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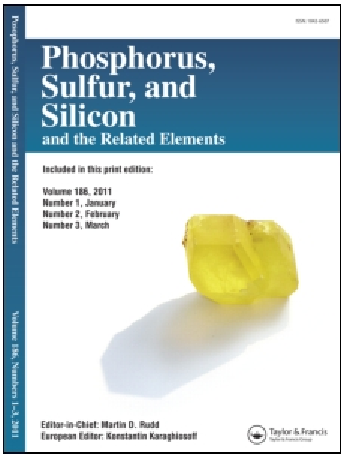

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The Reactions of Dialkyl Phosphites and Phosphine Oxides with Iodosylbenzene

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THE REACTIONS OF DIALKYL PHOSPHITES AND PHOSPHINE OXIDES WITH IODOSYLBENZENE

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The reaction of iodosylbenzene with >P(O)H type of acids (dialkyl phosphites, secondary phosphine oxides) was studied. The acids of >P(O)H type add to iodosylbenzene to yield intermediate **6** *which in the aprotic solvents yields oxidation products, it means >P(O)OH acids and/or anhydride of >P(O)OP(O)< type. On the other hand if the reaction is performed in alcohol as a solvent in the presence of sodium alcoholate >P(O)OR ester is the major product.*

Keywords: Alkyl phosphinates; dialkyl phosphates; H-phosphonates; iodosylbenzene; phosphine oxides; tetraalkyl pyrophosphate

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INTRODUCTION

Organic compounds of polycoordinated iodine have long been known, however, it is only recently that iodine compounds in the oxidation state +3 have gained synthetic and mechanistic significance, as described in several reviews.[1–6]

Iodosylbenzene, PhIO, is the most important and best investigated member of the family of iodosyl compounds. It has found wide synthetic application as a starting material in the preparation of numerous iodine(III) compounds and as an effective oxidant. However, to the best of our knowledge, iodosylbenzene hasn't been explored in phosphorus chemistry.

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As many iodine(III)-promoted reactions are thought to proceed via unstable intermediates, often phenyliodonium species, detailed studies on their mechanisms are scarce. In addition, it is often unclear as to whether this kind of iodine(III) chemistry proceeds via ionic or radical pathways. On the other hand it is well documented that, the reactivity of iodosylbenzene is related to the electrophilic center located on the iodine(III) atom and nucleophilic one on the oxygen atom. Iodosylbenzene is an effective oxidizing reagent, however, its insolubility due to its polymeric structure significantly restricts its practical usefulness. The overwhelming majority of the known reactions of PhIO require the presence of a hydroxylic solvent (water or methanol) or a catalyst (Lewis acid or complexes of transition metals), which actually results in the generation of activated monomeric species.

As early as in 1977 W. L. Foss at all.[7] presented the effectiveness of iodosylbenzene in the oxidation of the trivalent phosphorus organic compounds: phosphines and diphosphines which were transformed into phosphine oxides. For this transformation a phosphorus attack on the oxygen atom of iodosylbenzene was suggested.

In connection with our interest in the reactivity of phosphorus nucleophiles in the halophilic substitution reactions,[8] we took up the studies of the reaction between >P(O)H acids as well as >P—O$^-$ anions with iodosylbenzene. Because iodosylbenzene is known as an oxidizing agent one can expect the formation of dialkyl phosphates and phosphinates respectively in the reaction under investigation. On the other hand the effectiveness of such a oxidizing process, influence of solvent (especially hydroxylic solvents) and substituents on the phosphorus atom as well as on the course of the reaction were not obvious. Also the question should be answered: what is the mechanism of this reaction?

In this article we would present the results of our preliminary experiments.

RESULTS

From the theoretical point of view >P(O)H acids can add to iodosylbenzene to form 4-coordinate (σ^4, λ^5) and/or 3-coordinate (σ^3, λ^3) phosphorus intermediates (Scheme 1). Looking into the bonds energy the 4-coordinate phosphorus intermediate should be more stable, however both of them should collapse to iodobenzene and a >P(O)OH type acid.

In the first set of experiments we treated iodosylbenzene with dialkyl phosphites as well as secondary phosphine oxides in benzene or THF at the boiling point of the solvent. The reactions were carried out until the

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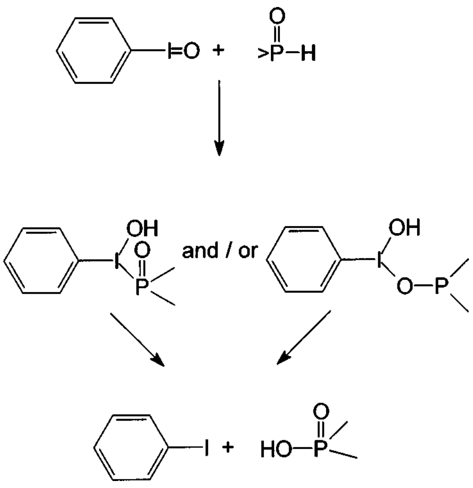
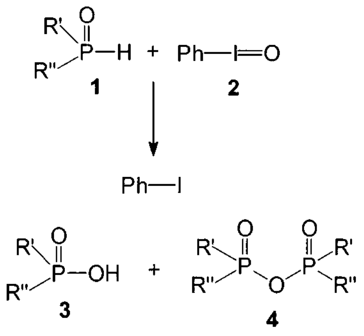


SCHEME 1

disappearance of solid iodosylbenzene. It should be pointed out that we observed much faster rate of the reaction between phosphine oxides and iodosylbenzene versus dialkyl phosphites; dialkyl phosphites required much longer reaction time.

