

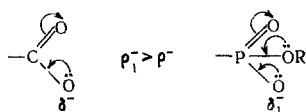
REACTIONS OF FLUORO OLEFINS

COMMUNICATION 18. ADDITION OF ACID PHOSPHONO-
AND PHOSPHORO-THIOIC ESTERS TO PERFLUORO OLEFINS

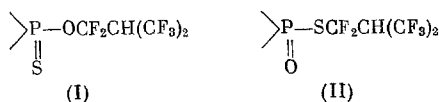
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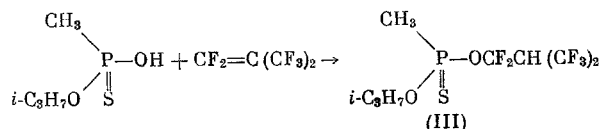
The ease with which nucleophilic reagents add at the double bond of perfluoro olefins is generally known. In these reactions an important factor is the magnitude of the nucleophilic power of the adding agent. For example, the nucleophilic power of amines and of alkoxide and azide ions is sufficient for the initial attack on the electrophilic perfluoro olefin molecule. On the other hand, the low nucleophilic power of a carboxylate ion, as compared with that of an alkoxide, leads as a result of the concentration of electron density between two equivalent oxygen atoms, to the inability of carboxylic acids to add to perfluoro olefins. The nucleophilic power of the anions of acid phosphoric and phosphonic esters should naturally be higher than that of a carboxylate ion because of the occurrence of conjugation, in which the unshared electron pair of the alkoxy group takes part:



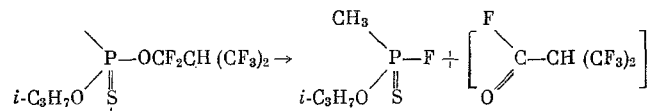
We have indeed shown that perfluoroisobutene and perfluorocyclobutene readily react with salts of acid methylphosphonic and methylphosphonothioic esters and of O,O-diisopropyl hydrogen phosphorothioate. It is known that salts of acid phosphorothioic O, O-diester show dual reactivity: in all known cases their acylation leads to O-acyl derivatives, whereas alkylation leads to S-alkyl derivatives [1]. Corresponding to this, the compounds which we prepared may have the structure (I) or (II):



It was shown that, depending on the reaction conditions, in their reaction with perfluoroisobutene these salts may react both in the thiol and in the thione form. The introduction of the perfluoro olefin into an ethereal solution of triethylammonium O-isopropyl methylphosphonothioate at below 0° with subsequent binding of the triethylamine liberated with hydrochloric acid leads to the formation of O-isopropyl O-[2H-pentafluoro-2-(trifluoromethyl)propyl]methylphosphonothioate (III):

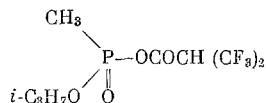


Proof of the structure of this compound is provided by its conversion into O-isopropyl methylphosphonofluoridothioate when it is heated with triethylamine:



The same fluoridothioic ester is formed if the reaction mixture is distilled without first removing the triethylamine. The reaction of perfluoroisobutene with triethylammonium diisopropyl phosphate goes analogously.

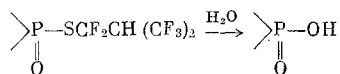
When the reaction of perfluoroisobutene with O-isopropyl hydrogen methylphosphonothioate is effected in acetic acid solution in presence of potassium acetate, then, depending on the conditions of treating the reaction mixture, the product is either a mixed anhydride of isopropyl hydrogen methylphosphonate and 2H-trifluoro-2-(trifluoromethyl)propionic acid



or isopropyl methylphosphonofluoridate (O,O-diisopropyl hydrogen phosphorothioate reacts similarly with perfluoroisobutene). Under these conditions the phosphorothioic and phosphonothioic compounds react in the thiol form: in the addition product then formed $\text{>P}-\text{SCF}_2\text{CH}(\text{CF}_3)_2$ the P—S bond is extremely

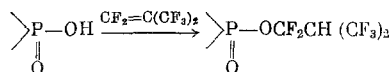


readily broken with formation of isopropyl hydrogen methylphosphonate:

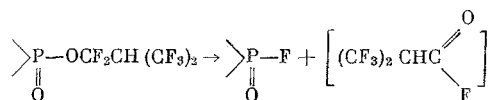


It has been shown recently that phosphonothioic esters are indeed readily converted into phosphonofluoridic esters — in presence of metal fluorides for example [2].

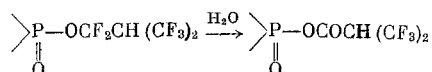
In its turn, the isopropyl hydrogen methylphosphonate adds to perfluoroisobutene:



However, we did not succeed in isolating this product, because in the direct distillation of the reaction mixture under the influence of the basic compounds present (potassium acetate) it is converted into isopropyl methylphosphonofluoridate:



If, however, potassium acetate is removed by first washing the reaction mixture with water, the above-mentioned mixed anhydride is formed:



This is still another example of the well-known ease of hydrolysis of fluorine atoms in the group — O — CF₂ — R [3].

