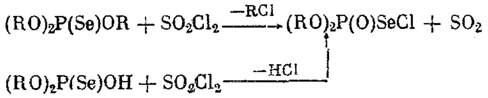
8. B. Tashkhodzhaev, L. G. Vorontsova, and F. D. Alashev, Zh. Strukt. Khim., 17, 886 (1976); Ya. L. Gol'dfarb, S. Z. Taits, F. D. Alashev, B. Tashkhodzhaev, L. G. Vorontsova, and O. S. Chizhov, First All-Union Conference on Organic Crystal Chemistry, Report Summaries [in Russian], Zinatne, Riga (1975), p. 52.
9. E. J. Corey and K. C. Nicolaou, J. Am. Chem. Soc., 96, 5614 (1974).
10. H. Hunsdieker and H. Erlbach, Chem. Ber., 80, 129 (1947).
11. L. Kaper, J. U. Veenland, and T. J. de Boer, Spectrochim. Acta, A23, 2605 (1967).
12. Ya. L. Gol'dfarb and P. A. Konstantinov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 121 (1959).
13. G. Bennett, W. H. Beaumont, and P. R. M. Brown, Veterinary Record, 235 (1974).
14. D. B. R. Johnston, C. A. Sawicki, T. B. Widholz, and A. A. Patchett, J. Med. Chem., 13, 941 (1970); R. H. Hurd and D. H. Shah, J. Med. Chem., 16, 543 (1973); C. A. Peters and R. N. Hurd, J. Med. Chem., 18, 215 (1975).
15. D. H. Shah and R. N. Hurd, US Patent No. 3839363 (1974); Chem. Abstr., 82, 31278 (1975); H. L. Wehrmeister and D. E. Robertson, J. Org. Chem., 33, 4173 (1968).
16. E. L. Eliel and A. W. Burgstahler, J. Am. Chem. Soc., 71, 2251 (1949).
17. W. Carruthers, A. G. Douglas, and J. Hill, J. Chem. Soc., 704 (1962).

REACTION PRODUCTS OF SELENOPHOSPHORUS ACID ESTERS WITH SULFURYL CHLORIDE

E. V. Bayandina, R. Kh. Giniyatullin,
and I. A. Nuretdinov

UDC 542.91:547.1'118

It was shown [1, 2] that selenophosphorus acid esters and free selenophosphorus acids react with So_2Cl_2 to form phosphorylated selenyl chlorides



$$(RO)_2P(Se)OR + SO_2Cl_2 \xrightarrow{-RCl} (RO)_2P(O)SeCl + SO_2$$
$$(RO)_2P(Se)OH + SO_2Cl_2 \xrightarrow{-HCl}$$

The phosphorylated selenyl chlorides were not characterized owing to their extreme thermolability.

It should be noted that the phosphorylated sulfenyl chlorides obtained by reaction of thiophosphorus acid derivatives with SO_2Cl_2 are considerably more stable products [3-5].

In the present work, we have investigated the reaction of selenophosphorus acid esters with SO_2Cl_2 to form different organoselenophosphorus compounds.

The reaction of the selenophosphorus acid esters with SO_2Cl_2 was conducted in $CHCl_3$ or toluene at −30 to −20°. The products decomposed on contact with moist air.

It was found that the elementary analyses and ^{31}P NMR data of a number of the products were at variance with the postulated formation of phosphorylated selenyl chlorides. In a preliminary communcation [6] we showed that the reaction of aryl selenophosphate esters with SO_2Cl_2 gives chloroselenophosphonium salts. Thus, it is common to all the reactions investigated that SO_2 is evolved; this was determined in the distillate of volatile products and solvent with the aid of an aqueous SeO_2 solution [7].

The stability of the selenophosphate reaction products depends on the nature of the substituents on the phosphorus atom. Thus, the reaction product of O,O-diphenyl O-ethyl selenophosphate with SO_2Cl_2 is stable up to 44°, while the analogous reaction of O,O,O-trimethyl selenophosphate with SO_2Cl_2 gives a substance which decomposes in solution at 5°.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 153-156, January, 1977. Original article submitted November 17, 1975.

