REACTION OF PERFLUORONITROSOALKANES WITH ESTERS OF PHOSPHOROUS ACID

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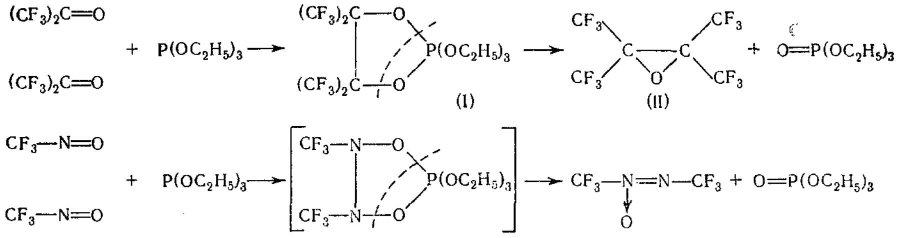
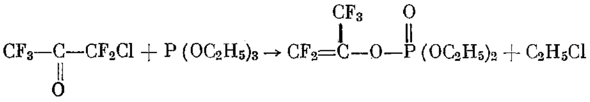
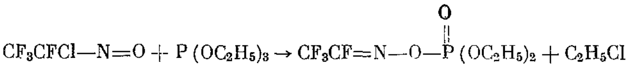
Together with other reactions, the reaction of fluoronitrosoalkanes with the esters of phosphorous acid can serve as clear examples of the chemical analogy between the nitroso group and the carbonyl group, going especially far in the series of organofluorine compounds. Thus, the formation of hexafluoroazoxymethane when triethyl phosphite is reacted with trifluoronitrosomethane [1] can be compared with the formation of tetrakis-trifluoromethylethylene oxide (II) as one of the products of the thermal decomposition of phosphorane (I) — the adduct of hexafluoroacetone and triethyl phosphite [2].



The reactions of triethyl phosphite with α-chloroperfluoro ketones [3] and α-chloroperfluoronitrosoalkanes [4] are completely analogous to each other.

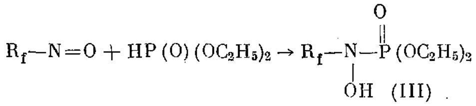


$$CF_3-\underset{\underset{O}{\|}}{C}-CF_2Cl + P(OC_2H_5)_3 \rightarrow CF_2=\overset{\overset{CF_3}{|}}{C}-O-\overset{\overset{O}{\|}}{P}(OC_2H_5)_2 + C_2H_5Cl$$



$$CF_3CFCl-N=O + P(OC_2H_5)_3 \rightarrow CF_3CF=N-O-\overset{\overset{O}{\|}}{P}(OC_2H_5)_2 + C_2H_5Cl$$

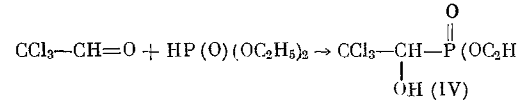
Trifluoronitrosomethane and tert-nitrosoperfluoroisobutane add acid phosphites to give the corresponding N-phosphorylated perfluoroalkylhydroxylamines (III) [5]. Aldehydes react in a similar manner in the presence of bases [6] (a catalyst is not required in the case of the perhalogenated aldehyde-chloral [7]).



$$R_f-N=O + HP(O)(OC_2H_5)_2 \rightarrow R_f-\underset{\underset{OH}{|}}{N}-\overset{\overset{O}{\|}}{P}(OC_2H_5)_2$$

(III)

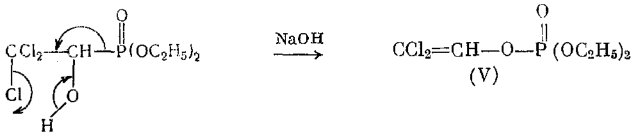
$R_f = CF_3, (CF_3)_3C$



$$CCl_3-CH=O + HP(O)(OC_2H_5)_2 \rightarrow CCl_3-\underset{\underset{OH}{|}}{CH}-\overset{\overset{O}{\|}}{P}(OC_2H_5)_2$$

(IV)

The treatment of (IV) with alkali leads to the product of the Perkov reaction, namely β,β-dichlorovinyl diethyl phosphate (V) [8].



