14.4 (23.4)
	(11)[f]	+11.9	128.0 (16.5)	151.2 (5.5)	48.2 (s)	118.0 (4.4)	129.9 (3.3)	125.0[g] (11.0)	125.3 (14.3)	43.7 (4.4)	18.0 (3.3)	21.6 (s)		14.6 (24.2)
	(18)[f,h]	+59.5	109.2 (80.2)	172.3 (25.3)	47.7 (6.6)	118.2[g] (8.8)	129.2 (s)	129.1 (17.6)	117.0[g] (3.3)	33.7 (50.5)	19.0 (16.5)	20.9 (s)		9.7(50.5) 8.5(50.5)
	(19)[c]	+65.5	119.3 (96.7)	161.8 (28.6)	43.8 (9.9)	115.4 (6.6)	129.4 (4.8)	126.5 (9.9)	119.5 (8.8)	37.4 (65.9)	17.7 (17.6)	20.8 (s)		16.3 (68.1)
	(20)[e,f]	+42.0	121.9 (100.0)	153.2 (14.3)	142.6 (28.6)	127.4[g] (9.9)	143.6 (2.2)	129.5[g] (11.0)	122.8 (11.0)	131.6 (39.6)	16.4 (16.5)	21.8 (s)		15.0 (71.4)
	(12)[e,f]	+6.7	125.5 (15.6)	155.6 (2.0)	50.7 (7.8)	122.8 (4.0)	122.3 (2.0)	118.7 (4.9)	134.1 (2.0)	44.2 (8.8)	18.3 (3.9)		23.3 (4.9)	10.3 (23.4)
	(21)[e,f,h]	+57.4	110.0 (81.3)	172.3 (24.2)	49.1 (6.6)	122.5[i] (5.5)	120.7[i] (2.2)	121.5[i] (7.7)	127.1 (7.7)	39.5 (45.0)	19.3 (15.4)		22.4 (2.2)	10.6(49.4) 8.4(49.4)
	(22)[e,f]	+68.6	122.5 (93.4)	161.0 (28.6)	46.5 (11.0)	123.1 (5.5)	119.7 (2.2)	118.6 (9.9)	131.6 (7.7)	47.8 (59.3)	19.3 (16.5)		23.0 (s)	15.2 (67.1)
	(23)[e,f]	+43.5	121.6 (100.0)	153.1 (14.3)	139.8 (8.8)	119.3 (12.1)	132.6[g] (2.2)	130.6[g] (s)	132.6 (s)	142.5 (28.6)	16.4 (16.5)		19.2 (4.4)	14.2 (70.3)

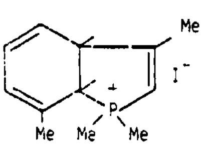
[a] In $CDCl_3$ unless otherwise noted. [b] $\underline{\delta}$ ppm from 85% H_3PO_4; downfield is positive. [c] $\underline{\delta}$ ppm downfield from Me_4Si; J_{PC} (Hz) in parentheses. Recorded at 22.5 MHz. [d] Spectrum published as No. 823 in "13C Nuclear Magnetic Resonance Spectral Data of Heterocyclic Phosphorus Compounds", Thermodynamics Research Center, Texas A and M University, College Stn., Tex., 1983. [e] Couplings confirmed at 15.0 MHz. [f] Assignments to 2°, 3°, and 4° carbons confirmed by INEPT program. [g] Could be reversed. [h] DMSO-d_6 solvent. [i] Assignment uncertain.

