# Reactions of *N*-alkyl- and *N*-aryltrihalogenoacetamides with phosphorus pentachloride

*A. D. Sinitsa,* A. A. Shalimov, A. M. Nesterenko, and D. M. Malenko*

*Institute of Organic Chemistry, National Academy of Sciences of the Ukraine,*
*5 ul. Murmanskaya, 02660 Kiev-94, Ukraine.*
*E-mail: ioch@bpci.kiev.ua*

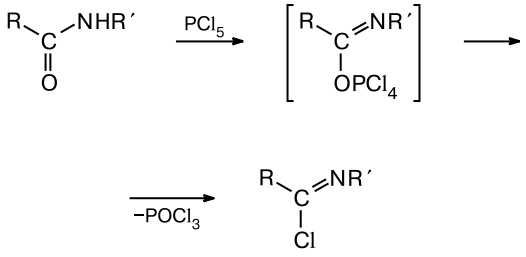
In the study of reactions of *N*-alkyl- and *N*-aryltrihalogenoacetamides with $PCl_5$, it was demonstrated for the first time that 3-alkyl(aryl)-2,2,2,4-tetrachloro-4-trihalomethyl-1,3,2-$\lambda^5$-oxazaphosphetanes are intermediates in the synthesis of trihaloacetimidoyl chlorides. According to quantum-chemical calculations, acyclic *N*-tetrachlorophosphoranes, which are the primary products in the reactions of trihaloacetamides with $PCl_5$, undergo rapid cyclization into the corresponding phosphorates and subsequent 1,3-chlorotropic migration gives rise to oxazaphosphetanes with the five-coordinate P atom.

**Key words:** trihaloacetamides, phosphorus pentachloride, tetrachlorophosphoranes, imidoyl chlorides, oxazaphosphetanes, quantum chemical calculations.

Reactions of *N*-monosubstituted carboxamides with $PCl_5$ and other chlorophosphoranes are most common and preparative routes to imidoyl chlorides.[1,2] Although the available experimental material concerning the synthesis of imidoyl chlorides is abundant, only a few studies have reported the attempts to isolate intermediate products in these reactions and investigate the reaction mechanisms. This mainly refers to halogeno carboxylic acid derivatives, for which the reaction pathways and the yields of final products have been found to depend on the nature of the halogen atom and the substituent at the N atom.

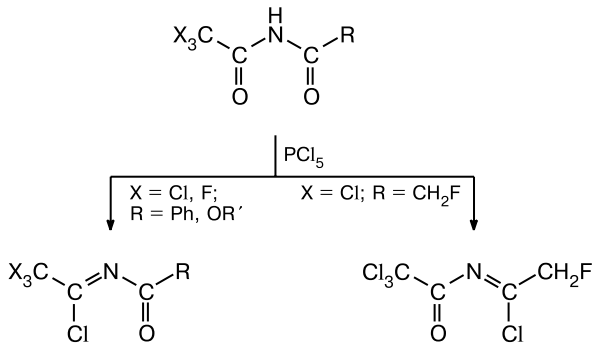
According to the generally accepted assumption,[3] reactions of *N*-substituted carboxamides with $PCl_5$ proceed *via* intermediate acyclic *O*-tetrachlorophosphoranes (Scheme 1).

**Scheme 1**



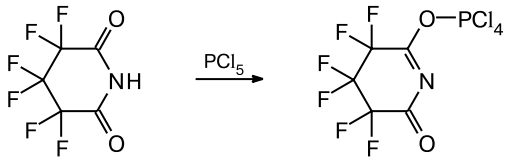

The reactions of imides (Scheme 2) with $PCl_5$ yield isomeric imidoyl chlorides.[4—6] The corresponding chlorophosphoranes as possible intermediates of these reactions have not been identified.

**Scheme 2**




Presumably,[7] the reaction of $PCl_5$ with perfluoroglutarimide affords *O*-tetrachlorophosphorane (Scheme 3); however, reliable data confirming its formation and structure are missing.

