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## **Reactions of Triaryl Derivatives of Group 5 with Selenium Dioxide**

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Triarylphosphines PR<sub>3</sub> (R = Ph, C<sub>6</sub>H<sub>4</sub>Me-o, -m, -p, or C<sub>6</sub>H<sub>4</sub>Cl-p) react with selenium dioxide suspended in benzene or in solution in ethanol to give triary phosphine oxides, PR<sub>3</sub>O, and triary phosphine selenides, PR<sub>3</sub>Se, or selenium, depending on the phosphine, the relative proportions of the reagents, and the solvent. Triarylarsines do not react with SeO<sub>2</sub> in ethanol, but reactions in benzene suspension give triarylarsine oxides or the addition compounds 2AsR<sub>3</sub>O·H<sub>2</sub>SeO<sub>3</sub> and selenium. Triphenylstibine reacts with SeO<sub>2</sub> suspended in benzene or in ethanol solution to give the addition compound SbPh<sub>3</sub>O·SeO<sub>2</sub> and selenium. Triarylbismuthines react with SeO<sub>2</sub> in benzeneethanol to give areneseleninic acids and bismuth(III)selenite. Possible mechanisms are discussed.

SELENIUM dioxide is a polymeric solid<sup>1</sup> which is insoluble in benzene but soluble in ethanol to give ethyl hydrogenselenite.<sup>2</sup> Melnikov and Rokitskaya<sup>3</sup> reported that triphenyl-phosphine, -arsine, and -stibine react with selenium dioxide suspended in benzene to give the oxides, PPh<sub>3</sub>O and AsPh<sub>3</sub>O, 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<sup>4</sup> or glyoxal,<sup>5</sup> water, and selenium, but oxidation of the solvents does not occur under the conditions described here.

<sup>1</sup> J. D. McCullough, J. Amer. Chem. Soc., 1937, **59**, 789. <sup>2</sup> S. Astin, L. de V. Moulds, and H. L. Riley, J. Chem. Soc.,

## RESULTS

Triphenylamine.—No reaction was observed between triphenylamine and SeO<sub>2</sub> 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.<sup>6</sup> 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<sub>2</sub> (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,<sup>7</sup> and it is shown here that triarylphosphine

<sup>5</sup> Y. Asahina, M. Ishidate, and T. Mamose, Ber., 1934, 67, 1432.

<sup>6</sup> T. W. J. Taylor and W. Baker, 'Sidgwick's Organic Chemistry of Nitrogen,' Oxford University Press, Oxford, 1942, ch. 3.
<sup>7</sup> P. Nicpon and D. W. Meek, *Inorg. Synth.*, 1967, 10, 157.

<sup>1935, 901.</sup> N. N. Melnikov and M. S. Rokitskaya, J. Gen. Chem.

<sup>(</sup>U.S.S.R.), 1938, **8**, 834. <sup>4</sup> N. N. Melnikov and M. S. Rokitskaya, J. Gen. Chem. (U.S.S.R.), 1937, **7**, 1532.

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.<sup>3</sup>

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

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

 $PR_3 + Se \longrightarrow PR_3Se$  (3)

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

Preliminary experiments suggested that tri-o-tolylphosphine does not react with SeO<sub>2</sub> suspended in boiling benzene.<sup>8</sup> 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<sub>2</sub>. Tri-o-tolylphosphine reacted readily with selenium in boiling benzene (1 h), but the reaction of tri-o-tolylphosphine selenide with SeO<sub>2</sub> was slow and incomplete (36 h).

Ethanol solutions. Triphenyl-, tri-p-tolyl-, and tri-m-tolyl-phosphine (3 mol) reacted with SeO<sub>2</sub> (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<sub>2</sub> (1 mol) in boiling ethanol. Some SeO<sub>2</sub> (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<sub>2</sub> 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<sub>2</sub> (1 mol) suspended in boiling benzene gave triphenylarsine oxide (2 mol), selenium (1 mol), and unchanged AsPh<sub>3</sub> (1 mol). Triphenylarsine (2 mol) reacted with SeO<sub>2</sub> (1 mol) to form triphenylarsine oxide and selenium [equation (5)]. It was difficult to remove the last traces of SeO<sub>2</sub> from the AsPh<sub>3</sub>O, and some unchanged AsPh<sub>3</sub> (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).

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

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

Reactions of triphenylarsine (2 mol) with  $\text{SeO}_2$  (3 mol) suspended in boiling benzene gave the addition compound  $\text{AsPh}_3\text{O}\cdot\text{SeO}_2$  and selenium [equation (6), M = As]. In the presence of moisture the final product was an addition compound of selenious acid. A crystal-structure deter-

mination <sup>9</sup> 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,<sup>10</sup> but it has not been prepared from reactions of AsPh<sub>3</sub> with SeO<sub>2</sub>.

