Translated from *Uspekhi Khimii* **58** 1869–1895 (1989) U.D.C. 547.241 + 547.239

Phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates

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ABSTRACT. In this review the information in the literature on the methods of synthesis, physicochemical properties, and application of phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates has been classified and correlated.

The bibliography includes 143 references.

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I. Introduction

Alkyl and aryl isocyanates have been known for over a hundred years. The first examples of phosphorus-containing organic isocyanates were not synthesised until 1956.[1] In recent years a considerable number of new types of alkyl and aryl isocyanates containing one or more phosphorus atoms in the molecule have been obtained and some of their properties have been studied. In 1973 a short review was published on phosphorus-containing alkyl, aryl, acyl, and sulphonyl isocyanates, including studies carried out before 1971;[2] it is now out of date. It is therefore of interest to correlate both the old and new information on the methods of synthesis and properties of phosphorus-containing organic isocyanates.

II. Methods of synthesis

1. Phosphorus-containing alkyl, alkenyl, and aryl isocyanates

(a) Reactions of chloroalkyl phosphates and chlorophosphoramidates with silver cyanate

On heating tris(trichloromethyl)phosphate with silver cyanate in benzene, tris(isocyanatomethyl)phosphate is formed:[3]

$$OP(OCH_2Cl)_3 + 3AgOCN \rightarrow 3AgCl + OP(OCH_2NCO)_3.$$

Diethyl 1,2,2,2-tetrachloroethylphosphoramidate reacts with silver cyanate by a similar route, but it is not possible to obtain the resulting diethyl 1-isocyanato-2,2,2-trichloroethylphosphoramidate in a pure form.[4]

(b) Phosgenation of phosphorus-containing amines and *N*-phosphorylated amidines

Diesters of α-aminoalkylphosphonic and α-aminoalkylphosphonothioic acids react fairly readily with phosgene, and depending on the concentration of the reactants they form either diesters of α-isocyanato-substituted alkylphosponic and alkylphosphonothioic acids or *N*,*N*′-bis[α-(dialkoxyphosphoryl)alkyl]ureas:[1,5]

$$(C_2H_5O)_2P(X)CRR^1NH_2 \xrightarrow{COCl_2} \begin{cases} \xrightarrow[X=O,\,S]{3:1} (C_2H_5O)_2P(X)CRR^1NCO \\ \xrightarrow[X=O]{4:1} [(C_2H_5O)_2P(X)CRR^1NH]_2CO \end{cases}$$

X = O: R = R^1 = CH_3 or R = H, R^1 = C_6H_5; X = S: R = R^1 = CH_3.

The aminophosphonate and aminophosphonothioate diesters required for these syntheses are obtained from dialkyl phosphites (or dialkyl phosphorothioites), aldehydes (or ketones), and ammonia:[5–7]

$$(C_2H_5O)_2P(X)H + RC(O)R^1 + NH_3 \rightarrow (C_2H_5O)_2P(X)CRR^1NH_2.$$

Esters of α-(dialkoxyphosphoryl)aminoacetic acid react with phosgene in a similar manner[8] to form the corresponding isocyanates.[9]

Treatment of (*S*)-(−)-α-(diethoxyphosphoryl)benzylamine with phosgene[10–12] in the presence of pyridine resulted in the synthesis of the first example of optically active α-phosphorylated organic isocyanates—(*S*)-(+)-α-(diethoxyphosphoryl)benzyl isocyanate ($[\alpha]_D^{20}$ + 35.5°, *c* = 2, CCl_4).[12–14]

When aminoaryl esters of phosphoric, phosphorothioic, phosphonic, phosphonothioic, and phosphinothioic acids are reacted with phosgene in inert organic solvents at 50–120 °C, isocyanatoaryl esters of the corresponding phosphorus acids are obtained:[15–23]

$$XP(OC_6H_4NCO\text{-}4)_3,\quad (C_2H_5O)_2P(X)OC_6H_4NCO\text{-}4 \quad (\text{where } X = O, S),$$

$$C_6H_5N(CH_3)P(O)(OC_6H_4NCO\text{-}4)_2,\quad C\left[\begin{array}{c}CH_2O\\ \diagdown\\ \diagup\\ CH_2O\end{array}\!\!>P(O)OC_6H_4NCO\text{-}4\right]_2,$$

$$C_6H_5CH{=}CHP(O)(OC_6H_3CH_3\text{-}4\text{-}NCO\text{-}3)_2,$$

$$(CH_3)_nP(S)(OC_6H_3CH_3\text{-}4\text{-}NCO\text{-}3)_{3-n}.$$

When *O*,*O*′-bis(4-aminophenyl)-*N*,*N*-dimethylphosphoramidate is treated with phosgene, cleavage of the P–N bond occurs together with phosgenation of the amino group and *O*,*O*′-bis(4-isocyanatophenyl)phosphorochloridate is formed:[20]

$$(CH_3)_2NP(O)(OC_6H_4NH_2\text{-}4)_2 \xrightarrow[-4HCl]{COCl_2} ClP(O)(OC_6H_4NCO\text{-}4)_2 + (CH_3)_2NCOCl.$$

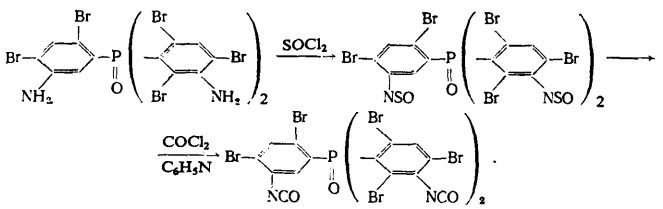
When phosgene reacts with aminoaryl phosphites the P—O bond is cleaved and isocyanatoaryl phosphites are not formed.[20]

Aminoaryl esters of phosphorus acids are obtained by reduction of the corresponding nitroaryl esters, by reaction of phosphorus acid chlorides with aminophenol, or by oxidation of aminoaryl phosphites.[16–18,20,24,25] Tris(*p*-nitrophenyl) phosphate is obtained by nitration of triphenyl phosphate. Nitrophenyl esters of other phosphorus acids are obtained by reaction of phosphorus acid chlorides with nitrophenols.[17,18,20,24]

Hexa(4-isocyanatophenoxy)triphosphonitrile is synthesised by phosgenation of hexa(4-aminophenoxy)triphosphonitrile:[26]

$$(P_3N_3)(OC_6H_4NH_2\text{-}4)_6 \xrightarrow{COCl_2} (P_3N_3)(OC_6H_4NCO\text{-}4)_6.$$

The conversion of aminoarylphosphine oxides to isocyanatoarylphosphine oxides by phosgenation of the intermediate $-N=S=O$ compounds has been reported:[27]



When *N*-(diphenoxyphosphoryl)benzamidine is boiled with phosgene, *N*-(diphenoxyphosphoryl)iminobenzoyl isocyanate $C_6H_5C[=NP(O)(OC_5H_5)_2]NCO$ is obtained.[28]

(c) Reaction of haloalkyl isocyanates with alkyl esters of trivalent phosphorus acids

Trialkyl phosphites and alkyl phosphinites undergo an Arbuzov rearrangement with chloromethyl isocyanate at –20 °C to form dialkoxy-, dialkyl-, or diaryl-phosphorylmethyl isocyanates.[29–32] When chloromethyl isocyanate reacts with alkyl phosphoro-dichloridites, alkyl phosphorodifluoridites, dialkyl phosphorochloridites, and dialkyl phosphorofluoridites, dihalophosphoryl- and alkoxy-halophosphoryl-methyl isocyanates are obtained. Reactions with dialkyl phosphorohalidites occur both in the presence of catalytic quantities of $FeCl_3$ and without it, while alkyl phosphorodihalidites react only in the presence of a catalyst.[30,32–35] Bromomethyl isocyanate also reacts in a similar manner with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphorodihalidites, but the reaction takes place under milder conditions:[14,35,36]

$$R_2POR^1 + XCH_2NCO \longrightarrow [R_2(R^1O)PCH_2NCO]^+X^- \xrightarrow{-R^1X} R_2P(O)CH_2NCO,$$
$$R = AlkO,\ Alk,\ Ar;\quad X = Cl,\ Br;$$
$$ROPX_2 + YCH_2NCO \xrightarrow[-RY]{FeCl_3} X_2P(O)CH_2NCO;$$
$$(RO)_2PX + YCH_2NCO \xrightarrow{-RY} X(RO)P(O)CH_2NCO,$$
$$R = Alk;\quad X = Cl,\ F;\quad Y = Cl,\ Br.$$

α,β-Dichloro- and α,β-dibromo-methyl isocyanates react with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphorodihalidites to form only α-phosphorylated β-chloro- or β-bromo-ethyl isocyanates. The reaction with alkyl phosphoro-dihalidites only takes place in the presence of catalysts. The halogen atoms at the β-position of these isocyanates are much less active and do not undergo reaction.[14,35,37–40]

α-Chlorobenzyl isocyanate undergoes a reaction with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphoro-dihalidites in a similar manner to chloromethyl isocyanate but under slightly more severe conditions.[14,35,41]

Diphenylchloromethyl isocyanate exists as a tautomeric mixture with *N*-chlorocarbonyldiphenylketimine and on reacting with ethyl diaryl phosphites gives two isomeric products in approximately equal quantities—α-(diaryloxyphosphoryl)diphenylmethyl isocyanate and the *N*-benzhydrylidenamide of phosphonoformic acid:[14,42,43]

$$\begin{array}{l}(C_6H_5)_2C(Cl)NCO \\ \quad\quad\uparrow\downarrow \\ (C_6H_5)_2C=NCOCl\end{array} \xrightarrow{C_2H_5OP(OAr)_2} (ArO)_2P(O)C(C_6H_5)_2NCO + \\ + (C_6H_5)_2C=NCOP(O)(OAr)_2.$$

In contrast to diphenylchloromethyl isocyanate, 1-chloro-1-phenyl-2,2,2-trifluoroethyl isocyanate exists only in the isocyanate form and when it reacts with triphenyl phosphite gives only the isocyanate:[44]

$$(C_2H_5O)_3P + C_6H_5CCl(CF_3)NCO \xrightarrow[-C_2H_5Cl]{} (C_2H_5O)_2P(O)C(C_6H_5)(CF_3)NCO.$$

It was reported[45] that when 1,2,2,2-tetrachloroethyl isocyanate is reacted with triethyl phosphite in carbon tetrachloride, 1-(diethoxyphosphoryl)-2,2,2-trichloroethyl isocyanate is obtained in good yield. It was later established that when this isocyanate is reacted with trialkyl phosphites and dialkyl phosphorohalidites, a mixture of 1-(dialkoxyphosphoryl)- or 1-(alkoxyhalophosphoryl)-substituted 2,2,2-trichloroethyl and 2,2-dichlorovinyl isocyanates is formed:[46]

$$(RO)_2PX + CCl_3CHClNCO \rightarrow X(RO)P(O)CH(CCl_3)NCO + \\ + X(RO)P(O)C(=CCl_2)NCO,$$
$$X = RO,\ Cl,\ F;\quad R = Alk.$$