In a special experiment we showed that in the reaction of isopropyl hydrogen methylphosphonate with perfluoroisobutene the product is indeed either isopropyl methylphosphonofluoridate or the mixed anhydride. The structure of this mixed anhydride was confirmed by its synthesis by the acylation of isopropyl hydrogen methylphosphonate with 2H-trifluoro-2-(trifluoromethyl)propionyl chloride.

EXPERIMENTAL

Reaction of Perfluoroisobutene with O-Isopropyl Hydrogen Methylphosphonothioate. A four-necked flask fitted with stirrer, inlet and outlet tubes for the passage of gas, and thermometer was charged with 60 ml of glacial acetic acid, 3.7 g of potassium acetate, and 5.1 g of O-isopropyl hydrogen methylphosphonothioate. The mixture was stirred while 15 ml of dry perfluoroisobutene was passed. Most of the acetic acid was distilled off under reduced pressure, the residue was dissolved in ether, and the solution was washed with water. After two fractionations we obtained 6.5 g (54%) of the mixed anhydride of 2H-trifluoro-2-(trifluoromethyl)propionic acid and isopropyl hydrogen methylphosphonate as a colorless liquid having: b. p. 72° (11 mm); d_4^{20} 1.3270, n_D^{20} 1.3440. Found: C 30.26; H 3.75; P 10.40; F 36.20%; MR 50.45. $C_6H_{11}O_4PF_6$. Calculated: C 30.38; H 3.48; P 9.81; F 36.20%; MR 50.92.

15 ml of perfluoroisobutene was bubbled into a stirred solution of 5.1 g of O-isopropyl hydrogen methylphosphonothioate in glacial acetic acid containing 3.7 g of potassium acetate at room temperature. The reaction mixture was distilled under reduced pressure. Acetic acid came off at 51° (3 mm). The residue contained 4.4 g of isopropyl methylphosphonofluoridate; b. p. 31° (3 mm); d_4^{20} 1.0905. Found: acid fluoride fluorine 14.00%. $C_4H_{10}O_2FP$. Calculated: acid fluoride fluorine 13.63%. [3] gives: b.p. 38.5-39° (6.3 mm); d_4^{20} 1.0980.

A four-necked flask fitted with stirrer, thermometer, and gas inlet and outlet tubes was charged with 50 ml of dry ether, 5.1 g of O-isopropyl hydrogen methylphosphonothioate, and 3.3 g of triethylamine. 15 ml of perfluoroisobutene was passed with stirring. The temperature was kept between -5 and 0°. In the fractionation of the reaction mixture we obtained 3.2 g of O-isopropyl methylphosphonofluoridate as a colorless liquid; b. p. 70-71° (50 mm); d_4^{19} 1.1056; n_D^{19} 1.4230. Found: C 31.62; H 6.93; P 20.13; S 19.36%; F (hydrolyzable) 12.80%; mol. wt. 155. $C_4H_{10}OSP$. Calculated: C 30.70; H 6.42; P 19.80; S 20.60; F (hydrolyzable) 12.30%; mol. wt. 156.

The flask was charged with 50 ml of dry ether, 3.9 g of O-isopropyl hydrogen methylphosphonothioate, and 2.4 g of triethylamine. 10 ml of perfluoroisobutene was passed through the stirred mixture at between -5 and -10°. The reaction mixture was washed with cold hydrochloric acid and then water. The ether layer was dried with magnesium sulfate. Ether was driven off, and the residue was distilled under reduced pressure. We obtained 3.6 g (40%) of O-isopropyl-O-[2H-pentafluoro-2-(trifluoromethyl)propyl] phosphorothioate; b. p. 50° (2 mm); d_4^{20} 1.4053; n_D^{20} 1.3770. Found: C 26.95; H 3.28; P 8.95; S 9.27; F 42.50%. $C_8H_{11}O_2PSF_8$. Calculated: C 27.20; H 3.10; P 8.75; S 9.04; F 42.50%.

Reaction of Perfluoroisobutene with O,O-Diisopropyl Hydrogen Phosphorothioate. A three-necked flask fitted with stirrer and gas inlet and outlet tubes was charged with 60 ml of glacial acetic acid, 8 g of O,O-diisopropyl hydrogen phosphorothioate, and 4 g of potassium acetate. 15 ml of perfluoroisobutene was passed into the stirred mixture. Acetic acid was driven off under reduced pressure, the residue was extracted with ether, and the extract was washed with water. Ether was driven off, and two distillations of the residue gave 7.5 g (50%) of the mixed anhydride of diisopropyl hydrogen phosphate and 2H-trifluoro-2-(trifluoromethyl)propionic acid; b. p. 71° (3 mm); d_4^{21} 1.2757; n_D^{21} 1.3540. Found: C 33.61; H 4.83; P 8.61; F 31.66%. $C_{10}H_{15}O_5PF_6$. Calculated: C 33.33; H 4.17; P 8.63; F 31.67%.

