THE PREPARATION OF ORGANO-PHOSPHORUS COMPOUNDS FROM THE ELEMENT†

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I should like to express my thanks to Professor Wittig and the other members of the scientific committee for their invitation to speak on this subject. My talk will be in the nature of a review and discussion of the highlights of work reported in the literature including research carried out in this field in the Central Research Laboratories of the American Cyanamid Company. This review does not pretend to be comprehensive, although it is not difficult to cover most of the important published reactions in which a carbon–phosphorus bond is formed directly from elemental phosphorus. The programme of study of the reactions of elemental phosphorus at the Cyanamid Laboratories was proposed by one of the finest people I have known, the late Dr Henry Storch. This research was designed to complement the programme in phosphine chemistry and, hopefully, eliminate the need for the intermediate preparation of phosphine as a raw material for synthesis. A number of types of reactions were carried out in this programme with phosphine to give a great variety of compounds. These were principally free radical reactions with olefins, acid-catalysed reactions with all types of carbonyl compounds and the base-catalysed addition of phosphine to acrylonitrile and similar active olefins. Phosphine for these reactions was prepared by the well-known hydrolysis of aluminium phosphide. The preparation of phosphine on a commercial scale appears to be receiving increased attention in many laboratories. In the past year, patents have been granted concerning the electrolytic reduction of phosphorus to phosphine[1] and improved alkaline hydrolytic procedures[2]. There is no doubt that phosphine is a versatile and sometimes indispensable raw material but it is obvious that direct reaction with elemental phosphorus, when possible, provides a much more economical and convenient route to organo-phosphorus compounds in the laboratory as well as the industrial plant.

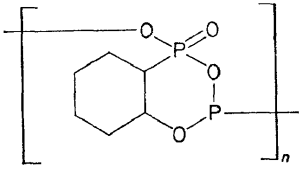
This review is divided into three parts dealing with the three main types of reactions of elemental phosphorus which give phosphorus to carbon bonds. These are free radical oxidation reactions, alkylation and arylation reactions and reactions with nucleophilic reagents. I will not discuss the reactions of metal phosphides with organic compounds although these systems are not very different from the nucleophilic reaction of organometallic reagents with phosphorus. I feel, even if somewhat arbitrarily, that the metal phosphides do not give direct synthesis from the element. You may also notice that I have not mentioned electrophilic reactions of the element. The

† This subject has recently been reviewed by M. M. Rauhut in *Topics in Phosphorus Chemistry*, Vol. I, Ed by M. Grayson and E. J. Griffith, John Wiley, N.Y. (1964).

compounds of phosphorus are frequently excellent nucleophiles and we might expect the element itself to attack electrophiles such as carbonyl compounds, olefins and alkyl halides. Reactions with alkyl halides are well known but one of the chief points I should like to develop in this review is that the initial stages of these reactions are free radical processes. A clear-cut electrophilic reaction of the element does not appear to me to have been reported in the literature.

Perhaps one of the best documented examples of a free radical reaction in which P–C bonds are formed is illustrated by the reaction of white phosphorus with olefins and an oxidizing agent. Probably the first observation of this reaction was made by Robert Boyle in 1681[3] when he noticed that turpentine affected the oxidation of phosphorus. In 1829 Graham reported that ethylene had a similar effect[4]. Of course, the radical chain nature of the oxidation of phosphorus was demonstrated much later. The first real investigation of the reaction with oxygen and simple olefins was reported in 1914 by Willstätter and Sonnenfeld[5].

Reaction with cyclohexene in benzene, for example, gave a typical "phosphorate" consisting of an adduct of the olefin and a P_2O_4 group. Essentially quantitative yields are obtained in this reaction. The structure of the "phosphorate" was depicted as a cyclic, monomeric material with both P–C and P–O bonds on the basis of the formation of phosphoric and cyclohexenephosphonic acids after treatment with nitric acid. The fact that the lead salt of the latter compound as well as the phosphorate itself are actually polymers was shown later by Walling and his co-workers[6]. They demonstrated that the reaction was indeed free radical in nature. An induction period was observed with peroxide-free cyclohexene. The reaction was initiated by azobisisobutyronitrile and inhibited by hydroquinone. They estimated a kinetic chain length of at least 7000 at 50°. Hydrolysis studies confirmed the presence of both P–C and ester bonds as proposed by Willstätter and Sonnenfeld. However, these are present as phosphonate and phosphite groups in the form of a polymeric anhydride structure. For example, solvolysis with several alcohols gave dialkylphosphites in about



