Some Ring Expansion and Related Reactions of
the Phosphindole System

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3-Butyl-1,2-diphenylphosphindole reacts smoothly with ethyl propiolate and water and with benzoyl chloride and water to give ring expanded products. The second of these products is further expanded to a seven-membered system by treatment with sodium hydride. With diiodomethane followed by hydroxide ion, cleavage of the phosphorus-containing ring occurs. The nmr and mass spectral data are analyzed in detail and the results are discussed in the context of related studies with simple phospholes and dibenzophospholes. Some of the results further illustrate that predictions regarding the types of reaction entered into by phosphorus heterocycles must be made with caution.

Although phospholes (I) are very weak nucleophiles compared with ordinary tertiary phosphines (1) and poor inorganic donors (2) for reasons which concern the possible aromatic character of the phosphole system and which are still the subject of considerable debate (1), certain phosphole derivatives will undergo ring expansions through reactions at the phosphorus atom. Similar reactions of dibenzophospholes (II) are also known and a variety of ring expanded monocyclic and tricyclic products may be formed by these methods.
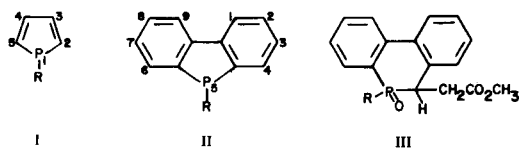

The first reaction of this type was observed (3,4) with 5-substituted-5*H*-dibenzophospholes (II, R = Me, Ph or CH_2Ph). This was the treatment of II with methyl propiolate and water to give the ring expanded products III (R = Me, Ph, CH_2Ph). The mechanism of this reaction has been discussed elsewhere (4) and involves attack of the phosphorus atom of II upon the triple bond of the ester, reaction of the zwitterionic adduct with water to form a vinylphosphonium hydroxide and rearrangement by apical migration from a trigonal bipyramidal interme-

diate. Yields vary from 16%-70% depending upon the substituent on the phosphorus atom of II.

A mechanistically related ring expansion of II (R = Me or Ph), shown in the sequence II → IV, was developed at about the same time (5).
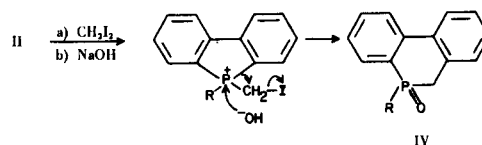

Until recently, similar one-carbon ring expansions of simple phospholes (I) directly involving the phosphorus atom as a nucleophile were unknown although other one-carbon ring expansions of phosphole oxides involving intermediate addition across the 2,3-bond of the phosphole ring had been observed (6,7). The two-step, 4-carbon expansion of 1,2,5-triphenylphosphole to the phosphonin V *via* the tricyclic ylide VI, formed by nucleophilic attack of the phosphorus atom of the phosphole upon two molecules of the ester followed by cyclization and intramolecular rearrangement (8,9), should also be mentioned.
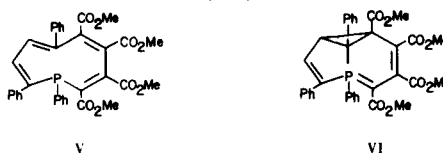
However, Mathey, et al. (10,11,12) have recently developed an ingenious and versatile double ring expansion of many simple phospholes by the sequence VII → VIII → IX → X. This expansion has not yet been duplicated with dibenzophospholes of type II.
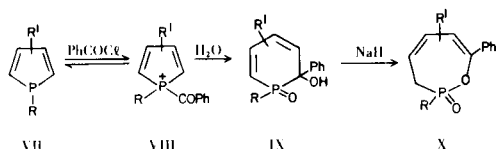
On the other hand, attempts to expand simple phospholes (e.g. 1,2,5-triphenylphosphole) with methyl propiolate and water in the manner of dibenzophospholes have been unsuccessful (13) presumably because of the very weak nucleophilic character of the phosphole system. Similar attempts (14) to ring expand simple phospholes by quaternization with diiodomethane followed by hydrolysis, again in the manner of dibenzophospholes (sequence II → IV), led to the formation of XI via the quaternary salt XII and the unexpected and most unusual 1,3-rearrangement product XIII.
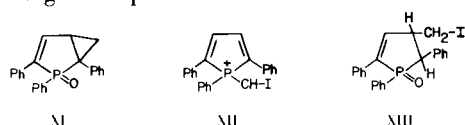
No similar studies have been carried out on the related but very little investigated (15) phosphindole (e.g. XIV) system and we decided to carry out such studies for several reasons. First, the simple phosphole (I) and dibenzophosphole (II) systems clearly behave quite differently in the reactions mentioned in the foregoing discussion, although a complete study has not yet been made, and it would be interesting to establish the behaviour of the related phosphindole system. In this connection, it should be mentioned that in reactions with dimethyl acetylenedicarboxylate, the phosphindole XIV not only behaves in a totally different manner from simple phospholes but also in a totally different manner from all other unsaturated phosphines so far studied (15).
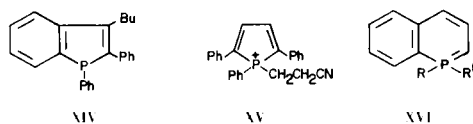