The major products we observed in such a reaction mixture were: phosphoric or phosphinic acids respectively and anhydrides of phosphoric and phosphinic acids (Scheme 2). The results of this set of experiments are collected in Table I.



SCHEME 2

As one can see from the data presented in the Table I dialkyl phosphites yield in the reaction with iodosylbenzene mainly pyrophosphates **4**. When diethyl phosphite was treated with iodosylbenzene in THF, the reaction mixture after 12 h was examined by means of

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TABLE I The Products Distribution in the Reaction of Iodosylbenzene with >P(O)H Acids in Aprotic Solvents

					Yield %	
Run	R′	R″	Solvent	Conditions	**3**	**4**
1	EtO	EtO	PhH	0.5 h, b.p.	11	77
2			THF	48 h, b.p.	90	5
3	iPrO	iPrO	PhH	0.5 h, b.p.	8	71
4			THF	48 h, b.p.		90
5	$OCH_2C(CH_3)_2\ CH_2O$		THF	12 h, b.p.	14	77
6			$PhCH_3$	0.5 h, b.p.	40	60
7	Ph	t-Bu	THF	12 h, b.p.	20	20[a]
8			$PhCH_3$	0.3 h, b.p.		70[b]
9	$PhCH_2$	$PhCH_2$	THF	3 h, b.p.	90	
10	n-C_6H_{13}	n-C_6H_{13}	THF	0.3 h, b.p.	95	

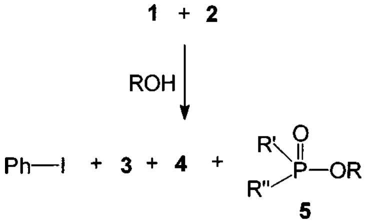
[a] From this reaction mixture beside **3** and **4** we isolated 1,4-di-O-t-butylphenylphosphinylbutandiol (40%).

[b] The yield was estimated from the NMR spectrum; 70% of **4** and 30% of starting material.

^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of this reaction mixture displayed one minor signal at $\delta_P = 4.7$ (diethyl phosphite) and two major signals with identical intensity $\delta_P = 0.96$ (diethyl phosphate) and $\delta_P = -12.10$ (tetraethyl pyrophosphate). Taking into consideration that in the reaction of dialkyl phosphite and iodosylbenzene pyrophosphate and water should be produced, somewhat surprisingly for us was the high yield of tetra*iso*propyl pyrophosphate observed in this reaction (Table I, runs 3 and 4). In a separate experiment the hydrolytic stability of tetra*iso*propyl pyrophosphate was checked under the reactions condition. It was found that compound **4** (R = R′ = iPrO) dissolved in THF with one equivalent of water at 56°C was stable within 24 h. The same hydrolytic stability we observed in case of 5,5,5′,5′-tetramethyl-2,2′-oxy-bis-[1,3,2]dioxaphosphinane 2,2′-dioxide **4**[R = R′ = $OCH_2C(CH_3)_2CH_2O$].

On the other hand secondary phosphine oxides in the reaction with iodosylbenzene produce phosphinic acids **3** as a major product (Table I, runs 9 and 10). Exemptions is *t*-butylphenylphosphine oxide, which in the reaction with iodosylbenzene in toluene produces the anhydride of *t*-butylphenylphosphinic acid **4** (R′ = tBu; R″ = Ph). In contrast to that when the reaction of *t*-butylphenylphosphine oxide with iodosylbenzene was performed in THF we isolated from the reaction mixture *t*-butylphenylphosphinic acid (20%) and the anhydride of *t*-butylphenylphosphinic acid (20%) beside 1,4-di-O-*t*-butylphenylphosphinylbutandiol (40%).

In the second set of experiments we treated >P(O)H type acids with iodosylbenzene in alcohol as a solvent in the presence as well as in the absence of the alcoholate as a base catalyst (Scheme 3). The results of this set of experiments are presented in the Table II.



