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SYNTHESIS OF 1,2-DIHYDRO-1-PHENYLINDENO[2,1-*b*]-PHOSPHOLE AS A POTENTIAL PRECURSOR OF A PHOSPHAPENTALENYL ANION[1]

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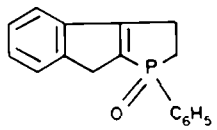
Abstract—3-Vinyl-1H-indene was employed for the first time as a diene in the McCormack cycloaddition with phenylphosphonous dibromide. The adduct was heated to rearrange the double bond, and on hydrolysis there was obtained 1,2,3,8-tetrahydro-1-phenylindeno[2,1-*b*]phosphole 1-oxide. The bromohydrin was formed with NBS in water; elimination of a molecule of HBr and of H_2O gave 1,2-dihydro-1-phenylindeno[2,1-*b*]phosphole oxide (I). The phosphine was formed by de-oxygenation with $HSiCl_3$-pyridine and has the proper saturation for formation of a benzophosphapentalenyl anion on abstraction of a proton. However, mixtures of products were obtained with various bases, and with *t*-butyllithium a 1,4-addition reaction occurred to form a compound identified as 3-*tert*-butyl-1,2,3,8-tetrahydro-1-phenylindeno[2,1-*b*]phosphole (isolated as the 1-oxide). Indications were obtained that *n*-butyllithium and lithium dicyclohexylamide also add to the diene unit of I. Another 1,4-addition (of the equivalent of H_2 occurred with I when the $HSiCl_3$ deoxygenation was attempted in the absence of pyridine. Products of this study were characterized by ^{31}P and ^{13}C NMR spectrometry. A new ring effect on ^{31}P shifts was noted; relative to cyclohexano[b]phosphol-2-ene derivatives, cyclopentano[b]phosphol-2-ene consistently have shifts displaced by 10–15 ppm upfield.

Until recently, trivalent phosphorus was largely ignored as a possible contributor to the establishment of a cyclic delocalized system. However, numerous studies[2] on the 5-membered phosphole ring have given some support to the notion that this system ought to be included along with the better known thiophene-pyrrole-furan series in considerations of this property. No direct determination of the resonance energy of a simple phosphole has been made, and it seems doubtful if the system will have a greater value than that of the rather weakly aromatic furan. Other π-excessive delocalized ring systems can be conceived of for phosphorus, and indeed we recently reported on the synthesis and properties of a derivative of the 9-membered phosphonin system[3] with ten π-electrons. Unfortunately, this derivative possessed two fused benzo groups which contributed to out-of-plane distortion of the ring and hindered orbital overlap. No example is yet known of the ten π-electron system resulting from substitution of trivalent phosphorus for an anionic carbon in the pentalenyl dianion system, although several examples exist of thia-, aza-, and oxa-derivatives.[4] We have therefore initiated work aimed at preparing suitable phosphine precursors (1 and 2) of such anions. In our first synthesis, we have prepared a benzo derivative 3 of system 1. This compound has not yet been successfully converted into the anion, due in some cases to interference by a competing reaction with the basic reagents used. This reaction, a nucleophilic 1,4-addition to the diene system of 3, is of interest in its own right, as is the accomplishment of the first synthesis of the indenophosphole ring system, represented by 3, which has an uncommon pattern of unsaturation. Our results are presented in this paper. Some other unusual reactions were encountered during the synthesis and are also described.

The synthetic scheme leading to 3 can be viewed as consisting of two phases. The tricyclic skeleton was first established in the form of phospholene oxide 4, and the phosphine 3 containing the requisite unsaturation was then constructed. Each phase of the synthesis is discussed below.



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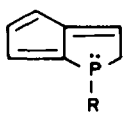
Construction of the tricyclic skeleton (*Scheme I*). The highly versatile McCormack cycloaddition of a diene with a P(III) halide was used to construct the requisite tricyclic system. This reaction required the ready availability of diene 6, a substance previously prepared by Bergamasco and Porter.[5] Their two-step sequence of the addition of vinylmagnesium bromide to 1-indanone, followed by dehydration of the resulting tertiary alcohol 5 with iodine-quinoline, provided the diene. Early in our work we discovered that the quality of this diene was crucial to success in the McCormack cycloaddition; a further complication is the pronounced tendency for the diene to polymerize. Best results were obtained when the diene was purified and mixed with the P(III) halide on the same day as it was prepared. The preferred pro-



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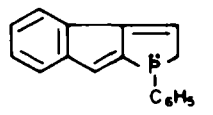

