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PHOSPHINE SULPHIDES AND THEIR COMPLEXES WITH METALS: ^{13}C NMR SPECTROSCOPY

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PHOSPHINE SULPHIDES AND THEIR COMPLEXES WITH METALS: ^{13}C NMR SPECTROSCOPY

S. RODERICK POSTLE†

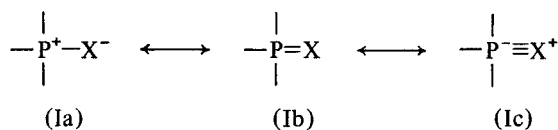
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^{13}C nuclear magnetic resonance data have been recorded for twenty-two tertiary phosphine sulphides. A discussion of the variation in chemical shifts and ^{31}P - ^{13}C coupling constants and a comparison of the data with some analogous phosphine oxides are included. The results are examined with respect to a description of the phosphoryl and thio-phosphoryl bonds. The ^{13}C and ^1H nmr and infra-red spectra of four gold (I) and aluminium (III) complexes of phosphine sulphides are recorded and commented upon.

INTRODUCTION

The controversy over a complete description of the bonding in the phosphoryl and thiophosphoryl groupings has raged long, without definite conclusions.¹ For example, electron diffraction studies² show that a bond order of two may be ascribed to the thio-phosphoryl bond, and that the bond order of the phosphoryl linkage is even greater. This may be taken to indicate that $d\pi$ - $p\pi$ overlap (Ib and Ic) is important in the formulation of these bonds.



(X = O, S, Se).

Bond dissociation energies³ indicate that the thio-phosphoryl linkage is energetically weaker than the phosphoryl linkage, possibly indicating that Ia is a more important contributor to the thiophosphoryl bond, whilst canonical forms Ib and Ic are more important in a description of the phosphoryl bond. In support of this statement, ^{31}P nmr data on triphenylphosphine oxide and triphenylphosphine sulphide⁴ show the phosphorus in the latter to be more deshielded, and to be relatively unaffected by protonation (Table I). Such a viewpoint must, however, be treated as an oversimplification, as the ^{31}P nmr data available for trialkylphosphine chalcides do not follow these

trends but are explicable rather upon a rationalization based upon chalcogen electronegativities.⁶ Furthermore, the data for the phosphine selenides are hard to rationalize solely on the assumption of contributions to the selenophosphoryl bond from canonicals Ia-Ic (and, in this case, there is the possibility of $d\pi$ - $d\pi$ overlap to consider).†

Our attention was also drawn to this general problem by a consideration of the ^1H nmr data recorded by ourselves and others,^{7,8} which shows protons on the

† We are grateful to a referee for drawing our attention to the dangers arising from comparison of data, drawn from different sources, without regard for solvent and concentration effects.

TABLE I
 ^{31}P nmr data for phosphine chalcides

Compound	δ^a
Ph_3PO	29.3
Ph_3OH^+	57.2
Ph_3PS	43.2
Ph_3PSH^+	42.6
Ph_3PSe	35.8
Bu_3^tPO	46.9
Bu_3^tPS	48.1
Me_3PO	41.0 ^b
Me_3PS	28.9 ^c
Me_3PSe	8.7 ^c

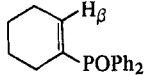
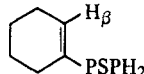
^a Downfield from 85% phosphoric acid: data are from Ref. 4 unless stated otherwise.

^b Ref. 5.

^c Ref. 6.

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TABLE II
¹H nmr data for some phosphine chalcides

Compound	H _α ^a	J _{P-H_α} ^b	H _β ^a	J _{P-H_β} ^b
Et ₃ PO ^c	8.35	11.9	8.90	16.3
Et ₃ PS	8.17	11.6	8.76	18.4
PhCH ₂ (O)Ph ₂ ^d	6.39	13.8		
PhCH ₂ P(S)Ph ₂	6.16	13.2		
Bu ^t P(O)Ph ₂			8.76	15.6
Bu ^t P(S)Ph ₂			8.76	16.0
HOCH ₂ CH ₂ (O)Ph ₂	7.40	10.0	6.02	15.0
HOCH ₂ CH ₂ P(S)Ph ₂	7.18	11.0	5.99	19.8
			3.65	21.0
			3.73	23.0

^a In Tau.

