CONCLUSIONS

In the presence of SbF_5 sulfur trioxide undergoes insertion reactions into the allylic C–F bonds of perfluoro-2-alkenes to give perfluoroalk-2-enyl fluorosulfates.

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SYNTHESIS AND STRUCTURE OF N-ETHYL-N-PROPARGYLPHOSPHONAMIDIC CHLORIDES

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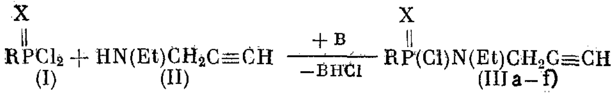
UDC 542.91:541.6:547.
1'118

Acetylenic organophosphorus compounds present interest as biologically active substances [1] and intermediate products in organic synthesis [2, 3]. Acid halides of N-propargylamidoacids of phosphorus are important initial compounds in the production of various organophosphorus compounds since the halogen atom is readily substituted on interacting with nucleophilic reagents. The synthesis of the acid dichlorides of some N-alkylpropargylamidophosphoric and thiophosphoric acids was described in the brief communication [4].

The present work describes the production of N-ethyl-N-propargylphosphonamidic, phosphonamidothioic, and phosphonamidoselenoic chlorides by reaction of the corresponding phosphonic dichloride (I) with N-ethyl-N-propargylamine (II) in the presence of base



$$\underset{(I)}{R\overset{\overset{X}{\|}}{P}Cl_2} + \underset{(II)}{HN(Et)CH_2C{\equiv}CH} \xrightarrow[-BHCl]{+B} \underset{(IIIa-f)}{R\overset{\overset{X}{\|}}{P}(Cl)N(Et)CH_2C{\equiv}CH}$$

R = Et, X = O (a); R = Et, X = S (b); R = Et, X = Se (c); R = Ph, X = O (d);
R = Ph, X = S (e); R = Ph, X = Se (f); B = Et_3N.

The compounds (IIIa-f) were obtained in an inert atmosphere in dry solvent. Compounds (IIIa-e) are liquids which are distilled *in vacuo*; but (IIIf) is a crystalline substance. It should be noted that the derivatives of selenophosphonic acids (IIIc) and (IIIf) are unstable in the presence of moisture in the air. The structure and the purity of the compounds obtained are confirmed by spectra methods and elemental analysis. The constants and some spectral characteristics of (IIIa-f) are presented in Table 1. A doublet characteristic of vibrations of the ≡C–H bond is observed in the IR spectra of (IIIa) and (IIId) in the region of 3200-3300 cm^{-1}, whereas one absorption band is observed in the spectra of the thio

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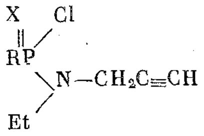
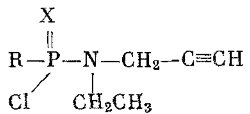
0568-5230/85/3408-1718$09.50

TABLE 1. Constants and Spectral Parameters for Compounds of General Formula



R	X	Yield, %	bp, °C (p, mm Hg), mp, °C	d_4^{20}	n_D^{20}	Found/calculated, %			δ^{31} P, ppm	IR spectrum, cm^{-1}	
						C	H	P		νC≡C	ν≡CH
Et	O	38,0	75 (0,05)	1,1318	1,4830	43,26 43,41	6,92 6,72	15,91 16,02	+29	2125	3242 3311
Et	S	64,3	71–72 (0,015)	1,1571	1,5361	40,06 40,09	6,90 6,20	14,83 14,79	+100	2121	3300
Et	Se	68,7	90–92 (0,008)	1,3807	1,5659	31,82 32,75	5,14 5,07	12,06 12,08	+96	2122	3300
Ph	O	56,5	115–117 (0,005)	1,1406	1,5440	54,78 54,66	5,50 5,38	12,76 12,84	+38	2118	3230 3302
Ph	S	58,6	126–127 (0,02)	1,2278	1,5940	51,56 51,26	5,21 5,05	12,45 12,04	+86	2125	3309
Ph	Se	63,0	57	–	–	43,66 43,35	4,49 4,27	10,28 10,19	+74	2130	3310

TABLE 2. Parameters of the PMR Spectra of the N-Propargyl Group in the Compounds of General Formula



(δ, ppm , J, Hz, $J_{\mathrm{H_A C\equiv CH}}=J_{\mathrm{H_B C\equiv CH}}=2{,}4$)

Compound	R	X	δH_A	δH_B	$\Delta\delta H_A - H_B$	δCH	$J_{H_AH_B}$	J_{PNCH_A}	J_{PNCH_B}
(IIIa)	Et	O	4,04	3,84	0;20	2,36	18,2	11.2	15,5
(IIIb)	Et	S	4,26	3,87	0,39	1,97	18,2	12,0	19,8
(IIIc)	Et	Se	4,35	3,91	0,44	1,97	18,3	12,0	20,7
(IIId)	Ph	O	3,78	3,66	0,11	2,04	18,1	12,5	14,5
(IIIe)	Ph	S	4,04	3,79	0,25	1,91	18,3	12,9	18,3
(IIIf)	Ph	Se	4,10	3,80	0,30	1,87	18,4	13,2	18,8

and seleno derivatives (IIIb, c, e, f). This is explained by the presence of strong intermolecular bonding of the acetylenic proton with the oxygen of the P=O group in (IIIa) and (IIId). The P=S and P=Se groups are weaker proton acceptors and evidently do not participate in such hydrogen-bonding. This is shown by the single absorption band in the region of 3300 cm^{-1}.

