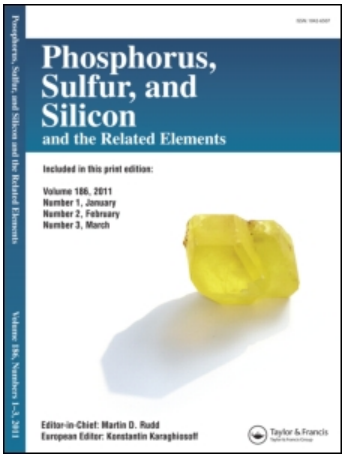

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DEMONSTRATION OF C-PROTONATION OF PHOSPHOLES AND OF δ-DESHIELDING OF ^{31}P USING MULTICYCLIC PHOSPHORUS COMPOUNDS[1]

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Cyclohexa[b]phospholes and 4,5-dihydrobenzo[e]phosphindoles were synthesized by the dehydrobromination of the appropriate diene-phosphonous dihalide cycloadducts. The benzo[g]phosphindole system was constructed by NBS bromination of the 2,3-dihydro derivative as the P-oxide, followed by deoxygenation and then DBU dehydrobromination. Dimerization of salts and oxides of the phospholes was a common property, even occurring for the fully unsaturated benzo[g]phosphindole oxide with sacrifice of its naphthalene character. Two of the phospholes were found to add anhydrous HCl, with proton-attachment to a ring carbon. A second mole of HCl was also added, giving chlorophospholenium chlorides as final products. The benzo[g] series of compounds proved useful in demonstrating a ^{31}P chemical shift effect similar to that found in ^{13}C NMR spectroscopy; when considered as naphthalenes containing a 1-phosphorus substituent, pronounced deshielding occurred on placement of a methyl group in the compressed 8-position. This δ-shielding effect was especially strong in the phosphines of this series.

In some of our recent work,[2-7] we have shown that the McCormack cycloaddition of dienes and P(III) halides can be readily adapted to the synthesis of multicyclic phosphorus heterocycles. In this paper we describe the synthesis of a number of specially designed tricyclic phospholene oxides and derivatives, and of some new types of phospholes derived from multicyclic phospholene precursors. The phospholes have proved of special value in that they exhibit a property never before observed: protonation on a ring carbon, and not on phosphorus, takes place on interaction with anhydrous HCl. Sensitivity of the ring carbons to electrophilic attack is a well known property of other 5-membered heteroaromatic systems, but this aspect of phosphole chemistry remains to be explored. The reaction will be shown to follow a course unique to the character of phosphorus, resulting in the net addition of two moles of HCl to form a chlorophospholenium ion. The multicyclic phospholene derivatives have also proved of value in demonstrating a new effect in ^{31}P NMR spectroscopy; their framework can be employed to install special steric interactions with the ^{31}P nucleus, and this has revealed for the first time that interaction with a δ-oriented substituent can cause substantial deshielding, just as is observed for the ^{13}C nucleus. Earlier preliminary reports on the formation of delocalized phosphole anions[8] and of ^{31}P NMR properties of dimers of P(IV) phosphole derivatives[9] made use of some of the multicyclic compounds to be described in this paper.

Synthesis of Multicyclic Phospholene Derivatives

Phospholene oxides with cycloalkano rings fused at the α,β-positions are conveniently prepared by applying the McCormack cycloaddition reaction to α-vinylcyclo-

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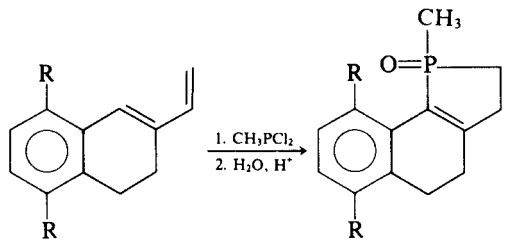
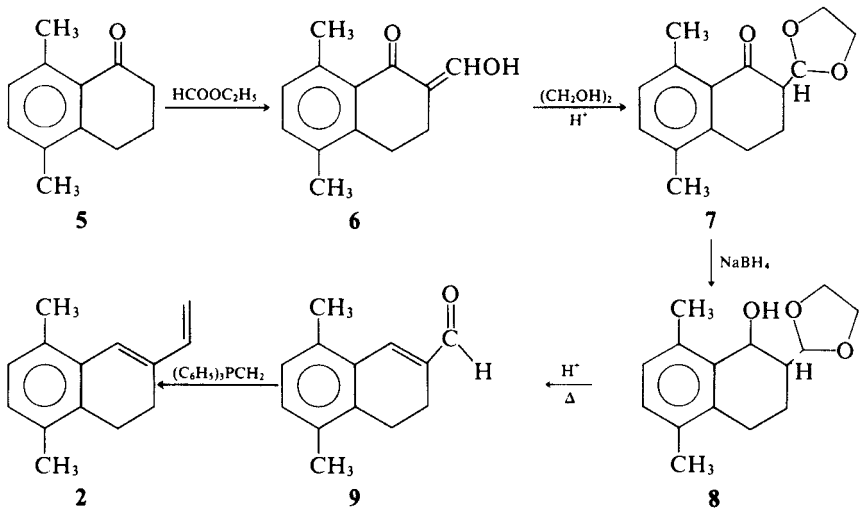
alkenes.[2-4] In the present study, the cycloadditions to form **3** and **4** were performed for the first time.



R = H, **1**
R = CH_3, **2**

3
4

Diene **1** was available from the previous study,[4] in which it was cyclized with $C_6H_5PBr_2$. The synthesis of the new diene **2** was performed by a similar method, which started with the known[10] α-tetralone **5**.

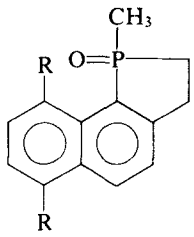


5 **6** **7**

2 **9** **8**

Diene **1** on cyclization with CH_3PCl_2 at room temperature probably provided the 3-phospholene framework in the cycloadduct, but hydrolysis was conducted under hot, acidic conditions to allow double-bond rearrangement[2] to **3**. From diene **2**, however, the 2-phospholene oxide **4** was the only product from either cold or hot cycloaddition, and has provided the only exception known so far to the generality[11a] that cold cycloadditions with CH_3PCl_2 can be relied on to provide 3-phospholene derivatives. Notable also is the slowness of this cycloaddition (43% after 4 months at room temperature). Conducting the reaction at higher temperatures gave very poor results due to diene instability. The steric congestion provided by the methyl on the aromatic ring must account for the slowness of the reaction, and may play a role in the double-bond migration.

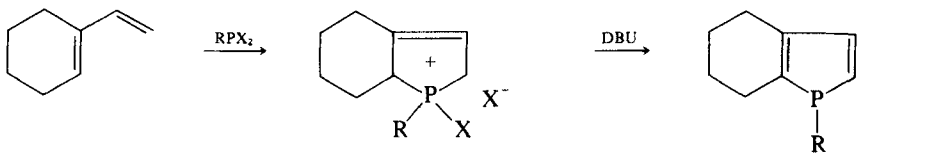
Both phospholenes responded well to aromatization[4] with palladium on charcoal, and provided the naphthalenophospholenes **10** and **11**.



10, R = H
11, R = CH_3

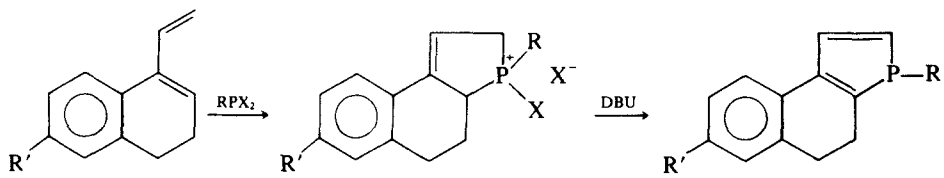
Synthesis of Phospholes

The Mathey dehydrohalogenation technique for converting McCormack cycloadducts to phospholes[12] was applied successfully to the synthesis of multicyclic phospholes **14**, **15**, **19**, **20** and **21** as shown below. DBU was used as the dehydrohalogenating agent; the low yields are typical of this process,[12-13] which nevertheless stands as a highly useful synthetic method.



