Nuclear Magnetic Resonance, Crystal, and Molecular Structure Analysis of 5,10-Dihydro-10-methyl-5-phenylacridophosphin-10-ol and Related "Butterfly" C–P Heterocycles. Evidence of a P···H—O Hydrogen Bond in the Crystal of the Title Compound

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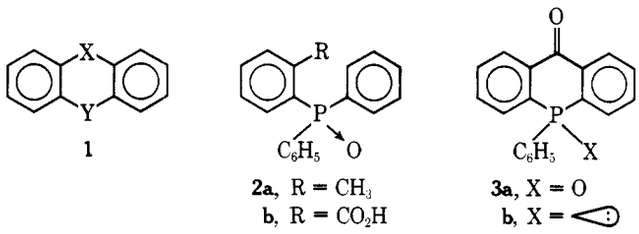
The synthesis of 5,10-dihydro-10-methyl-5-phenylacridophosphin-10-ol and several related analogues has been achieved by addition of methylmagnesium iodide to 5,10-dihydro-5-phenylacridophosphin-10-one. Variable temperature ^1H NMR analysis, ^{31}P NMR analysis, and a single-crystal analysis of the title compound confirmed the structure as a "butterfly" type molecule. Long-range P–C–C–C–C–H coupling ($^5J_{PH}$) of 1.6 Hz in the title compound was observed along with a coupling of H–C–C–C–CH of ≈0.45 Hz also detected, both being confirmed by ^1H and ^{31}P decoupling studies. Unit cell dimensions of the title compound are a = 6.1336, b = 8.8456, c = 15.4235 Å, α = 100.980°, β = 100.003°, γ = 83.150°; final R value is 0.04. The x-ray analysis revealed an intermolecular P···H—O hydrogen bond in the crystal, a phenomenom heretofore unreported. Although an equilibrium between two "butterfly" conformers in solution cannot be entirely eliminated via NMR analyses of the title compound in several solvents, only one form could be isolated and oxidation or quaternization produced only one oxide or quaternary salt, respectively.

Certain substituted derivatives of anthracene such as represented by **1** have been recognized for some time as candi-



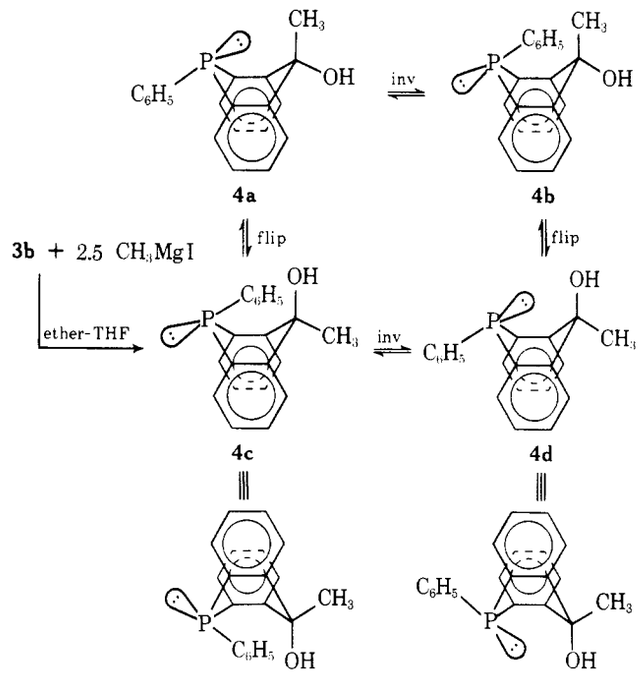
1 **2a**, R = CH_3; **b**, R = CO_2H **3a**, X = O; **b**, X =

dates to possess a folded conformation or "butterfly conformation" when C–X–C and C–Y–C angles deviated significantly from 120°.[3] Thus, heterocyclic analogues exist as folded structures. 5,10-Disubstituted 5,10-dihydrophosphanthrene systems were first obtained by Davis and Mann in 1964.[3c] Although no "ring fluttering" process was cited at that time in the system, the workers recognized such possibilities in a brief summary of the field in 1970.[4] In an effort to evaluate the possibility of "ring fluttering" and, if possible, inversion on P, we have prepared diphenyl-*o*-tolylphosphine oxide (**2a**)[5] which was oxidized to **2b**.[6] Cyclization with 115% PPA[7] of **2b** gave an improved yield of **3a** (reported while our work was in progress[6]). Reduction of **3a** with trichlorosilane gave **3b** in very high yield.[6,8] This paper reports our results on the chemistry and conformational analysis of **3b**, which is a member of a relatively rare C–P heterocyclic family of active interest.[8,9]

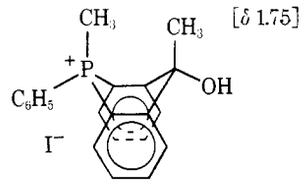
Reaction of **3b** with excess CH_3MgI in ether–THF gave, after workup, a crystalline solid (mp 156–157 °C, 81%) identified by evidence to be presented below as **4a**. This suggests that perhaps coordination of the magnesium with the lone pair on P could result in preferential attack on the carbonyl group from the "top" side, or side which is syn to the lone pair. However, as shown in Scheme I, a complex equilibrium is quite conceivable in which butterfly conformers and invertomers could be interconvertible by a series of inversions on P and flipping of the butterfly structures. The current investigation concerns an examination of this situation in solution and x-ray analysis of a single crystal of **4a**.

Since alkylation and oxidation of phosphines is known to proceed with *retention* of configuration,[10] some insight as to the stereochemistry in **4** might be gleaned from reactions of this type. For example, it was found that without meticulous

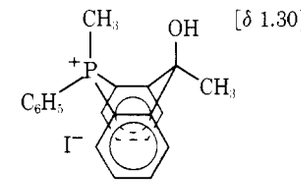
Scheme I



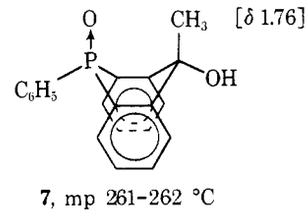
care to permit essentially all of the CH_3I to be converted to the corresponding Grignard reagent, two isomeric salts **5** and



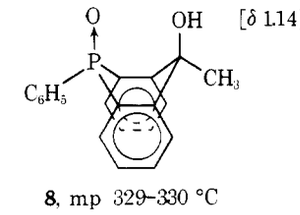
5, mp 276-277.5 °C



6, mp 282-283 °C



7, mp 261-262 °C



8, mp 329-330 °C

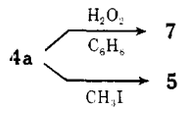
Table I. ^{1}H NMR Signals of C-CH_3 Protons for Products

Registry no	Compd	Solvent	δ value (J) relative to Me_4Si[a]
61279-12-7	**4a**[b]	$DCCl_3$	1.60 [d ($^5J_{PH}$ = 1.6 ± 0.2 Hz)]
		Me_2SO-d_6	1.40 [d ($^5J_{PH}$ = 1.6 ± 0.2 Hz)]
		C_6D_6 (or CH_3OD)	1.57 [dd ($^5J_{PH}$ = 1.6 ± 0.2; J_{HH} = 0.45 Hz)]
61279-13-8	**5**	Me_2SO-d_6	1.75 [bs]
61279-14-9	**6**	Me_2SO-d_6	1.30 [bs]
61279-15-0	**7**	Me_2SO-d_6	1.76 [bs]
61279-16-1	**8**	Me_2SO-d_6	1.14 [bs]

[a] dd = doublet of doublet; bs = broad singlet. [b] ^{31}P NMR ($DCCl_3$) spectrum showed broad singlet at +26.67 (relative to 85% H_3PO_4).

