Synthetic Approaches to Unsaturated Five-membered Heterocycles Containing Both Ring and Side-chain Phosphorus Atoms

Md. Amin, David G. Holah, Alan N. Hughes* and Thitima Rukachaisirikul

Department of Chemistry, Lakehead University
Thunder Bay, Ontario, Canada P7B 5E1

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The syntheses of several structurally interesting 2-diphenylphosphinyl-substituted 2-phospholenes and phospholanes are reported together with a discussion of the ^{31}P and ^{13}C nmr spectral properties of these compounds. Several of these syntheses were found to be highly stereoselective and the potential of some of the products of these reactions as precursors to phosphole derivatives bearing phosphorus-containing side-chains has also been explored. A new, and possibly general, route to 4-oxo-2-phospholene oxides or sulfides from the corresponding 4-methylene compounds is also reported. This route involves an unusual free-radical catalyzed oxidative cleavage of the 4-methylene group by molecular oxygen and a probable mechanism for this reaction is proposed.

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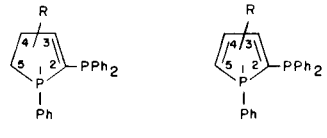
In connection with our studies on the coordination chemistry of phosphines [1] and phospholes [2] in general and bidentate phosphines [3] in particular, we have synthesized a range of novel unsaturated five-membered heterocycles containing both ring and side-chain phosphorus atoms. The majority contain the 2-substituted 2-phospholene structural unit shown in **1** and one of the as yet unrealized, though actively pursued, objectives of this study is the synthesis of the fully unsaturated phosphole system **2**.

These systems are of interest for a variety of reasons. For example, the two phosphorus atoms in **1** and **2** should



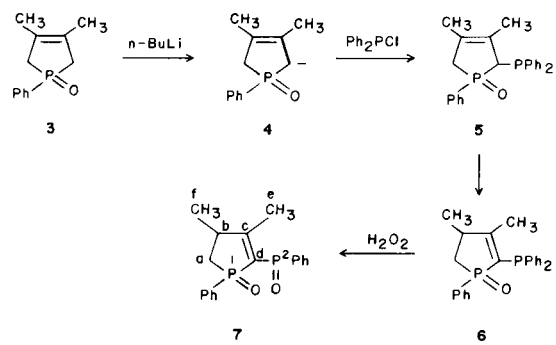
1 **2**

have quite different donor character which would be of interest not only in conventional coordination chemistry but also in the chemistry of potential homogeneous catalysts based upon these systems. These two non-equivalent P atoms should also show nmr coupling with each other and with the ring ^{13}C atoms. Indeed, the ^{13}C spectra of phosphorus heterocycles [4] and P-P coupling in a variety of bis-phosphines, bis-phosphine derivatives, and bis-phosphine complexes [5] have both received considerable attention recently.

In addition, phosphines in general and bis-phosphines in particular react readily with electrophilic alkyne derivatives to give a variety of unsaturated phosphorus heterocycles [6], some having quite unusual structures. The use of systems such as **1** and **2** in such reactions could therefore be of considerable value in the synthesis of complex, fused-ring phosphorus heterocycles.

Finally, fully unsaturated systems such as **2** have the potential for cyclic delocalization and may, in some sense, be regarded as potentially aromatic systems. This topic has been discussed extensively elsewhere [7] for simpler phosphole systems and will not be further explored here except to note that the properties of a system containing both a delocalized and non-delocalized phosphorus non-bonding pair could be very interesting indeed.

The framework of structures of type **1** is easily constructed by treating the readily accessible [8] 3-phospholene oxide **3** with *n*-butyllithium to generate the known anion **4** in the manner outlined in the literature [9]. This, in turn, was treated with chlorodiphenylphosphine to give the 2-phospholene derivative **6**. Presumably the 3-phospholene oxide **5** occurs as an intermediate in the transformation **4** → **6** but the very basic medium in which the reaction is carried out apparently induces rapid double bond migration. Although **6** is formed in good yield by this sequence of reactions, it is difficult to isolate it in pure form from the complex product mixture. A clean product separation is, however, achieved by oxidation of **6** to **7**. This 2-phospholene oxide can be crystallized directly from the reaction mixture but isolation is more conveniently achieved by chromatographic methods (see Experimental section).



3 **4** **5** **7** **6**

Table I

^{31}P NMR Spectral Data for 2-Diphenylphosphinyl-substituted 2-Phospholene and Phospholane Derivatives

Compound	δ Ring P Atom [a]	δ Side-Chain P Atom	$^{2}J_{P\text{-}P}$ (Hz)
7	58.08	20.82	39.6
8 (major isomer)	48.90	20.78	35.4
8 (minor isomer)	51.12	20.66	35.4
10	48.22	22.18	33.5
16	1.12	25.00	59.7
17	32.50	21.64	24.7
21a	46.50	20.27	31.7
21b	43.93	21.61	31.3
27	60.05	31.59	2.2
29	-28.44	23.70	51.2

[a] Positive shifts are downfield of 85% H_3PO_4.

Table II

^{13}C NMR Spectral Data for 2-Diphenylphosphinyl-substituted 2-Phospholene and Phospholane Derivatives and Related Compounds [a,b]

Compound	δ C Aromatic	δ C Ring and Side-chain (Multiplicity) [c] (J_{P^1C} Hz) (J_{P^2C} Hz) [e]					
		C_a	C_b	C_c	C_d	C_e	C_f
7	127.15-135.50 (m)	35.89 (dd) (68.36) (10.00)	43.37 (dd) (7.33) (13.42)	183.33 (dd) (21.97) (2.44)	[f]	19.15 (dd) (14.65) (6.10)	21.18 (s) (0) (0)
10	127.38-135.58 (m)	34.65 (dd) (72.33) (3.97)	144.45 (dd) (10.85) (17.29)	170.86 (dd) (14.24) (3.39)	[f]	15.85 (dd) (14.04) (5.49)	116.74 (d) (15.26) (0)
12	123.92-135.06 (m)	40.37 (d) (59.00) (—)	145.55 (d) (9.49) (—)	150.60 (d) (12.89) (—)	[f]	16.35 (d) (16.95) (—)	112.99 (d) (13.56) (—)
17	126.50-133.20 (m)	38.26 (d) (75.19) (0)	196.00 (t) (20.14) (20.14)	166.44 (t) (2.69) (2.69)	149.52 (dd) (73.86) (63.11)	13.23 (dd) (13.43) (5.37)	—
21a	123.86-138.62 (m)	33.83 (dd) (70.80) (3.66)	63.65 (t) (20.14) (20.14)	175.64 (dd) (11.60) (3.05)	[f]	13.45 (dd) (14.03) (5.49)	53.19 (d) (3.05) (0)
21b	127.50-134.55 (m)	34.60 (dd) (67.82) (3.39)	62.35 (dd) (23.05) (18.99)	175.60 (dd) (11.53) (2.71)	[f]	13.49 (dd) (13.90) (5.40)	52.52 (d) (3.39) (0)
22a	128.00-132.73 (m)	43.50 (d) (60.35) (—)	198.69 (d) (16.31) (—)	154.47 (d) (3.30) (—)	145.14 (d) (67.81) (—)	13.63 (d) (14.92) (—)	—
22b	129.05-133.00 (m)	37.94 (d) (74.60) (—)	196.97 (d) (6.70) (—)	158.42 (d) (6.10) (—)	143.71 (d) (83.41) (—)	13.71 (d) (15.60) (—)	—
27	127.60-133.54 (m)	39.31 (d) (66.46) (0)	[g]	44.11 (d) (8.81) (0)	49.59 (dd) (61.37) (48.83)	21.00 (d) (8.82) (0)	—

