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ISOPHOSPHINDOLE P-OXIDE
A REACTIVE INTERMEDIATE AND ITS REACTION AS A DIELS-ALDER DIENE[1]

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Abstract—2-Phenylisophosphindole 2-oxide (3) was generated as a reactive intermediate by the dehydrobromination of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide. The existence of 3 was confirmed by trapping with various dienophiles as the Diels–Alder adducts. The stereochemistry of the $[4+2]\pi$ cycloaddition was found to be stereospecific giving *endo* products with the phosphoryl group *syn* to the approaching dienophile. When the dienophile was an alkyne, the cycloadduct decomposed under the reaction conditions to give β-substituted naphthalene as the final product.

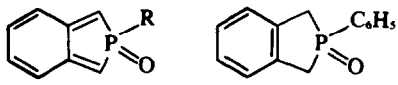
The remarkable difference between the chemistry of heteroindene (**1**, X = O, NR or S) and that of the isoconjugated isomer isoheteroindene (**2**, X = O, NR or S) is a subject of many theoretical[2] and experimental[3] investigations. A similar comparison of the chemistry of phosphindole (**1**, X = PR) with isophosphindole (**2**, X = PR) will be of considerable interest. Our recent work[4,5] on the phosphindole system indicated that there is considerable $p_\pi - p_\pi$ overlap between the phosphorus lone pair and the unsaturated system. The energy barrier to the phosphorus pyramidal inversion was found to be much lower than normal phosphines.[6] There is however very little known about the isophosphindole system. A semi-empirical CNDO/2 calculation[7] with parameters specifically developed for pyramidal inversion led to the prediction that the energy barrier to the phosphorus inversion in **2** (X = CH_3) could be exceptionally low (~6·9 kcal/mole), a result which is yet to be experimentally verified. On the other hand, the possibility of spiroconjugation was suggested for isophosphindole P-oxide (**3**) and experimental evidence was adduced in support of this prediction.[8]

We have recently developed a convenient synthesis[9,10] of 2-phenylisophosphindoline 2-oxide (**4**). With the ready availability of **4**, we began to explore the chemistry of the isophosphindole system.

Bromination of 2-phenylisophosphindole 2-oxide (**4**). 2-Phenylisophosphindole 2-oxide was brominated with equal molar quantity of N-bromosuccinimide, in the presence of a catalytic amount of benzoyl peroxide, in refluxing benzene for 12 hr. After removal of succinimide and the solvent, the mixture was separated by preparative TLC to furnish 50% yield of one major product. The spectroscopic data and elemental analysis of this compound were in accord with the structure of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (**5**). Also isolated as minor products were 10% yield of 1,1-dibromo-2-phenylisophosphindoline 2-oxide (**6**), 8% yield of *r*-1-*c*-3-dibromo-t-2-phenylisophosphindoline 2-oxide (**7**) and 5% yield of *trans*-1,3-dibromo-2-phenylisophosphindoline 2-oxide (**8**).

It is of interest to find out whether *r*-1-bromo-*c*-2-phenylisophosphindoline 2-oxide (**9**) was formed. Careful examination of the mixture by TLC showed that there was only a trace of this compound. Structural determination of these products was achieved by spectroscopy and mass spectrometry. All the bromo derivatives of 2-phenylisophosphindoline 2-oxide feature strong characteristic P=O stretching at about 1230 cm^{-1}.

1 **2**



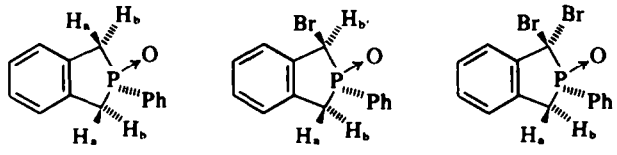
3 **4**

In the NMR spectra of all the above bromo compounds, the aromatic protons appear as multiplet in the region 7·2–7·8 δ, the benzylic protons attached to –Br give doublet and the other benzylic protons appear as part of an ABX pattern (X = ^{31}p). By careful examination of the NMR spectra of these compounds, it is possible to deduce the relative stereochemistry of the various isomers. This is based on two considerations. First, there is the shielding effect of the phenyl ring.[12] Secondly, the magnitude of the geminal ^2J(P–CH) coupling constants depends on the orientation of the phosphoryl group.[12,14] The shielding effect of phenyl ring in modifying the chemical shift of adjacent spin system is well documented and has been used for stereochemical assignment in the field of organophosphorus compounds. Examination of molecular models of the various isomers of the bromo derivatives of 2-phenylisophosphindoline 2-oxide suggests that the benzylic protons *cis* to the phenyl ring should be shielded, i.e. they should appear at a higher field (Table 1).