^b In Hertz, corrected to one decimal place.

^c Ref. 7.

^d Ref. 8.

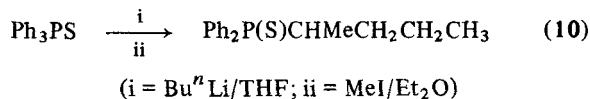
α- and β-carbons to phosphorus to be more deshielded in phosphine sulphides than in the corresponding phosphine oxides (Table II). It must be considered that the extra deshielding of the protons in the phosphine sulphides is due to anisotropic effects, the thiophosphoryl bond being more polarizable than the phosphoryl bond since the thiophosphoryl group is considered to be a less strongly electron-withdrawing group than the phosphoryl group (as evidenced by σ' values for the diphenylphosphinyl and diphenylphosphinthiaryl groupings⁹ and by the relative kinetic acidities of the methyldiphenylphosphine chalcides¹⁰).

In view of the problems arising from the above ³¹P and ¹H nmr data (noting also the strikingly different reactions of 2-hydroxyalkyldiphenylphosphine oxides and sulphides with base^{11,12}), it was concluded that a ¹³C nmr study of some phosphine sulphides and their complexes with metals would prove fruitful. A survey of ¹³C nmr data for some phosphine oxides has recently appeared in the literature.⁴

SYNTHESIS OF THE PHOSPHINE SULPHIDES

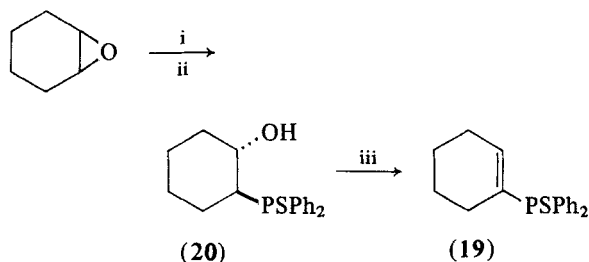
Most of the phosphine sulphides were prepared by known procedures.¹³ 1-Hexyldiphenylphosphine sulphide (11) was prepared in moderate yield by treating the corresponding phosphine oxide with an equimolar amount of phosphorus (V) sulphide in re-

fluxing benzene:¹⁴ such a procedure failed in the attempted preparation of ethenyldiphenylphosphine sulphide (4) and diphenyl 2-propylphosphine sulphide (6). The synthesis of 2-pentyl-diphenylphosphine sulphide (10) is the first recorded example of the alkylation of a phosphine sulphide-stabilized carbanion (Scheme 1).



SCHEME 1

1-Diphenylphosphinthiocylohexene (19) and *trans*-2-diphenylphosphinthiocylohexanol (20) were prepared as shown in Scheme 2¹².



(i = LiPPh₂/THF; ii = S₈; iii = KOBu^t/C₆H₆/reflux)

SCHEME 2

RESULTS AND DISCUSSION

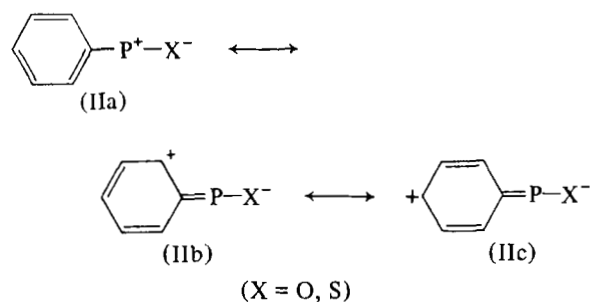
¹³C nmr data for the phosphine sulphides are summarized in Tables III (chemical shifts) and IV (coupling constants). By comparison with the ¹³C nmr data for phosphine oxides,⁴ the following points emerge from Tables III and IV†:

a) ¹δ_S ≈ ¹δ_O, but ¹δ_S > ¹δ_O (by 3–8 ppm)‡. This might reflect a greater measure of canonicals of type Ia in the ground-state bonding of thiophosphoryl linkage. However, where delocalization of charge *via* a π-

† The notation employed for convenience in this discussion is as follows: chemical shifts are referred to as "δ" and ³¹P-¹³C coupling constants as "J", superscripts referring to the carbon atom under consideration. Thus ¹J is the coupling constant for the *ipso*-carbon, and ²δ is the chemical shift of carbon-2 of the aliphatic chain (carbon-1 is α- to phosphorus). Subscripts, where employed, refer to corresponding phosphine oxides (O) and sulphides (S).