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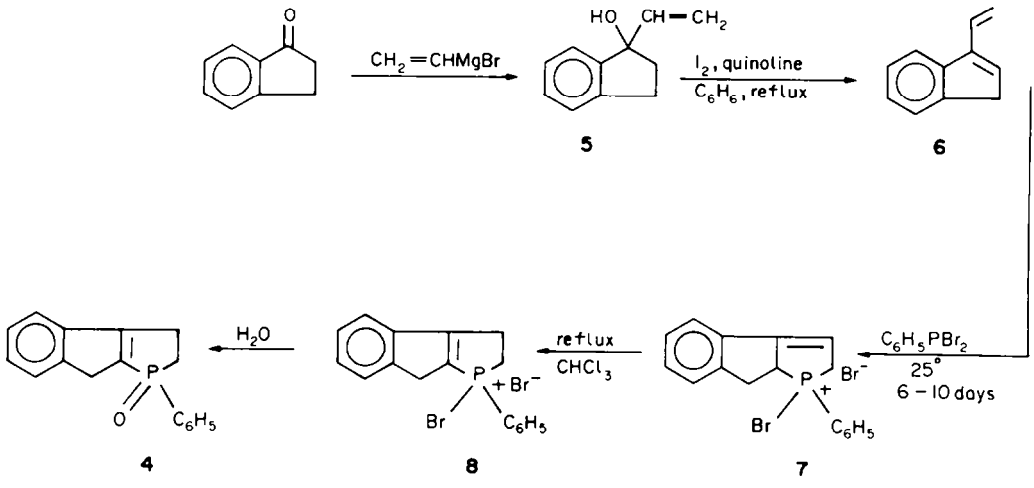
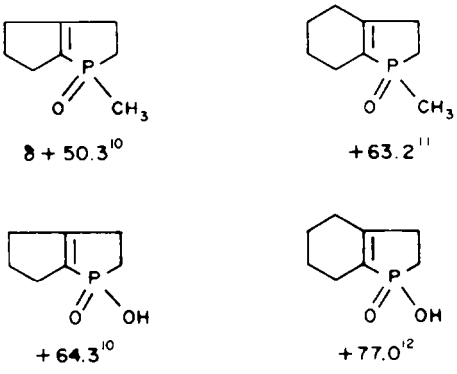


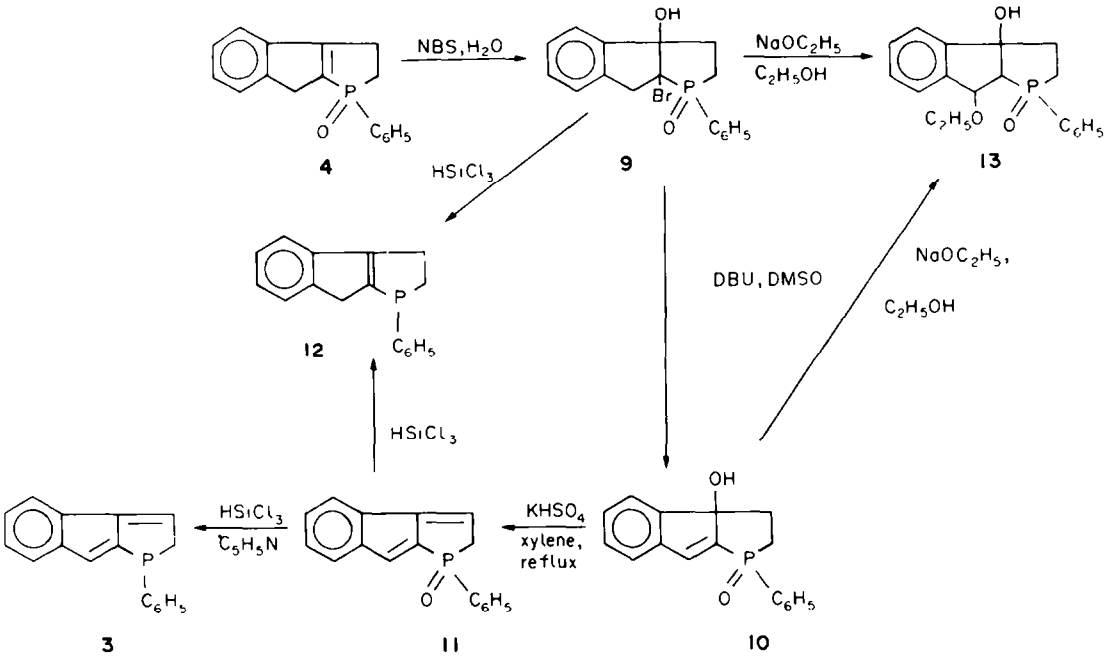
cedure for purifying the diene consisted simply of filtering the solution through a pad of dry silica gel, followed by vacuum-stripping of the solvent. Distillation is to be avoided, since polymerization is extensive. The procedure described in the Experimental Section, which has been repeated several times, is reasonably reliable, but minor deviations are likely to reduce the yield.

Diene **6** reacted very slowly with $C_6H_5PCl_2$, although the desired phospholene derivative with the double bond in the position shown in **4** was obtained. It was, however, more practical to use the faster reacting $C_6H_5PBr_2$, even though this reagent is known[6] to allow the double bond to remain in its initially established position as in **7**. Heating cycloadduct **7** in chloroform caused complete rearrangement to **8**, and hydrolysis then gave the desired phospholene oxide **4**. The success of the rearrangement of **7** to **8** is highly dependent on the quality of the cycloadduct; best results were obtained when the cycloadduct isolated was a pale yellow powdery solid, as is formed with high-purity diene. Occasionally the cycloadduct formed as an orange, sticky solid; yields of rearranged product were then low. A dark-brown, glassy form of the adduct was unsuitable and was discarded when obtained.

Phospholene oxide **4**, a crystalline solid, was readily characterized by NMR spectrometry. The position of the double bond was confirmed by the absence of olefinic proton signals. The ^{13}C NMR spectrum possessed three signals for sp^3 carbons, with only one having the large coupling associated with direct attachment to ^{31}P(δ 31.79, J_{PC} = 73.2 Hz). The C-3 and C-8 signals appeared at δ 23.26 (J = 2.9) and 34.39 (J = 10.7), respectively. These assignments were made by comparison with the spectrum of indene,[7] whose methylene carbon is markedly deshielded (δ 38.9). The slight upfield shifting in the spectrum of **4** can be attributed to γ-effects arising from the substituents on P, an effect we have observed in other systems.[8] The double bond carbons were easily distinguished from the two sets of aromatic carbons; conjugation with P = O causes pronounced downfield shifts of β-carbons,[9] here to δ 166.92 (J = 36.1), while α-carbons are recognized by large one-bond coupling (δ 138.97, J = 106.5). Some tentative assignments to aromatic carbons are given in the Experimental Section. The ^{31}P NMR signal for **4** appeared at δ 47.2; this value is substantially more upfield than might have been expected from comparison to the homolog with a 6-membered (δ 58.6[8]), rather than five-membered ring, fused to the 2-phospholene unit. This apparent ring effect has not been noted before, but on re-examining some published data other examples can be found.



