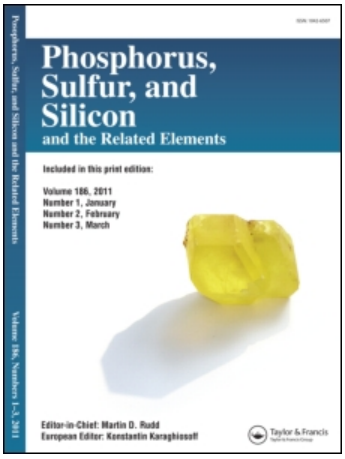


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# SYNTHESIS AND $^{31}$P NMR STUDY OF DIHYDRONAPHTHALENO- AND NAPHTHALENO-DERIVATIVES OF PHOSPHOLENE OXIDES

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**To cite this Article** Orton, William L. , Mesch, Keith A. and Quin, Louis D.(1979) 'SYNTHESIS AND $^{31}$P NMR STUDY OF DIHYDRONAPHTHALENO- AND NAPHTHALENO-DERIVATIVES OF PHOSPHOLENE OXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 5: 3, 349 — 357
**To link to this Article: DOI:** 10.1080/03086647908077737
**URL:** http://dx.doi.org/10.1080/03086647908077737

*Phosphorus and Sulfur*
1979, Vol. 5, pp. 349–357



# SYNTHESIS AND $^{31}P$ NMR STUDY OF DIHYDRONAPHTHALENO- AND NAPHTHALENO-DERIVATIVES OF PHOSPHOLENE OXIDES[1]

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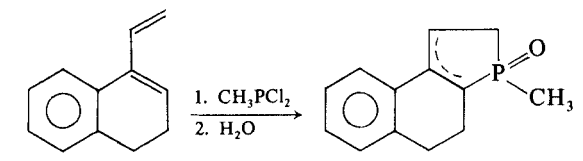
(*Received August 11, 1978*)

Naphthalenophospholenes (dihydrobenzo[*e*]- and [*g*]-phosphindoles) represent a new heterocyclic type that forms in 65–80% yield on dehydrogenation with Pd–C of the corresponding dihydronaphthaleno derivatives. The latter are readily accessible from hydrolysis of cycloadducts of certain vinyldihydronaphthalenes with P(III) chlorides. Six members of this family, as well as some derived phosphines and phosphonium salts, have been prepared. A phenanthrenophospholene oxide, also a new system, was synthesized similarly. $^{31}P$ nmr chemical shifts were appreciably (5–10 ppm) upfield in aromatized phosphine oxides relative to the dihydro forms. It is proposed that this shift results more from a change in the steric environment about phosphorus, as the carbon beta- to it in the adjacent ring changes from tetrahedral to planar geometry, rather than from a change in the degree of interaction of a carbon *p*-orbital with phosphorus. The upfield shift was even more pronounced (13 ppm) for a phosphine. Most of the new compounds were characterized also by $^{13}C$ nmr spectroscopy.

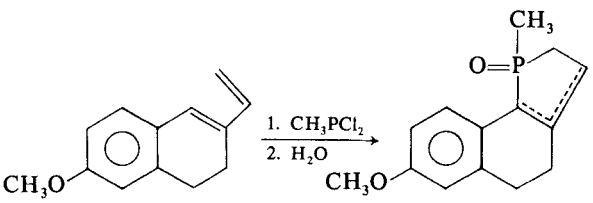


We recently showed[2] that the scope of the McCormack cycloaddition reaction could be greatly expanded by using 1-vinylcycloalkenes as the diene reactant with a phosphorus(III) halide. Benzo derivatives of these dienes also were used in the cycloadditions,[2,3] and compounds based on the previously unknown benzophosphindole ring systems as in (**2**) and (**4**) were constructed.

The location of the double bond in the phospholene ring can be maintained at the initially established 3,4-position with respect to phosphorus or allowed to rearrange to the 2,3-position. With the double bond in the latter position, the compounds can be viewed as dihydronaphthalene derivatives, and we have now found that dehydrogenation to the fully aromatic naphthalene system can be easily accomplished. Such compounds have not previously been prepared, and our work demonstrates yet another useful facet of the McCormack reaction in heterocyclic phosphorus chemistry. In this paper we describe the synthesis of several such naphthalene derivatives, as well as their dihydro precursors. Their availability has provided new opportunities in our continuing study[4] on structural effects on $^{31}P$ NMR chemical shifts.




(**1**) (**2**)




(**3**) (**4**)

