Pseudohalogenation of Phosphites

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Abstract: A new type of Atherton–Todd reaction for a convenient pseudohalogenation of phosphites has been developed. Direct azidation, cyanation, and thiocyanation of $(RO)_2P(O)H$ (R = Et, *i*-Bu, Ph) were accomplished readily with sodium pseudohalides in acetonitrile under mild modified Atherton–Todd conditions. The corresponding phosphorochloridates were demonstrated by GC/MS to be the intermediates. Pseudohalogenations of ethyl phenylphosphinate and diphenylphosphine oxide were also investigated.

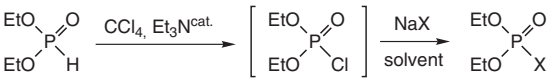
Key words: pseudohalophosphates, pseudohalogenation, phosphites, phosphorochloridates, Atherton–Todd reaction

Phosphorus compounds of the general type RR′P(O)H (where R, R′ = alkyl, aryl, hydroxyl, alkoxyl, aroxyl) undergo a variety of substitution reactions in which H is replaced by another atom or group such as deuterium,[1] halogen,[2] alkylmercapto,[3] β-substituted alkyl,[4] or α-hydroxyalkyl.[5] Among those reactions, Atherton–Todd method is one of the most widely used approaches, especially in the synthesis of a large part of biologically active species including phosphoramidates, organophosphates and polyphosphates; but it is still mainly limited to the formation of P–N compounds now.[6]

One the other hand, azide, cyanide, and thiocyanide are the most known and utilized pseudohalogens in organic chemistry and their corresponding pseudohalophosphates $(RO)_2P(O)X$ (where X = N_3, CN, NCS) are versatile reagents in organic synthesis.[7] Besides other methods for the preparation of phosphorazidates,[8] phosphorocyanidates,[9] and phosphor(isothiocyanatidate)s,[10] $(RO)_2P(O)X$ can be obtained from the corresponding phosphorochloridates. However, some require high temperature or long reaction time or special reagents, which mainly result from the low reactivity between organic compounds and inorganic ions. In addition, being essentially acid halides, phosphorochloridates are capable of many replacement side-reactions that involve the highly reactive halogen atom throughout the preparations.

Since phosphorochloridates are generally prepared from phosphites,[2b] direct pseudohalogenation of phosphites $(RO)_2P(O)H$ should be applicable. But, surprisingly, there are still no such reported practical procedures to date. The objective of the present work is thus to give a general methodology about convenient and direct pseudohalogenation of $(RO)_2P(O)H$ under modified Atherton–Todd conditions in view of the following reasons: a) the fact that phosphorochloridates are the in situ intermediates in Atherton–Todd reaction;[2b,11] b) the feasibility of pseudohalides of phosphorochloridates by alkali pseudohalogens under definite conditions;[8–10] and c) much more convenience of phosphites than phosphorochloridates in the preparation and availability as starting materials.

In order to optimize the reaction conditions, pseudohalogenation of diethyl phosphite was chosen as the representative reaction. It was found experimentally that no pseudohalogenation of diethyl phosphite occurred even at high temperature and long reaction time unless both carbon tetrachloride and catalytic triethylamine were used. This can be easily explained by the reaction mechanism demonstrated by GC/MS analysis of the reactions. Similar to the conventional Atherton–Todd reaction mechanism,[11] when treated with pseudohalides, carbon tetrachloride and triethylamine in selected solvents, diethyl phosphite was first converted into diethyl phosphorochloridate which was then pseudohalogenated immediately into the target compounds $(EtO)_2P(O)X$ (Scheme 1).



X=N_3, CN, SCN.

