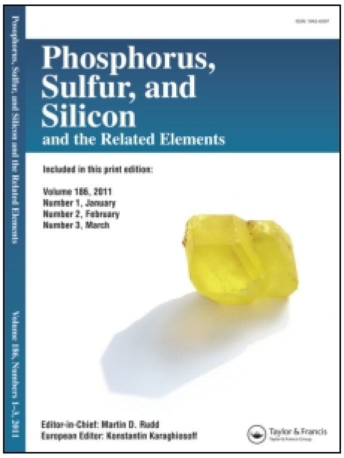

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ORGANOPHOSPHORUS COMPOUNDS, XXVIII. THE REACTION OF TRIPHENYLPHOSPHINE SULFIDE WITH TETRACHLOROBENZOQUINONES

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ORGANOPHOSPHORUS COMPOUNDS, XXVIII. THE REACTION OF TRIPHENYLPHOSPHINE SULFIDE WITH TETRACHLOROBENZOQUINONES

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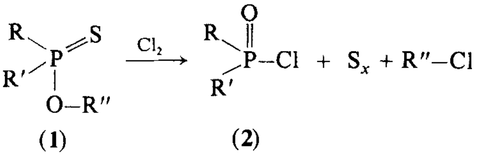
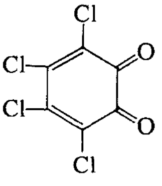
The reaction of triphenylphosphine sulfide with tetrachloro-*o*-benzoquinone gives a complex of the corresponding hydroquinone and triphenylphosphine oxide. Elemental sulfur is the other product. The tetrachloro-*p*-benzoquinone does not react to any noticeable extent under similar conditions. Several mechanisms are proposed to explain the results.

Tertiary phosphine sulfides are attacked by strong oxidizing agents, e.g. nitric acid and potassium permanganate to give the corresponding oxides.[1] On the other hand, chlorine oxidizes phosphorus thionoesters of type (**1**), producing chloridates (**2**), elemental sulfur and alkyl chlorides.[2] Although attack by organic oxidants[3,4] on tervalent phosphorus compounds has been frequently studied,[5–7] the action of the same reagents on triphenylphosphine sulfide (TPPS) has, however, attracted no attention. This prompted us to investigate the behaviour of tetrachloro-*o*-benzoquinone (**3**) and tetrachloro-*p*-benzoquinone (**4**) with TPPS.

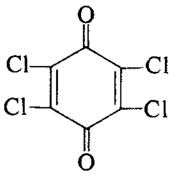
When an equimolar mixture of TPPS and quinone (**3**) in dry benzene was refluxed for 10 h, the complex (**7**) and elemental sulfur were isolated as the main reaction products. The reaction was, however, greatly enhanced when traces of water were admixed with benzene before the start of the reaction (cf. Experimental). The identity of complex (**7**) was established by mp, mixed mp and comparative mass spectra with an authentic specimen[8] prepared by the evaporation till dryness of an alcoholic solution of triphenylphosphine oxide (TPPO) and tetrachlorocatechol (**8**). Structure (**7**) was proposed by Ramirez *et al.*[8] to describe the same compound prepared by Horner and Klüpfel[9] by the reaction of quinone (**3**) with triphenylphosphine (TPP) in hydrated benzene and to which formula (**9**) was given.[9]



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



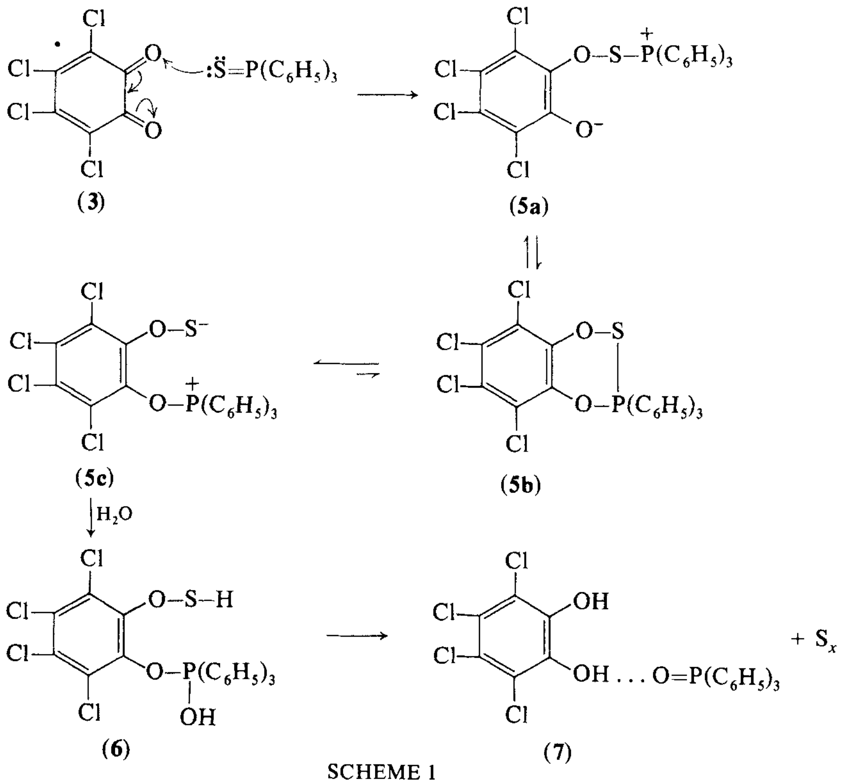
(**3**)