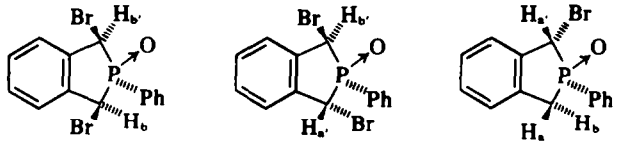
The dependence of the geminal coupling constant ^2J(P–C–H) on the phosphorus lone pair orientation has been observed.[12] In essence, a larger ^2J(P–C–H) coupling constant is attributed to the isomer in which the C–H bond is *cis* to the phosphorus lone pair and a smaller ^2J(P–C–H) coupling constant to the *trans*-isomer.

If one argues that, in cyclic phosphine oxides, the magnitude of the ^2J(P–C–H) coupling constant depends now on the orientation of the polar phosphoryl group, and that the dependence is in the same direction, then the proton *trans* to the phosphoryl group (i.e. *cis* to the phenyl group) should have the smaller coupling constant.

Table 1. The chemical shifts (δ in ppm) and geminal coupling constants (in Hz) of benzylic protons of some isophosphindolines



4 5 6



7 8 9

	4	6	5	7	8	9
$^a H_a$(^{2}J(PCH$_a$))	3·51(16)	3·59(17)	3·59(17)			3·59(17)
$^a H_b$(^{2}J(PCH$_b$))	3·35(9)	3·36(9)	3·36(9)			3·36(9)
$^a H_{a'}$(^{2}J(PCH$_{a'}$))					5·6(10)	5·6(10)
$^a H_{b'}$(^{2}J(PCH$_{b'}$))			5·2(2)	5·2(2)	5·3(2·5)	

The argument appears to be consistent with the data in Table 1. Similar dependence of geminal ^{2}J(C–C–H) coupling constants on the orientation of a polar group on carbon has been observed[15] and a theoretical explanation has been offered.[16]

With the stereochemistry of the various bromo compounds thus assigned, it is interesting to note that the *trans*-isomer **5** is formed in greater than 10-fold excess of the *cis*-isomer **9** even though the latter compound appears to be thermodynamically more stable (see later section). This stereoselectivity is rather unexpected because free radical bromination is not known to be so selective.[17] It may be that in the present case, with the constraint imposed by the bicyclic system, in the product formation step, the approach of the reagent bromine may come preferentially from the side opposite to the more bulky phenyl group.

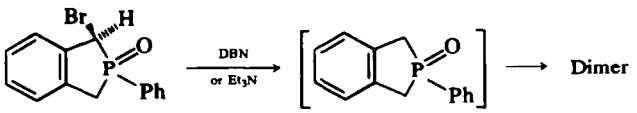
The formation of the dibromo compounds could not be minimized by decreasing either the reaction temperature or time.

On the other hand, treatment of 2-phenylisophosphindoline 2-oxide with phosphorus pentabromide in refluxing benzene for 24 hr led to the exclusive formation of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide, albeit in only 15% yield. Most of the starting material was recovered. It seems that phosphorus pentabromide behaves as a brominating agent and the same stereoselectivity is observed.