30 per cent yield. Some olefins such as styrene and cyclohexene gave insoluble phosphorates of this type with a P_2O_4 group. Other olefins, however, such as 1-octene formed soluble phosphorates which absorbed additional oxygen to give a second type with a P_2O_5 group. Molecular weight data on the product from hexadecene indicated a chain of five units with unknown end groups. From a mechanistic standpoint, Walling proposes only that a PO radical attacks the olefin followed by attack of a hydrocarbon radical on a phosphorus atom. This brief speculation is based on the observed structure of the products. Aside from questions of mechanism, the structures

of products obtained from acetylenes and halo-olefins remain unclear. For example, the phosphorate from *cis-dichloroethylene* appears to contain very little chlorine.

A related but less efficient reaction was first disclosed by Garwood and Hamilton in a patent in 1956 and described further in 1960 in a subsequent publication[7]. This is the reaction of an olefin with white phosphorus and a peroxide such as di-t-butyl peroxide at temperatures of 150–160°. A large excess of olefin is required to keep the phosphorus in solution and prevent the formation of red, polymeric phosphorus-containing solids. An excess of phosphorus compared to peroxide was also used to obtain maximum yields which were about 30 per cent. As indicated below, isobutylene was formed and in nearly quantitative yield. Isobutylene formation was shown to be dependent on the presence of the phosphorus but not the olefin.

$$n\mathrm{RCH{=}CH_2} + \mathrm{P_4} + (\text{t-BuO})_2 \longrightarrow R'_n\mathrm{P_4(OH)_2} + 2\mathrm{C_4H_8}$$

On this basis, the authors conclude that the reaction involves initial attack of alkoxy radical from the peroxide on the phosphorus tetrahedron. Isobutylene splits off rapidly and the reaction with the olefin occurs in some unknown sequence of steps. The presence of hydroxyl groups is conjectured largely on the basis of the stoichiometry rather than direct analysis. Oxidation with nitric acid indicated that over 90 per cent of the olefin was bonded to phosphorus. Both phosphonic and phosphinic acids were obtained. The presence of phosphine groups was confirmed by the characteristic red colours of the carbon disulphide test. Other chemical and physical tests indicated a complex material containing P–P bonds as well as P–H, P=O and acidic groups. This reaction is obviously far more complex than the oxygen case but serves to show the ease with which phosphorus will add a radical species and undergo chain reactions to give organo-phosphorus products. It is not unlikely that reactions of considerable preparative potential await more rigorous identification and control of the initiation and propagation stages of this kind of free radical oxidation process.

I should like to turn now to the subject of alkylation and arylation reactions of elemental phosphorus with organic halogen compounds. This topic follows logically after the free radical oxidation examples since, as I have already mentioned, I think this review will emphasize the predominantly free radical nature of the alkylation process.

The illustrious August Wilhelm Hofmann was the first to alkylate white phosphorus with ethyl iodide in the liquid phase in 1861[8]. He did this in the presence of metallic zinc which may actually have made this the first example of a nucleophilic reaction involving zinc alkyls. However, later workers showed that the metal was unnecessary. Masson and Kirkland actually isolated about 50 per cent of tetraethylphosphonium iodide by working up the crude product with aqueous hydrogen sulphide. The triethyl phosphine oxide was not isolated[9].

$$\mathrm{P_4} + \mathrm{CH_3CH_2I} \xrightarrow[(\mathrm{H_2O})]{185^\circ} (\mathrm{CH_3CH_2})_4\mathrm{P^+I^-} + (\mathrm{CH_3CH_2})_3\mathrm{PO}$$

