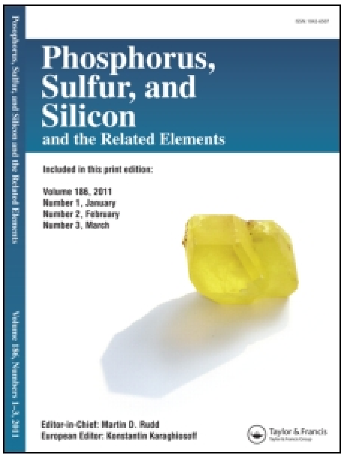

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THE REACTION OF TETRACHLORO-*o*-BENZOQUINONE WITH THE SULFIDES OF TRIPHENYLARSINE AND TRIPHENYLSTIBINE

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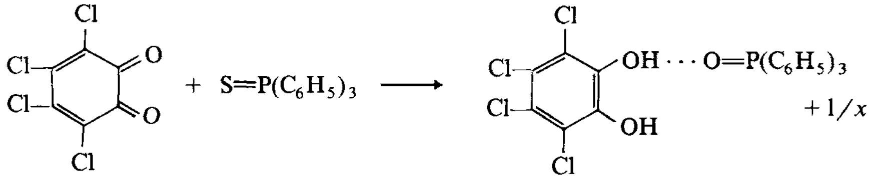
The reaction of tetrachloro-*o*-benzoquinone (1) with triphenylarsine sulfide gives a hydrogen-bonded complex of the corresponding hydroquinone and triphenylarsine oxide (5). The same quinone reacts with triphenylstibine sulfide yielding the cyclic adduct (9). In both cases, elemental sulfur is the other product.

Possible reaction mechanisms are considered and the structural assignments are based on analytical, chemical and spectroscopic results.

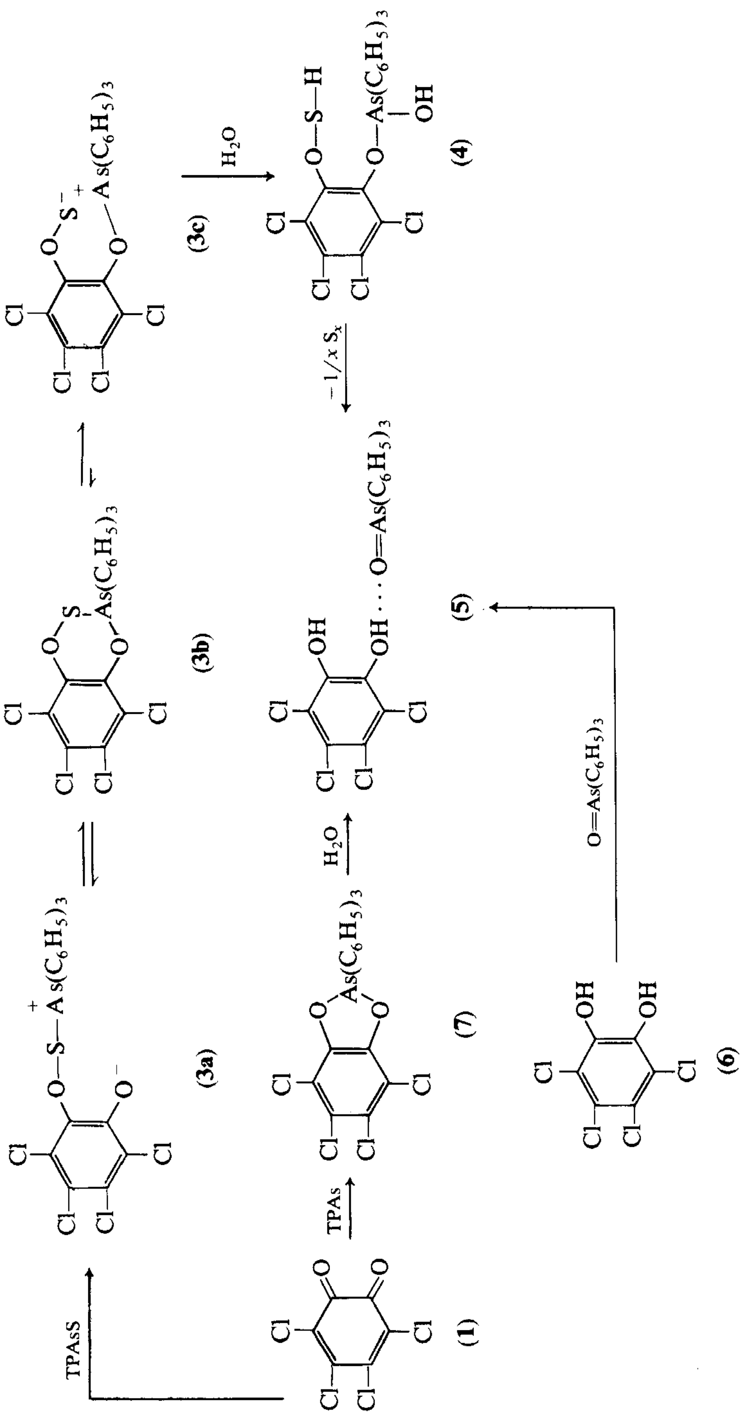
Recently,[1] we have shown that tetrachloro-*o*-benzoquinone (**1**) affects the oxidative desulfurization of triphenylphosphine sulfide (TPPS) to give the oxide-pyrocatechol complex (**2**).