12, R = CH_3, X = Cl
13, R = C_6H_5, X = Br

14 (18%, δ ^{31}P −7.6)
15 (25%, +10.5)

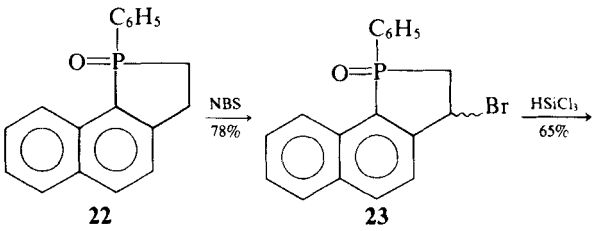


	R	*R'*	*X*
16,	CH_3	H	Cl
17,	C_6H_5	H	Br
18,	CH_3	OCH_3	Cl

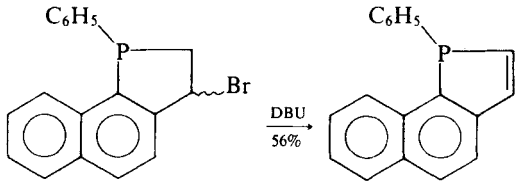
19 (20%, −4.1)
20 (~40%, +12.8)
21 (47%, −4.9)

Obtaining phospholes in analytically pure form is sometimes difficult because of their thermal and air sensitivity. The tricyclic phospholes **19**, **20**, and **21** were purified by column chromatography; the latter was obtained in analytically pure form as a crystalline solid by this procedure. The others were pure by spectroscopic analysis, but were analyzed as methiodide derivatives. The cyclohexaphospholes **14** and **15** were purified by vacuum distillation and also analyzed as derivatives.

A different method was employed for the synthesis of the benzophosphindole **25**. The synthesis, as outlined below, starts with a known[4] dihydro derivative **22**.



22 23

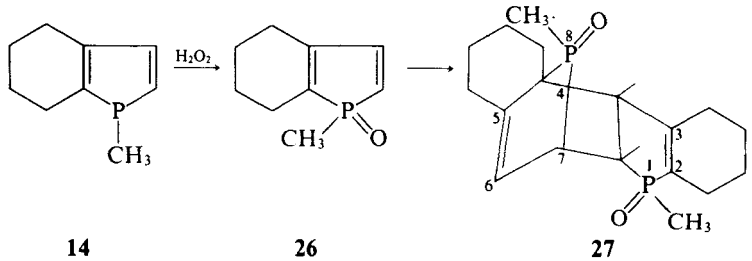


24 25 δ ^{31}P +0.1

The bromo derivative **23** was obtained as a mixture of stereoisomers; the sample gave two ^{31}P NMR signals (major δ +50.1, minor +44.8) and two sets of ^{13}C NMR signals for the sp^3 carbons. The α-effect of bromine caused substantial downfield shifting of C-3 in both isomers to the region δ 43–45, from δ 28.8[4] in the unsubstituted **22**. This bromo compound, as well as the corresponding phosphine (**24**), was difficult to purify, both being subject to decomposition, and analysis could not be obtained. The dehydrobromination of phosphine **24** to the phosphole was accomplished smoothly with DBU, but again the product could not be obtained in pure form. Partial purification by chromatography on alumina gave a colorless oil with the expected (see Experimental) spectral properties, but a persistent phosphorus-containing impurity could not be removed. The ^{31}P NMR shifts of phosphole **25**, as well as those of **14**, **15**, **19**, **20** and **21**, were in the expected relatively downfield region characteristic of this type of tertiary phosphine,[11b] and provide additional proof of the structures. Various derivatives (*vide infra*) provided further characterization.

Compound **25** is of special interest as it is the first known type of benzophosphindole other than the symmetrical dibenzo[bd]phosphindole.

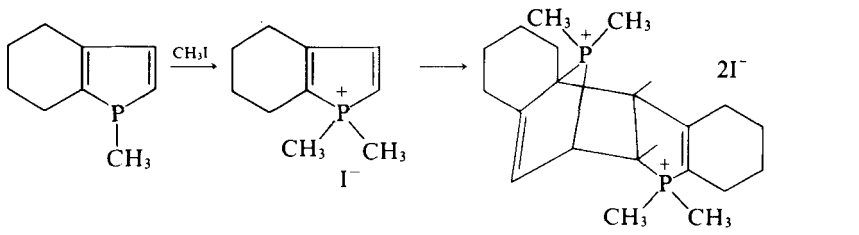
While phospholes are not known to dimerize in Diels-Alder fashion, P(IV) derivatives of phospholes are very prone to undergo this reaction. The new multicyclic phospholes were not exceptional, and when oxides were formed from them by H_2O_2 oxidation, the dimers were the exclusive products isolated. The dimerizations were, as usual,[14] regiospecific, forming only one of the several possible isomeric forms. The ^{31}P NMR shifts and 3-bond ^{31}P-^{31}P coupling constants[9] were quite similar to those reported[14] for dimers of monocyclic phosphole oxides; all possessed the especially downfield signal (δ +80 to +90) for the bridging P of the phosphanorbornene moiety. The 2-phospholene P was in the normal position of δ +52 to +59. The orientation of the dimerization is the same as that established for the monocyclic phosphole oxide dimers, as revealed by features of the ^{1}H and ^{13}C NMR spectra of a typical compound (**27**).



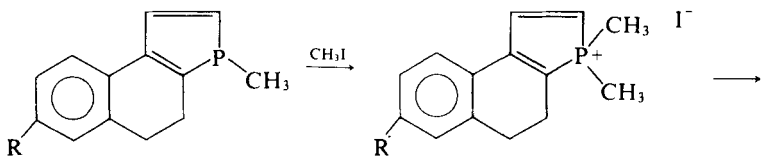
14 **26** **27**

Thus, the presence of only one olefinic proton in this dimer proves that the unsubstituted double bond of monomer **26** served as the dienophile. The *endo* ring fusion to the 7-phosphanorbornene moiety, an established fact for dimers of monocyclic phosphole oxides,[14] was indicated from the similarity of the chemical shifts for the protons attached to the fusion carbons. These shifts are distinctly downfield as a result of deshielding by the P=O group positioned over them. The substitution pattern in the 7-phosphanorbornene moiety is revealed by the ^{13}C NMR spectrum. The sp^2 carbons are coupled to the bridging P by nearly identical values (C-5, 10.7; C-6, 10.8 Hz) but only one of these is coupled also to the 2-phospholene P (5.0 Hz). This identifies the other sp^2 C as being remote (4 bonds) from the 2-phospholene P. The chemical shift of the remote C shows strong deshielding (δ 140.1) relative to the other sp^2 C (δ 122.3), and this carbon is thus revealed to carry a bond of the cyclohexane ring. This assignment was confirmed by off-resonance decoupling, where that signal suspected to be C-6 split to a doublet. The dimeric oxides from oxidation of the tricyclic phospholes **19**, **20** and **21**, (**28**, **29** and **30**, respectively) were assigned the same structural features as established for **27**.

Phospholium salts in this series were only partly dimerized in the course of their formation by quaternization of the phospholes, and this reaction led to various mixtures of the monomer and dimer. The mixtures were easily analyzed by ^{31}P NMR, however, since the dimers gave the usual doublet of doublets, and the monomers a singlet in the region typical of phospholium ions.[9] The dimers (**34–36**) are assumed to have formed with the same orientation of reactants as seen for the dimerization of the oxides.

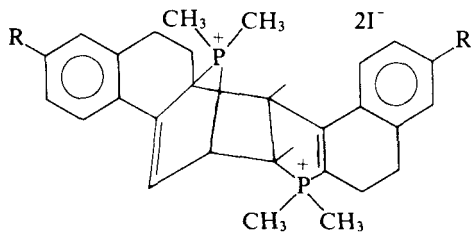


14 **31** **34**



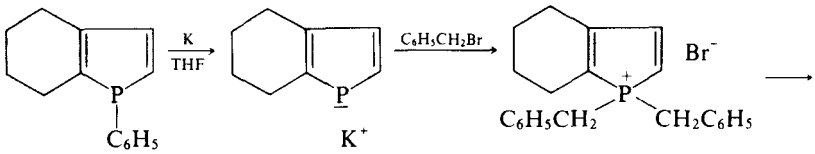
19, R = H
21, R = OCH_3

32
33

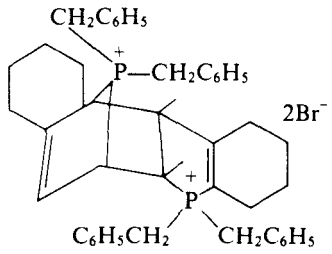


35
36

One dimeric salt was prepared by dialkylation of a phospholide ion.