If the product of the reaction is boiled with ethanol and then distilled from potassium hydroxide, the main product which is isolated is the triethylphosphine oxide. We know, of course, that the phosphonium salt will be converted to the oxide under these conditions. One also suspects that triethyldi-iodophosphorane is also present and is hydrolysed to the oxide. Crafts and Silva obtained 40–50 per cent conversions of phosphorus to the oxide and recovered large amounts of red phosphorus[10]. The possible reactivity of red phosphorus in this system has been explored recently. Kirsanov and his co-workers have obtained 50–80 per cent yields of tertiary phosphine oxides from red phosphorus and alkyl iodides in the presence of a catalytic amount of iodine after hydrolysis with aqueous sulphite[11]. Similar results were obtained with tetraiododiphosphine as the catalyst. Note, therefore, that just as with the free radical oxidation processes, the red phosphorus which is a byproduct under one set of conditions, may be a reactant and give the same products as white phosphorus with a small change in the reaction conditions. These workers had also shown that the reaction can take place with tetraiododiphosphine in molar amounts without elemental phosphorus being present. The same reaction was disclosed independently by Hoffman, Grunewald and Horner with benzyl chloride[12]. As a result of the existence of the separate reaction of tetraiododiphosphine with alkyl iodides, the Russian group has suggested that this compound is a *required* intermediate in the elemental phosphorus–alkyl iodide reactions catalysed by iodine. They feel that direct reaction of alkyl iodide with white or red phosphorus cannot occur. I think that we shall see that the weight of evidence supports the direct attack mechanism. In any case, no matter how the attack on phosphorus begins, we have to explain the formation of polyalkylated products such as the tertiary phosphine oxide and quaternary phosphonium salt. This has been done admirably by Hoffman, Grunewald and Horner in connection with their study of the tetraiododiphosphine reaction[12]. They have shown that a phosphonous dihalide will react with an alkyl halide to give a dialkyl trihalophosphorane. In addition, this compound or a phosphinous halide, as shown in the second equation, will react with more alkyl halide to give

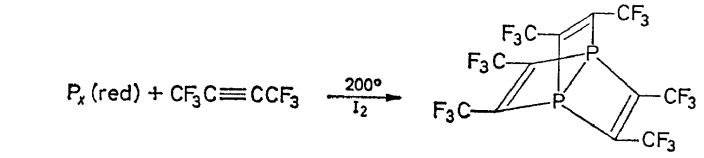
$$RPX_2 + RX \longrightarrow R_2PX_3$$

$$R_2PX + RX \longrightarrow R_3PX_2 \xrightarrow{H_2O} R_3PO$$

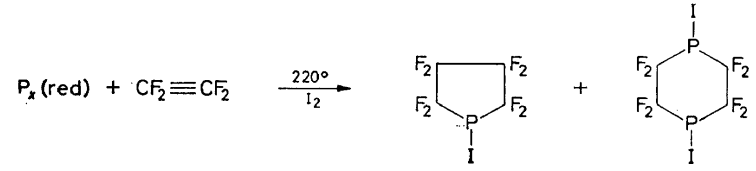
$$R_3PX_2 + RX \longrightarrow R_4P^+X_3^-$$

a trialkyl dihalophosphorane. Hydrolysis of such compounds is known to give tertiary phosphine oxides. Finally, quaternary phosphonium perhalides can be formed by further alkylation of the trialkyl phosphorane in the presence of excess alkyl halide. The last step was also proposed in the early literature by Dorken.[13] All of these steps can occur after the initial attack on elemental phosphorus, or the tetraiododiphosphine for that matter, and will acount for the products isolated. For information about the early stages of reaction, however, we have to look elsewhere. At this point we should mention some recent examples of the great synthetic possibilities that can be developed with this simple kind of direct reaction of elemental

phosphorus and organic halides. The preparation of a substituted diphosphabicyclo-octatriene or "phosphabarrelene" was reported by Krespan and co-workers by direct reaction of red phosphorus with the fluorinated acetylene in the presence of iodine[14]. With the preparation of the arsenic analogue, the di-iodide adduct of the acetylene worked equally well.



Similarly, reaction of red phosphorus with tetrafluoroethylene in the presence of iodine produced cyclic fluoroalkyliodophosphines that would have been extremely difficult to make by conventional methods[15]. It is probably significant that tetrafluoroethylene readily undergoes free radical reactions such as its violent homopolymerization. Historically, the first characteriza-



tion of simple halophosphines as the primary products of the direct reaction of white or red phosphorus with an alkyl halide was reported in 1953 by Bennett, Emeleus and Haszeldine[16]. Trifluoroiodomethane gave mixtures of the three compounds shown in amounts dependent on the reactant ratios and reaction time since these compounds can equilibrate quite readily. The electronegative fluoroalkyl group presumably prevents complete conversion to phosphonium salts by severely reducing the nucleophilic properties of the products.

$$CF_3I + P_4 \xrightarrow{220^\circ} CF_3PI_2 + (CF_3)_2PI + (CF_3)_3P$$

Two questions are raised by these results. First, are these reactions limited to condensed phase or liquid systems and second, are these reactions specific for fluoroalkyl halides?