‡ That is, carbon-1 is more deshielded in phosphine sulphides, than in the corresponding phosphine oxides.

system is possible (IIa-IIc), the effects of such a contribution are dampened.



b) $^1J_S < ^1J_O$ (by 15–20 Hz), and $^1J_S < ^1J_O$ (by 13–16 Hz). If the Fermi contact term is considered to be of predominant importance in determining these coupling constants,^{4,5,6,15} then one is perhaps drawn to the conclusion that the P-Cⁱ and P-C¹ bonds have a greater *p* orbital character in phosphine sulphides than in the corresponding oxides (the phosphorus-carbon bond is longer in trimethylphosphine sulphide than in trimethylphosphine oxide²).

c) 1J_S increases with increasing electronegativity of the groups attached to phosphorus [cf. (2), (1), and (21)]. The same trend has been observed in phosphine oxides and in phosphonium salts.⁴

TABLE III
¹³C Chemical shifts of some phosphine sulphides^a

Compound		i	o	m	p	l	2	3	4	5	6
Ph ₃ PS	1	132.9	132.1	128.5	131.8						
MePh ₂ PS	2	133.3	130.8	128.8	131.5	21.7					
EtPh ₂ PS	3	133.2	131.4	129.0	131.7	27.3	5.8				
CH ₂ =CHPSPPh ₂	4	131.8	131.3	128.9	131.8	129.7	132.4				
Pr ⁿ Ph ₂ PS	5	132.8	131.2	128.8	131.6	33.0	16.4	15.8			
Pr ⁱ Ph ₂ PS	6	132.3	131.6	128.8	131.7	28.6	16.3				
CH ₂ =CH·CH ₂ PSPPh ₂	7	131.8	130.8	128.6	131.5	39.0	127.3	121.2			
Bu ⁿ Ph ₂ PS	8	133.6	131.4	128.9	131.6	32.9	24.7	24.3	14.1		
1-C ₅ H ₁₁ PSPPh ₂	9	133.2	131.3	128.8	131.6	32.9	22.2	33.1	22.6	14.2	
2-C ₅ H ₁₁ PSPPh ₂	10	132.8	131.2	128.7	131.5	33.0	31.8	20.8	12.8		14.2 ^b
1-C ₆ H ₁₃ PSPPh ₂	11	133.3	131.3	128.9	131.6	33.0	22.6	30.8	31.7	22.9	14.5
Me ₂ PhPS	12	133.5	130.1	128.8	131.6	23.2					
Me ₃ PS	13 ^c					27.7					
Et ₂ PhPS	14	133.5	131.2	128.8	131.7	26.1	6.6				
Et ₃ PS	15					23.0	6.8				
Bu ₃ PS	16 ^d					30.8	24.5	23.9	13.6		
ClCH ₂ CH ₂ PSPPh ₂	17	133.8	131.0	129.3	131.9	34.1	50.5				
HOCH ₂ CH ₂ PSPPh ₂	18	133.5	131.2	129.0	131.9	35.2	57.8				
	19 ^e	131.6	132.4	128.7	131.6	131.8	142.9	27.1	21.9	22.8	25.2
	20 ^f	134.4	132.1	128.8	131.6	45.6	71.0	35.6	25.0	25.7	26.4
Ph ₂ PSCl	21	135.8	131.8	129.0	132.9						
Ph ₃ PSH ⁺	22 ^d	119.3	132.6	129.8	135.2						
Et ₂ PS·AuCl	23					22.7	6.9				
Ph ₃ PS·AuCl	24	128.1	132.2	129.8	134.0						
Et ₃ PS·AlBr ₃	25					22.6	7.1				
Ph ₃ PS·AlBr ₃	26	124.2	133.5	130.5	135.1						

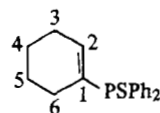
^a In ppm downfield from tetramethylsilane; carbon atoms are designated 0- ("ortho") etc. in phenyl rings, and 1- ("α-to phosphorus") etc. in aliphatic chains.

^b This is the value for carbon-2(Me).

^c From Ref. 6.

^d From Ref. 4.