Second, the retrocyanoethylation studies of cyanoethylphospholium salts such as XV (16) and the pyramidal inversion studies (17,18,19) of phospholes, phosphindoles and dibenzophospholes carried out by Mislow, et al., suggest that the phosphindole system should, in nucleophilic character, behave much more like the dibenzophospholes than the simple phospholes.

Finally, certain one-carbon ring expansions of phosphindoles could provide useful routes to the little studied

(20) phosphanaphthalenes (XVI).

This paper therefore reports the results of a preliminary study of phosphindole ring expansions. As with our earlier study (15) of phosphindole chemistry, the phosphindole chosen was 3-butyl-1,2-diphenylphosphindole (XIV) since it is the only one which is relatively easily available (though in small quantities) and the reactions of this system studied are summarized in Scheme 1.

Scheme 1
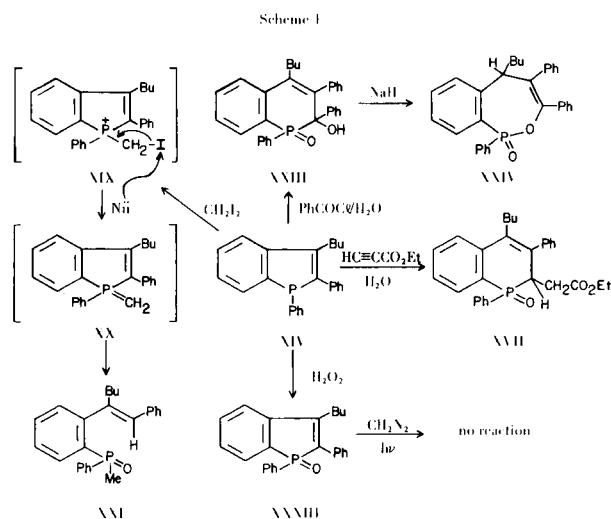
Treatment of the phosphindole XIV with ethyl propiolate in tetrahydrofuran containing a little water followed by heating under reflux for several hours gave, after work-up, a glass (35% yield) which analyzed very well for a 1:1:1 adduct of the phosphindole, the ester and water. That this adduct has the expected ring expanded structure XVII is shown by the ir, nmr and mass spectra. For example, the ir spectrum shows a typical ester carbonyl stretching frequency at 1745 cm^{-1} and a very broad band at 1210 cm^{-1} which is a superimposed ester C-O band and a P=O band. Furthermore, the nmr spectrum in deuterated chloroform shows twelve aromatic protons as a complex multiplet at τ 1.70-2.92 and two additional and somewhat more shielded aromatic protons occur as a broad multiplet centered on τ 3.30. The methylene protons of the ethoxy group and the allylic methine ring proton signals are superimposed and occur as a very complex multiplet at τ 5.85-6.70 while the allylic methylene protons of the butyl group occur as a poorly resolved multiplet in the usual (15) position at τ 7.61. The remaining butyl proton signals and the ester methyl proton signals occur as a complex multiplet at τ 8.35-9.60.