The first question is answered by Maier's demonstration that red phosphorus is alkylated by trifluoroiodomethane vapour over a copper catalyst[17]. The same products are obtained as in the liquid reaction although in reduced yields. The mono- and dialkylated compounds are the major products which is the reverse of the liquid system yields where the tris trifluoromethyl phosphine is usually the dominant product. I think this indicates that the phosphonous dihalide is a primary product of the reaction rather than a decomposition or disproportionation product. The second question has also been answered by Maier's heterogeneous vapour phase reactions of red phosphorus with various non-fluorinated methyl and ethyl halides[17, 18].

The principal product from these reactions is the phosphonous dihalide. The phosphinous halide is formed in small amount along with some phosphines and phosphorus trihalide. With methyl chloride, for example, methylphosphonous dichloride is produced in about 17 per cent conversion

$$P_x(\text{red}) + RX \xrightarrow[\text{Cu}]{280\text{–}370^\circ} RPX_2 + R_2PX$$

based on phosphorus after 10 hours at 360° and constitutes 95 per cent of the product. The proportion of dimethyl phosphinous halide in the product can be increased by quicker removal of products from the hot zone, indicating that this product is thermally unstable in the vapour state. This accounts for the different product distribution between liquid and vapour reactions. The important point in all this is that we seem to get the same initial products in all of the alkylation reactions regardless of alkyl halide structure, catalyst or reaction conditions. In the copper-catalysed reactions, furthermore, we have some analogy and precedent for the mechanistic pathway. As Maier points out, it seems reasonable to assume a mechanism like that proposed by Rochow for the direct synthesis of organosilicon compounds[19].

In these systems, the copper serves two functions. First, it acts as a carrier for alkyl radicals, as indicated in the first equation, by forming the unstable copper alkyl. In the second place, the cuprous halide which is formed at the same time acts as a chlorinating agent to give a halophosphorus radical adduct as shown in the second equation. This adduct can then add an alkyl radical or a halogen atom to give complex compounds from which the simple products are derived by additional radical or nucleophilic reactions. The last equation indicates one of the probable termination steps whereby inactive cupric halide is formed by disproportionation of cuprous halide. Maier has indicated that cupric bromode is inactive as a catalyst.

$$RX + 2Cu \longrightarrow CuX + (RCu) \longrightarrow R\cdot$$

$$CuX + P_x \longrightarrow XP_x\cdot$$

$$XP_x\cdot \xrightarrow[RX]{R\cdot} \begin{cases} XP_xR \\ XP_xX + R\cdot \end{cases}$$

$$2CuX \longrightarrow Cu + CuX_2$$

Additional support for the radical nature of the uncatalysed alkylation systems has been provided by the work of Petrov, Smirnov, and Emel'yanov[20]. Reactions with benzyl-, phenyl-, tolyl- and n-octyl chlorides and bromides with white phosphorus at elevated temperatures in a sealed tube gave the phosphonous and phosphinous halides. The phosphonous dihalide was the dominant product just as in the vapour phase reactions but here substantial conversion of phosphorus to the phosphinous halide was also observed. The best yields were obtained with the aryl halides and, with *meta*-tolyl bromide, where the correct stoichiometric ratio of three moles of halide to one gramme-atom of phosphorus was used, the total conversion of phosphorus was nearly 80 per cent. Petrov, Smirnov and Emel'yanov propose

that these reactions are radical in nature and involve the thermal homolysis of the carbon–halogen bond followed by addition of the radicals to the phosphorus tetrahedron. This type of radical addition with P–P bond cleavage is repeated until the final products of the reaction are produced. They reason that the homolytic cleavage of phosphorus itself does not begin until much higher temperatures are reached than those employed in these reactions. Dissociation of P_4 into P_2 fragments, for example, does not begin until 800°.

Perner and Henglein[21], in connection with a radiation study, found that carbon tetrachloride undergoes a similar thermal reaction with white phosphorus to give small amounts of red phosphorus, phosphorus trichloride, and trichloromethyl phosphonous dichloride. By studying the temperature dependence of phosphorus trichloride formation, Perner and Henglein estimated an activation energy of 22·2 kcal/m for the reaction. Furthermore, the rate of PCl_3 formation was nearly independent of phosphorus concentration over a wide range of concentration indicating that the uptake of radicals by phosphorus is very fast. Perner and Henglein also studied the photochemical reaction of white phosphorus with carbon tetrachloride. In this case, a red solid containing about 74 per cent phosphorus was the major product from room temperature to 100°. The other products were also formed but in quite low yields. Since the solution itself did not absorb light, primary activation of the suspended phosphorus was suggested with some reaction of the phosphorus polymerization intermediates with the solvent.