The stereochemistry of **11** is important in connection with the structure determination of an isomer (**12**) and is supported by several features. That the P—CH_3 group was *cis* with respect to the protons at 3a and 7a was confirmed from the magnitude of the two-bond ^{31}P—^{13}C coupling constants, which are well known to be large only when the lone pair on phosphorus is close to the coupled carbon and can be zero if remote.[8] In **11**, $^{2}J_{PC\text{-}3a}$ was in fact 0, while $^{2}J_{PC\text{-}7}$ was large (either 11.0 or 14.3, not assigned). Dreiding models show that the stereochemistry of structure **11** provides the proper lone pair disposition to give these couplings. A known effect for the dihydrophosphindole oxides is useful in confirming the *cis* ring fusion. With this fusion, the coupling to C-3 in the 2-phospholene moiety is large, since it is a result of two coupling pathways (^{2}J and ^{3}J) where the ^{3}J value will be large because of the dihedral angle[9] ($\underline{\theta} \sim 0°$) relating P to C-3. With *trans* ring fusion, this angle is closer to the minimum in the Karplus-like plot for $^{3}J_{PC}$ and consequently the sum of ^{2}J and ^{3}J will be smaller. This has been verified[6] with the P-phenyl counterpart of 7, which has $J_{PC\text{-}3} = 29.5$ Hz; the *trans*-fused product is known[10] to have $J_{PC\text{-}3} = 10.3$ Hz. Another ^{13}C effect in these compounds requires comment; the one-bond coupling in the phosphindole oxide (**20**) is much large (100 Hz) for olefinic C-2 than for aromatic C-7a (39.6 Hz). The reason for this difference is not obvious.

The ^{31}P NMR shifts (Table I) for the series were not exceptional. The relatively upfield value found on creating the phosphole oxide moiety in **20** ($\underline{\delta}$ + 42.0) is consistent with that of monocyclic compounds (e.g., 1,2,5-triphenylphosphole oxide, $\underline{\delta}$ + 41.5).[11]

Since the ^{1}H NMR spectrum of dihydrophosphindole (**11**) proved not to be very informative, this measurement (250 MHz) was made on the oxide of the aromatized derivative (**20**). Protons on the benzene ring were easily assigned; the proton on C-4 was readily recognized as it alone would give a singlet ($\underline{\delta}$ 7.17, slightly broadened), while the proton on C-7 was recognized from its pronounced downfield position ($\underline{\delta}$ 7.62) resulting from fixed proximity to the P=0 group[12]. The coupling patterns (see Experimental) for H-6 and H-7 were consistent with these assignments.

Dihydrophosphindole (**12**) was then shown to be isomeric with **11** from the value for M^+ in its mass spectrum. It was also characterized as derivatives **21**, **22**, and **23**.



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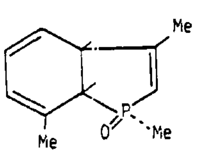

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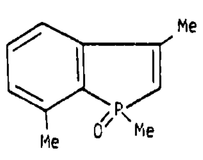

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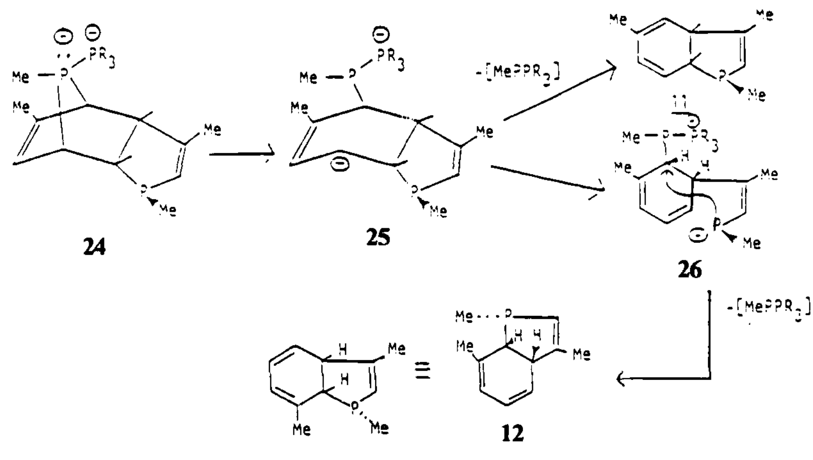
The ^{13}C NMR of **12** had features pointing to location of a methyl at the 7-position. Thus, the methyl carbon was coupled to ^{31}P by 4.9 Hz, consistent with a three-bond (but not a longer) connection. The P—CH_3 signal was noticeably displaced upfield ($\underline{\Delta\delta}$ 4.3 ppm) from **11** suggesting it to be sterically affected by location *cis* to the C-7 methyl. The inverted configuration at P was confirmed by the two-bond coupling constants to C-3a (7.8 Hz) and C-7 (2.0 Hz); these values are reversed from those in **11**, and consistent with the lone pair orientation proposed in **12**. The ^{13}C spectrum of oxide **22** had the expected large coupling for C-3 (28.6 Hz) as required by *cis* ring fusion. The ^{31}P shift for **12** ($\underline{\delta}$ + 6.7) was quite close to that for **11** (δ + 11.9), also consistent with the same ring fusion in both isomers. Conclusive proof of the presence of methyl on C-7 came from the 250 MHz ^{1}H NMR spectrum of phosphindole oxide **23**. The most downfield aromatic proton was found at δ 7.40, compared to δ 7.62 in **11** where P=O deshielding of an *ortho*-CH is present. The downfield signal is assigned to H-5 because of its *para* location to the phosphoryl group.[12] This signal is a triplet from the *ortho* coupling to H-4 and H-6 being of similar magnitude (^3J = 7.0 Hz), showing small splitting (1.1 Hz) from ^{31}P. H-4 and H-6 experience no special deshielding effects and both occur in an overlapping 2 H triplet-like signal at δ 7.18. No other location of the ring methyl could give these results. Finally, the 7-CH_3 protons of **12** are noticeably deshielded (δ 2.63) relative to the 5-CH_3 of **20**(δ 2.42) as a result of their proximity to the phosphoryl group.