The chemical shift (CS) of the acetylene proton of the propargyl group in the PMR spectra is strongly dependent on the environment at the P atom. In the case of (IIIa) and (IIId), a characteristic shift of the signal of the acetylene proton to weak field is observed. This is in conformity with the data of IR spectroscopy on the participation of this proton in the hydrogen bond with the P=O group.

In Table 2 are presented the CSs and spin–spin coupling constants of the protons of the N-propargyl group. It is evident from the PMR spectrum of compound (IIIa) (Fig. 1) that the methylene protons of the N-propargyl fragment are nonequivalent. The diastereotopicity of these protons is determined by the asymmetry of the fragment with the P atom [5]. It should be noted that the difference in CSs of the protons of the propargyl group reaches 0.44 ppm for compound (IIIc) and decreases in transposing to the thiophosphonic and phosphonic analogs (IIIb) and (IIIa) to 0.38 and 0.20 ppm, respectively. Analogous changes are also observed for the phenylphosphonates (IIId, e, f), although $\Delta\delta H_A H_B$ does not exceed 0.30 ppm in this series.

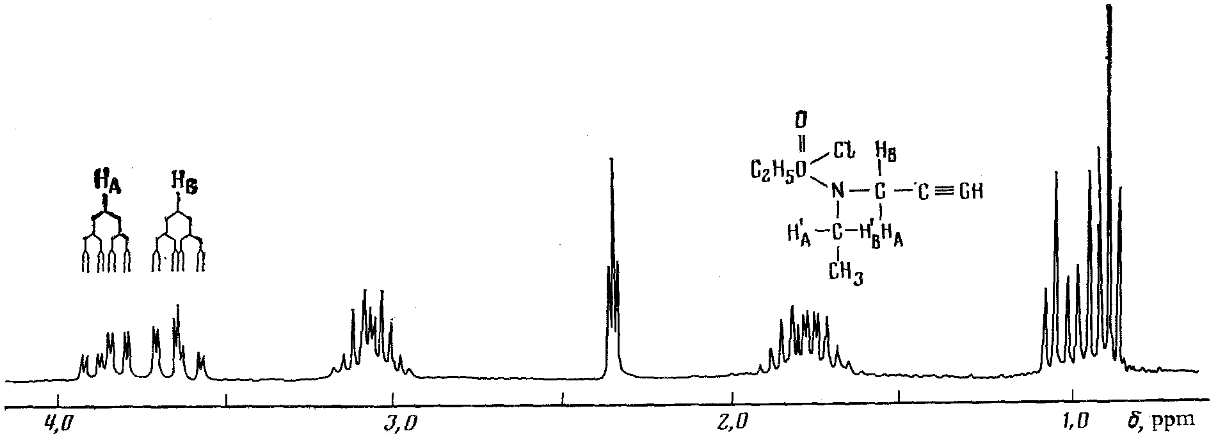


Fig. 1. The PMR spectrum of (IIIa).

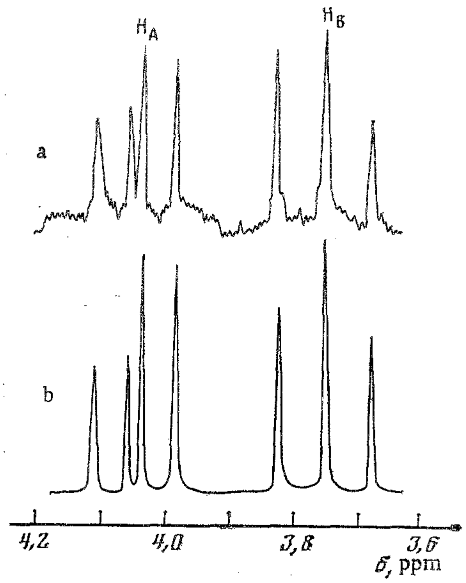


Fig. 2. The PMR spectrum of the methylene protons of the propargyl group of (IIIf) with suppression of the acetylenic proton (a) and the theoretical spectrum (b).

The diastereotopic protons H_A and H_B of the N-propargyl fragment form an ABX system with suppression of the spin–spin coupling with the acetylene proton (Fig. 2). The geminal constant $J_{H_AH_B}$ is little dependent on the nature of the other substituents on the P atom, and its magnitude changes in the limits 18.2 ± 0.2 Hz, whereas J_{PNCH_A} and J_{PNCH_B} differ strongly. It should be noted that J_{PNCH_B} significantly depends on the nature of X in the group P=X, and increases from 15.5 Hz for (IIIa) to 20.7 Hz for (IIIc). It is interesting that the methylene protons of the propargyl group in N-ethyl-N-propargyldichlorophosphates are equivalent. This is determined by the absence of chirality.