Unsaturated α-chlorovinyl isocyanate undergoes an Arbuzov reaction with triethyl phosphite in the same way as α-chloroalkyl isocyanates but the reaction takes place under more severe conditions:[47]

$$(C_2H_5O)_3P + CH_2=CClNCO \longrightarrow (C_2H_5O)_2P(O)C(=CH_2)NCO.$$

Dichloro- and trichloro-methyl isocyanates also readily undergo an Arbuzov rearrangement with phosphites, dialkyl phosphoro-halidites, and alkyl phosphorodihalidites. Under normal conditions dichloromethyl isocyanate exists as a tautomeric mixture with *N*-chloromethylenecarbamoyl chloride; this has been confirmed from its IR spectra. In the reaction with trialkyl phosphite nucleophilic attack by the phosphorus atom is directed on to both the carbon atom of the dichloromethyl group and the carbon atom of the chlorocarbonyl group so that a mixture of at least two products is formed. Only the isocyanate was isolated by vacuum fractionation:

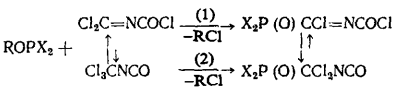
$$\begin{array}{l}Cl_2CHNCO \\ \quad\quad\uparrow\downarrow \\ ClCH=NCOCl\end{array} \xrightarrow{(C_2H_5O)_3P} (C_2H_5O)_2P(O)CHClNCO + \\ + ClCH=NC(O)P(O)(OC_2H_5)_2.$$

Reaction of dichloromethyl isocyanate with 2 moles of triethyl phosphite results in the formation of the bis-phosphorylated methyl isocyanate $[(C_2H_5O)_2P(O)]_2CHNCO$.[32,48]

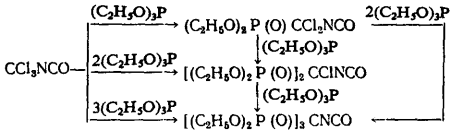
Diethyl phosphorofluoridite reacts with dichloromethyl isocyanate without a catalyst and depending on the ratio of the reactants (1 : 1 or 2 : 1) either ethoxyfluorophosphorylchloromethyl isocyanate or bis(ethoxyfluorophosphoryl)methyl isocyanate are formed.[32,35,49,50]

When dichloromethyl isocyanate reacts with diethyl phosphoro-chloridite, ethoxychlorophosphorylchloromethyl isocyanate is formed; in this case the second chlorine atom cannot be replaced by a phosphoryl group.[32,35,50] Dichloromethyl isocyanate reacts with alkyl phosphorodichloridites and phosphorodifluoridites in a similar manner to chloromethyl isocyanate, forming dihalophosphoryl-chloromethyl isocyanates.[32,35,50,51]

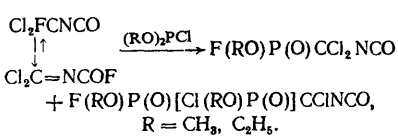
Under normal conditions trichloromethyl isocyanate exists in its tautomeric form—*N*-(dichloromethylene)carbamoyl chloride. On heating, the equilibrium is displaced towards the isocyanate form. When the tautomeric mixture reacts with alkyl phosphorodihalidites in the presence of catalytic quantities of $FeCl_3$, dihalophosphoryl-dichloromethyl isocyanates are obtained, and their formation can be represented by two routes.[32,52,53]



Depending on the ratio of the reactants (1 : 1 or 2 : 1), trichloromethyl isocyanate reacts with diethyl phosphorochloridite to form a mixture of mono- and bis-phosphorylated chloromethyl isocyanates or only bis-phosphorylated chloromethyl isocyanate. When diethyl phosphorofluoridite reacts with trichloromethyl isocyanate, only bis(ethoxyfluorophosphoryl)chloromethyl isocyanate can be isolated, whatever the ratio of the reactants (1 : 1, 2 : 1, or 3 : 1).[32,35,53] Trichloromethyl isocyanate reacts with one, two, and three moles of triethyl phosphite to form diethoxyphosphoryl-dichloromethyl, bis(diethoxyphosphoryl)chloromethyl, and tris(diethoxyphosphoryl)methyl isocyanates respectively. Bis- and tris-phosphorylated alkyl isocyanates are also obtained by reaction of mono- and bis-phosphorylated haloalkyl isocyanates with a suitable quantity of triethyl phosphite:[32,35,54]

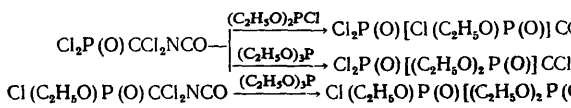


Dichlorofluoromethyl isocyanate, which exists mainly in the form of *N*-(dichloromethylene)carbamoyl fluoride (1 : 14), reacts with dialkyl phosphorochloridites in an interesting manner. In addition to formation of the expected alkoxychlorophosphorylchlorofluoro-methyl isocyanate and bis(alkoxychlorophosphoryl)fluoromethyl isocyanate, as in the case of the reaction with trichloromethyl isocyanate, a mixture of alkoxyfluorophosphoryldichloromethyl isocyanate and alkoxyfluorophosphoryl(alkoxychlorophosphoryl)chloromethyl isocyanate is formed with the latter predominating:[55]



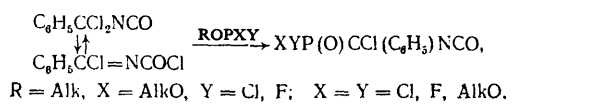
Tribromomethyl isocyanate reacts with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphorodihalidites in a similar manner to trichloromethyl isocyanate. However, it was only possible to isolate dichlorophosphoryldibromomethyl isocyanate $Cl_2P(O)CBr_2NCO$, tris(diethoxyphosphoryl)methyl isocyanate $[(C_2H_5O)_2P(O)]_3CNCO$, and difluorophosphoryldibromomethyl isocyanate $F_2P(O)CBr_2NCO$, in a pure form, with a small quantity of initial Br_3CNCO present.[40]

Dichlorophosphoryl- and ethoxychlorophosphoryl-dichloromethyl isocyanates also react with 1 mole of diethyl phosphorochloridite or triethyl phosphite to form mixed bis-phosphorylated chloromethyl isocyanates.[32,53]

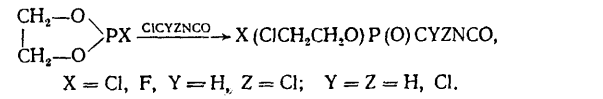


Ethoxyfluorophosphoryldichloromethyl isocyanate reacts with diethyl phosphorochloridite in a similar manner:[55]

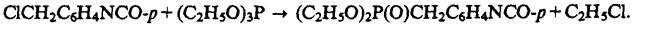
α,α-Dichlorobenzyl isocyanate reacts with esters and halide esters of trivalent phosphorus acids in a similar manner to α-chlorobenzyl isocyanate to form α-phosphorylated α-chlorobenzyl isocyanates. The reaction of α,α-dichlorobenzyl isocyanate with two (or more) moles of alkyl phosphorodichloridite or phosphorodifluoridite occurs with replacement of only a single chlorine atom by a dihalophosphoryl group, while when it is reacted with two moles of dialkyl phosphorohalidite or trialkyl phosphite a complex mixture is formed, from which pure compounds could not be isolated:[56]



The cyclic phosphites—2-chloro- and 2-fluoro-phospholanes—undergo an Arbuzov reaction with chloro-, dichloro-, and trichloro-methyl isocyanates with ring-opening:[32,35,57]

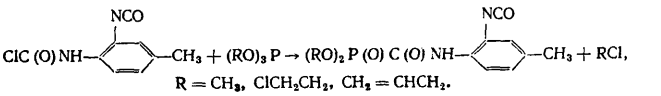


In contrast to α-chloroalkyl isocyanates, *p*-chloromethylphenyl isocyanate reacts with triethyl phosphite under more severe conditions (150–160 °C) without a solvent and *p*-(diethoxy-phosphorylmethyl)phenyl isocyanate is obtained in low yield:[30,31]

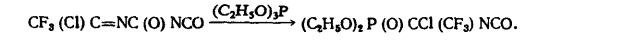


1-Chloromethyl- and 1-bromomethyl-2,4-diisocyanatobenzenes and bis(4-isocyanatophenyl)chloromethane also undergo an Arbuzov reaction with trialkyl phosphites but the corresponding isocyanates cannot be isolated as they probably polymerise in the presence of trialkyl phosphites.[20,58,59]

It should be mentioned that *N*-(isocyanatoaryl)carbamoyl chlorides also undergo a reaction with trialkyl phosphites, forming the corresponding phosphorus-containing aryl isocyanates:[20,60,61]



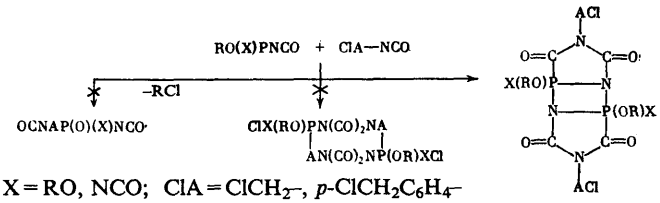
When *N*-(1-chloro-2,2,2-trifluoroethylidene)carbamoyl isocyanate reacts with triethyl phosphite, an isocyanate group rather than a chlorine atom is eliminated and 1-(diethoxyphosphoryl)-1-chloro-2,2,2-trifluoroethyl isocyanate is formed:[62,63]



N-(1-Methoxy-2,2,2-trifluoroethylidene)carbamoyl isocyanate reacts with triethyl phosphite in a similar manner.[62,63]

Chloromethyl isocyanate and *p*-chloromethylphenyl isocyanate also undergo a reaction with dialkyl phosphoroisocyanates and alkyl phosphorodiisocyanates but the products of Arbuzov rearrangement are not obtained. It was earlier suggested that quasiphosphonium compounds of dimeric structure are formed.[29,30,64] It was subsequently

established that tricyclic 1,3,2λ⁵4λ⁵-diazadiphosphetidine derivatives are obtained as a result of this reaction:[14,65–67]



X = RO, NCO; ClA = $ClCH_2$–, *p*-$ClCH_2C_6H_4$–

(d) Reaction of diaryl phosphites with α-chloroalkyl isocyanates

Diaryl phosphites readily react with a tautomeric mixture of diarylchloromethyl isocyanate with *N*-chlorocarbonyldiarylketimine in the presence of triethylamine to form diaryloxyphosphoryldiarylmethyl isocyanates:[42,43,68]

$$\begin{matrix} Ar_2C{=}NCOCl \\ \downarrow\uparrow \\ Ar_2C(Cl)NCO \end{matrix} + (Ar^1O)_2P(O)H \xrightarrow[-(C_2H_5)_3N{\cdot}HCl]{(C_2H_5)_3N} (Ar^1O)_2P(O)C(Ar)_2NCO.$$

(e) Reaction of chloroalkyl isocyanates with phosphorothioic acids

Chloromethyl isocyanate reacts with the potassium salts of *O,O'*-dialkylphosphorothioic and *O,O'*-dialkylphosphorodithioic acids to form the corresponding phosphorylated isocyanates:[29,69]

$$ClCH_2NCO + (RO)_2P(X)SK \rightarrow (RO)_2P(X)SCH_2NCO + KCl,$$
$$X = O, S.$$

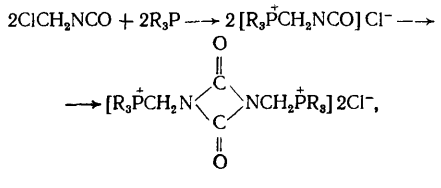
1-Chloro-1-phenyl-2,2,2-trifluoroethyl isocyanate reacts with *O,O'*-diisopropylphosphorodithioic acid in a similar manner.[44]

In contrast to chloromethyl and 1-chloro-1-phenyl-2,2,2-trifluoroethyl isocyanates, a tautomeric mixture of diphenylchloromethyl isocyanate and *N*-chlorocarbonyldiphenylketimine when reacted with *O,O'*-dialkylphosphorodithioic acids or their salts gives *O,O'*-dialkyl-*S*-(*N*-diphenylmethylenecarbamoyl)phosphorodithioates, which only in solution occur in tautomeric equilibrium with the corresponding isocyanates.[43,70]

$$\begin{matrix} (C_6H_5)_2C{=}NCOCl \\ \downarrow\uparrow \\ (C_6H_5)_2CClNCO \end{matrix} \xrightarrow{(RO)_2P(S)SH} \begin{matrix} (C_6H_5)_2C{=}N{-}C(O)SP(S)(OR)_2 \\ \downarrow\uparrow \\ (RO)_2P(S)SC(C_6H_5)_2NCO \end{matrix}$$

(f) Reaction of α-haloalkyl isocyanates with trialkyl- and triaryl-phosphines

Trialkyl- and triaryl-phosphines react very readily with chloromethyl isocyanate in inert solvents to form trialkyl- or triaryl-(isocyanatomethyl)phosphonium chlorides. Depending on the structure of the initial tertiary phosphines and also the reaction conditions and conditions for isolating the reaction products, either substituted isocyanatomethylphosphonium chlorides or their dimers can be obtained. In the case of triarylphosphines, both monomeric and dimeric products were obtained in a pure state, while in the case of trialkylphosphines only pure dimers were obtained:[29,71]



R = C_3H_7, C_8H_{17}, $C_{10}H_{21}$, C_6H_5, *p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$.