3,5-Dimethyl-1-phenyl-3a,7a-dihydrophosphindole (**15**) has been spectrally characterized in previous work,[2] although it has not yet been successfully obtained in pure form.

Mechanism of dihydrophosphindole formation. Since dihydrophosphindole formation from P-methylphosphole dimers is minimal in very dilute solutions or in the gas phase, it is strongly indicated that decomposition of the dimers to this structure depends on intermolecular interactions. There is no evidence for a unimolecular ejection of methylphosphinidene. The catalysis by *n*-Bu_3P provides a clue to the nature of the intermolecular reaction. It is known[13] that 7-phosphanorbornene phosphines have a strong tendency to add nucleophilic species, thus developing a geometry more favorable to the angle imposed on the C—P—C portion (79° in the *anti* isomer of the dimer of 1-phenyl-3-methylphosphole).[14] The bridging P of the dimers may therefore be considered to add a phosphine (either *n*-Bu_3P or another molecule of dimer) and create an adduct (a phosphoranide ion) such as **24**, where a lone pair occupies a site on the trigonal bipyramid. This species could undergo polytopal isomerization (pseudorotation or turnstile) before ejecting the nucleophile and before ring rupture occurs, thus accounting for the *syn* to *anti* inversion noticed at moderate temperatures. The events involving ring rupture are uncertain. One explanation of the process is shown below, and is attractive because a single intermediate (**25**) can account for the two isomers formed, as well as for the stereochemistry of each.



Phosphoranide (**24**) could also form **11** by retro-cycloaddition with elimination of $[MePPR_3]$, a fragment common to the above pathways and which then would decompose. In the presence of dienes[3], which compete for reaction at the bridging P, the intermolecular interaction process is retarded and only the expected dihydrophosphindole (**11**) is formed, by a retro-cycloaddition process of a P(V) adduct formed with the diene. No other mechanism than that shown seems capable of accounting for the apparent relocation of the methyl in **11** to the 7-position in **12**. A weakness in this scheme is that some of the phosphine with the opposite configuration at P found for **12** might have been expected from nucleophilic attack of the phosphide ion in **26** on the P fragment. However, steric interactions may prevent the adoption of the rotameric form needed for isomer formation. Alternative mechanisms that involve methyl migration in **11** to form **12** were ruled out by observing that pure **11** failed to form even a trace of **12** on thermal treatment. Another pathway ruled out involves generation of 1,3-dimethylphosphole which might redimerize by a different route; this phosphole when subjected to the same conditions formed no **12**, and indeed was extensively dimerized to form the usual framework but with the *anti*-7-PNB configuration (**13**). This is the first report of the dimerization of a phosphole by this pathway. The *anti*-dimer (**13**) was much more stable than *syn* (**9**), but at 145°C (0.4 M in xylene) considerable amounts of the isomeric dihydrophosphindoles (**11**) and (**12**) were formed.