**Scheme 3**




The formation of a mixture of *O*- and *N*-tetrachlorophosphoranes was postulated[8] for the reaction of *N*-methyltrifluoroacetamide (**1a**) with $PCl_5$ (Scheme 4). It was concluded that imidoyl chloride **2a** and $POCl_3$

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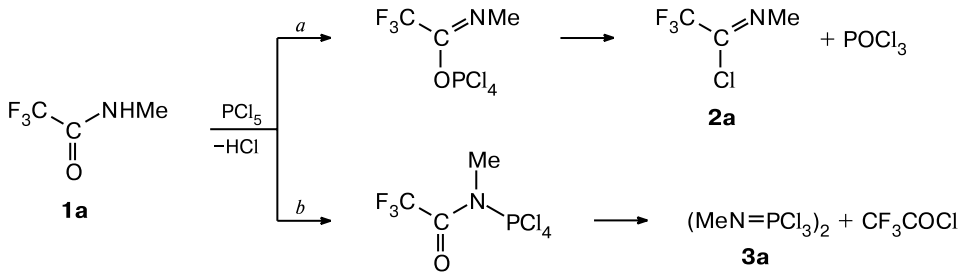
**Scheme 4**

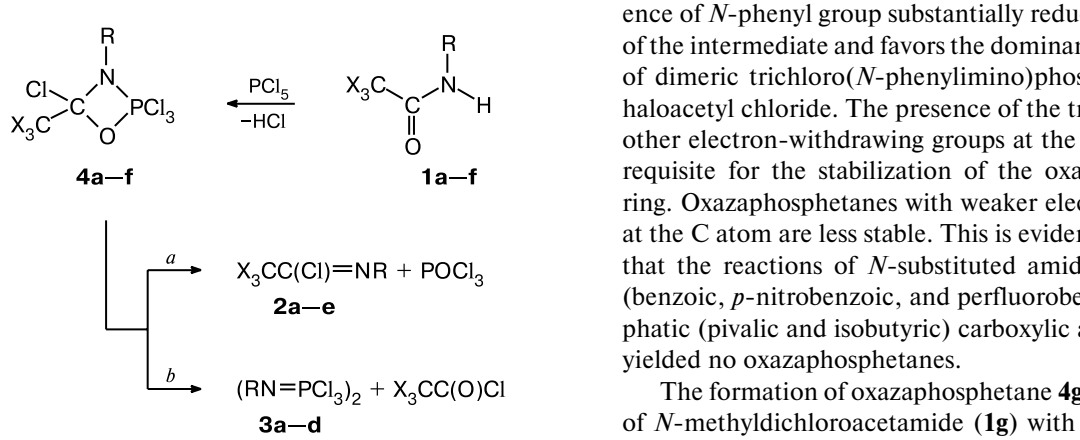


(pathway *a*) are formed from *O*-tetrachlorophosphorane, while the dimer of methylimidophosphine trichloride **3a** and trifluoroacetyl chloride (pathway *b*) are the decomposition products of *N*-tetrachlorophosphorane.

However, in this case too, neither type of chlorophosphoranes was isolated or characterized.

In continuation of investigations[9,10] into phosphorylation of halogeno carboxamides, we studied reactions of $PCl_5$ with *N*-alkyl- and *N*-arylpolyhalogenocarboxamides. *N*-Alkyltrihalogenoacetamides and trihalogenoacetanilides **1a—f** reacted with $PCl_5$ under mild conditions. The phosphorylation rate depended on the nature of the substituents at the N atom (*e.g.*, with the *tert*-butyl substituent, no reaction occurred). Oxazaphosphetanes **4a—f** were the reaction products (Scheme 5).

**Scheme 5**



X = F, R = Me (**a**), Bu (**b**), $Pr^i$ (**c**), Ph (**d**); X = Cl, R = Me (**e**), Ph (**f**).

The structures of oxazaphosphetanes **4** were confirmed by spectroscopic data; in addition, some of them (**4a,c,e**) were identical with compounds synthesized earlier[10] from *N*-chlorotrihaloacetamides and $PCl_3$.

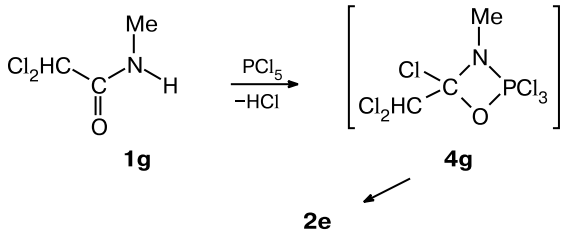
Most of the oxazaphosphetanes obtained are liquids that can be distilled *in vacuo* and are easily hydrolyzed by atmospheric moisture. Like dimeric trichloro(imino)phosphines, oxazaphosphetanes are resistant to $SO_2$.[11] The distilled liquids are stable for a long period of time. Hydrogen chloride catalyzes their decomposition, which was confirmed in an independent experiment. The use of *N*-trimethylsilylamides in the reactions with $PCl_5$ precludes the formation of HCl and affords the target products in high yields.