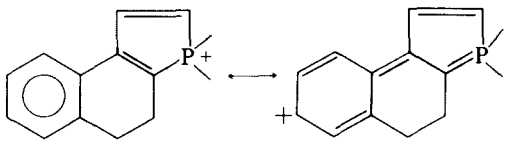
15 **37** **38**



39

The potassium cleavage of the phenyl group of **15** (and also of phosphole **20**), and the unique, low-field ^{31}P NMR signals indicative of considerable electron delocalization, have been reported elsewhere.[8] Experimental details are provided here.

While both the monomeric salts of the cyclohexaphospholium ion were colorless, salts in the benzo series were distinctly yellow. This may be attributed to the extended conjugation possible in this system as indicated by the resonance form **41**.

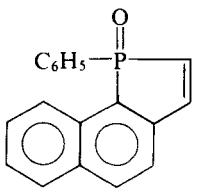


40 **41**

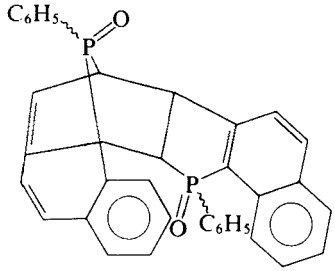
That positive phosphorus plays a role is evident from the fact that the corresponding oxides are colorless.

The tendency for P(IV) phosphole oxides to dimerize is so great that it occurs on formation of the oxide of the fully aromatic benzophosphindole **25**, even though this requires the disruption of the aromaticity of one of the benzene rings. When the oxide (**42**) was formed by dehydrobromination of bromo-oxide **23**, a product was

obtained whose complex ^{31}P NMR spectrum could be interpreted as consisting of a doublet of doublets, δ +40.5 and +57.7, $^{3}J_{PP} = 22$ Hz (with an extraneous signal at +40.4 superimposed on the upfield doublet). However, neither the chemical shifts nor the coupling constant match those found for the Diels-Alder dimers of more conventional P-phenyl phosphole oxides, where strong deshielding of the bridging P in the 7-phosphanorbornene moiety is present (e.g., δ +77.8 for dimer **29** with $^{3}J_{PP} = 35.6$ Hz). The more complex structure of a dimer from **42** may alter these relations, especially through a conjugative effect with the highly important double bond of the phosphanorbornene moiety as seen in a structure such as **43**. Other differences (e.g. exo *vs.* endo fusion) could also result from dimerization that could account for a departure from the commonly encountered dimer structure. In any case, the point seems established that phosphole oxide **42** tends to dimerize on formation.



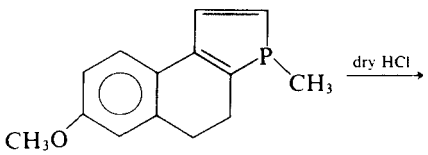
42



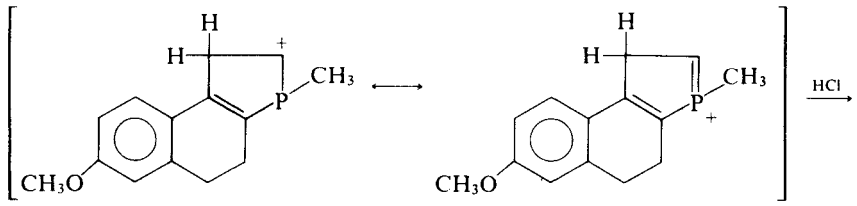
43

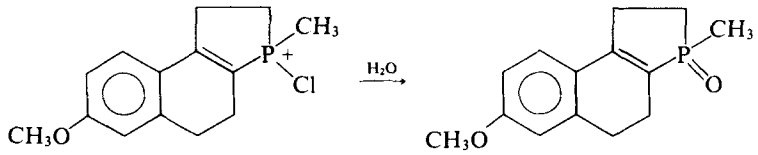
C-Protonation of the Phosphole Ring

Electron delocalization in phospholes[11d,13,15] should render the ring carbons sensitive to attack by electrophiles, although this possibility has received very little consideration to date, and there are no reports of electrophilic substitution at a ring carbon of a phosphole molecule. A striking example of this predicted sensitivity to electrophiles has been encountered with the phospholes of the present study: carbon (mostly β) is protonated exclusively and in high yield with anhydrous HCl. Addition of a second HCl molecule then occurs, to give, as depicted below for phosphole **21**, a chlorophospholenium ion (**44**) as the final product.



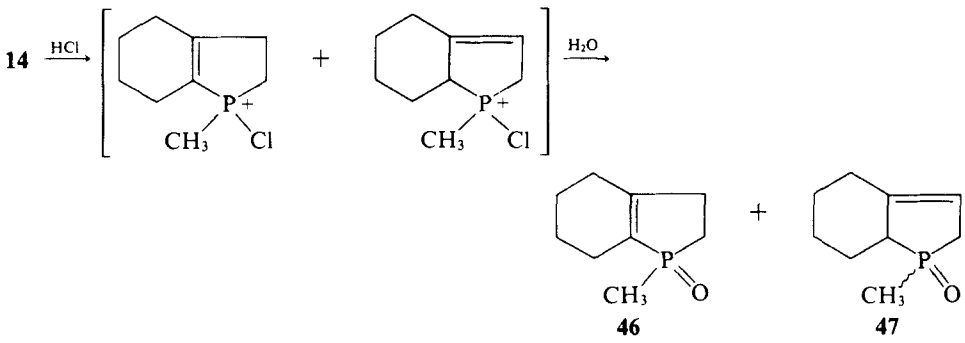
21





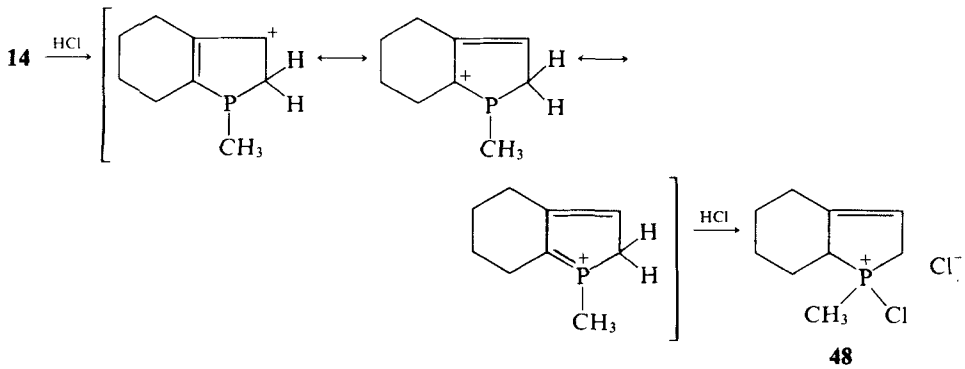
44 **45**

The chlorophospholenium character of the HCl addition product (**44**) was first revealed by its ^{31}P NMR shift of δ +103.0, a characteristic position for such structures,[16] and far downfield of the expected P-hydrochloride. The structure was established by hydrolysis of the HCl adduct to the known[4] 2-phospholene oxide **45**. The overall yield in the process was 84%. With phosphole **14**, the HCl reaction mixture gave a major ^{31}P signal at δ +119.0; hydrolysis provided not only the 2-phospholene oxide **46** (70%), but also the *cis* and *trans* isomers (30%) of the 3-phospholene oxide (**47**).



46 **47**

The proposed mechanism includes an intermediate that possesses a carbon-phosphorus double bond, which would provide an explanation for the attachment of a second proton to a carbon, and of chlorine to phosphorus. Double bonds to phosphoryl groups are highly reactive, with carbon rich in negative character,[17] and the same property may reside in salts. C-Protonation of pyrroles is, of course, a well-known property of this heterocycle,[18] but differs in that restoration of the full pyrrole system ensues. Both the α- and β-carbons of pyrroles may be protonated, with rather similar rates.[18] The dominating formation of the 2-phospholenium ion from phospholes is suggestive of β-attack, as is shown above in the mechanism outlined for phosphole **21**. However, α-attack could also occur, and may account for the formation, in the case of **14**, of a small amount of 3-phospholenium ion (**48**).



