An Unusual Synthesis of 2,3-Dihydrophosphindole 1-Oxides

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A very simple route to dimeric phosphole oxides is reported as is the pyrolytic decomposition of these phosphorus-bridged dimers. Like similar dimeric phosphole sulfides, these phosphole oxide dimers readily eliminate the bridging phosphorus grouping upon strong heating but, unlike the analogous sulfides, hydrogen transfer to give a 2,3-dihydrophosphindole 1-oxide rather than hydrogen elimination to give the fully unsaturated phosphindole oxide occurs. This hydrogen transfer is shown to be non-stereospecific and some mechanistic implications of this are briefly discussed.

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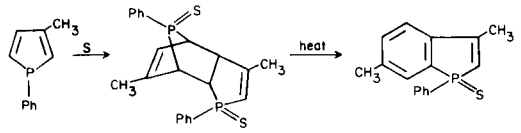
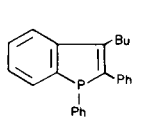
In a recent communication (1), we reported a synthesis of the relatively inaccessible phosphindole system in good yield by the potentially general route I → II → III. This route, if indeed it is general, would be particularly useful

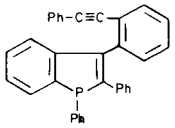


I II III

since other published syntheses of phosphindoles either lead to heavily substituted phosphindoles such as IV (2) and V (3) by methods which are not general or involve somewhat lengthy procedures (4,5) and sometimes expensive and not easily available reagents (4).



IV

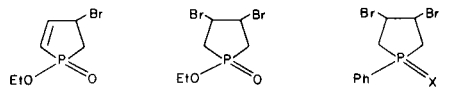


V

The simplicity of the sequence I → II → III is attractive for several reasons. Thus, simple phospholes of type I are now fairly easily available (though often in relatively small quantities) (6), the Diels-Alder phosphole sulfide dimer II loses the phosphorus bridge and a molecule of hydrogen in one experimental step on strong heating, numerous dimeric systems similar to II derived from simple phosphole oxides and sulfides (7-13) or phospholium salts (14) are known and it is also known that phosphindole oxides related to the sulfide III (4) and phosphine oxides and sulfides in general (15) are readily reduced to the corresponding phosphindoles or phosphines by silane derivatives.

We have therefore undertaken a further investigation of this promising synthesis with, initially, two objectives in mind. First, it would be desirable to bypass the direct use of simple phospholes since, as mentioned earlier, they are frequently available in only quite small quantities and low to medium yields and it is our experience that they deteriorate fairly rapidly on exposure to air and light. The second objective was to test the generality of the synthesis by extending it first to phosphole oxide dimers structurally related to the sulfide II and, later, to other dimeric systems such as those derived from simple phospholium salts.

Considering the first of these objectives, there have been a few brief reports that phosphole oxide (8,16) and phosphole sulfide (9) dimers similar to II have been prepared directly by dehydrohalogenation of phospholene and phospholane derivatives such as VI (8), VII (16) and VIII (X = O or S) (9) followed by spontaneous dimerization of the resulting transient intermediate phosphole oxides or sulfides. These dehydrohalogenations were carried



VI VII VIII

out by reaction of VI with dimethylamine followed by methylation and elimination catalyzed by ethoxide ion (8), by treatment of VII with triethylamine (16), by reaction of VIII (X = O) with potassium *t*-butoxide (9) and by similar treatment of VIII (X = S) with the powerful dehydrobrominating agent 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (9).

Generally, however, such reactions leading to dimeric phosphole oxides and sulfides have been considered undesirable since the main emphasis in reactions of this type has been the synthesis of a variety of monomeric sim-

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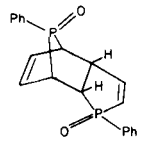
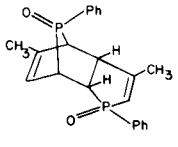
ple phospholes of type I. More usually, therefore, 3,4-dibromophospholane oxides of type VIII (X = O) have first been reduced by silane derivatives to give the corresponding dibromophospholanes and this has been followed by dehydrobromination using potassium *t*-butoxide (17,18) or DBU (10-12). This procedure leads to monomeric phosphole systems of type I rather than dimeric phosphole oxide systems related to II. In short, dimeric phosphole oxides and sulfides related to II and their syntheses by non-phosphole routes have received relatively little study although a range of such compounds is now known. In particular, syntheses and dehydrobrominations of dibromophospholane oxides of types VII and VIII (X = O) have been largely limited to such structures without further substitution at the 3- and 4-positions although Quin (18,19) has made brief mention of similar dibromo systems derived from 3-substituted and 3,4-disubstituted 1-methyl-3-phospholene 1-oxides.