Construction of the double bond system (*Scheme II*). The desired P-oxide with the proper location of unsaturation for conversion into a phosphapentalene is shown as **11**. Its construction from **4** commenced with the formation of bromohydrin **9** by reaction with *N*-bromosuccinimide in water. The orientation in the addition to the double bond had to be confirmed by the chemical properties of the product since its general insolubility hindered direct characterization by ^{13}C NMR spectroscopy. Thus, dehydrobromination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in DMSO gave an unsaturated alcohol (by IR and ^1H NMR) that clearly had the double bond in the position shown in **10** as seen from its NMR spectral properties. Only one of the two possible diastereoisomers was obtained. The characteristic benzylic CH_2 ^1H NMR signal of **4** was no longer present and the ^{13}C NMR spectrum had the carbinol carbon in the expected region (δ 90.52, J_{PC} = 26.4 Hz). The other sp^3 carbons had the expected characteristics, as did the sp^2 carbon (C-8a) attached directly to P (δ 150.39, J_{PC} = 99.6 Hz). However, the usual strong deshielding of a β-carbon was suppressed in this case by the influence of the benzo group; in indene, the corresponding carbon is noticeably shielded (tentatively assigned[7] to δ 120.9 or 123.6) and the conjugation with P = O does not shift this signal below δ 150. No definite assignment has been



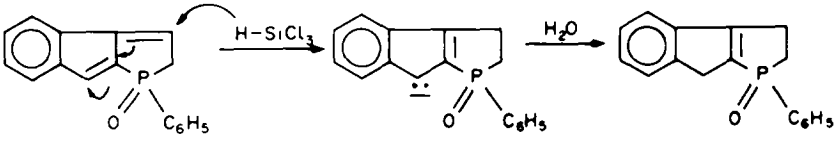
made to this carbon; the spectrum is complex and the three downfield doublets that can be recognized (δ 148.98, J = 8.79; 141.63, J = 13.6; 141.50, J = 7.8; coupling confirmed at a different field) can variously be assigned to C-3b, C-7a, or C-8. However, these characteristics are quite in accord with the assigned structure; the alternative structure (from the inverted positions of Br and OH in **9**) would have the double bond between C-3 and C-3a, which is ruled out. The ^{31}P NMR signal was displaced significantly upfield (from +47.2 in **4** to +33.9 in **10**). This shift effect was discovered in previous work[8] to be quite characteristic for the structural unit resulting from attachment of the phosphorus atom to an sp^2 carbon located at the ring fusion position. The combination of this effect with that arising from the 5-membered ring makes this shift appear at remarkably high field. The double bond effect has been noted[8] to conform with the empirical observation that shielding is increased as ^{31}P approaches an eclipsed relation with β-CH bonds, either on sp^2 or sp^3 carbon.[13]

The double bond of **10** was found to be very sensitive to nucleophilic attack. Thus, when the dehydrobromination of **9** to give **10** was first attempted with sodium ethoxide in ethanol, the product **13** was found by ^{1}H and ^{13}C NMR to contain an ethoxy group which presumably was introduced by Michael addition to the initially formed **10**. It was later shown that the Michael product could indeed be obtained in 85% yield by subjecting a pure sample of **10** to the same set of conditions. Reduction of the phosphine oxide group in bromohydrin **9** with trichlorosilane in an attempt to form the corresponding phosphine, so as to give a more soluble and spectrally characterizable derivative, was accompanied by complete loss of the elements of HO–Br, forming phosphine **12** instead. This compound, δ ^{31}P 12.45, was identified by its conversion into oxide **4** on treatment with H_2O_2. This reaction appears to be related to the debromination of vicinal dibromides with $HSiCl_3$, first encountered in earlier work in this laboratory[14] as a side reaction in the deoxygenation of 3,4-dibromophospholane oxides. Alcohol **10** reacted readily with numerous dehydrating agents (iodine–quinoline, $POCl_3$–pyridine, *p*-toluenesulfonic acid, H_2SO_4, DMSO, etc.), to give complex mixtures. However, the product mixture from refluxing a xylene solution of **10** over anhydrous $KHSO_4$ was more tractable, and the desired product was found to be remarkably easily separated from all of the rest by dry-column chromatography. Simply placing the dehydration mixture on silica gel, and eluting with chloroform, gave the desired product **11** as a cream-colored, analytically pure solid on removal of solvent. Yields as high as 40% have been obtained by this procedure. The product undergoes some minor decomposition on attempted recrystallization but is stable indefinitely at room temperature in the solid state, and gives spectral data that confirm the structural assignment. The ^{31}P NMR shift remains on the relatively high-field side (δ +29.2), proving that the original double bond had not migrated. ^{13}C NMR confirmed the structure by showing only one sp^3 carbon to be present, with the characteristically large coupling to be expected from direct attachment to ^{31}P (δ 41.61, J_{PC} = 74.2 Hz). The olefinic sp^2 carbons were not easily distinguished from the aromatic carbons on this complex spectrum; only C-8a is assigned with confidence (δ 137.02, J = 94.7), and again as in **10** the signal for the carbon β- to P = O was upfield-shifted and not clearly recognized. Integration of the ^{1}H NMR spectrum also indicated only one CH_2 group to be present, a multiplet at δ 3.40–3.68. One of the two olefinic protons was adequately resolved from the large, complex aromatic region to be detectable; it appears as a doublet from ^{31}P coupling (δ 6.94, $^3J_{PH}$ = 26 Hz) with further small splitting. These properties suggest assignment to the proton on C-3.

