ACID MONOCHLORIDES OF PHOSPHORUS AMIDOSELENO ACIDS AND THEIR PROPERTIES

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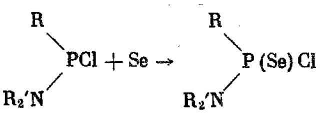
The synthesis and properties of acid chlorides of phosphorus seleno acids have been studied very little. Only several acid chlorides of alkylselenophosphinic, and of diethyl- and diphenylselenophosphoric acids have been reported [1-4]. No information is available on the properties of acid chlorides of phosphorus amidoseleno acids. In this article we give the results on the study of the conditions in the synthesis of acid chlorides of different phosphorus amidoseleno acids and some of their reactions with nucleophilic reagents.

It was found that acid chlorides of tetraalkyldiamidophosphorous acids reacted at 120-130°C with elemental selenium. A vacuum distillation of tetraalkyldiamidoselenochlorophosphates yielded liquids of high specific gravity which were soluble in most organic solvents and fairly sensitive toward the action of liquid air. The constants of diamidoselenochlorophosphates are given in Table 1 (compounds I, II). The addition of selenium to acid chlorides of morpholidoethylphosphinic and diethylamidophenylphosphinic acids takes place under similar conditions. The acid chloride of morpholidoethylselenophosphinic acid (VII) is a liquid whereas the acid chloride of diethylamidophenylselenophosphoric acid (VIII) is a crystalline solid. The reaction of acid chlorides of dialkylamidoalkyl(aryl)phosphorous acids with selenium proceeds at higher temperatures (130-160°). These reaction products frequently show the yellowish color of the liquid (Table 1, compounds III-VI).

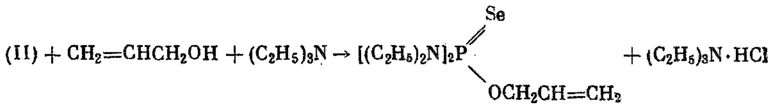
The IR spectra provide a good confirmation of the structure of acid chlorides of phosphorus amidoseleno acids. The most characteristic absorption for the compounds obtained by us was in the region of valence vibrations of P–Cl and P=Se groups. The spectra of all acid chlorides of phosphorus amidoseleno acids show good absorption in the 475-500 cm^{-1} region, corresponding to vibrations of the P–Cl groups [5]. No reliable correlations for vibration frequencies of the P=Se group have been reported in the literature. Some contradictory data obtained in the study of IR spectra of phosphorus seleno acid derivatives [6-8] can possibly be attributed to the small number of compounds studied. IR spectra of I-VIII display an absorption band in the 560 cm^{-1} region, which, we believe, belongs to P = Se group vibrations and this agrees with the data on the IR spectra of the acid dichloride of methylselenophosphinic acid [8] (Fig. 1a-1c). Thus, the reaction of acid chlorides of amido acids of trivalent phosphorus with selenium proceeds with the formation of acid chlorides of the corresponding phosphorus seleno acids



$$(R)(R'_2N)PCl + Se \rightarrow (R)(R'_2N)P(Se)Cl$$

R = alkyl, aryl R_2N, RO, ArO, R' = alkyl

A study has been made of the reactions of the selenochlorophosphates with some nucleophilic reagents. Thus, the reaction of II with allyl alcohol in the presence of triethylamine gave the tetraethylamide of allylselenophosphoric acid (IX)



$$(II) + CH_2{=}CHCH_2OH + (C_2H_5)_3N \rightarrow [(C_2H_5)_2N]_2P({=}Se)OCH_2CH{=}CH_2 + (C_2H_5)_3N \cdot HCl$$

(IX)