## SYNTHESIS

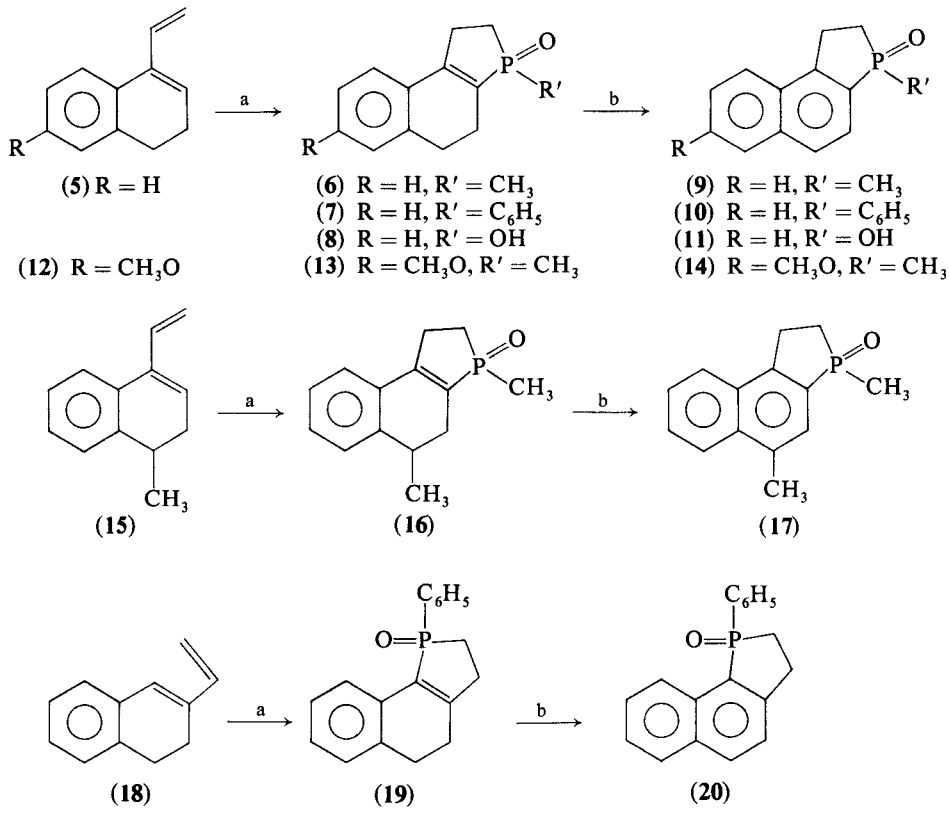
The reactions leading to the benzophosphindole derivatives are summarized in Scheme I. The starting dienes (**5**), (**12**), and (**15**) (1-vinyl-3,4-dihydronaphthalenes) were obtained from the commercially available α-tetralones of corresponding substitution by addition of vinylmagnesium bromide followed by dehydration of the resulting alcohol.[2,3] This scheme is not readily applied to β-tetralones,[3] and diene (**18**) (a 2-vinyl-3,4-dihydronaphthalene) was synthesized by a Wittig reaction involving

methylenetriphenylphosphorane with 2-formyl-3,4-dihydronaphthalene, in a manner already reported[3] for the corresponding 6-methoxy derivative. Cycloadditions of the 1-vinyl dienes in hexane were conducted at room temperature and were worked up after 7 days. As noted earlier,[3] the reaction of the 2-vinyl derivative (**18**) was noticeably slower and was refluxed for the 7-day period. The products were hydrolyzed in a warm acidic medium to promote the rearrangement to the desired 2-phospholene oxide system. The new phospholene oxides (**6**), (**7**), (**16**), and (**19**) were obtained in 30–70% yield. The yield of the novel phosphinic acid (**8**) (from cycloaddition with phosphorus tribromide) was 28%.

Proton nmr spectroscopy established for the products that the desired 2,3-phospholene structure had been obtained through the absence of an olefinic signal at $\delta$6–6.5.[2] In other aspects the spectra lacked useful structural information. The $^{13}C$ nmr spectra (*vide infra*) were more helpful in confirming the structures, however.

Dehydrogenation of the dihydronaphthalenes occurred in 65–80% yield with palladium-on-charcoal in refluxing cumene. No reduction of the phosphoryl group occurred, and the products generally crystallized from the reaction medium on chilling. For complete dehydrogenation, however, we found it necessary to use starting materials of high purity, since instances were encountered where the functioning of the palladium catalyst was inhibited. Subjecting the recovered material to recrystallization generally sufficed to overcome this problem in a repeated dehydrogenation.

From the examples described in Scheme I, it may be seen that the scope of this approach to naphthalenophospholenes is quite broad. It has been used to prepare both P-methyl and P-phenyl phosphine oxides, as well as a phosphinic acid (**11**). Examples with a substituent in either benzenoid ring are included, and from the use of a 2-vinyl (i.e. (**18**)) instead of a 1-vinyl derivative of the starting dihydronaphthalene, it is possible to produce the




(**5**) R = H; (**12**) R = $CH_3O$

(**6**) R = H, R′ = $CH_3$; (**7**) R = H, R′ = $C_6H_5$; (**8**) R = H, R′ = OH; (**13**) R = $CH_3O$, R′ = $CH_3$

(**9**) R = H, R′ = $CH_3$; (**10**) R = H, R′ = $C_6H_5$; (**11**) R = H, R′ = OH; (**14**) R = $CH_3O$, R′ = $CH_3$

(**15**) (**16**) (**17**)

(**18**) (**19**) (**20**)

a: P(III)chloride, then $H_2O$. b: Pd–C, Δ.

SCHEME I

benzo[*g*]phosphindole system (in (**20**)) in addition to the benzo[*e*]phosphindole system seen in the other derivatives. No other synthetic method has yet been described for producing naphthalenes with fused phospholene rings, in spite of the considerable current activity in multicyclic phosphorus chemistry.[5]

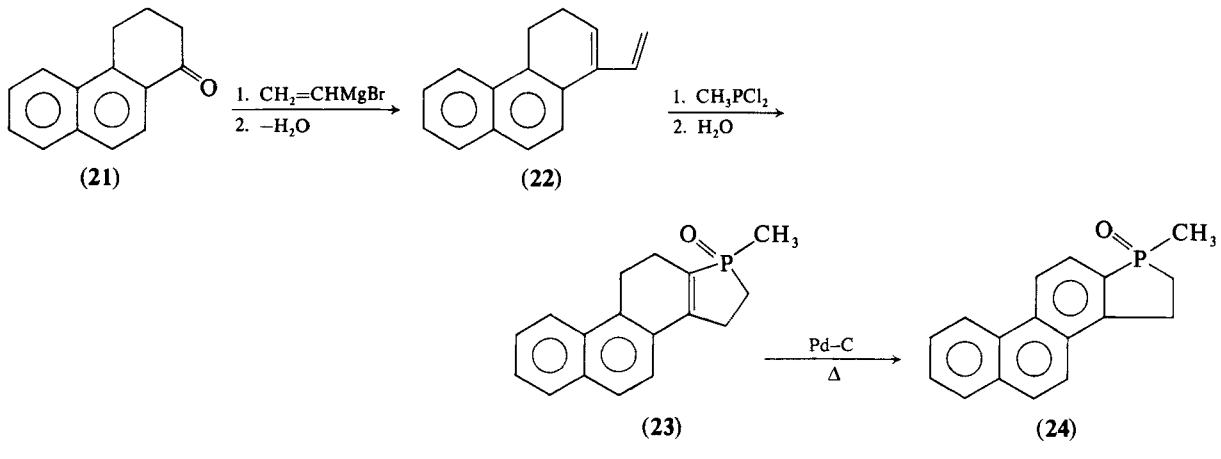
Our method is not necessarily limited to tricyclic compounds, and this has been demonstrated (Scheme II) by the synthesis of the new tetracyclic system based on fusion of the phenanthrene and phospholene rings (as in (**24**)). The dehydrogenation step proceeded in excellent yield (85%).