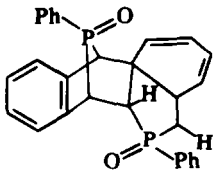
Dehydrobromination of r-1-*bromo-t-2-phenylisophosphindoline 2-oxide* (**5**). An easy entry into the isophosphindoline system can be achieved by dehydrobromination of *r*-1-bromo-t-2-phenylisophosphindole 2-oxide (**5**) with base. After **5** was treated with excess 1,5-diazabicyclo [3.4.0] nonene-5 (DBN) in refluxing benzene for 8 hr, the resulting mixture, on separation by preparative TLC afforded 62% yield of a new compound (Scheme 1). Its mass spectrum and elemental analysis were consistent with the dimer of 2-phenylisophosphindole 2-oxide (**10**). Dehydrobromination of **5** with excess triethylamine in refluxing benzene for 12 hr gave 50% yield of the same product. The formation of DBN·HBr and NEt_3·HBr salts in both reaction indicated that dehydrobromination has indeed taken place. The isolation of the dimer indicates that **10** if formed, must be unstable and it dimerizes too rapidly to allow its isolation. The dimerization of 2-phenylisophosphindole 2-oxide is not unexpected, in view of the strong tendency of unstable *o*-quinonoid system to undergo dimerization.[18]

The elucidation of the structure of the dimer is not an easy task. The mass spectrum of the dimer features a molecular ion at *m/e* 452. The infrared spectrum of the dimer exhibits a strong band at 1210 cm^{-1}, attributable to phosphoryl stretching and strong bands at 1440 cm^{-1}, 1120 cm^{-1} and 700–800 cm^{-1}, all associated with phenyl absorption. The 60 MHz, 100 MHz and 220 MHz NMR spectra all show a 14-H multiplet at 7·0–7·8 δ for aromatic protons, a 4-H multiplet at 6·3 δ for olefinic protons, a 1-H doublet of doublet at 5·3 δ for another olefinic proton (J_{P-CH} = 22 Hz), two 1-H multiplet at 4·2 δ and 3·9 δ for two nonequivalent methine protons and a 1-H multiplet at 3·4 δ for another methine protons.

If one considers that the dimer arises from two molecules of 2-phenylisophosphindole 2-oxide, there are at least 36 possible structures.[10] Some of these structures can be readily eliminated from consideration. For example, the complexity of the observed NMR spectra would rule out any symmetrical structure. At the moment, we favor structure **11** as the dimer, being consistent with the spectroscopic data. The stereochemical assignment is based solely on analogy with the behavior of 2-



Scheme 1.

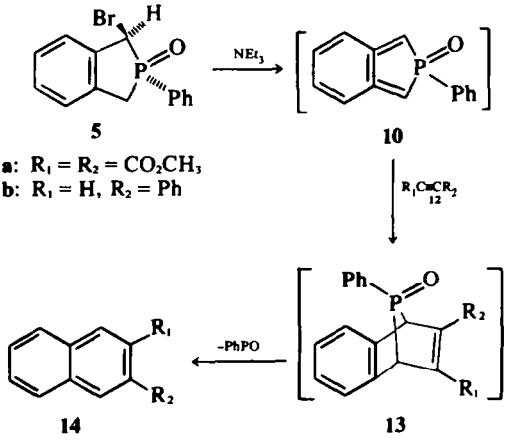


11

phenylisophosphindole 2-oxide in undergoing $[4+2]\pi$ cycloaddition (*vide infra*).

2-Phenylisophosphindole 2-oxide as Diels–Alder diene. The existence of many transient *o*-quinonoid intermediates has been confirmed by trapping with various dienophiles.[19-21]

In order to demonstrate that 2-phenylisophosphindoline 2-oxide is indeed the reaction intermediate, we sought to trap it in the form of the Diels–Alder adduct. Thus, treatment of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (**5**) with excess triethylamine in the presence of dimethyl acetylenedicarboxylate, in refluxing benzene for 48 hr, led to the isolation of 28% yield of a new compound by preparative TLC. It was identified as dimethyl 2,3-naphthalenedicarboxylate (**14a**) by comparison with an authentic sample. The formation of the ester can only arise from the Diels–Alder adduct **13** by the extrusion of the PhPO moiety, a process which has been well documented[22-24] (Scheme 2):



a: $R_1 = R_2 = CO_2CH_3$
b: $R_1 = H$, $R_2 = Ph$

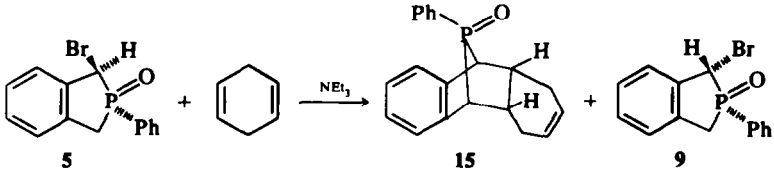
Scheme 2.

