

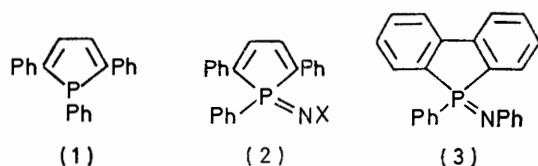
The Reactivity of Organophosphorus Compounds. Part XXX.¹ Imino-phospholes and a New Synthesis of Benzofurazans *via* Intramolecular Rearrangement of 1-*o*-Nitroarylimino-1,2,5-triphenylphospholes

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A series of *N*-substituted 1-imino-1,2,5-triphenylphospholes (2) have been synthesised. Reactions of aryl, methanesulphonyl, arylsulphonyl, ethoxycarbonyl, phenoxycarbonyl, and diphenylphosphinyl azides with 1,2,5-triphenylphosphole gave the corresponding *N*-substituted 1-imino-phospholes [2; X = Ar, MeSO₂, ArSO₂, EtO₂C, PhO₂C, and Ph₂P(O)] in good yields by non-nitrene routes. The tosylimino-phosphole (2; X = Tosyl) was also produced by reaction of anhydrous chloramine-T with the phosphole. Benzoyl azide reacted by decomposition followed by Curtius rearrangement rather than by reaction with the relatively weakly nucleophilic 1,2,5-triphenylphosphole (*cf.* Ph₃P). The electron deficient 4-nitrobenzoyl and 2,4-dinitrobenzoyl azides gave the corresponding 1-*o*-arylimino-1,2,5-triphenylphospholes [2; X = C₆H₄NO₂-*p* and 2,4-(NO₂)₂C₆H₃] in 6 and 55% yields respectively. 5,7-Dimethyltetrazolo[1,5-*a*]pyrimidine (13) in the presence of copper gave the 1-[(4,6-dimethylpyrimidin-2-yl)imino]phosphole (14). Thermolysis of 5-phenyl- and 5-*p*-nitrophenyl-1,3,4-dioxazol-2-ones (7) with 1,2,5-triphenylphosphole at 150° gave the corresponding 1-*o*-arylimino-1,2,5-triphenylphospholes (2; X = PhCO and *p*-NO₂-C₆H₄CO), but these decomposed at this temperature to give the corresponding aryl cyanides and the phosphole oxide. The use of copper-bronze reduced the decomposition point of the dioxazolidin-2-ones sufficiently for the imino-phospholes to be isolated. Base catalysed decomposition of ethyl *N*-(*p*-nitrophenylsulphonyloxy)carbamate (4) in the presence of the phosphole gave 1-ethoxycarbonylimino-1,2,5-triphenylphosphole (2; X = CO₂Et). In the last two reactions the phosphole is probably acting as a nitrene trap as it is in the thermolysis of the 1-phthalimidobenzofuro[2,3-*b*]azirine (9) to give the 1-phthalimidoiminophosphole.

Thermolysis of 1-*o*-nitroarylimino-1,2,5-triphenylphospholes at 150° gives 1,2,5-triphenylphosphole oxide and the corresponding substituted benzofurazans; this reaction is shown to proceed *via* intramolecular attack by an oxygen atom of the neighbouring nitro-group on the phosphorus atom. The corresponding *N*-*o*-nitrophenyliminotriphenylphosphorane and triethyl phosphorimidate [Ph₃P=NAr and (EtO)₃P=NAr] are stable, pointing to a special effect of the phosphole ring, believed to involve ring strain, at least in part.

WHILE ylides based on triphenylphosphine are among the best known organophosphorus reagents in general organic synthesis, little is known of the corresponding ylides of the readily accessible 1,2,5-triphenylphosphole (1). We expected that a combination of polar, resonance,

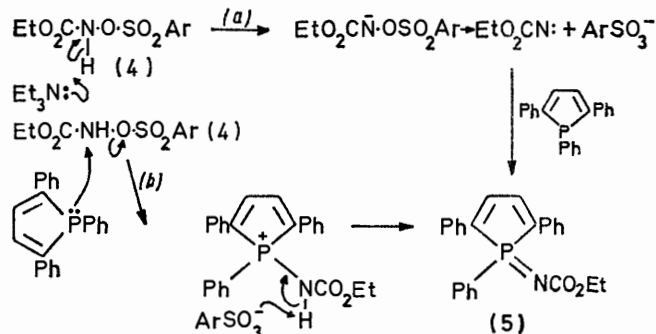


and ring strain effects would lead to a marked difference in reactivity of the latter compound, compared with that of triphenylphosphine.

We now describe the synthesis and reactions of a variety of *N*-substituted 1-imino-1,2,5-triphenylphospholes (2), which are *N*-analogues of ylides. This highly crystalline and highly coloured class of organophosphorus compounds has not been described previously, although the preparation of the related 5-phenyl-5-phenyliminodibenzophosphole (3) has been reported.²

Preparation of *N*-Substituted 1-Imino-1,2,5-triphenylphospholes.—(i) *By reaction of 1,2,5-triphenylphosphole with nitrene- or nitrenoid-sources.* Lwowski and Maricich³ have described the formation of ethoxycarbonylnitrene by triethylamine-induced α -elimination from ethyl *N*-(*p*-nitrophenylsulphonyloxy)carbamate (4). We found that the same reaction in the presence of 1,2,5-

triphenylphosphole gave 1-ethoxycarbonylimino-1,2,5-triphenylphosphole (5) (36%). No detectable reaction occurred in the absence of base, indicating that reaction had indeed occurred *via* α -elimination of the nitrene (Scheme 1, route *a*) rather than by nucleophilic attack by trivalent phosphorus (Scheme 1, route *b*). This is the converse of the corresponding reaction using triphenylphosphine,⁴ indicating the much reduced *P*-nucleophilicity of 1,2,5-triphenylphosphole compared with triphenylphosphine.



SCHEME 1 (Ar = *p*-NO₂-C₆H₄)

We attempted to prepare 1-benzoylimino-1,2,5-triphenylphosphole (6; Ar = Ph) and the *p*-nitrobenzoyl analogue (6; Ar = *p*-NO₂-C₆H₄) by reaction of 1,2,5-triphenylphosphole with the 5-aryl-1,3,4-dioxazol-2-ones (7; Ar = Ph or *p*-NO₂-C₆H₄), which have been shown

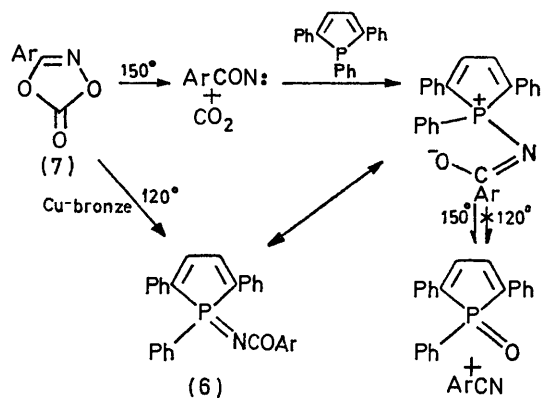
¹ Part XXIX, J. I. G. Cadogan and A. G. Rowley, *J.C.S. Perkin II*, 1974, 1030.