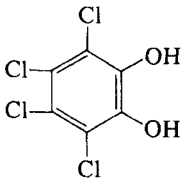
(**4**)

A mechanism accounting for the formation of the observed products is depicted in Scheme 1. It is based on the assumption of initial attack by the TPPS on quinone (**3**) to give the dipolar adduct (**5a**) which probably exists in equilibrium with the cyclic structure (**5b**). Compound (**5**), represented by the *O*-phosphonium form (**5c**), adds the elements of water to give the transient intermediate (**6**) which then loses elemental sulfur yielding the complex (**7**).

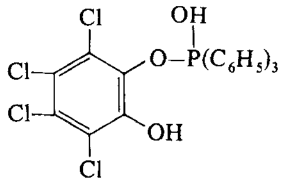
However, the mechanism given in Scheme 1 does not completely exclude an alternative one (Scheme 2) for the production of complex (**7**) and elemental sulfur from the reaction of TPPS with quinone (**3**). This comprises the primary reduction of tetrachloro-*o*-benzoquinone (**3**) with traces of water to yield the corresponding hydroquinone (**8**) and active oxygen |O|. This latter by virtue of its higher electronegativity, replaces sulfur from TPPS. The oxide formed adds through hydrogen bonding to the hydroquinone (**8**). The fact that elementary sulfur and not H_2S is isolated indicates that TPPO was generated by the assumed reaction and not through the intermediate reduction of TPPS. Further, the finding that hydroquinone (**8**) does not add to TPPS to any appreciable extent under the prevailing experimental conditions, adds complementary sup-



SCHEME 1

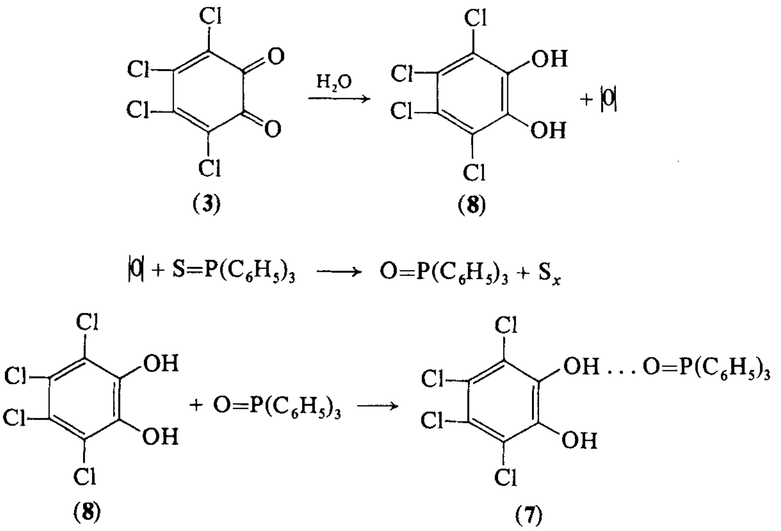


(8)



(9)

port to the conclusion that TPPO is formed simultaneously with generation of hydroquinone (**8**). It is of interest to remark here that tetrachloro-*p*-benzoquinone (**4**) does not react to any noticeable extent with TPPS under apparently similar conditions. This might find its explanation in the large disparity in the redox potentials of the two quinones



SCHEME 2

(**3**) and (**4**). Thus, while tetrachloro-*o*-benzoquinone (**3**) has an $\mathbf{E}_0$ value of 860 mV[10] (calomel), the corresponding value of the *p*-isomer is only 712 mV.[11]

EXPERIMENTAL

The benzene (thiophene-free) used was dried over sodium. Mixtures of benzene–ethyl acetate (3 : 1) and benzene–cyclohexane (3 : 17) were used as solvent systems (TLC). Iodine vapor was used as the visualizing agent.