Structure **11** represents the first known 3-phospholene with an exocyclic double bond at the 2-position. It is a tautomeric form of a phosphole oxide, but we have detected no tendency for rearrangement to occur to the phosphole oxide. Such a structure would have quite different spectral properties from those reported for **11**.

Deoxygenation of **11** occurred smoothly with trichlorosilane–pyridine, forming phosphine **3** in 88% yield. This phosphine, first obtained as an oil, crystallized on standing and gave the correct elemental analysis. That no rearrangement of the double bond accompanied the reduction was established by oxidizing the phosphine back to the starting oxide **11** with H_2O_2. The ^{31}P NMR shift of phosphine **3** (δ −39.3) had the same relatively upfield displacement as seen in the corresponding oxide; a monocyclic model for comparison would be 1-phenyl-3-phospholene, δ (neat) 25.3.[15] The ^{13}C NMR spectrum was too complex in the sp^2 region to be readily interpreted; the single sp^3 carbon was the expected doublet (δ 42.69, J = 14.3 Hz).

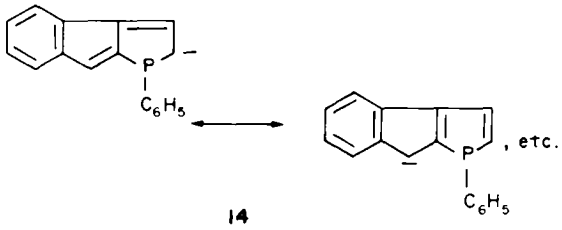
Accompanying phosphine **3** from the $HSiCl_3$–C_5H_5N reduction was a small amount (up to 10%) of another phosphine product with a ^{31}P NMR shift of δ −12.45. This shift, as well as that of the oxide formed with H_2O_2 (δ +47.2), indicated the product to be the previously characterized **12** (which forms oxide **4**, δ +47.2). It was also observed that, if the pyridine were omitted, the trichlorosilane reduction gave exclusively this dihydro product. This reducing property of $HSiCl_3$ towards a diene appears to be a new reaction. It may be specific, however, to the particular system used here where a benzo group is also present, for if $HSiCl_3$ can be viewed as a hydride donor to the β-position of oxide **11**, then the negative group placed on the organic molecule will be specially stabilized by the benzo group and constitute a driving force.



This mechanism is not established, however. Pyridine may act by diminishing the hydride-transferring power of trichlorosilane through complex formation. It will be seen in the next section that this diene system has other strong tendencies to undergo 1,4-additions, and the phosphorus function plays no necessary role.

Reaction of phosphine **3** *with bases.* With the expectation that a proton α- to phosphorus in phosphine **3** could be extractable with strong base, forming the stabilized phosphapentalenyl anion **14**, the phosphine was treated with a series of bases.

A reaction occurred at room temperature with a suspension of NaH in DMSO, and with KOC_4H_9-*t* in *t*-C_4H_9OH, but each product was a dark tar having



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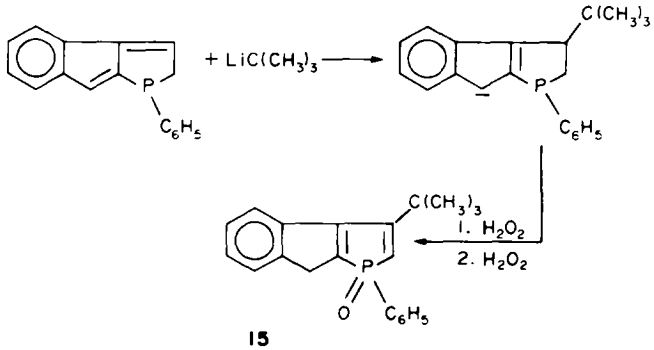
numerous ^{31}P NMR signals. Quenching the solutions with water, followed by oxidation with H_2O_2, gave equally forbidding products. Since none of the starting phosphine oxide **11** was recovered, it was clear that the bases had done more than just remove an α-proton. With *tert*-butyl lithium at room temperature, however, a definite reaction product could be isolated after oxidative quenching of the mixture. The product proved to be the 1,4-addition product **15**, isolated in 30–40% yield as a single diastereoisomer.

The elemental and mass spectral analyses proved that *tert*-butyl addition had occurred. The 1,4-orientation of the addition was clearly revealed by the ^{13}C NMR spectrum, which had signals for a double bond conjugated to P = O just as seen in the corresponding non-butyl compound **4**. These signals (C-3a, δ 167.92, J = 34.2 Hz, and C-8a, 141.22, J = 104.5) leave no doubt as to the position of the double bond. The "indene CH_2" (C-8) was also in the expected position (δ 34.1, J = 12.2); this prompted the assignment of the *t*-butyl group to C-3, and this was supported by the displacement of the C-3 signal in **4** (δ 23.26) to δ 48.81. This assignment was further supported by showing that C-8 acquired a hydrogen in the quenching of the anion by substituting D_2O for H_2O in the quench; the C-8 signal was appropriately reduced in magnitude by the diminution of the nuclear Overhauser effect. Finally, the ^1H NMR spectrum confirmed that a 2H benzylic group was present (δ 2.8–3.7) superimposed upon a low lying C-3 1H multiplet; the other 2H-multiplet (δ 2.4) was assigned to C-2. In the deuterated compound, only the downfield multiplet exhibited a change. When double irradiation was carried out at δ 2.4, the downfield multiplet showed only very minor changes and these were in the underlying C-3 methine multiplet, proving that the two 2H multiplets were too remote to be coupled.