^e Numbering system:



^f Numbering system:

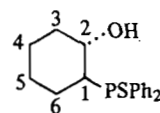


TABLE IV
 Phosphorus–Carbon coupling constants of some phosphine sulphides^a

Compound		i_J	o_J	m_J	p_J	1_J	2_J	3_J	4_J	5_J	6_J
Ph ₃ PS	1	85.5	10.6	12.2	2.5						
MePh ₂ PS	2	82.5	9.7	12.5	2.9	58.5					
EtPh ₂ PS	3	80.0	10.1	11.8	3.3	57.5	3.8				
CH ₂ =CHPSPPh ₂	4	84.2	10.3	12.6	3.3	76.1	10.2				
Pr ⁿ Ph ₂ PS	5	78.1	10.8	12.1	3.8	56.2	2.0	17.7			
Pr ⁱ Ph ₂ PS	6	77.1	9.1	11.3	3.0	56.2	0				
CH ₂ =CH·CH ₂ PSPPh ₂	7	82.5	10.8	10.9	3.4	52.5	8.6	13.4			
Bu ⁿ Ph ₂ PS	8	79.6	10.3	10.8	3.3	56.4	17.6	0			
1-C ₅ H ₁₁ PSPPh ₂	9	81.4	10.8	12.1	4.0	57.0	2.0	14.6	0	0	
2-C ₅ H ₁₁ PSPPh ₂	10	79.2	10.8	11.8	3.8	57.0	0	13.9	0		0 ^b
1-C ₆ H ₁₃ PSPPh ₂	11	82.6	10.1	11.3	3.4	56.7	2.3	16.4	0	0	0
Me ₂ PhPS	12	80.6	8.3	11.8	2.5	57.5					
Me ₃ PS	13 ^c					56.1					
Et ₂ PhPS	14	74.1	9.3	11.1	2.8	54.9	3.8				
Et ₃ PS	15					51.7	4.3				
Bu ₃ PS	16 ^d					50.5	3.8	15.4	*		
ClCH ₂ CH ₂ PSPPh ₂	17	78.6	9.6	12.3	4.3	66.0	0				
HOCH ₂ CH ₂ PSPPh ₂	18	79.2	10.1	12.1	3.3	56.7	0				
	19 ^e	82.7	10.1	12.1	3.3	78.9	8.6	14.9	0	8.8	10.1
	20 ^e	78.9	7.8	11.8	1.8	54.2	4.5	10.3	0	10.1	2.0
Ph ₂ PSCl	21	96.3	12.6	14.9	2.8						
Ph ₃ PSH ⁺	22 ^d	85.4	11.0	14.6	*						
Et ₃ PS·AuCl	23					46.1	5.0				
Ph ₃ PS·AuCl	24	84.9	10.6	13.4	3.3						
Et ₃ PS·AlBr ₃	25					48.9	4.5				
Ph ₃ PS·AlBr ₃	26	86.2	11.8	13.4	3.3						

^a In Hertz, corrected to one decimal place.^b This is the value for carbon-2 (Me)^c From Ref. 6^d From Ref. 4 (* indicates unresolved coupling)^e For numbering system, see footnotes to Table III.

d) $i_J \gg o_J < m_J$; $1_J \gg 2_J < 3_J$. $2J_S$ and $2J_O$ (Ref. 12) decrease with the presence of groups more electronegative than hydrogen on carbon-2 [c.f. (8), (3), (17), and (18)], or with an alkyl group on carbon-1 [c.f. (6) and (10)]. The absolute signs of 1_J and 2_J have been assigned as positive and negative, respectively.⁶ If electron-withdrawing substituents on carbon increase the s character of the other bonds to carbon,⁸ then the trend in 2_J is in the expected direction.

e) $m\delta < o\delta \leq p\delta < i\delta$. This follows from a consideration of the canonicals IIa–IIc.

f) 1_J , 2_J , and i_J are greater where the carbon is (nominally) sp^2 hybridized rather than sp^3 hybridized (cf. (1), (4), and (19)). This is attributable to the greater electronegativity of the ethenyl group, and from the increased s character of the P–C–C bonds.

