

CHEMISTRY OF PHOSPHORUS IODIDES

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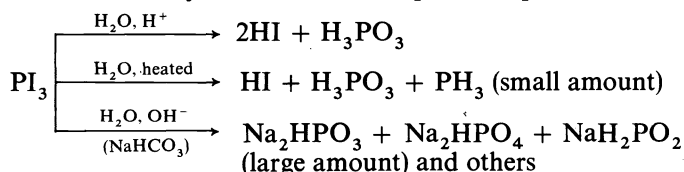
ABSTRACT

The present paper contains a review on chemistry of phosphorus triiodide and diiodide. Literature references—86.

Chemistry of phosphorus halides is of special interest, if only because it is out of phosphorus halides that the overwhelming majority or rather almost all known at present phosphorus-organic compounds are obtained.

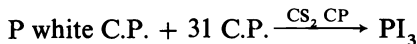
Out of phosphorus halides most extensively studied and most widely used are phosphorus chlorides, least of all—phosphorus iodides. Phosphorus chlorides are known in dozens of thousands, while phosphorus iodides hardly number a thousand. This is due to the fact that until recently the simplest phosphorus iodides were virtually inaccessible materials. Furthermore, the investigation of phosphorus iodides was and is hampered by their very pronounced peculiarities and by a striking difference between chemical properties of phosphorus iodides and phosphorus compounds with other halides. These very circumstances—the peculiar properties of phosphorus iodides and their being insufficiently studied—induced us to start some years ago an investigation of the reactivity of the simplest phosphorus iodides and, in particular, to determine the capability of the simplest phosphorus iodides to transform into phosphorus-organic compounds. This article gives a brief description of the present state of the art in the chemistry of phosphorus iodides.

The comparison of chemical properties of phosphorus chlorides and iodides would probably reveal more differences rather than any similarity. The simplest reactions of phosphorus chlorides usually proceed in one direction (direct reactions); for instance, the hydrolysis of phosphorus trichloride yields phosphorus acid in a particularly satisfactory amount. Very often the simplest reactions of phosphorus iodides proceed in several directions; for instance, the hydrolysis of phosphorus triiodide yields phosphorous acid, phosphine, phosphoric acid, hydrophosphorous acid and other products which have not yet been isolated as pure compounds^{1,2}.

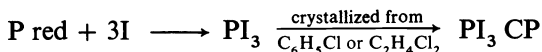


P—P-bonded compounds can be obtained from phosphorus chlorides only under special conditions, while from phosphorus iodides they are readily obtainable. Generally, the reactions of phosphorus iodides are much more complex compared with those of phosphorus chlorides and one may expect them to yield various surprising results.

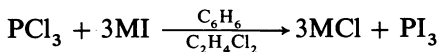
The simplest phosphorus iodide—phosphorus triiodide—was initially obtained in 1850, but its chemical properties were not fully investigated till 1959, since it was virtually inaccessible being synthesized from the pure red phosphorus or white phosphorus in the purest sulphur–hydrocarbon solution^{3,4,5}.



We succeeded in making phosphorus triiodide quite accessible, having realized the same synthesis, but from ordinary red phosphorus and iodine without solvents with further crystallization from phenyl chloride or dichloroethane⁶.

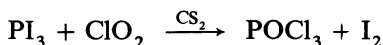


Phosphorus triiodide is also obtained in quite pure condition from phosphorus trichloride and alkali-metal iodides in benzol- or dichloroethane solution⁷.

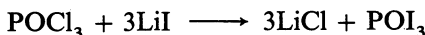
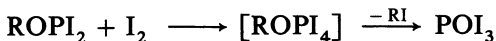


M: Li, Na, K

Phosphorus oxyiodide could not be prepared by means of the oxidation of phosphorus triiodide by oxygen⁸. Oxidation by chlorine dioxide leads to iodine and phosphorus oxychloride⁹.

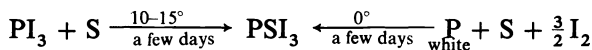


We managed to obtain phosphorus oxyiodide, previously unknown, by the interaction of alkoxydiiodophosphines and elemental iodine, as well as by the replacement of chlorine atoms by those of iodine in phosphorus oxychloride in reaction with lithium iodide¹⁰.