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The propensity for 1,4-addition to the diene system, as assisted by the benzo group acting to stabilize the initially formed anion, thus is again seen, and in the present case takes precedence over anion formation by proton–extraction. The same event seems to take place at lower temperatures; *n*-butyl lithium or lithium dicyclohexylamide were employed at −20° and while definite products have not been isolated from the complex mixtures, their spectral characteristics in each case suggested some incorporation of the anion in the molecule. The phosphine group is probably not playing a role in these additions; the benzo group appears to be responsible, and thus is clearly an undesirable structural feature when present in a molecule designed to test the concept of anion formation and its stabilization by cyclic delocalization. In any future work, the parent bicyclic system should be sought as the model for anion formation.

EXPERIMENTAL

General. Melting points were obtained on a Mel-Temp apparatus and are corrected. Proton NMR spectra were recorded using JEOL MH-100 (100 MHz), JEOL FX 90Q (90 MHz) or IBM NR 80 (80 MHz) Fourier Transform instruments. Proton chemical shifts (on $CDCl_3$ solutions unless otherwise stated) are expressed in ppm (δ) downfield relative to an internal tetramethylsilane standard, and were recorded at ambient temperatures unless otherwise noted. Proton noise-decoupled ^{13}C NMR spectra were obtained using a JEOL FX 90Q instrument at 22.5 MHz using $CDCl_3$ as both solvent and internal lock, with TMS as internal standard against which downfield chemical shifts are expressed in parts per million. In certain instances, the shifts of partially superimposed ^{13}C signals and the magnitudes of some P–C couplings were checked using a Bruker WH 250 instrument at 62.5 MHz or a JEOL FX-60 at 15.0 MHz. ^{31}P NMR spectra (FT proton noise-coupled) were obtained at 36.4 MHz using either hexafluorobenzene in a 3 mm coaxial insert as an external lock (Bruker HFX-10) or deuteriochloroform as an internal lock (Bruker HXF-10 and JEOL FX 90Q). Chemical shifts of ^{31}P NMR spectra are expressed in ppm relative to external 85% phosphoric acid, using the sign convention of (+) for signals downfield from that of the standard. Mass spectra were recorded at 80 eV using an Hitachi Perkin–Elmer model RMU-7 double-focusing mass spectrometer fitted with a direct heated inlet system. Elemental analyses were carried out by MHW Laboratories, Phoenix, Arizona. All procedures involving trivalent phosphorus were carried out in an oxygen-free atmosphere of dry nitrogen. Column chromatography employed silica gel, Woelm activity 3, DCC.

1-*Vinyl*-1-*indanol* **5**. This alcohol was prepared by a modified literature[5] method in the following manner. All operations were conducted under dry N_2. Vinyl bromide (54.6 g, 0.51 mol) in dry THF (100 ml) was added dropwise at room temperature to a vigorously stirred suspension of magnesium turnings (12.4 g, 0.51 g-atom) in dry THF (250 ml) to which a crystal of iodine had been added. The reaction, once started, was extremely vigorous and occasional ice-bath cooling was necessary. After completion of the dropwise addition, the reaction mixture was stirred for 1.5 h and then cooled to −5°. To the cooled solution was added dropwise a solution of 1-indanone (45.1 g, 0.34 mol) in THF (150 ml) over 2 h. After the addition was completed, the mixture was allowed to warm slowly to room temperature and the resulting solution was stirred for 12 h. It was found that these mild conditions kept side reactions, such as aldol-type condensations, to a minimum. The solution was then chilled in an ice bath and quenched very slowly with saturated aqueous NH_4Cl (250 ml) followed by sufficient H_2O (about 100 ml) to dissolve any precipitated inorganic material. The organic and aqueous layers were extracted with ether (4 × 100 ml). All organic fractions were combined, dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to give 52.8 g (96%) of the crude alcohol as a clear, yellow-orange, mobile oil; ^1H NMR δ 2.06–2.37 (m, 2H, $-CH_2-$), 2.73–3.15 (m, 2H, benzylic $-CH_2-$), 2.86 (broad s, 1H, OH), 5.05–5.30 (m, 2H, $-CH=CH_2$), 5.93–6.21 (m, 1H, $-CH=CH_2$), 7.19–7.23 (m, 4H, aromatic). Further purification of the alcohol was not attempted and it was used immediately for the preparation of 3-vinyl-1H-indene **6**.

3-*Vinyl*-1*H*-*indene* **6**. As with the precursor (**5**), this compound was prepared by modified literature methods.[5] Crude **5** (52.8 g, 0.33 mol), used within 1 h of its isolation, was dissolved in dry benzene (800 ml) in which quinoline (2.5 ml) and iodine (*ca.* 0.5 g) had been dissolved. The mixture was then heated under reflux until evolution of H_2O had ceased (1.75 h) as measured by a Dean and Stark apparatus. The quantity of H_2O evolved (*ca.* 6 ml) indicated virtually quantitative dehydration. The dark solution was cooled to room temperature and filtered through a thick pad (*ca.* 15 cm × 4 cm) of silica gel to remove traces of unreacted **5**, 1-indanone carried through from the previous synthesis, and some dark impurity. The resulting medium yellow solution was then evaporated under reduced pressure to give 42.0 g (90%) of the crude diene as a brownish-yellow viscous oil which, from spectroscopic examination, appeared to be reasonably free of impurities; ^1H NMR δ 3.34 (broad s, 2H, $-CH_2-$), 5.24–5.89 (m, 2H, $-CH=CH_2$), 6.46 (t, 1H, $-CH-CH=C$, $^3J_{H-H} = 2$ Hz), 6.61–6.90 (m, 1H, $-CH=CH_2$), 7.10–7.63 (m, 4H, aromatic). This spectrum did show a very weak complex multiplet due to polymeric impurities (δ 2.30–3.10), the intensity of which increases fairly rapidly over a few hours while the intensity of the broad peak at δ 3.34 decreases. This instability[5] led to the use of the diene within 1 h of its isolation.