g) Both i_J and 1_J decreases slightly with the substitution of alkyl groups for hydrogen [cf. (2), (3), and (6)]. Such an effect may be ascribed to changes in bond lengths and/or angles (with consequent differing hybridization patterns). This effect has also been noted in phosphine oxides.⁴

h) $1\delta_S$ and $1\delta_O$ both increase with increasing the number of alkyl groups at phosphorus, at the expense of phenyl groups in the series (1), (2), (12) and (13) and on the related series of phosphine oxides.⁴ This has been ascribed to the greater electronegativity of phenyl relative to methyl.⁴ For the ethyl- and butyl-phosphine sulphides ((3), (14), (15): (8), (16)), however, the trend in chemical shifts is reversed, and, furthermore, 1_J does not follow a particular pattern with increasing alkylation, as opposed to arylation, at

TABLE V
Chemical shift differences ($\Delta^1\delta$) between H—R and
 $\text{Ph}_2\text{P(X)—R}$ (X = O, S)

R—	$\Delta^1\delta_{\text{S}}$	$\Delta^1\delta_{\text{O}}$
Me—	24.0	18.8 ^a
Et—	21.6	17.0 ^a
Pr ⁱ —	12.7	11.0 ^a
<i>n</i> -C ₆ H ₁₃ —	19.3	15.5 ^b
HOCH ₂ CH ₂ —	16.0	13.7 ^c

^a Computed from data in Ref. 4.

^b A. H. Davidson, unpublished result.

^c Ref. 12.

phosphorus. Clearly, electronegativity differences are but one of the factors involved here.

i) A comparison of the chemical shifts of the phosphine sulphides with the corresponding alkanes¹⁶ reveals that the diphenylphosphinthiyl group has a large deshielding effect upon carbon-1, but effects of ± 1 ppm upon carbons 2 and 3. The diphenylphosphinyl group may be seen to have a similar, but smaller, effect upon carbon-1 (Table V). The relative deshielding abilities of the two substituents may perhaps be explained in terms of anisotropy effects (cf. the ¹H nmr data in Table II). Such effects do not seem to be so important in the chemical shifts of phosphine chalcides bearing aliphatic *sp*²-hybridized carbon (Table VI). Here the trend towards greater deshielding mirrors the greater electronegativity of oxygen relative to sulphur, and contributions from canonicals of the type IIIb may be of consequence.⁴

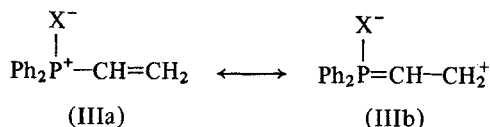


TABLE VI
Chemical shift differences between CHR=CHR and
 $\text{Ph}_2\text{P(X)CR}=\text{CHR}$ (X = O, S; R = H, alkyl).

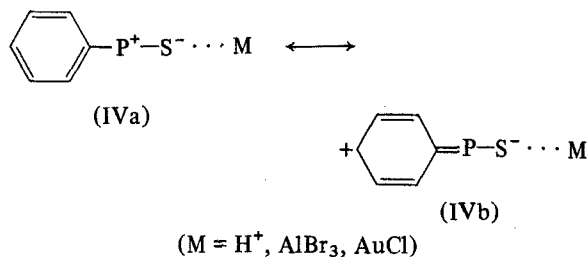
Compound	$\Delta^1\delta$	$\Delta^2\delta$
$\text{Ph}_2\text{P(O)CH}=\text{CH}_2$	8.3	11.6 ^a
$\text{Ph}_2\text{P(S)CH}=\text{CH}_2$	6.9	9.6 ^a
$\text{MeCH}=\text{CH}_2$	10.3	-7.8 ^a
$\text{Ph}_2\text{P(S)CH}_2\text{CH}=\text{CH}_2$	4.5	-1.6 ^a
phosphine sulphide (19)	4.4	15.5 ^b

^a Relative to ethene (δ 122.8) (Ref. 16).

^b Relative to cyclohexene (δ 127.4) (Ref. 16).

METAL COMPLEXES OF PHOSPHINE SULPHIDES

¹³C nmr data for two aluminium (III) and two gold (I) complexes of phosphine sulphides are shown in Tables III and IV. The results may be compared with those for the protonated form of triphenylphosphine sulphide (22) (Ref. 4). In the series (1), (22), (26), and (24), the *ipso*-carbon is significantly and increasingly shielded, and the remaining phenyl carbons are all slightly deshielded, the largest effect being for the *para*-carbon. A rationalization of these results must include significant contributions to the bonding patterns in these complexes from canonicals of the type IVb (*inter alia*).