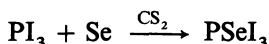
Phosphorus oxyiodide is a crystalline substance of dark violet colour with a low melting point (50–53°) which resembles elemental iodine in its appearance; it dissolves easily in water to form hydrogen iodide and phosphoric acid, being just slightly soluble in non-polar solvents and rather more so in alkyl iodides. Phosphorus oxyiodide has been identified by molecular weight determination, elementary analysis data and chemical conversions (into triphenylphosphate, calcium phosphate and phenylhydrazide of phosphoric acid).

The reaction of phosphorus triiodide and sulphur in carbon disulphide solution yields thioiodide—a substance of brick red colour with a melting point of 46–48°, which can also be prepared under analogous conditions from its elements¹¹.



Thioiodide of phosphorus triiodide is easily soluble in carbon disulphide, moderately soluble in non-polar solvents, and readily reacts with water, acetone and alcohols. Being stored or exposed to light thioiodide of phosphorus triiodide decomposes into phosphorus sulphide and phosphorus triiodide. The latter on being exposed to a moist atmosphere decomposes with the resulting elimination of hydrogen sulphide and hydrogen iodide.

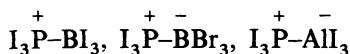
Phosphorus triiodide interacts with red selenium in boiling carbon disulphide¹².



Selenide of phosphorus triiodide, dark brown crystals with a melting point of 35–37°, can be also prepared from its elements taken in stoichiometric relationships.

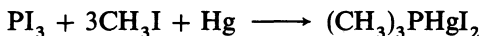
Crystalline selenide of phosphorus triiodide is stored in the dark and remains without transformation for a few days, but on being melted, dissolved or exposed to daylight disproportionates into phosphorus triiodide, iodine and P—Se-bonded products.

Phosphorus triiodide forms salts with some of the Lewis acids^{13–15}.

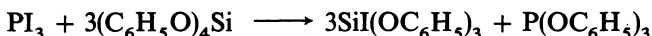


No published data are available to date concerning reactions of phosphorus triiodide with organometallic compounds.

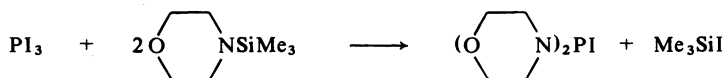
Phosphorus triiodide reacts with methyl iodide and mercury to form a substance which, by its composition, is close to a trimethylphosphine-mercury diiodide complex¹⁶.



As a result of the interaction of tetraphenoxysilane and phosphorus triiodide, triphenylphosphite is formed¹⁷.



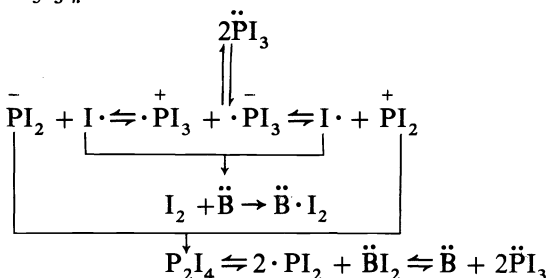
Phosphorus triiodide interacts with morpholyltrimethylsilane with the substitution of one or two iodine atoms, to yield morpholydodiiodophosphine or dimorpholydoiodophosphine, respectively¹⁸.



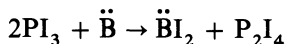
The substitution of three iodine atoms in phosphorus triiodide has not yet been accomplished even when using an excessive quantity of morpholyltrimethylsilane and in this case only two iodine atoms are substituted.

When ethers react with phosphorus triiodide in mild conditions, a peculiar reaction occurs: phosphorus triiodide is converted in equilibrium ratio into phosphorus diiodide and iodine which bonds with ether to form a complex^{19,7}.

It is very likely that the reaction proceeds according to the following mechanistic scheme which is consistent with the data of photolytic splitting of phosphorus triiodide to form iodine and a polymer of composition $(P_5I_3)_n$ ²⁰.