The mass spectrum confirms the structure XVII for the adduct since it shows a strong molecular ion peak at m/e 458 and a series of fragment ion peaks at m/e 415 (M - CH$_2$CH$_2$CH$_3$); 413 (M - OEt), 385 (M - CO$_2$Et) and 371 (M - CH$_2$CO$_2$Et). All of these peaks are consistent with the proposed structure since both M - CH$_2$CH$_2$CH$_3$

and M - CH_2CO_2Et should be formed readily by allylic cleavage and it is difficult to see how the -CH_2CO_2Et unit could arise by any other reaction pathway. Furthermore, another weaker peak occurs at m/e 358 which possibly corresponds to the ring contracted ion XVIII. In this reaction, therefore, the phosphindole XIV behaves as expected more like the benzophospholes (II) than the simple phospholes.
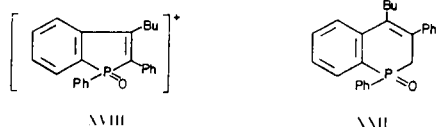
As will be seen later, the two unusually high field aromatic proton peaks in the nmr spectrum and the ring contraction under electron impact appear to be features of ring expanded structures such as XVII.

* Since XIV behaves like a dibenzophosphole in the above reaction, attempts were made to carry out a ring expansion with XIV analogous to that outlined in the sequence II → IV. The phosphindole reacts with undiluted diiodomethane at 100° in a sealed tube for several days to give a dark brown mass from which it proved impossible to isolate the expected iodomethyl salt XIX. However, on the assumption that the required salt was present in the mixture, the crude reaction product was dissolved in methanol and added to 10% aqueous sodium hydroxide and the resulting mixture was heated under reflux for several hours. Work-up of the reaction mixture gave a pale yellow viscous liquid in about 30% yield. Several repetitions of this experiment gave the same result.

The product shows the expected strong P=O band at 1180 cm^{-1} in the ir spectrum but, although the microanalytical results were poor and could not be improved either by preparative thin layer chromatography or by pumping at 10^{-6} Torr for several hours, the nmr and mass spectra showed clearly that the compound was a mixture composed mainly of the ring-cleaved product XXI and *not* the expected product XXII. Thus, the nmr spectrum showed a little over 14 aromatic protons at τ 1.95-3.33, one olefinic proton as a singlet at τ 3.80, two allylic protons of the butyl group as a broad hump at τ 7.55, three methyl protons as a doublet (J = 13 Hz) at τ 7.97 and 11 other aliphatic protons as two broad resonances at τ 8.75 and τ 9.24. This last signal represents four more aliphatic protons than is required for either structure XXI or XXII and it seems likely that the poor analysis is due to an impurity which is primarily aliphatic although a slightly more intense aromatic signal (between 0.5 and 1.5 protons for different samples) than is required for XXI or XXII suggests that the impurity may also have an aromatic component. The locations, integrations, multiplicities and coupling constants ($^2J_{P-H}$ = 13 Hz agrees well with litera-

ture (21) values) of the other signals are in excellent agreement with those expected for XXI and are incompatible with structure XXII.

Confirmation of this structure comes from the mass spectrum which shows a molecular ion peak (base peak) at m/e 374 as required by XXI. Furthermore, moderate to intense fragment ions appear (together with other fragments) at m/e 359 (M - CH_3), 345 (M - CH_2CH_3), 332 (McLafferty elimination of CH_2=CH-CH_3 from the butyl group), 331 (M - $CH_2CH_2CH_3$), 317 (M - $CH_2CH_2CH_2$-CH_3), 241 (332 - CH_2Ph), 215 (M - Bu-C=CHPh) and 139 (PhMePO). Again, this pattern is entirely consistent with the proposed structure XXI.