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<sub>3</sub> 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 <sup>3</sup> from SbPh<sub>3</sub> and SeO<sub>2</sub> is unlikely.

Triphenylstibine (2 mol) reacted completely with  $\text{SeO}_2$ (3 mol) in boiling benzene or ethanol to give the addition compound SbPh<sub>3</sub>O·SeO<sub>2</sub> 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<sub>3</sub>O 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.

$$2\text{BiR}_3 + 9\text{SeO}_2 + 3\text{H}_2\text{O} \longrightarrow \\ 6\text{RSeO}_2\text{H} + \text{Bi}_2[\text{SeO}_3]_3 \quad (7)$$

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

<sup>10</sup> K. A. Jensen and P. H. Nielsen, Acta Chem. Scand., 1963, **17**, 1875.

<sup>&</sup>lt;sup>8</sup> S. I. A. El Sheikh, B. C. Smith, and M. E. Sobeir, Angew. Chem. Internat. Edn., 1970, 9, 308.

<sup>&</sup>lt;sup>9</sup> S. Cameron, Acta Cryst., 1976, B32, 2094.

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similarly by S<sup>IV</sup> in dimethyl sulphoxide,<sup>11,12</sup> sulphur dioxide,<sup>13</sup> and thionyl chloride.<sup>14</sup> Tri-o-tolylphosphine reacts only slowly with SeO<sub>2</sub>, 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.

				Read	ctions w	itn se	elenium al	oxiae					
	Compound		SeO <sub>2</sub>		Reaction		MR <sub>3</sub> O		MR <sub>3</sub> Se		Se		
	amount/		amount/	%	Solv	vent	time,	amount/	%	amount/	%	amount/	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
DDh	6 1 1	202	9.09	100	CH	(95)	5	2 81	190	2 00	00		70
$D(C \cup M_{0} A)$	0.11	900	0.86	100	6116	(20)	3	171	100	0.95	00		
$P(C H Me_m)$	2.01	208	0.00	100		(50)	8	1.11	198	0.00	99		
$P(C H Me_{0})$	2.84	302	0.94	100		(25)	40	0.51	54	0.27	20		
PPh	7 91	200	3.61	100		(15)	5	7 10	100	0.21	20	3 54	98
$P(C H Me_{-h})$	1.26	200	0.63	100		(25)	5	1 25	198			0.63	100
$P(C H Me_m)$	2.86	200	1 43	100		(50)	7	2.83	198			1 38	97
$P(C, H, Me_0)$	0.79	202	0.39	100		(50)	24	0.20	51	0.11	28	1.00	
PPh.Se	2 52	200	1.26	100		(20)	5	2 59	206	0.11	<b>"</b> ()	3 67	296
P(C, H, Me-t).Se	2.34	200	1.17	100		(25)	5	2.31	197			3 41	291
$P(C_{*}H_{*}Me_{*}m)$ Se	1.51	199	0.76	100		(25)	ĕ	1.43	188			2.15	283
$P(C_{\bullet}H_{\bullet}Me_{\bullet})$ Se	0.23	192	0.12	100		(10)	36					0.14	117
PPh.	11.85	300	3.95	100	EtOH	(50)	10	7.80	197	3.84	97		
$P(C_{A}H_{A}Me-p)_{a}$	5.79	300	1.93	100		(25)	10	3.76	195	1.92	99		
P(C, H, Me-m).	3.89	299	1.30	100		(40)	9	2.47	190	1.27	98		
$P(C_{e}H_{A}Me-o)_{a}$	4.69	295	1.59	100		(30)	56	2.66	167	1.34	84		
PPh,	13.34	200	6.66	100		(25)	10	8.55	128	4.17	63		
$P(C_{a}H_{A}Me-p)_{3}$	2.73	199	1.37	100		(25)	1	1.81	132	0.89	<b>65</b>		
$P(C_{a}H_{4}Me-m)_{3}$	5.61	200	2.80	100		(40)	<b>2</b>	3.74	134	1.87	<b>67</b>		
$P(C_{a}H_{A}Me-o)_{3}$	2.22	200	1.11	100		(25)	40	1.20	108	0.59	53		
AsPh.	6.15	300	2.05	100	$C_6H_6$	(25)	40	3.97	194			2.02	96
U	7.23	300	3.61	100		(25)	44	7.30	<b>202</b>			3.54	- 98
$As(C_{6}H_{4}Me-p)_{3}$	1.98	<b>200</b>	0.99	100		(25)	18	2.11	213			0.76	77
$As(C_6H_4Me-m)_3$	1.98	<b>200</b>	0.99	100		(30)	24	2.03	205			0.76	77
$As(C_6H_4Me-0)_3$	1.98	<b>200</b>	0.99	100		(25)	40	2.19	221			1.01	102
	SbPh <sub>3</sub> O·SeO <sub>2</sub>												
SbPh <sub>3</sub>	2.31	<b>200</b>	3.46	<b>300</b>	EtOH	(30)	2	2.33	<b>202</b>			1.15	100
	3.51	<b>200</b>	5.27	300	$C_6H_6$	(25)	2	3.46	197			1.64	93
BiPh <sub>3</sub>	2.27	<b>200</b>	10.22	900	EtOH-	- (30)	10	6.56	578				
	2.27	<b>200</b>	10.22	900	C <sub>6</sub> H <sub>6</sub>	(30)	10	6.72	592				
$\operatorname{Bi}(C_6H_4Me-p)_3$	1.04	200	4.67	900		(35)	10	3.05	588				
$\operatorname{Bi}(C_6H_4\operatorname{Me}-m)_3$	4.16	200	18.69	900		(30)	10	11.42	550				
$Bi(C_{6}H_{4}Me-o)_{3}$	1.04	<b>200</b>	4.67	900		(30)	10	3.06	<b>590</b>				
$Bi(C_6H_4Cl-p)_3$	3.68	<b>200</b>	16.55	900		(30)	10	8.14	443				

