

Preparation and Properties of Tertiary *p*-Alkylarylphosphines containing Straight-chain Alkyl Groups

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A series of tris(*p*-alkylaryl)phosphines with straight chain alkyl groups, $P(p-C_6H_4-C_nH_{2n+1})_3$ where $n = 2-9$, have been prepared by reaction of phosphorus trichloride with the Grignard reagent derived from the corresponding *p*-bromoalkylbenzene. When $n = 2$ and 3 the phosphines are crystalline solids, but for $n > 3$ they are viscous oils up to $n = 9$, which is a waxy solid. The phosphines have been characterised by microanalysis, and i.r., 1H and ^{31}P n.m.r., and mass spectrometry. The *p*-substituted-arylphosphines are more sensitive than triphenylphosphine to air; aerial oxidation converts them exclusively into the corresponding phosphine oxide, in contrast to trialkylphosphines which are oxidised to a complex mixture of products. The complexing ability of the new phosphines (PAR_3) is demonstrated by their ready displacement of 1,5-cyclo-octadiene (cod) from $[M(cod)Cl_2]$ ($M = Pd$ and Pt) to yield *trans*- $[Pd(PAR_3)_2Cl_2]$ and *cis*- $[Pt(PAR_3)_2Cl_2]$, respectively.

TERTIARY phosphines are very good ligands for transition metals, and tertiary phosphine oxides for lanthanide and actinide elements. In a previous paper¹ we reported the preparation of such compounds with long straight-chain alkyl groups from which it is possible to prepare complexes that are freely soluble in hydrocarbon solvents, a property that is desirable for many applications including the preparation of homogeneous catalysts for the activation of alkanes and for the hydrogenation, isomerisation, hydroformylation, and hydrosilylation of

sensitive to oxygen both in solution and in the solid state. The sensitivity depended upon the length of the alkyl chain attached to the phenyl rings. Therefore, all steps in their preparation and characterisation were effected under a nitrogen atmosphere.

The tris(*p*-alkylaryl)phosphines were prepared by treating the Grignard reagent of the corresponding *p*-bromoalkylbenzenes with phosphorus trichloride in tetrahydrofuran solution. The lower members of the series were found to be crystalline solids which were purified by recrystallisation. However, the higher members ($n > 3$) were

TABLE I
Physical, analytical, and spectroscopic data for the triarylphosphines $P(p-C_6H_4R)_3$

R	Colour	Appearance	Yield ^a (%)	M.p. (°C)	B.p. (°C) ^b	³¹ P n.m.r. chemical shift ^c	Molecular ion M^+	Analysis (%) Found (calc.)	
								C	H
C_2H_5	White	crystalline solid	83	99		+10.6	346	82.5 (83.2)	7.9 (7.9)
C_3H_7	White	crystalline solid	71	45-48		+10.5	388	82.9 (83.5)	8.5 (8.6)
C_4H_9	Yellow	viscous oil	67		212 (0.005)	+10.6		83.7 (83.7)	9.1 (9.1)
C_6H_{11}	Yellow	viscous oil	69		296 (0.35)	+10.6	472	83.2 (83.9)	9.3 (9.6) ^d
C_8H_{13}	Yellow	viscous oil	66		Not distilled				
C_6H_{15}	Yellow	viscous oil	58		280 (0.005) ^e	+10.8	556		
C_8H_{17}	Yellow	viscous oil	63		Not distilled	+10.7			
C_9H_{19}	Yellow-green	viscous waxy solid	81		Not distilled	+10.8	640		

^a Yield based on PCl_3 . ^b Boiling point under reduced pressure, shown in mmHg in parentheses. ^c Measured relative to trimethylphosphate as an external standard, which lies -4.242 p.p.m. down-field from 85% H_3PO_4 (Lady Richards, personal communication). All values refer to solutions in $CDCl_3$. ^d Phosphorus: 6.7 (found), 6.6 (calculated). ^e Resulted in some decomposition of phosphine.

alkenes, as well as for the solvent-extraction of metals. In a number of these applications there are known to be significant differences between the properties of the complexes of aliphatic and aromatic tertiary phosphines. For example $[Rh(PR_3)_3Cl]$ complexes are much less effective as catalysts for the hydrogenation of olefins when R is an alkyl group than when it is an aryl group.^{2,3} Accordingly, in the present paper we describe the synthesis of a series of tris(*p*-alkylaryl)phosphines and their corresponding phosphine oxides, $P(p-C_nH_{2n+1}C_6H_4)_3$ and $O=P(p-C_nH_{2n+1}C_6H_4)_3$ in which $n = 2-9$, all of which are reported for the first time.