In our opinion, XXI is probably formed by the route XIV → XIX → XX → XXI as shown in Scheme 1 with attack of some nucleophile (see discussion below) upon the iodine atom of XIX to give the ylide XX which hydrolyzes in aqueous solution in the usual manner by protonation to give a phosphonium hydroxide. This then rearranges by apical elimination of the most stable carbanion to give XXI. Thus, although the expected intermediate iodomethylphosphindolium salt XIX is probably formed, nucleophilic attack upon the iodine atom rather than the expected hydroxide ion attack upon the phosphonium centre to give ring expansion (as with the synthesis of IV) occur.

This, however, is not entirely unexpected since it is well-known (22) that nucleophilic attack upon the halogen atom of an α-halogenoalkylphosphonium salt may occur under certain conditions. In particular, tertiary phosphines readily act (22) as nucleophiles in this type of reaction in hydroxylic solvents to give phosphonium ylides very cleanly. The nucleophile in the proposed step XIX → XX then may well be some remaining unquaternized phosphindole XIV rather than hydroxide ion.

Although we have as yet been unable to clarify further the steps in this proposed mechanism, it is clear that in this reaction the phosphindole system behaves in an entirely different manner from simple phospholes such as 1,2,5-triphenylphosphole (where 1,3-iodomethyl migration occurs (14)) and dibenzophospholes (where ring expansion occurs (5)). This again illustrates the difficulty in generalizing behaviour in heterocyclic phosphorus systems.

Turning now to phosphindole reactions analogous to the phosphole reactions of the type outlined in VII → VIII → IX → X, the phosphindole (XIV) reacts smoothly with benzoyl chloride in the presence of triethylamine in dry ether followed by treatment with water to give the ring expanded product XXIII. Microanalytical and spectroscopic data are in excellent agreement with this proposed structure. Thus, the ir spectrum shows a typical O-H stretching vibration as a broad peak at 3220 cm^{-1} and a strong, sharp P=O peak at 1190 cm^{-1}.

Similarly, the nmr spectrum shows 17 aromatic protons as a complex well-resolved multiplet at τ 1.85-3.08, 2 further aromatic protons (as observed for XVII) at slightly higher field as a broad hump at τ 3.13-3.76, two allylic protons of the butyl group as another broad hump at τ 7.18-7.90, one hydroxylic proton as a very sharp doublet (J = 16 Hz) centered on τ 8.21, the four remaining methylene protons of the butyl group as a multiplet at τ 8.31-9.08 and the three methyl protons of the butyl group as a highly distorted triplet (J = 5 Hz) centered on τ 9.23. Again, the locations and multiplicities of all the signals are consistent with the structure and $^3J_{P-OH}$ for the hydroxyl group is typical (12) of such systems. The -OH signal is also in the usual (12) location observed in related monocyclic systems of this type and, as expected, the signal vanishes on addition of deuterium oxide to the nmr sample.

Further support for the structure is given by the mass spectrum where a weak molecular ion peak is observed at m/e 464 together with fragment ion peaks associated with progressive degradation of the butyl group and loss of the hydroxyl group. However, major fragment ion peaks appear at m/e 359 (base peak) and 342 possibly corresponding to elimination of Ph-CO and then OH in a manner similar to that shown in XXV → XXVI → XXVII.

m/e 464   m/e 359   m/e 342
    \\\   \\\I'   \\\II
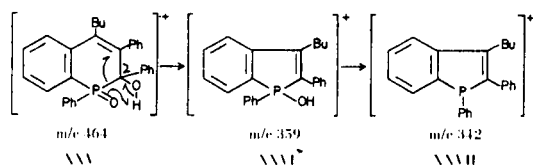
Some support for the idea that the fragmentation XXV → XXVI occurs in one step comes from the presence of a very weak metastable ion at ca. m/e 278 and also the appearance of a strong peak at m/e 105 corresponding possibly to Ph-C≡O⁺. Clearly this fragmentation cannot arise by simple cleavage of a PhCO-R bond since the ir spectrum of XXIII shows no trace of a carbonyl group and the ir and nmr spectra show that the only oxygen atoms occur in P=O and O-H functions.