SCHEME 3

From the reaction mixture of diethyl phosphite and iodosylbenzene in ethanol we isolated triethyl phosphate with a quantitative yield (Table II, run 1). The treatment of di*iso*propyl phosphite with iodosylbenzene in *iso*propanol produces tetra*iso*propyl pyrophosphate as a major product (60%) beside small amounts of di*iso*propyl phosphate (7%) and tri*iso*propyl phosphate (24%). In contrast to that the treatment of di*iso*propyl phosphite with iodosylbenzene in isopropanol in the presence of sodium *iso*propanolate (Table II, run 3) produces one major product, namely tri*iso*propyl phosphate (90%). On the other hand di-n-hexylphosphine oxide and dibenzylphosphine oxide yield in

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TABLE II The Products Distribution in the Reaction of Iodosylbenzene with >P(O)H Acids in Alcohols as a Solvent

						Yield %		
Run	R′	R″	R	Solvent	Conditions	**3**	**4**	**5**
1	EtO	EtO	Et	EtOH/THF	24 h, b.p.			100
2	iPrO	iPrO	iPr	iPrOH/THF	24 h, b.p.	7	60	24
3				iPrOH/iPrO$^-$ Na$^+$	1 h, b.p.			94
4	iPrO	iPrO	tBu	tBuOH/tBuO$^-$ K$^+$	1 h, b.p.	10		80[a]
5	nC_6H_{13}	nC_6H_{13}	Et	EtOH/THF	1 h, b.p.	70		
6			Me	MeOH	1 h, b.p.	62		30
7			Me	MeOH/MeO$^-$ Na$^+$	0.2 h, b.p.	25		69
8	$PhCH_2$	$PhCH_2$	Et	EtOH	0.25 h, b.p.	94		
9				EtOH/EtO$^-$	1 h, b.p.	[b]		
10	tBu	Ph	Me	MeOH/THF	3 h, b.p.	4	7	88
11				MeOH/MeO$^-$	1 h, b.p.			90

[a] Mixture of trialkylphosphates.

[b] Complex mixture of products (probably because of acidic protons in the benzylic positions).

the reaction with iodosylbenzene in alcohol oxidation products namely di-n-hexylphosphinic acid and dibenzylphosphinic acid, respectively (Table II, runs 5, 6, and 7). Exemption is *t*-butylphenylphosphine oxide, which under the above conditions produces the ester of *t*-butylphenylphosphinic acid as a major product (Table II, run 10).

As one can see from the data collected in the Table II the products distribution in the reaction under investigation strongly depends on the base catalyst. Trialkyl phosphates as well as alkyl esters of phosphinic acids are the major products when >P(O)H acids are treated with iodosylbenzene in alcohol in the presence of alcoholate anion.

DISCUSSION

The esters of phosphinic acids as well as trialkyl phosphates isolated from the reaction of >P(O)H acids with iodosobenzene in alcohol as a solvent strongly suggest the presence of phosphorylating agent in the reaction mixture. The formation of >P(O)OH acids, >P(O)OR esters, and pyrophosphates as well as in the reaction of >P(O)H acids with iodosylbenzene may be explained by the addition of >P(O)H acid to iodosylbenzene which will produce intermediate **6** possessing a four coordinate phosphorus atom. The intermediate **6** can collapse to >P(O)OH acid and iodobenzene. On the other hand the intermediate **6** can be the target for nucleophilic attack and can phosphorylate nucleophiles present in the reaction mixture (Scheme 4).

If the reaction is performed in aprotic solvent, in which the concentration of iodosylbenzene is low, intermediate **6** collapses into iodobenzene and >P(O)OH acid. In such a situation with the progress of the reaction the concentration of the >P(O)OH acid is growing in the reaction mixture and it can react with intermediate **6** to yield anhydrides **7**, what we observed in our experiments (see Table I).

We have obtained evidence in other studies that the mixture of iodosylbenzene and dialkyl phosphite is able to phosphorylate dialkylphosphates. We treated the mixture composed of 1 equivalent of di*iso*propyl phosphite and 1 equivalent of diethylphosphate with 1 equivalent of iodosylbenzene in THF solution, the ^{31}P NMR spectrum of such a reaction mixture displayed two resonance lines at $\delta_P = -12.50$ ppm (d, J = 36 Hz) and -14.20 ppm (d, J = 36 Hz), which were identified as the resonances of the anhydride **7** (R′=R=OEt) (Scheme 5).

In the separate experiment we treated the mixture composed of 1 equivalent of di*iso*propyl phosphite and 1 equivalent of *t*-butylphenylphosphinic acid with 1 equivalent of iodosylbenzene in $CHCl_3$ solution. The ^{31}P NMR spectrum of such a reaction mixture