Bromomethyl isocyanate[36] and α-chlorobenzyl isocyanate[41,72] react in a similar manner with triphenylphosphine to form triphenyl(isocyanatomethyl)phosphonium bromide and triphenyl-(α-isocyanatobenzyl)phosphonium chloride.

It has not been possible to synthesise triaryl(isocyanatomethyl)-phosphonium iodides by this method since iodomethyl isocyanate, which is required for their synthesis, has not been prepared up to the present time. Attempts to obtain iodomethyl isocyanate demonstrated that it is very unstable and decomposes as it is being formed with considerable elimination of free iodine. Another method was used to synthesise triaryl(isocyanatomethyl)phosphonium iodides. On heating triaryl(isocyanatomethyl)phosphonium chlorides with methyl iodide in methylene chloride (45–60 °C, 1–2 h), chlorine is exchanged for iodine and triaryl(isocyanatomethyl)phosphonium iodides are obtained. For the purpose of preparative synthesis there is no need to obtain and isolate triaryl(isocyanatomethyl)phosphonium chlorides in a pure form. It is sufficient to add triarylphosphine to a mixture of chloromethyl isocyanate and methyl iodide and heat the reaction mixture:[73]

$$\left.\begin{matrix} [Ar_3\overset{+}{P}CH_2NCO]Cl^- + CH_3I \\ Ar_3P + ClCH_2NCO + CH_3I \end{matrix}\right\rightarrow [Ar_3\overset{+}{P}CH_2NCO]I^- + CH_3Cl.$$

(g) Reaction of *N*-phosphorylated aziridines with chloromethyl isocyanate

When *N*-(dialkoxyphosphoryl)- and *N*-(tetraethyldiamino-phosphoryl)aziridines are reacted with chloromethyl isocyanate, the aziridine ring readily opens and *N*-phosphorylated aminomethyl isocyanates are formed:[74–76]

$$R_2P(O)N\begin{matrix}CH_2\\|\\CH_2\end{matrix} + ClCH_2NCO \rightarrow \begin{matrix}R_2P(O)N{-}CH_2NCO\\|\\CH_2CH_2Cl\end{matrix}$$

R = CH_3O, C_2H_5O, iso-C_3H_7, $(C_2H_5)_2N$.

(h) Reaction of phosphorus pentachloride with vinyl isocyanates

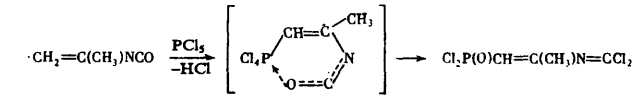
Vinyl isocyanate reacts with phosphorus pentachloride in the ratio 1 : 2 to form 2-(*N*-chlorocarbonylamino)vinyltrichloro-phosphonium hexachlorophosphorate, treatment of which with sulphur dioxide gives 2-(dichlorophosphoryl)vinylcarbamoyl chloride. The latter on heating under vacuum or by treatment with tertiary amines eliminates hydrogen chloride and is converted to 2-(dichlorophosphoryl)vinyl isocyanate:[77–80]

$$CH_2{=}CHNCO + PCl_4^+Cl^- \rightarrow [Cl_4PCH_2\overset{+}{C}HNCO]Cl^- \xrightarrow{-HCl}$$
$$\rightarrow [Cl_4PCH{=}CHNCO] \xrightarrow{PCl_5} [Cl_6\bar{P}Cl_3\overset{+}{P}CH{=}CHNCO] \xrightarrow{HCl}$$
$$\rightarrow [Cl_3PCH{=}CHNHCOCl]^+PCl_6^- \xrightarrow[-POCl_3,\ -SOCl_2]{SO_2}$$
$$\rightarrow Cl_2P(O)CH{=}CHNHCOCl \xrightarrow[-HCl]{} Cl_2P(O)CH{=}CHNCO.$$

When 2-(*N*-chlorocarbonylamino)vinyltrichlorophosphonium hexachlorophosphorate is treated with excess hydrogen sulphide or the calculated quantity of potassium xanthate, 2-(dichlorophosphoro-thioyl)vinyl isocyanate is obtained:[78,79]

$$[Cl_3PCH{=}CHNHCOCl]^+PCl_6^- \xrightarrow{H_2S \text{ or } CH_3OCSSK} Cl_2P(S)CH{=}CHNCO.$$

In contrast to vinyl isocyanate, 1-methylvinyl isocyanate reacts with phosphorus pentachloride in a 1 : 1 ratio of reactants to form *N*-[2-(dichlorophosphoryl)-1-methylvinyl]iminocarbonyl dichloride:[80,81]



It should be mentioned that the analogous dichloride is obtained on boiling 2-(*N*-chlorocarbonylamino)vinyltrichlorophosphonium hexachlorophosphorate in benzene or by treatment of it with methyl phosphorodichloridite at 60 °C:[80–82]

$$[Cl_3PCH{=}CHNHCOCl]^+PCl_6^- \xrightarrow{\Delta \text{ or } CH_3OPCl_2,\ 60\ ^\circ C} Cl_2P(O)CH{=}CHN{=}CCl_2.$$

When *N*-[2-(difluorophosphoryl)-1-methylvinyl]iminocarbonyl dichloride is treated with hexamethyldisiloxane, difluorophosphoryl-methylvinyl isocyanate is obtained:[83]

$$Cl_2P(O)CH{=}C(R)N{=}CCl_2 \xrightarrow{2C_2H_5OH} \rightarrow [Cl(C_2H_5O)P(O)CH{=}C(R)N{=}C(OC_2H_5)Cl] \rightarrow \rightarrow Cl(C_2H_5O)P(O)CH{=}C(R)NCO,$$
$$R = H,\ CH_3.$$

When *N*-[2-(difluorophosphoryl-1-methylvinyl]iminocarbonyl dichloride is treated with hexamethyldisiloxane, difluorophosphoryl-methylvinyl isocyanate is obtained:[83]

$$F_2P(O)CH{=}C(CH_3)N{=}CCl_2 \xrightarrow{[(CH_3)_3Si]_2O} F_2P(O)CH{=}C(CH_3)NCO.$$

(i) Reaction of dialkoxyphosphorylsulphenyl chlorides with vinyl and allyl isocyanates

Vinyl isocyanate undergoes a reaction with diethoxyphosphoryl-sulphenyl chloride to form *S*-(diethoxyphosphoryl)thiovinyl isocyanate:[77]

$$(C_2H_5O)_2P(O)SCl + CH_2{=}CHNCO \xrightarrow{-HCl} (C_2H_5O)_2P(O)SCH{=}CHNCO.$$

Dialkoxyphosphorylsulphenyl chloride readily adds on to the C=C double bond of allyl isocyanate in two directions to form a mixture of two isocyanates in the ratio 3 : 1:[84]

$$(RO)_2P(O)SCl + CH_2{=}CHCH_2NCO \rightarrow \rightarrow (RO)_2P(O)SCH_2CHClCH_2NCO + (RO)_2P(O)SCH(CH_2Cl)CH_2NCO.$$

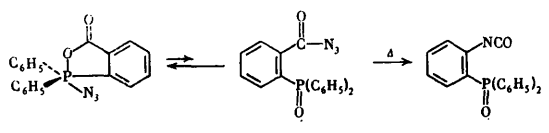
(j) Thermal decomposition of phosphorus-containing carboxylic acid azides

Thermal decomposition via the Curtius rearrangement of azides of phosphorus-containing fatty and aromatic carboxylic acids in toluene or without a solvent gives the corresponding phosphorus-containing alkyl and aryl isocyanates:[32,85–90]

$$R_2P(O)CH_2CH_2COCl \xrightarrow{NaN_3 \text{ or } (CH_3)_3SiN_3} \rightarrow [R_2P(O)CH_2CH_2CON_3] \xrightarrow[\text{toluene}]{\Delta} R_2P(O)CH_2CH_2NCO,$$
$$R = Cl,\ C_2H_5O,\ C_3H_7O,\ \text{iso-}C_3H_7O;$$
$$(RO)_2P(S)SCH_2CH_2COCl \xrightarrow{NaN_3 \text{ or } (CH_3)_3SiN_3} \rightarrow [(RO)_2P(S)SCH_2CH_2CON_3] \xrightarrow{\Delta} (RO)_2P(S)SCH_2CH_2NCO;$$

$$C_6H_5P(O)(C_6H_4COCl\text{-}p)_2 \xrightarrow{2NaN_3} [C_6H_5P(O)(C_6H_4CON_3\text{-}p)_2] \xrightarrow{\Delta} \rightarrow C_6H_5P(O)(C_6H_4NCO\text{-}p)_2;$$

$$(C_2H_5O)_2P(O)C(C_6H_5){=}C{=}O \xrightarrow{HN_3} (C_2H_5O)_2P(O)CH(C_6H_5)CON_3 \xrightarrow{\Delta} \rightarrow (C_2H_5O)_2P(O)CH(C_6H_5)NCO.$$



On boiling phosphorus-containing azides of aliphatic or aromatic carboxylic acids in absolute alcohol, nitrogen is eliminated and isocyanates are formed, immediately adding on alcohols and being converted to the corresponding urethanes $CH_3P(O)(C_6H_4NHCOOC_2H_5)_2$, $(C_6H_5)_2P(O)CH_2CH.(NHCOOC_2H_5)_2$, and $(C_6H_5)_2P(O)CH(NHCOOC_2H_5)(CH_2)_n.NHCOOC_2H_5$ (n = 1, 2).[63,92,93]

(k) Rearrangement of dialkyl- and diaryl-phosphinyl-acetohydroxamic acids and their *O*-benzoyl derivatives