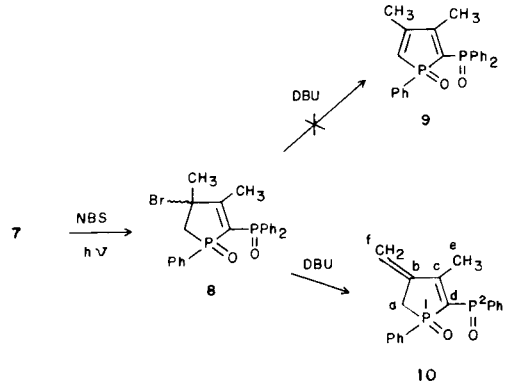
[a] Proton-decoupled. [b] The numbering and lettering of the C and P atoms are given on the structures in the text. [c] d = doublet, dd = doublet of doublets, m = multiplet, s = singlet, t = triplet. [e] P-C coupling constants have been assigned by analogy with related structures in the literature [4]. J_{P^1C} and J_{P^2C} may be transposed in certain cases. [f] Signal obscured by aromatic carbon signals. [g] Signal obscured by solvent signal (deuteriochloroform).

The 2-phospholene oxide **7** has, in fact, been prepared earlier [10] but since the product was not well characterized, we have carried out a thorough spectroscopic characterization. For example the ^{31}P nmr spectrum (Table I) shows the ring phosphorus atom with a chemical shift typical [11] of phosphorus in a 2-phospholene oxide and this is coupled, as expected, with the side-chain phosphorus atom. The ^{1}H spectrum (see Experimental) and the ^{13}C spectrum (Table II) are also in excellent agreement with the proposed structure but discussion of the rather complex ^{13}C spectrum will be deferred until later so that such spectra of this and related structures may be discussed as a whole.

Since the stereochemistry about the ring P atom would be fixed during the synthesis of **7**, two configurational stereoisomers of **7** are possible because of the chirality at C_b. The ^{31}P, ^{1}H and ^{13}C spectra show, rather surprisingly, that the sample of **7** isolated for each of the many times the synthesis was carried out consists of only one stereoisomer and a detailed chromatographic examination of the crude reaction mixture on several occasions showed no trace of the other possible stereoisomer. The reaction is,

therefore, highly stereoselective.

In an attempt to synthesize structures of type **2**, the 2-phospholene oxide **7** was subjected to a photochemically induced allylic bromination (using *N*-bromosuccinimide, NBS) to give **8**, with a subsequent dehydrobromination using the acidic ring methylene protons to give the 2-diphenylphosphinylphosphole derivative **9** in mind. Compound **8** is easily synthesized by this method in excellent yield but good analytical data could not be obtained for this compound because of its limited thermal stability even at room temperature. The characterization of **8** is, therefore,

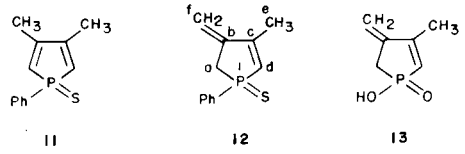


mainly on the basis of spectroscopic evidence, the nature of the precursor **7**, and the nature of the dehydrobromination product to be discussed shortly.

Regarding the spectroscopic evidence, the compound has sufficient thermal stability to show the expected molecular ion peaks at m/e = 484 (^{79}Br) and 486 (^{81}Br) in the mass spectrum although the peaks are quite weak. The ^{31}P nmr spectrum (Table I) of a freshly prepared solution is very clean and shows clearly that, as expected from the radical nature of the reaction leading to the formation of **8**, two configurational stereoisomers of **8** are formed in unequal quantities.

The ^{1}H nmr spectrum of **8** is also consistent with this and shows the aromatic protons as a complex multiplet at δ = 6.77 - 8.25 while the ring methylene protons appear as another multiplet at δ = 2.25 - 3.50. It is in the signals of the two methyl groups, however, that the presence of two stereoisomers becomes clear. Thus, the allylic methyl protons appear as two superimposed triplets of unequal area ($^{4}J_{P^1\text{-}H} = {}^{4}J_{P^2\text{-}H}$ = 2.0 Hz in both cases) with the multiplet centered on δ = 2.47 while the non-allylic methyl protons appear as two singlets of unequal area at δ = 2.06 and 2.12. It seems then that, as in the precursor **7**, both phosphorus atoms couple (equally) with the allylic methyl protons while neither of the phosphorus atoms couples with the non-allylic methyl protons. Integration of the various signals again indicates a high degree of purity for the freshly prepared material. Carbon spectra could not be obtained because of the limited stability of the product.

The dehydrobromination of **8**, occurs very readily with both 1,8-diazobicyclo[5.4.0]undec-5-ene (DBU) and gentle heating in the absence of other reagents with the second method giving a purer product. In fact, when a solution of **8** is allowed to stand in an nmr tube for any length of time the ^{31}P signals due to **8** decrease in intensity as new peaks due to a single dehydrobromination product appear. This reaction offers further evidence that **8** is indeed the product obtained by bromination of **7**. The reaction does not, however, give the phosphole oxide **9** and the isomeric 4-methylene-2-phospholene oxide derivative **10** is obtained instead. This is not entirely unexpected since the phosphole sulfide **11** may be readily transformed into **12** [12] while the related structure **13** is clearly preferred over the corresponding phosphole oxide form [13]. This type of tautomeric preference seems to operate when the phosphole

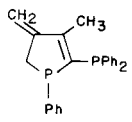


oxide or sulfide tautomer has methyl groups in both the 3-and 4-positions. It should perhaps also be noted that many simple phosphole oxides are difficult or impossible to isolate since they readily undergo a Diel-Alder type of dimerization [14].

The evidence that **10** is formed rather than the isomeric **9** is as follows. The ^{31}P spectrum (Table I) is consistent with either structure since it shows both a five membered ring phosphorus atom and a side-chain phosphorus atom with P-P coupling. However, the ^{1}H spectrum shows that two ring methylene protons remain in the dehydrobrominated structure, that only one methyl proton signal (allylic) appears in the spectrum, and that two non-equivalent olefinic protons are present. These, and other, details (see Experimental) are consistent only with **10** being the dehydrobromination product of **8**. The ^{13}C spectrum (Table II) is also entirely consistent with the proposed structure **10** but, apart from noting that the exocyclic methylene carbon atom is clearly seen as a doublet in the expected region at δ = 116.74, discussion will be deferred until later.