(**1**) (**2**)

Since arsenic and antimony are also members of the fifth group of the periodic table, it was of interest to investigate the action of the same quinone (**1**) on the sulfides of triphenylarsine and triphenylstibine to determine whether they behave in a similar manner.

When an equimolar mixture of triphenylarsine sulfide (TPAsS) and quinone (**1**) in dry benzene was refluxed for 10 h, the complex (**5**) was isolated as the main reaction product together with elemental sulfur. This reaction was markedly accelerated when a controlled amount of water was admixed with the solvent before starting the reaction. In favour of the proposed hydrogen-bonded structure (**5**) are: (a) Elemental analysis and molecular weight determination (MS) corresponded to $C_{24}H_{17}Cl_4AsO_3$. (b) The IR spectrum of complex (**5**), in KBr, showed bands at 3400 cm^{-1} (OH), 1550 cm^{-1} (C=C, aromatic) and at 740 cm^{-1} (Cl—Ar). The strong absorption bands present in the 1100–1000 cm^{-1} region are attributed to the As—C (phenyl) grouping.[2] (c) Upon thermolysis, complex (**5**) afforded tetrachloropyrocatechol (**6**) along with triphenylarsine oxide (TPAsO). (d) The oxide-pyrochatechol complex (**5**) was equally produced by the evaporation till dryness of an alcoholic solution of



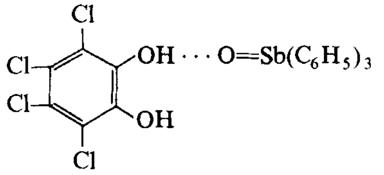
SCHEME 1

TPAsO and tetrachloropyrochatechol (**6**). (e) Furthermore, the identity of complex (**5**) was established by m.p., mixture m.p. and comparative IR spectra with a specimen prepared by an independent route. This was achieved by allowing triphenylarsine (TPAs) to react with quinone (**1**) in anhydrous benzene. The resulting colorless crystalline adduct was assigned the 1,3,2-benzodioxarsole structure (**7**), as inferred from its mass spectral analysis and its IR spectrum which lacks the —OH absorption. This cyclic adduct (**7**), upon treatment with water, yielded the hydrogen-bonded complex (**5**) (cf. Scheme 1).

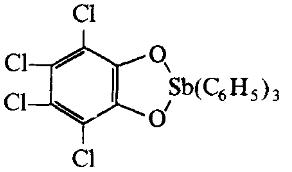
A mechanism for the formation of (**5**) is presented in Scheme 1. This comprises the initial attack by the TPAsS on quinone (**1**) to give the dipolar adduct (**3a**) which probably exists in equilibrium with the cyclic structure (**3b**). Compound (**3b**), represented by the species (**3c**), adds the elements of water to give the transient (**4**) which then loses elemental sulfur yielding the complex (**5**).