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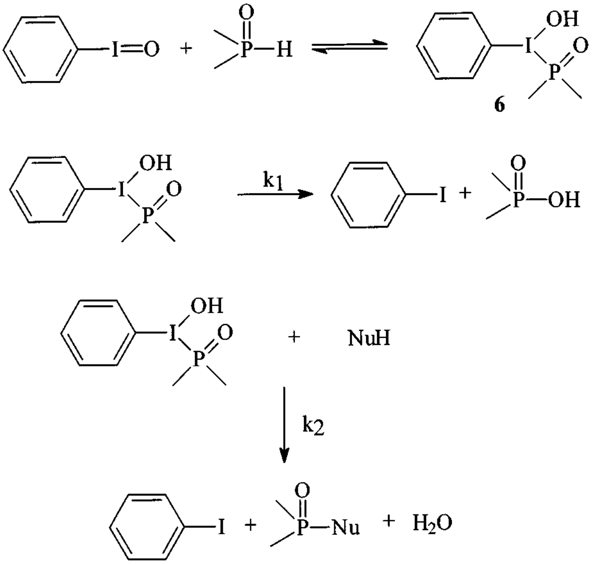
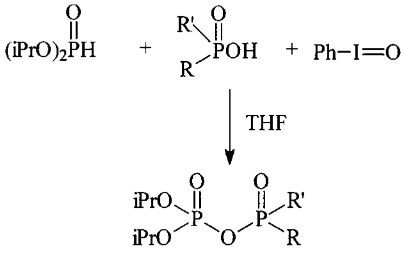


SCHEME 4

displayed two resonance lines at $\delta_P = 49.74$ ppm (d, J = 17 Hz) and −12.20 Hz ppm (d, J = 17 Hz), which were identified as the resonances of the anhydride **7** (R′ = tBu, R = Ph) (Scheme 5).



7

R	R'	^{31}P NMR [δ, ppm]		$J_{P\text{-}O\text{-}P}$ [Hz]
EtO	EtO	-12.58	-14.28	39
Ph	tBu	49.74	-12.22	17

SCHEME 5

The results of this experiments show that diethyl phosphate as well as *t*-butylphenylphosphinic acid undergo phosphorylation with a phosphite/iodosylbenzene mixture (probably by the intermediate **6**).

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We have to add, that the treatment of diethylphosphate and *t*-butylphenylphosphinic acid with iodosylbenzene under the same reaction conditions doesn't form neither tetraethyl pyrophosphate nor *t*-butylphenylphosphinic acid anhydride.

On the other hand if the reaction is performed in alcohol as a solvent, in which concentration of the iodosylbenzene is high, we have two competition processes: oxidation and nucleophilic attack of the alcohol on the phosphorus atom of the intermediate **6** to yield >P(O)OR esters. If the alcohol is a week nucleophile the formation of the >P(O)OR ester will compete with the anhydride formation (Table II, run 2). Alcoholate anion is a much better nucleophile than alcohol, in other words if reaction of iodosylbenzene with >P(O)H acid is performed in alcohol as a solvent in the presence of alcoholate anion, this anion can effectively compete with the >P(O)O$^-$ anion and will produce >P(O)OR ester. This situation is nicely demonstrated in the experiment with di*iso*propyl phosphite which in the reaction with iodosylbenzene in iPrOH gives 24% of tri*iso*propyl phosphate versus 94% in the case of the reaction carried out in the presence of sodium *iso*propanolate (Table II, runs 2 and 3). Likewise di-n-hexylphosphine oxide in the reaction with iodosylbenzene in methanol produces di-n-hexylphosphinic acid as a major product versus methyl di-n-hexylphosphinate (69%) in the case when the reaction is carried out in methanol in the presence of sodium methanolate (Table II, runs 6 and 7).

On the other hand one can also argue that esters **5** may be produced in the reaction of anhydrides **4** and alcohol; but in such a case esters **5** and acids **3** should be produced with an equal yield. In our experiments where the reaction was carried out in alcohol or in the mixture of alcohol and THF as a solvent, in the reaction mixture we observed the esters **5** in much higher concentration than acids **3** (Table II, runs 1, 3, 4, 7, 10, and 11). This observation strongly suggests that the esters **5** are produced (at least in part) in the direct reaction between intermediate **6** and alcohol. The reaction between >P(O)H acids and iodosylbenzene, as well as diacetoxyiodobenzene and Coser reagent is under investigation, and the results will be published subsequently.

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EXPERIMENTAL

The Reactions Between Iodosylbenzene and Dialkyl Phosphites in Aprotic Solvents

General Procedure

To a suspension of PhIO (5 mmol, 1.100 g) in 10 mL of the solvent (THF, benzene, toluene) a solution of $R_2P(O)H$ (5 mmol) in 2 mL of the same solvent was added. The reaction mixture was stirred for 0.5 to 48 h at the boiling point of the solvent. Then the solvent was removed in the vacuum and iodobenzene as well as tetraalkyl pyrophosphate was disstilled off under reduced pressure. The residue from the distillation was dissolved in 50 mL of ether and extracted with 20 mL of 5% $NaHCO_3$ water solution. The water layer was acidified with conc. HCl and extracted with ether (3 × 30 mL). The collected ether solutions were dried over $MgSO_4$, and after removal of the solvent gave dialkyl phosphate.

The results are collected in Table I.