In summary, all of the evidence is consistent with the proposed structure XXIII and, in particular, this compound shows the two aromatic protons at higher than usual field in the nmr spectrum and the ring contraction on electron impact observed for the structurally similar ring-expanded compound XVII. Presumably, these two high field protons are due to shielding of the two ortho protons of a freely rotating P - phenyl group by the remainder of the system although the reasons for this are not entirely clear.

Treatment of the compound XXIII with sodium hydride gave, as observed by Mathey (11,12) in similar reactions

for simple phospholes, a compound which analyzed very well for a rearrangement product of XXIII. However, the compound cannot be directly analogous to Mathey's rearrangement products of type X since the fused benzene ring of XXIII would block the carbon atom to which the hydrogen atom normally migrates. Such a rearrangement would have to give XXIV or the isomer XXVIII if the
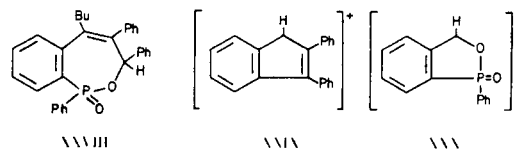
reaction follows the type of course proposed by Mathey. Alternatively, ring opening could occur. In fact, the product is XXIV as is shown clearly by the spectroscopic evidence.

For example, Mathey observed (12) in the infrared spectra of compounds of type X (using KBr discs) a P=O band at a slightly higher than usual location at 1250-1230 cm⁻¹ together with a doublet in the range 1067-1032 with a splitting of 14-24 cm⁻¹ tentatively assigned to the P-O-C vibration. For the rearrangement product tentatively formulated as XXIV we observed a very strong ir peak (using a Nujol mull) at 1245 cm⁻¹ assignable to P=O vibration together with a doublet (split by 14 cm⁻¹) at 1039 and 1025 cm⁻¹. Although the structure XXIV is not strictly analogous to compounds of type X, these infrared spectral features should be very similar in the two compounds. It should also be noted that the rearrangement product formulated as XXIV shows no OH vibration in the ir spectrum - neither is there any carbonyl vibration which might come from a ring-opened product.

Also, the signal averaged nmr spectrum of a very small sample of the rearrangement product showed a spectrum entirely consistent with XXIV. This spectrum showed 19 aromatic protons as a very broad and complex multiplet at τ 1.90-3.59, one allylic/benzylic proton as a distorted broadened triplet (J = 6 Hz) centered on τ 7.74 and 9 butyl protons as a broad multiplet at τ 8.25-9.59. Clearly, the butyl group is not on a double bond as in XIV, XXI and XXIII and the allylic single proton is obviously the tertiary proton in structure XXIV which should show the observed location and multiplicity. The spectrum also showed a very weak singlet impurity peak (less than half a proton) at τ 4.42.

Finally, the mass spectrum is again consistent with structure XXIV. The molecular ion peak appears, as expected, at m/e 464 together with the expected strong peak at m/e 407 corresponding to the easy loss of the allylic/benzylic butyl group. The next major peak occurs at m/e 267 and presumably corresponds to elimination of the PhP(O)-O unit from the 7-membered ring of the fragment ion at m/e 407 to give the ring-contracted ion XXIX.

A further medium peak at m/e 229 presumably corresponds to an alternative elimination of diphenylacetylene from the fragment ion at m/e 407 to give the ring contracted structure XXX.

Despite the structural and possible electronic differences between simple phospholes and phosphindoles then, phosphindoles undergo the typical phosphole double ring expansion observed by Mathey (10,11,12). However, as mentioned previously, no such studies have yet been carried out with dibenzophospholes. We therefore carried out similar reactions of 5-phenyl-5H-dibenzophosphole (II, R = Ph) with benzoyl chloride in the presence of triethylamine followed by treatment with water. As with the phosphindole, a product was obtained for which the analysis was in excellent agreement with the expected ring expanded adduct XXXI.