In the presence of HCl, phosphetanes **4** decompose just in the course of the reaction in two competitive pathways *a* and *b* (see Scheme 5). For *N*-methyltetrachloro(trifluoromethyl)oxazaphosphetane **4a**, the ratio of the imidoyl chloride **2a** and trifluoroacetyl chloride was virtually identical with that reported earlier.[8] Oxazaphosphetanes decomposed rapidly when heated to 80—120 °C. The decomposition temperature and the ratio of the products are determined by the nature of the substituents at the N atom. For R = Me and Bu, both decomposition pathways are approximately equally probable; the formation of imidoyl chloride and $POCl_3$ is dominant with a branched (*N*-isopropyl) radical. The presence of *N*-phenyl group substantially reduces the stability of the intermediate and favors the dominance (up to 75%) of dimeric trichloro(*N*-phenylimino)phosphine and trihaloacetyl chloride. The presence of the trihalomethyl or other electron-withdrawing groups at the C atom is prerequisite for the stabilization of the oxazaphosphetane ring. Oxazaphosphetanes with weaker electron acceptors at the C atom are less stable. This is evident from the fact that the reactions of *N*-substituted amides of aromatic (benzoic, *p*-nitrobenzoic, and perfluorobenzoic) and aliphatic (pivalic and isobutyric) carboxylic acids with $PCl_5$ yielded no oxazaphosphetanes.

The formation of oxazaphosphetane **4g** in the reaction of *N*-methyldichloroacetamide (**1g**) with $PCl_5$ was confirmed by spectroscopic methods. However, the final reaction product was trichloroacetimidoyl chloride (**2e**) rather than a dichloro analog as the result of chlorination of the dichloromethyl group (Scheme 6).

The formation of oxazaphosphetanes can proceed *via* intermediate acyclic *N*- or *O*-tetrachlorophosphoranes, which undergo cyclization into tetrachlorophosphorates upon the attack of the carbonyl O atom or the N atom on the electrophilic P atom. Subsequent 1,3-chlorotropic migration in the phosphorates leads to the corresponding tetrachlorooxazaphosphetanes with the five-coordinate

**Scheme 6**




P atom. Most likely, primary reaction products are *N*-phosphorylated derivatives. An alternative pathway implying a direct attack of the carbonyl O atom on the P atom seems to be less probable because in this case, the acyl substituents at the N atom, which enhance the electrophilicity of phosphorus, would favor cyclization and stabilization of oxazaphosphetanes.

To determine the most probable pathway for the formation of the phosphoranes, we performed *ab initio* RHF/6-31+G(d,p) and B3LYP/6-31+G(d,p) GAMESS[12] calculations of possible intermediates in the reactions of trihalogenoacetamides with $PCl_5$ with *N*-methyl- and *N*-phenyltrifluoroacetamides as examples (Scheme 7).

The results of the calculations are given in Table 1. According to the RHF/6-31+G(d,p) data, *N*-pre-reaction complexes **5** are thermodynamically more favorable ($\delta\Delta E$ = 56.8 (R = Me) and 72.7 kJ mol$^{-1}$ (R = Ph)) than their *O*-analogs (**6**). Although the initially formed putative *N*-tetrachlorophosphoranes (**7**) and *O*-isomers (**8**) are similar in thermodynamic stabilities, the formation of the former is more favorable ($\delta\Delta E$ = 13.3 (R = Me) and 10.6 kJ mol$^{-1}$ (R = Ph)). According to the scheme, the next reaction step is cyclization of *N*- or *O*-tetrachlorophosphoranes into phosphorates (**9**), which are more stable than acyclic isomers (**7**, **8**) ($\delta\Delta E$ = 4.6 and 17.9 kJ mol$^{-1}$ for R = Me and 2.9 and 13.8 kJ mol$^{-1}$ for R = Ph). Cyclic intermediates (**9**) are more polar (by 2 to 3 D) than acyclic ones (**7**, **8**), which also favors the cyclization along pathways *a* and *b* in polar media (see Scheme 7). Thus, acyclic *N*- or *O*-tetrachlorophosphoranes (**7**, **8**) can immediately be converted into phosphorates (**9**). The cyclization along pathway *a* occurs somewhat more easily because of its lower energy of activation (see Table 1).