Scheme 1 Pseudohalogenation of diethyl phosphite

Moreover, similar to our prior report about the cyanation of phosphorochloridates by potassium cyanide,[9a] azidation of diethyl phosphite can be stimulated, to a great extent, by use of solvents of the polar aprotic type, such as DMF and acetonitrile (Table 1). But in the protic methanol, $(EtO)_2PO_2Me$ was found to be the main product as anticipated. As stated before,[11] the base condition was vital importance to the generation of Atherton–Todd reactions, therefore, it is not surprising that no changes were detected in acetic acid. Acetonitrile is employed in our later experiments only because of its low boiling point, which would bring much convenience in the workup procedure.

Unexpectedly, it took only 30 minutes to accomplish the pseudohalogenation of diethyl phosphite in acetonitrile. The much shorter reaction time, compared with the usually several hours, when crude diethyl phosphorochloridate is used directly, may probably result from the higher reac-

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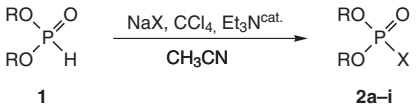
Table 1 Azidation of Diethyl Phosphite in Different Solvents[a]

Entry	Solvents	$E_T(30)$[b]	Yield of **2a** (%)[c]
1	methanol	55.5	6.3
2	acetic acid	51.2	0
3	acetonitrile	46.0	75.3
4	*N*,*N*-dimethylformamide	43.8	100
5	chloroform	39.1	20.7
6	tetrahydrofuran	37.4	29.3
7	benzene	34.5	13.7
8	carbon tetrachloride	32.5	22.7

[a] The lower reaction rate than that in experiments was due to the much lower concentration of the starting materials (2 mmol in10 mL).
[b] $E_T(30)$: experiential polarity parameter of solvent.[13,]
[c] Conversion of $(EtO)_2PHO$ to **2a** calculated from GC spectra after 1 h.

tivity of the 'fresh' phosphorochloridate formed in situ[12] and polar aprotic solvent used.[9a]

In common with the reactions of diethyl phosphite, azidation, cyanation, and thiocyanation of diisobutyl phosphite and diphenyl phosphite under the same conditions proceeded satisfactorily. Usually cooling is necessary to carry out the preparations because of the rather exothermic action. In addition, phosphorothiocyanidates formed at first were found to isomerize completely into phosphor(isothiocyanatidate)s in the distilled products which were characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and mass spectra. Therefore, a novel and convenient method in conducting direct pseudohalogenation of phosphites was performed as shown in Scheme 2.



Scheme 2 Pseudohalogenation of phosphites

Accordingly, results of synthesis of pseudohalophosphates $(RO)_2POX$ (X = N_3, CN, NCS) **2a–i** are shown in Table 2.

It is important to add a warning note about the thiocyanation of phosphites. Because sodium thiocyanide has very good solubility in acetonitrile and in products, but low in diethyl ether, thorough extractions of the crude products by diethyl ether and redistillations were needed for purification. Otherwise, sodium thiocyanide can occlude in the products during the distillation, which can be detected by the absorption of SCN in the IR spectra.

It is known that both alkylphosphinic acids $R(HO)P(O)H$[14] and dialkylphosphine oxides $R_2P(O)H$[15] can be esterified by alcoholysis to form the corresponding

Table 2 Synthesis of $(RO)_2P(O)X$ **2a–i** from $(RO)_2P(O)H$

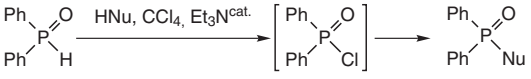
Entry	Product	R	X	Yield (%)[a]
1	**2a**	Et	N_3	85
2	**2b**	Et	CN	88
3	**2c**	Et	NCS	83
4	**2d**	*i*-Bu	N_3	85
5	**2e**	*i*-Bu	CN	81
6	**2f**	*i*-Bu	NCS	74
7	**2g**	Ph	N_3	76
8	**2h**	Ph	CN	83
9	**2i**	Ph	NCS	77

[a] Isolated yield.

phosphinates under conventional Atherton–Todd conditions. Moreover, pseudohalogenation of phosphonochloridates $R(R'O)P(O)Cl$[16] and phosphinic chlorides $RR'P(O)Cl$[17] by alkali pseudohalides have also been reported. We therefore investigated the possibility to apply the new procedure of phosphites to pseudohalogenation of those compounds possessing the functionality of P(O)H such as ethyl phenylphosphinate Ph(EtO)P(O)H and diphenylphosphine oxides $Ph_2P(O)H$.