Run 1. Iodobenzene 0.612 g (60%), b.p. = 30–40°C/0.3 mmHg, ^1H NMR ($CDCl_3$) $\delta = 6.51–7.02$ ppm (m, 3H), 7.22–7.53 ppm (m, 2H); tetraethyl pyrophosphate 0.558 g (77%), b.p. = 120–125°C/0.3 mmHg,[9] ^{31}P NMR ($CDCl_3$) $\delta = -12.20$ ppm;[10] diethyl phosphate 0.084 g (11%), ^{31}P NMR ($CDCl_3$) $\delta = -1.10$ ppm.[10]

Run 2. Iodobenzene 0.714 g (70%), b.p. = 30–40°C/0.3 mmHg, ^1H NMR ($CDCl_3$) $\delta = 6.51–7.02$ ppm (m, 3H), 7.22–7.53 ppm (m, 2H); tetraethyl pyrophosphate 0.036 g (5%), b.p. = 120–125°C/0.3 mmHg,[9] ^{31}P NMR ($CDCl_3$) $\delta = -12.20$ ppm;[10] diethyl phosphate 0.693 g (90%), ^{31}P NMR ($CDCl_3$) $\delta = -1.10$ ppm.[10]

Run 3. Iodobenzene 0.663 g (65%), b.p. = 30–40°C/0.3 mmHg, ^1H NMR ($CDCl_3$) $\delta = 6.51–7.02$ ppm (m, 3H), 7.22–7.53 ppm (m, 2H); tetra*iso*propyl pyrophosphate 0.614 g (71%), b.p. = 150–160°C/0.4 mmHg,[9] ^{31}P NMR ($CDCl_3$) $\delta = -14.20$ ppm;[11] di*iso*propyl phosphate 0.100 g (11%), ^{31}P NMR ($CDCl_3$) $\delta = -0.90$ ppm.[12]

Run 4. Iodobenzene 0.683 g (67%), b.p. = 30–40°C/0.3 mmHg, ^1H NMR ($CDCl_3$) $\delta = 6.52–7.02$ ppm (m, 3H), 7.22–7.53 ppm (m, 2H); tetra*iso*propyl pyrophosphate 0.778 g (90%), b.p. = 156–160°C/0.4 mmHg,[9] ^{31}P NMR ($CDCl_3$) $\delta = -14.20$ ppm.[11]

The Reactions Between Iodosylbenzene and 5,5-dimethyl-1,3-dioxaphosphorinan-2-oxide in Aprotic Solvents

To a suspension PhIO (5 mmol, 1.100 g) in 10 mL of the solvent (THF, toluene) a solution of 5,5-dimethyl-1,3-dioxaphosphorinan (5 mmol, 0.750 g) in 2 mL of the same solvent was added. The reaction mixture was stirred for 0.5 to 12 h at the boiling point of the solvent. Then the reaction mixture was diluted with 50 mL of ether and extracted with 20 mL of 5% $NaHCO_3$ water solution. The organic layer was dried over $MgSO_4$, evaporated to yield 2,2′-oxybis[5,5-dimetyl-1,

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3,2-dioxaphosphorinane]-2,2′-dioxide. The water layer was separated, acidified with conc. HCl and extracted with ether (3 × 30 mL). The combined ether solutions were dried over $MgSO_4$, filtered, and evaporated to yield 5,5-dimetyl-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinan. The results are presented in Table I.

Run 5. Iodobenzene 0.816 g (80%), ^1H NMR ($CDCl_3$) $\delta = 6.51$–7.02 ppm (m, 3H), 7.22–7.53 ppm (m, 2H); 2,2′-oxybis[5,5-dimetyl-1,3,2-dioxaphosphorinane]-2,2′-dioxide 0.604 g (77%), m.p. = 192–193°C (AcOEt/Hexane),[9] ^{31}P NMR ($CDCl_3$) $\delta = -20.07$ ppm;[10] 5,5-dimetyl-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinan 0.116 g (14%), m.p. = 170–171°C (AcOEt/Hexane),[9] ^{31}P NMR ($CDCl_3$) $\delta = -4.27$ ppm.[13]

Run 6. Iodobenzene 0.836 g (82%), ^1H NMR ($CDCl_3$) $\delta = 6.51$–7.02 ppm (m, 3H), 7.22–7.53 ppm (m, 2H); 2,2′-oxybis[5,5-dimetyl-1,3,2-dioxaphosphorinane]-2,2′-dioxide 0.471 g (60%), m.p. = 192–193°C (AcOEt/Hexane), ^{31}P NMR ($CDCl_3$) $\delta = -20.07$ ppm, 5,5-dimetyl-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinan 0.332 g (40%), m.p. = 170–171°C (AcOEt/Hexane), ^{31}P NMR ($CDCl_3$) $\delta = -4.27$ ppm.

