The Preparation and Properties of Tertiary Phosphines and Tertiary Phosphine Oxides with Long Alkyl Chains

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A series of tertiary phosphines and tertiary phosphine oxides with straight-chain alkyl groups of between ten and nineteen carbon atoms have been prepared. The tertiary phosphines are waxy, very air-sensitive solids, whereas the tertiary phosphine oxides are more crystalline, are stable in air, and do not show the deliquescence associated with the lower members of the series with alkyl chains containing between one and seven carbon atoms. The compounds were characterised by microanalysis, i.r., ^{1}H, and ^{31}P n.m.r, spectra, and mass spectrometry. The trialkylphosphines were found to form readily complexes [ML_2Cl_2] with palladium(II) and platinum(II) and the trialkylphosphine oxides formed complexes with elements, such as nickel(II) and copper(II), in the first transition series.

TERTIARY phosphines are very good ligands for transition metals, and tertiary phosphine oxides for lanthanide and actinide elements. It was therefore of interest to prepare complexes of these ligands with long straight-chain alkyl groups, $P(n\text{-}C_nH_{2n+1})_3$ and $PO\text{-}(n\text{-}C_nH_{2n+1})_3$, since such complexes would be expected to be freely soluble in hydrocarbon solvents which is desirable for many applications, including the preparation of homogeneous catalysts for the activation of alkanes and the preparation of new reagents for the solvent-extraction of metals. Accordingly we report here the preparation and characterisation of the complete series of tertiary phosphines and tertiary phosphine oxides with straight-chain alkyl groups comprising between ten and nineteen carbon atoms.

Prior to this work the only compounds which are reported here that have previously been described are $P(n\text{-}C_{10}H_{21})_3$,[1,2] $P(n\text{-}C_{12}H_{25})_3$,[3] $P(n\text{-}C_{14}H_{29})_3$,[4] $P\text{-}(n\text{-}C_{16}H_{33})_3$,[1] and $PO(n\text{-}C_{12}H_{25})_3$ [3] and none of these have been fully characterised.

EXPERIMENTAL

Preparation of the Trialkylphosphines.—The trialkylphosphines are extremely sensitive to oxygen. Accordingly all steps in their preparation and characterisation were effected under an atmosphere of nitrogen. The trialkylphosphines were prepared from the corresponding alkyl bromides by reacting the Grignard reagent with phosphorus

trichloride in tetrahydrofuran solution. The solutions were hydrolysed with a deoxygenated saturated aqueous solution of ammonium chloride.[5] The organic layer was syringed off into a Schlenk tube and dried over anhydrous sodium sulphate. The tetrahydrofuran was distilled off *in vacuo*, leaving the crude phosphine which was dried *in vacuo* at 80 °C for 24 h, followed by recrystallisation from chloroform and ethanol. The lower members were found to be extremely difficult to recrystallise due to their waxy states, but the higher members were easier to handle and were obtained in higher purity. Appearances, yields, and m.p.s are recorded in Table 1. All the alkyl bromides were available commercially except n-undecyl bromide and n-heptadecyl bromide which were prepared from the corresponding alcohols by the action of hydrobromic acid.[6]

Preparation of the Trialkylphosphine Oxides.—The trialkylphosphines were treated under nitrogen with a slight excess of hydrogen peroxide (6% w/v),[3] calculated on the basis of the reaction $PR_3 + H_2O_2 \rightarrow POR_3 + H_2O$. The trialkylphosphine oxides were extracted with chloroform, dried over anhydrous sodium sulphate, precipitated by the addition of ethanol, and recrystallised from acetone. Appearances, yields, m.p.s, and microanalytical data are given in Table 2.

Characterisation of the Trialkylphosphines.—The waxy state of the lower trialkylphosphines, coupled with the extreme sensitivity to oxygen, rendered purification and characterisation very difficult. Good microanalytical data were only obtained for the higher members of the series (see Table 1). Accordingly, complete characterisation