\\\I   \\\II
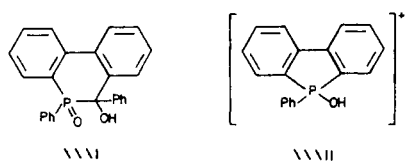
Spectroscopic evidence again strongly supports this structure with the ir spectrum (Nujol) showing a typical OH stretching frequency at 3220 cm^{-1} together with a P=O vibration at 1190 cm^{-1}. These vibrations are identical in location to those observed in the ir spectrum of XXIII. An nmr spectrum proved impossible to obtain because of the very low solubility of the adduct in the usual nmr solvents but the mass spectrum offered further evidence to support the proposed structure. The molecular ion peak appears at m/e 382 and fragment ion peaks occur at m/e 366 (loss of oxygen?) and m/e 365 (M - OH). The next important fragment ion occurs at m/e 277 and is presumably due to the ring contracted ion XXXII formed

by elimination of Ph-C$\overset{+}{\equiv}$O and analogous to the similar ion XXVI formed by electron impact on XXV. A weak

peak also occurs at m/e 260 (277 - OH) and the Ph-C$\overset{+}{\equiv}$O fragment occurs at m/e 105 as a peak of medium intensity. There can therefore be little doubt that the structure assignment is correct.

Treatment of the adduct XXXI with sodium hydride in dimethylformamide certainly led to the formation of a new product but the low carbon and hydrogen analyses (C = 56.99, H = 4.06%) show clearly that this is not the expected rearrangement product. The product is high melting (280°) and the low volatility rendered it impossible to record a mass spectrum. Furthermore, the compound has an extraordinarily low solubility in the conventional nmr solvents and the nmr spectrum could not be recorded even using prolonged signal averaging. The compound

therefore remains unidentified.

Finally, leaving reactions at the phosphorus atom of the phosphindole system, an attempt at photochemical addition of carbene (from diazomethane) across the double bond of the phosphindole oxide XXXIII was made. This would give an adduct analogous to XI (6) or lead to ring expansion as observed (6,7) with related systems. However, several attempts to carry out this reaction led only to the recovery of unchanged XXXIII. Presumably the double bond of the five membered ring in XXXIII is too hindered for addition to occur easily.

In summary, the phosphindole XIV behaves like simple phospholes in certain reactions (reaction with benzoyl chloride and water and treatment of the product with sodium hydride), like dibenzophospholes in other reactions (treatment with ethyl propiolate and water; treatment with benzoyl chloride and water) and like neither simple phospholes nor dibenzophospholes in yet other reactions (reaction with diiodomethane followed by hydroxide ion). This further illustrates the unpredictability of phosphorus heterocycles with regard to reactions at the phosphorus atom. However, it can be seen that ring expansion of the phosphindole system can be made to occur and that such ring expansions occur in sufficiently good yield to have potential value in the synthesis of phosphanaphthalene derivatives.

EXPERIMENTAL

Reaction of 3-Butyl-1,2-diphenylphosphindole (XIV) with Ethyl Propiolate and Water.

Ethyl propiolate (1 ml.) was added dropwise to a solution of 3-butyl-1,2-diphenylphosphindole (1 g., 2.9 mmoles) in tetrahydrofuran (15 ml.), containing 2 drops of water, at room temperature under nitrogen. The mixture was then heated under reflux for 20 hours. The solvent was removed by evaporation to give a glassy residue which was purified by preparative thin-layer chromatography using chloroform:ether (7:3) as eluent. Evaporation of the first fraction gave the phosphindole oxide XXXIII (0.23 g.) while the second fraction gave 4-butyl-2-(ethoxycarbonylmethyl)-1,2-diphenyl-1,2-dihydrobenzo[b]phosphorin 1-oxide (XVII) as a glass (0.46 g., 35%); ir (Nujol): ν max: 1745, 1210 cm^{-1} (broad); nmr (deuteriochloroform): τ 1.70-2.92 (m, 12H, aromatic), 3.30 (m, 2H, aromatic), 5.86-6.70 (m, 3H, CH$_2$ and CH), 7.61 (t, 2H, allylic butyl CH$_2$), 8.35-9.60 (m, 7H); ms: m/e 458 (M$^+$).