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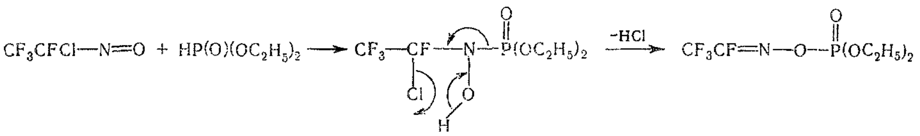
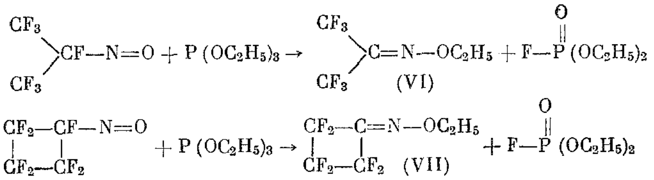
The adducts of acid phosphites and α-chloroperfluoronitrosoalkanes spontaneously cleave hydrogen chloride and give in one step the products of the Allen reaction, namely the phosphates of perfluoro oximes [4].

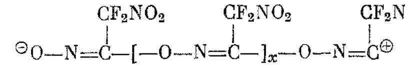


The reactions of phosphites with nitroso compounds, containing fluorine atoms in the α-position, proved to be very interesting. It could be postulated that these compounds will behave in a manner similar to either trifluoronitrosomethane or the α-chloroperfluoronitrosoalkanes. However, the course of the reaction is peculiar in this case. Secondary perfluoronitrosoalkanes, like 2-nitrosoperfluoropropane $(CF_3)_2CF-N=O$ and nitrosoperfluorocyclobutane $\overline{CF_2CF_2CF_2CF}-N=O$, react with triethyl phosphite with exceeding ease, even at -78°, in inert solvents, giving in good yields the ethyl ethers of the oximes of respectively hexafluoroacetone (VI) and perfluorocyclobutanone (VII), and diethyl fluorophosphate.



Compound (VI) was obtained by counter synthesis, by the alkylation of hexafluoroacetone oxime with ethyl iodide in the presence of alkali.

The reaction of triethyl phosphite with primary perfluoronitrosoalkanes, having two fluorine atoms α to the nitroso group, goes in more than one way. In the case of β-nitroperfluoronitrosoethane, $O_2NCF_2CF_2-N=O$, it proved possible to isolate a substance that in its properties corresponded to the polymer of difluoronitroacetonitrile oxide $(O_2NCF_2C\equiv N\rightarrow O)_n$ (VIII); the other reaction products that were identified included diethyl fluorophosphate and triethyl phosphate. (VIII) apparently has the following structure (cf. [9]).

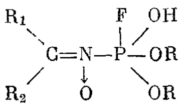


$$^{\ominus}O-N=\overset{CF_2NO_2}{\overset{|}{C}}-[-O-N=\overset{CF_2NO_2}{\overset{|}{C}}-]_x-O-N=\overset{CF_2NO_2}{\overset{|}{C}}{}^{\oplus}$$

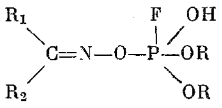
Diethyl phosphite reacts with $(CF_3)_2CF-N=O$, $\overline{CF_2CF_2CF_2CF}-N=O$, and $O_2NCF_2CF_2-N=O$, with cooling to 0°, forming 1 : 1 adducts, which by analogy with the reactions of $CF_3-N=O$ and $(CF_3)_3C-N=O$, can be assigned the structure of N-phosphorylperfluoroalkylhydroxylamines (III). However, the attention is attracted to the fact that the boiling points of these compounds are below the boiling point of trifluoromethyl-N-diethylphosphorylhydroxylamine. A detailed study revealed that the adducts actually have a different structure. Absorption maxima in the 1650-1700 cm^{-1} range are present in the infrared spectra of these compounds, i.e., in the absorption region of the C=N bond for polyfluoroorganic compounds, in which connection the frequency is close to the absorption maximum of the corresponding oxime in each case (Table 1). A doublet with a spin-spin coupling constant of the order of 1000 Hz is present in the F^{19} NMR spectra of all of the adducts, which is characteristic for a fluorine atom attached to phosphorus. The general character of the remainder of the spectrum is the same as for the corresponding oximes (Table 2). Structures of the type of (IXA) and (IXB) are in agreement with these data.