On heating dialkyl- and diaryl-phosphinylhydroxamic acids with an excess of triethyl orthoformate, they rearrange to phosphorylated alkyl isocyanates, which are converted during reaction to *N,N'*-bis(diarylphosphinylmethyl)ureas and ethyl *N*-[dialkyl(diaryl)-phosphinylmethyl]carbamates:[92,94]

$$R_2P(O)CH_2CONHOH \xrightarrow[-2R'OH,\ -R'OC(O)H]{(R'O)_3CH} [R_2P(O)CH_2NCO] \rightarrow$$
$$\rightarrow R_2P(O)CH_2NHCOOR' \quad (R'OH)$$
$$\rightarrow R_2P(O)CH_2NH_2 \xrightarrow{R_2P(O)CH_2NCO} [R_2P(O)CH_2NH]_2CO \quad (H_2O)$$
$$R = C_2H_5,\ C_6H_5,\ p\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4;\ R' = C_2H_5.$$

O-Benzoyl derivatives of diarylphosphinylacetohydroxamic acids when heated in aqueous alkaline solution also undergo the Lossen rearrangement to form phosphorylated methyl isocyanates, which are converted to symmetric *N,N'*-bis(diarylphosphinylmethyl)-ureas:[92,94]

$$R_2P(O)CH_2C(O)NHOC(O)C_6H_5 \xrightarrow[-H_2O]{KOH} \left[R_2P(O)CH_2C(=O)NOC(O)C_6H_5\right]^- K^+ \xrightarrow{-C_6H_5COOH}$$
$$\rightarrow \left[R_2P(O)CH_2C(=O)\ddot{N}:\right] \rightarrow R_2P(O)CH_2NCO \xrightarrow[-CO_2]{H_2O}$$
$$\rightarrow R_2P(O)CH_2NH_2 \xrightarrow{R_2P(O)CH_2NCO} [R_2P(O)CH_2NH]_2CO;$$
$$R = C_6H_5,\ p\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4.$$

(l) Isomerisation of *O,O'*-dialkyl *S*-(ethyleniminocarbonyl)phosphoro-dithioate

When *O,O'*-dialkyl *S*-(chlorocarbonyl)phosphorodithioates are treated with ethylenimine in the presence of triethylamine, *O,O'*-dialkyl *S*-(ethyleniminocarbonyl)phosphorodithioates are formed, which on boiling in toluene undergo complete isomerisation to phosphorus-containing alkyl isocyanates:[87,95]

$$(RO)_2P(S)SC(O)Cl \xrightarrow{HN\langle CH_2\text{–}CH_2,\ (C_2H_5)_3N} (RO)_2P(S)SC(O)N\langle CH_2\text{–}CH_2 \xrightarrow[\text{toluene}]{\Delta} \rightarrow (RO)_2P(S)SCH_2CH_2NCO.$$

(m) Reaction of *N,N'*-bis(alkylidene)ureas with dialkyl phosphites and dialkylphosphorodithioic acids

When *N,N'*-bis(1-phenyl-2,2,2-trifluoroethylidene)urea is boiled with diethyl phosphite or *O,O'*-diisopropyl phosphorodithioate in benzene, the corresponding phosphorus-containing isocyanates are obtained:[96]

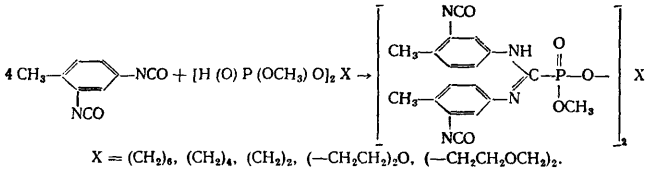
$$[C_6H_5(CF_3)C{=}N]_2CO \rightarrow$$
$$\rightarrow (C_2H_5O)_2P(O)C(C_6H_5)(CF_3)NCO \quad ((C_2H_5O)_2P(O)H)$$
$$\rightarrow (\text{iso-}C_3H_7O)_2P(S)SC(C_6H_5)(CF_3)NCO \quad ((\text{iso-}C_3H_7O)_2P(S)SH).$$

(n) Addition to 2,4-diisocyanatotoluene of phosphorus compounds containing active hydrogen atoms

2,4-Diisocyanatotoluene readily adds on 1 mole of dialkyl phosphite:[97–99]

$$(RO)_2P(O)H + CH_3C_6H_3(NCO)_2\text{-}2,4 \xrightarrow[\text{hexane}]{Na} \rightarrow (RO)_2P(O)C(O)NHC_6H_3NCO\text{-}3\text{-}CH_3\text{-}4.$$

Bis-phosphites react with excess 2,4-diisocyanatotoluene in the absence of catalysts to form phosphorus-containing aromatic isocyanates of complex structure:[100]



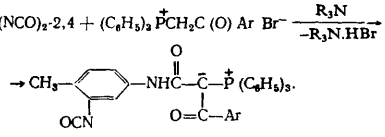
$X = (CH_2)_6$, $(CH_2)_4$, $(CH_2)_2$, $(-CH_2CH_2)_2O$, $(-CH_2CH_2OCH_2)_2$.

When 3 moles of 2,4-diisocyanatotoluene are reacted with tris(hydroxymethyl)phosphine or its oxide, aromatic isocyanates containing phosphorus are also obtained:[101]

$$XP(CH_2OH)_3 + CH_3C_6H_3(NCO)_2\text{-}2,4 \rightarrow XP[CH_2OC(O)NHC_6H_3NCO\text{-}3\text{-}.CH_3\text{-}4]_3,$$

X = O or unshared electron pair.

2,4-Diisocyanatotoluene reacts with triphenylphenacylphosphonium bromides in the presence of ethyldiisopropylamine to form a phosphorus ylide containing a free isocyanate group:[102]



(o) Treatment of phosphorus-containing urethanes with phosphorus pentachloride

When methyl *N*-[1-(diethoxyphosphoryl)]-, *N*-([1-ethoxyphenylphosphonyl)]- and *N*-[1-diphenylphosphinyl)]-2,2-dichlorovinylcarbamates are heated with phosphorus pentachloride, the corresponding 1-phosphorylated 2,2-dichlorovinyl isocyanates are obtained:[103,104]

$$C_2H_5O(X)P(O)C(=CCl_2)NHCOOCH_3 \xrightarrow{nPCl_5} Cl(Y)P(O)C(=CCl_2)NCO,$$
$$X = C_2H_5O,\ Y = Cl,\ n = 3;\quad X = Y = C_6H_5,\ n = 2;$$
$$(C_6H_5)_2P(O)C(=CCl_2)NHCOOCH_3 \xrightarrow{PCl_5} (C_6H_5)_2P(O)C(=CCl_2)NCO.$$

(p) Reaction of trichlorophosphazotrichloromethane with *N,N',N''*-trichloroisocyanuric acid

Trichlorophosphazotrichloromethane readily reacts with *N,N',N''*-trichloroisocyanuric acid, whereupon a chlorine molecule is eliminated and 1-trichlorophosphazo-1,1-dichloromethyl isocyanate is formed, which exists in equilibrium with its acid chloride form:[105,106]

$$Cl_3P{=}NCCl_3 \xrightarrow[-Cl_2]{1/3(ClNCO)_3} Cl_3P{=}NCCl_2NCO \rightleftarrows Cl_3P{=}NCCl{=}NCOCl.$$

(q) Reaction of isocyanates of trivalent phosphorus acids with alkylene oxides

When ethylene oxide is reacted with triisocyanatophosphine in the presence of catalytic quantities of a tertiary amine, *O,O'*-bis(2-isocyanatoethyl) phosphorus isocyanate is obtained:[107]

$$P(NCO)_3 + 2CH_2{-}CH_2 \rightarrow OCNP(OCH_2CH_2NCO)_2.$$
$$\quad\quad\quad

(t) Fluorination of dihalophosphorylalkyl, dihalophosphorylalkenyl, and alkoxychlorophosphorylalkyl isocyanates

Dichlorophosphorylalkyl, dichlorophosphorylalkenyl, and alkoxychlorophosphorylalkyl isocyanates are fluorinated with arsenic trifluoride[12–14,57,86] or antimony trifluoride:[37,38,53,83]

$$Cl_2P(O)—A—NCO \xrightarrow{AsF_3 \text{ or } SbF_3} F_2P(O)—A—NCO,$$
$$A=CH_2CH_2,\ CCl_2,\ C(=CH_2),\ CH=CH,\ CH(C_6H_5);$$
$$Cl(RO)P(O)CR^1R^2NCO \xrightarrow{AsF_3} F(RO)P(O)CR^1R^2NCO,$$
$$R^1=R^2=H,\ Cl;\ R^1=H,\ R^2=Cl,\ C_6H_5.$$

Reaction of difluorophosphorylalkenyl isocyanates with sulphur tetrafluoride gives 2-isocyanatoalkenyltetrafluorophosphoranes,[80,83] which are also formed when *N*-[dichloro(difluoro)phosphorylalkenyl]-iminocarbonyl dichloride is treated with sulphur tetrafluoride:[83]

$$F_2P(O)CH=C(R)NCO \xrightarrow{SF_4} F_4PCH=C(R)NCO$$
$$X_2P(O)CH=C(R)N=CCl_2 \xrightarrow{SF_4} [F_2P(O)CH=C(R)N=CF_2]$$
$$X=Cl,\ F;\ R=H,\ CH_3.$$

It should be mentioned that it is not possible to obtain 2-isocyanatoperchloroethyltetrafluorophosphorane by reaction of 2-dichlorophosphorylperchloroethyl isocyanate with sulphur tetrafluoride as cleavage of the P–C bond occurs:[108]

$$Cl_2P(O)CCl_2CCl_2NCO \xrightarrow{SF_4} Cl_3\overset{+}{S}\ P\overline{F}_6 + [F_3SCCl_2CClFNCO + S_2Cl_2].$$

(u) Elimination of chlorine, hydrogen chloride, or hydrogen bromide from phosphorylated haloalkyl isocyanates

When 1-(dihalophosphoryl)-, 1-(alkoxyhalophosphoryl)- and 1-(dialkoxyphosphoryl)-substituted 2-chloro- or 2-bromo-methyl isocyanates are treated with triethylamine, hydrogen chloride or bromide is readily eliminated and the corresponding phosphorylvinyl isocyanates are obtained.[14,38–40]

$$XYP(O)CH(CH_2Z)NCO \xrightarrow[-(C_2H_5)_3N.HZ]{(C_2H_5)_3N} XYP(O)C(=CH_2)NCO,$$
$$X=Y=Cl,\ F,\ OAlk,\ Z=Cl,\ Br;\ X=Cl,\ F,\ Y=C_2H_5O,\ Z=Br.$$

When 1-(dichlorophosphoryl)-1,2-dibromoethyl isocyanate is treated with triethylamine, (*E*)-1-(dichlorophosphoryl)-2-bromovinyl isocyanate is obtained.[14,40] When 2-(dichlorophosphoryl)tetrachloroethyl isocyanate is heated with methyl phosphorodichloridite, 2-(dichlorophosphoryl)-1,2-dichlorovinyl isocyanate is formed:[108]

$$Cl_2P(O)CCl_2CCl_2NCO \xrightarrow[-CH_3Cl,\ -POCl_3]{CH_3OPCl_2} Cl_2P(O)CCl=CClNCO.$$

(v) Reaction of 2-isocyanatoalkenyltetrafluorophosphoranes with hexamethyldisiloxane

On heating 2-isocyanatoalkenyltetrafluorophosphoranes with hexamethyldisiloxane, 2-(difluorophosphoryl)alkenyl isocyanates are obtained:[83]

$$F_4PCH=C(R)NCO \xrightarrow[-2(CH_3)_3SiF]{[(CH_3)_3Si]_2O} F_2P(O)CH=C(R)NCO,$$
$$R=H,\ CH_3.$$

(x) Cyclopolymerisation of diisocyanates in the presence of trialkyl phosphites

It has been shown[109] that when 2,4-toluylene diisocyanate, 1,6-hexamethylene diisocyanate, and 1,4-tetramethylene diisocyanate undergo cyclopolymerisation in the presence of trialkyl phosphites, phosphorylated isocyanates that contain isocyanurate rings are formed.