TABLE 1

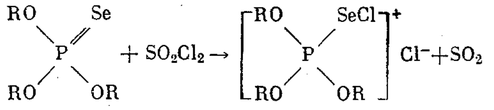
Starting material	^{31}P chemical shift, ppm	
	starting material	reaction product
$(C_6H_5O)_2P(Se)OC_2H_5$	−63	−31
$C_6H_5OP(Se)(OC_2H_5)_2$	−68	−34
$(C_2H_5O)_3PSe$	−73	−40 *
i-$C_4H_9OP(Se)(OCH_3)_2$	−77	−42 *
$C_6H_5P(Se)(OC_2H_5)_2$	−94	−72
$C_2H_5P(Se)(OC_2H_5)_2$	−108	−90 *

*At −20°.

On studying the ^{31}P NMR spectra of the reaction products indicated in Table 1, we found that the shielding of the ^{31}P nucleus in these compounds is always stronger than in the starting materials. These data are in accord with a phosphonium structure. It was shown in [8, 9] that similar changes in ^{31}P chemical shift (CS) occur on passing from neutral organic seleno- and thiophosphorus compounds to phosphonium derivatives.

It is known that there is little difference between the ^{31}P chemical shifts of organic seleno- and thiophosphorus compounds of the same type [10, 11]. Dialkyl selenophosphates have a ^{31}P CS in the vicinity of −20 ppm [12]. On the basis of this, we can conclude that compounds of general formula $(RO)_2P(O)SeCl$ will also have a CS in the vicinity of −20 ppm. As can be seen from Table 1, however, the CS values of the reaction products of the selenophosphates with SO_2Cl_2 are somewhat higher. These data, and also the elementary analyses of the products, give us to reason to suppose that the selenophosphate esters react with SO_2Cl_2 to form products with a different structure from the phosphorylated selenyl chlorides of [1, 2].

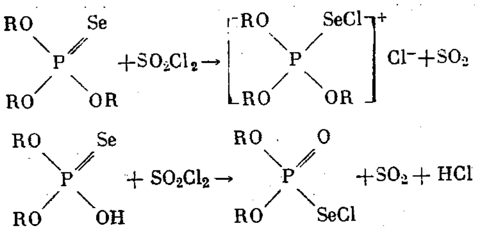
The general scheme for these reactions can be represented as follows:



As indicated above, the reaction product of O,O,O-triethyl selenophosphate and O,O-diethyl selenophosphoric acid with SO_2Cl_2 is one and the same, viz., O,O-diethyl Se-chloro selenophosphate [1, 2]. In view of the results that we have obtained by investigating the reaction of selenophosphate esters wtih SO_2Cl_2, it would be of interest to study the reaction of O,O-dialkyl selenophosphoric acids with SO_2Cl_2. After removing the volatile products and part of the solvent under vacuum at low temperature, we recorded the ^{31}P NMR spectra. The ^{31}P chemical shifts of the reaction products of O,O-dialkyl selenophosphoric acids with SO_2Cl_2 are in the vicinity of −20 ppm. When heated to >0-5°, these substances decompose to form elemental selenium.

The similarity in the ^{31}P NMR parameters of seleno- and thiophosphorus acid derivatives has been noted above [10, 11]. Therefore, on the assumption that O,O-dialkyl selenophosphoric acids react with SO_2Cl_2 to form phosphorylated selenyl chlorides, we prepared O,O-diethyl S-chloro thiophosphate and studied its ^{31}P NMR spectrum. This compound was prepared by reacting the O,O,O-triethyl thiophosphate with SO_2Cl_2 [3]. The ^{31}P CS of O,O-diethyl S-chloro thiophosphate is −19 ppm. Thus, we can conclude that O,O-dialkyl selenophosphoric acids react with SO_2Cl_2 to form O,O-dialkyl Se-chloro selenophosphates.

We can regard it as proven that, in contrast to the data in [1, 2], selenophosphate triesters and free selenophosphoric acids react with SO_2Cl_2 to form products with different structures



It has been established that when some of the crystalline products of the above reactions are heated, they decompose to form alkyl halide (identified by GLC) and elemental selenium. The phosphorus-containing substance remaining after decomposition is the corresponding chlorophosphate.

It is quite possible that the decomposition of the chloroselenophosphonium salt proceeds via alkyl chloride elimination and formation of a phosphorylated selenyl chloride, which decomposes to the chlorophosphate and elemental selenium under these conditions.

EXPERIMENTAL

The ^{31}P NMR spectra of $CHCl_3$ solutions of the selenophosphonium salts were obtained using a KGU-4 instrument with a working frequency of 10.2 MHz, at −20° in the case of thermolabile substances and at ~20° in the other cases. The chemical shifts are given relative to 85% H_3PO_4 as external standard.