TABLE 1. Infrared Spectra of Adducts of Perfluoronitrosoalkanes and Diethyl Phosphite

R_1	R_2	ν_{max} of adduct, cm^{-1}	ν_{max} of oxime, cm^{-1}
CF_3	CF_3	1656	1656
$-CF_2CF_2CF_2-$		1670	1690
F	O_2NCF_2	1705	1698 [10]



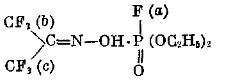
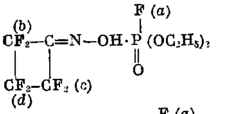
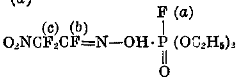
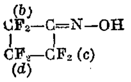
(IXA)



(IX B)

However, these compounds most probably represent complexes of the perfluoro oximes with diethyl fluorophosphate,

TABLE 2. F^{19} Chemical Shifts and P–F Coupling Constants for Adducts of Perfluoronitrosoalkanes with Diethyl Phosphite (internal standard – $C_6H_5CF_3$)

Compound	Chemical shifts, p.p.m.				J (P – F), Hz
	δ (F(a)) *	δ (F (b))	δF ((c))	δ (E (d))	
	18.4	2.0 †	3.7 †		967
	19.4	55.0	57.5	70.4	985
 $O_2NCF_2CF{=}N{-}OH \cdot P(O)F(OC_2H_5)_2$	18.9	25.4 ‡	27.8 **		975
		56.1	58.3	70.4	
$(C_2H_5)_2P(O)F$ (a)	18.8				985

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*The shifts are shown for the centers of the doublets, the splitting of which is determined by the J (P – F) constant.

†Quartets with the splitting J(CF_3–CF_3)≈14 Hz.

‡Triplet with J(CF_2–CF)≈13 Hz.

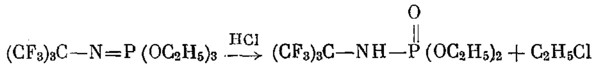
** The line is broad.

formed due to hydrogen bonding. This is confirmed by the presence of a broad absorption band in the infrared spectrum in the range 2800–3300 cm^{-1} (bound hydroxyl), and also by the fact that they are obtained by the simple mixing of equimolar amounts of the oximes and diethyl fluorophosphite. When the adducts are studied by the GLC method the oxime and diethyl fluorophosphate exit separately. As a result, the structure of the adducts can be depicted as $R_1R_2C{=}N{-}OH \cdot FP(O)(OC_2H_5)_2$ [X; a) $R_1{=}R_2{=}CF_3$; b) R_1, $R_2 = -(CF_2)_3-$; c) $R_1{=}F$, $R_2{=}O_2NCF_2$]. The formation of such adducts with electron-donor partners was described for the fluorides of perfluorohydroxamic acids [10] and perfluoroacetone oxime [11].

The question of how neutral phosphites react with tert-perfluoronitrosoalkanes has remained completely unanswered up to now. Study revealed that tert-nitrosoperfluoroisobutane reacts at –78° with 2 moles of triethyl phosphite, giving the corresponding phosphazo compound (XI) and triethyl phosphate.

$$(CF_3)_3C{-}N{=}O + 2P(OC_2H_5)_3 \rightarrow \underset{(XI)}{(CF_3)_3C{-}N{=}P(OC_2H_5)_3} + O{=}P(OC_2H_5)_3$$

The reaction of (XI) with hydrogen chloride gives the perfluorotert-butylamide of diethylphosphoric acid (XII).



$$(CF_3)_3C{-}N{=}P(OC_2H_5)_3 \xrightarrow{HCl} (CF_3)_3C{-}NH{-}P(O)(OC_2H_5)_2 + C_2H_5Cl$$

(XII)

The reaction of tert-nitrosoperfluoroisobutane with triphenylphosphine also leads to obtaining phosphazo compound (XIII).