Normal chemical properties of the phosphorus function are retained in these multicyclic structures. Thus, it was possible to effect deoxygenation of the phosphine oxide group to the phosphine, and this group in turn easily underwent quaternization to give phosphonium salts. An illustrative sequence in the naphthalene series is given in Scheme III.

## $^{31}$P NMR SPECTRAL PROPERTIES

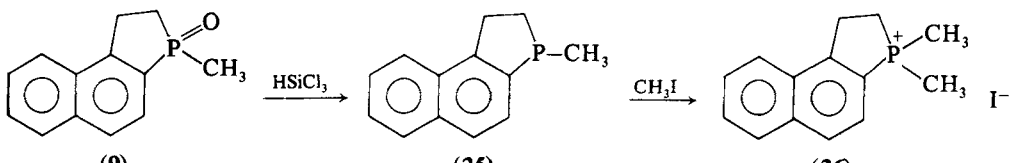
An observation made early in our study is that aromatization of the ring attached to the phospholene ring causes a very substantial upfield shift of the $^{31}$P nmr signal, especially in the P—$CH_3$ systems (e.g., from +65.1 for **6** to +56.1 for the naphthalene (**9**)). This was of special interest to us because of our general concern with spectral–structural relations. We proceeded to record $^{31}$P nmr spectra (Table I) for all of the compounds made in this study.

At first glance, one might suspect a change in $d\pi$–$p\pi$ conjugation to account for the shift observed on aromatization. It is a well established fact that aromatic groups attached directly to phosphorus functions cause upfield shifts of $\delta$ $^{31}$P with respect to structurally related non-aromatic derivatives. For phosphoryl groups, this has long been attributed to an increase in occupancy of the phosphorus d-orbitals by overlap with a $\pi$-orbital of carbon, and a recent study[6] makes use of this concept to account in part for certain nmr effects. In the present case, an explanation for the upfield shift in these terms would require that the $\beta$-naphthyl moiety be much more effective than a $\beta$-styryl moiety (in the dihydronaphthalene series) as a $\pi$-electron donor to phosphoryl. However, on further consideration of the structural change involved in the aromatization, it can be seen that a pronounced alteration in the steric environment in the vicinity of phosphorus also occurs. In the dihydro compounds, there is a methylene group attached to the doubly bonded




(**21**) (**22**) (**23**) (**24**)

SCHEME II




(**9**) (**25**) (**26**)

SCHEME III

TABLE I

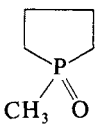
Properties of compounds

| Compound | Mp, °C | Formula | Calcd. C | Calcd. H | Calcd. P | Found C | Found H | Found P | $^1$H nmr[a] $\delta PCH_3$ ($J_{PH,Hz}$) | $^{31}$P nmr, $\delta$[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| (6) | 94–96 | $C_{13}H_{15}PO$ | 71.55 | 6.88 | 14.20 | 71.39 | 6.84 | 14.09 | 1.65(13) | +65.1 |
| (7) | 153–154 | $C_{18}H_{17}OP$ | 77.12 | 6.12 | 11.05 | 77.24 | 6.07 | 11.21 | | +58.6 |
| (8) | 195–196 | $C_{12}H_{13}O_2P$ | 65.48 | 5.91 | 14.07 | 65.51 | 5.86 | 14.19 | | +74.8 |
| (9) | 116–117 | $C_{13}H_{13}OP$ | 72.21 | 6.07 | 14.32 | 72.15 | 6.05 | 14.22 | 1.76(14) | +56.1 |
| (10) | 200–202 | $C_{18}H_{15}OP$ | 77.69 | 5.44 | 11.13 | 77.89 | 5.57 | 11.42 | | +55.3 |
| (11) | 212–216 | $C_{12}H_{11}O_2P$ | 66.06 | 5.08 | 14.19 | 66.12 | 5.20 | 14.55 | | +70.3 |
| (13) | 175.5–177[c] | | | | | | | | 1.58(12) | +66.4 |
| (14) | 147–148 | $C_{14}H_{15}O_2P$ | 68.28 | 6.15 | 12.58 | 68.15 | 6.07 | 12.69 | 1.82(14) | +55.2 |
| (16) | oil | | | | | | | | | +65.8, +66.1 |
| (17) | 122–123 | $C_{14}H_{15}OP$ | 73.03 | 6.57 | 13.45 | 72.79 | 6.56 | 13.31 | 1.76(14) | +55.9 |
| (19) | 151.5–154 | $C_{18}H_{17}OP$ | 77.13 | 6.11 | 11.05 | 77.18 | 6.00 | 11.17 | | +57.4 |
| (20) | 200–202 | $C_{18}H_{15}OP$ | 77.69 | 5.43 | 11.13 | 77.84 | 5.34 | 11.29 | | +55.6 |
| (23) | 227–230 | $C_{17}H_{17}OP$ | 76.99 | 6.40 | 11.54 | 76.72 | 6.44 | 11.95 | 1.60(12) | +65.5 |
| (24) | 236–237 | $C_{17}H_{15}OP$ | 76.61 | 5.60 | 11.64 | 76.36 | 5.34 | 11.40 | 1.70(13) | +60.0 |
| (25) | oil | | | | | | | | 1.1(2) | −18.6 |
| (26) | 300 dec | $C_{14}H_{16}IP$ | 49.14 | 4.72 | 9.05 | 48.86 | 4.77 | 9.23 | | —[d] |
| (32) | oil | | | | | | | | 1.21(2) | −5.8 |
| (33) | oil | | | | | | | | 1.14(2) | −5.9 |
| (34) | 283–284 | $C_{14}H_{18}IP$ | 48.86 | 5.27 | 9.00 | 48.80 | 5.26 | 8.87 | | +56.0[e] |
| (35) | 263–264 | $C_{15}H_{20}IOP$ | 48.15 | 5.39 | 8.28 | 48.02 | 5.14 | 8.16 | | +55.3[e] |