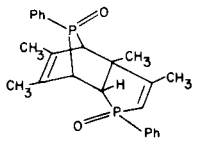
In this connection, we have found that the phosphole oxide dimers IX, X and XI (all of which are known and have previously been prepared by other methods usually involving phosphole intermediates (9,10,12)) can be prepared by an extremely simple process. Thus, as with the phospholene oxide XII (R′ = R″ = H) (9), both XII (R′ = H, R″ = CH_3) and XII (R′ = R″ = CH_3), prepared by



IX



X



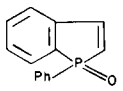
XI

XII

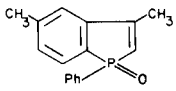
literature methods (20), readily add molecular bromine across the 3,4- double bond to give the corresponding 3,4-dibromophospholane oxides characterized (see experimental section) by isolation of a small sample of the pure adduct in each case. Chromatography of the crude dibromophospholane oxides obtained by this procedure, and also the known dibromophospholane oxide VIII (X = O), on neutral alumina leads to rapid dehydrobromination and dimerization on the column and the isolation, in high yield, of the dimers IX, X and XI from the appropriate dibromophospholane. These known adducts were characterized by analyses, mass spectral molecular weights and comparison of their melting points and nmr spectra with published data.

Thus, it seems that simple phosphole oxide dimers of this type are indeed generally very readily and conveniently available by non-phosphole routes. However, two further points from the literature regarding these bromination-dehydrobromination reactions should perhaps be noted here. The first is that Quin (19) has observed that certain 3- and 3,4-substituted 3,4-dibromo-1-methylphospholane 1-oxides also show a tendency to decompose *via* dehydrobromination (although details were not given) and these might therefore also serve as sources of phosphole oxide dimers. The second point is that, in contrast to the observations recorded above, 3,4-dibromo-3,4-dimethyl-1-phenoxyphospholane 1-oxide can be chromatographed on neutral alumina (21) apparently without any significant dehydrobromination and the above experimentally easy approach to phosphole oxide dimers therefore has some limitations.

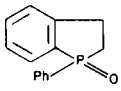
Turning now to the second objective of this study, pyrolysis of IX and X does *not* lead to the formation of the corresponding phosphindole oxides XIII and XIV as expected by analogy with the behaviour of II (1). Thus, although the expected loss of the bridging phosphorus grouping occurs in each case, this is *not* accompanied by the loss of hydrogen to give the phosphindole. Instead, a hydrogen-transfer reaction occurs and this leads to formation of the 2,3-dihydrophosphindole oxides XV and XVI from IX and X respectively. The evidence for this is presented below.



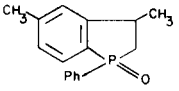
XIII



XIV

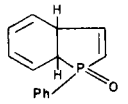


XV

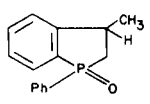


XVI

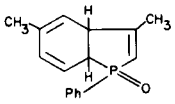
Pyrolysis of the phosphole oxide dimer IX followed by chromatographic purification leads to the isolation of a colourless solid, m.p. 100-102°, which analyzed well for $C_{14}H_{13}OP$. A mass spectrum confirmed the molecular weight as 228 and a precise mass determination confirmed the molecular formula (Found: 228.0704; Calcd. for $C_{14}H_{13}OP$: 228.0704). That this compound is the 2,3-dihydrophosphindole oxide XV (rather than the isomeric system XVII which might be expected to be formed, initially at least, by loss of the phosphorus-containing bridging group in IX) is shown by the ^1H nmr spectrum (τ



XVII



XVIII



XIX

2.10-2.95, m, 9H, aromatic; τ 6.15-7.00, m, CH_2; τ 7.10-7.80, m, CH_2) which is identical with that reported (4) for the 2,3-dihydrophosphindole XV which has been prepared (4) by a different method and which has a

reported melting point of 97-101°.

