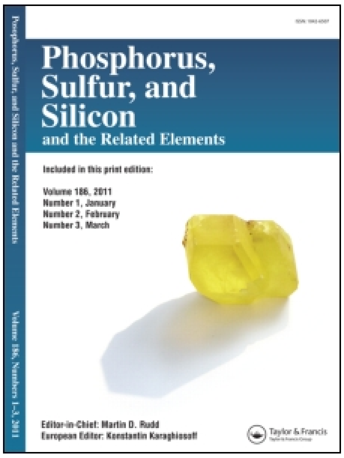

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Reaction of Selenoesters of Phosphorus Acids with Halogens

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REACTION OF SELENOESTERS OF PHOSPHORUS ACIDS WITH HALOGENS

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Abstract Reaction of phosphinoselenoates 1a-b with elemental chlorine, bromine, iodine as well as sulfuryl chloride involves halogenolysis of P-Se bond and formation of tert-butylphenylphosphinohalogenate 7. Intermediate products, containing one and two phosphorus atoms were detected by ^{31}P NMR. The similarities and differences in the behavior of phosphorus selenoesters and their thio-analogues are discussed.

INTRODUCTION

The problem of halogenation reaction of phosphorus thio- and selenoesters has two important aspects:

(i) the detoxification of phosphoroorganic poisons;

(ii) the access to optically active halogenoanhydrides of phosphorus acids.

This communication is an extension of earlier works from this Laboratory,[1-2] which were devoted to the stereochemical and mechanistic problems connected with the halogenation of phosphorus thioloesters.

The aim of this investigation is to examine what effects may bring the exchange of the sulfur atom in the studied system for selenium. Two effects could be expected: the inreased ability of the phosphorus selenoesters to form relative stable complexes with halogenes[3] (particulary Br_2 and I_2), because of the stronger donor character of selenium, and the increasing rate of nucleophilic substitution at the phosphorus atom due to the weakness of P-Se bond. The overall effect on the reaction course is difficult to anticipate.

RESULTS AND DISCUSSION

In this communication the results obtained for the model esters 1a-b will be described.

$Bu^tPhP(O)SeR$ 1a: R = Me
1b: R = Ph

Elemental chlorine, bromine, iodine, as well as sulfuryl chloride were used as halogenating reagents.
FT (^1H decoupled) ^{31}P NMR studies of the reacting system 1a-b + X_2 (X_2=Cl_2,Br_2,SO_2Cl_2) were performed in the temperature range 173-293 K in methylene chloride or toluene. In all cases similar spectral pattern was observed; characteristic set of signals (doublet of doublets) in the region +114 - +110 ppm and +59 - +60 ppm is ascribed to the intermediate 5 and +103 - +102 ppm and +66 - +67 ppm to the intermediate 6. Compounds 5 and 6 contain two phosphorus atoms bonded by the oxygen bridge. Due to the fact that 5 and 6 are formed as pairs of diastereoisomers, the signals are multipied by two (Fig. 1).

In addition to 5 and 6, two other intermediates containing one phosphorus atom are observed in the course of the studied reaction. The structure of selenonium salt 3 is ascribed to the compound with chemical shift about +92 ppm, while to the species with $\delta_P \approx +87$ ppm the structure of molecular complex 2. It is evident, that both species should remain in the equilibrium with substrates (Scheme I, steps (a) and (b)). The participation in equilibrium of selenurane 4 (path (c)) cannot be excluded. The position of the equilibrium depends on the structure of substrates, reaction medium and temperature.
Figure 1b illustrates the situation, when intermediates 2, 3 and 5 are observed at the same time.