2. Phosphorus-containing acyl isocyanates

(a) Reaction of *N*-(diethoxyphosphoryl)-*N*-(2-chloroethyl)carbamoyl chloride with trimethylsilyl isocyanate

N-(Diethoxyphosphoryl)-*N*-(2-chloroethyl)carbamoyl chloride reacts with trimethylsilyl isocyanate on boiling for 30 h in the presence of the catalyst $(C_4H_9)_4NI$ to form *N*-(diethoxyphosphoryl)-*N*-(2-chloroethyl)carbamoyl isocyanate:[110]

$$(C_2H_5O)_2P(O)NC(O)Cl + (CH_3)_3SiNCO \xrightarrow{Cat.\ (C_4H_9)_4NI}$$
$$\rightarrow (C_2H_5O)_2P(O)NC(O)NCO + (CH_3)_3SiCl.$$
$$CH_2CH_2Cl \qquad\qquad CH_2CH_2Cl$$

(b) Reaction of dialkoxyphosphorylcarboxamides and *N*-phosphorylated ureas with oxalyl chloride

Dialkoxyphosphorylcarboxamides react in carbon tetrachloride or chloroform at a temperature of 60–70 °C with oxalyl chloride to form dialkoxyphosphorylacyl isocyanates:[111–113]

$$(AlkO)_2P(O)CRR^1CONH_2 + (COCl)_2 \rightarrow (AlkO)_2P(O)CRR^1CONCO + 2HCl + CO,$$
$$R=R^1=H,\ Cl,\ CH_3;\ R=H,\ R^1=CH_3.$$

N-(Diethoxyphosphoryl)-*N*-(2-chloroethyl)urea reacts in a similar manner:[110]

$$(C_2H_5O)_2P(O)NC(O)NH_2 + (COCl)_2 \rightarrow (C_2H_5O)_2P(O)NC(O)NCO.$$
$$CH_2CH_2Cl \qquad\qquad CH_2CH_2Cl$$

(c) Treatment of *O,O'*-dialkyl *N*-alkylphosphoramidates with chlorocarbonyl isocyanate

When *O,O'*-dialkyl *N*-alkylphosphoramidates are boiled with chlorocarbonyl isocyanate in carbon tetrachloride, *N*-alkyl-*N*-(dialkoxyphosphoryl)carbamoyl isocyanates are obtained:[114]

$$(RO)_2P(O)NHR^1 + ClC(O)NCO \rightarrow (RO)_2P(O)N(R^1)C(O)NCO + HCl,$$
$$R=C_2H_5,\ R^1=CH_3,\ C_2H_5;\ R=\text{iso-}C_3H_7,\ R^1=C_2H_5.$$

(d) Reaction of *N*-phosphorylated ethylenimines with chlorocarbonyl isocyanate and dichloromethylenecarbamoyl chloride

When *O,O'*-dialkyl phosphoroethylenamidates are treated with chlorocarbonyl isocyanate, opening of the ethylenimine ring occurs with formation of *N*-(dialkoxyphosphoryl)-*N*-(2-chloroethyl)-carbamoyl isocyanates,[76,110] which are also obtained by the action of dichloromethylenecarbamoyl chloride followed by treatment of the intermediate with methanesulphonic acid:[75]

$$(RO)_2P(O)N\begin{array}{l}CH_2\\|\\CH_2\end{array}\begin{array}{l}\xrightarrow{ClC(O)NCO}\ (RO)_2P(O)N(CH_2CH_2Cl)C(O)NCO\\ \qquad\qquad\qquad\qquad\qquad\uparrow CH_3SO_2OH\\ \xrightarrow{ClC(O)=CCl_2}\ (RO)_2P(O)N(CH_2CH_2Cl)C(O)N=CCl_2\end{array}.$$

3. Phosphorus-containing sulphonyl isocyanates

(a) Addition of dialkyl phosphites to sulphuryl diisocyanate

One mole of dialkyl phosphite in ether solution at 0 °C adds on to one isocyanate group of sulphuryl diisocyanate to form the corresponding sulphonyl isocyanate.[115] With excess dialkyl phosphite products from the addition to both isocyanate groups are formed:[115,116]

$$SO_2(NCO)_2\begin{array}{l}\xrightarrow{(RO)_2P(O)H}\ (RO)_2P(O)C(O)NHSO_2NCO\\ \xrightarrow{2(RO)_2P(O)H}\ [(RO)_2P(O)C(O)NH]_2SO_2\end{array}.$$

(b) Treatment of *N*-isopropyl-*N'*-(triphenylphosphazosulphonyl)urea with phosgene

When *N*-isopropyl-*N'*-(triphenylphosphazosulphonyl)urea is boiled with phosgene in chlorobenzene, triphenylphosphazosulphonyl isocyanate is obtained:[117]

$$(C_6H_5)_3P{=}NSO_2NHCONHC_3H_7\text{-iso} \xrightarrow{COCl_2} (C_6H_5)_3P{=}NSO_2NCO.$$

III. Chemical properties

Phosphorylated organic isocyanates which contain no other reactive groups apart from the isocyanate are similar in their chemical properties to normal organic isocyanates. They readily react with alcohols, phenols, amines, and other compounds with an active hydrogen atom, forming the corresponding derivatives in good yield. Phosphorus-containing organic isocyanates which have other reactive sites in addition to the isocyanate group can undergo a reaction with nucleophilic reagents on one or more reaction sites. Some reactions of phosphorus-containing organic isocyanates which do not affect the isocyanate group and which give other phosphorus-containing organic isocyanates have been described above.

1. Reaction with water

The majority of phosphorus-containing alkyl and aryl isocyanates are very readily hydrolysed by atmospheric moisture and react with water; but only in certain cases have the reaction products—the corresponding phosphorus-containing symmetrical ureas—been isolated:[9,46,91,94,98]

$$[(C_2H_5O)_2P(O)C(=CCl_2)NH]_2CO,$$
$$\{2\text{-}CH_3\text{-}4\text{-}[(C_2H_5O)_2P(O)C(O)NH]C_6H_3NH\}_2CO,$$
$$[(C_6H_5)_2P(O)CH_2NH]_2CO,\ [(RO)_2P(O)CH(COOR^1)NH]_2CO,$$
$$\{2\text{-}[(C_6H_5)_2P(O)]C_6H_4NH\}_2CO.$$

When α-(diethoxyphosphoryl)benzyl isocyanate [racemate or (*S*)-(+)-enantiomer] is exposed to atmospheric moisture or a stoichiometric quantity of water in ether, racemic or (*SS*)-(−)-*N*,*N'*-bis[α-(diethoxyphosphoryl)benzyl]urea is obtained.[12]

When (*S*)-(+)-α-[bis-(trimethylsiloxy)phosphoryl]benzyl isocyanate is treated with excess water, (*S*)-(−)-α-aminobenzylphosphonic acid is obtained:[12,56]

$$C_6H_5\dot{C}H(NCO)P(O)[OSi(CH_3)_3]_2 \xrightarrow{H_2O} C_6H_5\dot{C}H(NH_2)P(O)(OH)_2.$$

Diethoxyphosphorylcarbonylamidosulphonyl isocyanate is hydrolysed with water to diethoxyphosphorylcarbonylamidosulphonamide:[115]

$$(C_2H_5O)_2P(O)C(O)NHSO_2NCO \xrightarrow{H_2O} (C_2H_5O)_2P(O)C(O)NHSO_2NH_2.$$

When bis(diethoxyphosphoryl)chloromethyl isocyanate is reacted with 2 moles of water in acetone, a compound containing a carbonyl group is formed:[118]

$$[(C_2H_5O)_2P(O)]_2CClNCO \xrightarrow{H_2O} [(C_2H_5O)_2P(O)]_2CClNHCOOH \xrightarrow{-CO_2}$$
$$\rightarrow [(C_2H_5O)_2P(O)]_2CClNH_2 \rightarrow [(C_2H_5O)_2P(O)]_2C{=}NH\cdot HCl \xrightarrow{H_2O}$$
$$\rightarrow [(C_2H_5O)_2P(O)]_2C{=}O.$$

In contrast to mono- and bis-phosphorylated alkyl isocyanates, tris(diethoxyphosphoryl)methyl isocyanate reacts with water only with great difficulty. It remains unchanged on boiling for 2 hours with a stoichiometric quantity of water in acetone. Only on boiling with a tenfold excess of water in dioxan for 3 h does the molecule decompose to form products with an undetermined structure.[118]

2. Reaction with alcohols and phenols

Phosphorus-containing alkyl, alkenyl, and aryl isocyanates that do not contain other groups can react with alcohols and phenols; they have the properties of normal organic isocyanates and readily add on alcohols,[1,4,5,12,26,27,30–32,36–38,40–42, 45–47, 54,68,69,74,75,88,89,91–95,107,119] glycols,[3,20,26,58,59,88,101,119,120] cresol,[20,58,59] and cellulose and cellulose acetate[99] to the isocyanate group. The reactions are usually carried out in inert solvents without a catalyst or in the presence of catalytic quantities of a tertiary amine.

$$R_{3-n}P(X)(ANCO)_n + nR^1OH \rightarrow R_{3-n}P(X)(ANHCOOR^1)_n,$$

$n = 1-3$; X = O, S; A—different bridging groups (see Methods of Synthesis)

It should be mentioned that tris(diethoxyphosphoryl)methyl isocyanate does not react at 20 °C even with a large excess of alcohol over a period of 10–15 days. Even in the presence of a base the reaction is only complete after 15 days under these conditions:[40,54]

$$[(C_2H_5O)_2P(O)]_3CNCO \xrightarrow[\text{Cat. } (C_2H_5)_3N]{ROH} [(C_2H_5O)_2P(O)]_3CNHCOOR.$$

Trialkyl- and triaryl-(isocyanatomethyl)phosphonium halides readily add on alcohols to the isocyanate group. Phenols add on only in the presence of catalytic quantities of a tertiary amine.[36,71,73]

$$[R_3PCH_2NCO]^+X^- + R^1OH \rightarrow [R_3PCH_2NHCOOR^1]^+X^-,$$
R, R^1=Alk, Ar; X=Cl, Br, I.

Phosphorus-containing acyl isocyanates[110–112] and sulphonyl isocyanates[115,117] also readily add alcohols to the isocyanate group to form the corresponding urethanes:

$$(RO)_3P(O)CCl_2CONHCOOR^1,\ (C_2H_5O)_2P(O)N(CH_3CH_2Cl)C(O)NHCOOC_2H_5,$$
$$(C_6H_5)_3P{=}NSO_2NHCOOR^2,\ (C_2H_5O)_2P(O)C(O)NHSO_2NHCOOC_2H_5$$

(where R = C_2H_5, C_4H_9; R^1 = CH_3, C_2H_5, iso-C_3H_7; R^2 = CH_3, iso-C_3H_7, tert-C_4H_9, cyclo-C_6H_{11}).