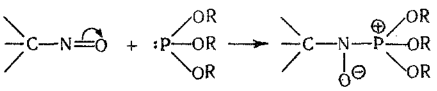
$$(CF_3)_3C{-}N{=}O + 2P(C_6H_5)_3 \rightarrow \underset{(XIII)}{(CF_3)_3C{-}N{=}P(C_6H_5)_3} + O{=}P(C_6H_5)_3$$

(XIII) is an exceedingly stable compound, and withstands heating with conc. H_2SO_4 at 60–70°.

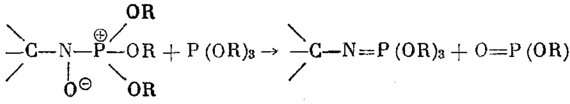
The reaction of 2-nitrosoperfluoropropane with triphenylphosphine gives an adduct, which could not be isolated in the crystalline state. Hydrolysis of the reaction mixture gave hexafluoroacetone oxime and triphenylphosphine oxide.

Concerning the mechanism of the Perkov–Allen reaction and related processes there exist, as is known, various theories, which can be grouped on the basis of the direction of the initial attack by the phosphite molecule: a) on the α-carbon atom; b) on carbonyl oxygen (oxygen of the nitroso group); c) on carbonyl carbon (nitrogen of the nitroso group); and d) on the α-halogen atom (see [4, 12]). According to modern concepts, the most probable mechanisms are the "c" and "d" types. Conclusive evidence for selecting between them is still lacking, and although many authors give preference to the mechanism involving attack of the phosphite on the positively polarized α-halogen atom, still experimental data exist in support of the fact that the site of attack (in the case of the α-chloroperfluoronitrosoalkanes) is the nitrogen atom of the nitroso group [4]. It is understood that, depending on the structure of the reactants, the mechanism of the reaction can be different and requires special study. Nevertheless, an attempt can be made to give a general scheme, if only for a certain gamut of processes. It seems to us that the concept of initial attack by the phosphorus atom, bearing an unshared electron pair, on the positively charged nitrogen atom of the nitroso group may be a general one for all of the reactions of the perfluoronitrosoalkanes with the esters of phosphorous acid and certain other compounds of trivalent phosphorus. This assumption is primarily in agreement with the fact that perfluoronitroso compounds of variable structure, independent of whether a chlorine atom is present in the α-position, enter with exceeding ease into the reaction. Chlorine in the α-position can be polarized positively, but such polarization is hardly possible for fluorine; in the case of the tert-perfluoronitrosoalkanes a halogen in the α-position is generally absent.

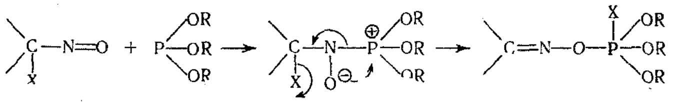
Attack of the phosphite on the nitrogen atom should first lead to the bipolar ion, the further fate of which depends on the character of the substituents attached to the carbon atom α to the nitrogen.



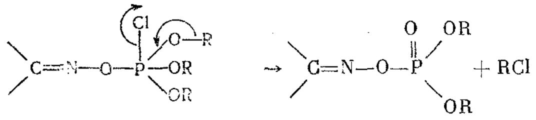
If all of the three substituents are perfluoroalkyl radicals, then reaction with a second phosphite molecule occurs, with the formation of the phosphazo compound.



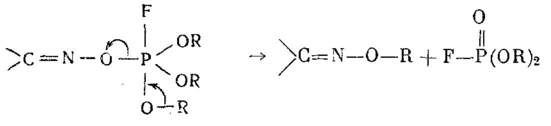
If one of the substituents in the α-position is halogen, then it migrates to the phosphorus, in which connection the bond system $C=N-O-P$ is formed.