To summarize, with no consideration of the reaction mechanism, the process proceeds according to the scheme:

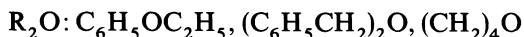


when B: $(C_2H_5)_2O$, $(C_3H_7)_2O$ and $(C_4H_9)_2O-PI_3$ 30%, P_2I_4 70% at 20°;

when B: $(C_6H_5)_2O$, $C_6H_5OCH_3-PI_3$ 80%, P_2I_4 20% at 100°.

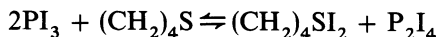
It would seem probable that equilibrium is strongly displaced to the phosphorus triiodide side; however, the nucleophiles being added, the iodine is bonded into complexes resulting in the displacement of equilibrium to the phosphorus diiodide side.

The higher the basicity of the ether and the less hampered the access to a nucleophilic atom of oxygen, the easier is the conversion of phosphorus triiodide into phosphorus diiodide. For instance, during simple washing of phosphorus triiodide with pure ether the former is practically completely converted into phosphorus diiodide. In some cases, alongside this process, the irreversible splitting of ethers occurs to form alkyl iodides¹⁹.



The rise in temperature increases the rate of phosphorus diiodide formation, but this is accompanied by a sharp increase in the secondary reaction rate.

Thioethers act in the same way as the ethers, but the carbon-sulphur bond is never split and the formation of alkyl iodides is not observed. The case with thiophane illustrates that, as with ethers, the conversion takes place in equilibrium ratio²¹ and proceeds according to the scheme



Diphenyl sulphide and dibenzyl sulphide do not cause the conversion of

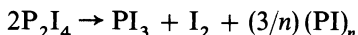
phosphorus triiodide into phosphorus diiodide and don't react with it. This is probably due to the low basicity of diphenyl sulphide and is confirmed by thermochemical data²².

The conversion of phosphorus triiodide into phosphorus diiodide in the reaction with tertiary amines proceeds very easily, but is accompanied by the formation of a large number of highly polymeric substances with low iodine content²¹.

Triphenylphosphine also causes equilibrium ratio conversion of phosphorus triiodide into phosphorus diiodide²³ according to the following schemes:



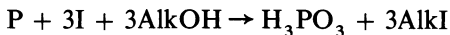
At 175° phosphorus triiodide is converted in equilibrium ratio into phosphorus diiodide and iodine without the action of other reagents, but the conversion is accompanied by a number of secondary irreversible (direct) reactions, in particular, by phosphorus diiodide splitting into phosphorus triiodide, iodine and a polymer of composition PI^{19} .



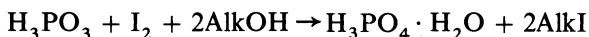
The resultant phosphorus triiodide is converted in equilibrium ratio into phosphorus diiodide which is further decomposed, etc.

It may be that at high temperatures the phosphorus triiodide as such acts as a nucleophilic agent.

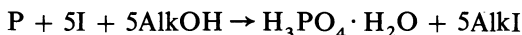
The reaction of phosphorus triiodide with alcohols or reaction of red phosphorus-iodine mixture with alcohols has been used for a long time to obtain alkyl iodides. Over more than 100 years the following scheme was employed^{25, 24}



In fact, if instead of introducing phosphorus triiodide into the reaction, the phosphorus-iodine mixture is used, the reaction doesn't stop at the phosphorous acid and alkyl iodides formation phase. The phosphorous acid is oxidized by iodine to phosphoric acid and the following reaction occurs in the presence of alcohols²⁶



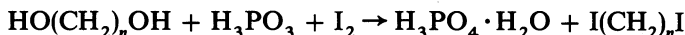
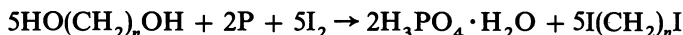
i.e. the reaction between primary and secondary alcohols, phosphorus and iodine proceeds practically quantitatively after the overall scheme²⁶.



With tertiary alcohols the dehydration also occurs, but with the conditions of the reaction slightly changed the tertiary iodides (triiodides) are obtainable in about 75 per cent yield.

Diiodoalkanes are synthesized to give high yields from glycols, iodine and red phosphorus or from glycols, iodine and phosphorous acid²⁷ according to the following schemes:

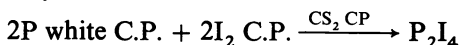
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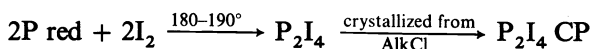
$n = 2-6, 10$.