² G. Wittig and E. Kochendoerfer, *Chem. Ber.*, 1964, **97**, 741.

³ W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, 1964, **86**, 3164.

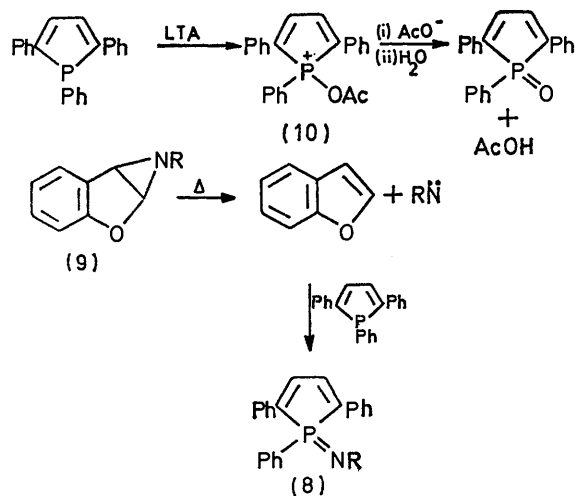
⁴ J. I. G. Cadogan and I. Gosney, unpublished results.

to give the corresponding benzoylnitrenes on thermolysis at 150°. At this temperature, however, the products were the corresponding benzonitrile and 1,2,5-triphenylphosphole oxide, thus suggesting that the iminophosphole (6) had indeed been formed *via* reaction of the aroylnitrene with 1,2,5-triphenylphosphole, but that the product had decomposed intramolecularly (Scheme 2)



SCHEME 2

in the manner previously established for benzoylimino-triphenylphosphorane ($\text{Ph}_3\text{P}=\text{NCOPh}$).⁶ The use of copper-bronze, however, lowered the decomposition point of the parent dioxazolone (7) to 120°, at which temperature the desired 1-aryylimino-1,2,5-triphenylphospholes (6) were stable, and hence ultimately isolable in 36–55% yields. It is likely that this reaction involves the intermediacy of a copper-nitrene complex



SCHEME 3

($\text{ArCO}\cdot\text{N}\rightarrow\text{Cu}$) similar to that proposed by Kwart and Khan⁷ to explain the acceleration of decomposition of arenesulphonyl azides by copper.

* The question of nitrene participation in LTA oxidations of amino- and amido-compounds is discussed elsewhere.¹⁰

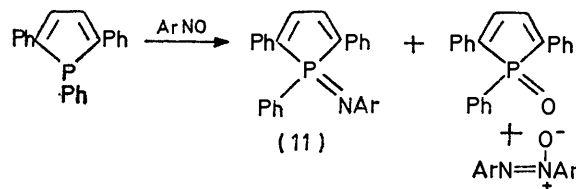
⁵ J. Sauer and K. K. Mayer, *Tetrahedron Letters*, 1968, 319.

⁶ L. Horner and A. Gross, *Annalen*, 1955, **591**, 117.

⁷ H. Kwart and A. A. Khan, *J. Amer. Chem. Soc.*, 1967, **89**, 1950.

Two routes to 1-phthalimidoimino-1,2,5-triphenylphosphole (8) were investigated involving (a) oxidation of *N*-aminophthalimide by lead tetra-acetate (LTA)⁸ and (b) thermolysis of the *N*-phthalimidonitrene* or a precursor that phthalimidonitrene* or a precursor would react suitably with 1,2,5-triphenylphosphole. In the former case, direct oxidation of the phosphole to 1,2,5-triphenylphosphole oxide (87%) took place at the expense of reaction with *N*-aminophthalimide (Scheme 3), possibly *via* the intermediacy of a phospholium acetate (10), by analogy with the corresponding reaction of LTA with triphenylarsine.¹⁰ Thermolysis of the 1-phthalimidobenzofuro[2,3-*b*]azirine (9), with 1,2,5-triphenylphosphole in boiling benzene, however, gave the required 1-phthalimidoimino-1,2,5-triphenylphosphole (8) in 22% yield.

The remaining nitrogenic route to iminophospholes investigated was the deoxygenation¹¹ of *p*-nitronitrosobenzene by the phosphole which gave 1-*p*-nitrophenylimino-1,2,5-triphenylphosphole (11) in only 8% yield, the major product being the corresponding azoxyarene¹¹ (Scheme 4).

SCHEME 4 (Ar = *p*-NO₂·C₆H₄)

(ii) *By reaction of 1,2,5-triphenylphosphole with azides.* Most reactions of triphenylphosphine with azides occur rapidly¹² *via* a non-nitrene route¹³ involving an unstable phosphorane diyltriazene to give iminotriphenylphosphoranes. We have now shown that 1,2,5-triphenylphosphole similarly reacts with aryl, arylsulphonyl, diphenylphosphinyl, aroyl, and ethoxycarbonyl azides to give the corresponding *N*-aryl- (2; X = Ar), *N*-arylsulphonyl- (2; X = ArSO₂), *N*-diphenylphosphinyl- [2; X = Ph₂P(O)], *N*-aroyl- (2; X = ArCO), and *N*-ethoxycarbonyl-1-imino-1,2,5-triphenylphospholes (2; X = EtO₂C) (Table 1). In general, 1,2,5-triphenylphosphole was very much less nucleophilic (reaction temperature *ca.* 100°) than triphenylphosphine in its reactions with azides. This reduced the scope of the reaction in cases where alternative thermally induced intramolecular reactions were possible. Thus 2-azidoacetophenone gave

$$\text{XN}_3 + \text{Ph}_3\text{P} \longrightarrow [\text{Ph}_3\text{P}=\text{N}=\text{N}=\text{NX}] \longrightarrow \text{Ph}_3\text{P}=\text{NX} + \text{N}_2$$

⁸ D. J. Anderson, D. C. Horwell, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc. (C)*, 1970, 576.

⁹ D. W. Jones, *J.C.S. Chem. Comm.*, 1972, 884; *J.C.S. Perkin I*, 1972, 225.

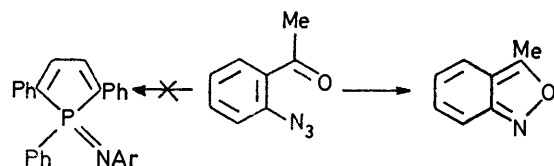
¹⁰ J. I. G. Cadogan and I. Gosney, *J.C.S. Perkin I*, 1974, 466.

¹¹ P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 1963, 42.

¹² H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

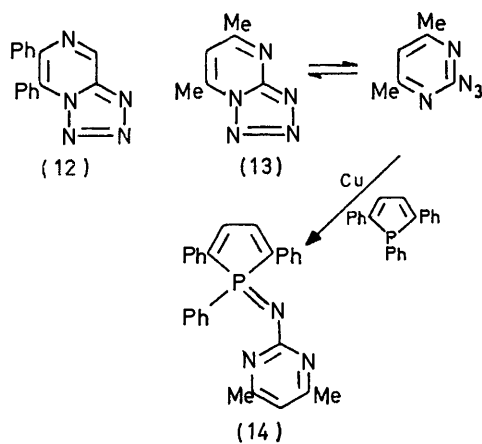
¹³ J. E. Leffler and R. D. Temple, *J. Amer. Chem. Soc.*, 1967, **89**, 5235.

anthranil rather than 1-(2-acetylphenyl)imino-1,2,5-triphenylphosphole (Scheme 5), while benzoyl azide pre-



ferred to undergo a Curtius rearrangement to phenyl isocyanate. In the latter case reduction of the electron density on the azide group by the use of *p*-nitro- and 2,4-dinitro-benzoyl azides led to increasing yields of the corresponding 1-aryliminophospholes (3 and 55%) formed at lower reaction temperatures.