It is worthy of mention that the reaction of quinone (**1**) with triphenylphosphine selenide (TPPSe) and triphenylarsine selenide (TPAsSe) afforded the corresponding pyrocatechol-oxide complexes (**2**) and (**5**) in high percentage yields. Elemental selenium was also isolated in each case. The oxidative deselenation reactions of TPPSe and TPAsSe by quinone (**1**) proceeded, however, much faster* as compared with the aforementioned oxidative desulfurization reactions of TPPS and TPAsS with the same quinone (**1**).

The reaction of quinone (**1**) with triphenylstibine sulfide (TPSbS), in benzene, was found not to give a pyrocatechol-oxide complex of type (**8**). It leads, however, to the formation of an addition product having structure (**9**). Elemental sulfur was also isolated.



(**8**)



(**9**)

The identity of adduct (**9**) was verified by the following evidence: (a) Elemental and mass spectroscopic analysis confirmed to be $C_{24}H_{15}Cl_4O_2Sb$. (b) The behaviour of adduct (**9**) under electron impact is in complete variance as compared with that of complex (**5**). Thus, the mass spectrum of adduct (**9**) shows no evidence for a fragmentation pattern of triphenylstibine oxide as well as of the tetrachloropyrocatechol moiety (cf. exper.). (c) The IR spectrum of adduct (**9**) does not reveal −OH absorption above 3000 cm^{-1}. (d) Adduct (**9**) was equally obtained and identified (comparative IR and Mass Spectra) by allowing quinone (**1**) to react with triphenylstibine in dry benzene. (e) Upon thermolysis, adduct (**9**) regenerates the starting quinone (**1**) and triphenylstibine, simulating thus what is known regarding the facile elimination of phosphorus from cyclic compounds.[5]

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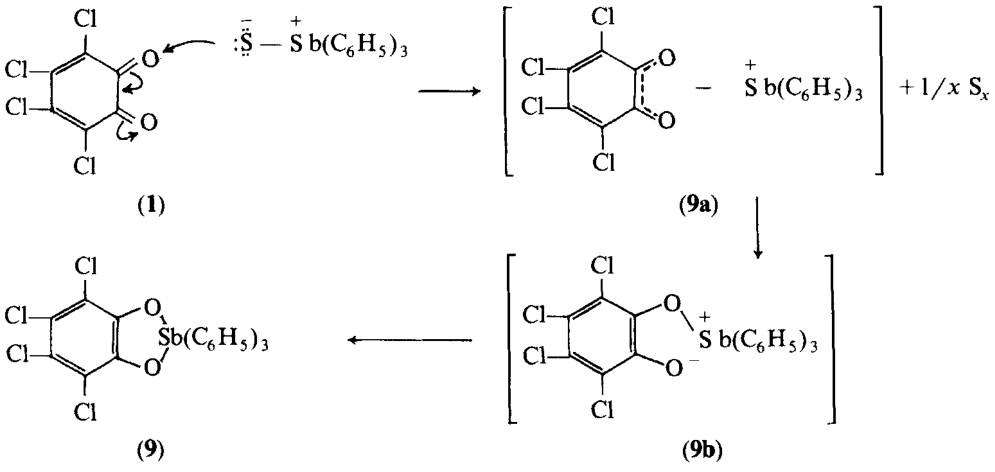
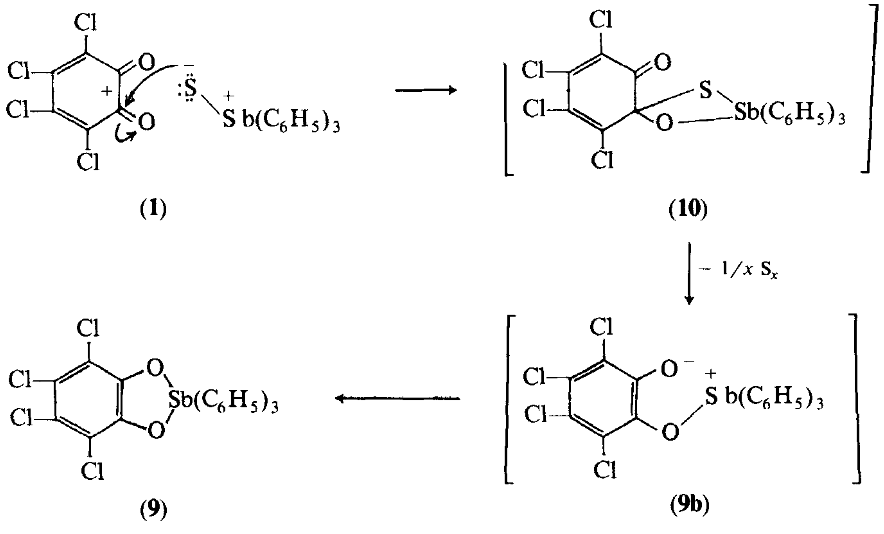
*Cf. the increase of reducing properties from sulfur to selenium (Refs. 3, 4).