1,2,3,8-*Tetrahydro*-1-*phenylindeno*[2,1-*b*]*phosphole* 1-*Oxide* **4**. Within 1 h of its isolation, the 3-vinyl-1H-indene (42.0 g, 0.30 mol) was dissolved in *n*-hexane (150 ml) in which copper stearate (2.5 g) had been suspended. Phenylphosphonous dibromide (80 g, 0.30 mol) was added and the resulting slightly turbid liquid was sealed under dry N_2 in an amber bottle and set aside at room temperature. Deposition of crystalline material began within 1 h and, after 8 days, the mixture became completely solid. The solid was then broken up, filtered under N_2, washed with *n*-hexane (*ca.* 500 ml), and dried by drawing dry N_2 through the very pale buff powdery mass to give 63.0 g (52%) of a mixture of the expected isomeric 3-phospholenium and 2-phospholenium McCormack adducts (**7** and **8**). Yields of up to 75% may occasionally be obtained but the above result is more typical. This mixture of adducts was converted into the 2-phospholenium isomer by heating under reflux a $CHCl_3$ (500 ml) solution (red) under N_2 for 42 h, during which time the solution became pale orange. Hydrolysis was effected by pouring the cooled solution slowly into saturated aqueous $NaHCO_3$ (300 ml) followed by the addition of sufficient solid $NaHCO_3$ in small portions to neutralize residual acids. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 125 ml). The organic layer and extracts were combined, dried ($MgSO_4$) and evaporated to give a viscous, medium brown oil (occasionally a dark grey solid). To this oil was added cold ethyl acetate (80 ml) and, after a few minutes, a dense mass of pale buff needles slowly separated out. Filtration and evaporation gave a small second crop and a total yield of 25.5 g (62% based on adduct) of **4**: m.p. 161–163° (recrystallization of a sample from hot ethyl acetate gave colourless needles but no change in mp); ^1H NMR δ 2.40–2.85 (m, 2H, $-P-CH_2-$), 2.85–3.35 (m, 2H, $-CH_2-$), 3.35–3.66 (m, 2H, benzylic $-CH_2-$), 7.15–7.88 (m, 9H, aromatic). ^{31}P NMR δ +47.18. ^{13}C NMR ($CDCl_3$ δ 23.26 (C-3, $J = 2.9$ Hz), 31.79 (*C*-2, $J = 73.2$), 34.39 (C-8, $J = 10.7$), 138.97 (*C*-8*a*, $J = 106.5$), 139.97 (C-7*a*, $J = 16.6$), 149.92 (C-3*b*, $J = 7.8$), 166.92 (*C*-3*a*, $J = 36.1$); singlets at 120.96, 124.86, 126.77, 126.86 for benzo carbons; phenyl signals unresolved. (Found: C, 76.52; H, 5.75; P, 11.47. Calc. for $C_{17}H_{15}OP$: C, 76.69; H, 5.64; P, 11.65%).

8*a* - *Bromo* - 1,2,3,3*a*,8,8*a* - *hexahydro* - 3*a* - *hydroxy* - 1 - *phenylindeno*[2,1-*b*]*phosphole* 1-*oxide* **9** *and attempted HSiCl*$_3$ *reduction.* To a solution of 9.0 g (0.034 mol) of **4** in THF (130 ml) and H_2O (50 ml) was added, with vigorous magnetic stirring, freshly recrystallized *N*-bromosuccinimide (7.0 g, 0.039 mol). The colourless solution immediately became a clear yellow and, after about 2 h, began to deposit a finely divided white solid until the reaction was apparently complete (22 h). The precipitate was

collected by filtration, washed with a little acetone followed by ether to remove a faint yellow colour, and then dried under reduced pressure to give the bromohydrin **9** (4.6 g, 38%; on other occasions, yields approached 60%) as a fine white powder of m.p. 228–230° dec. Recrystallization of a very small sample from hot ethanol gave the same mp; the most reproducible mp data were obtained by preheating the block to 200°; IR (Nujol) ν_{OH} 3150, $\nu_{P=O}$ 1160 cm^{-1}; low solubility prevented acquisition of NMR data. (Found: C, 56.17; H, 4.53; Br, 21.82; P, 8.62. Calc. for $C_{17}H_{16}BrO_2P$: C, 56.25; H, 4.44; Br, 22.01; P, 8.53%).

Attempted reduction of this product with trichlorosilane led to both P=O bond reduction and elimination of HOBr giving 1,2,3,8-tetrahydro-1-phenylindeno[2,1-*b*]phosphole **12** (^{31}P NMR δ −12.45) characterized as the corresponding oxide **4** (^{31}P NMR δ +47.18).