It has been shown¹⁴ that reactions between triphenylphosphine and tetrazolopolyazines, such as (12) give



iminophosphoranes *via* transition states identical with those involved in the corresponding reaction involving azides (Scheme 6). 1,2,5-Triphenylphosphole did not react at 130°, however, with the tetrazolopyrimidine (13),¹⁵ known to be in equilibrium with 2-azido-4,6-dimethylpyrimidine, until copper was added to the reaction. The resulting 1-[(4,6-dimethylpyrimidin-2-yl)imino]-1,2,5-triphenylphosphole (14) probably arose, therefore, *via* a copper-nitrenoid route in this case (Scheme 6).

The reduced nucleophilicity in the foregoing reactions, of 1,2,5-triphenylphosphole, compared with triphenylphosphine, is noteworthy. There are three possible contributing causes. First, there is the possibility that the reduction of lone pair availability on phosphorus is a result of aromaticity of the phosphole ring. Photoelectron spectroscopic evidence suggests¹⁶ that this is minimal, but other experimental evidence, mainly from Quin's school,¹⁷ points to some aromatic character.

¹⁴ T. Sasaki, K. Kanematsu, and M. Murata, *Tetrahedron*, 1972, **28**, 2383.

¹⁵ K. von Fraunberg and R. Huisgen, *Tetrahedron Letters*, 1969, 2599.

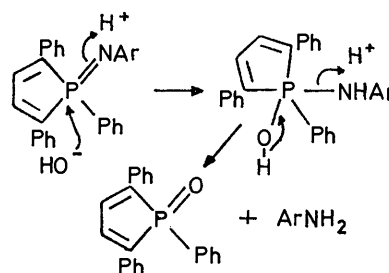
¹⁶ W. Schäfer, A. Schweig, G. Märkl, M. Hauptmann, and F. Mathey, *Angew. Chem. Internat. Edn.*, 1973, **12**, 145.

Secondly, steric effects of the three phenyl rings are bound to contribute to the reduced nucleophilicity, while thirdly, the increase in strain in the five membered phosphole ring on conversion from the trivalent state into the intermediate quaternary form would be expected to inhibit nucleophilic reactions of the phosphorus atom. The angle C(2)-P̂-C(5) in 1,2,5-triphenylphosphole has not been measured, but in 1-benzylphosphole it is 90.7°.¹⁸ On reaction with azide the phosphorus atom will assume a tetrahedral configuration thus unfavourably enlarging the C(2)-P̂-C(5) angle towards 109°.

Properties of Iminophospholes and Synthesis of Benzofurazans by Thermolysis of 1-o-Nitroarylimino-1,2,5-triphenylphospholes.—Most of the iminotriphenylphospholes described above are highly coloured, crystalline compounds, stable in the absence of water, and thus phospholes are possibly of some diagnostic value as nitrene traps or as stable derivatives of azides.

Although the colour of the crystalline iminophospholes varies widely according to the substituent these differences largely disappear in solution, the u.v. spectra showing very similar envelopes with transitions occurring at 210 (ϵ_{max} 30,000–45,000) and 380–405 nm (9000–34,000), with no significant shifts on substitution (Table 1). This suggests that the colour differences are a phenomenon of the crystalline state. The visible absorptions of the iminophospholes which are at longer wavelength than the P=N absorption generally found in aryliminotriphenylphosphoranes, may be due to spiro-conjugation, of the type invoked to explain the colour of phosphole oxides,¹⁹ involving through-space interaction between the π -system of the phosphole and the imino lone pair of electrons.

The relative ease with which hydrolysis to the corresponding amines and 1,2,5-triphenylphosphole oxide occurred, compared with the corresponding hydrolysis



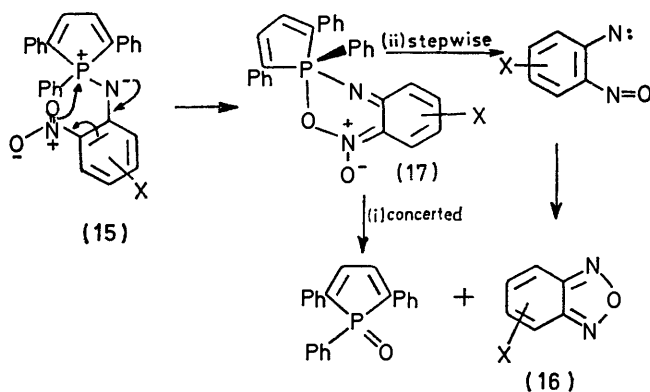
of phenyliminotriphenylphosphorane (Ph₃P=NPh), indicated a high electrophilicity of the phosphorus centre in the former (Scheme 7). This effect was particularly marked in 1-*o*-nitroarylimino-1,2,5-triphenylphospholes

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

¹⁸ P. Coggan, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, 1970, **92**, 5779.

¹⁹ J. M. Holland and D. W. Jones, *J.C.S. Perkin I*, 1973, 927.

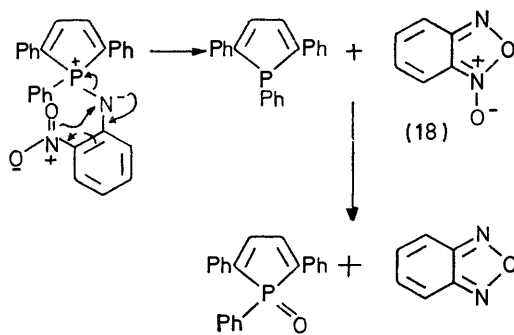
(15) which, on thermolysis, in mesitylene at 150°, underwent decomposition involving nucleophilic attack by the oxygen atom of the *o*-nitro-group on the phosphorus atom of the iminophosphole to give the corresponding benzofurazan (16) in 32–60% yields, together with the phosphole oxide. In accord with this, the reaction proceeded most readily with electron releasing substituents. In contrast, the corresponding acyclic *o*-nitrophenylimino-triphenylphosphoranes $\text{Ph}_3\text{P}=\text{NAr}$ and $(\text{EtO})_3\text{P}=\text{NAr}$ ($\text{Ar} = o\text{-NO}_2\cdot\text{C}_6\text{H}_4$), were stable under these conditions. This suggests reaction, as in Scheme 8, *via* intramolecular



SCHEME 8

attack of the nitro-group on the electrophilic phosphole phosphorus atom to give a bicyclic species (17) in which the phosphorus atom is now pentaco-ordinate, with trigonal bipyramidal configuration, and in which the phosphole ring is able to take up an apical-equatorial position which is strain free (*ca.* 90°). This is in contrast to the considerable strain present in the starting iminophosphole, in which the phosphorus atom has tetrahedral configuration. This is then followed by decomposition to give the phosphole oxide and the benzofurazan, either in a concerted step or stepwise *via* *o*-nitronitrosobenzene.

