Reactions of Triarylphosphines, Triphenylarsine, and Triphenylstibine with Thionyl Chloride and Sulphur Dichloride

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Triarylphosphines react with thionyl chloride by oxygen transfer to give the triarylphosphine oxide and sulphur dichloride. Further reaction with sulphur dichloride gives the triarylphosphine dichloride and triarylphosphine sulphide and/or sulphur, depending on the phosphine and the mole ratio. Triphenylarsine and triphenylstibine react with thionyl chloride by chlorine transfer to give the dichloride, sulphur dioxide, and sulphur, or with sulphur dichloride to give the dichloride and sulphur. Further reaction of triphenylarsine (but not triphenylstibine) with sulphur gives triphenylarsine sulphide.

TERVALENT phosphorus, arsenic, and antimony are oxidised to the quinquevalent state by various reagents, including thionyl chloride.[1,2] This paper describes reactions of triphenylphosphine, tritolylphosphines, triphenylarsine, and triphenylstibine with thionyl chloride or sulphur dichloride in benzene solution below room temperature. Possible reaction patterns are discussed.

Triarylphosphines.—Triphenylphosphine, tri-*p*-tolylphosphine, tri-*m*-tolylphosphine, or tri-*o*-tolylphosphine (3 mol equiv.) react with thionyl chloride (1 mol equiv.) to give a mixture of triarylphosphine oxide, triarylphosphine dichloride, and triarylphosphine sulphide. The triarylphosphine dichlorides are present in the lower of two layers of reaction products. They are not isolated but are hydrolysed and recovered as oxides.

$$\begin{tikzcd}[column sep=small] 3Ar_3P + SOCl_2 \arrow[r] & Ar_3PO + Ar_3PCl_2 + Ar_3PS \arrow[d, "H_2O"] \\ (Ar = Ph,\ p\text{-Tolyl},\ m\text{-Tolyl},\ o\text{-Tolyl}) & Ar_3PO + 2HCl \end{tikzcd}$$

Two distinct patterns of behaviour occur with lower mole ratios of triarylphosphine to thionyl chloride.

(*a*) Tri-*m*-tolylphosphine and tri-*o*-tolylphosphine give triarylphosphine oxide, triarylphosphine dichloride, and triarylphosphine sulphide, as before, and some unchanged thionyl chloride. No traces of sulphur are observed. Yields of triarylphosphine oxide are sometimes higher, and yields of triarylphosphine sulphide lower than might be expected, because of the slow side-reaction of triarylphosphine sulphide with thionyl chloride.[3]

$$Ar_3PS + SOCl_2 \longrightarrow Ar_3PO + S_2Cl_2$$

(*b*) Triphenylphosphine and tri-*p*-tolylphosphine give triarylphosphine oxide, triarylphosphine dichloride, and sulphur, with occasional traces of triarylphosphine sulphide (*ca.* 2%). Some thionyl chloride remains unchanged when the mole ratio of phosphine to thionyl chloride is less than 2.

$$\begin{tikzcd}[column sep=small] 2Ar_3P + SOCl_2 \arrow[r] & Ar_3PO + Ar_3PCl_2 \arrow[d, "H_2O"] + S \\ (Ar = Ph,\ p\text{-Tolyl} & Ar_3PO + 2HCl \end{tikzcd}$$

The triarylphosphines all react with sulphur dichloride to give triarylphosphine dichloride and sulphur and/or triarylphosphine sulphide, depending on the mole ratios of the reagents. It is well known that triarylphosphines will react with sulphur under these conditions.[4]

$$\begin{gathered} Ar_3P + SCl_2 \longrightarrow Ar_3PCl_2 + S \\ 2Ar_3P + SCl_2 \longrightarrow Ar_3PCl_2 + Ar_3PS \\ (Ar = Ph,\ p\text{-tolyl},\ m\text{-tolyl},\ o\text{-tolyl}) \end{gathered}$$

Possible mechanisms for the oxidation of phosphines by dimethyl sulphoxide are discussed at length elsewhere.[5] Thionyl chloride is a stronger electron acceptor than dimethyl sulphoxide, and has a similar structure. Nucleophilic attack by phosphorus on sulphur, followed by oxygen transfer, would give triarylphosphine oxide and sulphur dichloride as primary reaction products.