We propose Scheme 2 to account for this interesting observation. In the light of the bulkiness of the antimony atom as compared to phosphorus and arsenic, the weak electron density on that atom would result in a relatively feeble attraction between antimony and sulfur. Further, one can assume charge separation on the two carbonyl functions of the *o*-chloranil molecule, of which the partially positive side neutralizes the negatively charged sulfur atom of the additive, leading to the elimination of the elementary sulfur. In the meantime, charge redistribution on the two oxygen atoms of chloranil facilitates their combination with the positively charged antimony atom of the stibine reagent to yield the final product (**9**).



SCHEME 2



SCHEME 3

Another alternative pathway (cf. Scheme 3) which cannot be overlooked, involves a nucleophilic attack by triphenylstibine sulfide (TPSbS) on the carbon atom of the carbonyl function in quinone (**1**) (carbophilic attack). This leads to the intermediate adduct (**10**) which collapses with elimination of sulfur to the dipolar form (**9b**). The latter undergoes ring-closure giving the stable 1,3,2-benzodioxastibole (**9**).

From the results of the present investigation, it can be seen that compounds of the fifth group elements of the same structural type, namely TPP, TPAs, TPSb, their sulfides and their selenides, show remarkable similarities in their behaviour toward chloranil with gradation in properties from phosphorus to antimony as the element becomes more metallic.

EXPERIMENTAL SECTION†

All m.p.s are uncorrected. The benzene (thiophene-free) used, was dried over Na. Triphenylarsine sulfide (TPAsS),[6] triphenylstibine sulfide (TPSbS),[7] triphenylarsine oxide (TPAsO),[8] triphenylstibine oxide (TPSbO),[9] triphenylphosphine selenide (TPPSe)[10] and triphenylarsine selenide (TPAsSe),[11] were prepared according to known procedures. The IR spectra were run on a Beckmann Infracord Model 4220, in KBr or in $CHCl_3$, and the mass spectra were run at 70 eV on a Varian MAT 112 Mass Spectrometer.

Mixtures of benzene-ethylacetate (9 : 1 or 3 : 1) and benzene-cyclohexane (3 : 17) were used as solvent systems (TLC). Iodine vapour was used as a visualizing agent.