TABLE 1

Physical and analytical data for the trialkylphosphines

Phosphine	Colour	Appearance	Yield [a]	M.p. (°C)	^{1}H N.m.r.[b] chemical shifts		M^+ Found (Calc.)	Analysis Found (Calc.) C	H
$P(n\text{-}C_{10}H_{21})_3$	Cream	Soft wax	76%	37—40 [c,d]	0.88	1.27	454 (454)		
$P(n\text{-}C_{11}H_{23})_3$	Cream	Soft wax	69%	40—41	0.88	1.27			
$P(n\text{-}C_{12}H_{25})_3$	Cream	Soft wax	57%	44—45 [d]	0.88	1.27	538 (538)		
$P(n\text{-}C_{13}H_{27})_3$	White	Hard wax	61%	45—47	0.88	1.27	580 (580)		
$P(n\text{-}C_{14}H_{29})_3$	White	Hard wax	75%	48—52 [d]	0.88	1.27	622 (622)		
$P(n\text{-}C_{15}H_{31})_3$	White	Hard wax	78%	46—48	0.88	1.27	664 (664)		
$P(n\text{-}C_{16}H_{33})_3$	White	Crystalline solid	75%	59—61 [c,d]	0.88	1.27	706 (706)	79.9 (81.5)	13.7 (14.1)
$P(n\text{-}C_{17}H_{35})_3$	White	Crystalline solid	75%	60—61	0.88	1.27	748 (748)	81.1 (81.7)	14.0 (14.1)
$P(n\text{-}C_{18}H_{37})_3$	White	Crystalline solid	72%	62—64	0.88	1.27	790 (790)	81.0 (81.9)	14.4 (14.1)
$P(n\text{-}C_{19}H_{39})_3$	White	Crystalline solid	68%	60—62	0.88	1.27	832 (832)	81.8 (82.1)	14.1 (14.2)

[a] Yield based on PCl_3. [b] Recorded in $CDCl_3$ solution; δ in p.p.m. from $SiMe_4$. [c] See ref. 1. [d] See ref. 4.

TABLE 2

Physical and analytical data for the trialkylphosphine oxides

Phosphine oxide	Colour	Appearance	Yield (%) [a]	M.p. (°C)	N.m.r. chemical shifts		^{31}P [c]	M^+ Found (Calc.)	Analysis Found (Calc.)	
					^1H [b]				C	H
PO(n-C$_{10}$H$_{21}$)$_3$	White	Waxy solid	85	37	0.88	1.27	−42.64	470 (470)	76.1 (76.5)	13.3 (13.5)
PO(n-C$_{11}$H$_{23}$)$_3$	White	Waxy solid	80	40—41	0.88	1.27	−45.25	512 (512)	76.6 (77.3)	13.4 (13.6)
PO(n-C$_{12}$H$_{25}$)$_3$	White	Crystalline solid	78	50—52 [d]	0.88	1.27	−44.41	554 (554)	76.3 (77.9)	13.3 (13.6)
PO(n-C$_{13}$H$_{27}$)$_3$	White	Crystalline solid	80	59—60	0.88	1.27	−44.45	596 (596)	77.2 (78.5)	13.3 (13.7)
PO(n-C$_{14}$H$_{29}$)$_3$	White	Crystalline solid	81	57—58	0.88	1.27	−43.84	638 (638)	77.1 (78.9)	13.6 (13.7)
PO(n-C$_{15}$H$_{31}$)$_3$	White	Crystalline solid	78	60—61	0.88	1.27	−46.59	680 (680)	79.1 (79.3)	13.7 (13.8)
PO(n-C$_{16}$H$_{33}$)$_3$	White	Crystalline solid	79	60—61	0.88	1.27	−46.06	722 (722)	79.3 (79.7)	13.7 (13.8)
PO(n-C$_{17}$H$_{35}$)$_3$	White	Crystalline solid	88	74—75	0.88	1.27	−42.64	764 (764)	79.6 (80.0)	13.7 (13.8)
PO(n-C$_{18}$H$_{37}$)$_3$	White	Crystalline solid	94	73—75	0.88	1.27	−46.43	806 (806)	80.1 (80.3)	13.6 (13.9)
PO(n-C$_{19}$H$_{39}$)$_3$	White	Crystalline solid	93	69—71	0.88	1.27	−46.01	848 (848)	81.1 (80.6)	14.0 (13.9)

[a] Yield based on trialkylphosphine. [b] Recorded in CDCl$_3$ solution containing SiMe$_4$ as internal standard. [c] Recorded in CDCl$_3$ solution using TMP as external standard. [d] See ref. 3.

depended on a combination of physical techniques together with the characterisation, including microanalysis, of the corresponding trialkylphosphine oxide.