Further confirmation of this structure comes from the mass spectral fragmentation pattern which shows, in addition to the molecular ion peak (base peak), a peak at m/e 200 (22% of base peak) corresponding to M- $CH_2=CH_2$. That this fragmentation is a one-step process is confirmed by the presence of the appropriate metastable peak at m* = 175.4 and there can be little doubt that it is due to an ethylene elimination. This in turn shows (as does the nmr evidence) that the $-CH_2-CH_2-$ unit is present and hence confirms the structure. It should perhaps also be noted that although this fragment ion peak is apparently relatively weak compared with the base peak, almost all other significant peaks in the spectrum are of similar or lower relative intensity.

Considering now the thermal decomposition of the phosphole oxide dimer X, a similar reaction to that described above occurs and the dihydrophosphindole oxide XVI is obtained. Indeed, the product of this pyrolysis, normally isolated as a colourless glass by preparative thin layer chromatography, is a mixture of approximately equal quantities of two stereoisomers of the dihydrophosphindole XVI. That this is so is indicated by the analysis of the product which is in good agreement with the expected formula $C_{16}H_{17}OP$, the mass spectrum of the mixture which shows (at 15eV) a single molecular ion peak at m/e 256 and by the ^1H nmr spectrum which shows eight aromatic protons as a complex multiplet at τ 2.11-3.00, three benzylic methyl protons as a slightly broadened singlet at τ 7.59, three aliphatic methyl protons as two overlapping doublets of approximately equal area centered on τ 8.54 (with, in both cases, J = *ca.* 7 Hz) and three methylene and methine protons as a very broad and complex series of low intensity signals in the range τ 6.10-8.75. In this ^1H nmr spectrum, it is the fact that the methyl group on the five membered ring of XVI appears as two doublets rather than the expected one such doublet which indicates (as does the extreme complexity of the methine and methylene proton signals) that the product is a mixture of two isomers.

Later experimentation showed that it is possible to carry out an almost complete separation of these two stereoisomers although the actual method of separation owes much to chance since it relies upon cutting out and extracting different portions of the band produced by the two isomers on the preparative thin layer plate. However, by this method, one component was obtained as colourless crystals, m.p. 120-122°, while the other was obtained as a colourless, semi-crystalline material dispersed in a glassy matrix of uncrystallized product.

Both of the products show much simpler ^1H nmr spectra than the mixture. For example, the first of these products described above shows eight aromatic protons as a multiplet at τ 2.04-3.00, one methine proton as a closely spaced multiplet of five major peaks (main coupling constant = *ca* 6 Hz) with signs of further splitting centered on τ 6.18, three benzylic methyl protons as a sharp singlet at τ 7.55, 3 aliphatic methyl protons as a doublet at τ 8.56 (J = 7 Hz) with each peak of the doublet showing very slight additional coupling (*ca.* 1 Hz) and two non-equivalent methylene protons as a very complex multiplet between τ 6.50 and 8.65. This last signal shows two principal regions of absorption centered on *ca.* τ 7.10 and *ca* τ 8.10 respectively with these regions superimposed on the methyl signals mentioned above. That the methine proton at τ 6.18 and the methyl protons at τ 8.56 are indeed coupled as required by structure XVI was shown by double resonance experiments. Thus, double irradiation at the frequency of the methine multiplet causes the methyl doublet to collapse to a singlet while similar double irradiation of the methyl signal causes major changes in the methine signal.

The other stereoisomer of XVI shows a similar (but not identical) ^1H nmr spectrum with eight aromatic protons at τ 2.05-3.00, one methine proton signal similar in appearance to that described above but centered on τ 6.63, three benzylic methyl protons again as a sharp singlet at τ 7.52, three aliphatic methyl protons as a doublet (J = 7 Hz) at τ 8.46, and two methylene protons as a very complex series of weak signals at τ 7.05-8.70. As before, coupling between the methine proton and the appropriate methyl protons was confirmed by double irradiation experiments.