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The Reactions Between Iodosylbenzene and Phosphine Oxides in Aprotic Solvents

General Procedure

To a suspension of PhIO (5 mmol, 1.100 g) in 10 mL of the solvent (THF, toluene) a solution of dialkylphosphine oxides (5 mmol) in 2 mL of the same solvent was added. The reaction mixture was stirred for 0.3 to 12 h at the boiling point of the solvent. Then the reaction mixture was diluted with 50 mL of ether and extracted with 25 mL of 5% $NaHCO_3$ water solution. The organic layer was dried over $MgSO_4$, evaporated and separated by radial chromatography. The water layer was acidified with conc. HCl and extracted with ether (3 × 30 mL). The combined ether solutions were dried over $MgSO_4$, filtered and evaporated to yield phosphinic acids. The results are presented in Table I.

Run 7. Iodobenzene 0.816 g (80%), ^1H NMR ($CDCl_3$) $\delta = 6.51$–7.02 ppm (m, 3H), 7.22–7.53 ppm (m, 2H), *t*-butylphenylphosphinic acid 0.198 g (20%), m.p. = 150–152°C (AcOEt/Hexane),[14] ^{31}P NMR ($CDCl_3$) $\delta = 52.44$ ppm;[15] *t*-butylphenylphosphinic acid anhydride 0.190 g (20%), ^{31}P NMR ($CDCl_3$) $\delta = 50.89$; 50.37 ppm (mixture of diasteroisomers);[14] 1,4-di-O-*t*-butylphenylphosphinylbutanodiol 0.450 g (40%) (mixture of diasteroisomers), ^{31}P NMR ($CDCl_3$) $\delta = 52.25$; 52.29 ppm, ^1H NMR ($CDCl_3$) $\delta = 1.12$ ppm (d, 9H), 1.23 ppm (d, 9H), 1.71–1.90 ppm (m, 4H), 3.72–3.91 ppm (m, 2H), 4.00–4.25 ppm (m, 2H), 7.32–7.63 ppm (m, 6H), 7.72–7.91 ppm (m, 4H), FAB MASS M/e = 451 (M + 1) M/e = 253 $Ph^tBuP(O)(CH_2)_4$, M/e = 198 $Ph^tBuP(O)OH$.

Run 8. The yield was estimated from the ^{31}P NMR spectrum: *t*-butylphenylphosphinic acid anhydride 70%, ^{31}P NMR ($CDCl_3$) δ = 50.89; 50.37 ppm (mixture of diasteroisomers), *t*-butylphenylphosphine oxide 30% ^{31}P NMR ($CDCl_3$) δ = 48.71ppm.

Run 9. Iodobenzene 0.714 g (70%), ^1H NMR ($CDCl_3$) δ = 6.51–7.04 ppm (m, 3H), 7.22–7.53 ppm (m, 2H). Dibenzylphosphinic acid 1.107 g (90%), m.p. = 190–191°C (AcOEt/Hexane);[9] ^{31}P NMR ($CDCl_3$) δ = 51.70 ppm, ^1H NMR ($CDCl_3$) δ = 2.95 ppm, (d, 4H, J^2_{PH} = 16 Hz), 6.63–6.91 ppm (m, 10H).[16]

Run 10. Iodobenzene 0.765 g (75%), ^1H NMR ($CDCl_3$) δ = 6.54–7.03 ppm (m, 3H), 7.25–7.52 ppm (m, 2H); di-n-hexylphosphinic acid 1,111 g (95 %), m.p. = 75–76°C (AcOEt/Hexane);[9] ^{31}P NMR ($CDCl_3$) δ = 58.86 ppm.[10]

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The Reaction Between PhIO and > P(O)H Type Compounds in Alcohols

To a suspension of PhIO (5 mmol, 1.100 g) in 10 mL of the solvent (alcohol, or a mixture THF: alcohol = 1 : 1) 5 mmol of >P(O)H compound (diethyl phosphite, di*iso*propyl phosphite, di-n-hexylphosphine oxide, dibenzylphosphine oxide, *t*-butylphenylphosphine oxide) were added. The reaction mixture was stirred for 0.2 to 24 h at the boiling point of the solvent. The work up depends on the starting material used in the experiments.

Runs 1 and 2. The solvent was removed in the vacuum from the reaction mixture and the residue was separated by distillation under reduced pressure. The results are collected in Table II.

Run 1. Iodobenzene 0.612 g (60%), b.p. = 30–40°C/0.3 mmHg, ^1H NMR ($CDCl_3$) δ = 6.51–7.02 ppm (m, 3H), 7.22–7.51 ppm (m, 2H); triethyl phosphate 0.910 g (100%), b.p. = 60–65°C/0.4 mmHg, ^{31}P NMR ($CDCl_3$);[9] $\delta = -0.03$ ppm.[10]

Run 2. Iodobenzene 0.663 g (65%), b.p. = 30–40°C/0.3 mmHg, ^1H NMR ($CDCl_3$) δ = 6.51–7.02 ppm (m, 3H), 7.22–7.51 ppm (m, 2H); tetra*iso*propyl pyrophosphate 0.519 g (60%), b.p. = 160–170°C/0.5 mmHg, ^{31}P NMR ($CDCl_3$) $\delta = -14.01$ ppm; di*iso*propyl phosphate