The construction of 2-diphenylphosphinylphosphole oxides related to the 2-diphenylphosphinophosphole system **2** therefore apparently could not be achieved by the route outlined above because of the tendency of one of the double bonds to move exocyclic to the five-membered ring as a result of the presence of the methyl groups in the 3- and 4-positions of **9**. Therefore, an alternative approach was tried which involved reduction of the dioxide **10** with trichlorosilane in an attempt to give **14**. This reaction was attempted on the assumption that if the phosphole **15** tautomeric with **14** has significant aromatic character, the de-

localization energy in **15** might provide sufficient driving force for the isomerization **14** → **15** to occur. Use of a large excess of trichlorosilane gave a complex reaction



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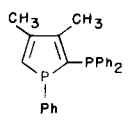

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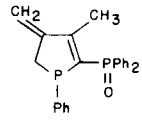

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mixture but use of a small excess of trichlorosilane in the presence of pyridine gave a mixture of three phosphorus-containing components (one major, two minor) which could not be separated by chromatography because virtually no separation occurred using a variety of solvents and adsorbents. It was, however, possible to establish that the major component had the structure **16** - *i.e.* reduction of the ring P=O bond had taken place but the side-chain P=O bond was untouched and the exocyclic double bond had not migrated into the ring upon reduction. This last observation indicates that the isomeric phosphole has little, if any, aromatic character.

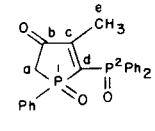
The evidence that **16** rather than **14** or **15** is the major product is as follows. First, the low-voltage (*ca.* 12 eV) mass spectrum of the mixture of the reaction products shows two molecular ion peaks at m/e 388 (major) and 390 (minor) corresponding to the loss of one oxygen atom and the loss of one oxygen atom accompainied by the addition of H_2 respectively. A further feature of the mass spectrum at 80 eV is the presence of a strong peak at m/e 201 which is characteristic of structures containing the $Ph_2P=O$ unit - *i.e.* the mass spectral evidence strongly indicates that it is the ring P=O bond which has been reduced. This conclusion is supported by the ^{31}P spectrum of the mixture which shows three pairs of doublets of very different intensities. The major component shows signals at δ = 1.12 and δ = 25.00 ($^2J_{P\text{-}P}$ = 59.7 Hz) and this suggests ring P=O reduction since the signal at δ = 25.00 is very close to that of the side-chain $Ph_2P=O$ group in the spectrum of the precursor **10** (δ = 22.18). A second component shows peaks of much lower intensity at δ = -16.50 and + 31.00 with $^2J_{P\text{-}P}$ = 74.2 Hz. Again, it seems to be the ring P=O which has been reduced. A third component shows all four peaks of the doublet of doublets as very low intensity signals in the δ = 13.00 - 15.50 range.

That the exocyclic methylene group is still intact in the major product of the reduction is shown by the ^1H spectrum of the mixture which shows two very narrow multiplets at δ = 5.25 and 5.43 (slightly upfield of the similar multiplets in the spectrum of **10** as would be expected from ring P=O reduction). Integration of these signals relative to those of the aromatic protons shows that about 50% of the mixture consists of this compound.

Reoxidation of the reaction product with hydrogen peroxide followed by chromatographic separation of the resulting mixture leads to the formation and isolation of pure **10** in about 50% yield. That **16** is the major product formed in the reduction of **10** with trichlorosilane therefore seems highly likely.

In another aspect of the investigation, several preparations of **10** were carried out in order to accumulate a large quantity for further studies. However, after the product of each preparation had been stored for some time, it was observed that the compound undergoes a spontaneous and very surprising oxidation in the solid state in the dark at low temperatures (refrigerator) which is almost complete in about two months.

The product of this oxidation has been unambiguously characterized as **17**. Thus, the mass spectrum shows a molecular ion peak at m/e 406, which is two atomic mass units more than the precursor **10**, while the ir spectrum (liquid film) shows a strong and sharp C=O stretching vibration at 1710 cm^{-1}. The ^{31}P spectrum of the compound (Table I) shows the ring P atom at the unusually high field value of δ = 32.50 while the side-chain P atom appears at the normal location. One would normally expect [7a] the ring P atom of a 2-phospholene oxide of this general type to resonate at around δ = 50 or at even lower field. However, similar anomalous shifts have been observed for the P atoms in a few other related structures. For example, **^{31}P shifts of** δ = 32.0 and δ = 29.2 have been observed for **18** [7a] and **19** [15] respectively and explanations for these shifts have been suggested. Compound **20**, closely related to **17**, also shows [16] an anomalous ^{31}P shift of δ = 36.5 although no explanation has yet been advanced for this. The ^1H spectrum and the ^{13}C spectrum of this compound (Table II) are also entirely consistent with the proposed structure and will be discussed, in general terms, later.



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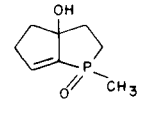

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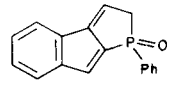

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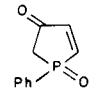

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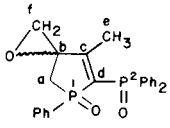
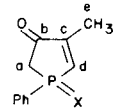
In an attempt to increase the rate of conversion of **10** into **17** and to obtain mechanistic information on this conversion, **10** was exposed to oxygen in the presence of the efficient radical initiator AIBN (azobisisobutyronitrile) under a variety of conditions since a radical mechanism seemed to be the most probable. It was found that under a slow stream of air, AIBN not only catalyzes the oxidation

of **10** to the ketone **17** relatively rapidly in benzene at 70° but also yields two isomeric epoxides (in unequal amounts) characterized as **21a** (major isomer) and **21b** (minor isomer). These were separated by column chromatography and while the gross structure of both epoxides was well characterized, the actual stereochemistry of each stereoisomer about C_b of the ring relative to the orientation of the



21a (major isomer)
21b (minor isomer)



22a (X = S)
22b (X = O)

P=O group has not been established. The two epoxide stereoisomers have different melting points, significant differences in their ^{31}P spectra (Table I), some minor differences in their ^{1}H (see Experimental) and ^{13}C (Table II) spectra, and the mass spectrum in each case confirms the molecular weight as 420. The ^{31}P chemical shift of the ring P atom in each case is also much more typical of a 5-membered phosphorus heterocycle than is the case in the spectrum of the ketone **17**.

These two epoxides, which are apparently the first reported spiro-oxirano phosphorus heterocycles, can be made much more easily and quickly by the conventional oxidation of **10** with *m*-chloroperbenzoic acid (MCPBA) which is quite frequently used [16] in such oxidations. Again, there is a stereochemical preference for what has been described as the major stereoisomer but this epoxidation seems to be less selective than the AIBN catalysed reaction.