48

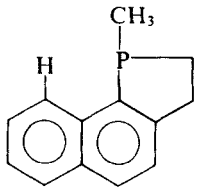
The position of the double bond in the final product does not necessarily reveal the site of initial protonation, as proton migrations could well follow the first attachment of a proton. However, for phosphole **21**, we have obtained support for a preference for β-protonation by replacing HCl by DCl and comparing the ^{13}C NMR spectra of both the 2-phospholenium ions and the phospholene oxide hydrolysis products (**45**). Attachment of D to carbon should provide a diminution of signal intensity, and this was clearly observed for the carbon attributed[19] to the β-position (δ 26.9 in the oxide[4]). The signal in both the ion and the oxide was reduced to nearly half its intensity when DCl was used. The effect at the α-carbon (δ 24.3) is less clearcut; there appears to be some diminution of signal intensity especially of the downfield half of the doublet, but the well-known poor reproducibility of ^{13}C intensities may be obscuring the point. It is, however, possible to say that β-protonation is clearly preferred over α-protonation in the case of phosphole **21**.

Little is known about the protonation of phospholes. The basicity of 1-methylphosphole towards 0.124 N HCl was determined[20] but the site of protonation was not established. The $TaCl_5$ complex of 1,2,5-triphenylphosphole (but not the free phosphole) gave the phosphole hydrochloride with anhydrous HCl;[21] the proton was located on phosphorus, as revealed by the presence of infrared absorption characteristic of a P—H bond. Anhydrous CF_3COOH has been reacted with the 1-phenyl and 1-*t*-butyl derivatives of 3,4-dimethylphosphole; after addition of NaOH, the corresponding 3-phospholene oxides were isolated in about 20% yields.[22] Two mechanisms have been proposed to account for these results, but no experimental evidence is available to discriminate between them. In the first report on this reaction, Mathey proposed protonation at the α-carbon, followed by attack of $\bar{O}H$ on phosphorus.[22] In a later paper,[23] the alternative of P-protonation, followed by $\bar{O}H$ attack to form a pentacovalent phosphorus species that underwent a proton migration to the 3-phospholene oxide, was put forward and was recently reiterated.[13] A similar mechanism might also be considered for the HCl reaction, but would involve attack of Cl^- on protonated phosphorus to form a pentacovalent intermediate for the proton migration to the α-carbon. The poor nucleophilicity of Cl^- compared to OH^-, associated with the well-known tendency of P(V) chlorides to ionize, makes this mechanism seem less attractive than that of direct C-protonation, but cannot be completely ruled out. The more distantly related secondary phosphine 2,5-diphenylphosphole has been reported to add HCl, but the site of proton attack was not established.[24] No other electrophilic reagents have been shown to attack ring carbons of phospholes.

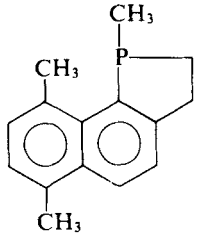
Deshielding of ^{31}P by a δ-Methyl Group

It is a well-established fact in ^{13}C NMR spectroscopy that steric interactions can cause either shielding or deshielding. The former is the better known, and is commonly found when a substituent atom is introduced into a γ-relation with regard to a particular carbon atom. The effect is reproduced in ^{31}P NMR.[11e] Deshielding occurs in ^{13}C NMR when an atom is introduced into the δ-position with regard to a carbon atom.[25] The effect is strongest when the interacting atoms are firmly held in a syn-axial relation.[26] An excellent example is provided by comparing the methyl chemical shifts in 1-methylnaphthalene and 1,8-dimethylnaphthalene; δ-deshielding of 7.1 ppm accompanies the introduction of the 8-methyl group.[27] To our knowledge, there is not yet a clear-cut example of the operation of the δ-deshielding effect in ^{31}P NMR spectroscopy. We have used the framework of the multicyclic phospho-

lenes to search for this effect. Thus, a phosphorus atom at the 1-position of naphthalene could be influenced by an 8-methyl group in the same way noted for 1,8-dimethylnaphthalene. The reality of the effect is quite clearly shown by the substantial (13.5 ppm) deshielding of ^{31}P in phosphine **50** relative to phosphine **49**. Both were prepared by $HSiCl_3$ reduction of the oxides.

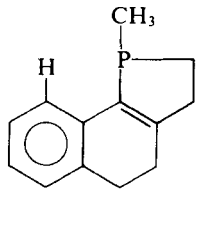


49, δ −23.7

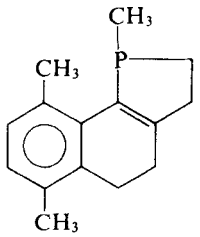


50, δ −10.2

The reverse effect is also detectable; the crowded 9-CH_3 of **50** has its ^{13}C shift at 25.7, while the less crowded 6-CH_3 is found at δ 20.2. The P-oxides of these phosphines show a similar ^{31}P difference, but of smaller magnitude (**10**, +61.3; **11**, +64.0). That a phosphine should be more sensitive to a structural change than an oxide is a common experience in ^{31}P NMR spectroscopy.[11b] The C—CH_3 groups of the oxides again have different shifts, attributable to δ-deshielding ($\Delta\delta$ 3.9). The dihydronaphthalenes provide another example where strong steric δ-interaction can occur, and indeed phosphine **52** is seen to be markedly downfield (10.7 ppm) of the uncrowded **51**.



51, δ −17.3



52, δ −6.6

Again the oxides show a smaller, rather unconvincing, shift difference (**3**, δ +63.0; **4**, δ +64.8). The δ-deshielding of the crowded C—CH_3 occurs in both the phosphine ($\Delta\delta$ 5.5) and the oxide ($\Delta\delta$ 3.0).

The concept of ^{31}P shifts, at least of P(III) derivatives, being sensitive to long-range deshielding influences, could be useful in the interpretation of spectra of complex and constrained heterocyclic phosphorus compounds, areas of increasing importance.

EXPERIMENTAL SECTION[28]

1-Methyl-2,3,4,5-tetrahydro-(1H)-benzo[g]phosphindole 1-Oxide (**3**).

A mixture of 25.6 g (0.16 mol) of diene **1**,[4] 26 g (0.16 mol) of methylphosphonous dichloride, 100 mL of pentane and 0.2 g of copper stearate was allowed to stand in the dark at room temperature for 5 weeks. The white precipitate was filtered from the mixture and hydrolyzed with 50 mL of hot (90°C) water. The

solution was neutralized with solid $NaHCO_3$, extracted with chloroform (3 × 100 mL) and the combined extracts dried ($MgSO_4$) and concentrated to give 7.6 g (22%) of **3** as a white solid. Recrystallization from toluene gave an analytical sample, mp 127–128°C; ^1H NMR ($CDCl_3$) δ 1.70 (d, $^2J_{P-H}$ = 12 Hz, P—CH_3), 2.00–3.00 (m, —CH_2), 7.10 (m, H-6,7,8), 7.66 (m, H-9); ^{31}P NMR ($CDCl_3$) δ +63.0.

Anal. Calcd for $C_{13}H_{15}OP$: C, 71.55; H, 6.93; P, 14.19. Found: C, 71.37; H, 7.13; P, 14.19.

1-Methyl-2,3,4,5-tetrahydro-(1H)-benzo[g]phosphindole (**51**).

To a solution of 1.3 g (6 mmol) of **3** and 30 mL of benzene was slowly added 2.0 g (15 mmol) of trichlorosilane. The mixture was refluxed for 2 h and then hydrolyzed with 20% NaOH. The layers were separated, and the organic layer was dried over $MgSO_4$ and concentrated to give 1.1 g (91%) of **51** as a clear oil; ^1H NMR ($CDCl_3$) δ 1.09 (d, $^2J_{P-H}$ = 3 Hz, P—CH_3), 1.48–2.98 (m, —CH_2—), 6.95–7.15 (m, Ar-*H*); ^{31}P NMR ($CDCl_3$) δ −17.6. The methyl iodide salt was prepared for analysis by adding an excess of iodomethane to a sample of **51** in pentane. Recrystallization from methanol give white needles, mp 277–279°C.

Anal. Calcd for $C_{14}H_{18}IP$: C, 48.86; H, 5.27; P, 9.00. Found: C, 48.64; H, 5.31; P, 9.28.

1-Methyl-2,3-dihydro-(1H)-benzo[g]phosphindole 1-Oxide (**10**).