0.064 g (7%), ^{31}P NMR ($CDCl_3$) $\delta = -1.57$ ppm; tri*iso*propyl phosphate 0.268 g (24%), b.p. = 70–75°C/0.5 mmHg,[9] ^{31}P NMR $\delta = -2.35$ ppm.[10]

Run 5. The reaction mixture was diluted with 50 mL of ether and extracted with 20 mL of 5% $NaHCO_3$ water solution. The organic layer was dried over $MgSO_4$, and evaporated to give iodobenzene 0.765 g (75%). The water layer was acidified with conc. HCl and extracted with ether (3 × 30 mL). The collected ether solutions were dried over $MgSO_4$, filtered and evaporated to gave di-n-hexylphosphinic acid 0.819 g (70%), m.p. = 75–76°C (AcOEt/Hexane), ^{31}P NMR ($CDCl_3$) $\delta =$ 58.86 ppm.

Run 6. The reaction mixture was diluted with 70 mL of ether and extracted with 20 mL of 5% $NaHCO_3$ water solution. The organic layer was dried over $MgSO_4$, evaporated, and separated by radial chromatography (CH_2Cl_2:MeOH: 20/1) to give methyl di-n-hexylphosphinate 0.390 g (30%), ^{31}P NMR ($CDCl_3$) $\delta = 59.83$ ppm, ^{1}H NMR ($CDCl_3$) $\delta = 0.82$–2.04 ppm (m, 26H), 3.34 ppm (d, $J^3_{PH} = 10$ Hz, 3H). The water layer was acidified with conc. HCl and extracted with ether (3 × 30 mL). The collected ether solutions were dried over $MgSO_4$, filtered and evaporated to gave di-n-hexylphosphinic acid 0.725 g (62%), m.p. = 75–76°C (AcOEt/Hexane), ^{31}P NMR ($CDCl_3$) $\delta = 58.86$ ppm.

Run 8. The reaction mixture was diluted with 70 mL of ether and extracted with 20 mL of 5% $NaHCO_3$ water solution. The water layer was acidified with conc. HCl and extracted with ether (3 × 30 mL). The collected ether solutions were dried over $MgSO_4$, filtered and evaporated to gave dibenzylphosphinic acid 1.107 g (90%), m.p. = 190–191°C (AcOEt/Hexane), ^{31}P NMR ($CDCl_3$) $\delta = 51.70$ ppm, ^{1}H NMR ($CDCl_3$) $\delta = 2.94$ ppm, (d, 4H, $J^2_{PH} = 16$ Hz), 6.64–6.91 ppm (m, 10H).

Run 10. The reaction mixture was diluted with 70 mL of ether and extracted with 20 mL of 5% $NaHCO_3$ water solution. The organic layer was dried over $MgSO_4$, filtered, evaporated and separated by radial chromatography (CH_2Cl_2 : MeOH = 50:1) to give iodobenzene 0.765 g (75%); *t*-butylphenylphosphinic acid anhydride 0.069 g (7%), ^{31}P NMR ($CDCl_3$) $\delta = 50.89$; 50.37 ppm (mixture of diasteroisomers); methyl *t*-butylphenylphosphinate 0.932 g (88%), ^{31}P NMR ($CDCl_3$) $\delta =$ 54.75 ppm, ^{1}H NMR ($CDCl_3$) $\delta = 7.05$–7.51 ppm (m, 5H), 3.53 ppm, (d, $J^3_{PH} = 10$ Hz, 3H), 1.02 ppm (d, $J^3_{PH} = 16$ Hz, 9H).[14] The water layer was acidified with conc. HCl and extracted with ether (3 × 30 mL). The collected ether solutions were dried over $MgSO_4$, filtered and evaporated to gave *t*-butyphenylphosphinic acid 0.198 g (4%), m.p. = 150–152°C (AcOEt/Hexane), ^{31}P NMR ($CDCl_3$) $\delta = 52.44$ ppm.

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The Reaction Between PhIO and > P(O)H Type Compounds in Alcohols in the Presence of Alkoholates

To the mixture composed of 10 mL of a solvent (alcohol, or a mixture THF : alcohol = 1 : 1), sodium alcoholate (5 mmol) and PhIO (5 mmol, 1.100 g), 5 mmol of >P(O)H type compounds (di*iso*propyl phosphite, di-n-hexylphosphine oxide, *t*-butylphenylphosphine oxide) were added. The reaction mixture was stirred for 0.2 to 1 h at the boiling point of the solvent. The work up depends on the starting material used in the experiments. The results are collected in Table II.

Run 3. From the reaction mixture the solvent was removed in the vacuum and the residue was separated by distillation under reduced pressure to give: iodobenzene 0.765 g (75%), b.p. = 30–40°C/0.3 mmHg), ^{1}H NMR ($CDCl_3$) $\delta = 6.51$–7.03 ppm (m, 3H), 7.22–7.51 ppm (m, 2H); tri*iso*propyl phosphate 1.052 g (94%), b.p. = 70–75°C/0.5 mmHg), ^{31}P NMR ($CDCl_3$) $\delta = -2.35$ ppm.