When azidation of ethyl phenylphosphinate was conducted under the same conditions, the target compound ethyl phenylphosphonazidate (**2j**) was obtained in 71% yield (see experimental). But cyanation and thiocyanation of ethyl phenylphosphinate did not occur even in refluxing acetonitrile. However, phenyl phosphinochloridate was not detected by GC/MS during the reactions. Attempt to prepare phenyl phosphinochloridate under typical Atherton–Todd conditions had also failed. The reaction may proceed with an unknown mechanism that needs further investigations.

In the case of diphenylphosphine oxide, the reaction became quite different. When a mixture of diphenylphosphine oxide, carbon tetrachloride, triethylamine and pseudohalides was stirred for a few minutes at room temperature, diphenylphosphinic acid, chloroform and triethylammonium chloride were detected by ^{31}P NMR spectroscopy and GC/MS, but without any pseudohalogen having been attached onto P atom. It is similar to the former report that the phosphine oxide may have been oxidized to diphenylphosphinic chloride which is then hydrolyzed by 'water originally associated with the phosphine oxide'[15a](Scheme 3).



Scheme 3 Atherton–Todd reactions of diphenylphosphine oxide

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As detected by GC, diphenylphosphine oxide was converted into the corresponding diphenylphosphinate and diphenylphosphinothioate easily by typical Atherton–Todd method. The reactions most probably proceeded by the formation of diphenylphosphinic chloride for that chloroform, the other typical product of Atherton–Todd reaction, was also detected by GC/MS (Scheme 3).

The lower reactivity of inorganic pseudohalogens mentioned above, compared with the homogenous nucleophiles in Scheme 3, may lead to the failure of pseudohalogenation of diphenylphosphine oxide.

To sum up, a new type of Atherton–Todd reaction has been performed based on the convenient azidation, cyanation, and thiocyanation of dialkyl and diaryl phosphites under mild conditions. Though only partly succeeded, pseudohalogenation of RR′P(O)H (where R, R′ = alkoxyl, aroxyl, alkyl, aryl) still deserve further investigation, and therefore the corresponding attempts with phase transfer catalysts are now under study in our laboratory.

More importantly, the methodology about direct pseudohalogenation of phosphites may also be applied to other phosphorylating reactions of those compounds with the general functionality of P(O)H.

Dialkyl phosphites,[18a] ethyl phenylphosphinate,[18b] and diphenylphosphine oxide[18c] were prepared by the known methods. Diphenyl phosphites and phenylphosphinic acid were purchased from Acros and used as such. GC-MS was recorded on a Varian CP-3800 and a Finnigan Mat TSQ70 spectrometer, IR on a Bio-Rad FTS185 spectrometer, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR (85% H_3PO_4 as external reference) on a Varian UNITY500 spectrometer.

Caution! Pseudohalogens and pseudohalophosphates are toxic or potentially explosive, appropriate precautions should be taken throughout the preparation of the products.

$(RO)_2P(O)X$ 2a–i from $(RO)_2P(O)H$; General Procedure

To a solution of the appropriate phosphite $(RO)_2PHO$ (20 mmol), CCl_4 (30 mmol), and sodium pseudohalide (30 mmol) in anhyd MeCN (50 mL) maintained at r.t. was added Et_3N (202 mg, 2 mmol) dropwise and very slowly. The mixture was then stirred intensively for 30 min. After filtration, the filtrate was concentrated in vacuo and then distilled to give the respective target products **2a–i** (Table 2).

Diethyl Phosphorazidate (2a)
Yield: 85%; bp 68–69 °C/2.0 mm.

IR (film): 1269.1 (P=O), 2163.2 cm^{-1} (N_3).