The mass spectra (at 80 eV) of the two isomers of XVI are less informative than that of XV. For example, whereas the spectrum of XV shows, as already mentioned, a major fragmentation at M-28 corresponding to the loss of the $-CH_2-CH_2$ grouping as ethylene, that of the first stereoisomer of XVI described above shows only a minor fragmentation at M-42 (*ca.* 5% of base peak at m/e 256) corresponding to the similar elimination of $CH_3-CH=CH_2$. However, in the case of XVI, this would be a less likely type of fragmentation than for XV since loss of the methyl group on the five-membered ring of XVI would be expected to occur to give a highly resonance stabilized benzyl type of carbonium ion. This indeed occurs as is shown by a strong peak at M-15 (55% of base peak) with the corresponding metastable peak at m/e 226.9. A similar spectrum is shown by the second isomer of XVI described above.

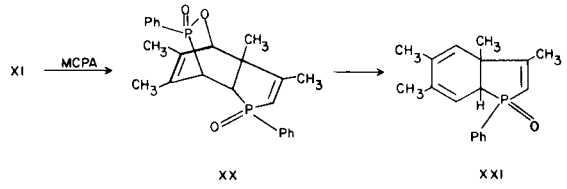
There can therefore be little doubt that the two products of the pyrolysis of X are indeed stereoisomers of XVI but, as XVI contains two asymmetric centres, four configurational stereoisomers are possible. However, since the geometry about the phosphorus atom is almost certainly fixed by the nature of X (the geometry of which is known (12) to be as shown as is the geometry of related phosphole oxide dimeric systems (22)), the two

stereoisomers of XVI obtained are probably those in which the methyl group on the five-membered ring is *cis* and *trans* to the configurationally fixed P=O linkage respectively.

Strong evidence that this is indeed the case is provided by comparison of the ^1H nmr spectra of the two stereoisomers of XVI with those of the very closely related system XVIII which has been synthesized (23,24) by two different routes and which has also been isolated (24) in two similar diastereomeric forms. The spectra of the two stereoisomers of XVIII (24) are virtually identical in chemical shifts and coupling constants with those of the two isomers of XVI with the exception of the additional methyl three-proton signal (on the six-membered ring) in the spectra of the latter.

The fact that pyrolysis of X gives two stereoisomers of XVI is more than just a mildly interesting observation since it throws some light upon the mechanism of the reaction. Thus, since the hydrogen transfer to the five-membered ring during the thermal decomposition of X is not stereospecific and gives rise to both *cis* and *trans* addition products, it is not a one-step reaction. Furthermore, it is probably an *inter*molecular reaction since the two hydrogens are in the *cis* arrangement in X and, as the basic carbon skeleton apparently remains intact during the reaction, it is reasonable to suppose that no C-C bonds are broken during the elimination and rearrangement. This would lead one to believe that any *intra*molecular transfer of two hydrogen atoms in this system would probably have to be *cis* even if the two hydrogens were transferred pyrolytically at different stages of the reaction. For example, this would almost certainly be the case if the two hydrogens are transferred independently by two thermally induced 1,3-sigmatropic rearrangements.

It is even probable that the expected intermediate XIX is not, in fact, an intermediate and that the hydrogen transfer steps occur either before loss of the phosphorus bridge commences or at the stage where only one P-C bond has been cleaved. The reason for this tentative deduction is not merely the apparently multistep nature of the reaction but also the fact that although the closely related system XVII is probably generated by photolytic (300 watt, high-pressure mercury lamp) extrusion of the PhP=O bridging group from the phosphole oxide dimer IX (25), all attempts to isolate or trap XVII were unsuccessful. Furthermore, the similar structure XXI, generated (26) by the unusual sequence XI → XX → XXI (MCPA = *m*-chloroperbenzoic acid), is also highly reactive and was trapped using 4-methyl-1,2,4-triazoline-3,5-dione. In this context, it is worth noting that in pyrolytic decompositions of XI similar to those described for IX and X, we have been unable to isolate any identifiable compound from the complex reaction product mixture which again was obtained as a very pale yellow glass. This could possibly be because a hydrogen transfer of the type already described above is not possible in the case of XI and formation of the reactive system XXI could well occur here.



Clearly, these mechanistic suggestions are highly speculative at this stage and equally clearly pyrolytic decompositions of phosphorus bridged species of the types discussed here merit further mechanistic as well as synthetic investigation. Thus, in addition to the points raised in the foregoing discussion, the question of why pyrolyses of phosphole oxide dimers do not follow the same route as similar treatment of the phosphole sulfide dimer II must also be answered. Indeed, do all phosphole sulfide dimers behave in the same manner as II? An obvious point here is that sulfur is a relatively good dehydrogenating agent and the differences between the behaviour of II and that of the phosphole oxide dimers might be due to generation of free sulfur during the reaction. However, addition of small amounts of free sulfur to the phosphole oxide dimers IX and X prior to pyrolysis made no difference to the course of the reaction. We have therefore commenced a further investigation of some of these facets of the problem.