Reaction of Tetrachloro-o-benzoquinone (**1**) *with TPAsS.*

(a) *In anhydrous benzene.* A mixture of quinone (**1**) (2.5 g, 0.01 mol) and TPAsS (3.4 g, 0.01 mol) in dry benzene (40 ml) was boiled under reflux for 10 h, then left for 12 h at room temperature. After evaporation of the solvent, *in vacuo*, the oily residue was treated with hot ethanol (15 ml, 90%) and the mixture kept at room temperature for 48 h. The solid material that separated was filtered off, washed with 5 ml cold CS_2 and recrystallised from benzene-petroleum ether (b.r. 40–60°) to give complex (**5**) in the form of colorless needles (4.2 g, 75%), m.p. 145–147°. Anal. Calcd. for $C_{24}H_{17}AsCl_4O_3$: C, 50.55, H, 3.00, As, 13.14, Cl, 24.87. Found: C, 50.37, H, 3.01, As, 13.12, Cl, 24.78. MS m/e: M^+ 322 $(C_6H_5)_3AsO^+$, M^+ 248 for $C_6H_2Cl_4O_2^+$ and base peak at m/e 152 $(C_{12}H_8)^+$. The IR spectrum had bands at 3420 cm^{-1} (OH), 1550 cm^{-1} (C=C, aromatic), 1100–1000 cm^{-1} (As—C, phenyl) and at 740 cm^{-1} (Cl—Ar).

The ethanol–CS_2 solution was reduced to a minimum volume then introduced to a column (1.5 × 30 cm) charged with silica gel (Kieselgel 60, particle size 0.2–0.5 mm, E. Merck, Darmstadt). Elution with petroleum ether (b.r. 40–60°) yielded elemental sulfur (ca. 0.25 g, 65%).

(b) *In hydrated benzene.* The complex (**5**) (80%) and elemental sulfur (70%) were isolated and in the same manner by reacting quinone (**1**) (0.01 mol) and TPAsS (0.01 mol) in boiling benzene (40 ml) containing water (1 ml) for 6 h. The working-up of the reaction mixture was as described before, *vide supra*.

Action of heat on 5. Complex (**5**) (0.5 g) was heated in a cold finger sublimator at 200°C (bath temperature) for 30 min, and the product treated with aq. NaOH (10%). The undissolved material (0.2 g, 80%) was recrystallized from ethanol to give colorless needles proved to be TPAsO (m.p. and mixture m.p.).[8]

After cooling the alkaline solution to 5°C, it was neutralised with aq. HCl (10%) under good stirring. The precipitated material was collected and recrystallised from benzene to give pale-yellow crystals proved to be tetrachloropyrocatechol (**6**) (m.p. and mixture m.p.),[12] (yield ca. 1.8 g, 90%).

Reaction of Tetrachloropyrocatechol (6) with TPAsO. An ethanolic solution of compound (**6**) (2.48 g, 0.01 mol) and TPAsO (3.22 g, 0.01 mol) was left to evaporate in an opened vessel at room temperature. The residual material was recrystallised from benzene-petroleum ether (b.r. 40–60°) to give colorless crystals proved to be complex (**5**) (m.p., mixture m.p. and comparative IR spectra), (yield 5 g, 90%).

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†The names of the compounds described in this paper are in line with IUPAC rules of organic nomenclature.

Reaction of Tetrachloro-o-benzoquinone (1) with TPAs. To a solution of quinone (**1**) (2.5 g, 0.01 mol) in dry benzene (30 ml), was added a solution of TPAs (0.01 mol) in the same solvent (20 ml). The color of the solution changes to deep red then fades gradually and in the same time evolution of heat was observed. After keeping the reaction for 10 h, at room temperature, colorless crystals of 4,5,6,7-tetrachloro-2,2,2-triphenyl-1,3,2-benzodioxarsole (**7**) were separated. Compound (**7**) was recrystallised from benzene-petroleum ether (b.r. 40–60°), m.p. 193–195°, (yield: 4.3 g, 80%). Anal. Calcd. for $C_{24}H_{15}AsCl_4O_2$: C, 52.20, H, 2.74, As, 13.57, Cl, 25.68. Found: C, 52.13, H, 2.69, As, 13.59, Cl, 25.72. Mol. Wt., Calcd.: 552, Found (MS): 552.

IR (expressed in cm^{-1}): Bands at 1550 (C=C, aromatic), 1100–1000 (As—C, phenyl) and at 740 (Cl—Ar).