An alternative mechanism which we have considered and discount (when $\text{X} = \text{H}$) as a result of our experiments is outlined in Scheme 9. This calls for a prior de-



SCHEME 9

composition into 1,2,5-triphenylphosphole and benzofurazan (18) which then react together to give the ob-

served phosphole oxide and benzofurazan, a deoxygenation which has precedent.²⁰ That this does not occur, and that reaction takes place as in Scheme 8, was shown as follows: (i) kinetic studies at 149° in bromobenzene as solvent at two concentrations, one half the other, of 1-*o*-nitrophenylimino-1,2,5-triphenylphosphole (15; $\text{X} = \text{H}$), showed the reactions to be first order in the iminophosphole ($t_{1/2} \sim 4$ h) and with rates independent of concentration ($k_1 = 3 \times 10^{-3} \text{ min}^{-1}$). Further, the rate constant was unchanged in the presence of added 1,2,5-triphenylphosphole. This established the unimolecular nature of the decomposition but did not differentiate between Schemes 8 and 9 because a control experiment established that deoxygenation of benzofuroxan by 1,2,5-triphenylphosphole was *faster* ($t_{1/2} \sim 2$ h) than the decomposition of the starting 1-*o*-nitrophenyliminophosphole. (ii) If Scheme 9 were operating, it would be expected that the presence of a 'foreign' phosphole of equal or nearly equal reactivity to that of 1,2,5-triphenylphosphole in the deoxygenation of benzofuroxan (18), would lead to the appearance of the 'foreign' phosphole oxide as well as 1,2,5-triphenylphosphole oxide among the products of thermolysis of the iminophosphole (15; $\text{X} = \text{H}$). If Scheme 8 were operative, the foreign phosphole would be expected to be unchanged. A competition experiment having established that 1,2,5-triphenylphosphole and 1,2-diphenyl-5-*p*-tolylphosphole deoxygenated benzofuroxan at identical rates, the thermolysis of the iminophosphole (15; $\text{X} = \text{H}$) in the presence of a mixture (*ca.* 2:1) of the diphenyl-*p*-tolyl- and triphenyl-phospholes gave an almost quantitative conversion into a fraction consisting of 1,2,5-triphenylphosphole and 1,2-diphenyl-5-*p*-tolylphosphole oxides in the ratio 7.5:1, corrected to 7:1 after allowing for 1,2,5-triphenylphosphole added to the reaction. At first sight this suggests that only 87.5% of the reaction is proceeding as in Scheme 8. The remaining 12.5% reaction is readily accounted for, however, by a competitive, direct, bimolecular deoxygenation of the starting *o*-nitrophenyliminophosphole by the added tervalent phospholes to give unidentified products. In support of this explanation is the observation that *o*-nitrophenyliminotriphenylphosphorane ($\text{Ph}_3\text{P}=\text{N}\cdot\text{C}_6\text{H}_4\text{-NO}_2\text{-}o$), is stable at 160° but reacts with added 1,2,5-triphenylphosphole to give the corresponding phosphole oxide. It should be noted, however, that Scheme 9 could become important in cases of strong electron-releasing groups in the *N*-aryl group of (15).

There remains to be considered only the reason for the high electrophilicity of the phosphorus atom in iminophospholes. This could be due to a combination of ring strain effects, discussed above, and the effect on the phosphorus atom resulting from aromaticity of the parent phosphole. This argument relies on the non-availability of the phosphorus lone pair electrons resulting from conjugation within the ring. When these electrons are utilised in bonding in the $\text{P}=\text{N}$ bond in the iminophosphole, destabilisation of the aromatic system

²⁰ A. Cameron-Wood, J. I. G. Cadogan, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.

would cause a large formal charge to reside on phosphorus. Against this, however, is the strong argument based on photoelectron spectroscopy.¹⁶ It should be noted that in the case of *o*-nitrophenyliminotrichlorophosphorane ($\text{Cl}_3\text{P}=\text{N}\cdot\text{C}_6\text{H}_4\text{NO}_2\text{-}o$), which does not contain a ring but which has a highly electrophilic phosphorus, we observed rearrangement to benzofurazan, although extrapolated arguments from this extreme case to those discussed above would be of little value.

Finally we draw attention to an unexpected experimental observation: we synthesised 1,2,5-triphenylphosphole by reaction of 1,4-diphenylbuta-1,3-diene with dichloro(phenyl)phosphine.²¹ Using 1-phenyl-4-*p*-tolylbuta-1,3-diene as the diene we expected to produce 1,2-diphenyl-5-*p*-tolylphosphole, but instead scrambling occurred to give 1,2,5-triphenylphosphole as an additional product. 1,4-Di-*p*-tolylbuta-1,3-diene and phenyl phosphonous dichloride gave at least three different phospholes. This scrambling effect, now being investigated, led to the use of mixtures of phospholes in some of our experiments described above. It is conceivable that this effect is a Lewis acid induced demethylation, of the type common in Friedel-Crafts reactions.

EXPERIMENTAL

Preparation of Materials.—Aryl azides were prepared from the corresponding anilines by diazotisation in 5*N*-HCl followed by reaction with sodium azide solution. The product was extracted into ether and purified by chromatography on alumina with ether as eluant. The azides (65–95%) so produced had the characteristic i.r. band at 2100 cm^{-1} and had m.p.s corresponding to those in the literature. New azides produced were 4-azidobenzene-sulphonamide, m.p. 105–106° (Found: *m/e*, 198. $\text{C}_6\text{H}_6\text{N}_4\text{O}_2\text{S}$ requires *m/e*, 198), and (2-azidophenyl)diphenylphosphine oxide, m.p. 140–142° (Found: *m/e*, 319. $\text{C}_{18}\text{H}_{14}\text{N}_3\text{OP}$ requires *m/e*, 319). 3-Azidophthalic anhydride and 2-azidobenzimidazole were kindly provided by Kodak Ltd.

Other known azides used in this investigation were prepared by standard methods and had the correct characteristics. 5-Phenyl- and 5-(*p*-nitrophenyl)-1,2,5-dioxazol-2-ones prepared by the method of Sauer and Mayer,⁵ had the correct m.p.s, as did *N*-aminophthalimide, prepared by Drew and Hatt's method.²² 1a,6b-Dihydro-1-phthalimidobenzofuro[2,3-*b*]azirine⁹ was kindly provided by Dr. I. Gosney.

1,2,5-Triphenylphosphole, m.p. 187–189° (lit.,²¹ 187–189°), was prepared by a modification of the literature method:²¹ a mixture of 1,4-diphenylbuta-1,3-diene (26.5 g, 0.13 mol) and dichloro(phenyl)phosphine (35 g, 0.2 mol) were heated at 215° for 6 h under nitrogen. The cooled mixture was triturated under ether. The solid was filtered off, washed with ether, dissolved in a minimum of hot chloroform, and filtered while still hot. Long yellow fluorescent needles of 1,2,5-triphenylphosphole formed on cooling (8–12 g, 25–35%). 1,2,5-Triphenylphosphole oxide, m.p. 236–238° (lit.,²¹ 237–239°), was best obtained (100%) by oxidation (almost instantaneous) of the phosphole with lead tetra-acetate (LTA) in methylene chloride, fol-

lowed by elution of the reaction mixture through a short alumina column.