^{1}H NMR ($CDCl_3$, 500 Hz): δ = 1.39 (t, *J* = 7.0 Hz, 3 H), 4.20 (q, *J* = 6.5 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 15.89, 64.75.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –0.30.

EI-MS: *m*/*z* (%) = 180 (M + 1, 6), 152 (85), 137 (25), 124 (52), 109 (100), 91(27), 81 (60), 29 (14).

Diethyl Phosphorocyanidate (2b)
Yield: 88%; bp 54–55 °C/0.7 mm.

IR (film): 1305.9 (P=O), 2209.5 cm^{-1} (C≡N).

^{1}H NMR ($CDCl_3$, 500 Hz): δ = 1.46 (t, *J* = 7.0 Hz, 3 H), 4.34 (q, *J* = 5.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 15.64, 66.88, 112.67, 114.38.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –20.60.

EI-MS: *m*/*z* (%) = 164 (M + 1, 4), 148 (2), 136 (30), 120 (35), 108 (100), 83 (10), 55 (35), 45 (14).

Diethyl Phosphor(isothiocyanidate) (2c)
Yield: 83%; bp 49–51 °C/0.3 mm.

IR (film): 1276.1 (P=O), 2004.9 cm^{-1} (N=C=S).

^{1}H NMR ($CDCl_3$, 500 Hz): δ = 1.53 (t, *J* = 7.0 Hz, 3 H), 2.99 (q, *J* = 7.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 15.19, 64.97, 111.85.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –18.00.

EI-MS: *m*/*z* (%) = 196 (M + 1, 3), 195 (M, 73), 168 (65), 140 (25), 124 (88), 122 (57), 109 (100), 81 (84).

Diisobutyl Phosphorazidate (2d)
Yield: 85%; bp 79–80 °C/0.1 mm.

IR (film): 1270.9 (P=O), 2163.0 cm^{-1} (N_3).

^{1}H NMR ($CDCl_3$, 500 Hz): δ = 0.97 (d, *J* = 7.0 Hz, 6 H), 1.96–2.04 (m, 1 H), 3.86–3.93 (m, 2 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 18.30, 28.82, 74.30.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –0.23.

EI-MS: *m*/*z* (%) = 236 (M + 1, 2), 193 (1), 180 (8), 164 (5), 137 (10), 124 (100), 81 (6), 57 (24).

Diisobutyl Phosphorocyanidate (2e)
Yield: 81%; bp 86–88 °C/1.0 mm.

IR (film): 1306.8 (P=O), 2208.9 cm^{-1} (C≡N).

^{1}H NMR ($CDCl_3$, 500 Hz): δ = 1.00 (d, *J* = 7.0 Hz, 6 H), 2.01–2.11 (m, 1 H), 4.01–4.07 (m, 2 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 18.38, 75.22, 28.76, 112.51, 114.24.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –19.60.

EI-MS: *m*/*z* (%) = 220 (M + 1, 2), 164 (8), 148 (7), 136 (3), 121(12), 108 (55), 57 (100), 41 (98).

Diisobutyl Phosphor(isothiocyanidate) (2f)
Yield: 74%; bp 84–85 °C/0.1 mm.

IR (film): 1286.9 (P=O), 2004.0 cm^{-1} (N=C=S).

^{1}H NMR ($CDCl_3$, 500 Hz): δ = 0.98 (d, *J* = 7.0 Hz, 6 H), 1.95–2.07 (m, 1 H), 3.90–3.94 (m, 2 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 18.43, 28.83, 74.68.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –17.52.

EI-MS: *m*/*z* (%) = 252 (M + 1, 2), 196 (M, 23), 180 (6), 153 (10), 140 (100), 123 (5), 57 (29), 41 (17).

Diphenyl Phosphorazidate (2g)
Yield: 76%; bp 137–139 °C/0.2 mm.

IR (film): 1289.1 (P=O), 2171.9 cm^{-1} (N_3).