A mixture of 2.2 g (10.1 mmol) of **3**, 25 mL of cumene and 200 mg of 10% palladium on charcoal was refluxed for 48 h, and then filtered while still hot. Upon cooling, **10** precipitated and was recrystallized from toluene to give 1.9 g of **10** (87%) as a white solid, mp 210.5–212.5°C; ^1H NMR ($CDCl_3$) δ 1.80 (d, $^2J_{P-H}$ = 13, P—CH_3), 2.38 (d of t, J_{HH} = 6, J_{HH} = 7, —CH_2—), 3.20 (m, —CH_2—), 7.20–7.90 (m, H-6,7,8), 8.40 (d, J_{HH} = 8 Hz, H-9); ^{31}P NMR ($CDCl_3$) δ +61.3.

Anal. Calcd for $C_{13}H_{13}OP$: C, 72.21; H, 6.06; P, 14.33. Found: C, 72.56; H, 6.23; P, 13.98.

1-Methyl-2,3-dihydro-(1H)-benzo[g]phosphindole (**49**).

To a solution of 1.1 g (5.1 mmol) of **10** and 30 mL of benzene was slowly added 2.0 g (15 mmol) of trichlorosilane. The mixture was refluxed for 2 h, and then hydrolyzed with 20% NaOH. The layers were separated and the organic layer was dried over $MgSO_4$ and concentrated to give 0.8 g (78%) of **49** as a yellow oil; ^1H NMR ($CDCl_3$) δ 1.10 (d, $^2J_{P-H}$ = 2 Hz, P—CH_3), 1.80–2.50 (m, —CH_2—), 3.00–3.80 (m, —CH_2—), 7.00–8.00 (m, Ar—*H*); ^{31}P NMR ($CDCl_3$) δ −23.3.

The methyl iodide salt was prepared for analysis by adding an excess of iodomethane to a pentane solution of **49**. Recrystallization from methanol gave white crystals, mp 296–297°.

Anal. Calcd for $C_{14}H_{16}IP$: C, 49.15; H, 4.71; P, 9.05. Found: C, 49.47; H, 4.82; P, 9.06.

2-Hydroxymethylene-5,8-dimethyl-1-tetralone (**6**).

To a hot slurry of 27.3 g (1.14 mol) of sodium hydride and 500 mL of toluene at 100°C was added dropwise a solution of 90.1 g (0.52 mol) of 5,8-dimethyl-1-tetralone (**5**), 115.5 g (1.56 mol) of ethyl formate and 100 mL of toluene over a 1 h period under a nitrogen atmosphere. When the slurry turned orange, the heating was discontinued and the mixture was allowed to stir overnight. Saturated $NaHCO_3$ (1 L) was added and the aqueous layer then acidified with 15% HCl and extracted with chloroform (3 × 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to a brown oil. Distillation gave 89.2 g (85%) of **6**, b.p. 101°C (0.08 mm); ^1H NMR ($CDCl_3$) δ 2.19 (s, —CH_3), 2.32 (t, $^3J_{HH}$ = 8, Ar—CH_2CH_2), 2.57 (s, —CH_3), 2.68 (t, $^3J_{HH}$ = 8, Ar—CH_2CH_2), 7.00 (AB, $^3J_{HH}$ = 7, *o*—Ar*H*), 7.83 (d, $^3J_{HH}$ = 8, C=C*H*—OH), 15.06 (d, $^3J_{HH}$ = 8 Hz, C=CH—O*H*); partial ^{13}C NMR ($CDCl_3$) δ 171.6 (C=*C*H—OH), 188.4 (C=O); IR (neat) $\nu_{C=O}$ 1640 cm^{-1}, $\nu_{C=COH}$ 1600 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.82; H, 6.94.

2-Ethylenedioxymethyl-5,8-dimethyl-1-tetralone (**7**).

A mixture of 89.2 g (0.44 mol) of **6**, 28.7 g (0.46 mol) of ethylene glycol, and 500 mg of *p*-toluenesulfonic acid in 350 mL of toluene was refluxed for 3 h while water was removed through a Dean-Stark trap. The mixture was then washed with saturated $NaHCO_3$ (3 × 100 mL), water (2 × 100 mL) and dried ($MgSO_4$). The solvent was removed under vacuum to give 108.7 g (100%) of **7** as an oil; ^1H NMR ($CDCl_3$) δ 2.18 (s, —CH_3), 1.80–2.40 (m, —CH_2—), 2.56 (s, —CH_3), 2.40–2.95 (m, —CH_2 and —C*H*—),

3.86 (m, —OCH_2—CH_2—), 5.40 (d, $^3J_{HH}$ = 4, —OC*H*O—), 6.98 (AB, $^3J_{HH}$ = 7 Hz, *o*—ArH); partial ^{13}C NMR ($CDCl_3$) δ 51.2 (—*C*H—), 102.8 (—H*C*—OCH_2CH_2O), 198.9 (C=O). This compound was used directly in the preparation of **8**.

2-Ethylenedioxymethyl-5,8-dimethyl-1,2,3,4-tetrahydro-1-naphthol (**8**).

To a solution of 108.7 g (0.44 mol) of **7** and 300 mL of methanol at 10°C was added 50.2 g (1.32 mol) of sodium borohydride over a period of 20 min. Following stirring at 10°C for 1 h and refluxing for 2 h, water (300 mL) was added and the methanol removed under vacuum. The aqueous layer was extracted with chloroform (3 × 150 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated to give 111.4 g (100%) of **8** as a clear oil; ^1H NMR ($CDCl_3$) δ 1.6–2.0 (m, —CH_2CH_2—), 2.12 (s, —CH_3), 2.36 (s, —CH_3), 2.30–2.80 (m, —*CH*—,), 3.86 (m, —OCH_2CH_2O—), 4.96 (m, —*CH*—OCH_2CH_2O—), 6.90 (s, Ar—H). This compound was used immediately in the next reaction for the synthesis of **9**.

2-Formyl-3,4-dihydro-5,8-dimethylnaphthalene (**9**).

A solution of 111.4 g (0.44 mol) of **8** and 200 mL of methanol was added to 200 mL of 10% HCl, and the mixture refluxed for 5 h. The methanol was removed under vacuum and the aqueous mixture extracted with chloroform (3 × 150 mL). The combined extracts were dried over $MgSO_4$ and concentrated to a yellow oil. Distillation gave 67.3 g (82%) of **9**, bp 118–120°C (0.05 mm); ^1H NMR ($CDCl_3$) δ 2.17 (s, —CH_3), 2.32 (s, —CH_3), 2.42 (t, $^3J_{HH}$ = 7, —CH_2—), 2.63 (t, $^3J_{HH}$ = 7, —CH_2—), 6.94 (AB, $^3J_{HH}$ = 7 Hz, *o*—Ar—*H*), 7.38 (s, Ar—*CH*=C), 9.59 (s, —C*H*O); partial ^{13}C NMR ($CDCl_3$) δ 192 (—*C*HO); IR (neat) $\gamma_{C=O}$ 1670 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.06; H, 7.41.

2-Vinyl-5,8-dimethyl-3,4-dihydronaphthalene (**2**).

A solution of 58.6 mL (0.13 mol) of *n*-butyllithium (2.22 M in hexane) was added slowly to 48.0 g (0.13 mol) of methyltriphenylphosphonium bromide in 150 mL of anhydrous ether over 30 min. The mixture was stirred at room temperature for 4 h, and then treated dropwise with 25.0 g (0.13 mol) of **9**. Following stirring at room temperature for 7 h, the mixture was filtered through Celite. The filtrate was washed with water (3 × 100 mL), dried ($MgSO_4$), and evaporated to a yellow oil. Distillation gave 8.8 g (35%) of **2**, bp 88–91°C (0.05 mm); ^1H NMR ($CDCl_3$) δ 2.11 (s, —CH_3), 2.19 (s, —CH_3) 2.35 (t, $^3J_{HH}$ = 8, —CH_2—), 2.41 (t, $^3J_{HH}$ = 8, —CH_2—), 5.05 (d, $^3J_{HH}$ = 10, —CH=CH_2), 5.24 (d, $^3J_{HH}$ = 17 Hz, —CH=CH_2), 6.48 (m, —*CH*=CH_2), 6.53 (s, Ar—*CH*=C), 6.76 (s, Ar—*H*'). Due to the instability of this compound, it was reacted immediately with methylphosphonous dichloride to prepare **4**.

1,6,9-Trimethyl-2,3,4,5-tetrahydro-(1H)-benzo[g]phosphindole 1-Oxide (**4**).