8 - *Ethoxy* - 1,2,3,3*a*,8,8*a* - *hexahydro* - 3*a* - *hydroxy* - 1 - *phenylindeno*[2,1-*b*] *phosphole* 1-*oxide* **13**. To absolute ethanol (25 ml) was added sodium metal (0.04 g, 0.0017 g-atom). After dissolution of the metal, the bromohydrin **9** (0.60 g, 0.0017 mol) was added rapidly and the mixture was then heated, with stirring, to 90°. The temperature was maintained at 90° for 20 min during which time some darkening of the solution occurred. After cooling the mixture at room temperature, it was poured onto cracked ice (50 g) and, after melting of the ice was complete, extracted with $CHCl_3$ (3 × 50 ml). The $CHCl_3$ extracts were combined, washed several times with water and then brine, dried ($MgSO_4$) and evaporated to give a tan solid. This was recrystallized from ethyl acetate to give 0.4 g (72%) of the ethoxy compound **13** as colourless plates: mp 232°; ^1H NMR ($CDCl_3$) δ 1.10 (t, 3H, $-OCH_2CH_3$, $^3J_{H-H}$ = 7 Hz), 1.68–2.64 (m, 5H, ring-CH_2– and –CH–P=O), 3.06–3.76 (m, 2H, $-OCH_2CH_3$), 4.62 (s, 1H, OH), 5.24 (d of d, 1H, $-CHOCH_2CH_3$, $^3J_{P-H}$ = 11 Hz, $^3J_{H-H}$ = 5 Hz), 7.17–7.97 (m, 9H, aromatic). ^{31}P NMR ($CDCl_3$) δ + 56.30. ^{13}C NMR at 15.0 MHz ($CDCl_3$) δ 15.29 (CH_3CH_2, s), 30.60 (C-2, J = 64.4 Hz), 36.0 (C-3, J = 3.9), 59.95 (C-8a, J = 66.3), 65.47 ($-CH_2O$, s), 89.4 (C-3a, J = 18.9), 141.78 (C-7a or C-3b, J = 6.3), 145.18 (C-7a or C-3b, J = 5.9); benzo and phenyl carbons not assigned; C-8 not observed. Mass spectra *m/e* 328 (M+). IR (Nujol) ν_{OH} 3200 (strong, broad), $\nu_{P=O}$ 1165 cm^{-1}. (Found: C, 69.37; H, 6.43. Calc. for $C_{19}H_{21}O_3P$: C, 69.50; H, 6.45%).

1,2,3,3*a* - *Tetrahydro* - 3*a* - *hydroxy* - 1 - *phenylindeno*[2, 1 - *b*]*phosphole* 1-*oxide* **10**. The bromohydrin **9** (5.1 g, 0.014 mol) was suspended with vigorous magnetic stirring in DMSO (120 ml) to which had been added DBU (4.2 g, 0.028 mol). A slight purple colour developed immediately. The temperature was then raised, with stirring, to 80° whereupon the suspended material slowly dissolved to give a deep purple solution. After dissolution was complete, the temperature was kept at 80° for 1 h. The mixture was then cooled, poured into water (300 ml), and the resulting aqueous solution extracted with $CHCl_3$ (4 × 150 ml). The $CHCl_3$ extracts were combined, washed with 10% HCl (3 × 120 ml) and then with water (3 × 120 ml). The resulting pale straw-coloured solution was dried ($MgSO_4$) and evaporated to give a pale brown solid. This was dissolved in $CHCl_3$ (*ca.* 50 ml) and sufficient hot benzene was added to give a solution which was saturated while boiling. Slow cooling of this solution gave 3.30 g (83%) of the alcohol **10** as fine colourless needles: m.p. 222–223°; ^1H NMR ($CDCl_3$) δ 1.67–3.00 (m, 4H, $-CH_2-$), 3.80 (broad, 1H, –OH, exchanged with D_2O), 7.08–8.13 (m, 10H, aromatic/olefinic). ^{31}P NMR δ +33.92. ^{13}C NMR ($CDCl_3$) δ 31.98 (C-3, $J \sim 0$ Hz), 35.48 (C-2, J = 71.3), 90.52 (C-3a, J = 26.4), 132.7 (phenyl *ipso* C, J = 105.5), 150.39 (C-8a, J = 99.6), doublets at 141.50 (J = 7.8), 141.63 (J = 13.6), and 148.98 (J = 8.79) for C-3b, C-7a, C-8 unassigned; phenyl and benzo signals poorly resolved. IR (Nujol) ν_{OH} 3160 (strong, broad), $\nu_{P=O}$ 1163 cm^{-1}. (Found: C, 72.22; H, 5.38; P, 10.81. Calc. for $C_{17}H_{15}O_2P$: C, 72.34; H, 5.36; P, 10.97%).

Treatment of this compound with sodium ethoxide gave the Michael addition product **13** described above.

1,2-*Dihydro*-1-*phenylindeno*[2,1-*b*]*phosphole* 1-*Oxide* **11**. The vinyl alcohol **10** (4.0 g, 0.14 mol) was suspended in cold xylene (130 ml) with vigorous magnetic stirring, and powdered, freshly dehydrated $KHSO_4$ (6.0 g, 0.044 mol) was added in small portions to give a very even dispersion. The temperature was then slowly raised under a slow stream of dry N_2 to reflux, which was maintained for 1 h. A bright yellow solution containing suspended clumps of partially hydrated $KHSO_4$ resulted. The cooled mixture was then poured onto a dry silica gel column (*ca.* 15 cm × 4 cm). The column was immediately eluted with benzene to remove all of the xylene and then with $CHCl_3$, which removed a band of pale yellow material. Elution was continued until a colourless eluate was obtained. The $CHCl_3$ eluate was evaporated under reduced pressure to give 1.20 g (32%) of pale cream coloured crystals of **11** from the deep yellow solution: mp slow dec above 170°; ^1H NMR δ 3.40–3.68 (m, 2H, P–CH_2–), 6.80–8.00 (m, 11H, aromatic/olefinic). ^{31}P NMR δ +29.14. ^{13}C NMR ($CDCl_3$) δ 41.61 (C-2, J = 74.2 Hz); the most downfield signals were 137.02 (C-8a, J = 94.7), 147.55 (J = 14.65), 151.26 (J = 33.2) with couplings confirmed at 15.0 MHz. (Found: C, 77.09; H, 4.83; P, 11.54. Calc. for $C_{17}H_{13}OP$: C, 77.27; H, 4.96; P, 11.72%).