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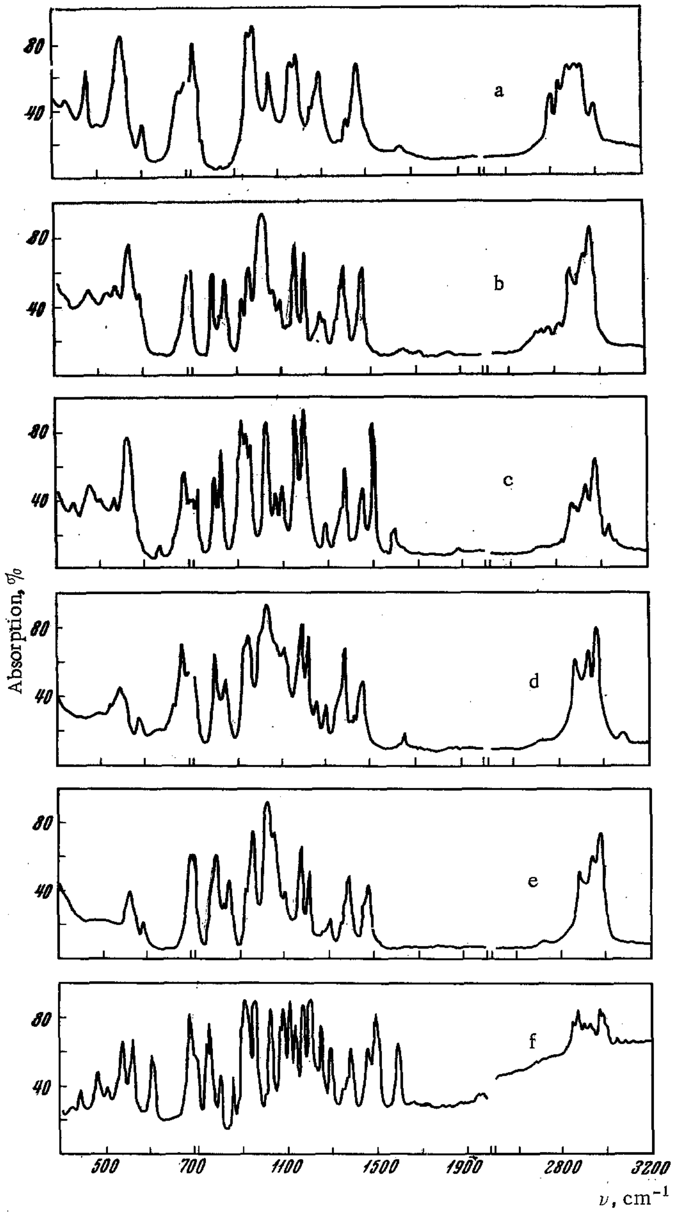
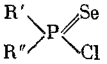
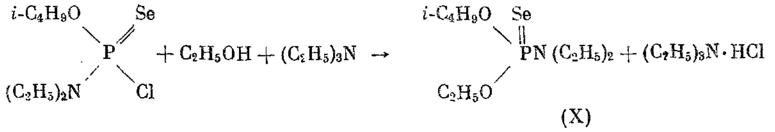


Fig. 1. IR spectra: (a) acid chloride of tetramethyldiamidoselenophosphoric acid; (b) acid chloride of isobutyldiethylamidoselenophosphoric acid; (c) acid chloride of phenyldiethylamidoselenophosphoric acid; (d) tetraethyldiamidoallylselenophosphoric acid; (e) diethylamide of O-isobutyl-O-ethylselenophosphoric acid; (f) morpholido-phenyldiethylamidoselenophosphoric acid (in vaseline oil).

IR spectrum of IX fully confirms the assumed structure (Fig. 1d). No absorption bands characteristic of the P—Cl group are given, whereas absorption bands characteristic of the double bond (1650, ν_{CH} 3080 cm^{-1}) are shown clearly. VI reacted readily with ethyl alcohol in the presence of a base to yield the diethylamide of O-isobutyl-O-ethylselenophosphoric acid (X).