It is of interest to note here that the minor stereoisomer, **21b**, is also sometimes isolated in trace amounts during the chromatographic purification of freshly prepared **10**.

The mechanism of the oxidation almost certainly involves an oxidation by molecular oxygen catalysed by a free radical initiator. In the case of the solid state reaction, the initiator remains unknown but, in solution, AIBN readily acts as an initiator. The mechanism is therefore probably basically the same as that of the autoxidation of styrene [17] which involves the addition of O_2 to the radical initiator to give $RO_2\cdot$ which then adds to the terminal methylene group of styrene to give $Ph\dot{C}HCH_2OOR$. This reacts with more O_2 and then more styrene to give a polyperoxide radical which then cleaves and "unzips" to give benzaldehyde, formaldehyde and styrene oxide.

However, extending this mechanism to the oxidation of **10**, in the decomposition of the polyperoxide radical derived from **10**, the first cleavage would occur at the end of a polymeric chain. This chain-end portion gives the major and minor epoxides (styrene oxide in the case of styrene). The remainder of the polyperoxide chain then "unzips" to give the ketone **17** and formaldehyde although attempts to detect formaldehyde were not made. The epoxide ring closure may occur either from the same side of the phospholene ring as the P=O group giving the *cis* isomer or from the opposite side of the ring giving the *trans* isomer although in a molecule as complex as this, it is difficult to predict which of these ring closures is sterically or electronically preferred.

During the spontaneous oxidation of **10**, the ketone **17** is the only product isolable. This suggests that, in the proposed pathway, the polyperoxide radicals formed have long chains because there are few initiating radicals present and, since cleavage of each chain gives only one epoxide molecule, but many ketone molecules, the ratio of ketone to epoxide formed is high. In this case, it is so high that epoxide formation is not observed. On the other hand, the AIBN catalysed oxidation always gives the ketone *and* the epoxides in moderate yields. If the mechanism proposed above is correct, this indicates that during the AIBN catalysed oxidation, relatively short-chain polyperoxide radicals are formed. Indeed, this might well be expected as there are many initiating radicals present. As the polyperoxide chains are short, the ratio of the ketone formed to epoxide formed should be relatively small and, as is in fact observed, reasonable amounts of the two possible epoxides should be formed. However, competing reactions are known [17] which can also lead to epoxide formation.

As has been noted elsewhere [16], 4-oxo-2-phospholene derivatives (*e.g.* **20**) containing a chiral tetracoordinate phosphorus atom have some potential as chiral reagents in a variety of heterocyclic syntheses. The relationship of the 4-oxo-compound **17** to these 4-oxo-2-phospholene oxides therefore raised the question of the possible generality of the free-radical catalysed oxidation of the 4-methylene-2-phospholene oxide **10** as an alternative route to the potentially useful 4-oxo-compounds.

In fact, we have shown that the 4-methylene-2-phospholene sulfide **12**, (δ ^{31}P = 48.94; ^{13}C spectrum, Table II) which is readily prepared [12] from **11**, undergoes the desired oxidation under similar reaction conditions to those employed in the oxidation of **10** to give the ketone **22a** with little evidence for the formation of epoxides corresponding to **21a** and **21b**. However, quite unexpectedly, another ketone, characterized as **22b**, has been isolated from the above reaction mixture. The mass spectra of the 4-oxo compounds **22a** and **22b** showed molecular ion peaks at the expected values of m/e 222 and m/e 206 respectively while the ^{31}P spectra show signals at δ = 31.98 and 30.71 respectively. Thus, the ^{31}P signals of **22a** and **22b** have the same unusually high field locations as those of the related structures **17** and **20** already discussed and the phenomenon seems, therefore, to be general to struc-

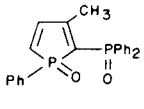
tures of this type.

The ir spectrum of **22a** shows a sharp C=O stretching vibration at 1708 cm^{-1} while that of **22b** shows a sharp carbonyl vibration at 1710 cm^{-1} and an additional P=O peak, not present in the spectrum of **22a**, appears at 1215 cm^{-1}. The ^1H spectrum of **22a** is very similar to that of **22b** (see Experimental) and these spectra and the ^{13}C spectra (Table II) of both products are entirely consistent with the proposed structures.

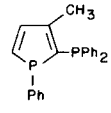
The formation of **22b** during the oxidation of the 4-methylene-2-phospholene sulfide **12** clearly results from the replacement of sulfur by oxygen in either **12** or **22a**. In view of the fact that the reaction was carried out under a constant flow of air for a considerable time (*ca.* 36 hours), such a replacement is not unreasonable but whether it is due to a radical catalysed process or is simply a conventional oxidation was not investigated.

The successful oxidation of both **10** and **12** (which differ considerably in substitution pattern) suggests that the reaction is general and a further route to 4-oxo-2-phospholene oxides or sulfides is therefore now available. Two examples of a reaction are not, however, sufficient to prove generality and other examples are under investigation.

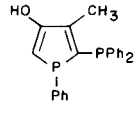
It is apparent that **17** has much potential as a precursor to a variety of phosphole derivatives such as **23**, **24** or **25** which could be derived from **17** by various reductive processes. Furthermore, these phosphole derivatives do not



23

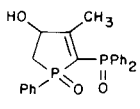


24

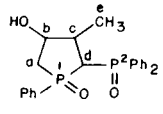


25

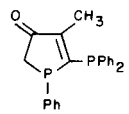
contain methyl groups in the 3- and 4-positions as is the case in **7**, the starting point of this investigation. Thus **17** was treated under nitrogen with 9-BBN (9-borabicyclo-[3.3.1]nonane) and with DIBAL-H (diisobutylaluminum hydride) which are normally [18, 19] very good reagents for the selective reduction of C=O groups in α,β-unsaturated carbonyl compounds, in an attempt to reduce the C=O group of **17**. Dehydration of the resulting alcohol **26** should then give the desired phosphole oxide **23**. However, in each case, a complex mixture of products was obtained as shown by the ^{31}P spectrum of the crude material. Repeated attempts to isolate pure components from these mixtures were not successful.



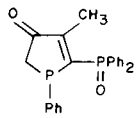
26



27



28



29

Although sodium tetrahydroborate is not particularly good as a selective reducing agent, there are reports [20,21] which show that it can occasionally be used successfully for the reduction of a C=O group in α,β-conjugated systems under very mild conditions. Furthermore, P=O groups are normally unaffected by this reducing agent. The ketone **17** was therefore treated with sodium tetrahydroborate according to the published procedure [20] and this produced, after column chromatography of the crude product, a pure colourless solid which has been characterized as the saturated alcohol **27** and not the desired unsaturated alcohol **26**. Thus, the mass spectrum showed a molecular ion peak at m/e 410 which corresponds to the addition of four hydrogen atoms to the starting material **17**.