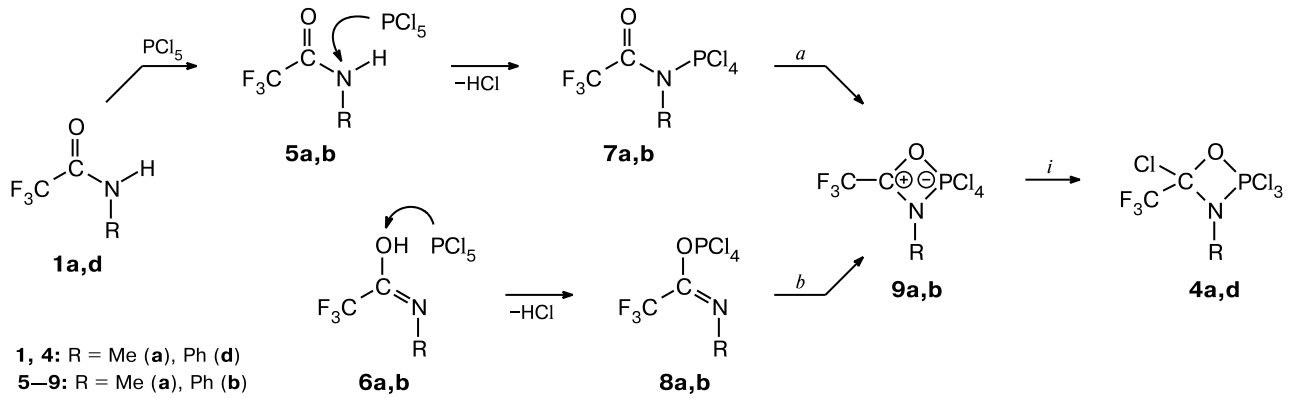
Subsequent 1,3-chlorotropic migration in phosphorates (**9**) gives tetrachlorooxazaphosphetanes (**4**) with the five-coordinate P atom; their energies are substantially lower than those of the corresponding bipolar isomers (**9**) ($\delta\Delta E$ = 84.4 (R = Me) and 83.2 kJ mol$^{-1}$ (R = Ph)). The fairly high energies of activation of 1,3-chlorotropic migration are lowered owing to coordination of the transition states with hydrogen chloride or to the solvation effects. Our data are in qualitative agreement with those obtained for tetrachlorodiazaphosphetanes.[13]

According to our calculations, the nature of substituent R (R = Me or Ph) at the amide N atom affects the course of the reactions insignificantly. It is worth noting that the thermodynamic characteristics of these processes *in vacuo* differ little from those obtained with consideration of the solvent effect in terms of the PCM model [14] ($\Delta E_{solv}$ = –25.2 (**7a**) and –16.3 kJ mol$^{-1}$ (**8a**)).

Introduction of halogen atoms into the aromatic ring of *N*-aryltrihalogenoacetamides significantly affects the direction of their reactions with $PCl_5$. For instance, *N*-pentafluorophenyltrifluoro- and -trichloroacetamides react with $PCl_5$ to give only trichloro(*N*-pentafluorophenylimino)phosphine,[15] while *N*-pentachlorophenyltrichloroacetamide affords the corresponding imidoyl chloride in moderate yield.[16]

Thus, our calculations showed that in the reactions of *N*-substituted trihalogenoacetamides with $PCl_5$, *N*-tetrachlorophosphoranes (**7**) are the most probable intermediates; they are rapidly converted into cyclic tetrachloro-

**Scheme 7**




*i*. 1,3-migration.

**Table 1.** Thermodynamic characteristics of the intermediates in the reactions of *N*-methyl- and *N*-phenyltrifluoroacetamides with $PCl_5$ according to the RHF/6-31+G(d,p) and B3LYP/6-31+G(d,p) calculations