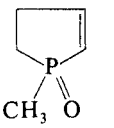
[a] In $CDCl_3$; Most spectral features were complex multiplets and not useful for structure verification. See Table II for $^{13}$C NMR.
[b] 85% $H_3PO_4$ reference; positive values are downfield, negative upfield; $CDCl_3$ solutions.
[c] Lit.[2] mp 174–177°C.
[d] Insolubility prevented spectral recording.
[e] DMSO solution.



carbon that also holds the phosphoryl group, whereas in the aromatized compounds this methylene carbon is converted to a planar $sp^2$ carbon. This carbon is $\beta$-oriented to phosphorus, and quite clearly this $CH_2$ group is in position to influence the environment of phosphorus. Steric changes produce far from trivial shifts on $\delta$ $^{31}$P, as has been seen, e.g., in our study[4,7] of cyclohexyl phosphorus compounds where a change of an electron-withdrawing phosphorus substituent such as a phosphoryl from a fixed axial to an equatorial position can be accompanied (depending on the nature of the phosphorus function) by an upfield shift of several ppm. Indeed, one major change that has been noticed[4] in the axial-equatorial interchange is a pronounced difference in the way the phosphorus function is also related to a $\beta$-carbon (axial:one *anti*, one *gauche* C–H; equatorial:two *gauche* C–H). In the dihydronaphthalene–naphthalene conversion, the phosphorus atom is relocated from a position on a plane lying between the two C–H bonds on the $\beta$-carbon to a position eclipsing the remaining hydrogen on the $\beta$-carbon, and it is possible that shielding develops from this new alignment of bond orbitals and atoms.[8] The p–d conjugation effect is always hard to isolate from other structural changes, but at least among phospholene oxides it is not associated with a large shift of $^{31}$P resonances. Thus, in the monocyclic system (where steric changes near phosphorus are also present) little effect accompanies installation of a double bond:

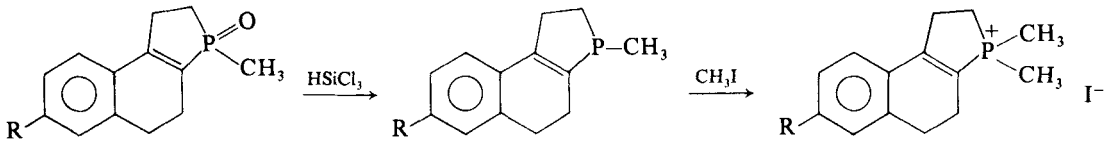



(**27**) (+65.8, $CDCl_3$)[9]




(**28**) (+66.5, $CDCl_3$)[9]

However, the phosphoryl group causes a very great change in the $^{13}$C nmr shifts of an attached double bond (for (**28**), $\delta$ C-2 = 126.9; $\delta$ C-3 = 150.6[9]). There can be no doubt that an interaction occurs between P=O and C=C, but the net reciprocal effect on $\delta$ $^{31}$P is negligible in this simple example. This is true in many similar examples we



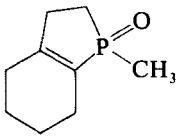

(6), R = H
(13), R = $CH_3O$

(32), R = H
(33), R = $CH_3O$

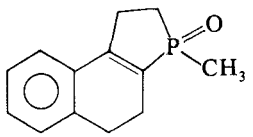
(34), R = H
(35), R = $CH_3O$

SCHEME IV

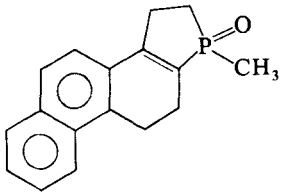
have studied.[9] Likewise, little change accompanies the benzannelation of the bicyclic 2-phospholene oxide (**29**):



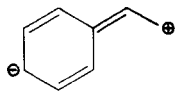
(**29**), $\delta$ $^{31}P$ + 63.2[2]



(**6**), +65.1



(**23**), +65.5

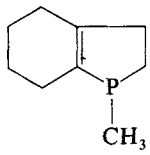


(**30**)

Steric changes would be small but finite in the (**29**) → (**6**) annelation, but largely absent in the (**6**) → (**23**) annelation. As noted, the $\delta$ $^{31}P$ change in the first annelation is a 2 ppm downfield shift (possibly a consequence of a change in electron density of the $\beta$-styryl carbon associated with resonance form (**30**)[10]) and nil in the second. The fact that three such different conjugated systems have $\delta$ $^{31}P$ values within 2 ppm of each other argues for no important role for a conjugative influence on $\delta$ $^{31}P$, and the change in the steric environment about P is just as likely to be responsible for the shift effects observed.