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[1] B. C. Smith and M. E. Sobeir, *Chem. and Ind.*, 1969, 621; S. I. A. El Sheikh, B. C. Smith, and M. E. Sobeir, *Angew. Chem.*, 1970, **82**, 326.

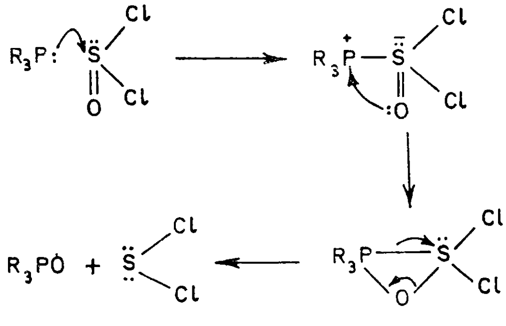
[2] A. C. Poshkus, J. E. Herweh, and L. F. Hass, *J. Amer. Chem. Soc.*, 1958, **80**, 5022, 5025.

[3] U.S.P. 3,082,256/1963 (*Chem. Abs.*, 1963, **59**, 10,121).

[4] P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, 1956, **78**, 3710.

[5] E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 4296.

The subsequent reaction pattern depends on the mole ratio of phosphine to thionyl chloride, and on the relative rates of reaction of the phosphine with thionyl chloride, sulphur dichloride, and sulphur. Equimolar mixtures of all four triarylphosphines with sulphur dichloride give triarylphosphine dichloride, but not triarylphosphine sulphide, which shows that reaction is faster with sulphur dichloride than with sulphur. Equimolar mixtures of tri-*o*-tolylphosphine or tri-*m*-tolylphosphine with thionyl chloride give triarylphosphine sulphide, but not sulphur, which shows that reaction is faster with sulphur than with thionyl chloride. Therefore the relative rates of reaction for these two phosphines must be: $SCl_2 > S > SOCl_2$.



Equimolar mixtures of triphenylphosphine or tri-*p*-tolylphosphine with thionyl chloride give sulphur, but not triarylphosphine sulphide, which shows that both these phosphines react faster with thionyl chloride than with sulphur. The quantities of sulphur produced: $Ph_3P \sim 35\%$; $(p\text{-Tol})_3P \sim 25\%$, are significantly less than the 50% predicted if the reaction with sulphur dichloride were faster than that with thionyl chloride. Hence, the relative rates of reaction for these two phosphines must be: $SOCl_2 > SCl_2 > S$.

The difference between the two pairs of triarylphosphines depend on differences in the rates of decomposition of the phosphine-thionyl chloride intermediates. The $P \rightarrow S$ co-ordinate bond is stabilised sufficiently by attractions between oxygen and methyl for the tri-*o*-tolylphosphine-sulphur dioxide complex to be isolated at room temperature.[2] Models show that similar interactions with thionyl chloride are expected for tri-*o*-tolylphosphine and are likely, although to a lesser extent, for tri-*m*-tolylphosphine. Both these phosphines are oxidised comparatively slowly by thionyl chloride below room temperature. Triphenylphosphine and tri-*p*-tolylphosphine form weaker complexes with thionyl chloride, and react much faster.

An alternative mechanism for the reaction of triarylphosphines with thionyl chloride involving chlorine transfer would give triarylphosphine dichloride and sulphur monoxide, which is unstable and decomposes spontaneously into sulphur and sulphur dioxide.[6] Thus the products of reaction of triarylphosphine (3 mol equiv.) with thionyl chloride (1 mol equiv.) would be: triarylphosphine dichloride (1 mol equiv.); triarylphosphine sulphide (0·5 mol equiv.); sulphur dioxide (0·5 mol equiv.); and triarylphosphine (1·5 mol equiv.), which does not react with sulphur dioxide under these conditions.[6,7] This reaction pattern does not occur with the triarylphosphines, but it is important for triphenylarsine.