| Process | Initial state | | | Transition state | | | | | Final state | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $-E$ | ZPE | μ /D | $-E$ | ZPE | $E^{\#}$ | $-\nu_1$ /cm$^{-1}$ | μ /D | $-E$ | ZPE | $\delta\Delta E$ | μ /D |
| | au | | | au | | | | | au | | | |
| | | | | | | RHF/6-31+G(d,p) | | | | | | |
| **5a** → **7a** | 3181.61587 | 0.09579 | 4.6 | — | — | — | — | — | 2721.54835 | 0.07651 | — | 3.7 |
| **7a** → **9a** | 2721.54835 | 0.07651 | 3.7 | 2721.54074 | 0.07632 | 5.0 | 116.4 | 4.4 | 2721.55012 | 0.07718 | −4.6 | 5.6 |
| **9a** → **4a** | 2721.55012 | 0.07718 | 5.6 | 2721.51958 | 0.07665 | 80.3 | 132.6 | 7.5 | 2721.58228 | 0.07775 | −84.4 | 2.4 |
| **6a** → **8a** | 3181.58819 | 0.09502 | 2.4 | — | — | — | — | — | 2721.54329 | 0.07592 | — | 2.2 |
| **8a** → **9a** | 2721.54329 | 0.07592 | 2.2 | 2721.54074 | 0.07632 | 6.7 | 116.4 | 3.3 | 2721.55012 | 0.07718 | −17.9 | 5.6 |
| **5b** → **7b** | 3372.22274 | 0.15243 | 4.0 | — | — | — | — | — | 2912.01348 | 0.12756 | — | 5.1 |
| **7b** → **9b** | 2912.01348 | 0.12756 | 5.1 | 2912. 01174 | 0.12759 | 4.6 | 119.6 | 5.5 | 2912.01464 | 0.12841 | −2.9 | 6.4 |
| **9b** → **4b** | 2912.01464 | 0.12841 | 6.4 | 2911.98340 | 0.12762 | 81.9 | 120.2 | 8.6 | 2912.04644 | 0.12888 | −83.2 | 3.5 |
| **6b** → **8b** | 3372.04860 | 0.15231 | 1.7 | — | — | — | — | — | 2912.00945 | 0.12734 | — | 2.3 |
| **8b** → **9b** | 2912.00945 | 0.12734 | 2.3 | 2912.00715 | 0.12775 | 5.6 | 73.8 | 3.6 | 2912.01464 | 0.12841 | −13.8 | 6.4 |
| | | | | | | B3LYP/6-31+G(d,p) | | | | | | |
| **7a** → **9a** | 2727.69402 | 0.07620 | 1.9 | 2727.69234 | 0.07637 | 4.6 | 34.8 | 2.8 | 2727.71137 | 0.07683 | −45.6 | 5.0 |
| **8a** → **9a** | 2727.69847 | 0.07564 | 2.1 | 2727.67482 | 0.07384 | 61.9 | 270.0 | 4.2 | 2727.71137 | 0.07683 | −33.9 | 5.0 |
| **9a** → **4a** | 2727.71137 | 0.07683 | 5.0 | 2727.67766 | 0.07616 | 88.6 | 250.7 | 4.6 | 2727.72548 | 0.07739 | −37.2 | 2.4 |

*Note*. $E^{\#}$ and $\delta\Delta E$ are expressed in kJ mol$^{-1}$.

phosphorates (**9**) and, upon triad migration of the Cl atom, into oxazaphosphetanes (**4**).

## Experimental

IR spectra were recorded on a UR-20 spectrophotometer. $^1$H, $^{19}$F, $^{31}$P, and $^{13}$C NMR spectra were recorded on a Varian VXR-300 spectrometer (299.15, 282.20, 121.42, and 75.43 MHz, respectively). Chemical shifts are referenced to HMDS ($^1$H, $^{13}$C) and $CFCl_3$ ($^{19}$F) as the internal standards and to 85% $H_3PO_4$ ($^{31}$P) as the external standard. The starting amides were prepared according to known procedures.[17]

**2,2,2,4-Tetrachloro-3-methyl-4-trifluoromethyl-1,3,2-λ$^5$-oxazaphosphetane (4a).** ***A.*** A solution of *N*-methyltrifluoroacetamide (**1a**) (0.1 mol) in $CH_2Cl_2$ (50 mL) was added to a suspension of $PCl_5$ (0.1 mol) in $CH_2Cl_2$ (100 mL). The reaction mixture was left at room temperature for 48 h (complete dissolution of $PCl_5$) and concentrated *in vacuo*; the residue was distilled. The yield of compound **4a** was 53%, b.p. 60—65 °C (10 Torr). $^{31}$P NMR ($CH_2Cl_2$), δ: −46.2 (q, $^3J_{PH}$ = 26.0 Hz). $^{19}$F NMR ($CH_2Cl_2$), δ: −81.9 (s), which agrees with the literature data.[9]

***B.*** Chlorotrimethylsilane (0.015 mol) was added at 10 °C to a stirred solution of *N*-methyltrifluoroacetamide (**1a**) (0.015 mol) and triethylamine (0.017 mol) in ether (50 mL). The reaction mixture was kept at room temperature for 96 h. The precipitate that formed was filtered off and washed with ether (10 mL). The solvent was removed under atmospheric pressure. The residue was dissolved in $CH_2Cl_2$ (15 mL) and the solution was added to a stirred suspension of $PCl_5$ (0.0136 mol) in $CH_2Cl_2$ (20 mL). The mixture was kept at room temperature for 24 h (complete dissolution of $PCl_5$) and concentrated *in vacuo*. The yield of compound **4a** was 94%.