The i.r. spectra (4 000—200 cm^{-1}), obtained without the need for a mulling agent, showed the absence of bands attributable to P=O or P–O stretching modes indicating the absence of significant amounts of oxidation products. Strong absorption bands at 3 000—2 860 cm^{-1} (C–H stretching modes in CH$_3$), 2 870—2 810 cm^{-1} (C–H stretching modes in CH$_2$), 1 490—1 400 and 1 385—1 360 cm^{-1} (C–H deformation modes), and 730—710 cm^{-1} (CH$_2$ rocking modes), which are all consistent with the presence of trialkylphosphines,[7] were observed. No bands assignable to P–C stretching modes were observed. Such bands are expected [7,8] between 750 and 650 cm^{-1} and are either too weak to be observed or are obscured by the strong CH$_2$ rocking modes.

The ^1H n.m.r. spectra showed multiplets at δ 1.27 and a triplet at δ 0.88 (downfield from SiMe$_4$) assigned to the methylene and methyl groups, respectively, of the long alkyl chains. Integrated intensities of these two peaks were consistent with the expected number of protons per alkyl chain. The absence of any further proton signals provided evidence of purity.

The mass spectra all showed the expected molecular ion. The fragmentation patterns were characteristic of the trialkylphosphines; no unexpected peaks were observed, nor were peaks containing oxygen, therefore the mass spectra provided further evidence of purity.

Attempts to use gas–liquid chromatography to provide an estimate of purity [9,10] were unsuccessful because decomposition occurred below the temperature necessary for elution. Thus using a 3 ft column of 10% SE 30 on 80—100 mesh Chromasorb WHP, a temperature programme from 140—300 °C at 8 °C min^{-1}, and both a flame-ionisation and a phosphorus detector, a number of peaks were obtained, at relatively short retention times, that did not contain phosphorus, together with a peak due to a phosphorus-containing compound after a relatively long interval of time; for P(C$_{10}$H$_{21}$)$_3$ this latter peak was observed after 17 min corresponding to a column temperature of 280 °C.

Characterisation of the Trialkylphosphine Oxides.—Good microanalytical data were obtained for all members of the series. The i.r. spectra, recorded in Nujol and hexachlorobutadiene mulls, showed a strong absorption band centred at about 1 148 cm^{-1} which was assigned to the P=O stretching vibration; [7,8] in other respects the spectra resembled those of the trialkylphosphines. The ^1H n.m.r. spectra were essentially identical to those of the trialkylphosphines in showing a multiplet at δ 1.27 due to the methylene protons and a triplet at δ 0.88 due to the terminal methyl protons. The absence of any further resonances, together with the fact that the relative integrated intensities of the two peaks were consistent with the anticipated formulae, was taken as an indication of purity. The phosphorus-31 n.m.r. spectra in CDCl$_3$ showed a single resonance in the range 43—46 p.p.m. downfield from trimethyl phosphate, which is consistent with the values reported previously for other members of the series.[3,11,12] In addition the single phosphorus resonance provided further evidence of purity.

The mass spectra all showed the expected molecular ion and the fragmentation patterns were characteristic of trialkylphosphine oxides, with no unexpected peaks.

Measurements.—Microanalytical data were determined in the Chemistry Department at University College, London. 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. Hydrogen-1 n.m.r. spectra were recorded in CDCl$_3$ solution containing tetramethylsilane as an internal standard, using a Perkin-Elmer R32 spectrometer. Phosphorus-31 n.m.r. spectra were recorded in CDCl$_3$ solution using a Brucker WH 90 spectrometer (10-mm phosphorus probe, 36.4 MHz). All chemical shifts were measured relative to trimethyl phosphate (TMP) as external standard.
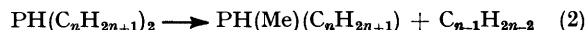
I.r. spectra were recorded in the range 4 000—250 cm^{-1} and 4 000—200 cm^{-1} using Perkin-Elmer spectrometers, models 457 and 577, respectively. Solids were run as mulls, using Nujol or hexachlorobutadiene as the mulling agent, and liquids as thin films using potassium bromide plates for the range 4 000—400 cm^{-1} and CsI or polythene plates below 450 cm^{-1}. All spectra were calibrated with a

standard polystyrene film. Gas–liquid chromatographic data were recorded using a Packard 419 gas–liquid chromatograph, equipped with a flame-photometric detector, a phosphorus probe, and a Curie point pyrolyser, for rapid injection of sample.