Earlier, Kraft and Parini[22] had established the formation of a phosphorus–carbon bond in the photochemical reaction of white phosphorus with alkyl halides. They irradiated saturated solutions of phosphorus in the halide at 20° and isolated the red phosphorus product containing organic groups. In this kind of reaction we are probably dealing with alkyl halide-derived radical initiation and termination of a phosphorus polymerization reaction and the proportion of organic groups is quite small. Nevertheless, Kraft and Parini isolated the lead salts of various phosphonic acids from such products after nitric acid oxidation. From this type of work, Kraft and Parini concluded that red phosphorus is a polymeric form of white phosphorus containing terminal groups such as halogen, hydroxyl and so forth. The different forms of red phosphorus depend on the degree of polymerization and the terminal groups. Red phosphorus is therefore never a pure material. Perner and Henglein[21] also carried out this same reaction in the presence of *gamma*-radiation from a Cobalt 60 source over a range of temperatures. *G*-values in terms of phosphorus converted per 100 eV absorbed are shown for the extremes of temperature which they report. Notice particularly the drop in red phosphorus yield at higher temperature with

$$P_4 + CCl_4 \xrightarrow{\gamma\text{-rays}} P_x(\text{red}) + PCl_3 + CCl_3PCl_2$$

G-values	25°	22	1·4	4·5
	130°	<0·5	9·5	41

concurrent increase in the phosphorus halide products. Perner and Henglein

conclude from this that the formation of red phosphorus and the low molecular weight phosphorus halide products takes place by concurrent processes involving the same intermediates but with different temperature dependence. The sudden increase in PCl_3 and trichloromethyl phosphonous dichloride above 100° indicates a radical chain reaction and the authors estimate the activation energy to be 8·2 kcal/mol for the formation of these products. The yield of low molecular weight products also increases with the dose rate. The fact that phosphorus traps chlorine atoms in preference to the trichloromethyl radical is indicated by the complete absence of compounds containing more than one trichloromethyl group. We will come back to the mechanism of these reactions in a moment.

The red phosphorus obtained by Perner and Henglein from the *gamma*-ray induced reaction actually contained only about 56 per cent phosphorus, much less than that observed by Kraft and Parini in their photochemical–alkyl iodide reaction. The complete analysis for chlorine and carbon as well as phosphorus corresponded to a formula with one trichloromethyl group for every seven phosphorus atoms. Halogenation, with bromide, for example, gave trichloromethylphosphonous dibromide which confirmed the presence of a phosphorus–carbon bond in the red phosphorus polymer.

Bartkus and the author also investigated the radiation chemistry of white phosphorus in the presence of various organic liquids such as alkyl halides, olefins and alcohols[23]. Radiations were carried out with 3 MeV electrons from a Van de Graaff generator at dose rates from about one-half to two mrads per pass. Total doses were from 19 to 84 mrads in most cases although higher doses were investigated. A typical case is the reaction of 1-chlorobutane. The main radiolysis product from this compound in the pure state is the isomeric 2-chlorobutane for which the *G*-value is 60[24]. In a saturated solution of phosphorus in 1-chlorobutane, the *G*-value for the isomerization is depressed to 8 or 10. The trapping of radicals by phosphorus is again indicated. Aside from a trace of phosphorus trichloride found by gas chromatography, the only product of electron irradiation after removal of unreacted phosphorus was a polymeric yellow-coloured solid containing from 56–75 per cent phosphorus with the remainder as carbon, hydrogen, halogen and some oxygen unavoidably introduced during purification. The empirical formula shown is typical of the results with the halides. If we disregard the halogen and oxygen, the ratio of alkyl groups to phosphorus

$$P_4 + n\text{-}C_4H_9Cl \rightsquigarrow (n\text{-}C_4H_9)_5P_{39}Cl_2O_{10}$$

is about 1:8, closely resembling the results obtained by Perner and Henglein. Chlorobenzene gave quite similar results. The presence of carbon–phosphorus bonds was shown with benzyl chloride by isolation of benzylphosphonic acid–aniline salt after nitric acid oxidation. Examination of the crude product by means of electron spin resonance spectroscopy immediately after radiolysis gave no indication of the presence of unpaired electrons.