The ^{31}P spectrum of the compound (Table I) shows coupled ring and side-chain P atoms although these are both somewhat downfield of the signals of the corresponding P atoms in the various products described so far in this report. The low coupling constant is presumably a result of the change in hybridization at the C atom attached to both of the P atoms which would greatly change the angular relationships. The downfield shifts for the signals of both the ring and the side-chain P atoms is presumably due to the hydrogenation of the ring double bond (which will be unambiguously proved shortly) at the position δ to the P(IV) atom since a C=C bond adjacent to a P(IV) atom normally (but not always) produces a shielding effect [7a]. This is because the d-orbitals share some of the electron density on the α-carbon and, in general, an increase in the d-orbital utilization produces shielding.

The ^1H spectrum of the compound deserves some comment. It shows the fifteen aromatic protons as a complex multiplet at δ = 6.80 - 7.95, the range being slightly upfield from the aromatic proton signals in the various 2-phospholene oxide precursors. The hydroxyl hydrogen atom appears as a doublet centered at δ = 6.12 (J = 8.75 Hz) which is at unexpectedly low field for an alcoholic hydrogen. However, the fact that the hydrogen is indeed alcoholic has been confirmed by addition of D_2O which causes the signal to vanish completely. Such a downfield shift of the alcoholic hydrogen might be explained by intramolecular or intermolecular H-bonding with the ring (or side-chain) P=O group. The relatively low frequency range (3200 - 3400 cm^{-1}) for the OH vibration observed in the ir spectrum of the compound is another indication of H-bonding.

The tertiary hydrogen at C_b appears as a doublet of multiplets centered at δ = 4.38 ($^3J_{P\text{-}H}$ = 27.0 Hz) and the ring methylene protons are observed as a narrow multiplet at δ = 2.9 - 3.41 which consists of eight peaks of unequal area apparently indicating that they are coupled with the ring P atom and the C_b tertiary proton. The two tertiary protons at C_c and C_d appear as a multiplet at δ = 2.42 -

2.77 and, finally, the methyl protons appear as a doublet centered at δ = 1.28 apparently coupled only with the adjacent tertiary proton ($^3J_{H-H}$ = 7.0 Hz). These methyl protons appear well upfield from the allylic methyl protons in the various 2-phospholene oxide precursors as would be expected.

Several double resonance ^1H experiments have been carried out to verify the couplings among the different protons. Thus, irradiation at the middle of the hydroxyl proton doublet brings changes only at the signals of the C_b tertiary proton and it follows that the hydroxyl proton is coupled only with the C_b tertiary proton ($^3J_{H-H}$ = 8.75 Hz). This coupling was confirmed by further irradiation at the middle of the C_b tertiary proton doublet of multiplets which caused the hydroxyl proton doublet to collapse to a singlet. During this particular irradiation, the multiplets of the ring methylene protons and the C_c and C_d protons also undergo some changes. Clearly, the tertiary proton at C_b is coupled with the ring P atom ($^3J_{P-H}$ = 27.0 Hz), the hydroxyl proton ($^3J_{H-H}$ = 8.75 Hz), the ring methylene protons and the C_c proton. Coupling with the C_d proton is very unlikely. Further double irradiation experiments confirmed the remainder of the suggested coupling pattern.

The ^{13}C spectrum (Table II) is also in agreement with the proposed structure **27**.

Although, in theory, **8** stereoisomers of the compound **27** are possible since there are three chiral centres (C_b, C_c and C_d) formed during the reduction, only one stereoisomer was isolated and the reduction (repeated many times) therefore shows considerable selectivity. However, the ^{31}P spectrum of the crude sodium tetrahydroborate reduction product showed a second, relatively weak, doublet of doublets at δ = 47.04 and 30.55 respectively with $^2J_{P-P}$ = 6.05 Hz. These shifts and the coupling constant indicate that this component could be another stereoisomer. The compound could not be isolated in pure form because it is retained so strongly by the chromatographic column. Clearly the carbonyl group of **17** is not easily selectively reduced.

A possible alternative route to a 2-diphenylphosphino-substituted phosphole derivative would be reduction of the P=O groups of the ketone **17** by trichlorosilane to give **28** on the assumption that if the phosphole **25**, isomeric with **28**, had significant aromatic character, the resonance energy in **25** might provide sufficient driving force for the isomerization of **28** to **25**.

It was found that, using only a slight excess of trichlorosilane (in the presence of pyridine), the ketone **17** undergoes reduction smoothly to give the 4-oxo-2-phospholene **29**. Varying the amount of trichlorosilane gave always the same result. Thus, trichlorosilane reduction of both **17** and **10** show that it is the ring P=O group which is the most sensitive to reduction. In this case, no ring hydrogenation was detected and the reduction appears to be very clean.

Compound **29** is a viscous, hygroscopic liquid which was well characterized spectroscopically. In particular, the ^{31}P spectrum (Table I) shows coupled ring and side-chain P atoms at δ = -28.44 and 23.70 respectively. These changes in the ^{31}P spectrum on reduction are similar to those observed in the spectrum of **16**, and indicate that the ring P=O group has been reduced whereas the side-chain P=O group has not. It should also be noted that the ring P resonance is upfield of that of **16** which again illustrates the strong shielding effect of the 4-oxo-group. The mass spectrum shows a molecular ion peak at m/e = 390 which is also in agreement with the fact that only one of the P=O groups is reduced and that no hydrogenation has occurred. Furthermore, a strong peak at m/e 201, characteristic of compounds contain the $Ph_2P=O$ group appears in the spectrum. The ^1H spectrum (see Experimental) is also in agreement with the proposed structure.

The structure of the compound was finally confirmed by reoxidation with H_2O_2 which regenerates the ketone **17** in quantitative yield.

The ^{13}C spectra (Table II) already referred to frequently deserve some brief comment because of the relative complexity which arises from the presence of two, non-equivalent, phosphorus atoms in the majority of the structures listed. Thus, it can be seen that the carbon atoms of the five-membered ring and of the side-chains normally appear as multiplets and P-C couplings though up to three bonds are the norm. The only exception to this is C_f in structure **7** which shows no P-C coupling.