The changes in ¹ δ follow the (presumed) order of polarizing power of the Lewis acids. Additionally, in complex (24), there exists the possibility of π back-bonding from gold to sulphur, to reduce contributions from canonicals of the type IVb.

In the series (15), (25), (23), there is no pronounced change in ¹ δ (although ¹*J* decreases slightly upon complexation). Here, of course, there is no π -system present to transmit electronic effects.

Table VII lists some ¹H nmr and infra-red spectroscopic data for the complexes. In a qualitative sense, at least, these data may be correlated with the findings of ¹³C nmr spectroscopy.

TABLE VII
Infra-red and proton magnetic resonance spectroscopic data
for some phosphine sulphide complexes

Compound	$\nu_{\text{P}=\text{S}}^a$	H_α^b	$J_{\text{P}-\text{H}_\alpha}^c$	H^b	$J_{\text{P}-\text{H}_\beta}^c$
Et ₃ PS	647	8.17	11.6	8.76	18.4
Et ₃ PS · AuCl	630	7.90	11.2	8.63	18.4
Et ₃ PS · AlBr ₃	637	8.01	10.8	8.75	19.2
Ph ₃ PS	637				
Ph ₃ PS · AuCl	589				
Ph ₃ PS · AlBr ₃	582				

^a In cm⁻¹: recorded as nujol mulls.

^b In Tau: H_α is attached to C¹.

^c In Hertz: $J_{\text{H}_\alpha-\text{H}_\beta}$ was measured in all three complexes as 7.2 Hz (to one decimal place).

CONCLUSIONS

The ^{13}C nmr spectra of tertiary phosphine sulphides can be qualitatively rationalized by assuming a greater contribution from the zwitterionic form Ia in the ground-state bonding pattern of the thiophosphoryl bond, than is present in the corresponding phosphoryl bond. Substitution effects at phosphorus, carbon-1, and carbon-2, may be correlated with electronegativity effects, assuming the Fermi contact term to be dominant in the determination of phosphorus-carbon coupling constants, and with anisotropic effects arising from the greater polarisability of the thiophosphoryl bond. Nevertheless, there are instances where empirical data contradict predicted trends (for instance, in the ^{31}P nmr spectra of phosphine chalcides in Table I, and, in the ^{13}C nmr, in the effect upon chemical shifts of decreasing the number of aryl groups attached to phosphorus relative to the number of alkyl groups), and a complete understanding of the nature of the chalcophosphoryl bond remains unresolved at present.

EXPERIMENTAL

Infra-red spectra were recorded as nujol mulls on a Perkin-Elmer 457 spectrophotometer. ^1H nuclear magnetic resonance spectra were recorded on a Varian CFT-20 instrument operating at 79.5 MHz, using ^2H -chloroform as solvent. ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL-100-15 instrument, operating at 25.2 MHz and employing a standard Varian FT programme, using ^2H -chloroform as solvent. Chemical shifts and coupling constants are given to one decimal place. Assignments of the spectra were made by a consideration of peak heights, coupling constants, and suitable off-resonance decoupling experiments.

Diphenyl 2-Propylphosphine Sulphide (6)

Chlorodiphenylphosphine (3.6 ml, 2×10^{-2} mol) was added over 15 min. to 2-propyl magnesium bromide (2×10^{-2} mol) in ether (20 ml), at 0° . The mixture was stirred at ambient temperature for 2h, then treated with 5M hydrochloric acid (40 ml). The ethereal layer was separated, and the aqueous phase extracted with ether (20 ml). The combined ether layers were washed with brine, dried (Na_2SO_4), and evaporated to dryness. The residue was treated with sulphur (0.47 g) and benzene (10 ml), and the benzene distilled off. The residue was taken up in methanol, filtered free of excess sulphur, and concentrated to ca. 2 ml under reduced pressure to give *diphenyl 2-propylphosphine sulphide* (3.21 g; 62%) as white crystals mp 93° (Found: C, 69.0; H, 6.7. $\text{C}_{15}\text{H}_{17}\text{PS}$ requires C, 69.2; H, 6.6%). τ 1.9–2.25 (4H), 2.5–2.65 (6H), 7.16 (d. sept., $J_{\text{P-H}} = 3$, $J_{\text{H-H}} = 7$; 1H), 8.85 (dd, $J_{\text{P-H}} = 19$; 6H).