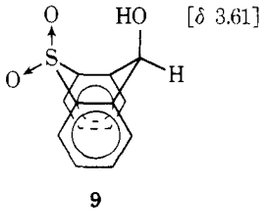
6 (mp 276–277.5 and 282–283 °C, respectively) formed from reaction with **4a** and could be separated but only by a difficult fractional recrystallization. Although the mixture of salts **5** and **6** perhaps suggested two butterfly conformer precursors, the possibility of invertomers (on phosphorus) could not be eliminated. Moreover, quaternization could have proceeded initially with CH_3I on **3b** followed by Grignard attack on the carbonyl group from two different directions. That the latter might be true was supported by the observation that addition of CH_3MgI to ketophosphine oxide **3a** furnished oxides **7** (mp 261–262 °C) and **8** (mp 329–330 °C). Extreme care in fractional recrystallization gave pure oxides **7** and **8**.

In view of the isolation of **4a** and x-ray analysis thereof (discussed later in this paper), the interrelationship of salts **5** and **6** and oxides **7** and **8** can be discerned. Direct oxidation



of **4a** dissolved in benzene by 10% H_2O_2 at *room temperature* (12 h) gave a quantitative yield of the *lower melting* oxide **7**. Similarly, quaternization of **4a** with CH_3I at room temperature (24 h) gave a quantitative yield of the lower melting salt **5**. In both cases also, the proton signal in the ^{1}H NMR spectrum for the protons in C-CH_3 occurred at lower field (δ 1.76 for **7** and δ 1.75 for **5** in Me_2SO-d_6) compared to the same signals for salt **6** (δ 1.30) and oxide **8** (δ 1.14), respectively (all spectra in Me_2SO-d_6 and all are slightly broadened singlets). Since ketophosphine oxide **3a** can reasonably give only two isomeric oxides from attack on either face of the carbonyl group, the assignments for structures **5–8** are defensible. An x-ray analysis of the lower melting salt **5** has confirmed the structure and will be reported later.

That the magnetic anisotropic effect of the P→O group on a proton of a CH_3 group in a near parallel arrangement can cause a paramagnetic shift has been strongly suggested in simple cyclic, geometric isomers.[11] This appears true also for the S→O group in related butterfly compounds **9** and **10** in



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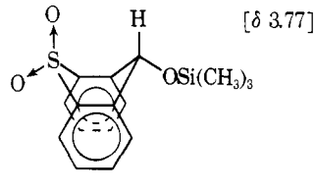

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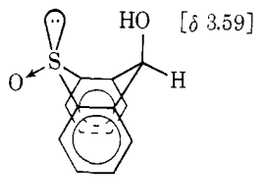
which the pseudoaxial proton of the latter occurs at lower field.[3b,12] Indeed, , similar chemical shifts of the proton signal in **9** related to that in **11** appears to be strong evidence for the arrangement shown. Moreover, crystalline **11** has been confirmed by x-ray analysis.[3b]

For comparison, reduction of ketophosphine oxide **3a** with $NaBH_4$ in ethanol gave a mixture, but one isomer [structure



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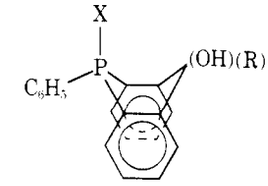
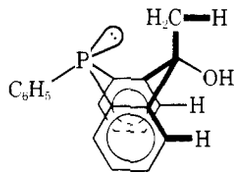


12a, R = H; X = O
b, R = $CH_2C(CH_3)_3$; X = O
c, R = $CH_2C(CH_3)_3$; X = lone pair

12a with the stereochemistry at >C(OH)H unspecified] was *heavily predominant*. The ^{1}H NMR spectrum showed a doublet at δ 6.40 [>C(OH)**H**]. Although heavily deshielded, assignment of this proton (C–H) to a particular isomer has not been possible. The ^{1}H NMR data for protons in C-CH_3 in **4a–8** have been summarized in Table I.

Neopentenylmagnesium chloride added to **3b** in THF–xylene gave a mixture from which phosphine oxide **12b** and phosphine **12c** could be isolated. Oxide **12b** had ^{1}H NMR signals ($DCCl_3$) at δ 0.81 [$(CH_3)_3C$), 2.03 (bd, J_{PCCCCH} = 3 Hz, CH_2)], and 7.16–8.16 (ArH). The broad doublet (CH_2) collapsed to a broadened singlet upon ^{31}P decoupling. Thus, long-range coupling of $J_{PCCCC-H}$ was confirmed in **12b**. Though not common, such a $^5J_{PH}$ coupling has been recorded in one conjugated system.[13] Interestingly, neither oxide **7** or **12b** showed a $^5J_{PH}$ coupling.

Careful ^{1}H NMR analysis of **4** and ^{31}P decoupling experiments produced unusual results. Considering only the protons of the C-CH_3 group, in C_6D_6 what appeared to be a doublet of doublets (greatly broadened) was observed at δ 1.60 (Table I) and a $^5J_{PH}$ = 1.6 ± 0.2 Hz, confirmed by decoupling ^{31}P to give two lines, J_{HH} = 0.45 ± 0.5 Hz. Interestingly, irradiation of the aromatic protons systematically from low to high field caused the ^{1}H–^{1}H doublet to greatly sharpen. In CH_3OD, the doublet was similarly split ($^5J_{PH}$ = 1.6 and $^5J_{HH}$ = 0.45 Hz) into two doublets and irradiation of the aromatic protons again caused the disappearance of the smaller coupling and gave a sharp doublet ($^5J_{P-H}$ = 1.6 Hz). Again this confirmed a $^5J_{PH}$ coupling. Reasonably, the smaller coupling J_{H-H} could result from peri hydrogen coupling to the protons of C-CH_3 as shown but a doublet of *triplets* would be predicted. It may



be that the decoupling is not totally complete and the broadened single doublet is the result of some residual P–H and H–H coupling.

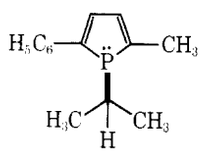
It was not unexpected that in benzene-d_6 there might be greater separation of the lines. "Benzene shifts" or aromatic solvent induced shifts (ASIS) are well known[14] in many sys-

tems but the possibility existed for the equilibrium as shown in Scheme I to be operative. This would seemingly necessitate fortuitously identical (or nearly so) $^5J_{PH}$ and $^5J_{HH}$ values in **4a** and supposedly **4d** [Courtauld models imply very large steric repulsive interactions in **4b** (C_6H_5 vs. CH_3) and **4c** (C_6H_5 vs. OH)].

Solubility limitations dictated that a variable temperature ^1H NMR study was only possible using a combination of three solvents for three temperature ranges (CH_3OD, −90 to 40 °C; $DCCl_3$, −40 to 40 °C; *o*-ClC_6H_4Cl, −20 to 110 °C). Assessment of the equilibria suggested in Scheme I was that high energy barriers to pyramidal inversion on P in phosphines[15] might retard "ring flipping" or, if such occurred, conformers **4a** and **4d** would predominate. Surprisingly, on cooling **4** ($DCCl_3$) to −20 °C, the broadened doublet coalesced to a broad singlet (Figure 1). When using CH_3OD, a similar phenomenon occurred and cooling to −90 °C did not change the intensity or shape of this broad singlet. Unfortunately, precipitation occurred below −95 °C as was observed also in $DCCl_3$ even at −40 °C (the spectra were nearly identical in $DCCl_3$ or in CH_3OD). This phenomenon was repeatable on several different samples.