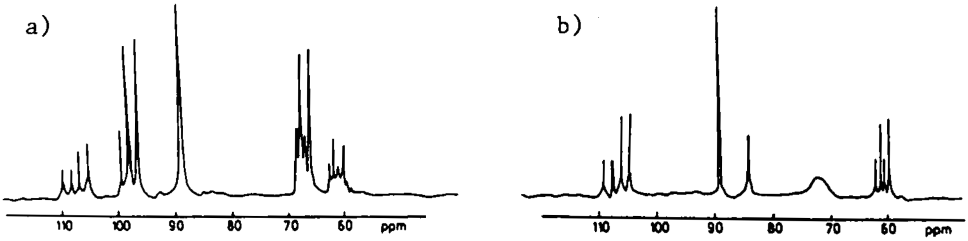
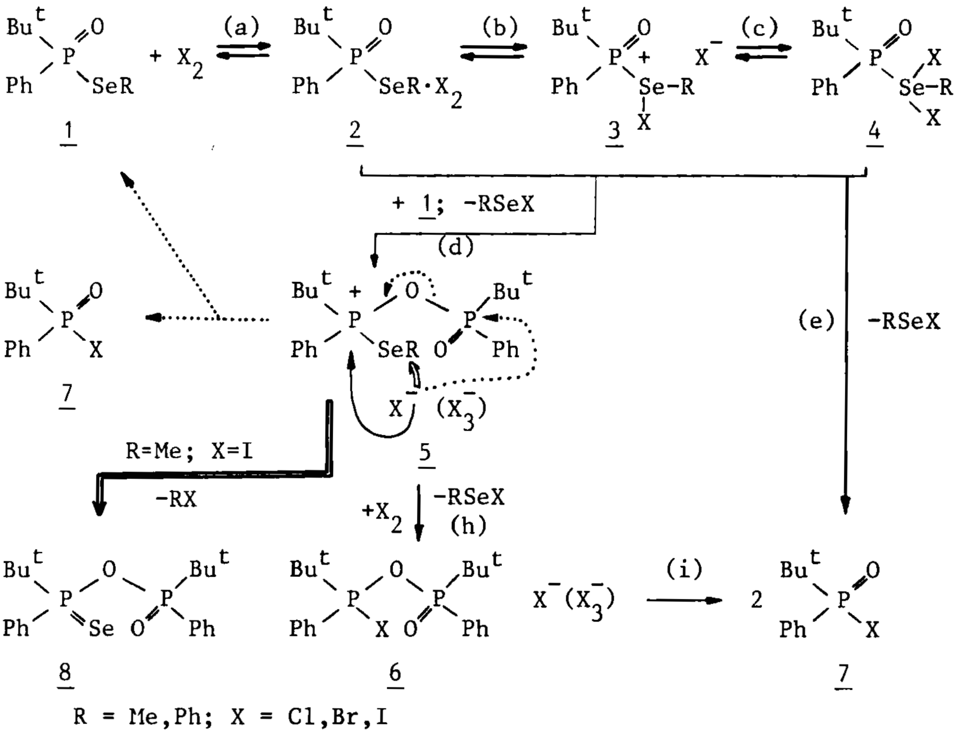


FIGURE 1 NMR spectra of (a) 1a + Cl_2, (b) 1a + SO_2Cl_2 (in CH_2Cl_2 at 193 K)

SCHEME I



Behavior of both studied models, 1a-b towards halogenating reagents is similar, and observed differences have rather quantitative character. The only exception is the reaction of 1a with elemental iodine. In this rather slow reaction - in addition to 7

(X = I) the product containing two phosphorus atom - 8 is obtained. The experimental results are in agreement with the mechanistic scheme presented above.

The scheme allows to rationalize the formation of all observed intermediates and reaction products. It is similar to the scheme proposed for the halogenolysis of phosphorus thioloesters.[1-2] However, some differences in behavior of selenoesters 1a-b are evident. The considerable enhancement of the reaction rate was observed, particulary with Br_2 and I_2. Moreover, during the reaction of 1 with Br_2 and I_2 the intermediates 6 (X = Br,I) are formed and 7 (X = Br,I) are the main reaction products, which was not observed for thio-analogues of 1.

It can be concluded, that -SeR group modified by coordination with halogenes is a better leaving group than -SR group. The strong affinity of selenium towards halogens assists in the process of nucleophilic substitution at phosphorus by shifting of the equilibrium $\underline{1} + X_2 \rightleftharpoons \underline{2} \rightleftharpoons \underline{3}$ towards selenonium salt 3.

ACKNOWLEDGEMENT

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REFERENCES

1. B. Krawiecka, J. Michalski and E. Tadeusiak, J.Am.Chem.Soc., 102, 6582 (1980) and references cited therein.
2. B. Krawiecka, J. Michalski and E. Tadeusiak, ACS Symposium Series, 171, 525 (1981).
3. V. Krishnan and R. Zingaro in Selenium, edited by R.A. Zingaro and W.C. Cooper (Van Nostrand Reinhold Company, New York, Cincinnati, Toronto, London, Melbourne, 1974), p. 367.