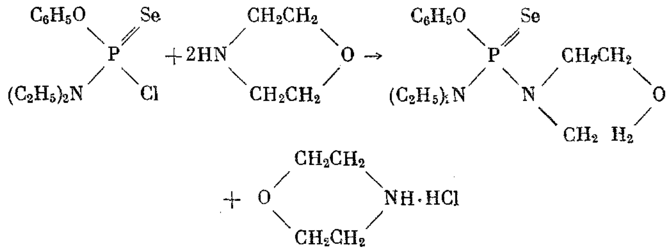
TABLE 1. Acid Monochlorides of Phosphorus Seleno Acids of General Formula: 

No. of compound	R′	R″	Yield, %	Bp (p, mm Hg)	d_4^{20}	n_D^{20}	Phosphorus, %	
							Found	Calculated
I	$(CH_3)_2N$	$(CH_3)_2N$	64,5	69 (0,1)	1,4114	1,5508	13,42	13,27
II	$(C_2H_5)_2N$	$(C_2H_5)_2N$	70,4	97 (0,5)	1,2558	1,5290	10,47	10,70
III	C_2H_5O	$(C_2H_5)_2N$	71,2	70—71 (0,1)	1,3114	1,5075	11,56	11,80
IV	C_4H_9O	$(C_2H_5)_2N$	68,1	74 (0,08)	1,2565	1,5048	10,58	10,67
V	C_6H_5O	$(C_2H_5)_2N$	63,6	123—125 (0,1)	1,3707	1,5660	10,08	9,93
VI	$CH_3C_6H_4O$	$(C_2H_5)_2N$	64,0	121—122 (0,07)	1,3390	1,5620	10,00	9,55
VII	C_2H_5		73,4	117—118 (0,2)	1,5054	1,5773	11,81	11,90
VIII	C_6H_5	$(C_2H_5)_2N$	60,1	Mp 42	—	—	10,42	10,52



(X)

A reaction of VII with morpholine yielded the phenyl ester of diethylamidomorpholidoselenophosphoric acid (XI).



The structure of X and XI was confirmed by elemental analyses and IR spectra (Fig. 1e, 1f).

EXPERIMENTAL

Preparation of II (typical experiment). A mixture of 23 g of acid chloride of tetraethyldiaminophosphorous acid and 8.63 g of a fine powder of selenium was heated with stirring to 120° and kept at this temperature for 10 min. With the temperature elevation to 130° all the selenium was dissolved. After cooling, the mixture was transferred to an Arbuzov flask and distilled. Yield 22.3 g (70.4%) of II with constants given in Table 1. I and III-VIII were prepared in a similar manner.

Reaction of VI with Ethyl Alcohol. Nine grams of VI in 30 ml of petroleum ether (40-70°) was added to a solution of 1.4 g of ethyl alcohol and 3.1 g of triethylamine in 100 ml of petroleum ether. The addition of VI was carried out while stirring and cooling to −5-0°. After the removal of triethylamine hydrochloride precipitate the solvent was evaporated in vacuo and the residue distilled. Yield 7.4 g (80.4%) of amide X, bp 74-75° (0.1 mm); d_4^{20} 1.1630; n_D^{20} 1.4820. Found: P 10.45; N 4.78%. $C_{10}H_{24}NO_2PSe$. Calculated: P 10.33; N 4.66%.

Amide IX was prepared by a similar procedure; bp 82-83° (0.05 mm); d_4^{20} 1.1619; n_D^{20} 1.5102. Yield 71%. Found: N 8.72; 8.68%. $C_{11}H_{25}N_2OPSe$. Calculated: N 9.00%.

Reaction of VII with Morpholine. A solution of 13 g of VII in 30 ml of benzene was added with stirring at a temperature of ~10° to a solution of 7.28 g of morpholine in 70 ml of benzene. After stirring for 2 h, the precipitate of morpholine hydrochloride was filtered off. The solvent was removed in vacuo. On the next day the residue crystallized. After recrystallization from petroleum ether, the mp was 61-62°. Yield 60%. Found: N 7.73; P 8.88%. $C_{14}H_{23}N_2OPSe$. Calculated: N 7.75; P 8.58%.

IR spectra were obtained on spectrophotometer UR-10 (liquid drops between KBr plates for I-X, emulsion in vaseline oil for XI).

CONCLUSIONS

1. Acid chlorides of various phosphorus amidoseleno acids were prepared and their IR spectra and chemical properties studied.

2. The acid chlorides of phosphorus amidoseleno acids reacted readily with alcohols and amines to yield the corresponding esters and amides of phosphorus seleno acids.

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