*Reaction of Dichloro(phenyl)phosphine with 1-Phenyl-4-*p*-tolylbuta-1,3-diene.*—The butadiene (21 g, 0.1 mol) was heated at 215° with the phosphine as described above. The yellow solid which formed on cooling was purified as above to give a fluorescent crystalline solid (7.00 g), m.p. 162–163°, τ (CDCl_3) 2.3–3.1 (aromatic) and 7.76 (methyl). The integration showed a ratio of aromatic : methyl protons of 31 : 3 while the required ratio is 21 : 3. Low eV mass spectrometry showed two peaks *m/e* 326 and 312 in the ratio 1.8 : 1. High speed liquid chromatography (h.s.l.c.) (DuPont 820) of the oxidised (LTA) product on alumina (Spherisorb A 20Y) with 30% dioxan in *n*-hexane showed two peaks, one of which had the same retention time as 1,2,5-triphenylphosphole 1-oxide, in an approximate ratio of 1.8 : 1.

Thus the product of the reaction appears to be a 1.8 : 1 mixture of 1,2-diphenyl-5-*p*-tolylphosphole and 1,2,5-triphenylphosphole. Analysis on both the initial and oxidised products corresponded to a 1.8 : 1 mixture: initial product (Found: C, 85.1; H, 6.0. $\text{C}_{22}\text{H}_{17}\text{P}$ requires C, 84.6; H, 5.5%). $\text{C}_{23}\text{H}_{19}\text{P}$ requires C, 84.7; H, 5.8%); oxidised product (Found: C, 80.4; H, 5.5. $\text{C}_{22}\text{H}_{17}\text{OP}$ requires C, 80.4; H, 5.2%. $\text{C}_{23}\text{H}_{19}\text{OP}$ requires C, 80.7; H, 5.6%).

*Reaction of Dichloro(phenyl)phosphine with 1,4-Di-*p*-tolylbuta-1,3-diene.*—The diene (4.02 g, 0.002 mol) and dichloro(phenyl)phosphine (7.00 g, 0.004 mol) were allowed to react as above to yield a yellow fluorescent product (0.98 g) after recrystallisation from chloroform-ether. The mother liquor was evaporated and the remaining solid dissolved in methylene chloride and oxidised with lead tetraacetate as described above. Chromatography on alumina with chloroform gave the mixed oxide (0.41 g). The low eV mass spectrum of the phosphole showed peaks at *m/e* 354, 340, 326, and 312 in the ratio 1 : 17 : 25 : 6, τ (CDCl_3) 2.2–3.2 (aromatic) and 7.73 (methyl). The ratio of aromatic : methyl protons of 30 : 7 corresponds well with mixture composition estimated by mass spectrometry (30 : 7). The low eV mass spectrum of the phosphole oxides showed the peaks *m/e* 360, 356, 342, and 328 in the ratio 1 : 29 : 35 : 7.

Analysis of the oxide mixture by h.s.l.c. showed three major components, two of which corresponded to 1,2,5-triphenylphosphole oxide and 1,2-diphenyl-5-*p*-tolylphosphole, the latter being the major component. Thus the product of the reaction is believed to be a mixture of 1,2,5-tri-*p*-tolyl-, 1-phenyl-2,5-di-*p*-tolyl-, 1,2-diphenyl-5-*p*-tolyl-, and 1,2,5-triphenylphosphole.

*Reaction of 1,4-Di-*p*-tolylbuta-1,3-diene with Dichloro(*p*-tolyl)phosphine.*—Dichloro(*p*-tolyl)phosphine was prepared by the method of Buchner and Lockhardt²³ by a Friedel-Crafts reaction between toluene and phosphorus trichloride in the presence of aluminium chloride. The product had b.p. 120° at 14 mmHg (lit.,²³ 120° at 13 mmHg), τ (CDCl_3) 2.1–2.9 (4H, m, aromatic) and 7.63 (3H, s, methyl protons).

The dichloro(tolyl)phosphine (4.00 g, 0.002 mol) was allowed to react with 1,4-di-*p*-tolylbuta-1,3-diene (3.00 g, 0.001 mol) under the conditions described for the preparation of 1,2,5-triphenylphosphole to yield a pale yellow, fluorescent, crystalline solid, m.p. 182–183° (0.58 g, 13%). Mass spectral and analytical data were consistent with the structure for 1,2,5-tri-*p*-tolylphosphole (Found: C, 85.1; H, 6.7%; *m/e*, 354. $\text{C}_{25}\text{H}_{23}\text{P}$ requires C, 84.4; H, 6.5%;

²¹ I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J. Chem. Soc. (C)*, 1965, 2184.

²² H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 1937, 16.

²³ B. Buchner and L. B. Lockhardt, *J. Amer. Chem. Soc.*, 1951, **73**, 755.

m/e, 354). The n.m.r. spectrum however, contained a complex absorption (3 lines) in the methyl region indicating a mixture of isomers; τ (CDCl₃) 2.5—3.1 (12H, m, aromatic), 7.6—7.8 (m, methyl protons) (total integration 9H).

A small quantity of product was oxidised to the phosphole oxide. H.s.l.c. analysis and low eV mass spectrometry indicated the presence of only one compound although the n.m.r. spectrum again showed a complex pattern for the methyl shifts.

Preparation of 1-Imino-1,2,5-triphenylphospholes.—1-Arylimino-1,2,5-triphenylphospholes. These were prepared by reaction of the phosphole (1 mol) with the azide (1 mol) in toluene (30 ml per g) at 100° under nitrogen until evolution of nitrogen had ceased (*ca.* 2 h). In some cases additional azide was used to ensure complete removal of phosphole, which was otherwise difficult to separate from the reaction mixture. Removal of the excess of solvent followed by crystallisation, usually from chloroform–ether, gave the 1-arylimino-1,2,5-triphenylphosphole (Table 1). These all had the expected n.m.r. spectra, and a P=N i.r. absorption at *ca.* 1300 cm⁻¹.

Preparations and Attempted Preparations of Iminophospholes from Nitrene and Nitrenoid Sources.—(a) Reaction of 1,2,5-triphenylphosphole with ethyl N-(p-nitrophenylsulphonyloxy)carbamate. The phosphole (2.02 g, 0.007 mol) was stirred vigorously with the carbamate (1.85 g, 0.007 mol) in methylene chloride (150 ml). Triethylamine (1.0 ml) was added dropwise over 0.5 h and the stirring continued for a further hour. The solvent was removed and the residue recrystallised from ethanol. The product was washed with a little ethylene dichloride to remove the last traces of unchanged phosphole. A further recrystallisation from chloroform–ether gave 1-ethoxycarbonylimino-1,2,5-triphenylphosphole (5) (0.91 g, 36%), m.p. and mixed m.p. with a sample obtained by reaction of ethyl azidoformate with 1,2,5-triphenylphosphole (Table 1) 219—221°. No reaction occurred in the absence of 10% triethylamine.