Triphenylarsine.—Equimolar reactions of triphenylarsine and thionyl chloride give triphenylarsine dichloride (1 mol. equiv.), sulphur dioxide (0·5 mol equiv.), and sulphur (0·5 mol equiv.). The dichloride formed initially is hydrolysed and isolated as triphenylarsine oxide hydrochloride.[8] Additional triphenylarsine (0·5 mol equiv.) reacts with the sulphur (0·5 mol equiv.) to produce triphenylarsine sulphide (0·5 mol equiv.), so that complete reaction occurs between triphenylarsine (1·5 mol equiv.) and thionyl chloride (1 mol. equiv.). Any larger excess of triphenylarsine is recovered unchanged: there is no reaction with sulphur dioxide under these conditions.[7]

$$Ph_3As + SOCl_2 \longrightarrow Ph_3AsCl_2 + \tfrac{1}{2}S + \tfrac{1}{2}SO_2$$

$$\Big\downarrow {\scriptstyle H_2O}$$

$$Ph_3AsOHCl + HCl$$

$$\tfrac{1}{2}Ph_3As + \tfrac{1}{2}S \longrightarrow \tfrac{1}{2}Ph_3AsS$$

The formation of these products indicates that the reaction takes place by chlorine-transfer. An alternative mechanism involving oxygen-transfer would give triphenylarsine oxide and sulphur dichloride. Triphenylarsine reacts with sulphur dichloride to give triphenylarsine dichloride and triphenylarsine sulphide and/or sulphur. Thus, if the mechanism involved oxygen-transfer, triphenylarsine (3 mol equiv.) would react with thionyl chloride (1 mol equiv.) to give triphenylarsine oxide (1 mol equiv.), triphenylarsine dichloride (1 mol equiv.), and triphenylarsine sulphide (1 mol equiv.). This reaction pattern for triphenylarsine can be rejected as incompatible with the products.

Triphenylstibine.—Equimolar reactions of triphenylstibine and thionyl chloride give triphenylstibine dichloride, sulphur, and sulphur dioxide. Triphenylstibine dichloride is stable in air and is only converted into the ' oxide ' by prolonged hydrolysis.[9] Triphenylstibine does not react with either sulphur dioxide [7] or sulphur under these conditions, and any excess is recovered from the reaction mixture.

$$Ph_3Sb + SOCl_2 \longrightarrow Ph_3SbCl_2 + \tfrac{1}{2}S + \tfrac{1}{2}SO_2$$

Triphenylstibine reacts with sulphur dichloride to give triphenylstibine dichloride and sulphur, but not triphenylstibine sulphide, which has only been prepared

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[6] See *e.g.*, B. C. Smith and G. H. Smith, *J. Chem. Soc.*, 1965, 5516.

[7] S. I. A. El Sheikh and B. C. Smith, *Chem. Comm.*, 1968, 1474.

[8] G. Ferguson and E. W. Macaulay, *Chem. Comm.*, 1968, 1288.

[9] See, *e.g.*, G. O. Doak and L. D. Freedman, ' Organometallic Compounds of Arsenic, Antimony, and Bismuth,' John Wiley, New York, 1970, ch. 7.

from the reaction of triphenylstibine dichloride with hydrogen sulphide.[10] The nature of the products shows that chlorine-transfer occurs and not the alternative mechanism involving oxygen-transfer.

TABLE 1

Reactions of triarylphosphines

	Ar_3P		$SOCl_2$		Ar_3PO		Ar_3PS		S	
	(g)	(mol %)	(g)	(mmol)	(g)	(mol %)	(g)	(mol %)	(g)	(mol %)
Ph_3P	7·52	100	5·10	42·9	6·71	84			0·34	37
Ph_3P	11·24	100	3·41	28·7	9·92	83			0·47	34
Ph_3P	17·90	200	4·06	34·1	18·56	195	0·20	2	0·91	83
Ph_3P	18·92	300	2·86	24·0	12·16	182	6·06	86		
Ph_3P	19·58	300	2·69	24·9	13·38	193	6·18	84		
(*p*-Tolyl)$_3$P	1·15	100	0·45	3·8	1·10	91			0·03	25
(*p*-Tolyl)$_3$P	1·25	100	0·49	4·1	1·31	99			0·03	23
(*p*-Tolyl)$_3$P	1·38	200	0·27	2·3	1·39	191			0·06	82
(*p*-Tolyl)$_3$P	3·76	300	0·49	4·1	2·74	185	1·21	87		
(*m*-Tolyl)$_3$P	0·79	99	0·31	2·6	0·63	78	0·13	15		
(*m*-Tolyl)$_3$P	1·79	200	0·35	2·9	1·37	146	0·38	38		
(*m*-Tolyl)$_3$P	2·53	300	0·33	2·8	1·61	198	0·55	64		
(*o*-Tolyl)$_3$P	1·23	100	0·48	4·0	0·83	64	0·29	21		
(*o*-Tolyl)$_3$P	2·05	200	0·40	3·4	1·58	147	0·61	54		
(*o*-Tolyl)$_3$P	3·15	300	0·41	3·5	1·78	161	1·13	97		
			SCl_2							
Ph_3P	5·63	100	2·21	21·5	5·10	85			0·64	93
Ph_3P	14·52	200	2·85	27·7	6·60	86	7·29	89		
(*p*-Tolyl)$_3$P	1·21	100	0·41	4·0	1·01	79			0·08	63
(*m*-Tolyl)$_3$P	1·43	100	0·56	4·7	1·12	74			0·12	79
(*o*-Tolyl)$_3$P	1·51	100	0·51	5·0	1·17	74			0·15	95
(*o*-Tolyl)$_3$P	2·07	200	0·35	3·4	1·07	98	0·59	51		