One final point should perhaps be noted and that is that although this synthetic approach did not yield phosphindoles directly as expected, other workers have found (4,5) that 2,3-dihydrophosphindoles may be converted into phosphindoles relatively easily.

EXPERIMENTAL

The ir spectra were recorded either as liquid films or, more usually, as Nujol mulls on a Beckman IR-20A spectrophotometer using sodium chloride cells. The nmr spectra were obtained with Varian A60-D and Bruker WP-80 FT nmr spectrometers using deuterated chloroform solutions containing tetramethylsilane as internal reference. Mass spectra were recorded using an Hitachi-Perkin-Elmer RMU-7 double focussing mass spectrometer equipped with a direct heated inlet system. Precise masses were determined using the peak matching technique. Carbon and hydrogen elemental analyses were obtained in our laboratories using a Perkin-Elmer model 240 elemental analyzer while phosphorus analyses were carried out by Dr. Franz Pascher of Bonn, West Germany.

Column chromatography was carried out using Merck Kieselgel 60 silica or Aluminum oxide 90 (active neutral) while thin-layer and preparative thin-layer chromatographic separations were carried out using Merck Kieselgel GF_{254} and Kieselgel 60 PF_{254} respectively.

Melting points are uncorrected.

Synthesis of 3,4-Dibromo-3-methyl-1-phenylphospholane 1-Oxide and 3,4-Dibromo-3,4-dimethyl-1-phenylphospholane 1-Oxide.

3-Methyl-1-phenyl-3-phospholene 1-oxide (XII; R′ = H, R″ = CH_3, prepared by literature (20) methods) (17.3 g., 0.09 mole) in chloroform (120 ml.) was chilled in an ice-bath and was then treated dropwise with a solution of bromine (9.1 ml., 0.18 mole) in chloroform (60 ml.) under dry, oxygen-free nitrogen with constant stirring. After the addition was com-

plete, the mixture was allowed to warm to room temperature and stirring was continued for a further three hours. Crushed ice was then added and the mixture was neutralized with dilute sodium bicarbonate solution. Excess of bromine was destroyed with saturated sodium thiosulfate solution. The organic layer was removed, washed several times with water, dried over anhydrous magnesium sulfate, filtered and evaporated to give a pale yellow solid. This crude product was crystallized by dissolution in the minimum amount of methanol followed by chilling of the solution. The colourless crystalline product was washed with acetone and dried to give the expected dibromophospholane oxide (6.95 g., 22%) as colourless crystals, m.p. 105-107°; ir (Nujol): ν max at 1434, 1397, 1380, 1274, 1248, 1200 (P=O), 1188, 1166, 1063, 990 (weak), 860, 813, 740, 728 and 689 cm^{-1}; nmr (deuteriochloroform): τ 1.79-2.63 (m, 5H, aromatic), 5.14 (doublet of triplets, 1H, methine, $^3J_{H\text{-}H}$ = 6.5 Hz, $^3J_{P\text{-}H}$ = 17 Hz), 6.94 (m, 4H, $2CH_2$) and 7.75 (s, 3H, CH_3). A reliable mass spectrum could not be obtained because of the thermal instability of the compound.

Anal. Calcd. for $C_{11}H_{13}Br_2OP$: C, 37.50; H, 3.69; P, 8.81. Found: C, 37.99; H, 3.85; P, 8.63. Analyses had to be obtained on very fresh samples because of air and moisture sensitivity of the material.

3,4-Dibromo-3,4-dimethyl-1-phenylphospholane 1-Oxide.