**3-Butyl-2,2,2,4-tetrachloro-4-trifluoromethyl-1,3,2-λ$^5$-oxazaphosphetane (4b).** *N*-Butyltrifluoroacetamide (**1b**) (0.186 mol) was added to a suspension of $PCl_5$ (0.186 mol) in $CH_2Cl_2$ (100 mL). The reaction mixture was kept at room temperature for 72 h (complete dissolution of $PCl_5$) and concentrated *in vacuo*; the residue was distilled. The yield of compound **4b** was 68%, b.p. 60—63 °C (0.07 Torr). Found (%): Cl, 41.65; N, 4.22; P, 9.17. $C_6H_9Cl_4F_3NOP$. Calculated (%): Cl, 41.59; N, 4.11; P, 9.09. $^{31}$P NMR ($CH_2Cl_2$), δ: −46.4 (q, $^3J_{PH}$ = 36.8 Hz). $^{19}$F NMR ($CH_2Cl_2$), δ: −81.9 (s). $^1$H NMR ($CDCl_3$), δ: 0.94 (t, 3 H, Me); 1.35 (sextet, 2 H, MeC$\underline{H}_2$); 1.77 (m, 2 H, MeCH$_2$C$\underline{H}_2$); 3.87 (dt, 2 H, NC$\underline{H}_2$, $^3J_{HP}$ = 36.4 Hz, $^3J$ = 8.1 Hz). IR ($CCl_4$), ν/cm$^{-1}$: 1080; 1210; 1400; 1475; 2980.

**2,2,2,4-Tetrachloro-3-isopropyl-4-trifluoromethyl-1,3,2-λ$^5$-oxazaphosphetane (4c).** A solution of *N*-isopropyltrifluoroacetamide (**1c**) (0.0436 mol) in $CH_2Cl_2$ (50 mL) was added to a suspension of $PCl_5$ (0.0436 mol) in $CH_2Cl_2$ (100 mL). The reaction mixture was heated at 40—45 °C for 8 h, and concentrated *in vacuo*; the residue was distilled. The yield of compound **4c** was 32%, b.p. 45—50 °C (0.07 Torr). $^{31}$P NMR ($CH_2Cl_2$), δ: −48.0 (d, $^3J_{PH}$ = 56.6 Hz). $^{19}$F NMR ($CH_2Cl_2$), δ: −81.1 (s), which agrees with the literature data.[9]

**2,2,2,4-Tetrachloro-3-phenyl-4-trifluoromethyl-1,3,2-λ$^5$-oxazaphosphetane (4d).** ***A.*** A solution of trifluoroacetanilide (**1d**) (0.05 mol) in $CH_2Cl_2$ (50 mL) was added to a suspension of $PCl_5$ (0.05 mol) in $CH_2Cl_2$ (150 mL). The reaction mixture was left at room temperature for 96 h (complete dissolution of $PCl_5$) and concentrated *in vacuo*. Trichloro(*N*-phenylimino)phosphine dimer was precipitated with light petroleum (40—60 °C, 50 mL) and filtered off. The solvent was removed *in vacuo*. The yield of compound **4d** was 38%, $n_D^{15}$ 1.3985. Found (%): Cl, 39.34; N, 3.92; P, 8.61. $C_8H_5Cl_4F_3NOP$. Calculated (%): Cl, 39.29; N, 3.88; P, 8.58. $^{31}$P NMR ($CH_2Cl_2$), δ: −45.2. $^{19}$F NMR ($CH_2Cl_2$), δ: −80.6 (s). $^{13}$C NMR ($CDCl_3$), δ: 98.50 (dq, $CF_3\underline{C}$,

$^2J_{CP}$ = 7.6 Hz, $^2J_{CF}$ = 40.7 Hz); 132.98 (d, $C_{ipso}$, $^2J_{CP}$ = 9.6 Hz); 131.02 (d, $C_o$, $^3J_{CP}$ = 6.7 Hz); 129.61 (s, $C_p$); 129.58 (d, $C_m$, $^4J_{CP}$ = 4.3 Hz); 119.40 (qd, $CF_3$, $J_{CF}$ = 285.7 Hz, $^3J_{CP}$ = 18.2 Hz). $^1$H NMR ($CDCl_3$), δ: 7.24 (t, 1 H, $H_p$); 7.39 (t, 2 H, $H_m$); 7.64 (d, 2 H, $H_o$). IR ($CCl_4$), ν/cm$^{-1}$: 1110; 1430; 1600; 1650.