Tentative conclusions initially were that an equilibrium could exist (although intermediates **4b** and **4c** could not be detected) between **4a** ⇄ **4d** in which, upon cooling, **4a** predominated since only **4a** could be obtained in crystalline form. As cited previously, this situation would assume nearly equal $^5J_{PH}$ and $^5J_{HH}$ coupling in **4a** and **4d**. If **4a** ⇄ **4d** exists, k_c for a single equilibrium cannot be calculated from the equation[16] $k_c = \pi\Delta\nu/\sqrt{2}$ since both inversion and flipping would be required in **4a** → **4d**. However, if an assumed multiequilibrium existed in the process in Scheme I, using a minimum $\Delta\nu = 0.2$ and maximum of 0.45 Hz at T_c, k_c has a range 0.44 to 0.99 s^{-1}, respectively. By the Eyring equation,[17] $\Delta G^{\ddagger}$ has a range of 14.7–15.1 kcal/mol, indicative of fast processes indeed, which would not be in keeping with simple systems.[15b]

Although pyramidal inversion barriers of phosphines are generally high,[15] racemization of **13** occurred at 25 °C.[17]



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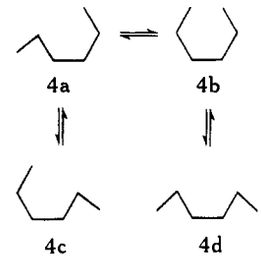
Presumably, strain imposed by the close proximity of substituents at positions 1, 2, and 5 facilitated the epimerization process. It is not unreasonable to expect preference of **4a** and **4d** in view of an expected high internal strain in **4b** and **4c**. However, at room temperature no two sets of doublet of doublets was ever observed when **4a** was dissolved in all useful solvents.

Another piece of evidence bears on the problem. *Rapid* oxidation of **4a** with 10% H_2O_2 in boiling benzene or acetone gave a crude solid, the ^1H NMR spectrum of which was nearly identical with that of pure **7** dissolved in the same solvent. A small signal for protons in the C–CH_3 group in **8** (δ 1.14 vs. δ 1.76 for **7**) could not be unequivocally assigned as it was barely outside the level of random noise in the baseline and at maximum amplitude. If **4a** and **4d** are present, oxidation must occur at rates with enormous differences so that **4a** is consumed to give **7** with concomitant shift of the equilibrium of **4d** to **4a** *without* oxidation of **4d**. This does *not* seem tenable since steric effects in **4a** or **4d** do not seem prohibitive from models.

Consequently, an alternative situation to evaluate is that the fluttering and P-inversion energy barriers are high. Unfortunately, low solubility characteristics of **4** permitted a variable temperature ^1H NMR study only in *o*-ClC_6H_4Cl (ODCB) and C_6H_5CN. In ODCB at 120 °C and after 24 h, several signals were observed. Singlets at δ 1.28 and 1.97 were confirmed for the protons of the –CCH_3 groups in high-melting oxide **8** and low-melting oxide **7**, respectively (approximately 1.4:1), by addition of authentic samples and the observation of a reinforcement of the peak intensities described. Thus, two phosphines, **4a** and **4d**, must have scav-



enged oxygen from solvent. Phosphine **4a** displayed the corresponding signal for protons of the C–CH_3 group at δ 1.58. Two doublets occurred at δ 1.05 and 1.68 in the ratio of 3:1. An important observation was that addition of 3 drops of 30% H_2O_2 to the NMR tube kept at 65 °C for 6 h and then allowed to stand for 12 h at room temperature resulted in the near disappearance of the signal at δ 1.58. Thus, phosphine **4a** was converted to oxide **7** which precipitated along with some **8**. Although **8** is less soluble than **7**, ^1H NMR analysis of the supernatant revealed the same signals for **7** and **8** (ca. 3:1) along with the two doublets at δ 1.05 and 1.65 (J = 7 Hz) but at decreased concentrations compared to the original mixture obtained from heating **4a** in ODCB at 120 °C for 24 h. A second oxidation of the new supernatant with excess 30% H_2O_2 at room temperature for 64 h resulted in the both oxides **7** and **8** with concomitant reduction by 60% of the doublets of δ 1.05 and 1.65. A reasonable assumption is that the peak at δ 1.05 is **4d**, the precursor of the high-melting oxide **8**. If one examines the bond distribution relating P to the CH_3 groups, the following arrangements pertain. Since **4a** has a $^5J_{PH} = 1.6 \pm 0.2$ Hz, it is not unreasonable to predict **4c** to have a similar J value. A tentative conclusion then might be that the signal at δ 1.65 is for **4b**. The J value for the signal at δ 1.05 is an identical 7 Hz, the same as for the doublet at δ 1.65. However, only oxides **7** and **8** were detected and isolated. The implication is that if the signal at δ 1.65 is due to **4b**, oxidation of this phosphine is slow as is true for the signal at δ 1.05 (assigned to **4d**). Courtauld molecular models suggest that the approach of any reagent to the trivalent P atom may be hindered, with possible strong intramolecular P···H—O bonding in **4d**. Phosphine **4a** looks more exposed at P than **4b** or **4c** and does not possess the P···HO bonding. Of course, we cannot rule out **4c** as displaying one of the signals at δ 1.05 or 1.65. Since the rates of oxidation of both of these phosphines are considerably slower than that for **4a**, we must assume that the P is hindered. Moreover, to invoke **4b** or **4c** as candidates for the signal at δ 1.05 or 1.65, we must assume a rapid equilibration with **4a** or **4d** since only oxides **7** and **8** are found. An identical experiment examined after 48 h showed similar results with slightly more oxides being formed and the peaks at δ 1.05 and 1.65 were slightly reduced in intensity.

When **4a** was heated in C_6H_5CN at 120 °C for 48 h, again oxides **7** and **8** formed as observed via ^1H NMR analysis at δ 2.01 and 1.37 along with that for **4a** at δ 1.65. A *very* small triplet centered at δ 1.12 appeared and a signal at δ 2.06, which may be part of a doublet obscured by the signal at δ 2.01 for the low-melting oxide **7**, was detected. Surprisingly, oxidation of this mixture with 5 drops of 30% H_2O_2 for 65 °C for 6 h (and then allowed to stand for 12 h) gave mostly low-melting oxide **7** and less than 10% of the high-melting oxide **8**. If the signal

