

## POLYHALOARYL COMPOUNDS CONTAINING PHOSPHORUS

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### SUMMARY

A number of (polyhaloaryl)phosphines, with one, two or three polyhaloaryl groups bound to phosphorus, have been synthesized by the addition of various chlorophosphines to a polyhaloaryllithium compound or Grignard reagent. Oxidation afforded the various phosphine oxides. IR and UV data are given.

### INTRODUCTION

We have synthesized a number of tertiary phosphines and their oxides containing polyhaloaryl substituents, such as the 4-(trimethylsilyl)-2,3,5,6-tetrafluorophenyl, 2,3,5,6-tetrafluorophenyl, pentachlorophenyl, 4-(trimethylsilyl)-2,3,5,6-tetrachlorophenyl, and 2,3,5,6-tetrachloro-4-pyridyl groups. We have also prepared the pentafluorophenyl-substituted phosphines,  $(C_6F_5)_nP(C_6H_5)_{3-n}$  ( $n=0-3$ ), and their oxides, and (pentachlorophenyl)diphenylphosphine, all of which have been previously described<sup>1-5</sup>, to study their spectral properties in connection with other hitherto unknown phosphines reported herein.

### RESULTS AND DISCUSSION

The polyhaloaryl-substituted phosphines were prepared by addition of diphenylchlorophosphine, phenyldichlorophosphine, or phosphorus trichloride to either a polyhaloaryllithium compound at  $-70^\circ$ , or to a polyhaloaryl Grignard reagent at  $0^\circ$ , in THF. The polyhaloaryl groups were those previously mentioned. Two silyl-substituted (polyhaloaryl)phosphines have been prepared by the consecutive addition of *n*-butyllithium and chlorotrimethylsilane to either bis(pentachlorophenyl)phenylphosphine or bis(2,3,5,6-tetrafluorophenyl)phenylphosphine. Both these silyl-substituted (polyhaloaryl)phosphines have also been synthesised in poor yields *via* addition of phenyldichlorophosphine to 4-(trimethylsilyl)-2,3,5,6-tetrachlorophenyllithium or 4-(trimethylsilyl)-2,3,5,6-tetrafluorophenyllithium. The poor yields may be due to cleavage of the silicon-carbon bond during preparation of the lithium compounds<sup>6,7</sup>. The reaction of pentachlorophenylmagnesium chloride with phosphorus trichloride failed to yield any tris(pentachlorophenyl)phosphine.

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All of the phosphines, except those containing the trimethylsilyl group, were oxidized to the corresponding oxides by a mixture of sodium dichromate, concentrated sulfuric acid, and glacial acetic acid<sup>1</sup>. For phosphines containing the tetrachloropyridyl group, as expected, no *N*-oxides were formed. Pentachloropyridine and its derivatives are resistant to oxidation by most reagents<sup>8</sup>.

The IR spectra of the (polyhaloaryl)phosphines and their oxides show absorptions associated with the polyhaloaryl group. In addition, those containing the phenyl group have an absorption at about  $1440\text{ cm}^{-1}$  which has been attributed<sup>9</sup> to the phosphorus-aryl absorption. The oxides have an absorption at about  $1204\text{ cm}^{-1}$  which may be that for the P=O stretching vibration<sup>10</sup>.

TABLE 1

UV SPECTRAL DATA OF POLYHALOARYL PHOSPHINES AND OXIDES<sup>a</sup>

Phosphine	$\lambda_{\text{max}}$ (nm)	$\epsilon \times 10^{-3}$	Phosphine oxide	$\lambda_{\text{max}}$ (nm)	$\epsilon \times 10^{-3}$
$\text{C}_6\text{F}_5\text{PPh}_2$	257	5.98	$\text{C}_6\text{F}_5\text{P(O)Ph}_2$	274	2.32
				266	2.47
$(\text{C}_6\text{F}_5)_2\text{PPh}$	257	11.9	$(\text{C}_6\text{F}_5)_2\text{P(O)Ph}$	275	3.44
				267	3.44
$(\text{C}_6\text{F}_5)_3\text{P}$	256	13.5	$(\text{C}_6\text{F}_5)_3\text{PO}^b$	275	2.53
				265	0.63
$\text{C}_6\text{Cl}_5\text{PPh}_2$	308	4.51	$\text{C}_6\text{Cl}_5\text{P(O)Ph}_2$	310	1.57
				301	1.27
$(\text{C}_6\text{Cl}_5)_2\text{PPh}$	312	9.5	$(\text{C}_6\text{Cl}_5)_2\text{P(O)Ph}$	314	3.03
				304	2.64
$(\text{C}_5\text{Cl}_4\text{N})_3\text{P}$	317	14.05			
$(4\text{-C}_5\text{Cl}_4\text{N})\text{PPh}_2$	310	6.9	$(4\text{-C}_5\text{Cl}_4\text{N})\text{P(O)Ph}_2$	313	6.2
				320 (sh)	
$(4\text{-C}_5\text{Cl}_4\text{N})_2\text{PPh}$	310	14.30	$(4\text{-C}_5\text{Cl}_4\text{N})_2\text{P(O)Ph}$	313	11.1
	239	26		324 (sh)	8.85
$(4\text{-C}_5\text{Cl}_4\text{N})_3\text{P}$	317	18.24	$(4\text{-C}_5\text{Cl}_4\text{N})_3\text{PO}$	325	17.5
	238	25.5			

