The Syntheses of Some Phosphonates and Sulfides Containing a Fluorovinyl Group

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As far as we know, little information has appeared in the literature concerning the syntheses of phosphonates and sulfides[1] containing a fluorovinyl group. In earlier papers, the radiation-induced addition reactions of dialkyl phosphonates[2] and thiols[3] to chlorofluoroethylenes were reported to give the corresponding 1 : 1 adducts, the dialkyl chlorofluoroethylphosphonates (I) and the alkyl chlorofluoroethyl sulfides (II). These 1 : 1 adducts were found to produce, in fair yields, the corresponding dialkyl fluorovinylphosphonates (III) and alkyl fluorovinyl sulfides (IV) by dechlorination with zinc dust in ethanol or diglyme. The yields and physical properties of the new phosphonates and sulfides with a fluorovinyl group are shown in Table 1.

$$\mathrm{CFCl{=}CX_2 + HP(O)(OR)_2 \xrightarrow{\gamma\text{-ray}}}$$

$$\mathrm{CHX_2CFClP(O)(OR)_2\ (I) \xrightarrow[EtOH]{Zn}}$$

$$\mathrm{CHX{=}CFP(O)(OR)_2\ \ (III)}$$

$$(\mathrm{X} = \mathrm{F\ or\ Cl};\ \mathrm{R} = \mathrm{CH_3},\ \mathrm{C_2H_5},\ \mathrm{or}\ n\text{-}\mathrm{C_3H_7})$$

$$\mathrm{CFCl{=}CFCl + RSH \longrightarrow CHFClCFClSR\ \ (II)}$$

$$\mathrm{\xrightarrow[Diglyme]{Zn} CHF{=}CFSR\ \ (IV)}$$

$$(\mathrm{R} = \mathrm{C_2H_5}\ \mathrm{or}\ i\text{-}\mathrm{C_3H_7})$$

The structures of the products were established mainly by means of the NMR spectra[4] of the proton and fluorine. In the NMR spectra of ethers containing a $-CF{=}CHCl$ group,[5] the coupling constants between the vicinal hydrogen and fluorine in the double bond were 25 cps for the trans form and 11 cps for the cis form. For the ethers with a $-CF{=}CHF$ group,[5] the coupling constants between the vicinal hydrogen and fluorine, J_{HF}^{trans} and J_{HF}^{cis}, were 17—18 cps and 7—8 cps respectively, while those between the vicinal fluorine and fluorine, J_{FF}^{trans} and J_{FF}^{cis}, were 135—137 cps and 9—11 cps respectively. The coupling constants between the vicinal hydrogen and fluorine of the dialkyl 1-fluoro-2-chlorovinyl- and 1, 2-difluorovinylphosphonates were 24—25 cps and 17 cps respectively, indicating that these proton and fluorine are in trans position. The measured coupling constants between the vicinal fluorine and fluorine (17 cps) also supported these structures. Thus, in the dechlorination of I, an isomer whose halogen (fluorine or chlorine) and phosphorus are in the trans position was almost exclusively formed.

On the other hand, the NMR spectra of the dechlorination product from II indicated the presence of the two isomers, trans and cis, in a ratio of about two to one. The assignments of isomers to the trans and cis forms were made from the values of J_{HF} and J_{FF}, as has been described in the case of difluorovinylphosphonates. The data of the NMR spectra of the products are summarized in Tables 2 and 3.

Experimental[6]

Material. The dialkyl chlorofluoroethylphosphonates and the alkyl chlorofluoroethyl sulfides used were prepared as has been reported[2,3] previously.

The Dialkyl 1-Fluoro-2-chlorovinyl- and 1, 2-Difluorovinyl-phosphonates. To 13.1 g (0.20 g-atom) of zinc dust in a flask equipped with a nitrogen inlet and a reflux condenser, a solution of 29.9 g (0.10 mol) of di-*n*-propyl 1, 2-dichloro-1, 2-difluoroethylphosphonate in 100 m*l* of ethanol was added, drop by drop, over a 1 hr period upon heating at 90°C; the reaction mixture was then heated under a nitrogen atmosphere for an additional 2 hr. After the unreacted zinc dust had been removed by centrifugation, the solvent was distilled off. To the residue, 40 m*l* of diluted hydrochloric acid was added, and then the solution was extracted with ether. The extract was washed with water and dried. After the removal of the ether, the distillation of the residue gave 19.0 g (0.83 mol, 83% yield) of di-*n*-propyl 1, 2-difluorovinylphosphonate, bp 80—82°C/2 mmHg. The infrared spectrum of the phosphonate obtained exhibited

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[1] I. L. Knunyants, A. V. Fokin, *Izvest. Akad. Nauk. SSSR, Otdel Khim. Nauk.*, **1952**, 261; *Chem. Abstr.*, **47**, 3221 (1953).

[2] K. Inukai, T. Ueda and H. Muramatsu, *J. Org. Chem.*, **29**, 2224 (1964).

[3] K. Inukai, T. Ueda and H. Muramatsu, This Bulletin, **39**, 2191 (1966).

[4] The NMR spectra were obtained for 25% solution in carbon tetrachloride, using a JNM-C-60 high resolution NMR spectrometer (60 Mc for ^{1}H and 56.446 Mc for ^{19}F). Tetramethylsilane was used for ^{1}H as internal standard and trifluoroacetic acid for ^{19}F as external standard.

[5] H. Muramatsu, K. Inukami, Y. Iwata and S. Murakami, This Bulletin, **40**, 1284, (1967).