The reaction of triphenylphosphine sulfide (TPPS) with tetrachloro-o-benzoquinone (3)

(a) *In dry benzene.* A mixture of TPPS[12] (2.94 g, 0.01 mol) and quinone (**3**) (2.46 g, 0.01 mol) in benzene (40 ml) was boiled under reflux for 10 h then left overnight at room temperature. After evaporating the solvent, *in vacuo*, the oily residue was treated with hot ethanol (25 ml, 95%) and the mixture kept aside at room temperature. The solid material that separated was filtered, washed with 5 ml cold CS_2, and recrystallized from chloroform–petroleum ether (bp 40–60°) to give colorless crystals (*ca.* 3.7 g, 70%) shown to be complex (**7**) (mp and mixed mp 122°).[8] Mol. wt. (MS): Calcd. 526, Found: 526.

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 (35–70 mesh ASTM) E. Merck, Darmstadt)]. Elution with petroleum ether (bp 40–60°) yielded elemental sulfur (*ca.* 0.25 g, 80%).

(b) *In hydrated benzene.* A mixture of TPPS (0.01 mol) and quinone (**3**) (0.01 mol) in 40 ml benzene containing 0.5 ml of water, was refluxed for 4 h. After evaporation of the volatile materials, *in vacuo*, the oily residue was treated with ethanol (20 ml) then left overnight at ambient temperature. Working-up as described above yielded complex (**7**) (*ca.* 85%), mp 122° either alone or upon admixture with a reference sample,[8] together with elemental sulfur (80%).

The reaction of triphenylphosphine sulfide (TPPS) with tetrachlorocatechol (8)

A mixture of TPPS (*ca.* 3 g, 0.01 mol) and tetrachlorocatechol (**8**) (2.5 g, 0.01 mol) in ethanol (40 ml, 95%) was refluxed for 10 h then allowed to evaporate slowly at room temperature. Benzene (15 ml) was added to the resulting solid material and the undissolved substance was filtered (2.3 g, 95%) and recrystallized from benzene to give pale-yellow crystals shown to be unchanged (**8**) (mp and mixed mp 194°).[13]

Petroleum ether (bp 40–60°) was added to the benzene-filtrate and the material that precipitated after cooling in the ice-chest was collected (2.9 g, 95%) then recrystallized from ethanol to give colorless needles shown to be TPPS (mp and mixed mp 157°).[12]

The reaction of triphenylphosphine sulfide (TPPS) with tetrachloro-p-benzoquinone (**4**)

A mixture of TPPS (*ca.* 3 g, 0.01 mol) and tetrachloro-*p*-benzoquinone (**4**) (*ca.* 2.5 g, 0.01 mol) in 40 ml benzene containing 0.5 ml of water was boiled under reflux for 10 h then left overnight at room temperature. After evaporation of the volatile materials, *in vacuo*, toluene (20 ml) was added. The toluene-insoluble material (2.3 g, 92%) was filtered and recrystallized from acetic acid to give golden yellow leaflets which were shown to be tetrachloro-*p*-benzoquinone (**4**) (mp and mixed mp 290°).[14] Petroleum ether (bp 40–60°) was added to the toluene filtrate and the precipitated material was collected (2.9 g, 95%) then recrystallized from ethanol to give colorless needles of TPPS (mp and mixed mp 157°).[12]

REFERENCES AND NOTES

1. G. M. Kosolapoff, *Organophosphorus Compounds* (John Wiley & Sons Inc., New York, 1958), Second Printing, p. 100.
2. J. Michalski, Abstracts of Papers, the 1st International Congress on Phosphorus Compounds, Oct. 1977, Rabat, Morocco, p. 19.
3. C. J. Timmons *Modern Reactions in Organic Synthesis* (Van Nostrand Reinhold Co., London, 1970, p. 84.
4. L. M. Jackman, *Adv. Org. Chem.* **2**, 329 (1961).
5. F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.* **78**, 5614 (1956).
6. F. Ramirez, E. H. Chen and S. Dershowitz, *J. Am. Chem. Soc.* **81**, 4338 (1959).
7. E. A. C. Lucken, F. Ramirez, V. P. Catto, D. Ruhm and S. Dershowitz, *Tetrahedron* **22**, 637 (1966).
8. F. Ramirez and S. Dershowitz, *J. Org. Chem.* **24**, 704 (1959).
9. L. Horner and H. Klüpfel, *Liebigs Ann. Chem.* **591**, 69 (1955).
10. D. E. Kvalnes, *J. Am. Chem. Soc.* **56**, 2487 (1934).
11. K. Wallenfels and W. Möhle, *Chem. Ber.* **76B**, 924 (1943).
12. A. Michaelis and L. Gleichman, *Chem. Ber.* **15**, 801 (1882).
13. Th. Zincke, *Chem. Ber.* **20**, 1779 (1887).
14. J. Erdèlyi, *Chem. Ber.* **63**, 1200 (1930).