RESULTS

The trialkylphosphines were all low-melting waxy solids that were extremely soluble in hexane and chlorinated solvents such as dichloromethane, chloroform, carbon tetrachloride, and 1,2-dichloroethane, and moderately soluble in tetrahydrofuran, benzene, and other aromatic solvents, hot alcohols such as methanol and ethanol, and warm acetone. They are, however, insoluble in cold methanol, ethanol, and acetone. These solubility characteristics are very similar to those of the alkyl bromides from which they are prepared, as well as of any decomposition products including the corresponding trialkylphosphine oxides.

ion peak; (ii) peaks due to the loss of olefins from the parent ion [two olefins are lost, C_nH_{2n} through reaction (1) and $C_{n-1}H_{2n-2}$ through (2); the ion formed by reaction (1) is

$$P(C_nH_{2n+1})_3 \longrightarrow PH(C_nH_{2n+1})_2 + C_nH_{2n} \qquad (1)$$

$$PH(C_nH_{2n+1})_2 \longrightarrow PH(Me)(C_nH_{2n+1}) + C_{n-1}H_{2n-2} \qquad (2)$$

dominant in most of the spectra]; (iii) ions at $m/e = 62$ and 76 due to $PHMe_2$ and PMe_3 respectively; and (iv) ions such as CH_3^+, $C_2H_5^+$, $C_3H_7^+$, $C_4H_9^+$, $C_5H_{11}^+$, etc., and $C_2H_3^+$, $C_3H_5^+$, $C_4H_7^+$, $C_5H_9^+$, etc., with slightly less of each alkenyl ion than of the corresponding alkyl ion. These ions are typical of those observed in the mass spectra of n-alkanes where they reach a maximum at around $C_3H_7^+$ and $C_4H_9^+$ and thereafter tail off rapidly in intensity,[17] as observed here. With branched-chain alkanes a very different pattern is observed. The mass spectra are thus consistent with the presence of
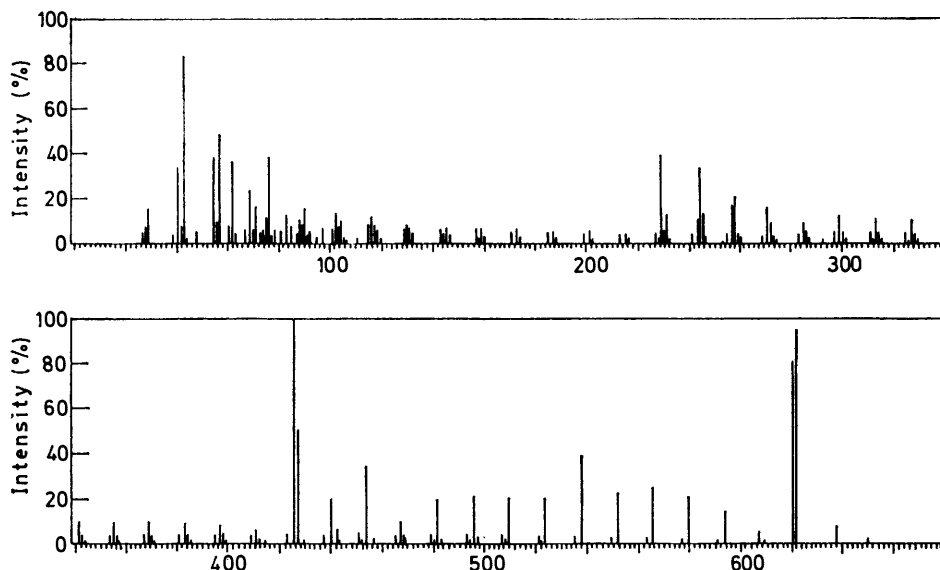

FIGURE 1   Mass spectrum of $P(C_{14}H_{29})_3$

Accordingly purification is difficult and necessitates multiple fractional recrystallisation. The trialkylphosphines are very sensitive to air, which results in the formation of a large number of oxidation products. Thus the ^{31}P n.m.r. spectrum of $P(C_{14}H_{29})_3$, after standing in chloroform solution in air for several hours, showed no absorption due to tris(tetradecyl)phosphine (ca. 30 p.p.m. upfield from TMP), but bands downfield from TMP at −45.62 (5), −42.99 (1.5), −29.96 (2), −27.45 (1), and −27.09 p.p.m. (2.5) where the figures in parentheses are the relative intensities. These bands are consistent with the formation of a series of oxidation products, $P(OR)_{3-n}R_n$ ($n = 1$ or 2) and $P(O)(OR)_{3-n}R_n$ ($n = 0$, 1, 2, or 3) as observed previously for the air oxidation of tri-n-butylphosphine.[13,14]