This is the sum of knowledge at present about the chemistry of phosphorus triiodides.

Tetraiododiphosphine, or briefly phosphorus diiodide, has already been known more than 150 years, but its chemical properties have not been studied adequately. Until recently phosphorus diiodide was obtained, similarly to phosphorus triiodide, from chemically pure white phosphorus and iodine in the solution of chemically pure carbon sulphide^{4, 28}.

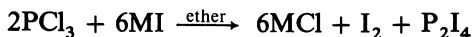


We succeeded in developing a simple and convenient method of phosphorus diiodide synthesis from red phosphorus and iodine without using fire-hazardous solvents; the process can be readily realized on a large scale; this enabled us to start a detailed investigation of the chemical properties of phosphorus diiodides⁶.

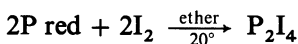
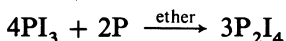
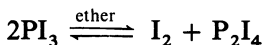


In the past it took an experienced chemist several days to obtain a few grams of phosphorus diiodide, while now an average-skill laboratory assistant can prepare during one day half a kilogram of phosphorus diiodide of considerably higher degree of purity than the one prepared according to the previously used technique. Strange as it may seem, up till now, the only technique reported in the literature abroad is an extremely inconvenient old method²⁸.

Phosphorus diiodide can also be obtained from phosphorus trichloride and alkali-metal iodides in ether or dioxan solution, from phosphorus triiodide using ethers (better in the presence of red phosphorus) or from red phosphorus and iodine in ether solution at 20°. In the latter case the yield is low—about 40 per cent—but the phosphorus diiodide obtained is extremely pure (melting point 126–127°)⁷.



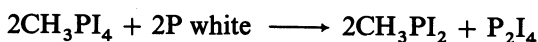
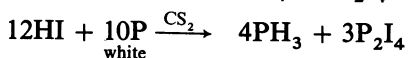
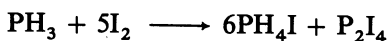
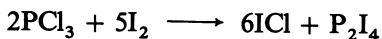
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To obtain dozens of grams of phosphorus diiodide the last of the above-mentioned techniques is the most suitable one, that is alloying phosphorus with iodine followed by crystallization.

Besides, a number of techniques for the synthesis of phosphorus diiodide have been described which have no preparative significance²⁹⁻³².

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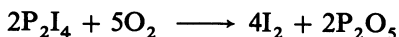


The mechanism of phosphorus diiodide formation from white phosphorus and iodine in carbon disulphide and carbon tetrachloride solutions at 15° has been discussed in a number of reports^{33, 34, 35}, but we believe that for the final judgement the available data are insufficient. It is more probable, that phosphorus diiodide is formed in the conditions mentioned without P—P-bond splitting, but the possibility that it will yield, as intermediate materials, phosphorus triiodide or substances close to it by composition, is not excluded.

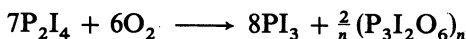
Phosphorus diiodide is crystallized to form beautiful orange needles with a melting point of 126–127°^{6, 7}. The molecule has a monomeric structure in vapour form and in the solution of carbon disulphide^{36, 37}, *trans*-isomeric structure in crystals and solution in carbon disulphide and carbon tetrachloride³⁸. If kept stored dry, the compound will remain without any transformation for an unlimited period of time.

Phosphorus diiodide is a compound of high reactivity. Many of the phosphorus diiodide reactions proceed by an extremely complex scheme, simultaneously in several directions, often leading to materials which are both difficult to split and to identify. Hydrolysis in ice-water gives a complex mixture of elemental phosphorus acids and phosphines^{39, 40}. Oxidative hydrolysis leads to an equally complex mixture of acids in which P—P and P—P—P units have been identified⁴¹. The barium salt of hypodiphosphorous acid has been isolated as a hydrolysis product in buffer barium acetate–acetic acid solution and from it, an extremely unstable free acid was obtained which is readily oxidized by oxygen in air and decomposes at as low a temperature as 20° with the elimination of phosphine^{42, 43}.