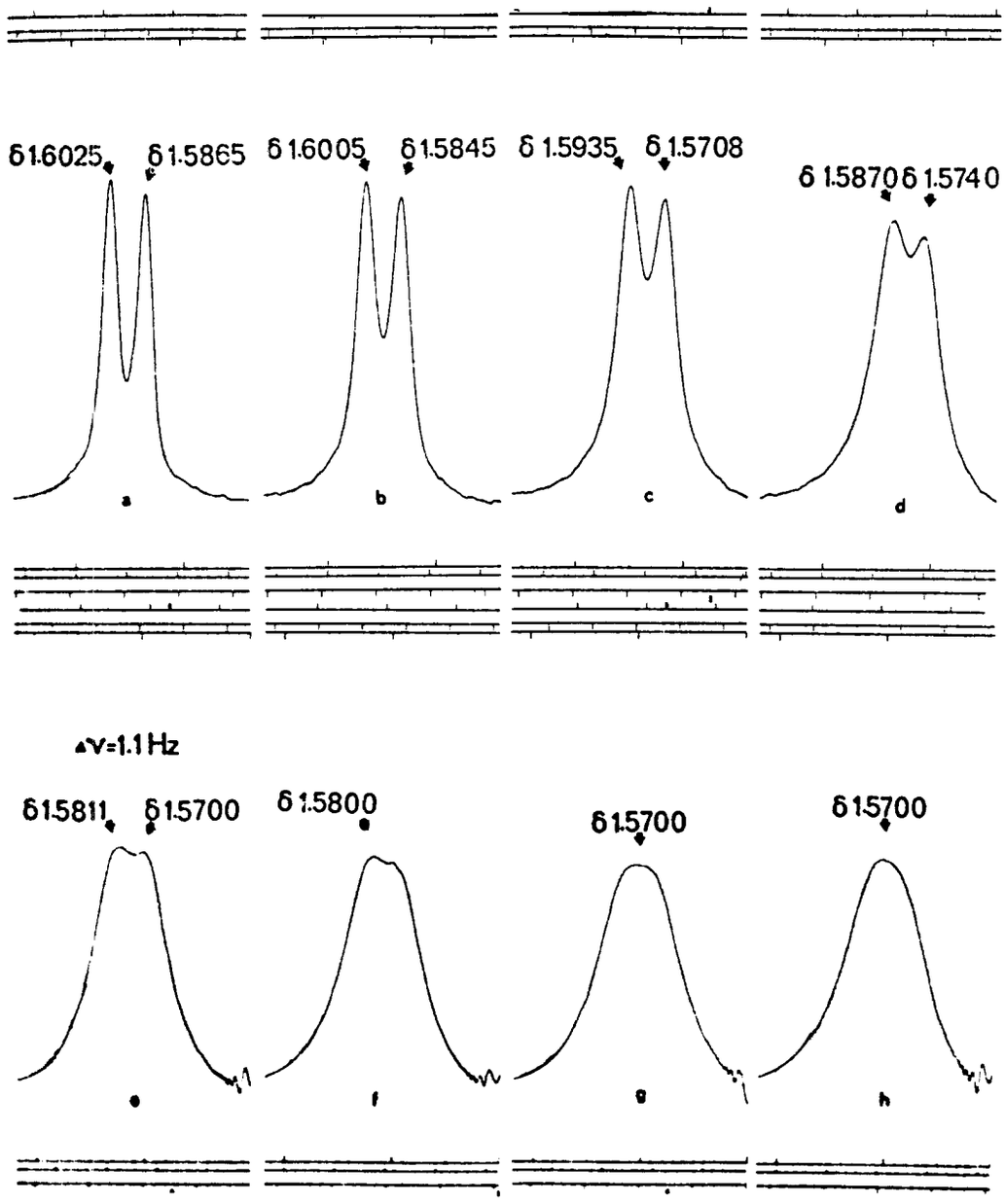
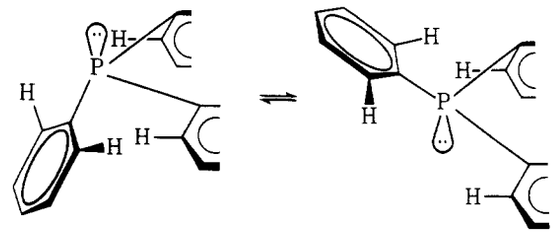


Figure 1. Methyl protons of **4a** in $DCCl_3$ at 100 MHz at various temperatures (°C): a, 30; b, 10; c, 0; d, −10; e, −18; f, −19; g, −20; h, −30.

at δ 2.06 is a doublet (it could not be separated from the peak for oxide **7** with a sweep width of 100 Hz and a resolution of 0.2 Hz), it may be due to **4d** but we cannot eliminate **4b** or **4c** from consideration since the latter could conceivably equilibrate to **4d** before it was consumed in the oxidation to oxide **8**. However, if the signal is due to **4b** or **4c**, it would imply that the inversion barrier for inversion on P in **4c** → **4d** or the flipping process in **4b** → **4d** is high. One would not expect these barriers to be as high for the reverse processes.

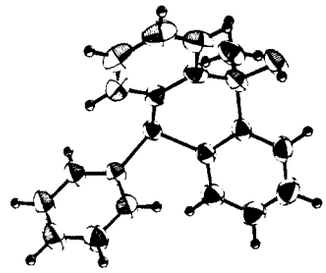
In the more polar benzonitrile under similar conditions, more high-melting oxide **8** is formed than low-melting oxide **7** after 48 h (1.5:1 for **8**:**7** in benzonitrile and 1:3 for **8**:**7** in ODCB). This suggests a higher conversion of **4a** to **4d** in benzonitrile but there is no simple mechanism whereby benzonitrile might promote this conversion. Unfortunately, it has not been possible to isolate from benzonitrile the compound with the signal at δ 2.06 or from ODCB the compound(s) giving signals at δ 1.05 and δ 1.68.

The P-inversion barrier (E_{inv}) in triarylphosphines has been estimated[15b] to be 27–29 kcal/mol. In the estimate it is assumed that pπ–dπ overlap is facilitated in the relatively planar transition state expected for the inversion process. Courtauld models imply that this transition state may possess increased hindrance relative to the ground state because of interaction between the P–C_6H_5 group and the two peri hydrogen atoms



on the fused ring system. Consequently, the barrier may approach 35 kcal/mol or greater (as observed for some trialkyl phosphines).[15b]

A discussion of the phenomena observed at low temperature is in order. If cooling to −20 °C slowed the fluttering process in **4**, one could expect the *average* P–C–C–C–CH angular arrangement to be different from that at room temperature and thus a new $^5J_{PH}$ coupling could result (in our case a smaller $^5J_{PH}$ as observed in Figure 1). Then, the average conformer



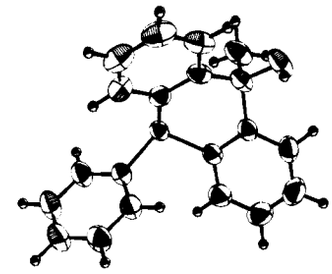


Figure 2. Stereoview of a single molecule of 4a.[35]

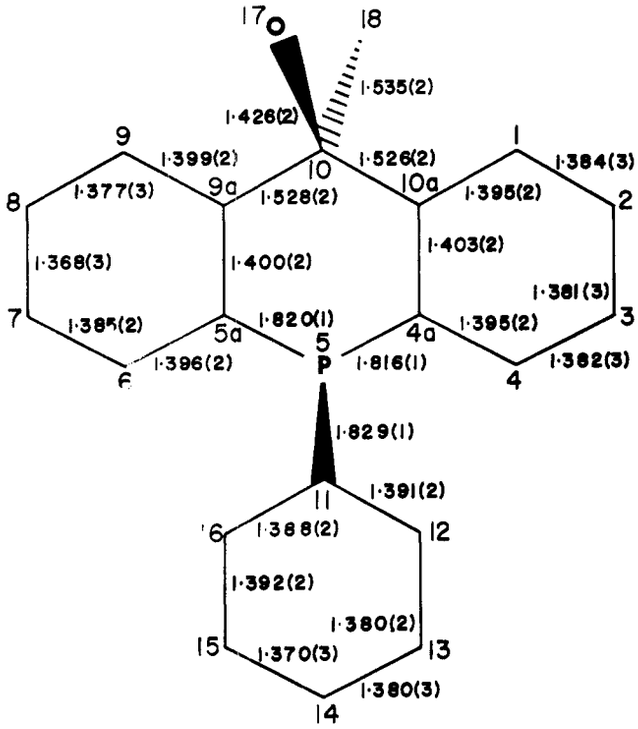


Figure 3. Bond distances and numbering scheme.

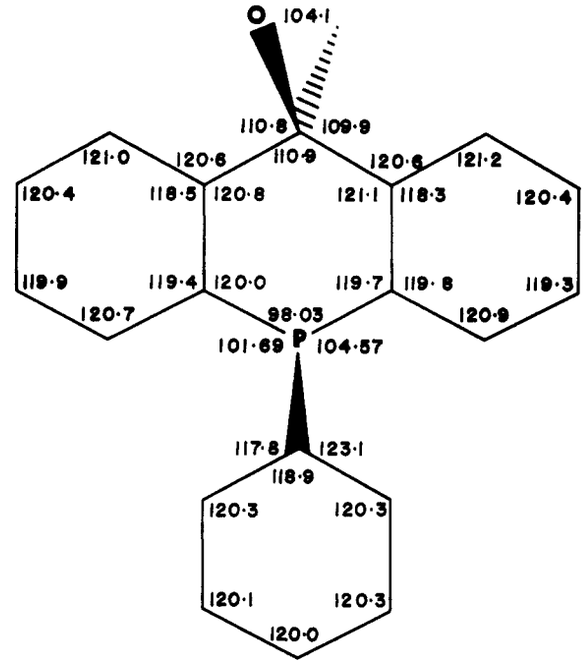


Figure 4. Bond angles. Standard deviations are between 0.06° (for C–P–C) and 0.2°. Additional angles are C(9a)–C(10)–C(18) = 110.3° and C(10a)–C(10)–O(17) = 110.6°.

in solution, perhaps more planar in nature, exists near −20 °C. We cannot exclude this possibility.