EXPERIMENTAL

Tris(p-alkylaryl)phosphines, $P(p-C_6H_4-C_nH_{2n+1})_3$ ($n = 2-9$).—The tris(*p*-alkylaryl)phosphines were found to be

found to be viscous liquids or waxy solids, and these, where possible, were purified by distillation. Appearances, yields, and analytical and spectroscopic data are recorded in Table I.

Tris(p-alkylaryl)phosphine Oxides, $O=P(p-C_6H_4-C_nH_{2n+1})_3$ ($n = 2-9$).—The tris(*p*-alkylaryl)phosphines were treated under nitrogen with a slight excess of 6% w/v hydrogen peroxide to yield the tris(*p*-alkylaryl)phosphine oxides, which were either recrystallised from acetone or heated at 80 °C *in vacuo* for 12 h to remove any excess of solvent. Appearances, melting points, and spectroscopic data are given Table 2.

p-Bromoalkylbenzenes, $p-BrC_6H_4-C_nH_{2n+1}$ ($n = 4-9$).—The *p*-bromoalkylbenzenes were not commercially available and so were prepared by the action of the Grignard reagent of an alkyl bromide on *p*-bromobenzaldehyde to produce an alcohol which was then dehydrated and hydrogenated to

give the desired product.⁴ *p*-Bromobenzaldehyde was treated with an excess of the alkylmagnesium halide in diethyl ether solution to yield the *p*-bromophenyl alcohol, which was then heated over freshly pulverized, fused potassium hydrogensulphate at 185 °C for 8 h or until the dehydration was complete. The dehydrated product was dis-

any solvent. Physical and microanalytical data are given in Table 4.

Materials.—Complexes [Pt(cod)Cl₂]⁵ and [Pd(cod)Cl₂]⁶ were prepared by standard procedures. The method of Clark was preferred for the platinum complex because it is easier and gives a whiter product. However the platinum(II)

TABLE 2
Physical, analytical, and spectroscopic data for the triarylphosphine oxides O=P(*p*-C₆H₄R)₃

R	Appearance	M.p. (°C)	³¹ P N.m.r. chemical (p.p.m.) *	Molecular ion M ⁺	Analysis (%)		
					Found (calc.)		
					C	H	P
C ₂ H ₅	White crystalline solid	148–152	–26.7	362	79.0 (79.5)	8.8 (8.6)	8.8 (8.6)
C ₃ H ₇	White crystalline solid	110–112	–26.3	404	79.6 (80.2)	8.1 (8.2)	7.8 (7.7)
C ₆ H ₁₁	Yellow oil		–26.3	488	80.6 (81.1)	9.1 (9.3)	5.7 (6.3)
C ₇ H ₁₅	Yellow oil		–25.3	572			
C ₉ H ₁₉	Yellow oil		–26.2	656			

* Chemical shifts measured relative to trimethyl phosphate as an external standard, which lies –4.242 p.p.m. down-field from 85% H₃PO₄ (Lady Richards, personal communication). All values refer to solutions in CDCl₃.

tilled under reduced pressure to yield the *p*-bromoalkenylbenzene, which was then dissolved in absolute ethanol (100 ml) and hydrogenated over Adam's catalyst (platinum oxide, PtO₂·2H₂O). Distillation gave the *p*-bromoalkylbenzene in good yield. Boiling points of all intermediates, together with yields, are given in Table 3.

p-Bromopropylbenzene.—This may be prepared by the above route, but it is more easily prepared by the reaction of allyl bromide with the mono-Grignard reagent of 1,4-di-

complex prepared according to ref. 6 gives excellent micro-analytical data.