I should like to conclude this discussion of alkylation and arylation reactions of elemental phosphorus with these equations depicting the mechanistic pathways proposed by Perner and Henglein for the radiation work with

CCl_4. These mechanisms apply in a general way to the radiation studies we have carried out as well as all of the thermal radical reactions we have discussed in which both red phosphorus polymers and low molecular weight products are formed. The first equation indicates the principal idea which seems to me to be common to all of these systems, namely that a radical

$$R\cdot + P_4 \longrightarrow R\text{–}P_4\cdot$$

$$RP_4\cdot \begin{cases} \xrightarrow{CCl_4} RP_4Cl + CCl_3\cdot \\ \xrightarrow{R\cdot} RP_4R \\ \xrightarrow{RP_4\cdot} R_2P_8 \\ \xrightarrow{P_4} RP_8\cdot \end{cases}$$

$$R = CCl_3,\ Cl,\ \textit{etc.}$$

generated thermally or by radiation from the alkyl or aryl halide attacks phosphorus to give an organo-phosphorus radical which can undergo one of four kinds of reactions. First, reaction with the alkyl halide solvent leads to further halogen substitution and formation of the chain-propagating organic radical. This is the step for which Perner and Henglein measured an activation energy of about 8 kcal/mol for CCl_4. The second equation indicates a radical coupling or termination step which is probably of minor significance in the presence of solvent and the relatively high concentrations of dissolved phosphorus. The last two equations describe the paths for formation of phosphorus polymers by coupling of two of these radicals or, more likely, the addition of the organophosphorus radical to phosphorus itself. Capture of halogen by the last species RP_8 would give a red phosphorus product of approximately the composition observed in the radiation work, namely one organic group for each 7 or 8 phosphorus atoms.

I should like to turn now to the third and last part of my talk which concerns the reactions of phosphorus with nucleophilic reagents. This brief but interesting topic has developed largely in the past few years through our work at the Cyanamid laboratories in Stamford.

The fact that phosphorus will react with nucleophilic reagents is indicated by the old and well-known reaction of white phosphorus with sodium hydroxide. The reaction products in water are phosphine and hydrogen gases and sodium hypophosphite and sodium phosphite. This is obviously a complex reaction involving a large number of steps none of which are well understood. In a similar way, reaction of white phosphorus with sodium ethoxide in ethanol gives a dark red solution which is not stable and slowly decomposes to give hydrogen, phosphine and sodium hypophosphite. The red solution formed in ethanol was shown[25] to have nucleophilic properties by Auger in 1904. Addition of methyl iodide to the freshly prepared solution of phosphorus in alkaline ethanol reportedly gave methyl phosphine, methyl phosphonic and dimethyl phosphinic acids and trimethylphosphine oxide.

In an analogous reaction, isoamyl iodide gave isoamylphosphonic acid in 59 per cent yield based on the iodide. Although these reactions are complex and not well understood, it seems reasonable to suppose that the first step probably involves attack by hydroxide ion on the phosphorus tetrahedron to give an anion with the negative charge on phosphorus[26]. This phosphide ion should be an active nucleophile capable of reaction with organic electrophilic reagents such as the alkyl iodides used by Auger. Furthermore, one might expect that other nucleophiles beside hydroxide ion should be capable of reaction with elemental phosphorus. This would give phosphide anions which may already contain a carbon–phosphorus bond and are capable of further reactions with electrophilic reagents. Reactions of both types have been discovered[26, 27]. First we will consider reactions with organic nucleophiles such as organometallic carbanions.