Phosphorus diiodide is readily oxidized by oxygen in air, but it is impossible to isolate the simplest products of oxidation—tetraiododiphosphine monoxides and dioxides. Oxidation using oxygen or nitrogen dioxide leads to the formation of iodine and phosphorus pentoxide⁴⁴.

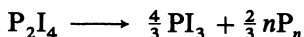


When oxygen reacts in carbon disulphide solution it gives a 60 per cent yield of phosphorus triiodide and an amorphous material of a variable composition, an average value being about $\text{P}_3\text{I}_2\text{O}_6$ ⁸.



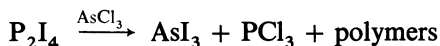
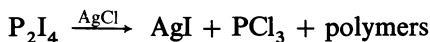
Oxidation in benzene solution at 80° gives a complex mixture of materials⁸.

When phosphorus diiodide is heated within a broad range of temperatures (from 20 to 300°) in an oxygen atmosphere, it is decomposed to form phosphorus pentoxide and iodine, whereas in a nitrogen atmosphere decomposition proceeds according to the scheme⁴⁵

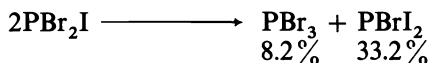
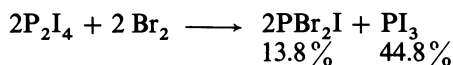


Phosphorus diiodide contains four mobile iodine atoms; their replacement by other atoms and groups leads one to expect the formation of P—P-bonded compounds. In most of these cases, however, the breaking of the P—P bond occurs to form a complex mixture of compounds with one phosphorus atom in a molecule and high-polymeric compounds. Alcohols, phenols and amines give mixtures of compounds from which pure substances could not be isolated⁴⁶.

The reactions with phenylmagnesium bromide lead to a complex mixture of polymers; from oxidation products of the latter small amounts of phenylphosphonic and diphenylphosphinic acids⁴⁷ have been isolated. The reaction with methylmagnesium iodide produces unidentifiable resins and a small amount of tetramethylphosphonium iodide⁴⁸, and by treatment with methyl-lithium a small amount of trimethylphosphine is obtained⁴⁹. With silver chloride⁵⁰ and arsenic trichloride⁵¹ not only are the iodine atoms replaced by the chlorine ones, but the P—P bond splitting occurs as well, that is tetra-chlorodiphosphine is not formed, but even if it is, it is immediately decomposed.

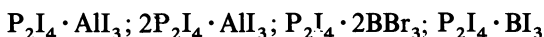


When bromine reacts with phosphorus diiodide, phosphorus triiodide and iodobrominophosphine are obtained of which the latter disproportionates to give phosphorus tribromide and diiodobrominophosphine⁵².

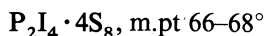


Diiodobrominophosphine is the only material which has been isolated as a pure compound; it presents cherry red crystals with a melting point of 8–12°. The amounts of the other products of the reaction were determined by means of indirect analyses and physical methods.

A series of phosphorus diiodide salts was obtained with Lewis acids^{53, 14}, for instance:

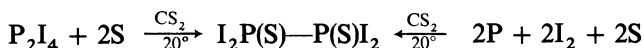


Phosphorus diiodide-sulphur complex and tetraiodoethane-sulphur complex $\text{C}_2\text{I}_4 \cdot 4\text{S}_8$ are isomorphous^{54, 55}



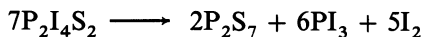
A few reactions of phosphorus diiodide proceeding without the P—P bond splitting are known.