The mass spectra of the long straight-chain trialkylphosphines were similar in appearance to the mass spectrum of the second member of the series, PEt_3.[15] However, since the spectra of the higher members of the series do not appear to have been reported,[16] and since there are some differences as compared with PEt_3, it is opportune to report the spectra in some detail. A typical mass spectrum is shown in Figure 1. The spectra show: (i) a strong parent-

linear alkyl tertiary phosphines. The fragments observed can be explained by the fragmentation pattern given in the Scheme. It is apparent from the relative abundances of the products that the principal fragmentation route for $P(C_{14}H_{29})_3$ involves P–C bond cleavage with loss of the olefin $C_{14}H_{28}$ and formation of $PH(C_{14}H_{29})_3$. This is consistent with the relative energies of the P–C and C–C bonds of ca. 276 and ca. 348 kJ mol⁻¹, respectively.[5,18,19]

The trialkylphosphine oxides are stable in air. They are solids that are more crystalline than the corresponding phosphines, and are thus easier to handle and purify. The phosphine oxides are very soluble in chlorinated solvents and saturated hydrocarbons, such as hexane, and moderately soluble in aromatic solvents, tetrahydrofuran, warm alcohols such as methanol and ethanol, and warm acetone. They are however insoluble in cold methanol, ethanol, and acetone. These solubility characteristics are very similar to those of the trialkylphosphines. In contrast to the lower members of the series [5,20] [i.e. those below $PO(C_8H_{17})_3$] the long-chain trialkylphosphine oxides were not deliquescent at all.

The mass spectra of the long straight-chain trialkyl-

$$C_{14}H_{28} \longrightarrow R + R'$$

$$C_{13}H_{26} \longrightarrow R + R'$$
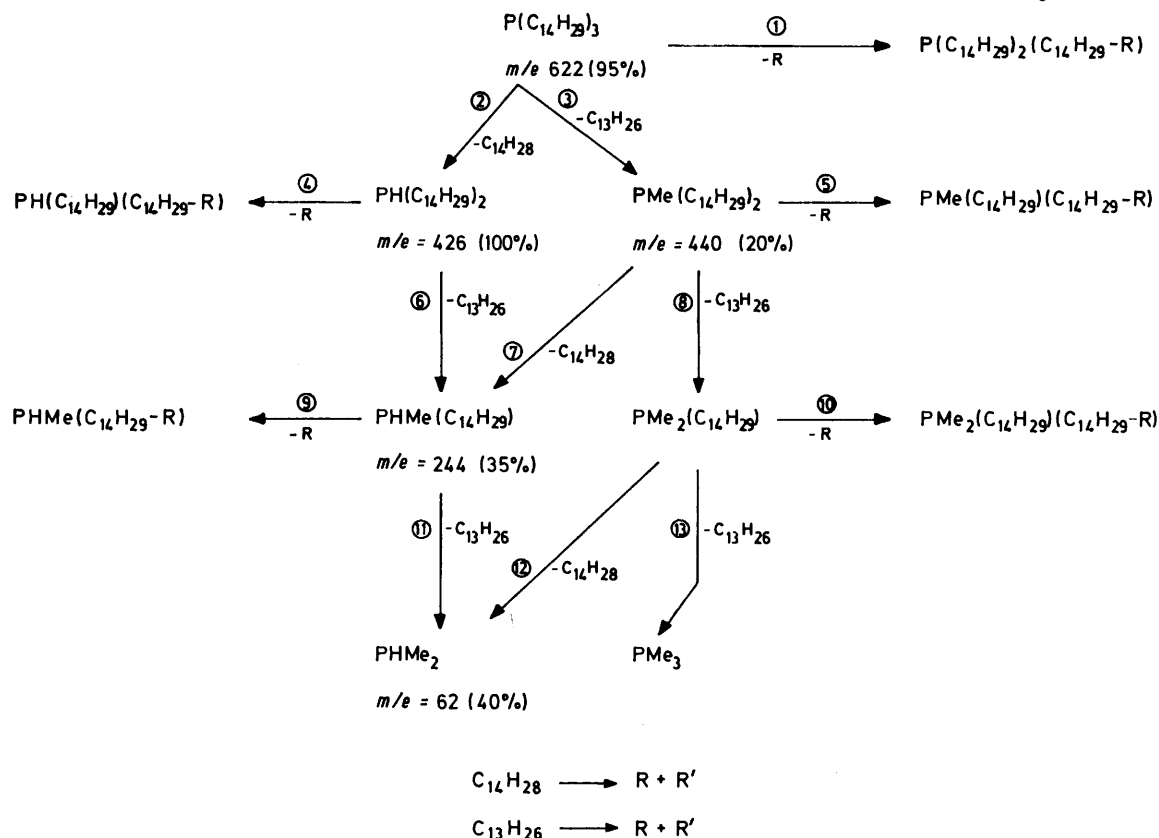
SCHEME Fragmentation pattern of $P(C_{14}H_{29})_3$; the percentage abundances of the uniquely determined species are shown in parentheses; $R = C_nH_{2n+1}$, $R' = C_nH_{2n-1}$