White phosphorus reacts completely with a molar excess of phenyl-lithium in diethyl ether after one to three hours to give a deep red solution[27]. Solutions of similar appearance are formed with other organo-metallic reagents. The primary phosphine is the major product obtained after hydrolysis but small amounts of secondary and tertiary phosphines were formed in a few cases. Neither phosphine nor hydrogen were observed during the hydrolysis. The major byproduct in all these reactions was an amorphous, insoluble, yellow solid containing 40–60 per cent phosphorus. Phenyl-lithium gave a 36 per cent yield of the primary phosphine under the best conditions. Use of a four-fold excess of phenyl-lithium gave 15 per cent of diphenylphosphine in addition to 27 per cent of the primary phosphine. Reaction with the phenyl Grignard reagent in tetrahydrofuran gave a 25 per cent yield of phenylphosphine after hydrolysis. The alkylorganometallics gave much poorer results. For example, only 7–9 per cent monobutylphosphine and 1 per cent of dibutylphosphine were obtained from either butyl-lithium or butyl Grignard reagent. Phenyl sodium and tri-isobutylaluminum gave only polyphosphide products. As anticipated, the organophosphide anions represented by the red solutions obtained from phosphorus and organo-metallic reagents were capable of further reactions.[28] Addition of butyl chloride to the completely reacted solution of white phosphorus and phenyl-lithium gave dibutylphenylphosphine and butyldiphenylphosphine after hydrolysis. The total conversion of phosphorus in this reaction is over 80 per cent. The solution produced by reaction of phosphorus with phenylsodium in toluene also reacted with butyl chloride to give over 70 per cent total yield of the mixed tertiary phosphines. You may recall that simple hydrolysis of the phosphorus-phenylsodium solution gave no low molecular weight products. These results indicate that the organo-phosphide intermediates from phenyl-lithium and phenylsodium have units in the phosphorus polymer with two phenyl groups attached to one phosphorus atom. The presence of a simple metal diphenylphosphide is unlikely except when excess organometallic is used since this would give diphenylphosphine on hydrolysis. Substituted aromatic lithium reagents also react with white phosphorus and butyl bromide to give both possible tertiary phosphines.[28] Alkyl organometallics, alkyl halides and white phosphorus also reacted to give secondary and tertiary phosphines[28]. Other electrophilic reagents besides alkyl halides will react with the organo-polyphosphide anions. For

example, propylene oxide and benzaldehyde gave various organo-phosphorus products after reaction with the organometallic-phosphorus solutions.

One of the most striking of the organometallic reactions carried out by Rauhut and Semsel gave tetrabutylcyclotetraphosphine as the major product from the reaction of butyl Grignard reagent, phosphorus and butyl bromide in refluxing tetrahydrofuran. This is in complete contrast to the results obtained with the more reactive butyl-lithium and aromatic reagents.

$$P_4 + 2n\text{-}C_4H_9M_9Br + 2\ n\text{-}C_4H_9Br \xrightarrow{THF} (C_4H_9P)_4$$

The final example in our review of reactions with nucleophilic reagents concerns the trapping of intermediates formed in the reaction of white phosphorus with hydroxide ion[26]. In this reaction, the carbon–phosphorus bonds are formed in a series of successive additions of nucleophilic phosphide ions to electrophilic, unsaturated compounds such as acrylamide and acrylonitrile. The reactions were generally carried out by addition of 10N potassium hydroxide to a finely divided suspension of phosphorus in the presence of the organic component. Potassium phosphite is formed in addition to the corresponding tertiary phosphine oxide. The stoichiometry expressed in the equation below seems to fit the maximum conversion of phosphorus to tris(2-carbamoylethyl)phosphine oxide, 74 per cent, which

$$P_4 + 2\ KOH + 4\ H_2O + 9\ CH_2{=}CHCONH_2 \xrightarrow[35^\circ]{EtOH} 3\ (NH_2COCH_2CH_2)_3PO + K_2HPO_3$$

was obtained at the highest ratio of acrylamide to phosphorus which was used. Under the best conditions, the conversion of phosphorus to tris-(2-cyanoethyl)phosphine oxide was somewhat lower. Little or no unreacted phosphorus was left at the end of the reaction. The normal conversion of phosphorus to phosphine is evidently suppressed with these efficient trapping reagents. With ethyl acrylate, however, the yield of tertiary phosphine oxide was quite low and a small amount of the corresponding tertiary phosphine was actually isolated. In this case the normal decomposition to phosphine evidently did occur followed by base-catalysed Michael addition to ethyl acrylate to give the tertiary phosphine. The mechanism proposed for these reactions involves trapping of the initial hydroxide–phosphorus anion by the unsaturated compound in a typical Michael addition followed by a sequence of successive P–P bond cleavages and similar trapping of phosphide anions until the products are obtained.

I will close this review of the direct synthesis of carbon–phosphorus bonds from elemental phosphorus with the safe conclusion that this versatile element shows great promise for still further discovery of useful synthetic methods for many types of organo-phosphorus compounds. If nothing else, I hope this talk will have stimulated your interest and curiosity and emphasized our need to know much more about the detailed mechanisms of these important reactions.

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