Measurements.—Microanalyses were determined in the Chemistry Departments at University College London and the University of Kent. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-7M mass spectrometer using a VG 2035 data system at the Materials Quality Assurance Directorate, Woolwich, London. Phosphorus-31 n.m.r. spectra were recorded in CDCl₃ solution using a Bruker WH-

TABLE 3
Physical data for *p*-bromoalkylbenzenes and precursors

<i>p</i> -Bromoalkylphenyl alcohol		<i>p</i> -Bromoalkenylbenzene			<i>p</i> -Bromoalkylbenzene			Overall yield ^g (%)
Formula	Yield ^a (%)	Formula	Yield ^b (%)	B.p. (°C) ^c	Formula	Yield ^d (%)	B.p. (°C) ^e	
<i>p</i> -BrC ₆ H ₄ CH(OH)C ₂ H ₅	86	<i>p</i> -BrC ₆ H ₄ -CH=CH ₂	79	98 (0.12)	<i>p</i> -BrC ₆ H ₄ C ₂ H ₅	93	56 (0.5)	60
<i>p</i> -BrC ₆ H ₄ CH(OH)C ₃ H ₇	73	<i>p</i> -BrC ₆ H ₄ -CH=CH-C ₂ H ₅	73	98 (0.2)	<i>p</i> -BrC ₆ H ₄ C ₃ H ₇	96	66 (0.03)	
<i>p</i> -BrC ₆ H ₄ CH(OH)C ₄ H ₉	73	<i>p</i> -BrC ₆ H ₄ -CH=CH-C ₃ H ₇	70	105 (0.05)	<i>p</i> -BrC ₆ H ₄ C ₄ H ₉	96	85 (0.1)	49
<i>p</i> -BrC ₆ H ₄ CH(OH)C ₅ H ₁₁	76	<i>p</i> -BrC ₆ H ₄ -CH=CH-C ₄ H ₉	71	130 (0.3)	<i>p</i> -BrC ₆ H ₄ C ₅ H ₁₁	94	86–88 (0.05)	51
<i>p</i> -BrC ₆ H ₄ CH(OH)C ₆ H ₁₃	63	<i>p</i> -BrC ₆ H ₄ -CH=CH-C ₅ H ₁₁	74	120 (0.15)	<i>p</i> -BrC ₆ H ₄ C ₆ H ₁₃	98	95 (0.15)	46
				100 (0.2)	<i>p</i> -BrC ₆ H ₄ C ₇ H ₁₅		95 (0.20)	
<i>p</i> -BrC ₆ H ₄ CH(OH)C ₇ H ₁₅	71	<i>p</i> -BrC ₆ H ₄ -CH=CH-C ₆ H ₁₃	79	113 (0.35)	<i>p</i> -BrC ₆ H ₄ C ₈ H ₁₇	86	104 (0.15)	48
<i>p</i> -BrC ₆ H ₄ CH(OH)C ₈ H ₁₇	74	<i>p</i> -BrC ₆ H ₄ -CH=CH-C ₇ H ₁₅	83	128 (0.1)	<i>p</i> -BrC ₆ H ₄ C ₉ H ₁₉	94	107 (0.2)	58
							112 (0.35)	

^a Yield based on *p*-bromobenzaldehyde. ^b Yield based on alcohol. ^c B.p. under reduced pressure, shown in mmHg in parentheses. ^d Yield based on alkenylbenzene. ^e Yield of *p*-bromoalkylbenzene based on *p*-bromobenzaldehyde.

bromobenzene, followed by hydrogenation of the resulting alkene to yield the desired product.⁴

Compounds [M(PAr₃)₂Cl₂] where M = Pd, Pt, Ar = *p*-C₆H₄-C_nH_{2n+1}.—All experiments were performed under a nitrogen atmosphere to prevent oxidation of the phosphine and decomposition of any intermediate complexes. Chloroform solutions of the phosphine PAr₃ (2 equiv.) and the cyclo-octadiene (cod) complex [M(cod)Cl₂] (1 equiv.) were mixed together and stirred for 4 h to yield [M(PAr₃)₂Cl₂]. The solutions were taken to dryness and, where possible, recrystallised from ethanol–chloroform (6 : 4). The higher members of this series could only be obtained as viscous oils. These were purified by pouring them onto a column of alumina (Brockman activity I, neutral) and eluting with chloroform–methanol (6 : 4). The solvent was removed and the complex heated at 50 °C *in vacuo* for 12 h to remove