Similarly dehydrobromination of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide with excess triethylamine in the presence of phenylacetylene in refluxing benzene for 48 hr, afforded 2-phenylnaphthalene (**14b**) in 15% yield. 2-Phenylisophosphindole 2-oxide dimer was also isolated in 25% yield. Hence, the dehydrobromination reaction of **5** in the presence of various alkynes, seems to offer a general method for the preparation of naphthalene derivatives. However, there remained the task of isolating a cycloadduct with the skeleton of the isophosphindole system intact. This was achieved by trapping **10** with alkenes. When *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide was dehydrobrominated with triethylamine in the presence of 1,4-cyclohexadiene, an adduct was isolated in 34% yield. Its spectroscopic properties and elemental analysis were in accord with structure **15**. Interestingly, from this reaction was also isolated *r*-1-bromo-*c*-2-phenylisophosphindoline 2-oxide (**9**). Presumably, it arose from a base-catalysed isomerization reaction (Scheme 3).

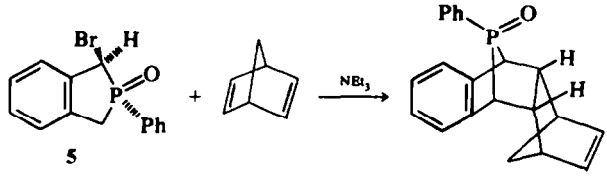
From the absence of coupling between phosphorus and the methine protons at the ring junction (Experimental) it is possible to assign the stereochemistry of the adduct **15** to be *endo*. Recently, Benezra[25] has reported the variation of vicinal ^{31}P–C–C–H couplings with dihedral angle and found a Karplus type relationship. It can be seen that in **15** the *endo* isomer would be expected to have a dihedral angle of 90°, thus a $^3J_{P-C-C-H}$ value of 0 Hz is within the experimental value. The stereochemistry at phosphorus in **15** has not been established with certainty.

We have however elucidated the complete stereochemistry of the $[4+2]\pi$ cycloadduct between 2-phenyl-isophosphindole 2-oxide and 2,5-norbornadiene. It was found that on treatment of **5** with excess triethylamine in the presence of excess 2,5-norbornadiene in refluxing benzene for 48 hr, there was obtained the adduct **14** in 25% yield (Scheme 4). In addition, *r*-1-bromo-*c*-2-phenylisophosphindoline 2-oxide (10% yield), the dimer of 2-phenylisophosphindole 2-oxide (20% yield) and the starting material (30%) were isolated. The adduct was assigned to the structure **16** on the basis of its spectroscopic data and elemental analysis. It was the only addition product isolated. The reaction was therefore stereospecific.

The 220 MHz NMR spectrum of **15** exhibits a 9-H multiplet at 7·2 δ for the aromatic protons, a 2-H singlet at 6·2 δ for the olefinic protons, a 2-H doublet at 3·7 δ for the methine protons adjacent to P=O ($J_{P-CH} = 10$ Hz), a



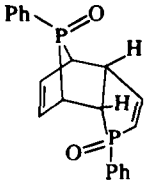
Scheme 3.



Scheme 4.