Of considerable interest is the reaction with sulphur proceeding in carbon disulphide solution, which results in the formation of tetraiododiphosphine disulphide also prepared from elements in carbon disulphide solution

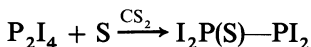


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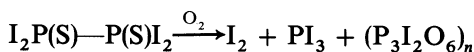
Tetraiododiphosphine disulphide presents orange crystals, m.pt 93–94°, with decomposition; it is stored without transformation at 20° in a helium atmosphere, in the dark for a period of one to two days. Then decomposition occurs and after 25 days P—P-bond frequencies completely disappear from the infra-red spectrum and are replaced by those of phosphorus triiodide and phosphorus sulphide. In the visible and ultra-violet spectrum the transformation rapidly proceeds according to the scheme^{56, 57}



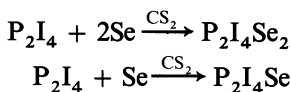
With a sulphur atom reacting with phosphorus diiodide in carbon disulphide solution a monosulphide is obtained—red crystals, m.pt 105–110° (with decomposition) which by its chemical properties is close to disulphide⁵⁶



When oxygen reacts with both the phosphorus diiodide sulphides, sulphur atoms are replaced by oxygen to give, instead of the corresponding oxides, iodine, phosphorus triiodide and a polymer of composition $\text{P}_3\text{I}_2\text{O}_6$ ⁵⁶.

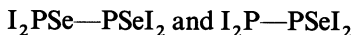


In boiling carbon disulphide phosphorus diiodide reacts with red elemental selenium in a molar ratio of 1:2 or 1:1 to form a reddish-brown solution from which, upon its being cooled down to –20°, brown-black crystals of phosphorus diiodide diselenide or monoselenide are recrystallized, respectively

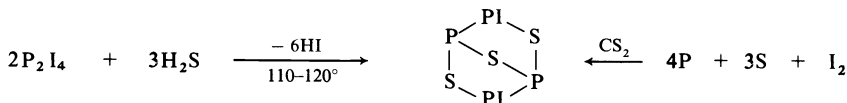


Being melted, dissolved or exposed to daylight both substances mentioned above are decomposed to form phosphorus triiodide, iodine, and some phosphorus- and selenium-containing compounds⁵⁸.

The structure of phosphorus diiodide selenides is as follows⁵⁸

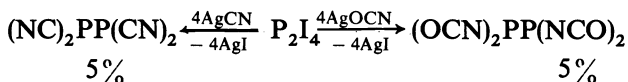


An interesting substance is obtained from phosphorus diiodide and hydrogen sulphide or from elements, in which the *trans*-isomeric structure of tetraiododiphosphine is transformed into a *cis*-isomeric structure^{59, 60, 61}

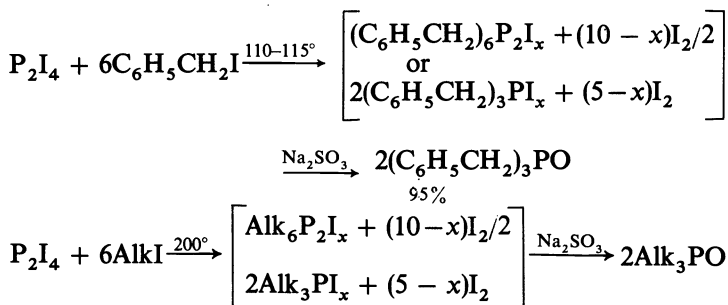


The reaction of phosphorus diiodide with silver cyanate and cyanide

results in the production of tetrakisocyanate- and tetracyan-diphosphines in small yields⁶²



The way in which phosphorus diiodide reacts with alkyl halides is very peculiar and complex. The interaction of benzyl iodide or lower alkyl iodides leads to complex compounds which, when decomposed by sodium sulphite and alkali, will be converted to triphosphine oxides in high yields⁶³:



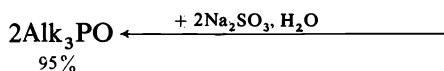
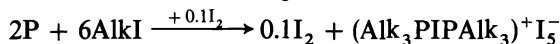
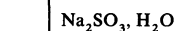
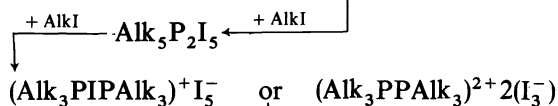
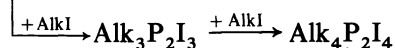
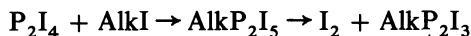
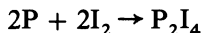
Since the reaction proceeds with phosphorus diiodide formation and is accompanied by free iodine elimination, there is no need to use finished phosphorus diiodide; red phosphorus and a small amount of iodine can be used instead to form a small quantity of phosphorus diiodide to allow initiation of the reaction.

