Reactions of Triaryl Derivatives of Group 5 with Selenium Dioxide

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Triarylphosphines PR_3 (R = Ph, C_6H_4Me-*o*, -*m*, -*p*, or C_6H_4Cl-*p*) react with selenium dioxide suspended in benzene or in solution in ethanol to give triarylphosphine oxides, PR_3O, and triarylphosphine selenides, PR_3Se, or selenium, depending on the phosphine, the relative proportions of the reagents, and the solvent. Triarylarsines do not react with SeO_2 in ethanol, but reactions in benzene suspension give triarylarsine oxides or the addition compounds $2AsR_3O{\cdot}H_2SeO_3$ and selenium. Triphenylstibine reacts with SeO_2 suspended in benzene or in ethanol solution to give the addition compound $SbPh_3O{\cdot}SeO_2$ and selenium. Triarylbismuthines react with SeO_2 in benzene–ethanol to give areneseleninic acids and bismuth(III)selenite. Possible mechanisms are discussed.

SELENIUM dioxide is a polymeric solid[1] which is insoluble in benzene but soluble in ethanol to give ethyl hydrogenselenite.[2] Melnikov and Rokitskaya[3] reported that triphenyl-phosphine, -arsine, and -stibine react with selenium dioxide suspended in benzene to give the oxides, PPh_3O and $AsPh_3O$, and the hydroxide, $SbPh_3(OH)_2$, and the selenides, MPh_3Se (M = P, As, or Sb), which were not isolated and whose formation was inferred from the presence of selenium in the crude products. Further investigations of the reactions of some triaryl derivatives of Group 5 with selenium dioxide in benzene and ethanol are reported here. Ethanol vapour reacts with selenium dioxide under vigorous conditions to give acetaldehyde[4] or glyoxal,[5] water, and selenium, but oxidation of the solvents does not occur under the conditions described here.

RESULTS

Triphenylamine.—No reaction was observed between triphenylamine and SeO_2 in boiling benzene or ethanol. Heating the mixtures in a sealed tube at 120 °C (1 week) gave trace amounts of a blue dye, typical of the oxidation products of arylamines.[6] The starting materials were recovered almost quantitatively.

Triarylphosphines.—Reactions in benzene suspension. Triphenyl-, tri-*p*-tolyl-, and tri-*m*-tolyl-phosphine (3 mol) reacted with SeO_2 (1 mol) suspended in boiling benzene (5 h) to give the triarylphosphine oxide and the triarylphosphine selenide. Similar reactions of the triarylphosphines (2 mol) with SeO_2 (1 mol) gave the triarylphosphine oxide and selenium, which appeared initially in the reactive red form and was converted slowly into the less reactive grey form. Triarylphosphine selenides were detected as reaction intermediates by thin-layer chromatography. Triarylphosphines react readily with red selenium,[7] and it is shown here that triarylphosphine

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[1] J. D. McCullough, *J. Amer. Chem. Soc.*, 1937, **59**, 789.

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[3] N. N. Melnikov and M. S. Rokitskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 834.

[4] N. N. Melnikov and M. S. Rokitskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1937, **7**, 1532.

[5] Y. Asahina, M. Ishidate, and T. Mamose, *Ber.*, 1934, **67**, 1432.

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selenides (2 mol) react with SeO_2 (1 mol) suspended in boiling benzene to give the triarylphosphine oxides and selenium.

Hence, these triarylphosphines react with selenium dioxide suspended in benzene to give triarylphosphine oxides and triarylphosphine selenides and/or selenium, depending on the proportions of the reagents. The following scheme (R = aryl) is consistent with the results of Melnikov and Rokitskaya.[3]

$$3PR_3 + SeO_2 \longrightarrow 2PR_3O + PR_3Se \qquad (1)$$

$$2PR_3 + SeO_2 \longrightarrow 2PR_3O + Se \qquad (2)$$

$$PR_3 + Se \longrightarrow PR_3Se \qquad (3)$$

$$2PR_3Se + SeO_2 \longrightarrow 2PR_3O + 3Se \qquad (4)$$

Preliminary experiments suggested that tri-*o*-tolylphosphine does not react with SeO_2 suspended in boiling benzene.[8] We have now found that trace amounts of tri-*o*-tolylphosphine oxide and tri-*o*-tolylphosphine selenide are formed slowly on prolonged boiling (36 h) but that selenium is not obtained, even with an excess of SeO_2. Tri-*o*-tolylphosphine reacted readily with selenium in boiling benzene (1 h), but the reaction of tri-*o*-tolylphosphine selenide with SeO_2 was slow and incomplete (36 h).