A mixture of 7.1 g (38.6 mmol) of **2**, 3.6 mL (41 mmol) of methylphosphonous dichloride and 0.3 g of copper stearate in 35 mL of pentane was allowed to stand for 4 months in the dark. The solvent and excess reactants were then decanted from the oily precipitate, which was dissolved in 50 mL of chloroform and hydrolyzed with 100 mL water. The aqueous layer was neutralized with solid $NaHCO_3$ and then extracted with chloroform (3 × 75 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to give 4.1 g (43%) of **4** as a slightly yellow oil. Partial purification was effected by chromatography on silica gel with chloroform eluant, giving 2.6 g (27%) of **4** as a sticky, non-crystalline solid; ^1H NMR ($CDCl_3$) δ 1.66 (d, $^2J_{P-H}$ = 12 Hz, P—CH_3), 1.90–3.00 (m, 8H), 2.20 (s, —CH_3), 2.70 (s, —CH_3), 6.87 (s, Ar—*H*); ^{31}P NMR ($CDCl_3$) δ +64.0.

1,6,9-Trimethyl-1,2,3,4-tetrahydro-(1H)-benzo[g]phosphindole (**52**).

To a solution of 700 mg (2.8 mmol) of **4** and 50 mL benzene was added 0.2 mL (10.3 mmol) of trichlorosilane under a nitrogen atmosphere. The mixture was stirred at ambient temperature overnight and then hydrolyzed with excess 20% NaOH. The aqueous layer was extracted with benzene (2 × 20 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated to a slightly yellow oil. Kugelrohr distillation gave 500 mg (78%) of **52**, bp 105° (0.03 mm); ^1H NMR ($CDCl_3$) δ 1 10 (d, $^2J_{P-H}$ = 2 Hz, P—CH_3), 2.31 (s, —CH_3), 2.70 (s, —CH_3), 1.5–3.2 (m, 8*H*), 7.06 (s, Ar—H); ^{31}P NMR ($CDCl_3$) δ −6.6.

The methyl iodide salt was prepared from **52** by reaction with an excess of iodomethane. Recrystallization from methanol-pentane gave white crystals, mp 254–256°C; ^{31}P NMR ($CDCl_3$) δ +50.9.

Anal. Calcd for $C_{16}H_{22}IP$: C, 51.63; H, 5.96; P, 8.32. Found: C, 51.75; H, 5.87; P, 8.64.

1,6,9-Trimethyl-2,3-dihydro-(1H)-benzo[g]phosphindole 1-Oxide (**11**).

A mixture of 400 mg (1.6 mmol) of **4**, 12 mL of cumene, and 200 mg of 10% palladium on charcoal catalyst was heated at reflux for 48 h, and then filtered while hot. Removal of the solvent under vacuum gave 300 mg (76%) of **11** as a white solid, mp 82–85°C; ^{1}H NMR ($CDCl_3$) δ 1.90 (d, $^2J_{P-H}$ = 13 Hz, P—CH_3), 2.44 (m, —CH_2—), 2.76 (s, —CH_3), 3.28 (s, —CH_3), 3.30 (m, —CH_2—), 7.30–8.30 (m, Ar—*H*); ^{31}P NMR ($CDCl_3$) δ +64.0; M/e calcd for $C_{15}H_{17}OP$: 244.1016, found: 244.1014.

1,6,9-Trimethyl-2,3-dihydro-(1H)-benzo[g]phosphindole (**50**).

To a solution of 300 mg (1.2 mmol) of **11** and 25 mL of benzene was slowly added 1.0 mL of trichlorosilane. The mixture was heated at reflux for 2 h and then hydrolyzed with 30% NaOH. The organic layer was separated, dried ($MgSO_4$), and concentrated to give 200 mg (73%) of **50** as a slightly yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, $^2J_{P-H}$ = 4, P—CH_3), 1.90 (m, —CH_2—), 2.68 (s, 6—CH_3), 3.12 (d, $^5J_{P-H}$ = 2 Hz, 9—CH_3), 3.40 (m, —CH_2—), 7.20–8.04 (m, Ar—*H*); ^{31}P NMR ($CDCl_3$) δ −10.3. The methyl iodide salt of **50** was prepared by addition of 0.5 mL of iodomethane to a $CDCl_3$ solution. Concentration of the mixture gave the salt as a white precipitate, which was recrystallized from methanol to yield white crystals, mp 239–240°; ^{31}P NMR ($CDCl_3$) δ +50.1.

Anal. Calcd for $C_{16}H_{20}IP$: C, 51.98; H, 5.45; P, 8.38. Found: C, 51.75; H, 5.32; P, 8.28.

1-Methyl-4,5,6,7-tetrahydrophosphindole (**14**) *and its Quaternization and Oxidation.*

A solution containing 16.8 g (88 mmol) of cycloadduct **12** dissolved in 45 mL of benzene-methylene chloride (2:1) was cooled at 0°. Over a period of 30 min, 23 g (180 mmol) of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) in 10 mL of benzene was added dropwise. The mixture was allowed to stir for 10.5 h at room temperature. In a glovebag, the solution was washed with 1% HCl to eliminate any excess DBU. The organic phase was separated, dried ($MgSO_4$) and concentrated to give a light brown oil. This oil was Kugelrohr-distilled at about 60° (0.03 mm) to give 2.28 g (18%) of phosphole **14** as a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, P—CH_3), 1.6–1.9 (m, CH_2), 2.35–2.7 (m, allylic CH_2), 6.67 (*A*BX, $^2J_{P-H}$ = 22, $^3J_{HH}$ = 7, *H*C—2), 6.93 (*A*BX, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, *H*C—3); ^{31}P NMR ($CDCl_3$) δ −7.6.

An excess of methyl iodide was added to a small portion of the phosphole in petroleum ether. After 10 h the white solid which had precipitated was collected by filtration. This proved to be the monomeric 1,1-dimethyl-4,5,6,7-tetrahydrophosphindolium iodide **31**, mp 133.5–135°; ^{31}P NMR ($CDCl_3$) δ +41.1.

Anal. Calcd for $C_{10}H_{16}IP$: C, 40.85; H, 5.44; P, 10.54. Found: C, 41.05; H, 5.48; P, 10.75.

Another small portion of the phosphole was oxidized with aqueous H_2O_2 to give the dimer (**27**) of the phosphole oxide, mp 224–225°C: ^{31}P NMR ($CDCl_3$) δ +90.0 (bridging P) and +59.0, d of d, $^3J_{PH}$ = 36.4 Hz; ^{1}H NMR[29] ($CDCl_3$) δ 1.50 (d, $^2J_{PH}$ = 13, P—CH_3), 1.56 (d, $^2J_{PH}$ = 12 Hz, P—CH_3), 1.72–2.20 (m, CH_2, 16H), 3.06 (m, CH, 2H), 3.50 (m, H—3a), 6.04 (m, H—6); partial ^{13}C NMR ($CDCl_3$) δ 5.1 (d, $^1J_{CP-8}$ = 63.5, CH_3P—8), 17.0 (d, $^1J_{CP-1}$ = 69.0, CH_3P—1), 38.5 (d of d, $^1J_{CP-1}$ = 77.6, $^2J_{CP-8}$ = 10.9, C—7a), 40.1 (d of d, $^1J_{CP-8}$ = 59.3, $^2J_{CP-1}$ = 3.0, C—7), 51.5 (d, $^1J_{CP-1}$ = 69.6, C—4), 56.3 (d of d, $^2J_{CP-1}$ = 15.3, $^2J_{CP-8}$ = 11.6), 140.1 (d, $^2J_{CP-8}$ = 10.7, C—5), 122.3 (d of d, $^2J_{CP-8}$ = 10.8, $^3J_{CP-1}$ = 5.0, C—6).

Anal. Calcd for $C_{18}H_{26}O_2P_2$: C, 64.28; H, 7.79; P, 18.42. Found: C, 64.11; H, 7.89; P, 18.44.

1-Phenyl-4,5,6,7-tetrahydrophosphindole (**15**).

The cycloadduct **13** was prepared in the usual way[2] from phenylphosphonous dibromide and 1-vinylcyclohexane (27.4% after 14 days). A solution of 40.2 g (0.107 mol) of **13** in 175 ml of benzene-methylene chloride (3:1) at 0°C was treated over a 30-min period with a solution of 32 mL (0.214 mol) of DBU in 18 mL of benzene. The solution was allowed to warm to room temperature and stirred for 1 h. In a glove bag, the solution was washed with 1% HCl to eliminate any excess DBU. The organic phase was dried ($MgSO_4$) and concentrated to give a dark orange oil. This oil was Kugelrohr-distilled at 135°C (0.9 mm) to give 5.8 g (25%) of **15** as a clear liquid; ^{1}H NMR ($CDCl_3$) δ 1.4–1.95 (m, CH_2), 1.9–2.8 (m, allylic CH_2), 6.2–6.6 (ABX, P—*CH*=*CH*), 7.1–7.6 (m, Ar—H); ^{31}P NMR ($CDCl_3$) δ +10.5. Mass spectrum: M/e calcd for $C_{14}H_{15}P$: 214.0911; found, 214.0914.