Certain more general points may be made. First, the ^{13}C chemical shifts are of the order which would be expected by analogy with related open chain and cyclic structures in the literature [4,7a]. Second, the expected [4,7a] high values for $^1J_{P-C}$ are observed in the signals of C_a and (where observable) C_d and these values range from 59.00 - 83.41 Hz. Third, in the spectra of those structures which contain the C=C-P=O or C=C-P=S unit (all structures except **27**) the signal of the sp^2 carbon atom β to the P=O or P=S linkage is at unusually low field (δ = 150 -183) and the effect is most pronounced in the spectra of those structures in which this sp^2 C atom is β to two such P=O groupings (**7**, **10**, **17**, **21a**, **21b**). In such cases, the signals fall in the range δ = 166 - 183. This effect has been noted in a variety of unsaturated phosphorus heterocycles [4,7a] and related open-chain structures [7a]. The signal of the sp_2 carbon atom α to the P=O or P=S unit in these structures (C_d) in the majority of cases listed in Table II falls under the aromatic carbon signals. However, in the spectra of **17**, **22a** and **22b**, the signal of this carbon atom is shifted into the readily observable region of δ = 143 -150 (with the expected multiplicity) because of the additional conjugation and inductive effect provided by the carbonyl group in these cases. As expected, the carbonyl carbon

atom (C_b) in these three structures appears as a doublet (**22a, 22b**) or triplet (**17**) in the δ = 196 - 199 range. Finally, where a side-chain P atom (P^2) is present, C_a couples with this P atom through the ring P atom (P^1) in the majority of such cases and coupling constants of up to $^3J_{P^2C}$ = 10 Hz are observable. No attempt was made to analyze the signals due to the aromatic carbon atoms.

In conclusion, we have shown that the route to five-membered heterocycles containing both ring and side-chain phosphorus atoms related in this paper is obviously quite satisfactory for compounds of the title type but the particular structural type in which the five-membered heterocycle is the fully unsaturated phosphole ring (as, for example, in **2**) is not readily attainable and some modification of the approach is required. One possible reaction which might be explored is the reduction of the ketone **17** with sodium tetrahydroborate in methanol in the presence of cerium(III) chloride. This system apparently [22] is highly selective for the reduction of carbonyl groups in α,β-unsaturated ketones in certain instances.

EXPERIMENTAL

All air-sensitive samples were properly protected from atmospheric hydrolysis or oxidation during weighing and data collection. Certain operations were carried out in a nitrogen-filled glove box. Infrared spectra were recorded on a Beckman IR-4250 spectrophotometer as Nujol mulls or as liquid films pressed between sodium chloride plates. The spectra were calibrated with a polystyrene reference film. A Bruker WP-80 Fourier-transform nmr spectrometer was used to record ^1H and ^{31}P (proton decoupled) and most of the ^{13}C (proton decoupled) spectra at 80, 32.3 and 20.1 MHz respectively. A few ^{13}C nmr spectra were recorded on a JEOL FX-90Q spectrometer [23]. The chemical shifts for the ^1H and ^{13}C spectra were measured relative to internal tetramethylsilane (TMS) using deuterated chloroform as both solvent and frequency lock. The ^{31}P chemical shifts were measured relative to external 85% phosphoric acid using chloroform as solvent and with deuterium oxide as the frequency lock. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-7 double focussing mass spectrometer using a direct heated inlet system. Microanalytical data for carbon and hydrogen were obtained from a Perkin-Elmer model 240 Elemental Analyzer in these laboratories with vanadium pentoxide used as a combustion aid. Phosphorus analyses were carried out commercially by Galbraith Laboratories, Inc., Knoxville, Tennessee. Column chromatography was carried out using silica gel (specially prepared for dry-column chromatography) obtained from ICN Pharmaceuticals, Inc., K & K Laboratories Division, as adsorbent. Thin-layer chromatography was carried out on microscope slides using a variety of adsorbent and solvents. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

3,4-Dimethyl-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-Oxide (**7**).

A solution of the readily accessible [8] 3,4-dimethyl-1-phenyl-3-phospholene 1-oxide (**3**) (10.38 g, 0.05 mole) in dry tetrahydrofuran (75 ml) was added slowly over a period of 45 minutes to a stirred solution of 1.6 *M* *n*-butyllithium (40 ml, 0.064 moles) in dry tetrahydrofuran (30 ml) at −75° under dry nitrogen. The resulting dark-red solution was stirred at −75° for 30 minutes. Chlorodiphenylphosphine (16.3 g, 0.073 moles) was then added over a period of 20 minutes to give a bright-red solution which was stirred at the same temperature for a further 3 hours. The temperature of the solution was then raised to -20° and dilute hydrochloric acid (1.0%) was added slowly until the solution was neutral. In this step, the colour changed from red to pale yellow. Water (25 ml) was added to increase the volume of the aqueous layer and the solution was then transferred to a round-bottomed flask for removal of the tetrahydrofuran by a rotary evaporator. The remaining aqueous layer was extracted with dichloromethane (3 × 50 ml) and the combined dichloromethane extracts were washed with 5% potassium carbonate solution (3 × 50 ml). The solution was further washed with water (3 × 50 ml) and then dried over anhydrous potassium carbonate. After concentrating the solution in a rotary evaporator, the residue was dried under reduced pressure (oil pump) to give yellow, viscous liquid (22.8 g).

The viscous liquid so obtained was dissolved in absolute ethanol (50 ml) and then treated with 30% hydrogen peroxide (ratio 2 drops of H_2O_2/1.0 g of the viscous liquid). The solvent was again removed on a rotary evaporator and the residue was dried under reduced pressure as before. The resulting viscous liquid was dissolved in chloroform (100 ml), washed with water (3 × 50 ml) and dried over anhydrous sodium sulfate. The viscous liquid obtained after removal of the chloroform was treated with ether to precipitate a filterable solid (4.85 g). This was recrystallised from acetone-water to give the pure desired product **7** (3.5 g, 17%), mp 236-239° (lit [10] mp 253°); ^1H nmr (deuteriochloroform): δ 1.40 (d, 3H, CH_3, $^3J_{H\text{-}H}$ = 7.5 Hz), 2.33 (t, 3H allylic CH_3, $^4J_{P^1\text{-}H}$ = $^4J_{P^2\text{-}H}$ = 2.0 Hz), 1.57-2.65 (m, 2H, CH_2), 2.65-3.50 (m, 1H), 6.70-8.26 (m, 15H, aromatic).

Anal. Calcd. for $C_{24}H_{24}P_2O_2$: C, 70.94; H, 5.91; P, 15.27. Found: C, 70.85; H, 5.97; P. 15.18.

4-Bromo-3,4-dimethyl-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-Oxide (**8**).

A solution of 3,4-dimethyl-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-oxide (**7**) (3.0 g, 0.008 mole) in dry dichloromethane (50 ml) was flushed with dry nitrogen to remove oxygen. The solution was placed in a 100 ml three-necked flask and then irradiated by a high pressure mercury lamp (Hanovia 654A10) under dry nitrogen. *N*-Bromosuccinimide (2.22 g, 0.012 mole) was added slowly, as a solid, to the above solution over a period of 15 minutes. After completion of the addition, the mixture was stirred and irradiated at room temperature under nitrogen for a further one hour. It was then transferred to a separatory funnel, extra dichloromethane (50 ml) was added to increase the volume and the solution was washed with water (8 × 50 ml). The organic layer was dried over anhydrous sodium sulfate and the solvent was removed carefully using a rotary evaporator at room temperature to give a pale-yellow viscous liquid. When the viscous liquid was further dried using an oil pump, a pale-yellow (foamy) semi-solid product characterized as **8** was obtained (3.76 g, 97%). A thin-layer chromatographic analysis showed that the crude product was, in fact, quite pure. Further purification was not attempted because of the thermal instability of this compound and, for the same reason, reliable analytical data could not be obtained. The compound has, however, been unambiguously characterized (see Discussion).