Run 4. The yield was estimated by ^{31}P NMR ($CDCl_3$) $\delta = -2.29$ ppm [$(iPrO)_3PO$, 31%]; −5.58 ppm [$(iPrO)_2$ t-BuOPO, 38%]; −9.14 ppm [$(t\text{-}BuO)_2$ iPrOPO, 15%]; −12.50 ppm [$(t\text{-}BuO)_3PO$, 1%]; 1.70 ppm [$(iPrO)_2P(O)OH$, 13%].

Run 7. The reaction was diluted with 50 mL of ether and washed with 10 mL of water. The ether layer was dried over $MgSO_4$, the solvent was removed in the vacuum and the residue was separated by radial chromatography (CH_2Cl_2 : MeOH : 20/1) to give: iodobenzene 0.785 g (77%), ^{1}H NMR ($CDCl_3$) $\delta = 6.54$–7.02 ppm (m, 3H), 7.22–7.51 ppm (m, 2H); methyl di-n-hexylphosphinate 0.855 g (69%), ^{31}P NMR ($CDCl_3$) $\delta = 59.83$ ppm, ^{1}H NMR ($CDCl_3$) $\delta = 0.82$–2.01 ppm (m, 26H), 3.32 ppm (d, 3H, $J^3_{PH} = 10$ Hz). The water layer was acidified with conc. HCl and extracted with ether (3 × 30 mL). The collected ether solutions were dried over $MgSO_4$, filtered, and evaporated to give di-n-hexylphosphinic acid 0.292 g (25%), m.p. = 75–76°C (AcOEt/Hexane), ^{31}P NMR ($CDCl_3$) $\delta = 58.86$ ppm.

Run 11. The reaction mixture was diluted with 50 mL of ether and washed with 10 mL of water. The ether layer was dried over $MgSO_4$, removed in the vacuum and the residue was separated by radial chromatography (CH_2Cl_2 : MeOH : 50/1) to give: iodobenzene 0.765 g (72%), ^{1}H NMR ($CDCl_3$) $\delta = 6.51$–7.02 ppm (m, 3H), 7.22–7.51 ppm (m, 2H); methyl *t*-butylphenylphosphinate 0.954 g (90%), ^{31}P NMR ($CDCl_3$) $\delta = 54.75$ ppm, ^{1}H NMR ($CDCl_3$) $\delta = 7.01$–7.53 ppm, (m, 5H), 3.51 ppm, (d, 3H, $J^3_{PH} = 10$ Hz), 1.01 ppm (d, 9H, $J^3_{PH} = 16$ Hz).

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The Reaction Between Iodosylbenzene and Di*iso*propyl Phosphite in the Presence of Diethyl Phosphate

To a suspension of PhIO (5 mmol, 1.100 g) in 10 mL of THF and di*iso*propyl phosphite (5 mmol; 0.830 g) diethyl phosphate (5 mmol, 0.770 g) was added. The reaction mixture was stirred for 24 h at the boiling point of the solvent. Then the solvent was removed in the vacuum and ^{31}P NMR ($CDCl_3$) was measured. The ^{31}P NMR spectrum exhibited five resonance lines: $\delta = 0.137$ ppm (intensity 40) di*iso*propyl phosphate; $\delta = -0.45$ ppm (intensity 50) diethylphosphate, $\delta = 5.30$ ppm (intensity 5) di*iso*propyl phosphite, $\delta = -12.58$ ppm (intensity 20), and -14.28 ppm (intensity 20) O,O-diethyl-O',O'-di*iso*propyl pyrophosphate.

The Reaction Between Iodosylbenzene and Di*iso*propyl Phosphite in the Presence of *t*-butylphenylphosphinic Acid

To a suspension of PhIO (5 mmol, 1.100 g) in 10 mL of $CHCl_3$ and di*iso*propyl phosphite (5 mmol, 0.830 g) phenyl t-butylphosphinate (5 mmol, 0.990 g) was added. The reaction mixture was stirred for 24 h at the boiling point of the solvent. Then the solvent was removed in the vacuum and ^{31}P NMR ($CDCl_3$) was measured. The ^{31}P NMR spectrum exhibited six resonance lines: $\delta = 0.16$ ppm (intensity 2) di*iso*propyl phosphate; $\delta = 52.90$ ppm (intensity 4) phenyl t-butylphosphinic acid; $\delta = 5.59$ ppm (intensity 10) di*iso*propyl phosphite, $\delta = -12.30$ ppm, d, $J^3_{PP} = 39$ Hz, (intensity 4) and 49.74 ppm, d, $J^3_{PP} = 39$ Hz (intensity 5) O',O'-di*iso*propylphenyl t-butylphosphate; $\delta = -13.95$ ppm (intensity 5) tertra*iso*propylpyrophosphate.

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