90 spectrometer (10-mm phosphorus probe, 36.4 MHz). All ³¹P chemical shifts were measured relative to trimethyl phosphate as an external standard. ¹H n.m.r. spectra were recorded in CDCl₃ solution containing SiMe₄ as an internal standard using a Perkin-Elmer R32 spectrometer.

I.r. spectra were recorded in the range 4 000–200 cm⁻¹ using Perkin-Elmer spectrometers, models 457 and 577. Solids were run as mulls, using Nujol or hexachlorobutadiene as the mulling agent, and liquids as thin films using potassium bromide plates for the range 4 000–400 cm⁻¹ and CsI plates below 400 cm⁻¹. All spectra were calibrated with a standard polystyrene film.

RESULTS AND DISCUSSION

The tris(*p*-alkylaryl)phosphines were prepared by treating phosphorus trichloride with the Grignard reagent

derived from the corresponding *p*-bromoalkylbenzene. The *p*-bromoalkylbenzenes are not commercially available and so it was necessary to develop a satisfactory procedure for making the pure *para*-isomer in good yield. We¹ and others⁷ have noted previously that, when preparing very soluble compounds of the present type, it is essential to use very pure starting materials to minimise the amount of purification needed at the end. This is because the products and their impurities have very similar properties, making separation difficult.

p-Halogenoalkylbenzenes have been prepared either by reaction of chlorobenzene with a terminal alkene in the presence of concentrated sulphuric acid⁸ or chlorobenzene with an alkyl bromide in the presence of aluminium tribromide or finely divided aluminium.⁹ However, we

the *para*-isomer in high yield. Reaction of an alkyl Grignard reagent with an arylaldehyde yields a secondary alcohol, which is then dehydrated to the alkenylbenzene and hydrogenated to the alkylbenzene.⁴ The materials used in this preparation are all readily available, isomeric mixtures are not formed and the final product is therefore easily purified, by fractional distillation. The best yields are obtained when a slight excess of the Grignard reagent is used. *p*-Bromopropylbenzene can be prepared in this way but it is more easily prepared as described in the Experimental section.

After completion of this work our attention was drawn to the synthetic procedure of Manassen and Dror,¹³ based upon the reaction of bromobenzene with an acyl chloride in the presence of aluminium trichloride, fol-

TABLE 4
Physical properties, spectroscopic, and analytical data for $[M\{P(C_6H_4R)_3\}_2Cl_2]$

R	M	Colour, appearance	M.p. (°C)	$\nu(M-Cl)/cm^{-1}$	³¹ P N.m.r.		Analysis (%)			
					$\delta/p.p.m.$	J_{P-P}/Hz	Found (calculated)			
							C	H	Cl	P
C ₂ H ₅	Pd	Yellow, crystalline solid	ca. 230 (decomp.)	360	-18.6		65.8 (66.3)	6.4 (6.3)	8.3 (8.2)	7.9 (7.1)
	Pt	Cream, crystalline solid	268 (decomp.)	295, 320	-9.2	3 695	59.8 (60.1)	5.7 (5.7)	7.6 (7.4)	
<i>n</i> -C ₃ H ₇	Pd	Yellow, crystalline solid	166 (decomp.)	360	-18.9		67.5 (67.9)	6.8 (7.0)	7.5 (7.4)	8.0 (7.5)
	Pt	Cream, crystalline solid	86 (decomp.)	295, 320	-9.3	3 696	61.7 (62.8)	6.3 (6.4)	6.8 (6.9)	5.8 (6.0)
<i>n</i> -C ₄ H ₉	Pd	Yellow, crystalline solid	164 (decomp.)	360	-18.7		69.7 (69.4)	7.8 (7.6)	6.9 (6.8)	5.8 (5.9)
	Pt	Cream, crystalline solid	136-138 (decomp.)	295, 320	-9.2	3 698	62.9 (63.9)	6.8 (7.0)	6.1 (6.3)	5.3 (5.5)
<i>n</i> -C ₅ H ₁₁	Pd	Yellow, crystalline solid	118 (decomp.)	360	-18.7		70.0 (70.6)	7.9 (8.1)	6.1 (6.3)	6.1 (5.5)
	Pt	Yellow, hard wax		295, 320	-9.3	3 694	63.5 (65.4)	7.2 (7.5)	6.2 (5.9)	4.9 (5.1)
<i>n</i> -C ₆ H ₁₃	Pd	Dark wax		365	-18.6		69.0 (71.7)	8.0 (8.5)	5.4 (5.9)	
<i>n</i> -C ₈ H ₁₉	Pd	Dark oil		365	-18.6		74.4 (74.1)	9.5 (9.5)	4.7 (4.9)	4.8 (4.3)