This compound (6.98 g., 19.5% yield) was prepared in a similar manner from 3,4-dimethyl-1-phenyl-3-phospholene 1-oxide (XII, R′ = R″ = CH_3, prepared by literature (21) methods) (20 g., 0.09 mole) and bromine (9.1 ml., 0.18 mole). The product was obtained as very hygroscopic, colourless crystals, m.p. 114-117°; ir (Nujol): ν max at 1434, 1390, 1257, 1198 (P=O), 1165, 1137, 1120, 1108, 1028, 990 (weak), 850, 780, 752, 734 and 695 cm^{-1}; nmr (deuteriochloroform): τ 1.68-2.80 (m, 5H, aromatic), 6.39-7.35 (m, 4H, $2CH_2$), 7.7 (d, 3H, CH_3, $^4J_{P\text{-}H}$ = 1 Hz) and 7.79 (d, 3H, CH_3, $^4J_{P\text{-}H}$ = 1 Hz). Similar problems to those outlined above were encountered with mass spectral studies.

Anal. Calcd. For $C_{12}H_{15}Br_2OP$: C, 39.34; H, 4.10; P, 8.47. Found: C, 39.65; H, 4.40; P, 8.47.

It should be noted that in the synthesis of each of the above dibromophospholanes, predominantly one stereoisomer appears to be formed. That this is so is indicated by the simplicity of the spectra. Thus, in the case of the first product, a very simple A_2MX methine pattern is observed and the spectrum shows only one very narrow CH_3 signal. Similarly the spectrum of the second compound is very simple in the methyl proton region although it is possible that what have been assigned as very small P-H coupling constants (*ca.* 1 Hz) in the methyl signals are in fact due to the presence of two stereoisomers in almost equal quantities.

Synthesis of the Phosphole Oxide Dimers IX, X and XI.

Pure 3,4-dibromo-1-phenylphospholane oxide (VIII, X = O, prepared by literature methods (9)) (8.18 g., 0.02 mole) was dissolved in the minimum amount of chloroform and chromatographed on a neutral (or basic) alumina column using chloroform as eluent. The first 200 ml. of eluate contained only unchanged starting material but later fractions contained only the dimeric phosphole oxide IX. The unchanged starting material was rechromatographed to give complete conversion to the dimer IX which was obtained by evaporation of the eluate as a white solid which was recrystallized from benzene (3.73 g., 88%), m.p. 234° (lit. (9) m.p. 234-237°); ir (Nujol): ν max at 1660 (C=C), 1580, 1440, 1326, 1213, 1180 (P=O), 1154, 1120, 1104, 996, 839, 789, 752, 740 and 692 cm^{-1}; nmr (deuteriochloroform): τ 2.00-2.88 (m, 10H, aromatic), 3.13-3.69 (m, 2H, olefinic), 3.69-4.16 (m, 2H, olefinic), 5.16-6.08 (m, 2H, methine) and 6.08-6.71 (m, 2H, methine). This nmr spectrum is entirely consistent with the dimeric structure IX and is very similar to the published spectrum which was recorded under somewhat different conditions (9) in trifluoroacetic acid solution with TMS as *external* reference. The mass spectrum showed a molecular ion peak at m/e 352 with a strong fragment ion peak at m/e 222 (M-PhPO) corresponding to loss of the bridging phosphorus grouping under electron impact.

The same procedure could be carried out with the crude, unrecrystallized dibromophospholane. Under these conditions, the phosphole oxide dimer IX was obtained contaminated with some tarry material. This tarry impurity could, however, be removed by washing the product with acetone.

Under similar conditions, pure 3,4-dibromo-3-methyl-1-phenylphospholane 1-oxide (5.26 g., 0.01 mole) yielded the corresponding dimer X in crude form and recrystallization from hot benzene gave pure X (2.69 g., 95.5%) as a white solid, m.p. 225° (lit. (12) m.p. 217-218°); ir (Nujol): ν max at 1662 (C=C), 1600, 1434, 1184 (P=O), 1176, 1126, 1115, 1098, 995 (weak), 848, 800, 741, 728, and 695 cm^{-1}; nmr (deuteriochloroform): τ 2.07-2.66 (m, 10H, aromatic), 3.56-4.05 (m, 2H, olefinic), 4.05-4.37 (m, 2H, olefinic), 5.54-6.15 (m, 2H, methine), 6.15-6.82 (m, 2H, methine), 7.90 (s, 3H, CH_3) and 8.30 (s, 3H, CH_3). This nmr spectrum is virtually identical to that reported (12) for X. The mass spectrum shows a molecular ion peak at m/e 380 together with the expected M-PhPO peak at m/e 256.