Ethanol solutions. Triphenyl-, tri-*p*-tolyl-, and tri-*m*-tolyl-phosphine (3 mol) reacted with SeO_2 (1 mol) in ethanol (2 h) to give the triarylphosphine oxides and triarylphosphine selenides [equation (1)]. The same products were obtained from attempted reactions of the triarylphosphines (2 mol) with SeO_2 (1 mol) in boiling ethanol. Some SeO_2 (0.33 mol) did not react, and selenium was not obtained as a product although it appeared as a transient intermediate. The triarylphosphines reacted readily with red selenium, but the triarylphosphine selenides did not react with SeO_2 in boiling ethanol, unless the solutions were evaporated to dryness.

Tri-*o*-tolylphosphine (2 or 3 mol) reacted slowly with SeO_2 (1 mol) in boiling ethanol (3 d) to give trace amounts of tri-*o*-tolylphosphine oxide and selenide.

Triarylarsines.—Reactions in benzene suspension. The attempted reaction of triphenylarsine (3 mol) with SeO_2 (1 mol) suspended in boiling benzene gave triphenylarsine oxide (2 mol), selenium (1 mol), and unchanged $AsPh_3$ (1 mol). Triphenylarsine (2 mol) reacted with SeO_2 (1 mol) to form triphenylarsine oxide and selenium [equation (5)]. It was difficult to remove the last traces of SeO_2 from the $AsPh_3O$, and some unchanged $AsPh_3$ (*ca.* 2%) was recovered, even after 15 h. Triphenylarsine did not react with red selenium in boiling organic solvents (or even with potassium selenocyanate in acetonitrile in a sealed tube at 200 °C).

$$2AsPh_3 + SeO_2 \longrightarrow 2AsPh_3O + Se \qquad (5)$$

$$2MPh_3 + 3SeO_2 \longrightarrow 2MPh_3O{\cdot}SeO_2 + Se \qquad (6)$$

Reactions of triphenylarsine (2 mol) with SeO_2 (3 mol) suspended in boiling benzene gave the addition compound $AsPh_3O{\cdot}SeO_2$ and selenium [equation (6), M = As]. In the presence of moisture the final product was an addition compound of selenious acid. A crystal-structure determination[9] has shown that two arsine oxide molecules are hydrogen-bonded to selenious acid, $Ph_3AsO \cdots HO{-}SeO{-}OH \cdots OAsPh_3$. It was disconcerting that early analyses ($C_{36}H_{32}As_2O_5Se$ requires C, 55.9; H, 4.1; As, 19.4%) suggested the composition $C_{18}H_{15}AsSe$ (Calc. for $C_{18}H_{15}AsSe$: C, 56.0; H, 3.9; As, 19.5%). Triphenylarsine selenide has been prepared from triphenylarsine dichloride and hydrogen selenide,[10] but it has not been prepared from reactions of $AsPh_3$ with SeO_2.

Tri-*m*- and tri-*o*-tolylarsine oxides form similar addition compounds, $2As(C_6H_4Me)_3O{\cdot}H_2SeO_3$.

Ethanol solutions. The most striking feature of the behaviour of the triarylarsines was their failure to react with SeO_2 in ethanol. The starting materials were recovered from solutions containing $AsPh_3$ (2 or 3 mol) and SeO_2 (1 mol) after boiling under reflux (24 h). The only indications of reaction occurred on evaporation, when red selenium formed on the surface of the SeO_2.