2-H singlet at 3·1 δ for the allylic methine protons, a 2-H singlet at 2·6 δ for the methine protons at the ring junction and two 1-H doublets at 0·8 δ and −0·3 δ for the two nonequivalent bridgehead methylene protons (J_{AB} = 10 Hz). A J_{AB} value of 9 Hz has been observed for the methylene protons of dichloronorbornadiene.[26] The *endo* stereochemistry of the adduct is assigned on the basis of the vicinal P–C–C–H coupling ($^3J_{PCCH}$ = 0 Hz). Molecular model shows that for the *exo* adduct the dihedral angle of P–C–C–H would be close to 180° and therefore a $^3J_{PCCH}$ of 40 Hz would be expected.[25] The assignment of the orientation of the methylene bridge is based on two factors. The rather large difference in chemical shifts of the two protons indicates that one of the protons must be strongly shielded (−0·3 δ) by the benzene ring. Also the absence of vicinal H–C–C–H coupling between the ring junction protons and the bridgehead protons shows that they are 90° with respect to each other. From inspection of molecular models, this is more likely for the structure proposed. In order to deduce the stereochemistry at phosphorus of the adduct **16**, the shift reagent tris(dipivalomethano)-praseodynium (**3**) [Pr(DPM)$_3$] was added in varying amounts to a $CDCl_3$ solution of **16**. A plot of chemical shift vs [Pr(DPM)$_3$]/[Substrate] ratio for various peaks in the NMR spectrum of **16** in $CDCl_3$ measured at 60 MHz gave linear relationship.[27] It was observed that the shift was in the decreasing order of phenyl ring protons attached to P=O ~ methine protons at the ring junction > allylic methine protons ~ methine protons adjacent to P=O. Using the assumption that the protons closest to the complexed Pr atom should display the greatest shift,[28] we can conclude that the P=O group is on the side of the ring junction whereas the phenyl group is away from it.

Thus, 2-phenylisophosphindole 2-oxide undergoes stereospecific [4+2]π cycloaddition with 2,5-norbornadiene to give the *endo-exo* adduct.[29] Stereochemical preference at phosphorus is probably governed by steric factor in that the more bulky phenyl group is away from the approaching dienophile. As far as we are aware, there is in the literature only one other example where the complete stereochemistry of the [4+2]π cycloadduct of phosphole oxide is known. This is in the dimerization of 1-ethoxyphosphole 1-oxide.[30] The structure of the dimer was determined by X-ray[31] and found to be **13**. It can be seen that the same stereochemical course was followed in the [4+2]π dimerization.



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CONCLUSIONS

2-Phenylisophosphindole 2-oxide (**4**) has been generated as a reactive intermediate. Its existence was demonstrated by trapping it with various dienophiles. The [4+2]π cycloaddition reaction with **4** as the 4π component, was found to be stereospecific, giving the *endo* adduct with the phosphonyl group *syn* to the 2π component. This stereospecificity appears to be general for phosphole oxides.

The reactivity of **4** should be contrasted with that of the P-oxide of **1** (X = PC_6H_5) which has been characterized as a stable solid.[4,5] The chemical pattern is in analogy with other heteroindene-isoheteroindene systems[2,3] or the simpler indene-isoindene system,[32,33] in that the *o*-quinonoid structure imposes considerable reactivity into the molecule.

EXPERIMENTAL

All m.ps are uncorrected. NMR spectra were recorded on Varian T-60 and Varian HA-100 spectrometers. The 220 MHz spectra were run by the 220 MHz laboratory, Sheridan Park, Ontario. Unless otherwise mentioned, all the NMR spectra were taken in $CDCl_3$ with TMS as either internal standard. All proton spectra are reported in δ units relative to TMS. Abbreviations used in reporting of NMR spectra are: s, singlet; d, doublet; t, triplet; q, quintet; m, multiplet. IR spectra were recorded on a Perkin–Elmer Model 257 spectrophotometer or a Unicam SP 1000 spectrophotometer with polystyrene calibration. Solid samples were taken as KBr pellets, and liquid samples either as thin film (neat) or in $CHCl_3$ or CCl_4. Mass spectra were recorded on an AEI MS-902 mass spectrometer at a temp of 100–150°. The operating conditions were a 70 eV electron energy, resolution of 1000 and 8 kV accelerating voltage. Organic Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Benzene and toluene were dried and distilled over sodium wire. Thin layer chromatograms were run on silica gel sheets with fluorescent indicator made by Eastman Organic Chemicals. Preparative TLC was performed on silica gel (HF 254+366 according to Stahl, made by E. M. Damsterdt Company, Germany) plates and were developed in ethyl acetate unless otherwise stated.