^{1}H NMR ($CDCl_3$, 500 Hz): δ = 7.20–7.40 (m, 5 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 115.26, 120.05, 120.24, 125.99, 126.31, 129.91.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –9.73.

EI-MS: *m*/*z* (%) = 276 (M + 1, 14), 275 (M, 100), 274 (M – 1, 36), 232 (5), 167 (28), 154 (12), 94 (8), 77 (22).

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Diphenyl Phosphorocyanidate (2h)
Yield: 83%; bp 128–130 °C/0.4 mm.

IR (film): 1322.0 (P=O), 2210.9 cm^{-1} (C≡N).

^1H NMR ($CDCl_3$, 500 Hz): δ = 7.17–7.41 (m, 5 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 111.36, 113.21, 119.91, 120.11, 125.90, 126.95, 129.76, 130.27.

^{31}P NMR ($CDCl_3$, 125Hz): δ = –29.20.

EI-MS: *m/z* (%) = 259 (M, 75), 166 (5), 140 (100), 119 (25), 94 (90), 77 (45), 65 (22), 51 (21).

Diphenyl Phosphor(isothiocyanidate) (2i)
Yield: 77%; bp 144–146 °C/0.2 mm.

IR (film): 1300.7 (P=O), 1986.9 cm^{-1} (N=C=S).

^1H NMR ($CDCl_3$, 500 Hz): δ = 7.07–7.42 (m, 5 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 120.13, 120.23, 124.76, 126.32, 129.51, 130.10.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = –27.71.

EI-MS: *m/z* (%) = 292 (M + 1, 7), 291 (M, 78), 258 (5), 215 (18), 170 (8), 140 (12), 94 (38), 77 (100).

Ethyl Phenylphosphonazidate (2j) from Ph(EtO)P(O)H
To a solution of Ph(EtO)P(O)H (3.40 g, 20 mmol), CCl_4 (30 mmol), and NaN_3 (1.95 g, 30 mmol) in MeCN (50 mL) maintained at r.t., was added Et_3N (2 mmol) dropwise and slowly. The mixture was then stirred for 30 min. After filtration, the filtrate was concentrated in vacuo and then distilled to give $Ph(EtO)P(O)N_3$.

Yield: 71%; bp 106–108 °C/0.25 mm.

IR (film): 1254.4 (P=O), 2154.3 cm^{-1} (N_3).

^1H NMR ($CDCl_3$, 500 Hz): δ = 1.41 (d, *J* = 7.0 Hz, 3 H), 2.05 (t, *J* = 9.0 Hz, 2 H), 7.50–7.87 (m, 5 H).

^{13}C NMR ($CDCl_3$, 125 Hz): δ = 16.10, 63.01, 128.30, 128.61, 131.24, 133.26.

^{31}P NMR ($CDCl_3$, 125 Hz): δ = 19.29.

EI-MS: *m/z* (%) = 211 (M, 6), 169 (27), 141 (100), 91 (7), 77 (44), 65 (7), 51 (18), 47 (14).

Atherton–Todd Reactions of Ph_2PHO
To a solution of Ph_2PHO (404 mg, 2 mmol) and HNu (Nu = O*i*-Bu, SPr; 2 mmol) in CCl_4 (5 mL) was added Et_3N (0.2 mmol). After stirring the mixture for 10 min, samples were taken without further isolation for ^{31}P NMR or GC-MS analysis.

Diphenylphosphonic Acid
^{31}P NMR ($CDCl_3$, 125 Hz): δ = 31.50.

Isobutyl Diphenylphosphonate
EI-MS: *m/z* (%) = 274 (M, 6), 219 (100), 201 (45), 141 (22), 132 (38), 77 (57), 51 (21).

***S*-Propyl Diphenylphosphinothioate**
EI-MS: *m/z* (%) = 276 (M, 15), 234 (30), 202 (90), 201 (100), 183 (8), 155 (12), 125 (11), 77 (17).

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