Anal. Calcd. for $C_{29}H_{31}O_3P$: C, 75.98; H, 6.77; P, 6.77. Found: C, 75.37; H, 7.21; P, 6.53.

Reaction of 3-Butyl-1,2-diphenylphosphindole (XIV) with Diiodomethane and Hydroxide Ion.

3-Butyl-1,2-diphenylphosphindole (1.03 g., 3 mmoles) and diiodomethane (1 ml., 12.3 mmoles) were mixed and heated in a sealed tube at 100° for 5 days according to the method of Hughes and Srivanavit (14). The resulting dark brown mixture was dissolved in methanol (100 ml.) and, without isolation of any reaction product, the solution was added slowly to aqueous sodium hydroxide (10%, 7 ml.) at room temperature with vigorous stirring. The reaction mixture was then heated under reflux for 24 hours, cooled and treated with dilute hydrochloric acid until just acid to litmus. Water (10 ml.) was added and the mixture was evaporated under reduced pressure to remove most of the methanol. The mixture was then extracted with chloroform (100 ml.) and the chloroform extract was dried over anhydrous sodium sulfate, evaporated to low bulk and chromatographed on a silica column using chloroform as the eluent. The main product from the column chromatography was rechromatographed by preparative thin layer chromatography on silica using chloroform:ether (9:1) as the eluent. Extraction of the main band gave a pale yellow viscous liquid characterized as the impure (see discussion) ring-opened compound XXI (0.34 g., 30%), ir (liquid film) ν max: 1180 cm^{-1} (P=O); nmr (deuteriochloroform): τ 1.95-3.33 (m, 14H, aromatic), 3.80 (s, 1H, olefinic), 7.55 (broad, 2H, allylic CH$_2$), 7.97 (d, 3H, CH$_3$, J = 13 Hz), 8.75 and 9.24 (broad, 11H, aliphatic); ms: m/e 374 (M$^+$).

Anal. Calcd. for $C_{25}H_{27}OP$: C, 80.21; H, 7.22; P, 8.29. Found: C, 78.75; H, 7.62; P, 3.95.

Numerous attempts to further purify this material were unsuccessful but the spectroscopic data (see discussion) leave no doubt that the product is mainly XXI.

Reaction of 3-Butyl-1,2-diphenylphosphindole (XIV) with Benzoyl Chloride and Water.

3-Butyl-1,2-diphenylphosphindole (1.04 g., 3 mmoles) in dry ether (80 ml.) containing triethylamine (1.5 ml., 12.9 mmoles) was treated dropwise with freshly distilled benzoyl chloride (3 ml., 20.7 mmoles) at room temperature with vigorous stirring under argon for 12 hours. The resulting mixture was hydrolyzed with water (50 ml.) and was then stirred at room temperature for a further 2 hours. The organic layer was washed with 5% sodium hydrogen carbonate solution and then water before drying over magnesium sulfate. The solution was evaporated to low bulk and the crude product was chromatographed on a silica column. Elution with light petroleum gave mainly 3-butyl-1,2-diphenylphosphindole oxide XXXIII (0.32 g.) and benzoic acid. Further elution with ether:methanol (4:1) gave a yellow oil which was rechromatographed on silica by preparative thin layer chromatography using chloroform:ether (7:3) as eluent. Extraction of the main band gave 4-butyl-2-hydroxy-1,2,3-triphenyl-1,2-dihydrobenzo[b]phosphorin 1-oxide (XXIII) as colourless crystals (0.18 g., 13%), m.p. 221-224°; ir (Nujol) ν max: 3220 (OH), 1190 (P=O) cm^{-1}; nmr (deuteriochloroform): τ 1.85-3.08 (m, 17H, aromatic), 3.13-3.76 (broad, 2H, aromatic), 7.18-7.90 (broad, 2H, allylic CH$_2$), 8.21 (d, 1H, OH, J = 16 Hz), 8.31-9.08 (m, 4H, 2CH$_2$), 9.23 (distorted t, 3H, CH$_3$, J = 5 Hz); ms: m/e 464 (M$^+$).