Reaction of 2-phenylisophosphindoline 2-oxide with N-bromosuccinimide. A mixture of 2-phenylisophosphindoline 2-oxide[9,10] (0·23 g; 1 mmole) and N-bromosuccinimide (recrystallized from water as described by Dauben and McCoy[34]) (0·18 g; 1 mmole) were refluxed in 40 ml dry benzene, in the presence of a catalytic amount of benzoyl peroxide for 12 hr. The mixture was cooled and washed twice with water to remove succinimide and the organic layer was dried over $MgSO_4$ and filtered. On evaporation of the solvent, followed by preparative TLC of the residue, there was obtained *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (0·15 g; 50%) m.p. 90–92° (ether). R_f value = 0·45 NMR: 7·5 (m, 4-H, Ar-H); 5·2 (d, 1-H, –CH); 3·3–4·0 (part of ABX, 2-H, $-CH_2$, $^2J_{P-CH_a}$ = 17, $^2J_{P-CH_b}$ = 9 Hz). IR: 1230 cm^{-1} (P=O); 1440 cm^{-1}, 1120–1100 cm^{-1} and 700–800 cm^{-1} (Ph); mass spectrum: *m/e* 308 (10%); 306 (10%); 227 (100%); 179 (30%); 149 (20%). (Found: C, 54·91; H, 4·13; Br, 25·5. Calcd for $C_{14}H_{12}POBr$: C, 54·75; H, 3·94; Br, 26·02%).

Also isolated as minor products were 1,1-dibromo-2-phenylisophosphindoline 2-oxide (0·03 g; 10%), m.p. 107–110° (chloroform/hexane), R_f value = 0·48, 0·025 g (8%) of *r*-1-, *c*-3-dibromo-t-2-phenylisophosphindoline 2-oxide, m.p. 186–188° (ether), R_f value = 0·53, 0·015 g (5%) of *trans*-1,3-dibromo-2-phenylisophosphindoline 2-oxide, m.p. 95–98° (chloroform/hexane), R_f value = 0·57, and a trace of *r*-1-bromo-*c*-2-phenylisophosphindoline 2-oxide, m.p. 140–142° (ether), R_f value = 0·4.

Spectral data of dibromo derivatives

1,1-Dibromo-2-phenylisophosphindoline 2-oxide. NMR: 7·3 (m, 4-H, Ar-H); 3·1–4·0 (part of ABX, 2-H, $-CH_2$, $^2J_{P-CH_a}$ = 17, $^2J_{P-CH_b}$ = 9 Hz; IR: 1240 cm^{-1} (P=O); 1440 cm^{-1}, 1120–1100 cm^{-1} and 700–800 cm^{-1} (Ph); mass spectrum: *m/e* 388 (5%); 386 (10%); 384 (5%); 307 (20%); 305 (20%); 226 (50%); 179 (20%); 178 (30%); 149 (100%); 102 (10%).

r-1-c-3-Dibromo-t-2-phenylisophosphindoline 2-oxide. NMR: 7·4 (m, 4-H, Ar-H); 5·3 (d, 1-H, –CH, $^2J_{P-CH_b}$ = 2·5 (Hz); 5·6 (d, 1-H, –CH, $^2J_{P-CH_a}$ = 10 Hz). IR: 1240 cm^{-1} (P=O), 1440 cm^{-1}, 1120–1100 cm^{-1} and 700–800 cm^{-1} (Ph); mass spectrum: *m/e* 388 (5%); 386 (10%); 384 (5%); 307 (20%); 305 (20%); 226 (25%); 225 (20%); 179 (100%); 178 (90%); 149 (80%); 102 (10%).

trans-1,3-*Dibromo-2-phenylisophosphindoline 2-oxide.* NMR: 7·3 (m, 4-H, Ar-H); 5·2 (d, 1-H, –CH, $^2J_{P-CH_b}$ = 2 Hz). IR: 1320

cm^{-1} (P=O); 1440 cm^{-1}, 1120–1100 cm^{-1} and 700–800 cm^{-1} (Ph); mass spectrum: *m/e* 388 (2%); 386 (4%); 384 (2%); 307 (21·3%); 305 (21·3%); 226 (5%); 225 (8%); 179 (100%); 178 (97%); 149 (31%); 102 (34%).