phosphine oxides are very similar in appearance to those of the corresponding phosphines, with the difference that all the ions containing phosphorus are sixteen mass units heavier due to the presence of an oxygen atom. This is consistent with the greater bond energy of the P=O than P–C bond, *ca.* 523 kJ mol⁻¹ (ref. 21) and *ca.* 276 kJ mol⁻¹ (refs. 5 and 18) respectively. A typical mass spectrum is shown in Figure 2.

The trialkylphosphines (L) were found to displace readily ligands such as cyclo-octadiene (COD) from complexes of palladium(II) and platinum(II) to give compounds of general formula $[ML_2Cl_2]$ corresponding to those formed by lower

$$[M^{II}(COD)Cl_2] + 2L \longrightarrow [M^{II}L_2Cl_2] \qquad (3)$$
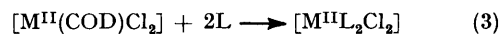
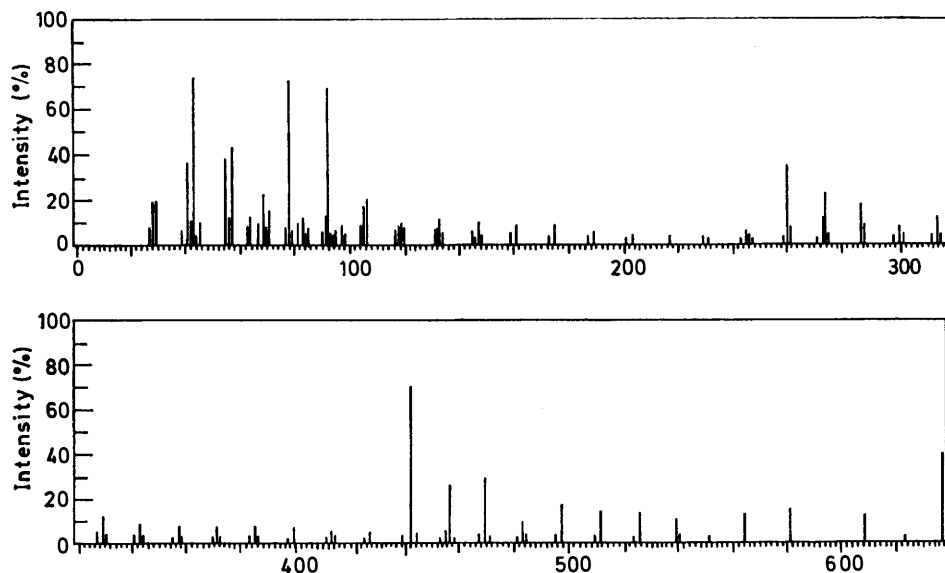members of the series.[21] The long-chain trialkylphosphine oxides (L′) complex with first-row transition metal elements

FIGURE 2   Mass spectrum of $PO(C_{14}H_{29})_3$

such as nickel(II) and copper(II), in a similar manner to shorter-chain trialkylphosphine oxides.[18] The characteristic colour of the nickel–phosphine oxide complexes may be used for the detection of tertiary phosphine oxides.[22,23]

$$Ni[ClO_4]_2 + 4L' \longrightarrow [NiL'_4][ClO_4]_2 \quad (4)$$
$$\text{Red-rose}$$

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