Action of water on compound (7). Compound (**7**) (0.01 mol) in 40 ml benzene containing water (1 ml), was refluxed for 4 h. After evaporation of the volatile materials under reduced pressure, the oily residue was treated with ethanol (10 ml), then left for 12 h, at room temperature. Recrystallisation of the resulting solid material from benzene-petroleum ether (b.r. 40–60°) afforded colorless crystals (95%) proved to be complex (**5**) (m.p., mixture m.p. and comparative IR spectra).

Reaction of quinone (1) with TPPSe. A mixture of quinone (**1**) (2.5 g, 0.01 mol) and TPPSe (3.41 g, 0.01 mol) was either refluxed in 40 ml dry benzene for 5 h, or boiled in benzene containing water (40 : 0.5 ml, v/v) for 3 h. The black powder of selenium was filtered off and the filtrate freed from the volatile materials, *in vacuo*. The residual material was recrystallised from chloroform-petroleum ether (b.r. 40–60°) to give colorless crystals (4.2 g, 80%) proved to be complex (**2**) (m.p. and mixture m.p. 122°).[1,13] Similarly, complex (**5**) was obtained (ca. 85%) and identified (m.p., mixture m.p. and comparative IR spectra) together with elemental selenium, upon allowing equimolecular quantities of quinone (**1**) and TPAsSe to reflux either in dry benzene or in benzene-water mixture, for 6 h.

Reaction of quinone (1) with TPSbS. A mixture of quinone (**1**) (2.5 g, 0.01 mol) and TPSbS (3.8 g, 0.01 mol) was refluxed in 40 ml of dry benzene for 10 h, then left for 12 h, at room temperature. After evaporation of the solvent, *in vacuo*, the residual material was washed thoroughly first with ethanol then with CS_2 (10 ml of each). The undissolved material was filtered off (5 g, 85%) and recrystallised from chloroform-petroleum ether (b.r. 40–60°) to give 4,5,6,7-tetrachloro-2,2-dihydro-2,2,2-triphenyl-1,3,2-benzodioxastibole (**9**) as colorless crystals, m.p. 185–187°. Anal. Calcd. for $C_{24}H_{15}Cl_4SbO_2$: C, 46.87, H, 2.46, Cl, 23.06, Sb, 19.74. Found: C, 47.75, H, 2.42, Cl, 23.12, Sb, 19.42. Mol. Wt. Calcd.: 596, Found (MS) m/e: M^+ 596 for $C_{24}H_{15}Cl_4SbO_2^{+\cdot}$, base peak at 198 for $C_6H_5Sb^+$.

The IR spectrum had bands at 1550 cm^{-1} (C=C, aromatic) and at 740 cm^{-1} (Cl–Ar).

The reaction of quinone (1) with TPSb. A mixture of quinone (**1**) (2.5 g, 0.01 mol) in dry benzene (20 ml) and TPSb (3.5 g, 0.01 mol) in the same solvent (30 ml), was left for 12 h, at room temperature. After evaporation of the solvent, *in vacuo*, the residue was triturated with petroleum ether (b.r. 40–60°). The solid material, so formed, was collected (4.9 g, 80%) and recrystallized from chloroform-petroleum ether (b.r. 40–60°) to give colorless crystals proved to be compound (**9**) (m.p. and mixture m.p. 185°). MS: m/e 596 (M^+ corresponding to $C_{24}H_{15}Cl_4SbO_2$).

Action of heat on (9). Compound (**9**) (0.1 g) was heated in a cold finger sublimator at 250° (bath temperature) for about 20 minutes under reduced pressure (10 mm/Hg). The substance that sublimed was boiled in petroleum ether (b.r. 60–80°). The undissolved material was then recrystallised from benzene, and proved to be tetrachloro-*o*-benzoquinone (**1**) (m.p. and mixture m.p. 129°).[14]

The petroleum ether solution was concentrated to half its volume and cooled in the refrigerator. The crystals that separated were filtered off and proved to be triphenylstibine (TPSb) (m.p. and mixture m.p. 50°).[9]

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