Triphenylstibine.—Triphenylstibine (2 or 3 mol) reacted immediately with SeO_2 (1 mol) in benzene or ethanol at room temperature to give a slight precipitate of red selenium, but the reaction was incomplete. Most of the $SbPh_3$ did not react, even on boiling (16 h) or on heating in a sealed tube at 120 °C. Triphenylstibine did not react with selenium in boiling organic solvents. There appear to be no authentic reports of the preparation of triphenylstibine selenide, and its preparation[3] from $SbPh_3$ and SeO_2 is unlikely.

Triphenylstibine (2 mol) reacted completely with SeO_2 (3 mol) in boiling benzene or ethanol to give the addition compound $SbPh_3O{\cdot}SeO_2$ and selenium [equation (6), M = Sb]. Triphenylstibine reacted slowly with the addition compound in boiling solvents to give trace amounts of selenium (50 h), but pure $SbPh_3O$ was not obtained.

Triarylbismuthines.—Saturated solutions of triphenylbismuth (2 mol) and SeO_2 (9 mol) in benzene–ethanol (equal volumes) reacted at room temperature to give a white precipitate. Further reaction occurred on boiling under reflux in air (10 h). High yields of benzeneseleninic acid (5.5 mol) were obtained from the filtrate, but the predominantly inorganic precipitate contained trace amounts of organic material. Similar reactions of tri-*p*-, tri-*m*-, and tri-*o*-tolylbismuthines gave the corresponding tolueneseleninic acids.

$$2BiR_3 + 9SeO_2 + 3H_2O \longrightarrow 6RSeO_2H + Bi_2[SeO_3]_3 \qquad (7)$$

DISCUSSION

Triphenylamine.—Triphenylamine is not oxidised by selenium dioxide in boiling benzene or ethanol. Triphenylamine oxide and selenide are unknown.

Triarylphosphines.—Triarylphosphines are electron donors which form complexes with many electron acceptors. The first stage of the reactions with SeO_2 presumably involves nucleophilic attack by P^{III} on Se^{IV}. The cyclic intermediates decompose into triarylphosphine oxides and 'selenium monoxide' which disproportionates into selenium dioxide and selenium, which in turn reacts with the triarylphosphines to give triarylphosphine selenides. Phosphorus(III) is oxidised

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similarly by S^{IV} in dimethyl sulphoxide,[11,12] sulphur dioxide,[13] and thionyl chloride.[14] Tri-*o*-tolylphosphine reacts only slowly with SeO_2, because of steric hindrance from the *o*-methyl groups.

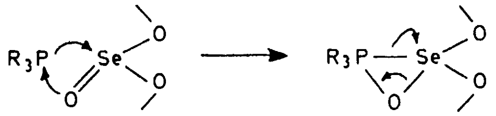
dioxide. Tri-*o*-tolylphosphine selenide does not react with polymeric selenium dioxide because the *o*-methyl groups hinder nucleophilic attack by oxygen on phosphorus.