Single Crystal Analysis. A stereoview of a single molecule of **4a** is shown in Figure 2. The crystals were obtained via sublimation (see Experimental Section) of a solid sample. That no structural change had occurred during sublimation was confirmed by no depression in the mixture melting point determination of the solid sample and sublimed product. Also the melting point values were identical as were the ^{1}H NMR spectra. Bond distances and the numbering scheme are given in Figure 3 while bond angles are given in Figure 4. For comparison, five structures of phosphine molecules containing P–C(sp^2) bonds were selected from the literature[18–22] based on accuracy of the structure determinations and similarity to the present molecule. The average bond distance for the 12 P–C(sp^2) bonds in these five structures is 1.833 Å. The P(5)–C(11) bond length of 1.829 Å is not significantly different from this average. The two P–C bonds contained in the six-membered ring, however, are slightly shortened [P(5)–(4a) = 1.816 and P(5)–C(5a) = 1.820 Å] compared to the average for P–C(sp^2) bonds in acyclic phosphorus systems. The value of 98.03° for the C(4a)–P(5)–C(5a) angle is on the low side of the range of value reported for six-membered rings containing a P atom.[23]

The identities of the –OH and –CH_3 groups were determined from the weights of vectors in the Patterson map, the behavior of the temperature factors during refinement of the structure, the final bond distances, and the fact that three hydrogen atoms were found attached to C(18) while only one peak was associated with O(17). The –CH_3 group was found to occupy the pseudoaxial position while the –OH and –C_6H_5 groups are in the pseudoequatorial positions. The six-membered heterocyclic ring is in a boat conformation. The internal torsion angles are 4a–5 = −34.9; 5–5a = 38.0; 5a–9a = −2.1; 9a–10 = −43.6; 10–10a = 47.0; 10a–4a = −3.8°. The fold angle (the dihedral angle between the two benzene rings) is found to be 137.4°. Because there are no similar phosphorus compounds for comparison, the phenothiazene system has been chosen to serve as a basis for comparison. A wide variety of values has been reported[24] for the fold angle in phenothiazene systems ranging from 135.6 to 158.5°. It is also interesting to note that in the two crystal forms of phenothiazene[24,25] a difference in fold angles of about 5° is observed and in a phenothiazene derivative[26] containing two molecules per asymmetric unit a difference of about 10° in the fold angle is observed for the two independent molecules. It is therefore unclear how the packing forces and electronic structure affect this conformational parameter. The phenyl group is in an unusual conformation described by the torsion angles C(4a)–P(5)–C(11)–C(12) of 34.1° and C(5a)–P(5)–C(11)–C(16) of 108.3°, and is thus tilted such that H(C12) is located close to C(4) and C(4a) with distances of 2.90 and 2.82 Å, respectively. It is therefore noted that the P(5)–C(11)–C(12) angle is en-

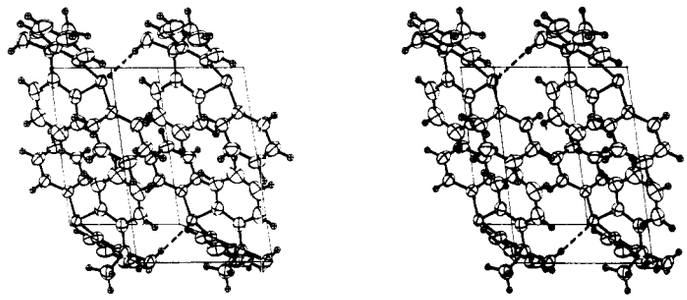


Figure 5. Stereoview of crystal packing axes are $a \rightarrow c \uparrow b$.[35] The hydrogen bond is shown with the dotted line.

larged a significant amount from 120° and that C(11)–P(5)–C(4a) angle is larger than the C(11)–P(5)–C(5a) angle. There is also observed a difference in deviation of P(5) from the phenyl rings in the heterocyclic system. Looking at Figure 3, P(5) is −0.036 Å from the plane of C(1)–C(2)–C(3)–C(4)–C(4a)–C(10a) and +1.01 Å from the plane of C(5a)–C(6)–C(7)–C(8)–C(9)–C(9a).

A packing diagram is shown in Figure 5. The most interesting feature is the occurrence of a P···H—O hydrogen bond. The P···O distance is 3.379 Å, the O–H distance is 0.85 Å, and the P···H distance is 2.526 Å. The O and H atoms are transformed by $1 + x, y, z$. This last value is about 0.6 Å less than the sum of the van der Waals radii of 3.1 Å. The P···H—O angle is 177°. We believe that this is the first observation of an intermolecular P···H—O hydrogen bond in a crystal structure, although evidence has been presented for the P–H group as a hydrogen bond donor.[23,27,28] It is interesting to note that in the crystal structure of *trans*-1-methyl-4-*tert*-butyl-4-phosphorinanol,[29] which contains the necessary molecular features (i.e., a trivalent P atom and a strong donor group), no P···H—O hydrogen bond is reported. Instead an O—H···O hydrogen bond is found between the two independent molecules in the asymmetric unit.

Listing of the anisotropic temperature factors and hydrogen parameters may be obtained in the supplementary material upon request. F_o and F_c tables may be obtained from the senior authors.

Experimental Section

General Data. Melting points were obtained with a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Beckman IR-5A spectrometer. ^1H and ^{31}P NMR spectra were obtained with a XL-100(15) Varian spectrometer. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. *o*-Carboxyphenyldiphenylphosphine oxide (**2b**)[6] was prepared from *o*-tolyldiphenylphosphine oxide (**2a**).[5] Ketophosphine oxide **3a**[6] was obtained via cyclization of **2b** with 115% PPA by a technique described previously[7] for alkenylphosphonium salts. Reduction of **3a** to **3b**[8] with $HSiCl_3$ was accomplished in the standard manner.[6,8] All spectral data and melting point values for **2a, 2b, 3a,** and **3b** were essentially identical with those reported in the references given. All J values were checked at sweep width 250, 100, and 25 Hz for accuracy.

For the purpose of x-ray diffraction studies of **4a** a prismatic crystal (0.35 × 0.22 × 0.20 mm) was cut from one of the larger ones obtained from sublimation at 135 °C (0.025 mm). Initial examination of the crystal showed it to be triclinic with two molecules per unit cell. The crystal data follow: $C_{20}H_{17}OP$; mol wt 304.33; triclinic; a = 6.1336 (4), b = 8.8457 (4), c = 15.4235 (7) Å, α = 100.980 (4), β = 100.003 (3), γ = 83.150 (3)°; V = 805.79 Å;[26] Z = 2; ρ_{obsd} = 1.252 g cm^{-3}, ρ_{calcd} = 1.254 g cm^{-3}; $F(000)$ = 320; space group $P\bar{1}$ as confirmed by structure determination; Ni filtered Cu Kα radiations, λ(Cu Kα_1) 1.54051 Å for least-squares cell data and λ(Cu K$\bar{\alpha}$) 1.54178 Å for intensity; μ(Cu K$\bar{\alpha}$) = 14.8 cm^{-1}.