***B.*** Chlorotrimethylsilane (0.032 mol) was added to a stirred solution of trifluoroacetanilide (**1d**) (0.032 mol) and triethylamine (0.036 mol) in benzene (200 mL). The reaction mixture was refluxed for 8 h. The precipitate that formed was filtered off and washed with benzene (30 mL). The solvent was removed *in vacuo*. The residue was dissolved in $CH_2Cl_2$ (20 mL) and the solution was added to a stirred suspension of $PCl_5$ (0.0314 mol) in $CH_2Cl_2$ (30 mL). The reaction mixture was kept at room temperature for 48 h (complete dissolution of $PCl_5$) and concentrated *in vacuo*. Trichloro(*N*-phenylimino)phosphine dimer was precipitated with light petroleum (30 mL) and filtered off. The solvent was removed *in vacuo* to give compound **4d** in 93% yield.

**2,2,2,4-Tetrachloro-3-methyl-4-trichloromethyl-1,3,2-λ$^5$-oxazaphosphetane (4e).** ***A.*** *N*-Methyltrichloroacetamide (**1e**) (0.12 mol) was added to a suspension of $PCl_5$ (0.12 mol) in $CH_2Cl_2$ (250 mL). The reaction mixture was refluxed for 18 h and concentrated *in vacuo*. The residue was treated with light petroleum (60 mL). The precipitate that formed was filtered off and washed with light petroleum—benzene (2 : 1) (40 mL). The yield of compound **4e** was 45%, m.p. 40—41 °C. $^{31}$P NMR ($CH_2Cl_2$), δ: −46.8 (q, $^3J_{PH}$ = 27.4 Hz), which agrees with the literature data.[9]

***B.*** Chlorotrimethylsilane (0.02 mol) was added at 10 °C to a stirred solution of *N*-methyltrichloroacetamide (**1e**) (0.021 mol) and triethylamine (0.025 mol) in ether (100 mL). The reaction mixture was kept at room temperature for 96 h. The precipitate that formed was filtered off and washed with ether (20 mL). The solvent was removed *in vacuo* and the residue was dissolved in $CH_2Cl_2$ (30 mL). The solution was added to a stirred suspension of $PCl_5$ (0.02 mol) in $CH_2Cl_2$ (30 mL). The mixture was kept at room temperature for 48 h (complete dissolution of $PCl_5$) and concentrated *in vacuo*. The yield of compound **4e** was 96%.

**2,2,2,4-Tetrachloro-3-phenyl-4-trichloromethyl-1,3,2-λ$^5$-oxazaphosphetane (4f).** Chlorotrimethylsilane (0.0113 mol) was added to a stirred solution of trichloroacetanilide (**1f**) (0.0113 mol) and triethylamine (0.014 mol) in benzene (50 mL). The reaction mixture was kept at room temperature for 96 h. The precipitate that formed was filtered off and washed with benzene (20 mL). The solvent was removed *in vacuo* and the residue was dissolved in $CH_2Cl_2$ (15 mL). The solution was added to a stirred suspension of $PCl_5$ (0.0113 mol) in $CH_2Cl_2$ (30 mL). The mixture was kept at room temperature for 48 h (complete dissolution of $PCl_5$) and two thirds of the solvent was distilled off *in vacuo*. The precipitate that formed was filtered off and the filtrate was concentrated *in vacuo*. Trichloro(*N*-phenylimino)phosphine dimer was precipitated with light petroleum—benzene (1 : 1) (30 mL) at 0 to 5 °C and filtered off. The solvents were removed *in vacuo*. The yield of compound **4f** was 62% (90% purity), m.p. 67—70 °C (decomp.). Found (%): Cl, 60.72; N, 3.60; P, 7.84. $C_8H_5Cl_7NOP$. Calculated (%): Cl, 60.49; N, 3.41; P, 7.55. IR ($CCl_4$), ν/cm$^{-1}$: 1100; 1360; 1600; 1660. $^{31}$P NMR ($CH_2Cl_2$), δ: −45.6. $^1$H NMR ($CDCl_3$), δ: 7.22 (t, 1 H, $H_p$); 7.34 (t, 2 H, $H_m$); 7.56 (d, 2 H, $H_o$).