1,1-Dibenzyl-4,5,6,7-tetrahydrophosphindolium Bromide and its Dimer (**39**) *from Potassium 4,5,6,7-Tetrahydrophosphindolide* (**37**).

To a solution containing 1.8 g (8.4 mmol) of phosphole **15** in 50 mL of dry THF was added 0.72 g (18 mmol) of freshly shaved potassium metal. (Caution: Extreme care must be exercised when using potassium metal as fires and detonation are both possible!) The reaction began immediately as observed by the appearance of the typically red phosphide anion. Within 30 min all the potassium metal had dissolved and the solution was deep red. An aliquot of the solution of **37** was removed for ^{31}P NMR analysis (δ +73.3[8]). Another aliquot was removed and reacted with an excess of benzyl bromide. The solution changed color from red to yellow, and a solid (KBr) precipitated within 5 min. The solid was filtered and the filtrate was concentrated to yield a yellow oil. Trituration of this oil with pentane gave a pale yellow solid which was a mixture of monomer **38** (δ ^{31}P +50.1, $CDCl_3$) and dimer **39** (δ ^{31}P +89.7 and +61.5, d of d, $^3J_{PP}$ = 36 Hz[9]).

*3-Methyl-4,5-dihydro-(3*H*)-benzo[e]phosphindole* (**19**).

To a slurry of 51.0 g (0.19 mol) of cycloadduct **16**[4] in 300 mL of benzene-methylene chloride (2:3) was added 57.8 g (0.38 mol) of DBU over a 1 h period. The solution was stirred for 48 h at room temperature and then poured into 10% HCl. The organic layer was separated, washed with water (2 × 150 mL) and dried over $MgSO_4$. Concentration gave a yellow oil which was chromatographed on neutral alumina with benzene as eluting agent to give 7.7 g (20%) of **19** as a clear oil; ^{1}H NMR δ 1.32 (s, P—C*H*$_3$), 2.40–2.92 (m, C*H*$_2$), 6.70 (d of d, $^2J_{P-H}$ = 37, $^3J_{HH}$ = 7 Hz, P—C*H*=C), 7.0–7.42 (m, Ar—H); ^{13}C NMR ($CDCl_3$) δ 6.9 (d, $^1J_{PC}$ = 17 Hz, P—*C*H$_3$); ^{31}P NMR ($CDCl_3$) δ −4.1. It was converted to the methyl iodide salt, prepared in pentane at room temperature (overnight), but this proved to be a mixture of monomer **32** (δ ^{31}P, $CDCl_3$, +48.3) and dimer **35** (δ ^{31}P[9] $(CD_3)_2SO$, d of d, +101.0 bridging P, and +57.5, $^3J_{PP}$ = 38.0 Hz).

Anal. Calcd for $C_{14}H_{16}IP$: C, 49.15; H, 4.71; P, 9.05. Found: C, 49.19; H, 4.52; P, 9.21.

The oxide dimer (**28**) was then prepared as a derivative. A solution of 5.5 g (27 mmol) of **19** in chloroform (50 mL) was shaken with 10% hydrogen peroxide (50 mL) at room temperature for 10 min. The organic phase was washed with 50 mL of water, 50 mL of saturated sodium thiosulfate and then dried ($MgSO_4$) and concentrated to give 5.9 g (99%) of dimer **28**. Recrystallization from toluene gave an analytical sample, mp 263–264°C (dec); ^{1}H NMR[29] ($CDCl_3$) δ 1.56 (d, $^2J_{PH}$ = 14, both P—C*H*$_3$), 1.96–2.60 (m, C*H*$_2$—C*H*$_2$), 3.32–3.50 (m, H—4, H—7a), 4.80 (m, H—3a), 6.76–7.55 (m, Ar-*H*, 8H); ^{13}C NMR ($CDCl_3$) δ 6.4 (d, $^1J_{PC}$ = 62, bridge P—*C*H$_3$), 17.7 (d, $^1J_{PC}$ = 71 Hz, 2-phospholene P—*C*H$_3$); ^{31}P NMR[9] ($CDCl_3$) δ +89.0 (bridge P) and +57.3 (d of d, $^3J_{PC}$ = 35.0 Hz).

Anal. Calcd for $C_{26}H_{26}O_2P_2$: C, 72.21; H, 6.06; P, 14.33. Found: C, 72.28; H, 5.94; P, 14.51.

*4,5-Dihydro-3-phenyl-(3*H*)-benzo[e]phosphindole* (**20**) *from Cycloadduct* (**17**).

A solution containing 28.1 g (66 mmol) of **17** (from $C_6H_5PBr_2$ and 1,2-dihydro-4-vinylnaphthalene[2], 45% after 7 days) in 150 mL of benzene-methylene chloride (3:1) was cooled to 0°C. Over a period of 30 min, 21.3 g (140 mmol) of DBU dissolved in 18 mL of benzene was added in 5 mL portions using a syringe. The solution was then stirred at room temperature for 1 h. In a glovebag the solution was washed with 1% HCl to eliminate any excess DBU. The organic phase was dried ($MgSO_4$) and concentrated to give a dark orange oil (7.2 g, 40%). The product (**20**) could not be purified by distillation. Although some purification was effected by chromatography on alumina with benzene as eluent; ^{31}P NMR ($CDCl_3$) δ +12.8; ^{13}C NMR δ 22.9 (d, $^2J_{PC}$ = 17.7 Hz, C—4) 28.9 (d, $^3J_{PC}$ = 5.5 Hz, C—5). The phosphole was converted to its oxide dimer **29** by shaking a chloroform solution with excess 10% H_2O_2. The chloroform layer, and several chloroform extracts of the aqueous layer, were washed with a few mL of saturated sodium thiosulfate and then dried ($MgSO_4$). Evaporation gave **29**, which was recrystallized from toluene, mp 229–230°C dec; δ ^{31}P NMR ($CDCl_3$) +77.8 (bridging P) and +51.8, d of d, $^3J_{PP}$ = 35.6 Hz).Analysis showed that there was one mole of toluene of solvation, confirmed by mass spectroscopy (m/e M-1 91).

Anal. Calcd for $C_{36}H_{30}O_2P_2C_7H_8$: C, 79.60; H, 5.57; P, 9.52. Found: C, 79.60; H, 5.90; P, 9.55.

*3-Methyl-7-methoxy-4,5-dihydro-(3*H*)-benzo[e]phosphindole* (**21**).

To 13.8 g (0.046 mol) of cycloadduct **18**[4] in 75 mL of benzene-methylene chloride (2:3) was added 18.0 g (0.12 mol) of DBU over a 1 h period at room temperature. After being stirred for 48 h, the solution was washed with saturated $NaHCO_3$ (2 × 100 mL) and water (2 × 100 mL). The separated organic phase was dried ($MgSO_4$) and concentrated to a brown oil which was purified by chromatography on neutral

alumina with elution by benzene to give 5.0 g (47%) of **21** as a white solid, mp 50–52°; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, P—CH_3), 2.78 (m, —CH_2—), 3.76 (s, O—CH_3), 6.56–7.52 (m, Ar—H); ^{13}C NMR ($CDCl_3$) δ 7.3 (d, $^1J_{PC}$ = 17.7 Hz, P—CH_3), 55.1 (s, O—CH_3); ^{31}P NMR ($CDCl_3$) δ −4.9.

Anal. Calcd for $C_{14}H_{15}OP$: C, 73.03; H, 6.57; P, 13.45. Found: C, 73.27; H, 6.73; P, 13.29.

A solution of 1.0 g (4.3 mmol) of **21** and 20 mL of benzene was treated with an excess of iodomethane and allowed to stand for 48 h. Filtration and recrystallization from ethanol gave 1.6 (100%) of a yellow mixture of monomeric methiodide **33** (^{31}P NMR, d_6-DMSO δ +46.4) and its dimer **36** (^{31}P δ +96.0, bridging P, and +52.6, d of d, $^3J_{PP}$ = 44 Hz).