The unit cell parameters were determined by a least-squares fit to the $+2\theta$ and -2θ of 60 reflections distributed through all octants of reciprocal space. The density was measured by flotation in a mixture of CCl_4 and cyclohexane. A total of 3313 intensities with $\theta \leq 75°$ were measured on a Nonius CAD-4 automatic diffractometer using θ–2θ scan techniques. A variable scan width was calculated as (1.1 + 0.11 tan θ)° for each reflection. A receiving aperture with variable width (4.0 + 0.86 tan θ) mm and a constant height of 6 mm was located 173 mm from the crystal. A reflection was scanned for a maximum time of 90 s with ⅔ of that time spent scanning the peak (P) and ⅙ of the time spent scanning each the left and right backgrounds (LB and RB). The unscaled intensity was calculated as $I = P - 2(LB + RB)$. The scan time was less than 90 s for those intensities where a value of 40 000 for I could be attained with a faster scan speed than the normal one of 1.1°/min. A monitor reflection was measured every 30 reflections. Three oreintation control reflections were centered after every 200 measurements. In the case that any of the θ, ω, ϕ, or K angles of these reflections were changed by 0.1°, a new orientation matrix was automatically determined from a list of 11 reflections; 268 reflections were considered indistinguishable from the background having $I \leq 2\sigma(I)$ and were assigned an intensity equal to 1.4 $T^{1/2}$ ($T = P + 2LB + 2RB$) for the purpose of least-squares refinement. A Gaussian method[30] was employed to make the absorption correction by using 216 sampling points. The transmission coefficient ranged from 0.681 to 0.774. Each structure factor was assigned a weight given by $w_F = 1/\sigma_F^2$ where σ_F is defined as

$$\sigma_F = \tfrac{1}{2}\left[\frac{\sigma^2 + (0.04I\nu)^2}{(\mathrm{Lp})(\mathrm{I}\nu)}\right]^{1/2}$$

$\sigma = (T^{1/2})\nu$, ν is scan speed, and Lp is the Lorentz-polarization factor.

A sharpened Patterson map was calculated from which the positions of all 22 nonhydrogen atoms were located resulting in an initial R value ($= \Sigma|kF_o - F_c|/\Sigma|kF_c|$) of 0.24. After several cycles of refinement[31] (9 × 9 block diagonal) these atoms were given anisotropic temperature factors. The hydrogen atoms were located from a difference Fourier synthesis. Least-squares refinement with isotropic temperature factors for hydrogen atoms and anisotropic temperature factors for nonhydrogen atoms was terminated when all shifts were small fractions of the corresponding estimated standard deviations.

The scattering factors for P, O, and C atoms were taken from the International Tables for X-Ray Crystallography[32] and those for hydrogen atoms from Stewart, Davidson, and Simpson.[33]

The R value based on final parameters (Table II and supplementary material[34]) is 0.040 for all 3313 data. The least-squares refinement minimized the quantity $\Sigma w_F(kF_o - F_c)^2$. The average values of $w_F\Delta F^2$ did not vary significantly with either $|F_o|$ or sin θ/λ thus validating the weighting scheme which was used.[34] A final difference Fourier map showed no peaks larger than 0.17 e A^{-3} or less than −0.23 e A^{-3}.

5,10-Dihydro-10-methyl-5-phenylacridophosphin-10-ol (4a). Methylmagnesium iodide was prepared by adding methyl iodide (1.78 g, 12.5 mmol) in 20 ml of anhydrous ether to magnesium turnings (0.304 g, 0.0125 g-atom) covered with 10 ml of anhydrous ether. The reaction was completed in 4 h when all the magnesium was consumed. Cold THF (100 ml) was poured into the Grignard solution and again ether was distilled out. Ketophosphine **3b**[6] (1.44 g, 5 mmol) in 50 ml of freshly distilled THF was added to the Grignard solution at room temperature under N_2. After the addition (≈1 h), the reaction mixture was stirred at room temperature for 1 h and heated for 2 h at gentle reflux. After the mixture was cooled, saturated NH_4Cl solution (10 ml) was added along with ether. The organic layer was separated, and the aqueous layer was extracted with two 50-ml portions of benzene. The combined organic layers were dried (magnesium sulfate). Removal of the solvent using a rotary evaporator gave 1.45 g of crude alcohol **4a.** Recrystallization (benzene–hexane) gave **4a** in colorless crystal form (1.25 g,[17] 81%, mp 141–142 °C). The ^1H NMR spectrum showed the presence of recrystallization solvent (apparently, it had been trapped in the crystals) which could not be removed by vacuum drying (110 °C, 0.01 mm). However, a small amount of the crystals was ground to a fine powder and then sublimed at 135 °C (0.025 mm) to give pure phosphine **4a** (mp 156–157 °C).

Anal. Calcd for $C_{20}H_{17}OP$: C, 78.95; H, 5.59; P, 10.20. Found: C, 79.28; H, 5.51; P, 10.25.

Phosphine **4a** (100 mg) in 20 ml of benzene was converted to the oxide **7** by using an excess of 10% H_2O_2. After stirring at room temperature for 12 h, a quantitative yield of the oxide (mp 261 °C) was obtained. On the basis of melting point, mixture melting point, ^1H NMR, and IR spectral data, the product was found to be identical with compound **7** cited latter. Phosphine **4a** (100 mg) was converted to phosphonium salt **5** by addition of an excess of methyl iodide (93.4 mg, 0.7 mmol). After stirring at room temperature for 24 h, the mixture gave a quantitative yield of the methyl iodide salt. On the basis of the melting point (276–277 °C), mixture melting point, NMR, and

Table II. Final Fractional Coordinates for Nonhydrogen Atoms[a]

	x	y	z
C(1)	−4487 (3)	−1957 (2)	1541 (1)
C(2)	−4427 (4)	−2152 (2)	633 (1)
C(3)	−2813 (4)	−1529 (2)	324 (1)
C(4)	−1304 (3)	−661 (2)	928 (1)
C(4a)	−1396 (2)	−406 (1)	1842 (1)
P(5)	584.3 (5)	748.7 (4)	2626.9 (2)
C(5a)	−1219 (2)	1576 (2)	3451 (1)
C(6)	−1053 (3)	3088 (2)	3911 (1)
C(7)	−2347 (3)	3696 (2)	4569 (1)
C(8)	−3791 (3)	2805 (3)	4777 (1)
C(9)	−4001 (3)	1317 (2)	4324 (1)
C(9a)	−2731 (2)	675 (2)	3651 (1)
C(10)	−2949 (3)	−985 .(2)	3163 (1)
C(10a)	−2965 (2)	−1100 (1)	2162 (1)
C(11)	750 (2)	2409 (2)	2101 (1)
C(12)	−1055 (2)	3071 (2)	1578 (1)
C(13)	−859 (3)	4381 (2)	1244 (1)
C(14)	1122 (3)	5059 (2)	1436 (1)
C(15)	2908 (3)	4428 (2)	1956 (1)
C(16)	2742 (2)	3090 (2)	2282 (1)
O(17)	−4899 (2)	−1551 (1)	3322 (1)
C(18)	−1037 (3)	−2072 (2)	3547 (1)

[a] The x, y, and z values are all $\times 10^4$. Standard deviations for the last digit are in parentheses.

IR spectral data, the salt was identical with compound **5** cited later.

***cis*- and *trans*-5,10-Dihydro-10-methyl-5-phenylacridophosphin-10-ol 5-Oxide (7, 8).** Methylmagnesium iodide was prepared as cited previously by adding methyl iodide (14.2 g, 0.1 mol) to magnesium turnings (2.43 g, 0.1 g-atom). Ketophosphine oxide **3a**[6] (6.08 g, 0.02 mol), previously dissolved in 200 ml of hot anhydrous THF, was added through an addition funnel dropwise but rapidly into the Grignard solution, kept at room temperature. The reaction mixture was then boiled for 10 h under N_2. After cooling in the ice–water bath, the mixture was concentrated to approximately 20 ml; this was followed by hydrolysis with saturated NH_4Cl solution (20 ml) and the resulting mixture was stirred for 1 h and allowed to stand for 1 h more. The crude product precipitated out as a white solid which was filtered off and recrystallized (absolute ethanol) to give pure oxide **8** (1.53 g, 24% yield), mp 329–330 °C.