***N*-Methyltrichloroacetimidoyl chloride (2e).** A solution of *N*-methyldichloroacetamide (**1g**) (0.2 mol) in $CH_2Cl_2$ (50 mL) was added to a suspension of $PCl_5$ (0.2 mol) in $CH_2Cl_2$ (250 mL). The reaction mixture was left at room temperature until the dissolution of $PCl_5$ was completed. The formation of 2,2,2,4-tetrachloro-4-dichloromethyl-3-methyl-1,3,2-λ$^5$-oxazaphosphetane (**4g**) was evidenced by an intense signal at δ −48.5 ($^3J_{PH}$ = 27.5 Hz) in the $^{31}$P NMR spectrum of the reaction mixture. After five days, the solvent was removed *in vacuo* and the residue was fractionated. The yield of compound **2e** was 37%, b.p. 54—56 °C (10 Torr), which agrees with the literature data.[18]

**Thermolysis of oxazaphosphetane 4a.** A solution of compound **4a** (0.02 mol) in xylene (8 mL) was refluxed for 18 h. The mixture was distilled under atmospheric pressure. The yield of imidoyl chloride **2a** was 1 g (35%), b.p. 49—50 °C (*cf.* Ref. 8). The residue was kept *in vacuo* and treated with light petroleum (5 mL). The precipitate that formed was filtered off to give 2,2,2,4,4,4-hexachloro-1,3-dimethyl-1,3,2,4-diazadiphosphetane (**3a**) (1.4 g, 50%), m.p. 175—177 °C (*cf.* Ref. 19).

**Thermolysis of oxazaphosphetane 4b.** Compound **4b** (0.036 mol) was heated to 130 to 135 °C and kept at this temperature for 3 h. The mixture was fractionated under atmospheric pressure. According to $^{31}$P and $^{19}$F NMR data, the fraction with b.p. 100—105 °C (9.2 g) consisted of *N*-butyltrifluoroacetimidoyl chloride (**2b**) ($\delta_F$ −71.8) and $POCl_3$ ($\delta_P$ 3.0). The residue was kept *in vacuo* at 50 °C for 4 h to give 1,3-dibutyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetane (**3b**) (3.68 g, 50%), m.p. 74—75 °C (*cf.* Ref. 19).

**Thermolysis of oxazaphosphetane 4c.** Compound **4c** (0.08 mol) was heated at 125—130 °C for 4 h. The mixture was fractionated *in vacuo*. According to $^{31}$P and $^{19}$F NMR data, the fraction (6.5 g) with b.p. 35—40 °C (20 Torr) consisted of *N*-isopropyltrifluoroacetimidoyl chloride (**2c**) ($\delta_F$ −71.6) and $POCl_3$ ($\delta_P$ 3.0).

**Thermolysis of oxazaphosphetane 4d.** A solution of compound **4d** (0.0363 mol) in toluene (15 mL) was refluxed for 20 min. Two thirds of the solvent was distilled off *in vacuo* and the precipitate that formed was filtered off and washed with light petroleum (10 mL). The yield of 2,2,2,4,4,4-hexachloro-1,3-diphenyl-1,3,2,4-diazadiphosphetane (**3d**) was 6.2 g (75%), m.p. 179—180 °C (*cf.* Ref. 11). Light petroleum was removed *in vacuo* from the filtrate and the residue was distilled to give *N*-phenyltrifluoroacetimidoyl chloride (**2d**) (1.9 g, 24%), b.p. 51—53 °C (10 Torr) (*cf.* Ref. 20).

**Thermolysis of oxazaphosphetane 4e.** A solution of compound **4e** (0.01 mol) in xylene (5 mL) was refluxed for 18 h and then distilled *in vacuo*. The yield of *N*-methyltrichloroacetimidoyl chloride (**2e**) was 0.8 g (41%), b.p. 53—55 °C (10 Torr) (*cf.* Ref. 18). The residue was treated with light petroleum (10 mL) and the precipitate that formed was filtered off to give 2,2,2,4,4,4-hexachloro-1,3-dimethyl-1,3,2,4-diazadiphosphetane (**3a**) (0.9 g, 50%), m.p. 174—176 °C.

**Thermolysis of oxazaphosphetane 4f.** A solution of compound **4f** (0.032 mol) in toluene (80 mL) was refluxed for 20 min and concentrated *in vacuo*. The precipitate that formed was washed with light petroleum (30 mL). The yield of 2,2,2,4,4,4-hexachloro-1,3-diphenyl-1,3,2,4-diazadiphosphetane (**3d**) was 5 g (75%), m.p. 179—180 °C.

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