Little information is available on the effect of replacement of a ring H by various substituents on an aryl phosphine oxide. Our compounds include one such substitution (H by $CH_3O$) in both the dihydronaphthyl ((**6**) → (**13**) and naphthyl series ((**9**) → (**14**)), but in neither case did the effect on $\delta$ $^{31}P$ exceed 1 ppm, which cannot be considered significant. This is consistent with observations for other series; methoxy is known to cause weak shielding (2.5 ppm) in phenylphosphonic dichloride,[11] no effect on some phenylphosphonates,[11] but weak deshielding in phenylphosphonic acid[12] (0.5 ppm) and difluoride[13] (1.4 ppm).

To evaluate $^{31}P$ nmr effects among phosphines in the tricyclic series, the additional synthetic work outlined in Scheme IV was performed on the dihydronaphthyl system. By comparing (**32**) to the corresponding naphthalene (**25**), it will be seen that the same strong upfield shift occurs on aromatizing the central ring. The effect (12.8 ppm) is even larger than that for phosphine oxides, which is certainly more difficult to explain by a conjugative than a steric argument. If tricyclic (**32**) is viewed as a benzannelation product of bicyclic phosphine (**36**), then it is again seen that any conjugative effect of the benzo group is small, for (**36**) was found to have the value −7.7 for $\delta$ $^{31}P$ while (**32**) has the value −5.8.



(**36**)

The methoxy substituent effect is again seen to be negligible in the $\beta$-styryl system, both for the phosphines ($\Delta\delta$ $^{31}P$ (**32**)–(**33**) is 0.1 ppm) and phosphonium salts ($\Delta\delta$ $^{31}P$ for (**34**)–(**35**) is 0.7 ppm).

## CARBON-13 NMR SPECTRA

In Table II are given partial $^{13}C$ nmr spectra for most of the compounds prepared in this study. While assignment of peaks to the aromatic and olefinic carbons was made difficult and unreliable by the number and proximity of the signals, the $sp^3$ carbons were relatively easily assigned, and these are the subject of Table II.

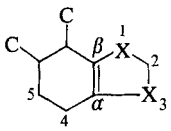
For the oxides, the $sp^3$ carbon alpha- to phosphorus is immediately obvious from its large one-bond coupling to $^{31}P$. In the naphthalene series, this bares the other $sp^3$ carbon for assignment. The chemical shifts for both carbons fall in the narrow range $\delta$ 25.7–28.3 for all compounds studied. This

TABLE II

Partial $^{13}C$ nmr spectra[a]

| Compound | C-1 | C-2 | C-4 | C-5 | $CH_3$–P | Others |
|---|---|---|---|---|---|---|
| | | | A. Dihydro compounds | | | |
| (**6**) | 27.7(6) | 24.4(58) | 19.6(9) | 26.9(4) | 15.9(68) | |
| (**7**) | 27.7(6.7)[b] | 21.0(50.7) | 19.9(s) | 27.6(7.3)[b] | | C-$\beta$ 154.4(32.4) |
| (**13**) | 26.9(1.8)[c] | 24.4(59.8) | 19.5(9.8) | 28.3(6.1)[c] | 15.9(67.1) | C-$\beta$ 149.7(31.7) |
| (**16**)[d] | 26.2–27.9[b] | 24.3(56) | 26.2–27.9[b] | 32.1(6) | 15.9(67) | C-$\beta$ 147.8(30) |
| (**19**) | —[e] | 26.8(72) | 27.7(s)[c] | 27.0(s)[c] | | |
| (**23**) | 27.3(2.5) | 25.9(62.3) | 19.3(8.6) | 22.6(s) | 16.1(67.5) | C-$\beta$ 149.0(31) |
| (**32**) | 32.2(4.2) | 23.1(13.5) | 24.0(s)[f] | 28.4(5.1) | 13.0(24) | |
| (**33**) | 32.4(4.3) | 23.2(13.5) | 24.0(s)[f] | 29.0(4.9) | 13.1(21) | |
| | | | B. Aromatized compounds | | | |
| (**9**) | 26.1(4) | 26.3(70) | | | 17.4(32) | |
| (**10**) | 26.6(5) | 27.4(71) | | | | |
| (**14**) | 25.7(4) | 26.1(67) | | | 17.2(67) | |
| (**17**) | 26.0(5) | 26.3(70) | | | 17.4(67) | 5-$CH_3$ 19.6 |
| (**20**) | —[g] | 28.3(71) | | | | |
| (**24**) | 26.3(5) | 26.3(63.2) | | | 17.4(67.8) | |
| (**25**) | 32.4(5.5) | 25.6(6.7) | | | 14.4(20.7) | |

[a] For convenience, the numbering is made consistent for all ring systems by use of the generalized structure




where one X may be P. Chemical shifts are referenced to TMS as O in $CDCl_3$ solutions. Numbers in parentheses are $^{31}P$–$^{13}C$ coupling constants (Hz).

[b] Overlapping signals.

[c] Assignment uncertain.

[d] *Cis, trans* mixture. Separate signals were only clearly discernible for $CH_3$ at C-5 ($\delta$ 20.0 and 21.0).

[e] C-3 $\delta$ 31.6 (6.7 Hz).

[f] Coupling uncertain; signal may overlap with C-2 signal.