Anal. Calcd for $C_{20}H_{17}O_2P$: C, 75.00; H, 5.31; P, 9.70. Found: C, 75.10; H, 5.48; P, 9.74.

The solvent from the mother liquor was evaporated to give a gummy solid which was dissolved in 10 ml of benzene; these solutions, standing for 5 h, slowly deposited a small amount of white solid. This was identified by IR analysis to be starting material ketophosphine oxide **3a**. The benzene layer was then decanted and evaporated to give a gummy solid which was recrystallized by dissolving the solid in minimum benzene and slowly adding hexane to cloudiness. A white solid precipitated slowly (overnight). According to the ^1H NMR spectrum, the product appeared to be a mixture of both isomers **7** and **8**. By the ratio of ^1H NMR signals for methyl protons at δ 1.14 and 1.76, isomer **8** (δ 1.76) constituted approximately 80% of this mixture. In each of three recrystallizations, the compound was dissolved in minimum ethanol and benzene was added; the solution was concentrated to ½ volume, diluted with more benzene, concentrated again, and allowed to stand overnight. By such purification, isomer **7** was obtained in pure crystal form (1.2 g, 20%, mp 261–262 °C).

Anal. Calcd for $C_{20}H_{17}O_2P$: C, 75.00; H, 5.31; P, 9.70. Found: C, 75.30; H, 5.27; P, 9.73.

***cis*- and *trans*-5,10-Dihydro-10-hydroxy-5,10-dimethyl-5-phenylacridophosphinium Iodide (5, 6).** To the Grignard reagent prepared by adding methyl iodide (9.94 g, 70 mmol) in 30 ml of THF to magnesium (1.215 g, 0.05 g-atom) covered with 25 ml of THF was added slowly, with cooling, ketophosphine **3b** (1.44 g, 5 mmol) in 50 ml of freshly distilled THF. After the addition was completed, the reaction mixture was boiled overnight (about 12 h). After cooling in the ice–water bath, hydrolysis was performed by slowly adding saturated NH_4Cl solution (20 ml). The product was a gummy solid which would not dissolve in the THF but was, however, soluble in methylene chloride (50 ml). Consequently, the organic layer was separated and the aqueous layer was extracted with 50 ml of methylene chloride. The combined organic layers were dried (magnesium sulfate). Removal of the solvent using a rotary evaporator gave 1.5 g of crude product. Recrystallization twice from benzene [as described for purification of isomer **8** except that more ethanol (≈20 ml) was used] and then once from absolute ethanol gave shiny crystals of pure salt **5** (0.16 g, 8%, mp 282–283 °C).

Anal. Calcd for $C_{21}H_{20}OPI$: C, 56.50; H, 4.48; P, 6.95. Found: C, 56.63; H, 4.57; P, 6.96.

All the mother liquors were combined and the solution was concentrated to give a mixture of isomer **5** and **6** verified by NMR analysis. After two recrystallizations (benzene–ethanol), isomer **6** was obtained in the pure crystal form (0.7 g, 29%, mp 276–277.5 °C).

Anal. Calcd for $C_{21}H_{20}OPI$: C, 56.50; H, 4.48; P, 6.95. Found: C, 56.52; H, 4.11; P, 7.12.

5,10-Dihydro-10-neopentyl-5-phenylacridophosphin-10-ol (12c). Freshly washed and dried Mg (0.63 g, 0.026 g-atom) in 40 ml of sodium-dried xylene (3.8 g, 0.052 mol), freshly distilled THF, and 0.01 g of I_2 were heated to 123 °C with stirring. 1-Chloro-2,2-dimethylpropane (2.8 g, 0.026 mol) in 10 ml of xylene was slowly added over 2 h. The temperature decreased to 118 °C. The reaction mixture was stirred and heated to gentle reflux for 6 h. During this time, almost all the magnesium was consumed. To the cooled mixture, ketophosphine **3b** (2.88 g, 0.01 mol) in 45 ml of THF was slowly added over a 2-h period under N_2. The temperature rose from 26 to 30 °C. The reaction mixture was then allowed to stir overnight at room temperature and was then gently heated (80 °C) for 6 h. To the cooled reaction mixture was added 20 ml of saturated NH_4Cl solution with caution. The mixture was then stirred for 3 h. Two layers formed and the organic layer was separated, all under N_2. Two 50-ml extracts (xylene) of the aqueous layer were added to the original organic layer. The combined organic phases were dried ($MgSO_4$) overnight under N_2. Evaporation left a gummy solid to which was added a small amount (~10 ml) of CH_3CN with shaking. A white solid formed (0.8 g, 22.2%) and was dissolved in a minimum of $HCCl_3$. Reprecipitation was effected by slow addition of anhydrous hexane until the solution became cloudy. After standing in a refrigerator for 10 h, a solid formed and was filtered, 0.7 g (mp 195–197 °C) of phosphine **12c**: ^1H NMR ($DCCl_3$) δ 0.81 [s, $C(CH_3)_3$, 9 H], 2.039 (d, J_{PCCCH} = 3 Hz, CH_2, 2 H), 2.16 (s, OH, 1 H), and 6.81–7.96 (m, ArH, 13 H).

Anal. Calcd for $C_{24}H_{25}OP$: C, 79.97; H, 6.99; P. 8.59. Found: C, 79.80; H, 6.98; P, 8.57.

5,10-Dihydro-10-neopentyl-5-phenylacridophosphin-10-ol 5-Oxide (12b). The mother liquor (CH_3CN) from the above experiment was concentrated and allowed to stand in a refrigerator over 30 h. A heavy oil formed and with scratching, a solid slowly formed, 0.61 g (16%). Recrystallization of the solid from ethyl acetate and then from CH_3OH–H_2O (2:1) gave oxide **12b**: 0.5 g (mp 286–290 °C); ^1H NMR ($DCCl_3$) δ 0.73 [s, $C(CH_3)_3$, 9 H], 2.4 (s, CH_2, 2 H), and 7.16–8.16 (m, ArH, 13 H); ^{31}P NMR ($DCCl_3$) −13.40 ppm.

Anal. Calcd for $C_{24}H_{25}O_2P$: C, 76.57; H, 6.69; P, 8.22. Found: C, 76.59; H, 6.66; P, 8.27.

Reduction of Ketophosphine Oxide 3a. Preparation of 5,10-Dihydro-5-phenylacridophosphin-10-ol 5-Oxide (12a). Ketophosphine oxide **3b** (0.76 g, 2.5 mmol) was dissolved in 70 ml of hot 95% ethanol. After the solution had slowly cooled to room temperature, it was treated with sodium borohydride powder (0.28 g, 7.5 mmol) slowly. After being stirred at room temperature for 2 h, the reaction mixture was treated with water (5 ml) and warmed on a steam bath for 5 min. The mixture was cooled in an ice bath, and the resulting solid was filtered off to afford 0.76 g of crude **12a** (mp 225–230 °C, 100%). The solid was recrystallized from absolute ethanol to give 0.6 g of pure product **12a** in crystalline form (mp 249.5–250.5 °C, 80%): IR (KBr) 3350 (broad, O–H), 1179 cm^{-1} (P=O); ^1H NMR (Me_2SO-d_6) δ 5.15 [bs, >C(OH), 1 H], 6.40 (bd, $^4J_{PH}$ = 8 Hz, CH, 1 H), 7.2–8.3 (m, ArH, 13 H).

Anal. Calcd for $C_{19}H_{15}O_2P$: C, 74.51; H, 4.90; P, 10.13. Found: C, 74.33; H, 5.04; P, 10.05.

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Registry No.—**3a,** 54086-38-3; **3b,** 54086-39-4; **12a,** 61279-17-2; **12b,** 61279-18-3; **12c,** 61279-19-4; 1-chloro-2,2-dimethylpropane, 753-89-9.