<sup>a</sup> Solvent: cyclohexane. <sup>b</sup> Lit.<sup>1</sup> (methanol)  $\lambda_{\text{max}}$ : 275 ( $\epsilon$  2600) and 250 nm ( $\epsilon$  750).

The UV spectra (Table 1) of the (polyhaloaryl)phosphines and phosphine oxides are in agreement with the generalizations made by Jaffe<sup>11</sup> for the triphenyl derivatives of Group V elements and their oxides. Due to the presence of electron-withdrawing groups such as  $\text{C}_6\text{F}_5$ ,  $\text{C}_6\text{Cl}_5$  and  $4\text{-C}_5\text{Cl}_4\text{N}$ , there is considerable delocalization in the (polyhaloaryl)phosphines due to both the  $\pi(p \rightarrow p)$  donation of the phosphorus lone pair to the ring and the  $\pi(p \rightarrow d)$  withdrawal of electrons from the ring by the phosphorus *d* orbitals<sup>12</sup>. This conjugation is quite significant on changing from mono- to tris(polyhaloaryl)phosphines. The extinction coefficients increase in a fairly additive manner, showing that each polyhaloaryl group makes its individual contribution to the intensity of that peak.

Oxidation of the phosphines to phosphine oxides produces a bathochromic shift in the secondary band. The result is the appearance of the unperturbed or weakly perturbed vibrational pattern, with two, low intensity, prominent bands and shoulders

or inflections at shorter wavelengths. In the oxidation, the lone pair on phosphorus has been removed but delocalization still occurs due to  $\pi(p \rightarrow d)$  withdrawal of electrons from the ring by the phosphorus  $d$  orbitals<sup>12</sup>. The lower extinction coefficients are indicative of less conjugative interaction of the polyhaloaryl group with the phosphorus atom in (polyhaloaryl)phosphine oxides than in the corresponding (polyhaloaryl)phosphines.

#### EXPERIMENTAL

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. All glassware used in these experiments was dried in an oven at 120°, assembled while hot and flushed with nitrogen. THF was dried over sodium and distilled from sodium benzophenone ketyl. The IR and UV spectra were recorded employing, respectively, a Perkin-Elmer 21 and a Cary-14R spectrophotometer. Molecular weights were determined by mass spectrometry. All melting and boiling points are uncorrected.

#### *(Polyhaloaryl)phosphines and phosphine oxides*

The organometallic compounds were prepared as described: pentafluorophenyllithium<sup>13</sup>; pentachlorophenyllithium<sup>5</sup>; 4-(trimethylsilyl)-2,3,5,6-tetrachlorophenyllithium<sup>14</sup>; 4-(trimethylsilyl)-2,3,5,6-tetrafluorophenyllithium<sup>6</sup>; 2,3,5,6-tetrachloro-4-pyridyllithium<sup>15</sup>; pentachlorophenylmagnesium chloride<sup>16</sup>; and 2,3,5,6-tetrachloro-4-pyridylmagnesium chloride<sup>17</sup>.

The chlorophosphine was added to the appropriate polyhaloarylithium compound at -70° in THF and stirred until Color Test I<sup>18</sup> was negative. In reactions with Grignard reagents the mixture was stirred for ca. 15 h. The mixture was hydrolysed with dilute HCl, extracted with ether, and the extract dried (MgSO<sub>4</sub>). For preparations involving C<sub>6</sub>Cl<sub>5</sub>MgCl and C<sub>5</sub>Cl<sub>4</sub>NMgCl the solvent was evaporated and the residue chromatographed on a column of silica gel in CCl<sub>4</sub>. For all others, the solvent was evaporated, the residue dissolved in an appropriate solvent and then crystallized.

An alternative work-up procedure, especially for pentachlorophenyl-substituted phosphines, involves evaporation of the reaction mixture to dryness and extraction with hot benzene or another suitable solvent.

The oxidations were carried out by a reported procedure<sup>1</sup>.

All experimental data are recorded in Table 2.