In an analogous fashion there was prepared 1-pentyl *diphenylphosphine sulphide* (9) as white crystals (45%) mp 58° (hexane/ethyl ethanoate) (Found: C, 70.7; H, 7.35. $\text{C}_{17}\text{H}_{21}\text{PS}$ requires C, 70.8; H, 7.35%). τ 2.15–2.7 (10H), 7.6–7.75 (m; 2H), 8.35–9.2 (m; 9H).

2-Pentyl Diphenylphosphine Sulphide (10)

Triphenylphosphine sulphide (2.94 g, 10^{-2} mol), under nitrogen in tetrahydrofuran (20 ml), was treated dropwise with butyllithium in hexane (1.7M; 5.9 ml, 10^{-2} mol), and the mixture was stirred at ambient temperature for 3.5 h. Iodomethane (1.56 g, 1.1×10^{-2} mol) was added, initiating a vigorous reaction. The whole was quenched with water (20 ml) and ether (20 ml), and the ethereal layer separated, washed with brine, dried (MgSO_4), and evaporated to yield a yellow oil, which crystallized upon standing, partially. The crystals were dried upon filter paper and recrystallized twice from hexane/ethyl ethanoate, to yield 2-pentyl *diphenylphosphine sulphide* as white crystals (1.21 g; 44%) mp $84\text{--}5^\circ$ (Found: C, 70.95; H, 7.15. $\text{C}_{17}\text{H}_{21}\text{PS}$ requires C, 70.8; H, 7.35%). τ 2.15–2.7 (10H), 7.6–7.85 (m; 1H), 8.3–9.15 (m, 10H).

2-Chloroethyl Diphenylphosphine Sulphide (17)

2-Hydroxyethyldiphenylphosphine sulphide (1.88 g, 7.1×10^{-3} mol) in benzene (20 ml) was treated with phosphorus (V) chloride (1.49 g 7.1×10^{-2} mol) at 0° . The mixture was then heated under reflux for 30 min., cooled, and the upper layer decanted, washed with saturated aqueous sodium hydrogen carbonate, brine, dried, and evaporated to yield a yellow oil. This was purified by chromatography (acetone/silica) to yield 2-chloroethyldiphenylphosphine sulphide as colourless crystals (1.13 g; 57%) mp $60\text{--}1^\circ$ (Found: C, 59.8; H, 5.15. $\text{C}_{14}\text{H}_{14}\text{ClPS}$ requires C, 59.9; H, 5.05%) τ 2.0–2.45 (10H), 6.29 (dt, $J_{\text{P-H}} = 11$, $J_{\text{H-H}} = 7$, 2H), 7.05 (dt, $J_{\text{P-H}} = 10$; 2H).

Triethylphosphine Sulphide Gold (I) Chloride (23)

Dimethylsulphide gold (I) chloride 17 (0.59 g, 2×10^{-3} mol) and triethylphosphine sulphide (0.03 g, 2×10^{-3} mol) were mixed in dichloromethane (2 ml). The solution was filtered, concentrated to ca. 1 ml under reduced pressure, and treated with ether until it became cloudy. Storing the solution at -10° gave a crop of off-white crystals. The mother liquors were concentrated twice more to yield a total of 0.46 g (60%) of *triethylphosphine sulphide gold (I) chloride* mp 57° (Found: C, 18.5; H, 3.7. $\text{C}_6\text{H}_{15}\text{AuClPS}$ requires C, 18.85; H, 3.95%).

Triethylphosphine Sulphide Aluminium (III) Bromide (25)

Aluminium (III) bromide (0.27 g, 10^{-3} mol), in dibromomethane (0.5 ml), and triethylphosphine sulphide (0.15 g, 10^{-3} mol), in carbon disulphide (5 ml), were mixed under a stream of dry nitrogen. An orange oil separated, and the mixture was evaporated to dryness, and washed with three portions of boiling carbon tetrachloride. The residue, after prolonged evaporation, was a clear orange oil (0.30 g; 71%) of *triethylphosphine sulphide aluminium (III) bromide* (Found: C, 16.9; H, 3.35. $\text{C}_6\text{H}_{15}\text{AlBr}_3\text{PS}$ requires C, 17.3; H, 3.65%).

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