When this research program was started, it was anticipated that the 7-phosphanorbornene moiety could well serve as a generator of phosphinidenes, a little-known, highly reactive species for which versatile synthetic methods do not yet exist. However, it is now clear that the thermal degradation of phosphole dimers follows a much more complicated pathway started by intermolecular interactions of P(III) units. This conclusion is similar to that made in the reaction of dienes with the 7-methyl-PNB system; substantial amounts of 1-methyl-3-phospholenes form in this process but result from a direct interaction of the diene with the 7-phospha atom, followed by a retro-cycloaddition. There is no evidence that the 3-phospholenes are formed from a release of methylphosphinidene followed by cycloaddition with the diene. The possibility remains, however, that the 7-PNB system in other compounds may decompose with phosphinidene formation.

The concept of an interaction between neutral P(III) species has been employed by others,[15] but these reports do not include a reaction between tertiary phosphines, as is proposed here. It is the unusual tendency of the bridging P to increase its covalency that allows the event to occur in the present case.

EXPERIMENTAL[16]

Thermolysis of phosphole dimers. Solvents (usually *n*-decane or toluene) were carefully dried and degassed, and used to prepare solutions of known molarity with the phosphole dimers. The reaction vessel was a heavy-walled tube fitted with a Teflon plug operated by a screw cap (Kontes). The vessel was flame-dried and flushed with argon, and then charged with the solution. It was placed in an oil bath at a pre-set temperature, which was maintained for a definite reaction time. Experiments testing the catalytic activity of definite amounts of tri-*n*-butylphosphine were conducted similarly. Product analysis was performed directly on the solutions by ^{31}P NMR measurements, using peak heights as an approximate measure of product ratios. Frequently the solutions contained 10–20 components, most of which were not identified. Significant results of the analyses are provided in the section "Results of Thermal Decompositions". Somewhat different conditions were used in experiments where phospholes or dihydrophosphindoles were to be isolated; these are described in subsequent sections.

Identification of 1-methylphosphole. The mixture obtained after refluxing for 1 h a solution of 0.6 g (3.1 mmol) of phosphole dimer **5** and 6 ml of dry mesitylene (under argon) was placed on a vacuum line and the volatile material transferred to a tube chilled with liquid N_2. About 5–6 ml were collected, leaving a viscous residue; a sample in C_6D_6 gave a single ^{31}P NMR signal at δ −8.7 (lit.[17] for 1-methylphosphole (**6**), −8.7 neat). The product was further characterized by oxidation in a two-phase medium with 5 ml of 10% H_2O_2. The layers were separated after 5 min of shaking, and the aqueous layer extracted with three 5-ml portions of $CHCl_3$. The combined organic layers were dried ($MgSO_4$) and concentrated to yield 0.1 g of a mixture of phosphole oxide dimer (**16**), 85%, δ ^{31}P NMR ($CDCl_3$) +91.3 and +61.7 ($^3J_{PP}$ = 35.4 Hz) and 1-methyl-*cis*-3a,7a-dihydrophosphindole-1-oxide[2], 15%, δ ^{31}P NMR ($CDCl_3$) +11.7.

Identification of 1,3-dimethylphosphole. A solution of 0.5 g (2.2 mmol) of phosphole dimer **9** and 0.5 ml of dry pristane, sealed under argon, was heated at 185 ± 2° for 1 h. Bulb-to-bulb transfer on the vacuum line provided 0.05 g of liquid that gave only one ^{31}P NMR signal; δ ($CDCl_3$) −6.6 (lit.[18] −6.9 for neat 1,3-dimethylphosphole); MS, *m/z* 112 (parent peak); calcd for C_6H_9P, M^+ 112.

1,3,5-Trimethyl-cis-3a,7a-dihydrophosphindole-1-oxide (**19**). To a solution of 0.4 g (2.2 mmol) of crude **11** in 20 ml of $CHCl_3$ was added 10 ml of 10% H_2O_2 dropwise over 5 min. The biphase was then vigorously stirred for 1 h, separated, and the aqueous layer extracted with five 20-ml portions of $CHCl_3$. The combined $CHCl_3$ layers were washed with 5 ml of H_2O and then with 5 ml of saturated sodium thiosulfate solution. The $CHCl_3$ layer was then dried (Na_2SO_4 and $MgSO_4$) and evaporated to yield 0.2 g (46%) of **19** as a white solid of about 90% purity. All attempted purifications by recrystallization led to aromatization of the dihydro ring: ^{13}C and ^{31}P NMR, see Table I.