The substances were purified by reprecipitation from chloroform with ether. After removal of all traces of solvent under a vacuum of ~0.06 mm at 0° for 2 h, some of the compounds had a definite melting point. The melting point of substances decomposing below 20° was determined under a layer of dry VM-1 mineral oil.

Reaction of O-Phenyl O,O-Diethyl Selenophosphate with SO_2Cl_2 (Standard Experiment). A chloroform solution of 2.3 g SO_2Cl_2 (1:2) was added dropwise at −20° to a stirred solution of 5.0 g O-phenyl O,O-diethyl selenophosphate in $CHCl_3$ (1:2). The mixture was kept at −20° for 30 min, and the volatile products were evacuated with a water-jet pump through a trap cooled with liquid nitrogen, and then passed through an aqueous solution of SeO_2. The amount of selenium liberated (0.63 g) was used to determine the amount of SO_2 (1.03 g, 94.5%). The reaction mixture was then treated with 70 ml ether. After 1 h at −0°, the solvent was decanted off from the precipitated crystals, which were repeatedly treated with ether and dried at 0.06 mm and 0° for 2 h to give 4.6 g (74.0%) of phenoxydiethoxychloroselenophosphonium chloride, mp 33-34°, $\delta_{^{31}P} = -34.0$ ppm. Found: C 33.47; H 4.29; P. 8.11%. $C_{10}H_{15}Cl_2O_3PSe$. Calculated: C 32.97; H 4.12; P 8.52%.

Analogously, 4.5 g (70.7%) of diphenoxyethoxychloroselenophosphonium chloride was prepared at −20 to −30° from 5.7 g of O-ethyl O,O-diphenyl selenophosphate in $CHCl_3$ (1:2) and 2.28 g of SO_2Cl_2 in $CHCl_3$ (1:2), mp 38-39°, $\delta_{^{31}P} = -31.0$ ppm. Found: C 41.13; H 3.64; P 7.52%. $C_{14}H_{15}Cl_2O_3PSe$. Calculated: C 40.78; H 3.43; P 7.52%.

Reaction of 4.9 g O,O-diethyl phenylselenophosphonate in 5 ml $CHCl_3$ with 2.4 g SO_2Cl_2 in 3 ml $CHCl_3$ at −20 to −30° gave 3.6 g (65.2%) of diethoxychloroselenophenylphosphonium chloride, mp 31-32°, $\delta_{^{31}P} = -72$ ppm. Found: C 34.59; H 3.95; P 8.48%. $C_{10}H_{15}Cl_2O_2PSe$. Calculated: C 34.48; H 4.31; P 8.90%.

Reaction of 10.0 g O,O-diethyl ethylselenophosphonate in 10 ml $CHCl_3$ with 5.9 g SO_2Cl_2 in 6 ml $CHCl_3$ at −30° gave a substance with a mp of −14°,* decomposition point 11-12°, $\delta_{^{31}P} = -90$ ppm.

Reaction of 10.0 g O,O-dimethyl O-isobutyl selenophosphate in 10 ml $CHCl_3$ with 5.5 g SO_2Cl_2 in 6 ml at −20 to −30° gave a substance with $\delta_{^{31}P} = -42$ ppm.

Reaction of 20.0 g triethyl selenophosphate in $CHCl_3$ (1:2) with 11.02 g SO_2Cl_2 in $CHCl_3$ (1:2) at −30° gave a substance with $\delta_{^{31}P} = -40$ ppm, which decomposed at 5°.

Reaction of O,O-Diethyl Selenophosphoric Acid with SO_2Cl_2. A solution of 3.1 g SO_2Cl_2 in 5 ml toluene was added at −40 to −45° to a stirred solution of 5.0 g O,O-diethyl selenophosphoric acid in 5 ml toluene. The mixture was stirred at the same temperature for 0.5 h. The volatile products were distilled off under a vacuum of ~10 mm to give a substance with a $\delta_{^{31}P}$ of −22 ppm at −20°.

Analogously, reaction of 7.0 g O,O-di-n-butyl selenophosphoric acid in 10 ml toluene with 3.5 g SO_2Cl_2 in 5 ml toluene at −40 to −45° gave a substance with a $\delta_{^{31}P}$ of −17 ppm at −20°.