1,2 - *Dihydro* - 1 - *phenylindeno*[2,1 - *b*] - *phosphole* (**3**). Trichlorosilane (1.36 g, 0.01 mol) and pyridine (2.37 g, 0.03 mol) were mixed carefully in dry benzene (40 ml) under dry N_2 and the oxide **11** (0.528 g, 0.002 mol) in benzene (20 ml) was added in one portion. The resulting buff suspension was then heated under reflux for 1 h yielding a bright yellow suspension. The mixture was cooled in an ice bath and quenched under N_2 with 30% aqueous NaOH (16 ml) keeping the mixture ice-cold during the quenching. Water (20 ml) was added to increase the volume of the aqueous layer. The sealed reaction vessel was then transferred to a nitrogen-filled glove bag where the benzene layer was separated; the aqueous layer was washed with benzene (30 ml) and the two benzene extracts were combined and dried ($MgSO_4$). The bright yellow solution was evaporated under reduced pressure (aspirator) with magnetic stirring to remove the solvent, leaving a yellow glass which, after pumping at 0.8 Torr for 1 h followed by standing overnight, gave 0.437 g (88%) of the slightly sticky, yellow crystalline dihydro phosphine **3**: m.p. 80–81°; ^1H NMR δ 2.20–3.48 (complex m, 2H, –P–CH_2–), 6.12–6.39 (m, 1H, =CH–CH_2–P), 6.67 (slightly broadened s, 1H, –P–C=CH, 6.75–7.60 (m, 9H, aromatic). ^{31}P NMR δ −39.77 with very minor impurity peaks at *ca.* −13. ^{13}C NMR ($CDCl_3$) δ 42.69 (C-2, J = 14.3 Hz). (Found: C, 82.06; H, 5.38; P, 12.28. Calc. for $C_{17}H_{13}P$: C, 82.25; H, 5.28; P, 12.48%).

If the pyridine is omitted from the initial reaction mixture, the reaction follows an entirely different course to give mainly the 1,2,3,8-tetrahydro-1-phenylindeno[2,1-*b*]phosphole **12** as pale yellow crystals embedded in a pale yellow glass in yields of *ca.* 85%. This was characterized by H_2O_2 oxidation to the corresponding oxide **4**.

3 - *tert* - *Butyl* - 1,2,3,8 - *tetrahydro* - 1 - *phenylindeno*[2,1 - *b*]*phosphole* 1-*Oxide* **15**. Phosphine **3** (0.37 g, 0.0015 mol) was dissolved in dry benzene (10 ml) under N_2 and *tert*-butyllithium in pentane (2.1 *M*, 4 ml, *ca.* 0.008 mol) was added by hypodermic injection in one portion to the vigorously stirred solution. The mixture immediately turned dark red and some brown granular material precipitated. After the reaction mixture had been stirred at room temperature for 15 min, H_2O (10 ml) was slowly added followed by dil HCl (10 ml) to neutralize the mixture. Hydrogen peroxide (30%, 2 ml) was then added to oxidize any phosphine present. The resulting suspension was extracted with $CHCl_3$ (2 × 10 ml) and the extracts were combined, dried ($MgSO_4$) and evaporated to low bulk (*ca.* 5 ml). The resulting clear yellow solution was placed on a column of dry silica gel (1 cm × 20 cm) which was eluted first with benzene to remove hydrocarbons and then with $CHCl_3$ until coloured material had moved close to the bottom of the column. The chloroform eluate was evaporated under reduced pressure to low bulk; further slow evaporation at room temperature led to the formation of 0.15 g (32%) of the *tert*-butyl addition product **15** as colourless needles: mp 207.5–209°; ^1H NMR δ 1.04 (s, 9H, CH_3), 2.20–2.60 (m, 2H, –P–CH_2–), 2.78–3.68 (m, 3H, benzylic–CH_2 and –P–CH_2–CH–), 6.95–7.80 (m, 9H, aromatic); double irradiation of the signal at 2.20–2.60 shows that coupling of this signal with *part* of the multiplet at 2.78–3.68 occurs. ^{31}P NMR δ +39.71. ^{13}C NMR sp^3 region at 62.5 MHz ($CDCl_3$): δ 28.95 (CH_3, s), 34.14 (C-8, J = 12.2 Hz), 35.25 ($C(CH_3)_3$, s), 35.51 (C-2, J = 76.3), 48.81 (C-3, s); sp^2 region at 22.5 MHz, 132.91 (phenyl *ipso* C, J = 102.5), 140.27 (C-7a, J =

16.6), 141.22 (C-8a, J = 104.5), 148.83 (C-3b, J = 7.82), 167.92 (C-3a, J = 34.2); benzo carbons 122.69, 123.69, 123.78, 125.34, unassigned; phenyl carbons not resolved. Mass spectrum *m/e* 322 (M+). (Found: C, 77.47; H, 7.28; P, 9.43. Calc. for $C_{21}H_{23}OP$: C, 78.24; H, 7.19; P, 9.61%). The mass spectrum showed that traces of chloroform were tenaciously retained by the compound even after pumping at $\sim 10^{-7}$ Torr for several hours, accounting for the low C value.

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