[g] C-3 $\delta$ 28.8 (4.5).

knowledge led to recognition of the corresponding carbons in the dihydronaphthalene series, although in the benzo[*e*] series there remains some ambiguity with regard to the assignment of the carbon alpha- to the benzene ring in the central ring. For example, in (**13**), the signals appear at $\delta$ 26.9 ($J_{PC}$ = 1.8 Hz) and 28.3 ($J_{PC}$ = 6.1 Hz). A possible basis for their distinction is the upfield shift of the carbon *beta* to phosphorus in the 5-membered ring of bicyclic compound (**29**)[2] ($\delta$ 28.5, $J_{PC}$ = 10 Hz) that might be experienced by $\gamma$-crowding with the nearby aromatic ring carbon. This might make $\delta$ 26.9 for (**13**) assignable to the *beta* carbon (C-1 in Table II), leaving a quite reasonable $\delta$ 28.3 for the carbon alpha to the benzene ring (C-5 in Table II). This assignment places the *beta* carbon in good agreement with the comparable carbon in the naphthalene counterpart (**14**, $\delta$ 25.7, $J_{PC}$ = 4 Hz). This leaves the remaining signal ($\delta$ 19.5, $J_{PC}$ = 9.8 Hz) for assignment to the allylic carbon of the central ring (C-4 in Table II). This high-field position is easily explained by the $\gamma$-shielding of the two substituents on phosphorus. To confirm this assignment, data for the C-methyl derivative (**16**) can be considered. Although *cis, trans* isomers result from this substitution (and are clearly evident in the $^{31}P$ spectrum), the only new signal on the $^{13}C$ spectrum is that for a second C–$CH_3$ (singlet). This methyl moves the carbon of attachment downfield to $\delta$ 32.1. More importantly, the upfield signal ($\delta$ 19.6 in (**6**)) vanishes and reappears at about $\delta$ 27. This is clearly a $\beta$-effect of the $CH_3$ group, leaving no doubt as to the origin of the upfield signal.

In the single member (**19**) of the benzo[*g*] series, the carbon *alpha-* to the benzene ring is four bonds removed from phosphorus and hence is a singlet. There are two singlets in the spectrum ($\delta$ 27.7 and 27.0), and hence one is the $\alpha$-carbon, the other probably the adjacent carbon. The two coupled carbons are easily assigned to the phospholene ring;

the downfield position ($\delta$ 31.6) adopted by C-3 of this ring, also adjacent to benzene, is reasonable.

$^{31}P-^{13}C$ coupling between two and three bonds showed small variations with structural changes, but we were not able to use the changes reliably to aid the assignments.

In the dihydronaphthalene series, one $sp^2$ carbon was consistently downfield (in the region $\delta$ 148–154 with $J \sim 30$ Hz) of the complex pattern for the others. This appears to be the olefinic carbon *beta*- to phosphorus from its similarity to the comparable carbon of (**29**)[2] ($\delta$ 144.1, $J = 30$ Hz).

Fewer data are available for the phosphines. The two $sp^3$ carbons of the naphthalene (**25**) had widely different (7 ppm) chemical shifts, and the upfield signal is assignable to the carbon attached to phosphorus due to the relatively weak *alpha*-effect of phosphino groups.[14] For the two dihydronaphthalenes (**32**) and (**33**), the remaining $sp^3$ carbon signals are easily distinguishable by the upfield position ($\delta$ 24.0) of the allylic carbon, shielded by the $\gamma$-effect of the substituent on phosphorus.

## EXPERIMENTAL

### *General*

Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. All manipulations of phosphines were performed in a glove bag with a nitrogen atmosphere. Elemental analyses were performed by MHW Laboratories, Phoenix, Ariz. $^1H$ nmr spectra were taken with a JEOL MH-100 spectrometer. $^{31}P$ FT nmr spectra were obtained with a Bruker HFX-10 system at 36.43 MHz with proton noise-decoupling and are referenced to 85% $H_3PO_4$. Positive shifts are downfield, negative upfield. $^{13}C$ FT nmr spectra were obtained with a JEOL FX-60 spectrometer at 15 MHz with proton noise-decoupling; TMS was used as reference.

### *3-Methyl-1, 2, 4, 5-tetrahydro-3(H)-benzo[e]phosphindole-1-oxide* (**6**)

The $\Delta^{9b(1)}$ isomer of (**6**) was available from a previously reported study,[2] having been formed by cycloaddition of diene (**5**) with $CH_3PCl_2$. It was isomerized to (**6**) by heating a 1-g sample in 5 ml of 6 N HCl at 75°C for 1 h. Neutralization with 6 N NaOH followed by extraction with 3 20-ml portions of chloroform gave a gummy solid purified by sublimation at 80°C (0.05 nm); yield 0.75 g (75%). Analysis and other properties are given in Tables I and II.

### *3-Phenyl-1,2,4,5-tetrahydro-3(H)-benzo[e]phosphindole-1-oxide* (**7**)

The precipitate from 7 days' standing of a mixture of 40 g (0.25 mol) of diene (**5**),[2] 45.8 g of $C_6H_5PCl_2$, 0.1 g of copper stearate and 250 ml of cyclohexane was washed with pentane and then dissolved in 50 ml of chloroform. Without cooling, the solution was slowly neutralized with saturated $NaHCO_3$. The aqueous layer was separated and extracted with 3 × 100 ml of chloroform. The extracts were dried ($MgSO_4$); stripping of solvent left an oil which crystallized on trituration with pentane. Cyclohexene was a useful solvent for recrystallization, yielding 19.6 g (28%) of (**7**); properties appear in Tables I and II.

### *3-Hydroxy-1,2,4,5-tetrahydro-3(H)-benzo[e]phosphindole-1-oxide* (**8**)

The white precipitate formed after 7 days' standing at room temperature of a mixture of 17.2 g (0.11 mol) of diene (**5**),[2] 29.8 g (0.11 mol) of $PBr_3$, 0.1 g of copper stearate and 150 ml of pentane was collected and washed with pentane. The solid was added in portions to 200 ml of 10% NaOH. Liquid was decanted from an insoluble gum and acidified with 10% HCl. The precipitated (**8**) was collected and combined with an additional crop obtained from a chloroform extraction (3 × 100 ml) of the acid solution. This crop was initially an oil but trituration with pentane gave a tan solid. Recrystallization of the combined crops of (**8**) from cumene gave 6.0 g (25%) of (**8**), whose properties are given in Tables I and II.