A weighed sample of the compound was introduced into a flask containing 0.1 N KOH. The flask was shaken carefully, and then the excess of alkali was back-titrated and the percent fluorine content of the hydrolyzate was determined. Found: F 32.20%. $C_{10}H_{15}O_5PF_6$. Calculated F 31.67%.

A flask was charged with 50 ml of dry ether, 12 g of O,O-diisopropyl hydrogen phosphorothioate, and 5 g of triethylamine. 20 ml of perfluoroisobutene was passed into the stirred mixture at between -5 and -10°. The reaction mixture was washed with cold hydrochloric acid and water. The ether layer was dried over magnesium sulfate. Ether was driven off, and the residue was distilled under reduced pressure. We obtained 14 g (58%) of O,O-diisopropyl-O-[2H-pentafluoro-2-(trifluoromethyl)propyl] phosphorothioate; b. p. 65° (2 mm); d_2^{22} 1.3215; n_D^{22} 1.3820. Found: C 30.16; H 3.95; P 7.83; S 9.02; F 38.30%. $C_{10}H_{15}O_3PF_8S$. Calculated: C 30.04; H 3.80; P 7.80; S 8.10; F 38.40%.

Reaction of Perfluoroisobutene with Isopropyl Hydrogen Methylphosphonate. A flask was charged with 50 ml of dry ether, 7 g of isopropyl hydrogen methylphosphonate, and 5 g of triethylamine. 10 ml of perfluoroisobutene was bubbled through the stirred mixture at -10° . The reaction mixture was washed with hydrochloric acid and water. The ether layer was dried over magnesium sulfate, ether was driven off, and the residue was distilled under reduced pressure. We obtained 6 g (37%) of the mixed anhydride of isopropyl hydrogen methylphosphonate and 2H-trifluoro-2-(trifluoromethyl)propionic acid; b. p. 72° (11 mm); d_4^{20} 1.2987; n_D^{20} 1.3432. Found: C 30.10; H 3.86; P 9.21; F 36.42%. $C_8H_{11}F_6O_4P$. Calculated: C 30.38; H 3.86; P 9.81; F 38.30%.

Reaction of Perfluorocyclobutene with O,O-Diisopropyl Hydrogen Phosphorothioate. The procedure was analogous to that of the preceding experiment. From 6 g of O,O-diisopropyl hydrogen phosphorothioate and 15 ml of perfluorocyclobutene (and 2.5 g of triethylamine) we obtained 8.4 g (77%) of O-(2H-hexafluorocyclobutyl)-O,O-diisopropyl phosphorothioate; b. p. 67° (3 mm); d_4^{20} 1.3206; n_D^{20} 1.3752. Found: P 8.56; F 31.46; S 9.36%. $C_{10}H_{15}O_3PSF_6$. Calculated: P 8.61; F 31.66; S 8.90%.

Mixed Anhydride of Isopropyl Hydrogen Methylphosphonate and 2H-Trifluoro-2-(trifluoromethyl)propionic Acid. A flask was charged with a solution of 7 g of isopropyl hydrogen methylphosphonate in dry ether, an equimolecular amount of triethylamine was added, and then at $0-5^{\circ}$ 10 g of 2H-trifluoro-2-trifluoro-2-(trifluoromethyl)propionyl chloride was added dropwise. The reaction mixture was washed with water, and the ether layer was separated and dried over magnesium sulfate. Ether was driven off, and we obtained 9 g (49%) of the mixed anhydride of isopropyl hydrogen methylphosphonate and 2H-trifluoro-2-(trifluoromethyl)propionic acid; b. p. $69-70^{\circ}$ (10 mm); d_4^{20} 1.3271, n_D^{20} 1.3447.

A weighed sample of the compound was introduced into a flask containing 0.1 N KOH, the mixture was shaken vigorously, excess of alkali was back-titrated, and the percent fluorine content was determined. Found: F 31.85%. $C_8H_{11}O_4F_6P$. Calculated: F 31.67%.

CONCLUSIONS

1. Salts of acid alkylphosphonic, alkylphosphonothioic, and phosphorothioic esters readily add to perfluoro olefins with formation of the corresponding fluoroalkyl esters; depending on the conditions, the salts of the acid thio esters react in the thiol or the thione form.

2. The O-alkyl-O-1,1-difluoroalkyl alkylphosphonothioates and O,O-dialkyl-O-1,1-difluoroalkyl phosphorothioates formed have the character of mixed anhydrides.

LITERATURE CITED

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2. O. Saville, J. Chem. Soc., 1961, 4624.
3. J. A. Young and P. Tarrant, J. Amer. Chem. Soc., 71, 2432 (1949).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