TABLE 1

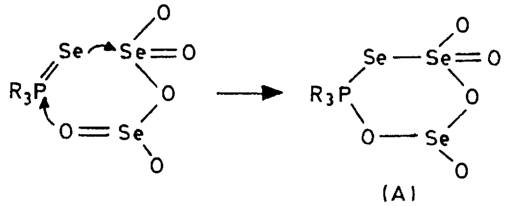
Reactions with selenium dioxide

	Compound		SeO_2				MR_3O		MR_3Se		Se	
	amount/ mmol	%	amount/ mmol	%	Solvent (V/cm^3)	Reaction time, t/h	amount/ mmol	%	amount/ mmol	%	amount/ mmol	%
PPh_3	6.11	302	2.02	100	C_6H_6 (25)	5	3.81	189	2.00	99		
$P(C_6H_4Me\text{-}p)_3$	2.57	299	0.86	100	(30)	3	1.71	199	0.85	99		
$P(C_6H_4Me\text{-}m)_3$	2.83	298	0.95	100	(50)	8	1.88	198	0.94	99		
$P(C_6H_4Me\text{-}o)_3$	2.84	302	0.94	100	(25)	40	0.51	54	0.27	29		
PPh_3	7.21	200	3.61	100	(15)	5	7.19	199			3.54	98
$P(C_6H_4Me\text{-}p)_3$	1.26	200	0.63	100	(25)	5	1.25	198			0.63	100
$P(C_6H_4Me\text{-}m)_3$	2.86	200	1.43	100	(50)	7	2.83	198			1.38	97
$P(C_6H_4Me\text{-}o)_3$	0.79	202	0.39	100	(50)	24	0.20	51	0.11	28		
PPh_3Se	2.52	200	1.26	100	(20)	5	2.59	206			3.67	296
$P(C_6H_4Me\text{-}p)_3Se$	2.34	200	1.17	100	(25)	5	2.31	197			3.41	291
$P(C_6H_4Me\text{-}m)_3Se$	1.51	199	0.76	100	(25)	6	1.43	188			2.15	283
$P(C_6H_4Me\text{-}o)_3Se$	0.23	192	0.12	100	(10)	36					0.14	117
PPh_3	11.85	300	3.95	100	EtOH (50)	10	7.80	197	3.84	97		
$P(C_6H_4Me\text{-}p)_3$	5.79	300	1.93	100	(25)	10	3.76	195	1.92	99		
$P(C_6H_4Me\text{-}m)_3$	3.89	299	1.30	100	(40)	9	2.47	190	1.27	98		
$P(C_6H_4Me\text{-}o)_3$	4.69	295	1.59	100	(30)	56	2.66	167	1.34	84		
PPh_3	13.34	200	6.66	100	(25)	10	8.55	128	4.17	63		
$P(C_6H_4Me\text{-}p)_3$	2.73	199	1.37	100	(25)	1	1.81	132	0.89	65		
$P(C_6H_4Me\text{-}m)_3$	5.61	200	2.80	100	(40)	2	3.74	134	1.87	67		
$P(C_6H_4Me\text{-}o)_3$	2.22	200	1.11	100	(25)	40	1.20	108	0.59	53		
$AsPh_3$	6.15	300	2.05	100	C_6H_6 (25)	40	3.97	194			2.02	96
	7.23	300	3.61	100	(25)	44	7.30	202			3.54	98
$As(C_6H_4Me\text{-}p)_3$	1.98	200	0.99	100	(25)	18	2.11	213			0.76	77
$As(C_6H_4Me\text{-}m)_3$	1.98	200	0.99	100	(30)	24	2.03	205			0.76	77
$As(C_6H_4Me\text{-}o)_3$	1.98	200	0.99	100	(25)	40	2.19	221			1.01	102
							$SbPh_3O{\cdot}SeO_2$					
$SbPh_3$	2.31	200	3.46	300	EtOH (30)	2	2.33	202			1.15	100
	3.51	200	5.27	300	C_6H_6 (25)	2	3.46	197			1.64	93
$BiPh_3$	2.27	200	10.22	900	EtOH– (30)	10	6.56	578				
	2.27	200	10.22	900	C_6H_6 (30)	10	6.72	592				
$Bi(C_6H_4Me\text{-}p)_3$	1.04	200	4.67	900	(35)	10	3.05	588				
$Bi(C_6H_4Me\text{-}m)_3$	4.16	200	18.69	900	(30)	10	11.42	550				
$Bi(C_6H_4Me\text{-}o)_3$	1.04	200	4.67	900	(30)	10	3.06	590				
$Bi(C_6H_4Cl\text{-}p)_3$	3.68	200	16.55	900	(30)	10	8.14	443				

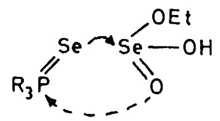
The subsequent reaction patterns depend on the different reactivities of triarylphosphine selenides in benzene and ethanol. The reactions of PPh_3Se with polymeric selenium dioxide may proceed *via* a six-membered cyclic intermediate (A) involving oxygen from a neighbouring selenium. The products are triphenylphosphine oxide and ' diselenium monoxide ' which disproportionates into selenium dioxide and selenium. A six-membered cyclic intermediate is not possible with monomeric ethyl hydrogenselenite, and the intermediate (B) does not react further. Triarylphosphine selenides do not react with solutions of SeO_2 in ethanol, except when evaporation of the solvent leads to the formation of polymeric selenites or solid selenium