3-Methyl-4-methylene-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-Oxide (**10**).

The crude bromo product **8** (3.76 g, 0.0087 mole) was heated at 90-100° in a rotary evaporator for about 45 minutes during which time the initial pale-yellow semi-solid compound turned to a dark-brown viscous liquid. This liquid was dissolved in dichloromethane (100 ml) and transferred to a separatory funnel where it was washed with 5% sodium bicarbonate solution (3 × 50 ml) and then with water (3 × 50 ml). Drying of the organic layer was carried out over anhydrous sodium sulfate and another dark-brown viscous liquid was obtained after removing the solvent under reduced pressure. The crude product was purified by dry-column chromatography (chloroform as eluent) on silica to give the pure product **10** as a colorless, glassy solid (1.73 g, 56%) mp 58-60°; ^1H nmr (deuteriochloroform): δ 2.46 (t, CH_3, $^4J_{P^1\text{-}H}$ = $^4J_{P^2\text{-}H}$ = 2.0 Hz), 2.75-3.37 (m, 2H, CH_2), 5.48 (m, 1H, olefinic), 5.75 (m, 1H, olefinic), 6.78-8.25 (m, 15H, aromatic). Double irradiation at δ = 3.00 causes each of the two olefinic proton signals to collapse to a doublet ($^4J_{P^1\text{-}H}$ = 2.0 Hz in each case).

Anal. Calcd. for $C_{24}H_{22}P_2O_2$: C, 71.28; H, 5.45. Found: C, 71.11; H,

5.65. A reliable phosphorus analysis could not be obtained because of the sensitivity of this compound to molecular oxygen (see Discussion).

Reduction of 3-Methyl-4-methylene-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-Oxide (**10**) by Trichlorosilane.

A 250 ml three-necked flask fitted with a condenser was flushed with dry nitrogen for 10 minutes. Trichlorosilane (2.72 g, 0.02 mole) and pyridine (5.45 g, 0.06 mole) were mixed carefully in dry benzene (50 ml) in the flask under nitrogen and the oxide **10** (0.8 g, 0.002 mole) in dry benzene (25 ml) was added in one portion. The resulting suspension was heated under reflux for 2 hours during which time a light yellow suspension was produced. The mixture was cooled in an ice bath and quenched under nitrogen with saturated aqueous sodium hydroxide (20 ml) keeping the mixture ice-cold during quenching. Water (40 ml) was added to increase the volume of the aqueous layer. The sealed reaction flask was then transferred to a nitrogen-filled glove box where the benzene layer was separated and the aqueous layer was again washed with benzene (40 ml). The two benzene extracts were combined and dried over magnesium sulfate. A yellow viscous material was obtained on concentrating the solution under reduced pressure with magnetic stirring to remove the solvent. The crude material was chromatographed on a dry silica column (chloroform as eluent) to give a yellow, viscous liquid (0.32 g) which was characterized as outlined in the Discussion. Reoxidation of this material with hydrogen peroxide (30% solution) in ethanol gave **10** which was obtained in pure form (*ca.* 50% yield) by dry column chromatography in the usual manner.

Formation of 3-methyl-4-oxo-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-Oxide (**17**) by Spontaneous Oxidation of **10**.

3-Methyl-4-methylene-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-oxide (**10**) (1.0 g, 0.0025 mole) was sealed in a small flask and the flask was placed in the refrigerator. After a few days, the ^{31}P spectrum showed that the compound had commenced oxidation and this oxidation was complete after *ca.* 2 months. On purification by dry column chromatography on silica (chloroform as eluent), a colorless glassy solid characterized as **17** was obtained (0.75 g, 75%), mp 55-58°; ^1H nmr (deuteriochloroform): δ 2.35 (t, 3H, allylic CH_3, $^4J_{P^1\text{-}H} = {}^4J_{P^2\text{-}H} = 2.0$ Hz), 2.65-3.30 (m, 2H, CH_2), 6.75-8.25 (m, 15H, aromatic); ir (Nujol): ν max, ν CO 1710 cm^{-1}.

Anal. Calcd. for $C_{23}H_{20}P_2O_3$: C, 67.98; H, 4.92. Found: C, 67.88; H, 4.98.

The very hygroscopic nature of **17** prevented the acquisition of a P analysis.

Preparation of the Ketone **17** and the Stereoisomeric Epoxides **21a** and **21b** by AIBN Catalyzed Oxidation of **10**.

3-Methyl-4-methylene-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-oxide (**10**) (1.0 g, 0.0025 mole) in benzene (35 ml) was placed in a 100 ml flask fitted with a condenser, a thermometer and an air inlet, and AIBN (0.04 g, 0.0024 mole) in benzene (5 ml) was added. A slow stream of air was bubbled through the solution and the mixture was heated at 70° with constant stirring. The solution gradually turned yellow. AIBN (0.04 g) was added twice more at 12 hour intervals and heating was continued for 48 hours. The benzene was then removed under reduced pressure to give a yellow viscous liquid.

The ^{31}P spectrum of the crude product showed that it was a mixture of three compounds. Separation was effected by dry silica column chromatography (chloroform-benzene (4:1) as eluent yielded the first fraction and chloroform as eluent yielded the next two fractions) which gave first the ketone **17** (0.253 g, 25%), then the minor epoxide **21b** (0.106 g, 10%), mp 180° dec; ^1H nmr (deuteriochloroform): δ 2.12 (t, 3H, allylic CH_3, $^4J_{P^1\text{-}H} = {}^4J_{P^2\text{-}H} = 2.0$ Hz), 2.20-3.00 (m, 2H, ring CH_2), 3.17 and 3.24 (dd, AB pattern, 2H, OCH_2, $^2J_{H\text{-}H} = 5.5$ Hz), 6.67-8.32 (m, 15H, aromatic) and, finally, the major epoxide **21a** (0.295 g, 28%), mp 65-66°; ^1H nmr (deuteriochloroform): δ 2.10 (t, 3H, allylic CH_3, $^4J_{P^1\text{-}H} = {}^4J_{P^2\text{-}H} = 2.0$ Hz), 2.27-2.82 (m, 2H, ring CH_2), 3.17 and 3.28 (dd, AB pattern, 2H, OCH_2, $^2J_{H\text{-}H} = 5.0$ Hz), 6.70-8.25 (m, 15H, aromatic).

Anal. Calcd. for $C_{24}H_{22}P_2O_3$: C, 68.57; H, 5.24; P, 14.76. Found: (for **21a**): C, 68.53; H, 5.44; P, 14.39. Found (for **21b**): C, 68.47; H, 5.38; P, 14.35.