The phosphole oxide dimer XI (1.99 g., 40%) was obtained similarly from 3,4-dibromo-3,4-dimethyl-1-phenylphospholane 1-oxide (8.85 g., 0.02 mole) as a white solid (which required careful recrystallization from benzene to remove impurities), m.p. 243-246° (lit. (12) m.p. 277°); ir (Nujol): ν max at 1602, 1440, 1294, 1190 (P=O), 1135, 1114, 995 (weak), 855, 816, 758, 748, 730, 706 and 698 cm^{-1}; nmr (deuteriochloroform): τ 1.90-2.63 (m, 10H, aromatic), 4.00 (doublet of doublets, 1H, olefinic, $^2J_{P\text{-}H}$ = 24 Hz, $^3J_{P\text{-}H}$? = 4.5 Hz), 6.30-7.05 (m, 3H, 3 methine), 7.93 (d, 3H, CH_3, J = 1.5 Hz), 8.15 (s, 6H, $2CH_3$) and 8.43 (d, 3H, CH_3, J = 1.5 Hz). This nmr spectrum is virtually identical to that reported (12) (with less complete data) for XI. The mass spectrum showed a molecular ion peak at m/e 408 with the expected M-PhPO fragment at m/e 284. Although on the above evidence there could be little doubt that the product was XI, because of the discrepancy between the measured and reported melting points, some analytical data were obtained as a check on purity.

Anal. Calcd. for $C_{24}H_{26}O_2P_2$: C, 70.58; H, 6.37. Found: C, 70.71; H, 6.26.

Pyrolysis of the Phosphole Oxide Dimers IX, X and XI.

The dimer IX of 1-phenylphosphole 1-oxide (1.23 g., 3.5 mole) was heated as a solid under nitrogen over a free flame until it began to melt. At this point, the pressure in the system was reduced to *ca.* 1 Torr and heating to just above the melting point was continued for a further five minutes so that volatile decomposition products could be removed under reduced pressure. After cooling, the yellowish viscous residue was dissolved in the minimum amount of methanol. This solution was extracted several times with petroleum ether (60-80° fraction), the petroleum ether extracts were concentrated and the resulting mixture was separated by preparative thin-layer chromatography on silica using 5% ether in chloroform. The major band was cut from the chromatographic plate, extracted with chloroform and the extract evaporated to give 2,3-dihydro-1-phenylphosphindole 1-oxide (XV) (0.132 g., 17%) as a very pale yellow glass. On one occasion, recrystallization from benzene-petroleum ether yielded this product as a white solid, m.p. 101-103° (lit. (4) m.p. 97-101°); ir (Nujol): ν max at 1588, 1449, 1430, 1249, 1192 (P=O), 1131, 1110, 1064, 995 (weak), 772, 760, 738, 712 and 690 cm^{-1}; nmr (deuteriochloroform): τ 2.10-2.95 (m, 9H, aromatic), 6.15-7.00 (m, 2H, CH_2) and 7.10-7.80 (m, 2H, CH_2). This is identical with the published (4) nmr spectrum. A mass spectrum showed a molecular ion peak at m/e 228 with a precise mass of 228.0704 (calculated, 228.0704).

By the same procedure, the phosphole oxide dimer X (1.32 g., 3.5 mmole) was pyrolysed and purified to give 2,3-dihydro-3,5-dimethyl-1-phenylphosphindole 1-oxide (XVI) (0.288 g., 32.5%) as a pale yellow glass; ir (liquid): ν max at 1599, 1448, 1434, 1204 (P=O), 1180, 1140, 1107, 994, 743 and 690 cm^{-1}.

Anal. Calcd. for $C_{16}H_{17}OP$: C, 75.00; H, 6.64; P, 12.11. Found: C, 74.73; H, 6.97; P, 11.78.

On most occasions, the compound was obtained in the above manner as a mixture of stereoisomers in approximately equal amounts (see discussion of nmr data) but careful removal of different portions of the chromatographic band followed by crystallization from benzene-petroleum ether was found to lead to the isolation of the two stereosiomers as separate entities. One of these was obtained as a white crystalline material, m.p. 120-122°; nmr (deuteriochloroform): τ 2.04-3.00

(m, 8H, aromatic), 6.18 (m, 1H, methine), 7.55 (s, 3H, CH_3), 8.56 (d, 3H, CH_3, $^3J_{H\text{-}H}$ = 7 Hz, $^4J_{P\text{-}H}$ = 1 Hz) and 6.50-8.65 (m, 2H, CH_2, with maxima at τ 7.10 and 8.10). The other stereoisomer was obtained as a semicrystalline colourless material; nmr (deuteriochloroform): τ 2.05-3.00 (m, 8H, aromatic), 6.63 (m, 1H, methine), 7.52 (s, 3H, CH_3), 8.46 (d, 3H, CH_3, $^3J_{H\text{-}H}$ = 7 Hz) and 7.05-8.70 (m, 2H, CH_2). The isomers showed virtually identical mass spectra with molecular ion peaks at m/e 256.