### *1,2 Dihydro-1-methyl-4-vinylnaphthalene* (**15**)

To a solution of vinylmagnesium bromide, prepared from 19.3 g (0.18 mol) of vinyl bromide and 4.4 g (0.18 g-atom) of magnesium in 200 ml of THF, was added a solution of 25 g (0.16 mol) of 4-methyl-1-tetralone (Aldrich Chem. Co.) in 100 ml of THF. The addition required 1 h; the mixture was then refluxed for 2 h, cooled to 0°C, and treated with 200 ml of saturated $NH_4Cl$. The organic layer was separated and combined with the organic layers from extraction of the aqueous layer with chloroform (3 × 100 ml). Drying ($MgSO_4$) and concentration gave 28.3 g (86%) of crude 4-methyl-1,2,3,4-tetrahydro-1-vinyl-1-naphthol, which was used directly in the next step.

The alcohol was dissolved in 200 ml of benzene containing 1 ml of quinoline and 0.5 g of iodine. The theoretical amount of water was removed by refluxing with a Dean–Stark apparatus. The solution was washed in sequence with 100 ml of saturated NaCl, 100 ml of saturated $Na_2S_2O_3$ and 100 ml of saturated NaCl and then dried ($MgSO_4$) and concentrated. The diene [(**15**), 85%, $^1H$ nmr ($CDCl_3$) $\delta$ 1.2 (d, $^2J_{HH} = 8$ Hz, $CH_3$), 1.9–3.0 (m, $-CH-CH_2$), 5.1–5.7 (*ABX*, $-CH=CH_2$), 3.05 (broad *t*, $^3J_{HH} = 3$ Hz, ring olefinic H), 6.5–6.8 (AB*X*, $-CH=CH_2$), 6.9–7.7 (m, ArH)] was used immediately in the cycloaddition to form (**16**).

### *3,5-Dimethyl-1,2,4,5-tetrahydro-3(H)-benzo[e]phosphindole-1-oxide* (**16**)

A mixture of 13 g (7.6 mmol) of diene (**15**), 9 g (7.6 mmol) of freshly distilled $CH_3PCl_2$, 0.5 g of copper stearate, and 150 ml of pentane was sealed in a wide-mouth bottle and allowed to stand for 7 days. The white precipitate was filtered off in a glove bag, washed with pentane, and then dissolved in 50 ml of chloroform. Neutralization with $NaHCO_3$ and extraction were performed as for (**7**). The chloroform extracts were dried ($MgSO_4$) and concentrated to a brown oil (17 g) whose $^1H$ nmr spectrum ($\delta$ 5.9–6.6, m) suggested the presence of olefinic H of unrearranged phospholene oxide. The product was then heated in 50 ml of 6 N HCl for 1 h; the mixture was neutralized (30% NaOH) and extracted with 5 × 50 ml of chloroform. The dried ($MgSO_4$) solution on concentration left a non-crystallizing oil

which was distilled at 115–120°C (0.05 mm); yield 11.6 g (70%). Spectral data are reported in Tables I and II.

*3,4-Dihydro-2-formylnaphthalene*

2-Ethylenedioxymethyl-1-tetralone was prepared as described[15] from 2-formyl-1-tetralone[16] and had mp 63–65°C (lit.[15] mp 63.5–65°C). To a solution of 24 g (0.11 mol) of this acetal in 500 ml of methanol was added 12.5 g (0.33 mol) of $NaBH_4$ over a 45-min period. The mixture was refluxed 1 h and then stripped of methanol. The residue was taken up in 100 ml of water and extracted with $CH_2Cl_2$ (3 × 100 ml). The extract was dried $MgSO_4$) and concentrated to give crude 2-ethylenedioxymethyl-1,2,3,4-tetrahydro-1-naphthol (23.7 g, 98%), used directly in the next step.

The alcohol in a solution of 300 ml of methanol, 120 ml of water, and 10 ml of conc. HCl, was refluxed for 4 h and was then freed of methanol by distillation. The aqueous solution was extracted with $CH_2Cl_2$ (5 × 100 ml), and the extract was dried ($MgSO_4$) and distilled to give 19 g (80%) of 3,4-dihydro-2-formylnaphthalene, bp 80–85°C (0.35 mm); $^1H$ nmr ($CDCl_3$) $\delta$ 2.3–2.9 (m, $CH_2$), 6.9–7.3 (m, olefinic and ArH), 9.5 (s, –CHO). A semicarbazone, recrystallized from ethanol, had mp 234–236°.

*Anal.* Calcd. for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.86; H, 6.04; N, 19.71.

*1,2-Dihydro-3-vinylnaphthalene* (**18**)

The Wittig reagent prepared from 71 ml of 2.4 M *n*-butyllithium (in hexane, 0.17 mol) and 61 g (0.17 mol) of methyltriphenylphosphonium bromide in 400 ml of ether was treated with a solution of 27 g (0.17 mol) of 3,4-dihydro-2-formylnaphthalene in 200 ml of ether. After 24 h of reflux, the mixture was filtered and the filtrate washed with water until the washings were neutral. The ether solution was dried ($MgSO_4$) and distilled to give 12.5 g (75%) of (**18**), bp 58–61°C (0.22 mm); $^1H$ nmr ($CDCl_3$) $\delta$ 2.4–3.0 (m, $CH_2$), 5.0–5.5 (m, $C{=}CH_2$, 6.4–6.8 (m, Ar*CH*=C and *CH*=$CH_2$), 7.0–7.3 (m, ArH). The diene was used immediately in the synthesis of (**19**).