(b) **Oxidation of N-aminophthalimide with lead tetra-acetate in the presence of 1,2,5-triphenylphosphole.** N-Aminophthalimide (0.65 g, 0.004 mol) and 1,2,5-triphenylphosphole (1.04 g, 0.003 mol) were stirred in dry methylene chloride at room temperature. Solid, dry lead tetra-acetate (1.24 g, 0.004 mol) was added and the solution turned deep red. Gradually (over 15—30 min) the solution turned fluorescent yellow-green. The mixture was filtered through Celite and the solvent evaporated off. The residue was chromatographed on dry column alumina with ether to give the phosphole oxide (1.18 g, 87%), m.p. 228—230° (lit.,²¹ 237—239°), i.r. identical with an authentic sample. The other component of the mixture, N-aminophthalimide, was identified by t.l.c. only.

(c) **Reaction of 1,2,5-triphenylphosphole with 1a,6b-dihydro-1-phthalimidobenzofuro[2,3-b]azirine (9).** The aziridine (1.00 g, 0.003 mol) was boiled under reflux in ethylene dichloride with the phosphole (0.90 g, 0.003 mol) for 4 h. The resultant red solution was evaporated to dryness and the residue, a red gum, triturated under ether. 1-Phthalimidoimino-1,2,5-triphenylphosphole (8) was thus obtained as an orange solid and recrystallised from chloroform–ether to yield deep red cubes (0.29 g), m.p. 231—235°. Two parent peaks were found in the mass spectrum: *m/e* 472 (Found: 472.133391. C₃₀H₂₁N₂O₂P requires 472.134058) and *m/e* 488 (Found: 488.127884; C₃₀H₂₁N₂O₃P requires 488.128972), ν_{\max} . 1760, 1740, 1720, 1690 (C=O), and 1365 (P=N) cm⁻¹, λ_{\max} . (ethanol) 212 (ϵ 24,000) and 392 nm

(8000). The mother liquor was concentrated to yield 1,2,5-triphenylphosphole oxide (0.41 g, 24%), m.p. 232—233°, identical with an authentic sample. The remaining mother liquor contained a mixture of products including unchanged phosphole, phosphole oxide, and N-amino-phthalimide (t.l.c.).

(d) **Reaction of 1,2,5-triphenylphosphole with 5,7-dimethyl-tetrazolo[1,5-a]pyrimidine.** The phosphole (1.04 g, 0.003 mol) and the tetrazole (0.45 g, 0.003 mol) were boiled under reflux in toluene (50 ml) for 2 h. No reaction occurred (t.l.c.). A catalytic quantity of copper-bronze was added and the solution maintained at 80°. Nitrogen was evolved and the reaction was complete in 30 min. The solvent was removed and the residue chromatographed on dry column alumina with ether to give yellow crystals of 1-[(4,6-dimethylpyrimidin-2-yl)imino]-1,2,5-triphenylphosphole (14) (0.51 g, 35%). The mass spectrum showed the correct parent ion, *m/e* 433 (Found: 433.170992. C₂₈H₂₄N₃P requires 433.170777), τ 1.68—2.10 (2H, m, *ortho*-protons PhP), 2.20—2.92 (15H, m, aromatic), 3.73 (1H, s, pyrimidyl ring proton), and 7.88 (6H, s, methyl protons), ν_{\max} . 1338 (P=N) cm⁻¹.

(e) **Reaction of 1,2,5-triphenylphosphole with p-nitronitrosobenzene.** p-Nitronitrosobenzene (0.50 g, 0.003 mol) in ethylene dichloride (10 ml) was added dropwise to a solution of 1,2,5-triphenylphosphole (1.04 g, 0.003 mol) and triethyl phosphite (0.55 g, 0.003 mol) in ethylene dichloride (30 ml) at room temperature. The resultant dark brown solution was evaporated to dryness and the residue chromatographed on dry column alumina with ether. Recrystallisation from chloroform–ether gave 1-o-nitrophenylimino-1,2,5-triphenylphosphole (0.12 g, 8%), m.p. 207—210°, mixed m.p. 212—214°, with a sample prepared by thermolysis of p-nitrophenyl azide (above), i.r. spectrum identical with this authentic sample.

Preparation of Iminophospholes by Reaction of Chloramine-T with 1,2,5-Triphenylphosphole.—Anhydrous chloramine-T (3.5 g, 15 mmol) in ethanol (20 ml) was added slowly to 1,2,5-triphenylphosphole following the method of Cadogan and Moulden²⁴ for the formation of triethyltosylimino-phosphorane. The mixture was boiled under reflux for 12 h, cooled, and water (100 ml) and ether (200 ml) were added. Work-up of the ether layer gave 1-tosylimino-1,2,5-triphenylphosphole (54%), m.p. 245—247°, undepressed on admixture with a sample produced from tosyl azide and the phosphole (Table 1).

Preparation of Iminophosphoranes.—(a) o-Nitrophenyl-iminotriphenylphosphorane. Triphenylphosphine (3.22 g, 0.012 mol) in ether (20 ml) was mixed with o-azidonitrobenzene in ether (20 ml). No nitrogen evolution was observed. After 30 min a yellow crystalline solid formed which was filtered off and washed with ether. Warming this compound released nitrogen and thus it was assumed to be the intermediate triazene (2.92 g, 42%). The triazene was boiled under reflux in chloroform (10 ml) until nitrogen evolution ceased (*ca.* 15 min). Addition of excess of ether to the hot solution gave yellow crystals of the iminophosphorane (1.41 g, 34%), m.p. 141—142° (Found: C, 72.1; H, 4.8; N, 7.0. Calc. for C₂₄H₁₉N₂O₂P: C, 72.3; H, 5.0; N, 7.0%). The mass spectrum showed the correct parent ion; *m/e* 398 (Found: 398.117737. C₂₄H₁₉N₂O₂P requires 398.118417). **N.B.** Azides were always mixed with triphenylphosphine as solutions or under a solvent.

²⁴ J. I. G. Cadogan and H. N. Moulden, *J. Chem. Soc.*, 1961, 3079.