1,3,5-Trimethylphosphindole-1-oxide (**20**). To a solution of 0.3 g (1.5 mmol) of dihydrophosphindole oxide (**19**) in 20 ml of cumene was added 0.1 g of 10% Pd on C. The mixture was refluxed under N_2 for 66.5 h, diluted with 50 ml of $CHCl_3$, and filtered through Celite. Rotoevaporation and high-vacuum yielded an oil with suspended black particles. This was dissolved in several ml of $CHCl_3$ and passed through a silica gel column (0.5 × 6.5 cm) using $CHCl_3$ as the eluent. Rotoevaporation and high-vacuum drying gave a light-yellow oil. The oil darkened on standing and was Kugelrohr-distilled at 115–119°C (0.03 mm) to yield 0.1 g (34%) of **20** as a white oily solid. Further purification by either column chromatography or recrystallization was not effective; ^1H NMR (250 MHz, $CDCl_3$) δ 1.73 (*d*, $^2J_{PH} = 13.5$ Hz, $P—C\underline{H}_3$), 2.23 (pseudo-*t*, $^4J_{PH} = {}^4J_{H_2H} = 1.5$ Hz, $=C—C\underline{H}_3$), 2.42 (s, $Ar—C\underline{H}_3$), 6.10 (*d* of *d*, $^2J_{PH_2} = 25.9$ Hz, $^4J_{H_2H} = 1.5$ Hz, H_2), 7.17 (s, H_4), 7.22 (*d* of *d*, $^3J_{H_6H_7} = 7.4$ Hz, $^4J_{PH_6} = 3.8$ Hz), H_6, 7.62 (*d* of *d*, $^3J_{PH_7} = 9.2$ Hz, $^3J_{H_7H_6}) = 7.4$ Hz, H_7; ^{13}C and ^{31}P NMR, see Table I; high resolution MS, *m/z* 192.0705; calcd for $C_{11}H_{13}OP$, M^+ 192.0704.

Synthesis of 1,3,7-trimethyl-cis-3a,7a-dihydrophosphindole (**12**). To a flame-dried reaction tube was added 0.7 g (3.1 mmol) of crude **9**. The tube was sealed under Ar and heated at 124 ± 7°C for 12.5 h. The product was Kugelrohr-distilled at 62–66°C (0.07 mm) to yield 0.3 g (54%) of fairly pure **12** as a clear oil: partial ^1H NMR ($CDCl_3$) δ 0.97 (*d*, $^2J_{PH} = 2.6$ Hz, $P—C\underline{H}_3$), 1.82 (s, $C—C\underline{H}_3$), 1.94 (s, $C—C\underline{H}_3$), 5.2–6.1 (m, 4H, $C\underline{H}=$); ^{13}C and ^{31}P, see Table I; MS *m/z* (relative intensity) $[M^+ + 1]$ 179.0 (12.2), M^+ 178.0 (97.3), $[M^+ - 1]$ 177.0 (100), $[M—CH_3]^+$ 163.0 (62.0), 161.0 (12.5), 147.0 (15.6). The phosphine (**12**) was converted to its methiodide by reaction in pentane with excess iodomethane. Immediate cloudiness occurred and the sample was stored in the freezer for 4 days. The white solid that had formed was filtered and washed with pentane. High-vacuum drying produced 0.32 g (59%) of **21** as a white hygroscopic solid. Recrystallization from MeOH-EtOAc removed most of the impurities and gave a sample with mp 183.5–187.5°C, but analytical purity could not be obtained; ^{13}C and ^{31}P NMR, see Table I.

1,3,7-Trimethyl-cis-3a,7a-dihydrophosphindole-1-oxide (**22**). To a solution of 0.9 g (5.1 mmol) of phosphine **12** in 30 ml of $CHCl_3$ was added dropwise 20 ml of ice-cold 10% H_2O_2 in an ice-water bath. The mixture was vigorously stirred at room temperature overnight, then cooled in an ice-bath while the excess H_2O_2 was quenched with saturated sodium thiosulfate. The aqueous layer was continuously extracted with $CHCl_3$ for 21 h. The $CHCl_3$ extract was dried over Na_2SO_4 and $MgSO_4$. Rotoevaporation and high-vacuum drying gave 0.3 g (31%) of a white solid with **22** as the main component. Attempted purification by recrystallization led to partial aromatization (see below) of the dihydro ring: ^{13}C and ^{31}P NMR, see Table I.