#### *Bis[4-(trimethylsilyl)-2,3,5,6-tetrafluorophenyl]phenylphosphine from bis(2,3,5,6-tetrafluorophenyl)phenylphosphine*

n-Butyllithium (14.2 ml, 0.02 mole) was added to bis(2,3,5,6-tetrafluorophenyl)phenylphosphine (4.0 g, 0.01 mole) in THF (100 ml) at -70°. After 1 h, chlorotrimethylsilane (4.3 g, 0.048 mole) in THF (20 ml) was added and the mixture stirred for 3 h at -70°. The solvent was removed, sodium hydroxide solution (5%, 100 ml) added, and the mixture extracted with ether. Evaporation of the solvent afforded a pale yellow liquid which was distilled under reduced pressure to give a colorless liquid. The latter solidified on cooling, and from pentane yielded white crystals of bis[4-(trimethylsilyl)-2,3,5,6-tetrafluorophenyl]phenylphosphine (0.75 g, 13.6%), m.p. 54-55°.

TABLE 2

## POLYHALOARYLPHOSPHINES AND OXIDES

Compound	Method <sup>a</sup>	Moles of RM	Moles of phosphine	Yield (%)	M.p. (°C)	Analysis found (calcd.)			
						C	H	Cl	P
C <sub>6</sub> Cl <sub>5</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	B	0.1	0.1	55	133–134 <sup>b</sup>				
C <sub>6</sub> Cl <sub>5</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>			0.02	33	215–216			39.44 (39.40)	6.76 (6.88)
C <sub>6</sub> F <sub>5</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	B	0.1	0.1	79	68–69 <sup>c</sup>				8.88 (8.81)
(C <sub>5</sub> Cl <sub>4</sub> N)P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	A	0.08	0.08	58	127–128			35.07 (35.41)	7.79 (7.73)
(C <sub>5</sub> Cl <sub>4</sub> N)P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>						B	0.08	0.08	57
(C <sub>5</sub> Cl <sub>4</sub> N)P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	B	0.08	0.08	53	196–198			34.31 (34.05)	7.49 (7.43)
(C <sub>6</sub> Cl <sub>5</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>5</sub>			A	0.1	0.05	20	238–240		
(C <sub>6</sub> Cl <sub>5</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>5</sub>	B	0.05	0.025	47	238–240	35.96 (35.58)	1.16 (0.82)		
(C <sub>6</sub> Cl <sub>5</sub> ) <sub>2</sub> P(O)C <sub>6</sub> H <sub>5</sub>							0.0033	84	246–248
(C <sub>5</sub> Cl <sub>4</sub> N) <sub>2</sub> PC <sub>6</sub> H <sub>5</sub>	A	0.1	0.05	58	221–223			52.69 (52.59)	5.74 (5.74)
(C <sub>5</sub> Cl <sub>4</sub> N) <sub>2</sub> PC <sub>6</sub> H <sub>5</sub>	B	0.1	0.05	52	221–223				
(C <sub>5</sub> Cl <sub>4</sub> N) <sub>2</sub> P(O)C <sub>6</sub> H <sub>5</sub>			0.01	80	223–225			51.00 (51.07)	5.69 (5.58)
(C <sub>6</sub> Cl <sub>5</sub> ) <sub>3</sub> P	B	0.1	0.03	10	286–288	27.63 (27.71)			
(C <sub>5</sub> Cl <sub>4</sub> N) <sub>3</sub> P	A	0.1	0.03	40	296–298			62.77 (62.74)	4.56 (4.56)
(C <sub>5</sub> Cl <sub>4</sub> N) <sub>3</sub> P(O)							0.044	97	270–272
(4-Me <sub>3</sub> SiC <sub>6</sub> F <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>5</sub>	B	0.05	0.025	9.4	54–55	52.16 (52.36)	4.06 (4.18)		
(4-Me <sub>3</sub> SiC <sub>6</sub> Cl <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>5</sub>						B	0.05	0.025	42

<sup>a</sup> A *via* Grignard reagent; B *via* lithium compound. <sup>b</sup> Cited<sup>5</sup>: 131.8–132.4°. <sup>c</sup> Cited<sup>3</sup>: 70°.

*Bis[4-(trimethylsilyl)-2,3,5,6-tetrachlorophenyl]phenylphosphine from bis(pentachlorophenyl)phenylphosphine*

n-Butyllithium (5 ml, 0.0072 mole) was added to bis(pentachlorophenyl)phenylphosphine (2.2 g, 0.0036 mole) in THF (200 ml) at –70°. Chlorotrimethylsilane (4.0 g, 0.04 mole) in THF (5 ml) was added and the mixture stirred until Color Test I was negative (30 min). The usual work-up gave pale yellow crystals of bis[4-(trimethylsilyl)-2,3,5,6-tetrachlorophenyl]phenylphosphine (1.7 g, 75%), m.p. 74–75°, from methanol.

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*Note added in proof.* There has just appeared an article on tetrafluoroaryl derivatives of phosphorus and sulfur by P. G. Eller and D. W. Meek, *J. Organometal. Chem.*, 22 (1970) 631.

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