Supplementary Material Available. Listing of the anisotropic temperature factors and hydrogen atom parameters (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Research Assistant, 1974–1975; (b) Research Associate, 1976, Oklahoma State University.
(2) (a) Research Assistant, 1972–1976, University of Oklahoma.
(3) Much of the work in the few related systems examined appears to be summarized in the following records. (a) For arsenics: J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1184 (1940); E. R. H. Jones and F. G. Mann, *ibid.*, 411 (1955); O. Kennard, F. G. Mann, D. G. Watson, J. K. Fawcett, and K. A. Kerr, *Chem. Commun.*, 268 (1968); K. Mislow, A. Zimmerman, and J. T. Melillo, *J. Am. Chem. Soc.*, **85,** 594 (1963); O. Kinnard, F. G. Mann, D. G. Watson, J. F. Fawcett, and K. A. Kerr, *Chem. Commun.*, 269 (1968). (b) For sulfur analogues: A. L. Ternay, Jr., D. W. Chasar, and M. Sax, *J. Org. Chem.*, **32,** 2465 (1967); A. L. Ternay, Jr., and D. W. Chasar, *ibid.*, **32,** 3814 (1967); **33,** 2237 (1968). (c) For a few dihydrophosphanthrene systems: M. Davis and F. G. Mann, *Chem. Ind. (London)*, 1539 (1962); *J. Chem. Soc.*, 4266 (1963); 3770 (1964). The early nomenclature of dihydrophosphanthrene has been continued by some workers but we have elected to use names designated by Dr. K. Loening, Director of Nomenclature of Chemical Abstracts. (d) For sila-, germa-, and stannadihydroanthracenes: P. Jutzi, *Chem. Ber.*, **104,** 1455 (1971). (e) For a general review, see M. J. Gallagher and I. D. Jenkins, *Top. Stereochem.*, **3,** 1 (1968).
(4) F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth", Wiley-Interscience, New York, N.Y., 1970.
(5) C. E. Griffin, R. B. Davison, and M. Gordon, *Tetrahedron*, **22,** 561 (1966).
(6) Y. Segall, I. Granoth, and A. Kalir, *J. Chem. Soc., Chem. Commun.*, 501 (1974).
(7) For the general procedure see W. R. Purdum, G. A. Dilbeck, and K. D. Berlin, *J. Org. Chem.*, **40,** 3763 (1975).
(8) G. Jongsma, R. Lourens, and F. Bickelhaupt, *Tetrahedron*, **32,** 121 (1976).
(9) C. Jongsma, F. J. M. Freijee, and F. Bickelhaupt, *Tetrahedron Lett.*, 481 (1976).
(10) D. B. Denny and J. W. Hanifin, *Tetrahedron Lett.*, 2178 (1963).
(11) K. L. Marsi and R. T. Clark, *J. Am. Chem. Soc.*, **92,** 3791 (1970); M. El-Deek, G. D. Macdonell, S. D. Venkataramu, and K. D. Berlin, *J. Org. Chem.*, **41,** 1403 (1976).
(12) S. A. Evans and A. L. Ternay, Jr., *J. Org. Chem.*, **40,** 2993 (1975); A. L. Ternay, Jr., L. Eus, J. Herrmann, and S. Evans, *ibid.*, **34,** 940 (1969), and references cited therein.
(13) A. G. Moritz, J. D. Saxby, and S. Sternhell, *Aust. J. Chem.*, **21,** 2566 (1968).
(14) J. Ronayne and D. H. Williams, *Chem. Commun.*, 712 (1966).
(15) (a) R. D. Beachler and K. Mislow, *J. Am. Chem. Soc.*, **92,** 3090 (1970); (b) K. Mislow, *Trans. N.Y. Acad. Sci., Ser. 11,* **35,** 227 (1973); (c) For a review on the stereochemistry of P compounds, see W. E. McEwen and K. D. Berlin, Ed., "Organophosphorus Stereochemistry", Parts I and II, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1975, and for a new theoretical approach to the inversion barrier, see W. Cherry and N. Epiotis, *J. Am. Chem. Soc.*, **98,** 1135 (1976).
(16) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Am. Chem. Soc.*, **89,** 357 (1967).
(17) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **92,** 1442 (1970).
(18) A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Am. Chem. Soc.*, **93,** 2574 (1971).
(19) J. J. Daly and S. A. Zuerich, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **118,** 332 (1963).
(20) J. C. J. Bart, *Acta Crystallogr., Sect. B,* **25,** 489 (1969).
(21) T. S. Cameron and K. Millar, *Cryst. Struct. Commun.*, **3,** 489 (1974).
(22) C. Kruger and P. J. Roberts, *Cryst. Struct. Commun.*, **3,** 707 (1974).
(23) D. E. C. Corbridge, "The Structural Chemistry of Phosphorus", American Elsevier, New York, N.Y., 1974.
(24) J. J. H. McDowell, *Acta Crystallogr., Sect. B,* **32,** 5 (1976).
(25) J. D. Bell, J. F. Blount, O. V. Briscoe, and H. C. Freeman, *Chem. Commun.*, 1656 (1968).
(26) S. S. C. Chu and D. van der Helm, *Acta Crystallogr., Sec. B,* **32,** 1012 (1976).
(27) L. W. Schroeder and J. J. Rush, *J. Chem. Phys.*, **54,** 1968 (1971).
(28) A. Sequeira and W. C. Hamilton, *J. Chem. Phys.*, **47,** 1818 (1967).
(29) A. T. McPhail, P. A. Luhan, S. I. Featherman, and L. D. Quin, *J. Am. Chem. Soc.*, **94,** 2126 (1972).
(30) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18,** 1035 (1965).
(31) F. R. Ahmed, S.F.L.S. program, NRC-10 Ottawa, National Research Council, 1966.
(32) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962.
(33) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42,** 3175 (1965).
(34) For a listing of aniostropic temperature factors, hydrogen parameters, and observed and calculated structure factors see paragraph at end of paper regarding supplementary material.
(35) C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Studies on the Syntheses of Heterocyclic Compounds. 696.[1] Stereochemistry of Four Isomeric 4a-Cyano-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1-methoxycarbonyl-1-methylphenanthrenes

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Thermolysis of 1-cyano-4-methoxy-1-(4-methoxycarbonyl-4-vinylpentyl)benzocyclobutene gave four stereoisomers of 4a-cyano-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1-methoxycarbonyl-1-methylphenanthrene, whose structures were revealed by the conversion of each octahydrophenanthrene into the known compounds. The structure elucidation and the chemistry of these compounds are presented.

There have been many reports on a discussion of the stereochemistry of stereoisomeric diterpenoids by physical and chemical means.[2,3] In general, naturally occurring diterpenoids have a trans A/B ring junction and are classified into podocarpic acid and abietic acid types of compounds depending upon the stereochemistry of C-1 substituents. Structures having a cis A/B ring junction are, however, possible and, in fact, there are several papers concerning the stereochemistry of four synthetic isomers.[4]

Previously, we have reported the synthesis of a key intermediate for diterpene alkaloids using the thermocyclization of a benzocyclobutene derivative.[5] In the course of investigation for this reaction, we could obtain four possible stereoisomeric octahydrophenanthrenes and reveal each structure using physical and chemical procedures.

As we have previously reported,[5] the thermolysis of 1-cyano-4-methoxy-1-(4-methoxycarbonyl-4-vinylpentyl)-benzocyclobutene (1) at 180–230 °C for 3 h gave 4aα-cyano-1,2,3,4a,9,10,10aα-octahydro-7-methoxy-1α-methoxycarbonyl-1β-methylphenanthrene (2) in a stereocontrolled manner, but the starting material was also recovered. Therefore, the benzocyclobutene 1 was treated under more