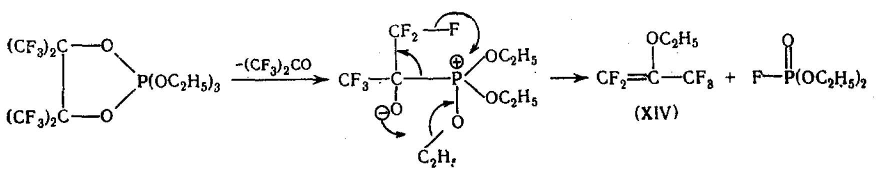
When $X=Cl$, alkyl chloride is eliminated (Allen reaction),



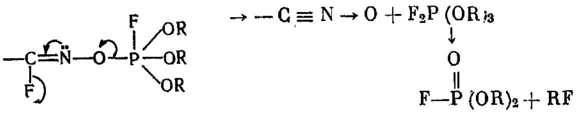
whereas when $X=F$, the alkyl ether of the oxime of the perfluoro ketone is cleaved.



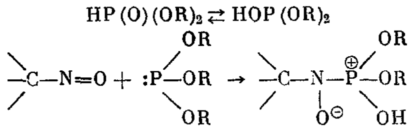
In the latter case it is not halogen, but rather the moiety $>C=N-O-$ that is cleaved, manifesting in this manner "pseudohalogen" properties. It should be mentioned that this reaction also has its direct analogy in the series of perfluorocarbonyl compounds. Besides the already mentioned oxide (II), the decomposition of phosphorane (I) also leads to obtaining 2-ethoxyperfluoropropylene (XIV) and diethyl fluorophosphate [2, 3] according to the following scheme



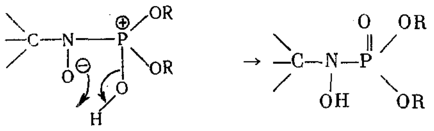
The formation of the nitrile oxide from the initial nitroso compound can be depicted by the scheme



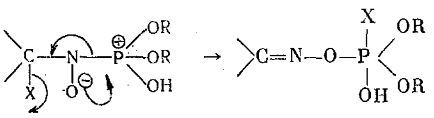
The reaction of perfluoronitrosoalkanes with acid phosphites can be depicted in the following manner:



of tert-perfluoronitrosoalkanes:

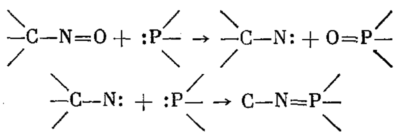


of secondary and primary perfluoronitrosoalkanes:

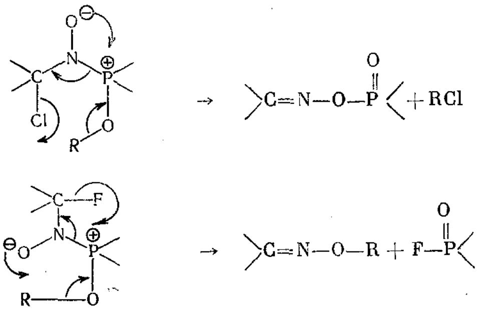


(XV)

If X=Cl, then HCl is cleaved and the product of the Allen reaction is formed; when X=F (XV), decomposition is to the oxime and diethyl fluorophosphate. The separate steps of the above given discussion permit, it is understood, a different treatment. Thus, the formation of the phosphazo compounds can be accomplished via the nitrene:



The transformation of the bipolar ion to the end reaction products can be depicted as being one-step:



The reactions of electron transfer can occur at definite stages (see [13]). In this connection the concept of initial attack by the phosphorus atom, bearing an unshared pair of electrons, on the positively charged nitrogen atom of the nitroso group, retains its universal character.