Reaction of 7.5 g O,O,O-triethyl thiophosphate in 10 ml toluene with 5.11 g SO_2Cl_2 in 5 ml toluene at −5° gave 3.86 g (49.8%) of O,O-diethyl S-chloro thiophosphate, bp 30-31°/0.08 mm, $n_D^{20} = 1.4668$, $\delta_{^{31}P} = -19$ ppm. According to [3], bp = 49-50°/0.02 mm, $n_D^{20} = 1.4672$.

Decomposition of Phenoxydiethoxychloroselenophosphonium Chloride. Phenoxydiethoxychloroselenophosphonium chloride (6.8 g) was heated to 40° for 10 min. Violent decomposition occurred with evolution of alkyl chloride, which was identified by GLC. In addition, 1.45 g selenium was formed, this amount corresponding to the theoretical amount (1.48 g). Distillation of the decomposition products gave 1.2 g (29.1% yield) of O-phenyl O-ethyl chlorophosphate, bp 78-79°/0.05 mm, $n_D^{20} = 1.5015$, $d_4^{20} = 1.2420$, $\delta_{^{31}P} = +3.5$ ppm. Found: P 14.07%; MR 52.34. $C_8H_{10}ClO_3P$. Calculated: P 14.06; MR 51.13.

---

*Melting point determined under a layer of dry mineral oil.

CONCLUSIONS

Selenophosphorus acid esters react with SO_2Cl_2 to form chloroselenophosphonium salts, while reaction of O,O-dialkyl selenophosphoric acids with SO_2Cl_2 under analogous conditions gives O,O-dialkyl Se-chloro selenophosphates.

LITERATURE CITED

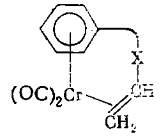
1. J. Michalski and A. Markowska, Dokl. Akad. Nauk SSSR, 136, 108 (1961).
2. A. Markowska, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 15, 153 (1967).
3. J. Michalski and A. Skowronska, Chem. Ind., 1199 (1958).
4. Cz. Borecki, J. Michalski, and St. Musierowiez, J. Chem. Soc., 4081 (1958).
5. Yu. G. Gololobov and V. V. Semidetko, Zh. Obshch. Khim., 36, 950 (1966).
6. I. A. Nuretdinov, R. Kh. Giniyatullin, and E. V. Bayandina, Izv. Akad. Nauk SSSR, Ser. Khim., 726 (1975).
7. I. I. Nazarenko and A. N. Ermakov, Analytical Chemistry of Selenium and Tellurium [in Russian], Nauka (1971), p. 28.
8. I. A. Nuretdinov, N. A. Buina, and N. P. Grechkin, Izv. Akad. Nauk SSSR, Ser. Khim., 169 (1969).
9. A. Schmidpeter and B. Brecht, Z. Naturforsch., 24, 179 (1969).
10. E. I. Loginova, Dissertation, Kazan (1972).
11. M. Grayson and E. Griffith (editors), Topics in Phosphorus Chemistry, Wiley, New York (1967), p. 5.
12. N. P. Grechkin, I. A. Nuretdinov, N. A. Buina, and L. K. Nikonorova, Chemistry and Use of Organophosphorus Compounds [in Russian], Nauka (1972), p. 350.

REACTION OF THE CARBONYLS OF GROUP VI METALS WITH BENZONITRILE AND ω-CYANOALKYLBENZENES

A. N. Nesmeyanov, V. S. Kaganovich,
V. V. Krivykh, and M. I. Rybinskaya

UDC 542.91:541.49:547.582.4:546.765

Earlier we reported [1] on the production of new chelate complexes of type (I):



(I)

$X = (CH_2)_n$ $(n = 2 - 4)$; OCH_2

In a continuation of research into the possibility of synthesizing complexes of such a type from group VI metals with other chelate groups we synthesized the ω-cyanoalkyl derivatives of arenechromium tricarbonyls and tried to obtain chelates from them.

In order to obtain the arenemetal tricarbonyl complexes we again studied the reaction of the hexacarbonyls of group VI metals with ω-cyanoalkylarenes, in spite of the fact that (according to [2]) nitriles, including those containing an arene ring, only give complexes of the $(RCN)_nM(CO)_{6-n}$ type (where n = 1-3) at the nitrogen atom. It should be noted that only reactions with nitriles in which the CN group is directly attached to the aromatic ring or is separated from it by one CH_2 unit have so far been investigated. It seemed of interest to determine whether the outcome of the reaction of group VI metal carbonyls with arene-containing nitriles would be affected by different degrees of separation of the CN group from the aryl ring, by the nature of the metal,

---

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 156-160, January, 1977. Original article submitted November 27, 1975.