Synthesis of the Epoxides **21a** and **21b** by *m*-Chloroperbenzoic Acid Oxidation of **10**.

3-Methyl-4-methylene-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-oxide (**10**) (0.5 g, 0.00125 mole) in dichloromethane (5 ml) was placed in a 25 ml flask fitted with a condenser and *m*-chloroperbenzoic acid (0.3 g, 0.00174 mole) was added in one portion. The resulting mixture was heated under reflux for 24 hours with constant stirring. At this stage an orange solution was obtained. The solution was neutralized by 10% sodium bicarbonate solution and the aqueous layer was extracted with chloroform (3 × 15 ml). The combined extracts were washed with water (3 × 20 ml) and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave a yellow, viscous liquid. Purification of this crude product by dry column chromatography on silica (chloroform as eluent) gave first the minor epoxide **21b** (0.117 g, 23%) followed by the major epoxide **21a** (0.200 g, 38%) in pure form.

Synthesis of 3-Methyl-4-oxo-1-phenyl-2-phospholene 1-Sulfide (**22a**) and the Corresponding 1-Oxide **22b** by the AIBN Catalyzed Oxidation of **12**.

The oxidation of the readily prepared **12** [12] (0.5 g, 0.0023 mole) in the presence of AIBN (0.05 g, 0.0003 mole) was carried out in a similar manner to that described for the similar oxidation of **10**. In this case, the reaction was complete in 36 hours and, as the reaction was proceeding, some insoluble material was formed. After completion of the reaction, the flask was cooled, and the benzene solution was decanted. The solvent was removed under reduced pressure when a yellow, viscous liquid was obtained. The crude material was then chromatographed in the usual manner on dry silica (benzene as eluent) to give the yellow sulfide **22a** as a viscous liquid (0.151 g, 30%); ^1H nmr (deuteriochloroform): δ 2.12 (dd, 3H, allylic CH_3, $^4J_{P\text{-}H} = 2$ Hz, $^4J_{H\text{-}H} = 1.5$ Hz), 2.75-3.30 (m, 2H, ring CH_2), 7.18 (dq, 1H, olefinic, $^2J_{P\text{-}H} = 19.5$ Hz, $^4J_{H\text{-}H} = 1.5$ Hz), 7.35-8.12 (m, 5H, aromatic); ir (liquid film): ν max ν CO 1710 cm^{-1}. Further elution of the column with benzene-chloroform (1:1) gave the yellow oxide **22b** as another viscous liquid (0.047 g, 10%); ^1H nmr: δ 2.13 (t, 3H, allylic CH_3, $^4J_{P\text{-}H} = {}^4J_{H\text{-}H} = 2.0$ Hz), 2.50-3.30 (m, 2H, ring CH_2), 7.24 (dq, 1H, olefinic, $^2J_{P\text{-}H} = 15.0$ Hz, $^4J_{H\text{-}H} = 2.0$ Hz), 7.38-7.92 (m, 5H, aromatic); ir; ν max, ν CO = 1710 cm^{-1}, ν P=O = 1215 cm^{-1}.

Anal. Calcd. for $C_{11}H_{11}PSO$ (**22a**): C, 59.46; H, 4.95. Found: C, 59.20; H, 5.01.

Anal. Calcd. for $C_{11}H_{11}PO_2$ (**22b**): C, 64.07; H, 5.34. Found: C, 63.96; H, 5.70.

A further fraction was eluted from the column between the two main fractions as another viscous liquid (0.01 g, ^{31}P nmr: δ = 49.79) but further characterization of this compound was not attempted because of the small quantity available.

Synthesis of 4-Hydroxy-3-methyl-2-diphenylphosphinyl-1-phenylphospholane 1-Oxide (**27**).

Sodium tetrahydroborate (0.03 g, 0.0008 mole) was added to a cold solution of **17** (0.2 g, 0.00049 mole) in 95% ethanol (10 ml). A yellow solution was immediately obtained. The mixture was stirred for 1.5 hours at 0-5° and then acidified with dilute hydrochloric acid while still cold. After removing the solvent under reduced pressure, water (10 ml) was added to increase the volume of the aqueous layer and the resulting slurry was extracted with chloroform (3 × 20 ml). The chloroform extracts were combined and dried over anhydrus sodium sulfate. On removing the solvent under reduced pressure, a solid was obtained. This was purified by dry column chromatography on silica in the usual manner. Some trace impurities were initially eluted from the column with chloroform-acetone (9:1) as eluent and further elution with chloroform-acetone (4:1) yielded 4-hydroxy-3-methyl-2-diphenylphosphinyl-1-phenylphospholane 1-oxide (**27**) as a colourless solid (0.051 g, 25%), mp 242-244°.

Anal. Calcd. for $C_{23}H_{24}P_2O_3$: C, 67.31; H, 5.85; P, 15.12. Found: C, 67.16; H, 5.86; P, 15.03.

Further elution of the column with methanol gave an impure solid

(0.068 g); mp 130-135° (not sharp); ^{31}P nmr: $\delta P^1 = 47.04$; $\delta P^2 = 30.46$, $^2J_{P\text{-}P} = 6.05$ Hz with other minor peaks. Due to purification problems, the characterization of this compound was abandoned.

Reduction of 3-Methyl-4-oxo-2-diphenylphosphinyl-1-phenyl-2-phospholene 1-Oxide (**17**) by Trichlorosilane.

Reduction of the ketone **17** (0.812 g, 0.002 mole) was carried out in a similar manner to that described earlier for **10** by trichlorosilane (2.72 g, 0.02 mole) in the presence of pyridine (5.46 g, 0.06 mole). In this case, however, a benzene-insoluble reddish-brown oil was obtained after quenching the reaction mixture with saturated sodium hydroxide solution.

The benzene layer was decanted, the oil was dissolved in chloroform (50 ml), and the resulting solution was dried over anhydrous sodium sulfate. The solvent was then removed under reduced pressure and the crude product was chromatographed on a dry silica column (chloroform as eluent) to give a reddish-brown viscous oil characterized as 3-methyl-4-oxo-2-diphenylphosphinyl-2-phospholene (**29**) (0.27 g, 35%); ^1H nmr (deuteriochloroform): δ 2.15 (dd, 3H, allylic CH_3, $^4J_{P^1\text{-}H} = 2.0$ Hz, $^4J_{P^2\text{-}H} = 2.25$ or *vice versa*), 2.23-2.75 (m, 2H, ring CH_2), 6.50-8.05 (m, 15H, aromatic); ir (liquid film): ν max ν CO = 1710 cm^{-1}. This compound was not further characterized apart from spectroscopic study (see Discussion), since on hydrogen peroxide oxidation, it produced the starting ketone **17**.

The reduction was also carried out in the absence of pyridine and similar results were obtained.

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