Reaction of 2-phenylisophosphindoline 2-oxide with phosphorus pentabromide. A soln of $PrBr_5$ (0·43 g; 1 mmole) in 35 ml dry benzene was added dropwise to a soln of 2-phenylisophosphindoline 2-oxide (0·23 g; 1 mmole) in 30 ml of dry benzene under N_2. The mixture was refluxed for 24 hr and the solvent was evaporated. The crude mixture was separated by preparative TLC to give 0·045 g (15%) of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide, identical in all respects with the product obtained by bromination of 2-phenylisophosphindoline 2-oxide with N-bromosuccinimide. Starting material was also recovered (75%).

Dehydrobromination of r-1-bromo-t-2-phenylisophosphindoline 2-oxide with 1,5-diazabicyclo [3.4.0] *nonene-5* (DBN). To a soln of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (0·31 g; 1 mmole) in 40 ml dry benzene was added DBN (0·20 g; 1·5 mmole) and the mixture was refluxed for 8 hr. The mixture became cloudy with formation of DBN·HBr salt after 20 min. The mixture was cooled and filtered, and excess DBN was neutralized with 5% H_2SO_4. The organic layer was washed twice with water, dried over $MgSO_4$, filtered and the solvent was removed. Preparative TLC of the residue afforded 0·14 g (62%) of 2-phenylisophosphindole 2-oxide dimer. It was recrystallized from chloroform/hexane to give hygroscopic white solid, m.p. 216–220° (dec). NMR (220 MHz): 7·0–7·8 (m, 14-H, Ar-H); 6·3 (m, 4-H, =CH); 5·3 (d of d, 1-H, =CH, J_{P-CH} = 22 Hz); 4·2 (m, 1-H, –CH); 3·9 (m, 1-H, –CH); 3·4 (m, 1-H, –CH); IR: 1210 cm^{-1} (P=O); 1440 cm^{-1}, 1120 cm^{-1} and 700–800 cm^{-1} (Ph); mass spectrum: *m/e* 452 (10%); 228 (25%); 150 (25%); 149 (100%). (Found: C, 70·87; H, 5·12. Calcd for $C_{28}H_{22}P_2O_2 \cdot H_2O$: C, 71·48; H, 5·14%).

Dehydrobromination of r-1-bromo-t-2-phenylisophosphindoline 2-oxide with triethylamine. To a soln of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (0·31 g; 1 mmole) in 40 ml dry benzene was added triethylamine (0·40 g; 4 mmole) and the mixture was refluxed for 12 hr. After cooling, the mixture was filtered and the solvent was evaporated. Preparative TLC of the residue resulted in the isolation of 2-phenylisophosphindole 2-oxide dimer (0·12 g; 50%), m.p. 216–220° (dec) (chloroform/hexane).

Trapping of 2-phenylisophosphindole 2-oxide with dimethyl acetylenedicarboxylate. To a mixture of Et_3N (0·30 g; 3 mmole) and of dimethyl acetylenedicarboxylate (0·28 g; 2 mmole) in 20 ml dry benzene was added dropwise a soln of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (0·31 g; 1 mmole) in 20 ml dry benzene at room temp. After the addition, the mixture was refluxed for 48 hr and then cooled. It was then filtered to remove the $Et_3N \cdot HBr$. The filtrate was evaporated and the residue was separated by preparative TLC (solvent-chloroform) to give 0·07 g (28%) of dimethyl-2,3-naphthalene dicarboxylate m.p. 45–46° (ether/petroleum ether), (lit.[35] m.p. 47°), identical in all respects with an authentic sample.

Dehydrobromination of r-1-bromo-t-2-phenylisophosphindoline 2-oxide in the presence of phenylacetylene. To a mixture of Et_3N (0·3 g; 3 mmole) and phenylacetylene (0·2 g; 2 mmole) in 20 ml dry benzene was added dropwise a soln of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (0·3 g; 1 mmole) in 20 ml dry benzene, under N_2, at room temp. The mixture was refluxed for 48 hr, after the addition. It was cooled and the solvent was evaporated. The crude residue was separated by preparative TLC to give 0·03 g (15%) of 2-phenylnaphthalene m.p. 101–102° (EtOH). (Lit.[35] m.p. 103–104°). Also isolated was 0·06 g (25%) of 2-phenylisophosphindole 2-oxide dimer.