1,3,7-Trimethylphosphindole-1-oxide (**23**). To a solution of 0.5 g (2.6 mmol) of oxide **22** in 15 ml of cumene was added 0.2 g of 10% Pd on C. The mixture was refluxed under N_2 for 48 h, and then diluted with 30 ml of $CHCl_3$ and filtered through Celite. Rotoevaporation and high-vacuum drying yielded 0.3 g (61%) of a green-yellow oil. The oil was dissolved in several ml of $CHCl_3$ and passed through a short silica gel column (0.5 × 6.5 cm) using $CHCl_3$ as the eluent. Rotoevaporation and high-vacuum drying gave a light-yellow oil which darkened on standing. It was Kugelrohr-distilled at 139–145°C (0.03 mm) to yield 0.2 g (40%) of **23** as a yellow oil. No purification occurred on column chromatography using silica gel, but some purification was accomplished using reverse-phase column chromatography (Adsorbosil C8, 200–425 mesh) with 20% H_2O—MeOH as eluent. Fractions with R_f 0.66 on Whatman TLC plates ($KC_{18}/KC_{18}F$), when concentrated by rotoevaporation and high vacuum, gave 0.1 g (20%) of **23** as the main component, a colorless clear oil: ^1H NMR (250 MHz, $CDCl_3$) 1.77 (*d*, $^2J_{PH} = 13.3$ Hz, P—C$\underline{H}_3$), 2.22 (pseudo-*t*, $^4J_{PH} = {}^4J_{H_2H} = 1.5$ Hz, =C—C$\underline{H}_3$), 2.63 (s, Ar—C$\underline{H}_3$), 6.09 (*d* of *d*, $^2J_{PH_2} = 26.8$ Hz, $^4J_{H_2H} = 1.5$ Hz, H_2), 7.18 (broad *t*, 2 H, H_4 and H_6), 7.40 (*t*, $^3J_{H_5H_6} = {}^3J_{H_4H_6} = 7.0$ Hz, split with $^4J_{PH_6} = 1.1$ Hz, 1 H, H_5); ^{13}C and ^{31}P NMR, see Table I; high resolution MS, *m/z* 192.0705; calcd for $C_{11}H_{13}OP$, M^+ 192.0704.

Attempted rearrangement of 1,3,5-trimethyl-3a,7a-dihydrophosphindole (**11**). To a flame-dried reaction vessel was added 0.2 g (1.1 mmol) of a mixture of **11** (68%) and its isomer **12** (32%). The oil was diluted with 5 ml of xylene and heated at 117–121°C for 10.7 h under Ar. ^{31}P NMR analysis showed no significant concentration changes.

Pyrolysis of 1,3-dimethylphosphole (**10**). To a flame-dried reaction tube was added 0.2 g (1.8 mmol) of **10**, prepared by flash vacuum pyrolysis[5] of dimer **9**, and 0.5 ml of dry, degassed xylene. The tube was sealed under Ar and heated at 120–121°C for 17 h to yield a light brown solution. The solution was analyzed by ^{31}P NMR (C_6D_6); main components were **10** (36%), *anti*-dimer **13** (42%), and *syn*-dimer **9** (9%). No signal for 1,3,7-trimethyl-3a,7a-dihydrophosphindole was present.

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program) or a JEOL FX-60 spectrometer at 22.5 MHz and 15.0 MHz, respectively, using TMS as an internal standard, unless otherwise noted. Phosphorus-31 NMR spectra were obtained on a JEOL FX-90Q or a Bruker HFX-10 spectrometer at 36.2 MHz and 36.4 MHz, respectively, using 85% H_3PO_4 as an external standard with an internal deuterium lock; positive chemical shifts (ppm) are downfield of the reference. Broad-band proton noise-decoupling was employed on all carbon-13 and phosphorus-31 NMR spectra. Mass spectra were obtained on a Hewlett Packard 5992A GC-MS at 70 eV or on an AEI MS 903 Spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Procedures involving trivalent phosphorus compounds were performed under a nitrogen or an argon atmosphere.

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