TABLE 2

Reactions of triphenylarsine

Ph_3As		$SOCl_2$		$Ph_3AsOHCl$		Ph_3AsS		S		Ph_3As	
(g)	(mol %)	(g)	(mmol)	(g)	(mol %)	(g)	(mol %)	(g)	(mol %)	(g)	(mol %)
1·72	100	0·67	5·6	1·90	94			0·07	39	*a*	
6·76	100	2·63	22·1	7·74	98			0·34	48		
1·89	150	0·49	4·1	1·38	93	0·57	41			*b*	
4·12	200	0·80	6·7	1·91	79	0·99	37			0·85	48
10·73	300	1·39	11·7	3·91	93	1·74	44			5·71	160
		SCl_2									
		(g)	(mmol)								
1·81	100	0·61	5·9	1·70	80			0·18	95		

[a] SO_2(+HCl) evolved: 31 mol %. SO_2(+HCl) evolved: 30 mol %.

TABLE 3

Reactions of triphenylstibine

Ph_3Sb		$SOCl_2$		Ph_3SbCl_2		S		Ph_3Sb	
(g)	(mol %)	(g)	(mmol)	(g)	(mol %)	(g)	(mol %)	(g)	(mol %)
2·05	100	0·69	5·8	2·22	90	0·08	43		
2·17	100	0·73	6·1	2·40	92	0·07	39	*a*	
16·71	150	3·76	31·6	11·32	84	0·39	38	4·42	40
4·51	200	0·76	6·4	2·37	88	0·08	40	1·42	63
		SCl_2							
		(g)	(mmol)						
1·44	100	0·42	4·1	1·54	89	0·06	46		
1·99	200	0·29	2·8	1·08	90	0·06	66	0·67	67

[a] SO_2 evolved: 2·28 mmol, 37 mol %.

The change from oxygen-transfer for all four triarylphosphines to chlorine-transfer for triphenylarsine and triphenylstibine is an important feature of this work. The favoured reaction patterns depend on changes in the relative stabilities of the oxides and dichlorides of the triaryl derivatives of Group V. Similarly, metals whose oxides have larger negative standard heats of formation than their chlorides (*e.g.* Al) react with thionyl chloride vapour to give the metal oxides, whereas metals with more stable chlorides (*e.g.* Ag) react to give the metal chlorides.[11]

EXPERIMENTAL

Similar conditions were used for all reactions. Weighed quantities of redistilled thionyl chloride [12] or sulphur di-

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[10] W. J. Lile and R. C. Menzies, *J. Chem. Soc.*, 1950, 617.

[11] P. W. Schenk and H. Platz, *Z. anorg. Chem.*, 1933, **215**, 113.

[12] L. Friedman and W. P. Wetter, *J. Chem. Soc.* (*A*), 1967, 36.

chloride in benzene (20 ml) were added slowly to a stirred solution of the triaryl derivative in benzene or benzene–toluene (25 ml) at *ca.* 10°. Reactions occurred immediately, and the mixtures were allowed to warm to room temperature. Liquid layers were decanted, solvents were removed on a rotary evaporator, and solids were separated by fractional crystallisation. Unchanged thionyl chloride was recognised by a band at 1235 cm^{-1} in the i.r. spectra of the distillate.

Typical reactions of triarylphosphines, triphenylarsine, and triphenylstibine, are summarised in Tables 1—3. The products had satisfactory m.p.s and analyses. Mole percentages are referred to 100% thionyl chloride or sulphur dichloride. Sulphur dioxide was determined volumetrically with alkali.

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