Dehydrobromination of r-1-bromo-t-2-phenylisophosphindoline 2-oxide in the presence of 1,4-cyclohexadiene. To a mixture of Et_3N (0·3 g; 3 mmole) and 3 ml 1,4-cyclohexadiene in 25 ml dry benzene was added dropwise a soln of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (0·3 g; 1 mmole) in 15 ml dry benzene under N_2, and the mixture was refluxed for 48 hr. After removal of the solvent, the crude mixture was separated by preparative TLC to give 0·11 g (34%) of 2-phenylisophosphindole 2-oxide-1,4-cyclohexadiene adduct as white crystals, m.p. 185–187° (chloroform/hexane). NMR: 7·2 (m, 9-H, Ar-H); 5·7 (m, 2-H, CH=CH); 3·5 (d, 2-H, –CHP=O); 3·2 (m, 2-H, C–H); 2·2 (m, 2-H, equatorial allylic); 1·3 (d of d, 2-H, axial allylic). IR: 1210 cm^{-1} (P=O); mass spectrum: *m/e* 306 (9·4%); 228 (27·2%); 182 (22·8%); 180 (100%); 150 (9·4%); 128 (74%); 104 (22·8%); 91 (13·6%); 77 (27·2%). (Found: C, 77·72; H, 6·39. Calcd. for $C_{20}H_{19}PO$: C, 78·42; H, 6·25%).

Also isolated as minor product was *r*-1-bromo-*c*-2-phenylisophosphindoline 2-oxide (0·03 g; 10%) as white crystals, m.p. 140–142° (ether). NMR: 7·5 (m, 4-H, Ar-H); 5·6 (d, 1-H, –C–H, J_{P-CH} = 10 Hz); 3·3–3·9 (part of ABX, 2-H, $-CH_2$, J_{P-CH_a} = 17; J_{P-CH_b} = 9 Hz); IR: 1240 cm^{-1} (P=O); mass spectrum: *m/e* 308 (6·6%); 306 (6·6%); 227 (100%); 179 (26·6%); 149 (26·6%). (Found: C, 55·35; H, 4·14; Br, 26·09. Calcd. for $C_{14}H_{12}POBr$: C, 54·75; H, 3·94; Br, 26·02%).

Dehydrobromination of r-1-bromo-t-2-phenylisophosphindoline 2-oxide in the presence of 2,5-norbornadiene. To Et_3N (0·1 g; 1 mmole) and 2 ml norbornadiene in 15 ml dry benzene was added a soln of *r*-1-bromo-t-2-phenylisophosphindoline 2-oxide (0·1 g; 0·03 mmole) in 15 ml dry benzene, under N_2. After the addition, the mixture was refluxed for 48 hr and cooled. It was then filtered to remove the $Et_3N \cdot HBr$. The filtrate was evaporated and preparative TLC of the crude residue afforded 0·03 g (25%) of 2-phenylisophosphindole 2-oxide-norbornadiene adduct as white crystals, m.p. 156–158° (chloroform/hexane). NMR: (220 MHz): 7·2 (m, 9-H, Ar-H); 6·2 (m, 2-H, –CH=CH); 3·7–3·6 (m, 2-H, –CHP=O); 3·1 (m, 2-H, –CH); 2·6 (m, 2-H, –CH); 0·8 (d, 1-H, –CH); 0·3 (d, 1-H, –CH). IR: 1200 cm^{-1} (P=O); 1450 cm^{-1}, 1100 cm^{-1} and 700–800 cm^{-1} (Ph); mass spectrum: *m/e* 318 (6%); 252 (5%); 228 (5%); 227 (5%); 179 (5%); 178 (8%); 128 (100%). (Found: C, 76·24; H, 6·04. Calcd. for $C_{21}H_{19}PO \cdot 3/4H_2O$: C, 76·07; H, 6·22%).

r-1-Bromo-*c*-2-phenylisophosphindoline 2-oxide (0·01 g; 10%) was also isolated.

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