TABLE I
Synthesis of *N*-substituted 1-imino-1,2,5-triphenylphospholes (2) *

X in (2)	Yield (%)	M.p. (°)	λ_{max} (nm)	ϵ_{max} $\times 10^{-3}$	Analysis †		
					C(%)	H(%)	N(%)
Ph	42	218—219	385	14.5	83.45 83.3 80.0 80.0	5.25 5.5 5.7 5.6	3.3 3.5 2.8 3.2
<i>p</i> -MeOC ₆ H ₄	65	196—198	386	12.8	81.0 81.3	4.9 4.9	6.5 6.5
<i>p</i> -NCC ₆ H ₄	43	209—210			83.7 83.4	5.6 5.25	3.2 3.25
<i>p</i> -MeC ₆ H ₄	92	196—199	388	12.0	74.7 75.0	4.7 4.7	6.3 6.2
<i>p</i> -NO ₂ C ₆ H ₄	67	212—214	384	33.5	77.6 77.6	5.0 4.9	3.2 3.1
<i>p</i> -HO ₂ C·C ₆ H ₄	88	268—269	387		63.9 63.5	4.0 4.0	3.0 2.7
<i>p</i> -IC ₆ H ₄	57	218—222	375	14.0	77.5 77.5	5.1 4.9	7.9 7.9
<i>p</i> -PhN ₂ ·C ₆ H ₄	38	252—254	393	39.0	69.9 69.6	4.4 4.4	2.7 2.9
<i>m</i> -BrC ₆ H ₄	71	210—212			83.7 83.5	5.7 5.8	3.1 3.4
<i>m</i> -MeC ₆ H ₄	71	196—197			82.2 82.5	5.4 5.1	2.9 2.8
<i>o</i> -PhCO·C ₆ H ₄	45	191—192			74.9 75.0	4.8 4.8	6.0 6.2
<i>o</i> -NO ₂ ·C ₆ H ₄	77	188—190	390	17.6	68.6 69.5	4.9 4.8	5.8 5.8
<i>p</i> -NH ₂ SO ₂ ·C ₆ H ₄	90	208—211	388		80.1 80.0	5.7 5.5	3.3 3.2
<i>m</i> -MeO·C ₆ H ₄	66	187—189					
<i>o</i> -O ₂ CH·C ₆ H ₄	44	158—159	394		72.0 72.6	5.0 4.8	5.9 5.9
2-NO ₂ ,4-MeO·C ₆ H ₃	59	172—173	394	16.0	75.3 75.4	5.0 5.0	6.1 6.1
2-NO ₂ ,4-Me·C ₆ H ₃	42	154—156	392		67.6 68.3	4.4 4.1	8.4 8.5
2,4-(NO ₂) ₂ C ₆ H ₃	26	151—152	374	32.0	66.9 67.4	3.9 3.9	5.4 5.6
2-NO ₂ ,4-CF ₃ ·C ₆ H ₃	50	186—187			74.7 75.4	5.1 5.0	6.0 6.1
2-NO ₂ ,6-MeC ₆ H ₃	81	195—196					
2-NO ₂ ,5-MeC ₆ H ₃	35	195—196			78.5 79.5	5.3 5.1	2.2 2.3
<i>o</i> -Ph ₂ P(O)·C ₆ H ₄	20	278—279	390	10.5	76.0 76.0	4.9 4.7	11.9 12.6
<i>p</i> -N ₃ ·C ₆ H ₄	35	120—121	390	16.8			
<i>p</i> -Ph ₃ P=N·C ₆ H ₄	78	222—224	384		68.7 69.0	5.6 5.6	5.2 5.2
<i>p</i> -(MeO) ₃ P=N·C ₆ H ₄	89	207—210	388	13.0	77.9 77.6	4.7 4.6	5.6 5.6
1-NO ₂ -2-Naphthyl	24	212—214					
Benzimidazol-2-yl	43	178—180	390	9.1			
2,3-Oxydicarbonylphenyl	73	209—211	390	15.7			
CO ₂ Ph	30	185—187	394	12.5	76.9 76.9	5.0 4.9	2.9 3.1
CO ₂ Et	82	221—222	398		74.2 75.2	5.6 5.5	3.75 3.5
MeSO ₂	92	242—243			68.1 68.2	5.1 5.0	3.4 3.5
Tosyl	78	249—252	403	13.5	72.1 72.4	4.7 5.0	3.0 2.9
<i>p</i> -NO ₂ ·C ₆ H ₄ SO ₂	72	222—223			65.5 65.5	4.1 4.1	5.5 5.4
Ph ₂ P(O)	32	218—222	396	10.0	76.6 77.3	5.2 5.1	2.6 2.6
PhCO	54	210			80.2 80.6	5.2 5.1	3.2 3.3
<i>p</i> -NO ₂ ·C ₆ H ₄ ·CO	36	192—193			73.2 73.1	4.6 4.4	6.0 5.9
2,4-(NO ₂) ₂ ·C ₆ H ₃ ·CO	55	222—223			66.5 66.6	3.8 3.8	7.9 8.1

* Mass spectral data consistent with the assigned structures were obtained in all cases. † The top row refers to 'Found,' and the bottom to 'Required' values.

In the absence of solvent violent, almost explosive, reactions have been found to occur.

(b) *4-Methyl-2-nitrophenyliminotriphenylphosphorane*.

Triphenylphosphine (2.20 g, 0.010 mol) and 4-azido-3-nitrotoluene were treated as in (a) to yield the triazene (2.40 g, 80%) which was decomposed as above to give the iminophosphorane (0.86 g, 30%) (Found: C, 72.4; H, 5.2; N, 6.8%; *m/e*, 412. $C_{25}H_{21}N_2O_2P$ requires C, 72.8; H, 5.1; N, 6.8%; *m/e*, 412).

2,4-Dinitrophenyliminotriphenylphosphorane, m.p. 190—192° (lit.,²⁵ 201—202°) (Found: C, 64.8; H, 4.2; N, 9.4%; *m/e*, 443. Calc. for $C_{24}H_{18}N_3O_4P$: C, 64.9; H, 4.1; N, 9.5%; *m/e*, 443), 8-nitro-2-naphthyliminotriphenylphosphorane, m.p. 210—212° (Found: C, 74.9; H, 4.8; N, 6.3%; *m/e*, 448. $C_{28}H_{21}N_2O_2P$ requires C, 75.0; H, 4.7; N, 6.2%; *m/e*, 448), and picryliminotriphenylphosphorane, m.p. 183—184° (lit.,²⁴ 183—184°) (Found: C, 58.9; H, 3.7; N, 11.7. Calc. for $C_{24}H_{17}N_4O_6P$: C, 59.0; H, 3.5; N, 11.5%) were prepared similarly. In the last case the intermediate triazene triphenyl-(3-picryltriazen-2-enylidene)phosphorane, was isolated and characterised, decomp. 90° (Found: C, 55.1; H, 3.3; N, 16.3. $C_{24}H_{17}N_6O_6P$ requires C, 55.7; H, 3.3; N, 16.2%).

Trichloro-(o-nitrophenylimino)phosphorane. This was prepared by a modification of Kirsanov's procedure.²⁶ *o*-Nitroaniline hydrochloride (2.12 g, 0.012 mol) and phosphorus pentachloride (4.20 g, 0.020 mol) were boiled under reflux in toluene (50 ml) until evolution of hydrogen chloride ceased. Dry petroleum (100 ml) was added to the mixture and the precipitated material discarded. The filtered solution was tightly sealed and stored at 0° for 2 days. Brown crystals of trichloro-(*o*-nitrophenylimino)phosphorane (3.40 g, 99%), m.p. 110—112° (lit.,²⁵ 109—111°), were filtered off in a dry-box and washed thoroughly with anhydrous ether (Found: C, 26.8; H, 1.6; N, 10.0. Calc. for $C_6H_4Cl_3N_2O_2P$: C, 26.4; H, 1.4; N, 10.2%). The mass spectrum showed the correct parent ions expected for the trichloro-compound; *m/e* 278/276/274/272.

Triethyl N-(o-nitrophenyl)phosphorimidate. This was prepared by reaction of triethyl phosphite (0.012 mol) with *o*-azidonitrobenzene (0.012 mol) in boiling benzene (20 ml). After 1 h, chromatography on alumina gave the phosphorimidate (82%) as a yellow oil (Found: *m/e*, 302. $C_{12}H_{19}N_2O_5P$ requires *m/e*, 302), τ (CCl₄) 2.4—3.6 (4H, m, aromatic), 5.6—6.2 (6H, m, CH₃CH₂OP), and 8.65 (9H, t, CH₃CH₂OP).