Dihalo- and alkoxyhalo-phosphoryl-substituted alkyl and alkenyl isocyanates have two reaction sites—the carbon atom of the isocyanate group and the phosphorus atom. Depending on the structure of the phosphorylated isocyanate, the alcohol reacting with it, the solubility of the product formed, the reaction conditions, etc., either only the isocyanate group reacts with an equimolar quantity of alcohol or replacement of a halogen atom on phosphorus by an alkoxy group takes place at the same time as addition. Thus, addition products of alcohols only on the isocyanate group have been obtained for the following types of isocyanates:[30,32,34,40,41,64,78,81,83,86,108,121–123]

$$XYP(O)CH_2NCO\ (X{=}Y{=}Cl;\ X{=}F,\ Y{=}RO);\ Cl_2P(O)CH(CH_2Br)NCO;$$
$$Cl_2P(O)CH(C_6H_5)NCO;\ F(C_2H_5O)P(O)CH(C_6H_5)NCO;\ F_2P(O)CH_2CH_2NCO;$$
$$Cl(RO)P(O)CH{=}CHNCO;\ X_2P(Y)CH{=}C(R)NCO$$
$$(X = Cl, F;\ Y = O, S;\ R = H, CH_3);$$
$$Cl_2P(O)CX{=}CHNCO\ (X = Cl, Br).$$

It is not possible to obtain products from the addition of 1 mole of a primary alcohol only to the isocyanate group of difluorophosphorylmethyl, alkoxychlorophosphorylmethyl, 2-(dichlorophosphoryl)ethyl, 1-(dichlorophosphoryl)vinyl, α-(difluorophosphoryl)benzyl, and α-(alkoxychlorophosphoryl)benzyl isocyanates.[30,34,38,40,41,64,86] However, when tertiary butyl alcohol is reacted with 1-(dichlorophosphoryl)vinyl isocyanate, the urethane $Cl_2P(O)C(=CH_2)NHCOOC(CH_3)_3$ is obtained.[38]

When difluorophosphorylmethyl isocyanate is treated with 2 moles of alcohol, alkyl *N*-(alkoxyfluorophosphorylmethyl)carbamate is

obtained in good yield.[30,34,64] With excess alcohol in the presence of tertiary amines, all dihalophosphoryl- and alkoxyhalophosphoryl-substituted alkyl and alkenyl isocyanates give alkyl *N*-[dialkoxyphosphorylalkyl(alkenyl)]carbamates.[30,34,38,40,41,46,64,86,108]

When 1-dichlorophosphoryl-2-chloro(bromo)ethyl isocyanates react with excess alcohol in the presence of triethylamine, as well as addition of the alcohol to the isocyanate group and replacement of the chlorine atom on phosphorus there is elimination of hydrogen chloride or bromide to give alkyl *N*-(1-dialkoxyphosphorylvinyl)-carbamate;[38,40] the same esters are obtained when 1-(dialkoxyphosphoryl)-2-bromoethyl isocyanate is treated with 1 mole of alcohol in the presence of triethylamine:[40]

$$\left.\begin{array}{l} Cl_2P(O)CH(CH_2X)NCO \xrightarrow[3(C_2H_5)_3N]{3ROH} \\ X=Cl,\ Br \\ (RO)_2P(O)CH(CH_2Br)NCO \xrightarrow[(C_2H_5)_3N]{ROH} \end{array}\right| \rightarrow (RO)_2P(O)C(=CH_2)NHCOOR.$$

α-(Dialkoxyphosphoryl)-α-chlorobenzyl isocyanate has two reaction sites—the carbon atoms of the isocyanate group and the substituted methylene group. When α-(diethoxyphosphoryl)-α-chlorobenzyl isocyanate in ether solution is treated with an equimolar quantity of methanol it appears that addition of methanol to the isocyanate group mainly occurs, and methyl *N*-[α-(diethoxyphosphoryll)-α-chlorobenzyl]carbamate, which is soluble with difficulty in ether, can be isolated in 50% yield. In the presence of triethylamine, methyl *N*-[α-(diethoxyphosphoryl)-benzylidene]carbamate is obtained in high yield.[56]

$$C_6H_5CCl(NCO)P(O)(OC_2H_5)_2 \longrightarrow \left|\begin{array}{l} \xrightarrow{CH_3OH} C_6H_5CCl(NHCOOCH_3)P(O)(OC_2H_5)_2 \\ \xrightarrow[CH_3OH,\ (C_2H_5)_3N]{} C_6H_5C(=NCOOCH_3)P(O)(OC_2H_5)_2. \end{array}\right.$$

Diethoxy phosphoryldichloromethyl and bis(diethoxyphosphoryl)-chloromethyl isocyanates react in a similar manner:[32,54]

$$(RO)_2P(O)C(X)ClNCO \xrightarrow{R'OH} [(RO)_2P(O)C(X)ClNHCOOR'] \xrightarrow{[(C_2H_5)_3N]} \rightarrow (RO)_2P(O)C(X)=NCOOR',$$
$$X=Cl,\ (RO)_2P(O).$$

In the case of the halophosphoryl compounds $Hal(X)P(O)C(Hal)_2.NCO$ and Hal(X)P(O)CH(Hal)NCO (X = Hal or OR) there is a third reaction site—the phosphorus atom.

Depending on the structure of the isocyanate and the nucleophilic reagent reacting with it as well as their stoichiometric ratio, initially only the isocyanate group participates, then the phosphorus atom and the halogen on the α-carbon atom, or all reaction sites simultaneously.

Dichloro- and difluoro-phosphorylchloromethyl isocyanates add 1 mole of alcohol to form crystalline alkyl *N*-(dihalophosphoryl-chloromethyl)carbamates:[50]

$$X_2P(O)CHClNCO \xrightarrow{ROH} X_2P(O)CHClNHCOOR,$$
$$X=Cl,\ F.$$

Dichlorophosphoryldichloromethyl isocyanate, and alkoxychloro-, alkoxyfluoro-phosphorylchloromethyl isocyanates also react with 1 mole of alcohol mainly on the isocyanate group alone. However, the urethanes formed are very unstable and on evaporating the solutions, vacuum distillation, or treatment with tertiary amines they readily eliminate a hydrogen chloride molecule and are converted to the corresponding compounds with a C=N bond. It was only possible to isolate the stable alkyl *N*-(dichlorophosphorylchloro-methylene)carbamates in a pure form.[50,52-54] Dichlorophosphoryl-dibromomethyl isocyanate reacts with alcohols in a similar manner:[40]

$$Cl_2P(O)CX_2NCO \xrightarrow{ROH} [Cl_2P(O)CX_2NHCOOR] \xrightarrow{(C_2H_5)_3N} \rightarrow Cl_2P(O)CX=NCOOR,$$
$$X=Cl,\ Br.$$

It should be mentioned that it is not possible to add 1 mole of alcohol to the isocyanate group of difluorophosphoryl- or alkoxyfluorophosphoryl-dichloromethyl isocyanate. Reaction takes place simultaneously on two reaction sites—the carbon atom of the NCO group and the phosphorus atom—and a mixture of products is formed, from which pure compounds could not be isolated.[53,118] However, in the case of 2-chloroethoxychlorophosphoryldichloro-methyl isocyanate, *N*-(2-chloroethoxychlorophosphorylchloro-methylene)carbamate was obtained.[57]

When dichloro- or alkoxychloro-phosphoryldichloromethyl isocyanate reacts with excess alcohol in the presence of a tertiary amine, alkyl *N*-(dialkoxyphosphorylchloromethylene)carbamates are obtained,[32,52,53] while dichloro- and alkoxychloro-phosphorylchloro-methyl isocyanates under the same conditions give alkyl *N*-[alkoxy-(dialkoxyphosphoryl)methyl]carbamates:[50]

$$Cl(X)P(O)CCl_2NCO \xrightarrow[(C_2H_5)_3N]{ROH} (RO)_2P(O)C(Cl)=NCOOR,$$
$$Cl(X)P(O)CHClNCO \xrightarrow[(C_2H_5)_3N]{ROH} (RO)_2P(O)CH(OR)NHCOOR,$$
$$X=Cl,\ RO.$$

α-(Dichlorophosphoryl)-α-chlorobenzyl isocyanate reacts with excess methanol in a similar manner to dichlorophosphoryldichloro-methyl isocyanate, forming the urethane $C_6H_5C(=NCOOCH_3)P(O).(OCH_3)_2$.[56]

When dichlorophosphoryldibromomethyl isocyanate is treated with 4 moles of sodium ethoxide in ethanol, ethyl *N*-[diethoxy-phosphoryl(ethoxy)methylene]carbamate is obtained:[40]

$$Cl_2P(O)CBr_2NCO \xrightarrow{4C_2H_5ONa} (C_2H_5O)_2P(O)C(OC_2H_5)=NCOOC_2H_5.$$

2-(Dichlorophosphoryl)perchloroethyl isocyanate reacts with alcohols in a similar manner to dichlorophosphoryldichloromethyl isocyanate, forming urethanes $(RO)_2P(O)CCl_2CCl=NCOOR$.[108]

When difluorophosphorylchloromethyl isocyanate is treated with 3 moles of alcohol or alkoxyfluorophosphorylchloromethyl isocyanate is treated with 2 moles of alcohol in the presence of triethylamine, alkyl *N*-[alkoxy(alkoxyfluorophosphoryl)methyl carbamates are obtained:[50]

$$\left.\begin{array}{l} F_2P(O)CHClNCO \xrightarrow[2(C_2H_5)_3N]{3\ ROH} \\ F(RO)P(O)CHClNCO \xrightarrow[(C_2H_5)_3N]{2ROH} \end{array}\right| \rightarrow F(RO)P(O)CH(OR)NHCOOR.$$

It is not possible to add 1 mole of alcohol just to the isocyanate group of bis(alkoxyfluorophosphoryl)chloromethyl isocyanate, and when the latter is treated with 3 moles of alcohol in the presence of triethylamine the reaction proceeds thus:[53]

$$[F(RO)P(O)]_2CClNCO \xrightarrow[3(C_2H_5)_3N]{3\ ROH} [(RO)_2P(O)]_2C=NCOOR.$$

Bis(alkoxyfluorophosphoryl)methyl isocyanate and its corresponding α-chloro-substituted compound when reacted with alcohols give urethanes.[50,53]

$$[F(RO)P(O)]_2CHNCO \xrightarrow{ROH} [F(RO)P(O)]_2CHNHCOOR,$$
$$[F(RO)P(O)]_2CClNCO \xrightarrow[(C_2H_5)_3N]{ROH} [F(RO)P(O)]_2C=NCOOR.$$

The addition of phenols and glucose tetraacetate to dichloro-phosphorylvinyl isocyanate has been reported.[121-123]

3. Reaction with thiols

Thiols add to phosphorylated alkyl isocyanates with much greater difficulty than alcohols. Thioethanol reacts with 1-diethoxyphosphoryl- and 1-diethoxyphosphorothioyl-1-methylethyl isocyanates only in the presence of triethylamine on heating in a sealed tube on a boiling water bath:[1,5]

$$(C_2H_5O)_2P(X)C(CH_3)_2NCO \xrightarrow[(C_2H_5)_3N]{C_2H_5SH} (C_2H_5O)_2P(X)C(CH_3)_2NHC(O)SC_2H_5$$
X=O, S.

4. Reactions with ammonia and amines

Dialkoxyphosphorylalkyl isocyanates, in the same way as alkyl and aryl isocyanates, readily react with ammonia to form *N*-(dialkoxyphosphorylalkyl)ureas:[1,5,31,75,90]

$$(RO)_2P(X)—A—NCO + NH_3 \rightarrow (RO)_2P(X)—A—NHCONH_2,$$
X=O: A=CH_2, $C(CH_3)_2$, $CH(C_6H_5)$, —N$(CH_2CH_2Cl)CH_2$—;
X=S: A=$C(CH_3)_2$.