During the further investigation of phosphorus diiodide alkylation with various alkyls optimum reaction conditions were found and the effect of the nature of the alkyls on the reaction rate was determined. With normal alkyl iodides having 7-9 carbon atoms the reaction is accomplished within 10-12 h at 200-210°.

With increasing molecular weight of alkyl iodides and for alkyl iodides of iso-structure the reaction rate decreases. The reaction rate is not increased when employing u.v. illumination or adding radical formation initiators. In phosphorus diiodide electron paramagnetic spectra, as well as in phosphorus diiodide-alkyl iodide mixtures and in mixtures of red phosphorus, alkyl iodides and iodine no signal of electron paramagnetic resonance was found at 25-250°. The reaction rate is considerably increased as a result of addition of the finite product of phosphorus diiodide alkylation with the same or any other alkyl iodide. Thus, phosphorus diiodide alkylation is an autocatalytic reaction and, in all likelihood, has an ionic and not a radical mechanism.

A series of special experiments have proved that alkylation of a red phosphorus-iodine mixture proceeds through the phosphorus diiodide formation stage⁶⁴⁻⁷⁰.

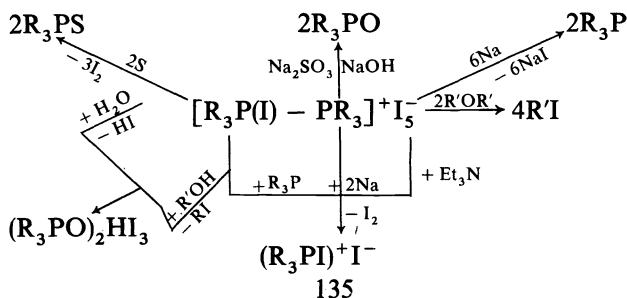
Considering what has been said above, the following scheme is proposed for the synthesis of triphosphine oxides from phosphorus diiodide and alkyl iodides or from red phosphorus and alkyl iodides in the presence of small quantities of iodine^{71, 72}:



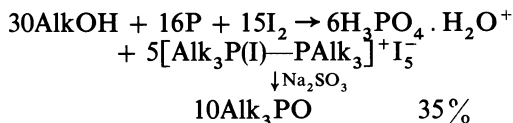
It is probable that one or two alkyl iodide molecules combine with phosphorus diiodide, which is followed by iodine elimination resulting in the conversion of the phosphorus atom back to its trivalent and nucleophilic state. The elimination of iodine probably occurs because the $\text{P}^{\text{V}}\text{—I}$ bond is not remunerative (due to its being unstable).

Not a single intermediate product has been isolated, which is quite reasonable since in every succeeding product the phosphorus atom is to be more nucleophilic than in the previous one and, consequently, every succeeding reaction is to proceed more rapidly than the previous one. In some cases finite products have been isolated as pure compounds. Based on molecular weight, electrical conductivity, electron paramagnetic resonance spectroscopy, elemental chemical composition and chemical transformation data, their structure is identical to that of pentaiodated hexaalkylidodiphosphorane-phosphoniums or bis-triiodated hexaalkyl-diphosphoniums. So far preference has not been given to either of the two formulas.

Pentaiodated hexaalkylidodiphosphorane-phosphoniums are crystal- or oil-like substances of brown or red-violet colour. They possess high reactivity and react easily with water, alcohols, ethers, trialkylphosphines, metals and sulphur. In general, reactions result in high yields and occasionally make it possible readily to obtain the compounds which are not easily accessible^{70, 73-78}.

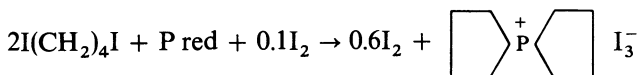
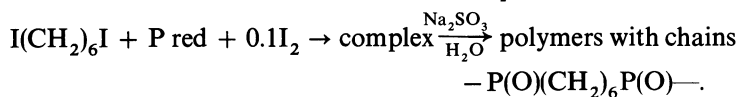
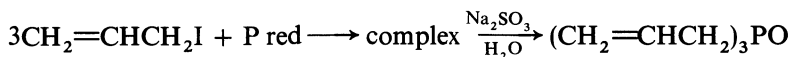


Even in early experiments in phosphorus diiodide alkylation it was observed that the hydrolysis of the reaction products gives, along with a large number of tertiary phosphine oxides, a small amount of phosphinic and phosphonic acids. Detailed research in the elaboration of convenient techniques for the preparation of phosphine oxides has proved that phosphine oxides can be obtained directly from alcohols without isolating alkyl iodides, that is by red phosphorus alkylation with alcohols in the presence of iodine⁷⁰.