Decomposition of (o-Nitrophenylimino)phosphoranes and Formation of Benzofurazans.—(a) *Thermolysis of 1-o-nitrophenylimino-1,2,5-triphenylphosphole in mesitylene*. The iminophosphole (1.04 g, 0.002 mol) was boiled under reflux in mesitylene (25 ml) for 48 h under nitrogen. Buff crystals of the phosphole oxide (0.48 g, 64%), m.p. 212—213°, i.r. spectrum identical with that of an authentic sample, formed on cooling. Chromatography of the mother liquor on alumina provided further phosphole oxide (0.18 g, 24%, overall yield 88%).

(b) *Thermolysis of 1-o-nitrophenylimino-1,2,5-triphenylphosphole in sealed tubes at 160°*. Sealed tubes containing the iminophosphole (0.2—0.3 g) in mesitylene (1 ml) were heated in an oil-bath at 160° for 48 h. G.l.c. analysis (10% FFAP, 150°; 5% Carbowax, 160°) showed a peak corresponding to benzofurazan; m.s.-g.l.c. (5% Carbowax, 160°)

gave the correct parent ion, *m/e* 120. Preparative g.l.c. was performed on the D.6 gas density balance (10% Carbowax) to give a sample of benzofurazan (65%; estimated using biphenyl as internal standard) identical with an authentic sample (Found: *m/e*, 120-032666. $C_6H_4N_2O$ requires *m/e*, 120-032360).

Various 1-*o*-nitroarylimino-1,2,5-triphenylphospholes were thermolysed under the same conditions. The reactions were quantified by g.l.c. using biphenyl as an internal standard and the products were isolated by preparative g.l.c. The results are summarised in Table 2.

TABLE 2

Benzofurazans (16) from 1- <i>o</i> -nitroaryliminotriphenylphospholes (15) ^a			
X in (15)	X in (16)	Yield (%)	Exact mass ^b
H	H	65	120-032666 120-032360
6-Me	4-Me	50	134-047791 134-048010
5-Me	5-Me	32	134-048054 134-048010
4-Me ^c	5-Me	46	134-048053 134-048010
4-MeO ^d	5-MeO	44	150-042803 150-042924

^a The (1-nitro-2-naphthylimino)phosphole gave the corresponding naphthofurazan in 8% yield. No benzofurazans were obtained from the 2,4-dinitrophenyl- and 2-nitro-4-trifluoromethyl derivatives. ^b The top row refers to 'Found,' and the bottom to 'Calc.' values. ^c 5-Methylbenzofurazan had m.p. 33—35° (lit.,²⁷ 37°). ^d 5-Methoxybenzofurazan had m.p. 95—98° (lit.,²⁷ 99°).

(2-Nitroarylimino)triphenylphosphoranes (aryl = Ph, *p*-MeC₆H₄, and *p*-NO₂·C₆H₄), (8-nitro-1-naphthylimino)triphenylphosphorane, and triethyl *N*-(*o*-nitrophenyl)phosphorimidate were all stable under the conditions described in the foregoing experiment. (*o*-Nitrophenylimino)trichlorophosphorane underwent considerable decomposition to a tar (ca. 50%) but a small yield (ca. 20%) of benzofurazan was detected by m.s.-g.l.c.

Kinetics of Benzofurazan Formation.—1-*o*-Nitrophenylimino-1,2,5-triphenylphosphole (0.38 g) and biphenyl (0.15 g) (internal standard) were dissolved in bromobenzene (10 ml) and the solution was divided into two equal parts. To one part was added 1,2,5-triphenylphosphole (0.18 g). A third solution was prepared containing the iminophosphole (0.18 g) and biphenyl (0.07 g) in bromobenzene (10 ml). Several aliquot portions (0.25 ml) of each solution were placed in sealed tubes and heated at 149° in an oil-bath. The progress of each reaction was followed by g.l.c. (5% Carbowax, 150°) and the benzofurazan concentration was measured as a fraction of the internal standard. In all cases the reactions were found to follow first-order kinetics. Rate plots were fitted by the method of least squares and gave the following first-order rate constants (*k*₁), (i) 2.8 × 10⁻³ min⁻¹ for thermolysis of the iminophosphole (0.38 g in 10 ml) alone, (ii) 3.0 × 10⁻³ min⁻¹ for thermolysis at half this concentration (0.18 g in 10 ml), and (iii) 2.7 × 10⁻³ min⁻¹ with added 1,2,5-triphenylphosphole (1 mol. equiv.).

Decomposition of 1-o-Nitrophenylimino-1,2,5-triphenylphosphole in the Presence of 1,2-Diphenyl-5-p-tolylphosphole.—The iminophosphole (2.23 g, 0.005 mol) and a mixture of

²⁵ L. Horner and H. Oediger, *Annalen*, 1959, **627**, 142.

²⁶ I. N. Zhmurova and A. K. Kirsanov, *Zhur. obshchei. Khim.*, 1960, **30**, 3044.

²⁷ J. M. Prokipcak and P. A. Forte, *Canad. J. Chem.*, 1970, **48**, 3059.

1,2,5-triphenylphosphole and 1,2-diphenyl-5-*p*-tolylphosphole (1 : 2.8; 1.63 g, 0.005 mol) were heated in mesitylene (100 ml) for 72 h. After LTA oxidation the phosphole oxide fraction (1.58 g, 95–100%) was separated by chromatography on alumina. N.m.r. and low eV mass spectrometry both showed a mixture of 1,2,5-triphenylphosphole 1-oxide and 1,2-diphenyl-5-*p*-tolylphosphole 1-oxide in the ratio 7.5 : 1. After correction for 1,2,5-triphenylphosphole added, it was found that the ratio of oxide originating from the iminophosphole to that formed from the phosphole was 7 : 1.

Competitive Deoxygenation of Benzofuroxan by 1,2,5-Triphenylphosphole and 1,2-Diphenyl-5-p-tolylphosphole.—A solution of benzofuroxan (0.20 g, 0.0015 mol), 1,2,5-triphenylphosphole (0.52 g, 0.0017 mol), and the previously obtained mixture of 1,2-diphenyl-5-*p*-tolylphosphole and 1,2,5-triphenylphosphole (0.54 g; 1.8 : 1) in benzene was boiled under reflux for 4 h. The solvent was removed and the residue was chromatographed on alumina to give a mixture of inseparable phosphole oxides (0.48 g, 96%), the

composition of which was determined by low eV mass spectrometry and by n.m.r. analysis. The ratio of 1,2,5-triphenylphosphole 1-oxide to 1,2-diphenyl-5-*p*-tolylphosphole 1-oxide was found from both methods to be 1.4 : 1, which after correction for the excess of 1,2,5-triphenylphosphole indicated almost identical rates of deoxygenation of benzofuroxan by the two phospholes.

Reaction of 1,2,5-Triphenylphosphole with (o-Nitrophenylimino)triphenylphosphorane.—The iminophosphorane (1.00 g, 0.003 mol) and 1,2,5-triphenylphosphole (1.00 g, 0.003 mol) were heated in mesitylene at 150° for 72 h. 1,2,5-Triphenylphosphole 1-oxide (0.12 g, 8%) was isolated from the reaction mixture.

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