N-(Diethoxyphosphoryl)-*N*-(2-chloroethyl)aminocarbonyl isocyanate[110] and triphenylphosphazosulphonyl isocyanate[117] add ammonia in a similar manner.

Phosphorus-containing alkyl,[1,4,5,9,12,30–32,36,37,41,42,45–48,54,68,74,75,85,88,92,94,95,124] alkenyl,[46,47] and aryl [30,31,89,98] isocyanates as well as isocyanates of *N*-phosphorylated iminocarboxylic acids[28] which apart from the isocyanate group have no other reaction sites very readily add primary[1,5,46] and secondary[30–32,54,72,75] aliphatic amines, phosphorylated alkylamines,[12,92,94] primary aromatic amines,[1,4,5,9,12,28,30–32,36,37,41,42,45–48,54,68,74,75,85,88,89,95,98,124] and morpholine[41,124] to form the respective ureas.

$$[R_2P(X)]_nANCO + R^1R^2NH \rightarrow [R_2P(X)]_nANHCONHR^1R^2,$$
n=1: R=Alk, Ar, AlkO, ArO; A=CH_2, $(CH_2)_2$, $\dot{C}H(C_6H_5)$, $\dot{C}H(C_6H_5)$, $CH(CH_2Cl)CH(CCl_3)$, $CHCOOR^3$, $C(CH_3)_2$, $C(C_6H_5)_2$, $C(C_{10}H_7\text{-}\alpha)_2$, $S(CH_2)_2$, $—CH_2C_6H_4—$, $C(=CH_2)$, $C(=CCl_2)$, $N=C(C_6H_5)$ etc.;
n = 2: R=AlkO, A=CH; *n* = 3, R=AlkO, A=C;

$$C_6H_5P(O)(C_6H_4NCO\text{-}p)_2 + 2C_6H_5NH_2 \rightarrow C_6H_5P(O)(C_6H_4NHCONHC_6H_5\text{-}p)_2.$$

Triaryl(isocyanatomethyl)phosphonium halides add 1 mole of an aromatic amine to the isocyanate group, forming compounds of the type $[Ar_3PCH_2NHCONHAr^1]^+X^-$ (X = Cl, Br, I).[36,73]

Phosphorus-containing acyl isocyanates[110–113] and sulphonyl isocyanates[115,117] also add primary aromatic amines,[110–113,115] and diethyl- and cyclohexyl-amine[117] to the isocyanate group, forming ureas

$$(AlkO)_2P(O)C(R)(R')CONHCONHAr,\ (C_6H_5)_3P{=}NSO_2NHCONRR',$$
$$(C_2H_5O)_2P(O)N(CH_2CH_2Cl)CONHCONHAr,$$
$$(C_2H_5O)_2P(O)C(O)NHSO_2NHCONHC_6H_5.$$

When dialkoxyphosphoryldichloro- or bis(dialkoxyphosphoryl)-chloro-methyl isocyanate is treated with 2 moles of an aromatic amine or 1 mole of an aromatic amine in the presence of triethylamine, hydrogen chloride is eliminated at the same time as addition of the amine to the isocyanate group:[48,54]

$$(RO)_2P(O)CXClNCO \xrightarrow[(C_2H_5)_3N]{ArNH_2} (RO)_2P(O)CX{=}NCONHAr,$$
X=Cl, $(RO)_2P(O)$.

One mole of a primary aromatic amine reacts with difluorophosphorylated alkyl and alkenyl isocyanates,[30,34,36,40,41,83,86] fluoroalkoxyphosphorylalkyl isocyanates,[30,34,36,41,57] and bis(ethoxyfluorophosphoryl)methyl isocyanate[50] only on the isocyanate group.

$$F_2P(O)ANCO + ArNH_2 \rightarrow F_2P(O)ANHCONHAr,$$
A=CH_2, $CHCH_2Br$, CHC_6H_5, $C(=CH_2)$, CH_2CH_2, CH=CH, $CH{=}C(CH_3)$;

$$F(AlkO)P(O)ANCO + ArNH_2 \rightarrow F(AlkO)P(O)ANHCONHAr,$$
A=CH_2, CHC_6H_5;

$$[F(C_2H_5O)P(O)_2CHNCO + p\text{-}ClC_6H_4NH_2 \rightarrow$$
$$\rightarrow [F(C_2H_5O)P(O)]_2CHNHCONHC_6H_4Cl\text{-}p.$$

2-(Dichlorophosphoryl)- and 2-(alkoxychlorophosphoryl)-vinyl isocyanates[78,79,81,108] as well as 2-(chlorazidophosphoryl)ethyl isocyanate[86] react in a similar manner.

It is not possible to add 1 mole of amine just to the isocyanate group of dichlorophosphorylalkyl, alkoxychlorophosphorylalkyl, 1-(dichlorophosphoryl)vinyl, 1-(dichlorophosphoryl)-2,2-dichlorovinyl and 1-(phenylchlorophosphonyl)-2,2-dichlorovinyl isocyanates or to isolate pure compounds. Reaction occurs simultaneously on the carbon atom of the isocyanate group and the phosphorus atom. With excess amine, as well as addition to the isocyanate group the chlorine atoms are completely replaced by amino groups[30,34,36,38,41,86,103,124] and the following ureas are formed: $(RR^1N)_2P(O)—A—NHCONRR^1$, $ArNH(R^2)P(O)—A—NHCONHAr$ [A = CH_2, CHC_6H_5, $(CH_2)_2$, $C(=CH_2)$, $C(=CCl_2)$, R^2 = AlkO, C_6H_5].

In the case of 1-(dichlorophosphoryl)- and 1-(phenylchlorophosphonyl)-2,2-dichlorovinyl isocyanates, treatment of the reaction mixture with water or alcohol gives products in which one chlorine atom on phosphorus has been replaced by a hydroxyl or alkoxyl group $R^2O(X)P(O)C(=CCl_2)NHCONRR^1$ (X = C_6H_5, RR^1N; R_2 = H, Alk).[103,124]

Depending on the structure of the isocyanate, α-halogen atoms are also replaced by an amino group or eliminated as hydrogen halides,[38,40,50,53,56] for example:

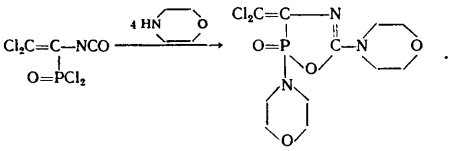
$$Cl_2P(O)CHClNCO \xrightarrow[3(C_2H_5)_3N]{4RR^1NH} (RR^1N)_2P(O)CH(NRR^1)NHCONRR^1,$$

$$[Cl(RO)P(O)]_2CClNCO \xrightarrow[3(C_2H_5)_3N]{3R^1R^2NH} [R^1R^2N(RO)P(O)]_2C{=}NCONR^1R^2.$$

In the case of bis(ethoxyfluorophosphoryl)chloromethyl isocyanate the fluorine atoms are not exchanged for amino groups under similar conditions:[53]

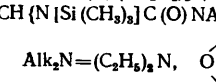
$$[F(C_2H_5O)P(O)]_2CClNCO \xrightarrow[(C_2H_5)_3N]{ArNH_2} [F(C_2H_5O)P(O)]_2C{=}NHCONHAr.$$

When 1-(dichlorophosphoryl)-2,2-dichlorovinyl isocyanate is reacted with 4 moles of morpholine, a cyclic compound—2,5-dimorpholino-4-dichloromethylene-5-oxo-5-phospha-2-oxazoline—is obtained:[103]



The addition of dialkyltrimethylsilylamines to α-(diethoxyphosphoryl)benzyl isocyanate and to triphenyl(α-isocyanatobenzyl)-phosphonium chloride has been reported:

$$C_6H_5CH(NCO)P(O)(OC_2H_5)_2 + Alk_2NSi(CH_3)_3 \rightarrow$$
$$\rightarrow C_6H_5CH\{N[Si(CH_3)_3]C(O)NAlk_2\}P(O)(OC_2H_5)_2,$$



In the latter case the addition product decomposes immediately it is formed at 15–20 °C, so that azomethine, triphenylphosphine, and trimethylchlorosilane are obtained.[72]

Diphenylketimines react similarly to amines with $(RO)_2P(S)SCH_2.CH_2NCO$ [95] and triphenylphosphazohydride reacts similarly with $Cl(X)P(O)CH_2NCO$ (X = Cl, RO) and $Cl_2P(O)CH=CHNCO$.[125,126]

α-Isocyanatophosphonoacetates add on hydrazine and 2,4-dinitrophenylhydrazine to form the corresponding semicarbazides:[9]

$$(RO)_2P(O)CH(COOR^1)NCO + R^2NHNH_2 \rightarrow \rightarrow (RO)_2P(O)CH(COOR^1)NHCONHNHR^2.$$

When bis(dialkoxyphosphoryl)chloromethyl isocyanate is reacted with amidines in the presence of triethylamine, phosphorylated 1,3,5-triazine derivatives are obtained.[127]

$$[(RO)_2P(O)]_2CClNCO \xrightarrow[(C_2H_5)_3N]{RC(=NH)NH_2} [(RO)_2P(O)]_2C\begin{array}{l}NH{-}C{=}O\\ \quad\quad\ \ \backslash\\ \quad N{=}C\\ \quad\quad\ \ /\\ \quad\quad R\end{array}NH.$$

5. Addition of hydrogen chloride and hydrazoic acid

When hydrogen chloride is passed through an ether solution of 2-(dichlorophosphoryl)ethyl isocyanate, *N*-[2-dichlorophosphoryl)-ethyl]carbamoyl chloride is obtained:[86]

$$Cl_2P(O)CH_2CH_2NCO \xrightarrow{HCl} Cl_2P(O)CH_2CH_2NHCOCl.$$

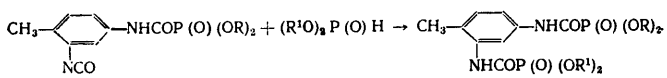
2-(Dichlorophosphoryl)vinyl isocyanate adds on hydrogen chloride when exposed to UV radiation, while 2-(dichlorophosphorothioyl)vinyl isocyanate does not react with hydrogen chloride under similar conditions.[78]

The addition of hydrazoic acid to diethoxyphosphoryldichloroacetyl isocyanate has been reported:[128]

$$(C_2H_5O)_2P(O)CCl_2C(O)NCO + HN_3 \rightarrow (C_2H_5O)_2P(O)CCl_2C(O)NHC(O)N_3.$$

6. Addition of dialkyl phosphites

2-Methyl-5-(dialkoxyphosphorylcarbonylamino)phenyl isocyanate in dioxan adds dialkyl phosphites:[98]



Diethoxyphosphorylcarbonylaminosulphonyl isocyanate adds diethyl phosphite to form *N*,*N*^{1}-bis(diethoxyphosphorylcarbonyl)-diamides of sulphuric acid:[115,116]

$$(C_2H_5O)_2P(O)C(O)NHSO_2NCO + (C_2H_5O)_2P(O)H \rightarrow \rightarrow [(C_2H_5O)_2P(O)C(O)NH]_2SO_2.$$

Similar compounds are obtained when sulphuryl diisocyanate is treated with 2 moles of dialkyl phosphite. The reaction evidently occurs in two stages.[115,116]

7. Reaction with phosphazo compounds

Phosphorylated alkyl isocyanates undergo the Staudinger reaction with triphenylphosphazo hydrocarbons to form phosphorylated carbodiimides.[62,129–131]

$$(RO)_2P(X)YC(CF_3)(C_6H_5)NCO + (C_6H_5)_3P{=}NR^1 \rightarrow \rightarrow (RO)_2P(X)YC(CF_3)(C_6H_5)N{=}C{=}NR^1 + (C_6H_5)_3PO,$$

X = O, Y – bond; X = Y = S.