In this case, however, besides tertiary phosphine oxides large amounts of alkylphosphonic acids (from alcohols with 5–10 carbon atoms—up to 52 per cent) or dialkyl phosphinic acids (from alcohols with 3–4 carbon atoms—up to 50 per cent) are obtained. The formation of phosphonic and phosphinic acids is probably explained by the fact that the hydrate of phosphoric acids obtained in the first reaction stage either interrupts alkylation after one or two alkyls have combined with the phosphorus atom, or interacts with phosphorus diiodide to form a complex in which the phosphorus atom combines with only one or two alkyls.

Undoubtedly, during the alkylation of red phosphorus with allyl iodide⁷⁹, 1,6-diiodohexane⁸⁰, or 1,4-diiodobutane⁸¹ the alkylation of phosphorus diiodide actually occurs, the latter being formed as an intermediate product.



It is likely that in all cases when C—P-bonded compounds are formed from C—I-bonded compounds and red or white phosphorus, phosphorus diiodide will be obtained as an intermediate product, if the reaction proceeds at a temperature up to 250°, e.g. during phosphorylation of iodo-fluorocarbons^{82, 83}.

Particularly interesting heterocyclic phosphorus-containing perfluorides obtained from unsaturated perfluorocarbons and red phosphorus in the presence of iodine are probably also formed as a result of phosphorus diiodide alkylation with iodo-fluorocarbons, which are intermediate products of the reaction^{84–86}.

In recent years the chemistry of phosphorus iodides has made significant progress.

First, simple and convenient techniques have been developed for the preparation of the simplest phosphorus iodides, the triiodide and diiodide, which until recently were considered virtually inaccessible, and now can be obtained readily in any desired quantity.

Secondly, several new quite unexpected reactions of phosphorus iodides have been found. Of particular significance and interest is the phosphorus triiodide equilibrium ratio conversion into phosphorus diiodide in the most liberal (mild) conditions, with ethers, sulphides, amines, tertiary phosphines and phosphites at a temperature such as 10°, and the formation of various interesting phosphorus diiodide sulphides.

Another new striking feature of phosphorus iodides is as follows: the Arbuzov and the Michaelis-Becker reactions make it possible to obtain from trivalent phosphorus compounds pentavalent ones with one additional phosphorus-carbon bond, and with phosphorus diiodide alkylation second and third phosphorus-carbon bonds are automatically formed, more rapidly than the first one. Actually, phosphorus diiodide alkylation implies the extension of limits for the employment of the Arbuzov reaction; it is a special modification of the Arbuzov reaction, which does not stop at the trivalent phosphorus monoalkylation stage, and owing to the peculiar properties of the phosphorus-iodine bond reaches the trialkylation stage.

No less important and interesting are the new types of compounds which have been obtained in the course of investigative work in the chemistry of phosphorus iodides. Those are pentaiodated hexaalkyl-iodophosphorane-phosphoniums or bis-triodated hexaalkyl-diphosphoniums, highly stable complexes of two trialkyl-phosphine oxide molecules with triiodohydrogen, and numerous iodophosphorane derivatives having a variety of properties.

Some peculiar features of the phosphorus iodides compared with other phosphorus halides are explained in the first place by a large iodine atomic radius and, probably, by the much greater capability of iodine atom vacant orbitals to form bonds in the intermediate products of the reactions. More substantiated, more general or more profound conclusions cannot be made for the time being—there is too little factual material in the chemistry of phosphorus iodides.

It is necessary to continue research in new phosphorus iodide reactions, new forms of phosphorus iodides and, especially, in the investigation of the physical properties of phosphorus iodides and their mechanisms of reaction, which is being pursued now.

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