* Chemical shifts measured relative to trimethyl phosphite as external standard. All spectra were recorded in CDCl₃.

found that both routes give rise to mixtures of isomers that are very difficult to separate on a preparative scale for all but the lower alkyl groups. It is well known that the halogenation of alkylbenzenes proceeds quite rapidly under varying reaction conditions.^{10,11} In the presence of acid catalysts and at low temperatures halogenation of the aromatic ring occurs, but again a mixture of *ortho*- and *para*-isomers is formed. It has been shown that silver trifluoroacetate catalyses the reaction between iodine and both benzene and toluene to form iodobenzene and *p*-iodotoluene respectively.¹² We have extended this reaction to the iodination of heptylbenzene and have formed the *para*-substituted product exclusively. However the yield is low and a large excess of alkylbenzene must be present in the system, which presents difficulties in the separation of the product from the reaction mixture.

Although all the above procedures are simple one-step processes they each have obvious disadvantages. The difficulties in separating the *para*-isomer, together with the low yields which are often obtained, render these processes unsuitable for large-scale procedures. Accordingly, it was decided to use a three-stage synthesis to prepare the *p*-halogenoalkylbenzenes which gave solely

lowed by a Wolff-Kischner reduction of the acyl group to an alkyl group using alkaline hydrazine. The product is claimed to be solely the *para*-isomer with no *ortho*-contaminant. However, although the overall yield is not given, the original discoverers¹⁴ report that the acylation step yields only 30% of the desired product together with 25% of PhCOR. By contrast, overall yields in the present synthesis of *p*-bromoalkylbenzenes are 46-60% (Table 3).

Characterisation of the Tris(p-alkylaryl)phosphines.— Good microanalyses were obtained for the lower members of the series; however, the high members could not be distilled without decomposition, and therefore the waxy state of these phosphines coupled with the increased sensitivity to oxygen when compared with triphenylphosphine rendered purification and characterisation difficult. Accordingly a complete characterisation of the whole series depended on a combination of physical techniques, as well as characterisation of derivatives including the phosphine oxides (Table 2) and the bis-(phosphine)dichloro-palladium(II) and platinum(II) complexes (Table 4). The mass spectra showed the presence of the expected molecular ions (Table 1).

The i.r. spectra (4 000-200 cm⁻¹) showed the absence

of bands attributable to P=O or P-O stretching modes, indicating the absence of significant amounts of oxidation products. The spectra were very similar to those of the *para*-bromoalkylbenzenes from which they were prepared. No bands assignable to P-C stretching modes were observed, which is in agreement with their absence in the spectra of trialkylphosphines characterised previously.^{1, 15, 16}

The relative intensities of the signals in the ¹H n.m.r. spectra (Table 5) were consistent with the proposed number of protons in each molecule. The ³¹P n.m.r. spectra in deuteriochloroform (Table 1) showed a single resonance *ca.* +10.66 p.p.m. up-field from trimethylphosphate (*ca.* 6.4 p.p.m. upfield from 85% H₃PO₄) which is consistent with the values reported previously for other tertiary aromatic phosphines.^{17, 18} In addition the