[6] All temperature readings are uncorrected.

TABLE 1. YIELDS AND PHYSICAL PROPERTIES OF PHOSPHONATES AND SULFIDES WITH FLUOROVINYL GROUP

R	Yield %	Bp °C/mmHg	n_D^{20}	d_4^{20}	MR_D		P, %		Cl, %		M.w.		$\nu_{C=C}$ cm^{-1}
					Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	
				$CHCl=CFP(O)(OR)_2$									
CH_3	56	64—65/2	1.4382	1.358	36.5	36.0	15.7	16.5	18.6	18.8	198	188.5	1637, 1619
C_2H_5	44	80—81/2	1.4358	1.238	45.7	45.3	13.3	14.3	16.5	16.4	218	216.5	1629
n-C_3H_7	59	105—106/2	1.4377	1.165	55.1	54.5	11.9	12.7	14.2	14.5	242	244.5	1640, 1615
				$CHF=CFP(O)(OR)_2$									
CH_3	31	52—53/3	1.3976	1.325	31.3	31.2	17.1	18.0					1677
C_2H_5	62	55—57/2	1.4025	1.208	40.4	40.5	15.4	15.5			212	200	1677
n-C_3H_7	83	80—82/2	1.4123	1.148	49.5	49.7	12.7	13.6			232	228	1677

R	Yield %	Bp °C	n_D^{20}	d_4^{20}	MR_D		F, %		$\nu_{C=C}$ cm^{-1}
					Found	Calcd	Found	Calcd	
				$CHF=CFSR$					
C_2H_5	31	92—95	1.4213	1.115	28.2	28.2	30.3	30.7	1670
i-C_3H_7	55	102—105	1.4236	1.079	32.6	32.8	27.4	27.5	1669

TABLE 2. NMR SPECTRA OF DIALKYL 1-FLUORO-2-CHLOROVINYL- AND 1,2-DIFLUOROVINYLPHOSPHONATES

$CHCl=CF-P(O)(OR)_2$

R	Chemical shift[a] of fluorine, ppm δ	Coupling constant, cps		
		J_{HF}	J_{PF}	J_{HP}
CH_3	46.4	24.8	82.6	4.5
C_2H_5	45.9	24.3	82.6	4.5
n-C_3H_7	45.7	24.3	81.9	4.5

$CHF=CF-P(O)(OR)_2$
(x) (y)

R	Chemical shift[a] of florine, ppm		Coupling constant, cps					
	δ_x	δ_y	$J_{HF(x)}$	$J_{HF(y)}$	J_{FF}	$J_{PF(x)}$	$J_{PF(y)}$	J_{HP}
CH_3	57.0	78.2	70.0	16.9	16.9	27.7	70.6	1.5
C_2H_5	58.4	77.5	70.8	16.9	16.9	27.6	69.2	1.5
n-C_3H_7	58.2	77.3	70.6	16.9	16.9	28.2	70.6	1.5

a) ^{19}F shifts, δ, are with respect to external trifluoroacetic acid increasing to high field.

TABLE 3. NMR SPECTRA OF ALKYL 1, 2-DIFLUOROVINYL SULFIDES

$$\underset{(x)}{\mathrm{CHF}}=\underset{(y)}{\mathrm{CF}}\text{-S-R}$$

R	Isomer	Chemical shift[a] of fluorine, ppm		Coupling constant cps		
		δ_x	δ_y	$J_{HF(x)}$	$J_{HF(y)}$	J_{FF}
C_2H_5	trans	81.8	60.5	78.0		145
	cis	57.0	35.2	72.2	12.3	14.0
i-C_3H_7	trans	79.5	56.0	78.8		149
	cis	55.4	31.1	73.6	12.0	15.1

a) ^{19}F shifts, δ, are with respect to external trifluoroacetic acid increasing to high field.

C=C absorption bands at 1677 cm^{-1} and 1639 cm^{-1} (sh.) and a P=O absorption band at 1270 cm^{-1}. Although the spectrum of the gas chromatograph of the product consisted of two peaks, indicating the existence of two isomers, the ratio of the two peak areas was 1 : 10. The predominant isomer was found from its NMR spectrum to have a structure with fluorine and phosphorus in the trans position on a double bond.

Using the same procedure, other dialkyl 1, 2-dichloro-1, 2-difluoroethyl- and 1, 2, 2-trichloro-1-fluoroethylphosphonates were dechlorinated. The yields and physical properties are listed in Table 1.

The Alkyl 1, 2-Difluorovinyl Sulfides. To 19.5 g (0.30 g-atom) of zinc dust in a flask, 21.5 g (0.10 mol) of isopropyl 1, 2-dichloro-1, 2-difluoroethyl sulfide in 50 ml of diglyme was added, drop by drop, over a 50 min period under a nitrogen atmosphere at 110°C; the reaction mixture was then stirred at 130°C for an additional 2 hr. The product formed upon heating was distilled and collected in a trap cooled in dry ice-acetone. The crude product in the trap was distilled to give 7.8 g (0.056 mol, 55% yield) of isopropyl 1, 2-difluorovinyl sulfide, bp 102—105°C. The infrared spectrum of the vinyl sulfide showed an C=C absorption band at 1669 cm^{-1}. The spectrum of its gas chromatograph consisted of two peaks with an area ratio of 1 : 2.4.

Ethyl 1, 2-difluorovinyl sulfide was synthesized in a similar way.

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