TABLE 1 ---4 . . . • • •

The subsequent reaction patterns depend on the different reactivities of triarylphosphine selenides in



benzene and ethanol. The reactions of PPhaSe with polymeric selenium dioxide may proceed via a sixmembered 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<sub>2</sub> in ethanol, except when evaporation of the solvent leads to the formation of polymeric selenites or solid selenium

<sup>11</sup> S. K. Ray, R. A. Shaw, and B. C. Smith, Nature, 1962, 196,

Triarylarsines.--Triarylarsines do not react with red selenium in boiling organic solvents, and on reaction with SeO<sub>2</sub> in benzene they give triarylarsine oxides and selenium, but not triarylarsine selenides. Triarylarsine



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

<sup>372.</sup> <sup>12</sup> E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, J. Chem. Soc., 1965, 6250.

B. C. Smith and G. H. Smith, *J. Chem. Soc.*, 1965, 5516.
E. H. Kustan, B. C. Smith, M. E. Sobeir, A. N. Swamy, and M. Woods, J.C.S. Dalton, 1972, 1326.

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 triaryl-phosphines is that triarylarsines do not react with  $\text{SeO}_2$  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.



Triphenylstibine.—Triphenylstibine reacts with  $\text{SeO}_2$ 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<sub>2</sub>.

*Triarylbismuthines.*—Triarylbismuthines are relatively strong electron acceptors, and carbon-bismuth bonds are relatively weak. Nucleophilic attack by selenitooxygen on bismuth is accompanied by migration of phenyl to selenium. Triarylbismuthines undergo similar insertion reactions with sulphur dioxide.<sup>15</sup> Addition <sup>15</sup> B. C. Smith and C. B. Waller, J. Organometallic Chem., 1971, **32**, C11. 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 benzenelight petroleum (b.p. 60–80 °C). Their analytical data are recorded in Table 2. The areneseleninic acids <sup>16</sup> were recrystallised from benzene-n-pentane.

## TABLE 2

Analytical data for addition compounds

	Mn	Analysis (%) "				
Compound	$(\theta_{e}/^{\circ}C)$	С	н			
2AsPh <sub>3</sub> O·H <sub>2</sub> SeO <sub>3</sub> <sup>b</sup>	131-160	55.95 (55.9)	4.2(4.1)			
2As(C,H4Me-m)3O·H2SeO3	115 - 125	58.85 (58.8)	5.3 (5.1)			
2As(C,H4Me-o),O·H2SeO3	145 - 175	59.1 (58.8)	5.2(5.1)			
SbPh <sub>3</sub> O·SeO <sub>2</sub>	235 - 237	45.85 (45.0)	3.2(3.1)			
<sup>a</sup> Calculated values are a	riven in parer	theses. <sup>b</sup> Fo	ound: As			

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Found: As, 19.3; Se, 10.15. Calc.: As, 19.4; Se, 10.2%.

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<sup>16</sup> W. H. Porritt, *J. Chem. Soc.*, 1927, 27; D. Behaghel and H. Seibert, *Ber.*, 1933, **B66**, 708.