TABLE 5

¹H N.m.r. chemical shifts * for the triarylphosphines

Phosphine	Me	CH ₂ not CH ₂ adjacent		Aromatic protons
		adjacent to aromatic ring	to the aromatic ring	
P(<i>p</i> -C ₆ H ₄ -C ₂ H ₅) ₃	1.20		2.60	7.20
P(<i>p</i> -C ₆ H ₄ -C ₃ H ₇) ₃	0.95	1.65	2.60	7.20
P(<i>p</i> -C ₆ H ₄ -C ₄ H ₉) ₃	0.92	1.50	2.60	7.20
P(<i>p</i> -C ₆ H ₄ -C ₅ H ₁₁) ₃	0.88	1.28	2.60	7.20
P(<i>p</i> -C ₆ H ₄ -C ₆ H ₁₃) ₃	0.88	1.27	2.60	7.20
P(<i>p</i> -C ₆ H ₄ -C ₇ H ₁₅) ₃	0.88	1.27	2.60	7.20
P(<i>p</i> -C ₆ H ₄ -C ₈ H ₁₇) ₃	0.88	1.27	2.60	7.20
P(<i>p</i> -C ₆ H ₄ -C ₉ H ₁₉) ₃	0.88	1.27	2.60	7.20

* All spectra recorded in CDCl₃ using SiMe₄ as internal standard.

single phosphorus resonance provided further evidence of purity. Upon oxidation to the phosphine oxide, O=P(*p*-C₆H₄R)₃, the chemical shift moves down-field by *ca.* 37 p.p.m. (Table 2), which is consistent with results observed with other triaryl- and trialkyl-phosphines.^{1, 19-21}

Properties of the Tris(p-alkylaryl)phosphines.—The triarylphosphines were either crystalline solids or viscous oils that were extremely soluble in hexane and chlorinated solvents such as dichloromethane, chloroform, and carbon tetrachloride, and moderately soluble in tetrahydrofuran, diethyl ether, and aromatic solvents such as benzene and toluene. The lower members of the series were found to be soluble in ethanol but this ability decreased as the length of the alkyl group on the phenyl rings increased. The higher members of the series are insoluble in cold ethanol, methanol, and other polar solvents. The corresponding phosphine oxides were also found to have similar physical properties and solubility characteristics.

These new phosphines were found to be sensitive to oxygen both as solids or oils, and in solution, whereas triphenylphosphine has been shown to be stable towards oxidation as a solid and in solution, and in fact has been used as an oxidation inhibitor in solutions of other oxygen-sensitive phosphines.²² Unlike trialkylphosphines, which yield a mixture of products on oxidation in air (auto-oxidation),^{1, 23} these new triarylphosphines appear to give exclusively the phosphine oxide. The oxidation properties were studied using ³¹P n.m.r.

spectroscopy. Tri(*p*-ethylphenyl)phosphine was allowed to stand in air for several days, after which significant amounts of the phosphine oxide could be detected *ca.* 36 p.p.m. downfield from the parent phosphine. Only two peaks were observed in the spectra. Similar results were found using tris(*p*-propylphenyl)phosphine. The sensitivity of the *para*-substituted triarylphosphines towards oxidation appeared to increase as the alkyl chain on the phenyl ring increased in length. This may be due to an increase in the aliphatic character of the phosphine, which results from changes in the stereochemistry of the molecule due to the presence of the long alkyl chains. Electronic factors may be ruled out because the ethyl and nonyl groups should not differ appreciably in their electron-donor properties at the phosphorus atom.

Palladium(II) and Platinum(II) Complexes.—The tris(*p*-alkylaryl)phosphines were found to readily displace co-ordinated dienes and other weak donor-ligands from complexes of palladium and platinum to yield bis(phosphine)dichloro-complexes. I.r. and ³¹P n.m.r. spectroscopy indicate that the palladium complexes have the *trans*-configuration whereas the platinum(II) complexes are *cis* (Table 4).²⁴ It is noteworthy that in each series the melting or decomposition points decrease as the alkyl group increases in length; this is immediately apparent from the physical appearance of the complexes, those with longer alkyl chains being waxy solids whereas those with shorter alkyl chains are crystalline. Clearly as the alkyl chain gets longer it becomes more difficult to pack the molecules into a crystal.

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