Anal. Calcd. for $C_{31}H_{29}O_2P$: C, 80.17; H, 6.25; P, 6.68. Found: C, 79.93; H, 6.10; P, 6.65.

Reaction of 4-Butyl-2-hydroxy-1,2,3-triphenyl-1,2-dihydrobenzo-[b]phosphorin 1-Oxide (XXIII) with Sodium Hydride.

The dihydrobenzo[b]phosphorin oxide XXIII (0.40 g., 0.86 mmole) in dry N,N-dimethylformamide (10 ml.) was treated with a catalytic amount of sodium hydride (prewashed with light petroleum) with vigorous stirring under argon. Immediately after the addition of sodium hydride, a violet colour developed but this disappeared again after a very short time. Stirring at room temperature was continued for a further 6 hours and then water (0.5 ml.) was added. The resulting mixture was carefully neutralized with dilute hydrochloric acid and the solvent removed by reduced pressure distillation. The brownish residue was chromatographed on silica by preparative thin layer chromatography using ethyl acetate as the eluent. The band of R_f value 0.41 was removed from the plate and extracted (soxhlet) with ether. The extract was evaporated to give a light brown glass (0.07 g., 18%) identified as the crude rearrangement product XXIV. The pure product (0.023 g.) was isolated by treating the glass with a small amount of cold ether followed by filtration to give colourless crystals, m.p. 164-166°; ir (Nujol) ν max: 1245 (P=O), 1039, 1025 (P-O-C) cm^{-1}; nmr (100% deuteriochloroform, signal averaged): τ 1.90-3.59 (m, 19H, aromatic), 7.74 (t, 1H, allylic CH, J = 6 Hz), 8.25-9.59 (m, 9H, butyl group); ms: m/e 464 (M$^+$).

Anal. Calcd. for $C_{31}H_{29}O_2P$: C, 80.17; H, 6.25; P, 6.68. Found: C, 79.77; H, 6.32; P, 6.50.

Reduction of 5-Phenyl-5H-dibenzophosphole (II, R = Ph) with Benzoyl Chloride and Water.

A solution of 5-phenyl-5H-dibenzophosphole (1.04 g., 4 mmoles) in vigorously stirred dry ether (80 ml.) containing triethylamine (1.5 ml., 12.9 mmoles) was treated dropwise at room temperature under argon with freshly distilled benzoyl chloride (3 ml., 20.7 mmoles). The resulting mixture was stirred under argon for 3 days and then hydrolyzed with water (50 ml.) for 2 hours. The mixture was filtered and a pale yellow solid was collected. This crude product was crystallized from toluene:methanol (3:1) to give a colourless crystalline solid (0.47 g., 31%) characterized as the ring expanded adduct XXXI, m.p. 270-272° dec.; ir (Nujol) ν max: 3220 (OH), 1190 (P=O) cm^{-1}; nmr: solubility too low; ms: m/e 382 (M$^+$).

Anal. Calcd. for $C_{25}H_{19}O_2P$: C, 78.53; H, 4.97; P, 8.12. Found: C, 78.29; H, 5.19; P, 7.89.

Some starting material (0.26 g.) was recovered on chromatographic treatment (silica - light petroleum) of the ethereal layer of the initial filtrate.

Attempts to further ring expand the product XXXI by treatment with sodium hydride in the manner outlined for XXIII, gave only a high melting (274-278°) colourless solid which was too involatile to merit further investigation other than to establish that the carbon and hydrogen content of this product are unexpectedly low.

Anal. Found: C, 58.66; H, 4.17.

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