Triarylarsines.—Triarylarsines do not react with red selenium in boiling organic solvents, and on reaction with SeO_2 in benzene they give triarylarsine oxides and selenium, but not triarylarsine selenides. Triarylarsine



(A)



(B)

oxides, which are stronger electron donors than triarylphosphine oxides, form solid addition compounds with

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[11] S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature*, 1962, **196**, 372.

[12] E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 6250.

[13] B. C. Smith and G. H. Smith, *J. Chem. Soc.*, 1965, 5516.

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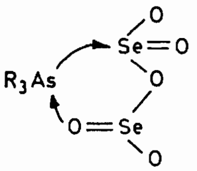
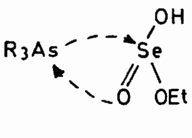
the appropriate excess of selenium dioxide or selenious acid. Tri-*o*-tolylarsine behaves like triphenylarsine and, unlike tri-*o*-tolylphosphine, reacts readily with SeO_2 in benzene.

The oxidation of triarylarsines by polymeric selenium dioxide may proceed *via* a five-membered cyclic intermediate, (C), involving oxygen from a neighbouring selenium. The most surprising difference from triarylphosphines is that triarylarsines do not react with SeO_2 in ethanol. It is clear that reactions involving intermediate (D) do not occur, presumably because of the larger size of arsenic and its weaker donor properties.


(C)


(D)

Triphenylstibine.—Triphenylstibine reacts with SeO_2 in benzene or ethanol, although antimony is even larger than arsenic. Triphenylstibine is a weaker electron donor than triphenylarsine, and a three-membered cyclic intermediate appears less likely than direct nucleophilic attack by oxygen on antimony. Triphenylstibine oxide, a stronger electron donor than triphenylarsine oxide, forms a particularly stable addition compound with SeO_2.

Triarylbismuthines.—Triarylbismuthines are relatively strong electron acceptors, and carbon–bismuth bonds are relatively weak. Nucleophilic attack by selenito-oxygen on bismuth is accompanied by migration of phenyl to selenium. Triarylbismuthines undergo similar insertion reactions with sulphur dioxide.[15] Addition compounds of triarylbismuthines with SeO_2 have not been isolated, but areneseleninic acids are formed by hydrolysis.

EXPERIMENTAL

Weighed quantities of triaryl derivatives and selenium dioxide were allowed to react in boiling benzene suspension or ethanol solution. The experimental data are summarised in Table 1. Selenium and unchanged selenium dioxide were removed by filtration and separated by washing with hot water. Triarylphosphine oxides and selenides were separated by fractional crystallisation from ethanol. *Addition compounds* of the triarylarsine oxides and triphenylstibine oxide were recrystallised from benzene–light petroleum (b.p. 60—80 °C). Their analytical data are recorded in Table 2. The areneseleninic acids [16] were recrystallised from benzene–n-pentane.

TABLE 2

Analytical data for addition compounds

Compound	M.p. (θ_c/°C)	Analysis (%) [a] C	H
$2AsPh_3O{\cdot}H_2SeO_3$ [b]	131—160	55.95 (55.9)	4.2 (4.1)
$2As(C_6H_4Me\text{-}m)_3O{\cdot}H_2SeO_3$	115—125	58.85 (58.8)	5.3 (5.1)
$2As(C_6H_4Me\text{-}o)_3O{\cdot}H_2SeO_3$	145—175	59.1 (58.8)	5.2 (5.1)
$SbPh_3O{\cdot}SeO_2$	235—237	45.85 (45.0)	3.2(3.1)

[a] Calculated values are given in parentheses. [b] Found: As, 19.3; Se, 10.15. Calc.: As, 19.4; Se, 10.2%.

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[15] B. C. Smith and C. B. Waller, *J. Organometallic Chem.*, 1971, **32**, C11.

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