Investigation of the spectra of the N-ethyl fragment with suppression of the spin–spin coupling of the protons of the methyl group rendered apparent the diastereotopicity of the methylene protons H_A' and H_B'. For compound (IIId), the following constants were determined: $J_{H_A'H_B'}$ = 14.3 Hz, $J_{PNCH_A'}$ = 11.1 Hz, and $J_{PNCH_B'}$ = 13.2 Hz. The CSs of these protons differ by 0.08 ppm. This part of the work on the diastereotopicity of the protons in the NCH_2R group will be considered separately in greater detail.

EXPERIMENTAL

PMR spectra were taken on a Bruker WM-250 spectrometer with a working frequency of 250.132 MHz in benzene. CSs were measured relative to TMS. Theoretical PMR spectra were computed on an ASPECT-2000 computer. The ^{31}P NMR spectra were obtained on a KGU-4 spectrometer with suppression of the spin–spin coupling of the ^{31}P and ^1H nuclei. The working frequency was 10.2 MHz. IR spectra were recorded on a UR-20 spectrophotometer (a drop of liquid between disks of KBr).

General Method for Obtaining N-Ethyl-N-propargylphosphonamidic Chlorides (IIIa-f). To a solution of 0.05 mole of the dichloride (I) in 100 ml of abs. ether or benzene at 0°C was added a mixture of 0.05 mole of (II) and 0.05 mole of Et_3N in 20 ml of abs. ether. The mixture was stirred for 1 h at ∿20°C. The residue was separated. The filtrate was concentrated, and the residue was distilled *in vacuo*. In the case of (IIIf), the residue was washed with hot petroleum ether, and the solution was decanted. White crystals were obtained on concentration *in vacuo*.

CONCLUSIONS

N-Ethyl-N-propargylethyl(phenyl)phosphonamidic, -phosphonamidothioic, and -phosphonamidoselenoic chlorides were obtained.

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REACTION OF MONOVALENT GOLD COMPLEX SALTS WITH FERROCENE THIO DERIVATIVES

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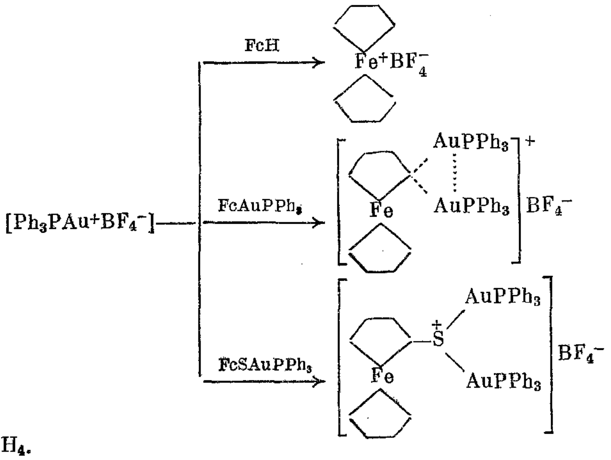
UDC 542.91:541.49:546.59-38:547.1'13:546.72

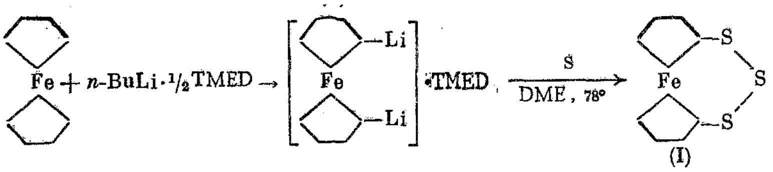
In our previous work [1, 2], we showed that incompletely coordinated and reactive triphenylphosphinegold tetrafluoroborate oxidizes ferrocene at the iron atom and the reaction with ferrocenyl(triphenylphosphine)gold proceeds at the gold atom to give a binuclear organogold complex $[C_5H_5FeC_5H_5(AuPPh_3)_2]^+BF_4^-$ with an Au—Au bond [1, 2]. If the gold atom is removed from the ferrocenyl ring by a sulfur atom, the attack of $[AuPPh_3]^+BF_4^-$ proceeds at the sulfur atom to form a binuclear gold-containing sulfonium complex [3]



$Fc = C_5H_5FeC_5H_4$.

Thus, we expected that the reaction of aurous complex salts $[Ph_3PAu]^+BF_4^-$ and $[(Ph_3PAu)_3O]^+BF_4^-$ with various ferrocene thio derivatives would lead to new gold-containing complexes. We studied the reaction of aurous complex salts with 1,2,3-trithia[3]ferrocenophane (I) [4] and 1,1'-ferrocenylenedithiol (II) [4, 5].

Starting compounds (I) and (II) were synthesized by the procedures of Davison et al. [4]. The reaction of $[(C_5H_4Li)_2Fe]\cdot$TMED (TMED = tetramethylethylenediamine) with sulfur gave (I) in 72% yield, while (II) was obtained by the reduction of (I).



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0568-5230/85/3408-1722$09.50