Pyrolysis of the phosphole oxide dimer XI again gave a pale yellow glass but nmr and mass spectral studies showed this to a very complex mixture and all attempts to isolate and characterize individual components were unsuccessful. However, as outlined in the discussion section, a different reaction pathway would be expected for this dimer.

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REFERENCES AND NOTES

(1) D. G. Holah, A. N. Hughes and D. Kleemola, *J. Heterocylic Chem.*, **14**, 705 (1977).

(2) M. D. Rausch and L. P. Klemann, *J. Am. Chem. Soc.*, **89**, 5732 (1967).

(3) W. Winter, *Tetrahedron Letters*, 3913 (1975); *Chem. Ber.* **110**, 2168 (1977).

(4) T. H. Chan and L. T. L. Wong, *Can. J. Chem.*, **49**, 530 (1971).

(5) D. J. Collins, L. E. Rowley and J. M. Swan, *Aust. J. Chem.*, **27**, 831 (1974).

(6) For a brief survey, see A. N. Hughes and D. Kleemola, *J. Heterocyclic Chem.*, **13**, 1 (1976).

(7) R. E. Donadio, *Diss. Abstr.*, **20**, 495 (1959).

(8) D. A. Usher and F. Westheimer, *J. Am. Chem. Soc.*, **86**, 4732 (1964).

(9) G. Märkl and R. Potthast, *Tetrahedron Letters*, 1755 (1968).

(10) F. Mathey, *Compt. Rend.*, **269C**, 1066 (1969).

(11) F. Mathey, R. Mankowski-Favelier and R. Maillet, *Bull. Soc. Chim. France*, 4433 (1970).

(12) F. Mathey and R. Mankowski-Favelier, *Org. Magn. Reson.*, **4**, 171 (1972).

(13) F. Mathey, *Tetrahedron*, **28**, 4171 (1972).

(14) L. D. Quin, S. G. Borleske and J. F. Engel, *J. Org. Chem.*, **38**, 1954 (1973).

(15) K. Naumann, G. Zon and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969); G. Zon, K. E. DeBruin, K. Naumann and K. Mislow, *ibid.*, **91**, 7023 (1969); K. E. DeBruin, G. Zon, K. Naumann and K. Mislow, *ibid.*, **91**, 7027 (1969).

(16) R. Kluger, F. Kerst, D. G. Lee and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 3919 (1967).

(17) L. D. Quin and J. G. Bryson, *ibid.*, **89**, 5984 (1967); L. D. Quin, J. G. Bryson and C. G. Moreland, *ibid.*, **91**, 3308 (1969).

(18) L. D. Quin, S. G. Borleske and J. F. Engel, *J. Org. Chem.*, **38**, 1858 (1973).

(19) L. D. Quin, J. P. Gratz and T. P. Barket, *ibid.*, **33**, 1034 (1968).

(20) For a review of these syntheses, see F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth", Wiley-Interscience, New York, N.Y., 1970.

(21) F. B. Clarke and F. H. Westheimer, *J. Am. Chem. Soc.*, **93**, 4541 (1971).

(22) Y. H. Chiu and W. N. Lipscomb, *ibid.*, **91**, 4150 (1969).

(23) W. Egan, R. Tang, G. Zon and K. Mislow, *ibid.*, **93**, 6205 (1971).

(24) M. El-Deek, G. D. Macdonell, S. D. Venkataramu and K. D. Berlin, *J. Org. Chem.*, **41**, 1403 (1976).

(25) H. Tomioka, Y. Hirano and Y. Izawa, *Tetrahedron Letters*, 4477 (1974).

(26) Y. Kashman and O. Awerbouch, *Tetrahedron*, **31**, 53 (1975).