*1-Phenyl-2,3,4,5-tetrahydro-1*(H)*-benzo*[*g*]*phosphindole-1-oxide* (**19**)

Diene (**18**), (12.5 g, 0.08 mol) and $C_6H_5PBr_2$[17] (11.5 g, 0.08 mol) were refluxed in hexane (50 ml) containing 0.3 g of copper stearate for 7 days. The yellow oil that precipitated was taken up in chloroform and hydrolyzed as for (**7**). Stripping of solvent left an oil that crystallized on pentane trituration. Recrystallization from cumene gave 10.1 g (45%) of (**19**), whose properties are reported in Tables I and II.

*3,4-Dihydro-1-vinylphenanthrene* (**22**)

Vinylmagnesium bromide was added to 60.7 g (0.31 mol) of 1-keto-1,2,3,4-tetrahydrophenanthrene (**21**)[18] as described in the synthesis of (**15**); the reaction was completed with a 16-h reflux period (crude yield 69.4 g, 100%). Dehydration of the alcohol was also accomplished as for (**15**), yielding 15.0 g (80%) of diene (**22**) as an oil, which was used directly for cycloaddition; $\delta$ $^1H$ nmr 2.12 (*d*, $J$ = 5 Hz, of *t*, $J$ = 9 Hz, H-2) 2.85 (*t*, $J$ = 9 Hz, H-1), 5.10 (*d* of *d*, $J$ = 9 and 2 Hz, $\begin{matrix} C \\ \diagdown \\ \end{matrix}C{=}C\begin{matrix} \diagup H \\ \diagdown H \end{matrix}$) 5.45 (*d* of *d*, $J$ = 17 and 2 Hz, $\begin{matrix} C \\ \diagdown \\ \end{matrix}C{=}C\begin{matrix} \diagup H \\ \diagdown H \end{matrix}$), 6.05 (*t*, $J$ = 5 Hz, H-3), 6.54 (*d* of *d*, $J$ = 17 and 9 Hz, –*CH*=$CH_2$), 7.08–7.90 (ArH).

*1-Methyl-2,3,10,11-tetrahydro-1H-naphtho*[*2,1-e*]*phosphindole-1-oxide* (**23**)

Diene (**22**) (15.0 g, 0.073 mol) was reacted with 9.8 g (0.083 mol) of $CH_3PCl_2$ in the usual way in hexane. The adduct that precipitated after 3 days was collected, dissolved in chloroform, and hydrolyzed by addition to an ice–$H_2O$ slush. The organic layer was recovered after neutralization with $NaHCO_3$, and was washed with 5% NaOH. On removing solvent, there was left 14.2 g (72.5%) of yellow solid, shown by $^1H$ nmr ($\delta$ 6.21, *d*, $^3J_{PH}$ = 27 Hz) to contain the 3-phospholene oxide moiety. The product was rearranged by heating in 300 ml of 6 N HCl at 80° for 4 h. The mixture was extracted with chloroform, and the extract was washed with water until the washings were neutral. Removal of solvent left a brown solid (12.1 g, 62% from diene (**22**)). A sample recrystallized from toluene gave a white solid; data are given in Tables I and II.

*Aromatization Procedure*

The following general procedure was used for the various aromatization reactions. The carefully purified dihydro derivative (5 g) was completely dissolved in the proper volume (generally 75–100 ml, except 250 ml for acid (**8**)) of cumene at about 70–80°C. The Pd-on-charcoal (5%, 1.5 g) was then added and the mixture was brought to reflux. A slow stream of dry nitrogen was passed through the solution while it was refluxed for 48 h. The mixture was filtered while hot and the filtrate chilled to 0°C. The product crystallized on standing: (**9**), 70% after recrystallization from $CCl_4$; (**10**), 83%, analytically pure as received; (**11**), 65% from acetone; (**14**), 65% from $CCl_4$; (**17**) and (**20**), both 80% analytically pure as received; (**24**), 85%, analytically pure as received. Properties for all products are recorded in Tables I and II.

*Preparation and Quaternization of Phosphines*

The following procedure for synthesis of phosphine (**25**) is typical. To a solution of oxide (**9**) (3.0 g, 14 mmol) in 50 ml of benzene was added 5.7 ml (56 mmol) of trichlorosilane in 10 ml of benzene, over a 30-min period. The mixture was stirred for 1 h and then refluxed for 12 h. The solution at 0°C was treated with 20% NaOH and the benzene layer was recovered. The aqueous layer was extracted with chloroform (3 × 100 ml), and the combined organic solutions were dried ($MgSO_4$) and freed of solvent to leave (**25**) as an oil (2.0 g, 71%) whose spectral features are given in Tables I and II. The methiodide (**26**) crystallized rapidly from treatment of a benzene solution of (**25**) with $CH_3I$ and was analyzed directly (Table I), since its solubility in various solvents was very low.

Similarly were prepared phosphine (**32**) and its methiodide (**34**) and phosphine (**33**) and its methiodide (**35**). Spectral data for (**32**) and (**33**) are given in Tables I and II. These methiodides, unlike (**26**), were recrystallizable from ethanol; analyses are given in Table I.

Phosphine (**36**) was prepared by the same procedure from oxide (**29**) in 76% yield (crude): $^{31}P$ nmr ($CDCl_3$) $\delta$–7.7; partial $^{13}C$ nmr $\delta$ 12.7 (*d*, $^1J_{PC}$ = 18 Hz, $CH_3$), 25.0 (*d*, $^1J_{PC}$ = 21 Hz, C-2), 37.6 (*d*, $^2J_{PC}$ = 4 Hz, C-3), 134.0 (broad *s*, C-7a), 144.4 (broad *s*, C-3a); methiodide (mp 185–186°C from methanol-ethyl acetate).

Calcd. for $C_{10}H_{18}IP$: C, 40.56; H, 6.13; P, 10.46. Found: C, 40.33; H, 6.15; P, 10.27.

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