8. Elimination of carbon dioxide from phosphorylated alkyl isocyanates

On heating the racemate of (*S*)-(+)-enantiomer of α-diethoxyphosphoryl)benzyl isocyanate for 1–2 h at 100–110 °C in the presence of a catalytic quantity of 1,3-dimethylphosphol-3-ene in anhydrous toluene, the corresponding racemic and optically active *N*,*N*′-bis[α-(diethoxyphosphoryl)benzyl]carbodiimides are obtained:[12]

$$2\,C_6H_5CH(NCO)P(O)(OC_2H_5)_2 \xrightarrow{\Delta} [(C_2H_5O)_2P(O)(C_6H_5)CHN{=}]_2C + CO_2.$$

9. Reaction with chlorine

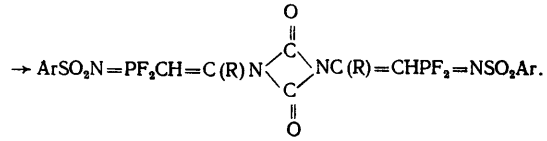
When dimethoxyphosphorothioylthiomethyl isocyanate is chlorinated, dimethyl phosphorochloridothioate and (probably) isocyanatomethylsulphenyl chloride are obtained:[69]

$$(RO)_2P(S)SCH_2NCO \xrightarrow{Cl_2} (RO)_2P(S)Cl + [ClSCH_2NCO].$$

10. Reaction with *N*,*N*-bis(trimethylsilyl)arenesulphonamides

2-Isocyanatoalkenyltetrafluorophosphoranes, when treated with *N*,*N*-bis(trimethylsilyl)arenesulphonamides, form phosphazo isocyanate dimers:[83]

$$F_4PCH{=}C(R)NCO + 2[(CH_3)_3Si]_2NSO_2Ar \rightarrow$$



IV. IR and NMR spectra

The IR spectra of phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates contain absorption bands that are characteristic of vibrations of the –N=C=O group. They are very intense in the region 2250–2280 cm^{-1} (asymmetric stretching vibrations),[4,9,12,28,31,34,36–38,40–50,52–57,62,69–71,75,78,81,83–85,86,88,90,91,93,95,96,102,103,106,108,110,112,114,115,117,120,132] weak in the region 1415 to 1470 cm^{-1} (symmetric stretching vibrations),[12,34,40,41,56,85,86,88] and strong in the region of about 600 cm^{-1} (bending vibrations).[12,41,56] The absorption bands from the asymmetric stretching vibrations of the isocyanate group in phosphorylated alkyl and alkenyl isocyanates are displaced to lower frequency by 10–25 cm^{-1} relative to the isocyanates of phosphorus acids and they occur in approximately the same region as for organic isocyanates not containing phosphorus substituents.[132,133] It was established by IR spectroscopy that the majority of α-chloro-substituted phosphorylated alkyl isocyanates occur solely in the isocyanate form, but some phosphorylated α,α-dichloroalkyl isocyanates exist in equilibrium with their chlorocarbonyl form:[54,106,108]

$$(C_2H_5O)_2P(O)CCl_2NCO \rightleftarrows (C_2H_5O)_2P(O)CCl{=}NCOCl,$$
$$Cl_2P(O)CCl_2CCl_2NCO \rightleftarrows Cl_2P(O)CCl_2CCl{=}NCOCl,$$
$$Cl_3P{=}NCCl_2NCO \rightleftarrows Cl_3P{=}NCCl{=}NCOCl.$$

In order to confirm the structure of phosphorus-containing alkyl, alkenyl, and aryl isocyanates, the ^{1}H NMR spectra of the following isocyanates were studied: $(RO)_2P(O)CH(NCO)COOR'$ (R = C_2H_5, iso-C_3H_7; R′ = CH_3, C_2H_5, iso-C_3H_7),[9] $Cl_2P(O)C(=CH_2)NCO$,[38] and $(C_2H_5O)_2P(S)SCH_2CH_2NCO$.[95]

The following isocyanates were studied using ^{1}H NMR and ^{31}P NMR: Cl(X)P(O)CY(CH_2Br)NCO (X = Cl, C_2H_5O; Y = H, Br)

and $Cl_2P(O)C(=CHX)NCO$ (X = H, Br),[40] $C_6H_5CH(NCO)P(O)(OR)_2$ (R = CH_3, C_2H_5),[41,90] $C_6H_5CH(NCO)P(O)(X)Cl$ (X = Cl, C_2H_5O),[41] $(RO)_2P(O)CH(CCl_3)NCO$ and $(RO)_2P(O)C(=CCl_2)NCO$ (R = CH_3, C_2H_5),[46] $C_6H_5CCl(NCO)P(O)(OR)_2$ (R = CH_3, C_2H_5), $C_6H_5CCl(NCO)P(O)(X)Cl$ (X = Cl, C_2H_5O),[56] and $(C_2H_5O)_2P(S).SCH_2CH_2NCO$.[88]

The following isocyanates were studied using ^{31}P NMR: (*S*)-(+)-$C_6H_5CH(NCO)P(O)(OR)_2$ [R = C_2H_5, $Si(CH_3)_3$],[12] a mixture of $(RO)_2P(O)SCH_2CHClCH_2NCO$ and $(RO)_2P(O)SCH.(CH_2Cl)CH_2NCO$ (R = CH_3, iso-C_3H_7),[84] $X(C_2H_5O)P(O)CH_2CH_2.NCO$ (X = Cl, C_2H_5O),[86] and *o*-$(C_6H_5)_2P(O)C_6H_4NCO$.[91]

The following isocyanates were studied using ^{31}P and ^{19}F NMR: $F(X)P(O)C(=CH_2)NCO$ (X = F, C_2H_5O),[40] $F(RO)P(O)CCl_2NCO$ (R = CH_3, C_2H_5),[55] and $(C_2H_5O)_2P(O)C(CF_3)(R)NCO$ (R = Cl, CH_3O).[62]

^1H NMR was used to study the diastereotopicity of the hydrogen atoms of the CH_2Br group in the isocyanates $X_2P(O)CH(CH_2Br)NCO$ (X = Cl, F) [40] and also the methoxyl groups in the isocyanates $C_6H_5CH(NCO)P(O)(OCH_3)_2$ [41] and $C_6H_5CCl(NCO)P(O)(OCH_3)_2$.[56]

^{31}P, $^{31}P-\{^1H\}$, ^{19}F, and ^1H NMR were used to confirm the structure and study the diastereotopicity of the fluorine atoms on phosphorus in isocyanates with a chiral carbon atom: (*S*)-(−)-$C_6H_5\dot{C}H(NCO)P(O)F_2$,[12] $C_6H_5\dot{C}H(NCO)P(O)F_2$,[12,41] $F_2P(O)\dot{C}H(CH_2Br)NCO$,[39,40] $F_2P(O)\dot{C}Br(CH_2Br)NCO$,[40] $C_6H_5\dot{C}Cl(NCO)P(O)F_2$ [56] and the diastereomeric anisochronism of isocyanates with chiral phosphorus and carbon atoms:

$(S)(+)\text{-}C_6H_5\dot{C}H(NCO)\dot{P}(O)(OC_2H_5)F$ (Ref.12),

$C_6H_5\dot{C}H(NCO)\dot{P}(O)(OC_2H_5)F$ (Refs.12, 41),

$F(C_2H_5O)\dot{P}(O)\dot{C}H(CH_2Br)NCO$ (Refs.39, 40),

$F(C_2H_5O)\dot{P}(O)\dot{C}Br(CH_2Br)NCO$ (Ref.40),

$C_6H_5\dot{C}Cl(NCO)\dot{P}(O)(OC_2H_5)F$ (Ref.56).

In addition, $^{19}F-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR were used to study the structure and diastereomeric anisochromism of bis-phosphorylated chloromethyl isocyanates with chiral phosphorus atoms:[55]

$F(RO)\dot{P}(O)[Cl(RO)\dot{P}(O)]\dot{C}ClNCO$ (R = CH_3, C_2H_5),

$[F(C_2H_5O)\dot{P}(O)]_2CClNCO$ и $[Cl(C_2H_5O)\dot{P}(O)]_2CClNCO$.

A quantum-chemical calculation using the Hofmann method was carried out on the isocyanates $F_4PCH=CHNCO$ and $Cl_4PCH=CHNCO$ and also their isomers $F_2P(O)CH=CHNCF_2$ and $Cl_2P(O)CH=CHNCCl_2$, and it was established that the phosphorane form is stable for fluorine-containing compounds while for chlorine-containing compounds the dichloride form is stable.[80]

V. Use of phosphorus-containing isocyanates for obtaining polymers

Phosphorylated organic isocyanates that contain several isocyanate groups in the molecule when reacted with polyfunctional compounds containing an active hydrogen atom (hydroxyl and amino groups, etc.) form fire-resistant, thermally stable polymers—polyurethanes, polyureas, polyurethanoureas, etc. These polymers are used for the production of rubbers, glues, varnish coatings, films, foamed plastics, moulded products, finishing materials for fabrics, etc. Phosphorus-containing organic isocyanates are used as additives for plastics and cellulose in order to impart fire-resistant properties or as vulcanising agents. Tris(*p*-isocyanatophenyl) phosphorothioate (Desmodur RF) has been used in West Germany as a cross-linking agent in adhesive rubber solutions.[3,15,18,20,26,58,61,89,99–101,107,109,119,120,134–139]

VI. Physiological activity of compounds obtained from phosphorus-containing isocyanates

Esters and amides of phosphorylated *N*-alkyl- and *N*-alkenylcarbamic acids possess high insecticidal, acaricidal, and fungicidal activity.[56,64,118,140,141] *N*-[2-Diethylenediamidophosphoryl)vinyl]-substituted urethanes and *N'*-arylureas exhibit antitumorigenic activity.[76,79,121,123] The phosphonium salt $[(C_6H_5)_3PCH_2NH.COOC_{10}H_{21}]^+Cl^-$ has antimicrobial properties.[142] The compounds $SO_2[NHC(O)P(O)(OR)_2]_2$, obtained from sulphuryl diisocyanate, have fungicidical, nematocidal, and herbicidal activity.[116]

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It is evident from the above that there has been an extensive development of the chemistry of phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates which are derivatives of synthetic and natural aminophosphonic acids[143] (the two hydrogen atoms on nitrogen replaced by a =C=O group), playing a definite role in biology. Phosphorus-containing organic isocyanates are starting to be used as raw materials for the synthesis of various types of aminophosphonic acids—analogues of aminocarboxylic acids. Moreover, phosphorus-containing organic isocyanates are very convenient and highly reactive compounds for introducing phosphorus into different organic products. They have already been used for the synthesis of phosphorus-containing polymers and biologically active compounds. From the theoretical point of view phosphorus-containing alkyl isocyanates have proved convenient subjects for studying the phenomena of diastereomeric anisochronism and diastereotopicity of atoms and groups in molecules with chiral carbon and phosphorus atoms.

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