Anal. Calcd for $C_{15}H_{18}IOP$: C, 48.47; H, 5.13; P, 8.33. Found: C, 48.30; H, 5.26; P, 8.10.

Dimer (**30**) *of 3-Methyl-7-methoxy-4,5-dihydro-(3H)-benzo[e]phosphindole 3-Oxide.*

A solution of 1.5 g (6.6 mmol) of phosphole **21** in 50 mL of chloroform was shaken with 50 mL of 5% hydrogen peroxide for 5 min at room temperature. The layers were separated and the organic layer was washed with water (2 × 25 mL), saturated sodium thiosulfate (30 mL) and then water (2 × 25 mL). It was dried ($MgSO_4$) and then concentrated under vacuum to give 1.7 g (99%) of dimeric oxide **30**, mp 234–237°C; ^{1}H NMR ($CDCl_3$) δ 1.46 (d, $^2J_{PH}$ = 12 Hz, P—CH_3), 1.80–2.72 (m, —CH_2—, 8H), 3.18–3.48 (m, —CH—, 2H), 3.63 (s, O—CH_3), 3.72 (s, O—CH_3), 4.64 (m, —CH^{29}—), 6.32–7.40 (m, Ar—H); ^{13}C NMR ($CDCl_3$) δ 6.2 (d, $^1J_{PC}$ = 61, P—CH_3), 17.7 (d, $^1J_{PC}$ = 71 Hz, P—CH_3), 55.07 (s, O—CH_3), 55.15 (s, O—CH_3), 159.25 (s, C—OCH$_3$), ^{31}P NMR ($CDCl_3$) δ +88.3 (bridging P) and +56.4 (d of d, $^3J_{PP}$ = 35 Hz); mass spectrum M/e calcd for $C_{28}H_{30}P_2O_4$: 492.1617. Found: 492.1612.

1-Phenyl-(1H)-benzo[g]phosphindole (**25**) *from 1-Phenyl-2,3-dihydro-(1H)-benzo[g]phosphindole 1-Oxide* (**22**).

To a solution of 1.5 g (5 mmol) of **22** in 35 mL of warm CCl_4 was added 0.96 g (5 mmol) of N-bromosuccinimide and 0.1 g of benzoyl peroxide. After being refluxed for 4 h, the mixture was cooled, filtered to remove the insoluble succinimide, and then washed with 1% NaOH to complete the removal of succinimide. The CCl_4 solution was dried ($MgSO_4$) and evaporated under vacuum to yield 1.5 g (78%) of crude bromide **23** as a mixture of diastereomers; ^{1}H NMR ($CDCl_3$) δ 2.6–3.4 (m, CH_2), 5.4–5.9 (m, CHBr), 7.0–8.1 (m, Ar—H); ^{31}P NMR ($CDCl_3$) δ major isomer + 50.1, minor isomer + 44.8; ^{13}C NMR ($CDCl_3$) major isomer δ 39.7 (d, $^2J_{PC}$ = 67.8, C—2), 45.5 (d, $^3J_{PC}$ = 7.9 Hz, C—3), minor isomer 40.7 (d, $^2J_{PC}$ = 64.7, C—2), 43.5 (d, $^3J_{PC}$ = 10.4 Hz, C—3).

The isomer mixture was converted to the corresponding phosphines (**24**) by treating 1.5 g (4.2 mmol) in 40 mL of dry benzene with 2.3 g (4.2 mmol) of $HSiCl_3$ in 10 mL of benzene over a period of 30 min. This solution was stirred for 1 h at room temperature and then refluxed for 12 h. The excess trichlorosilane was hydrolyzed at 0°C with 20% NaOH. The slightly basic aqueous layer was extracted with $CHCl_3$ (3 × 50 mL) and the organic phases were combined, dried ($MgSO_4$) and concentrated to yield 0.654 g (65%) of **24** as a yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.4 (m, CH_3), 3.5–3.65 (m, CHBr), 6.9–7.9 (m, Ar—H). Instability of the product prevented further characterization, and it was subjected directly to dehydrobromination with DBU (0.7 mL, 5 mmol) in benzene at 0°C, added over a 10-min period. The reaction was continued at room temperature for 4 h, and then terminated with a wash of 10% HCl. The benzene layer was dried ($MgSO_4$) and evaporated to give a yellow oil. Partial purification was accomplished on a silica gel column (elution with benzene) giving **25** as a colorless oil (0.4 g, 56%). The product showed no aliphatic protons in the ^{1}H NMR spectrum; ^{31}P NMR ($CDCl_3$) δ +0.1. An impurity with δ ^{31}P −5.4 could not be removed. Quaternization with benzyl bromide gave a solid salt, with δ ^{31}P ($CDCl_3$) +40.5, but all attempts to purify the substance by recrystallization from several solvents failed due to accompanying decomposition.

Attempted Preparation of 1-Phenyl-(1H)-benzo[g]phosphindole 1-Oxide (**42**).

A solution of 2.5 g (7.0 mmol) of bromo oxide **23** in benzene was cooled to about 5°C and treated with 1.1 mL (7 mmol) of DBU in benzene. The mixture was stirred for 20 min, and then warmed to room temperature. The precipitated DBU·HBr and any excess DBU were removed with a 1% HCl wash. Stripping the benzene left a yellow oil whose ^{1}H NMR spectrum showed no detectable aliphatic protons; ^{31}P NMR ($CDCl_3$) δ +40.2, +40.4 (overlapping), +40.8, +57.4, +58.0.

Reaction of 7-Methoxy-3-methyl-4,5-dihydro-(1H)-benzo[e]phosphindole (**21**) *with Hydrogen Chloride.*

An excess of hydrogen chloride gas was bubbled through a solution of 600 mg (2.6 mmol) of phosphole **21** and 5 mL of benzene. The mixture was stirred at room temperature for 3 h and then concentrated to

give 650 mg (84%) of 3-chloro-7-methoxy-3-methyl-1,2,4,5-tetrahydro-1(H)-phosphindolium chloride (**44**), ^{31}P NMR ($CDCl_3$) δ +103.0, as a yellow tar. Hydrolysis and work-up as for the synthesis of **3** gave 600 mg of 3-methyl-7-methoxy-1,2,4,5-tetrahydro-1(H)-phosphindole-3-oxide (**45**) having ^{1}H, ^{13}C and ^{31}P NMR spectra identical to reported values[4].

Reaction of 1-Methyl-4,5,6,7-tetrahydro-(1H)-phosphindole (**14**) *with Hydrogen Chloride.*

An excess of hydrogen chloride gas was bubbled through a solution of 1.0 g (6.6 mmol) of phosphole **14** and 20 mL of benzene. A yellow oil separated and the supernatant liquid was decanted. The ^{31}P NMR ($CDCl_3$) showed a major signal, presumably for 2,3,4,5,6,7-hexahydro-1-methyl-1-chloro-1(H)-phosphindolium chloride at δ +119.0. The mixture was hydrolyzed and extracted with $CHCl_3$; the extract was analyzed directly by ^{31}P NMR and found to be a 70:30 mixture of 2,3,4,5,6,7-hexahydro-1-methyl-1(H)-phosphindole-1-oxide (**46**),[2] ^{31}P NMR ($CDCl_3$) δ +65.6 and 2,4,5,6,7,7a-hexahydro-1-methyl-1(H)-phosphindole 1-oxide (**47**),[2] ^{31}P NMR ($CDCl_3$) +68.6 (cis), +61.5 (*trans*).

Reaction of 7-Methoxy-3-methyl-4,5-dihydro-(1H)-benzo[e]phosphindole (**21**) *with Deuterium Chloride.*

Anhydrous deuterium chloride was passed through a benzene solution of phosphole **21**. Work-up as for the HCl reaction with **21** gave the tetrahydrophosphindole oxide. The ^{13}C NMR spectrum ($CDCl_3$) had the doublet for C—1 (δ 26.9, $^2J_{PC}$ = 6.2 Hz[19]) of approximately half the intensity of the protonated form (**45**), relative to the adjacent doublet for C—5 as intensity reference (δ 28.3, J_{PC} = 6.1 Hz). Signals due to ^{2}D—^{13}C coupling were not observable. The downfield half (at 26.3 ppm) of the C—2 doublet also showed reduced intensity, but the upfield half (22.5 ppm) seemed unchanged in intensity.

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29. For confirmation of the assignment of H-3a, which is strongly deshielded by P=O, see Ref. 14.