EXPERIMENTAL

Ethyl Ether of Hexafluoroacetone Oxime (VI). To a solution of 7.8 g of 2-nitrosoperfluoropropane in 10 ml of difluorochloromethane at -78° was slowly added 6.5 g of triethyl phosphite. The solvent was evaporated, and the volatile reaction product was vacuum-distilled into a trap, cooled to -78°. Distillation of the high-boiling residue gave 5.7 g (93.2%) of diethyl fluorophosphate, bp 71-73° (17 mm); n_D^{20} 1.3750, identified by the GLC method with the authentic specimen (literature data [14]: bp 49-52° (3 mm); n_D^{20} 1.3720). The trap contents were distilled. We obtained 6.1 g (74.3%) of (VI), bp 64.5-65.5°; n_D^{20} 1.3089; d_4^{20} 1.2832. Found%: C 28.86; H 2.37; F 54.42; N 6.82. MR 31.29. $C_5H_5F_6NO$. Calculated%: C 28.73; H 2.42; F 54.53; N 6.70. MR 30.57. Infrared spectrum: ν_{max} 1626 cm^{-1} (C=N).

Hexafluoroacetone oxime [15] was dissolved in 50% aqueous dioxane, after which an equimolar amount of KOH and ethyl iodide was added, and the mixture was heated in a sealed ampule on the water bath (80°) for 8 h. We obtained 42.8% of (VI), which was identified by the GLC method.

Ethyl Ether of Perfluorobutanone Oxime (VII). Ether (VII) was obtained in a similar manner from 8.5 g of nitrosoperfluorocyclobutane and 6.7 g of triethyl phosphite in 10 ml of difluorodichloromethane. Yield of (VII) 5.0 g (56.2%), bp 92.5-94°; n_D^{20} 1.3425; d_4^{20} 1.3301. Found%: C 32.65; H 2.62; F 51.23; N 6.08. $C_6H_5F_6NO$. Calculated%: C 32.59; H 2.28; F 52.01; N 6.34. Infrared spectrum: ν_{max} 1652 cm^{-1} (C=N).

Reaction of Triethyl Phosphite with β-Nitroperfluoronitrosoethane. To a solution of 11.2 g of β-nitroperfluoronitrosoethane in 10 ml of trifluorotrichloroethane at -78° was gradually added 10.6 g of triethyl phosphite, and the mixture was allowed to stand overnight at room temperature. The obtained crystals were filtered (5.0 g). Recrystallization from benzene gave a substance that melted with vigorous decomposition at 188-188.5°. The crystals are soluble in acetone, and are insoluble in most organic solvents and in water. Found%: C 16.93; F 26.73; N 20.19. $C_2F_2N_2O_3$. Calculated%: C 17.41; F 27.57; N 20.31. Infrared spectrum: ν_{max} 1617 (NO_2), 1686 (C=N) cm^{-1}.

Reaction of Diethyl Phosphite with Perfluoronitrosoalkanes. With 2-Nitrosoperfluoropropane. A mixture of 8.6 g of 2-nitrosoperfluoropropane and 5.9 g of diethyl phosphite was mixed at 0° and allowed to stand overnight in a sealed glass ampule at room temperature, after which it was vacuum-distilled. We obtained 8.2 g of the adduct (Xa), bp 57-62° (7 mm); n_D^{20} 1.3410; yield 56.6%. After redistillation, bp 58-58.5° (7 mm); n_D^{20} 1.3367; d_4^{20} 1.3112. Found%: C 25.22; H 3.64; N 4.17; P 10.20. $C_7H_{11}F_7NO_4P$. Calculated%: C 24.94; H 3.30; N 4.16; P 9.20. Infrared spectrum: ν_{max} 1656 cm^{-1} (C=N).

With Nitrosoperfluorocyclobutane. Into a flask, fitted with a gas-inlet tube and a reflux condenser, and cooled to -78°, was charged 2.9 g of diethyl phosphite and then, with cooling to 0°, 4.4 g of nitrosoperfluorocyclobutane was added gradually. The mixture was allowed to stand overnight at room temperature, and then it was distilled. We obtained 4.7 g (64.6%) of the adduct (Xb), bp 71-75° (7.5 mm). After redistillation, bp 62-63° (6 mm); n_D^{20} 1.3525; d_4^{20} 1.3365. Found%: C 27.51; H 3.28; N 4.13. $C_8H_{11}F_7NO_4P$. Calculated%: C 27.52; H 3.18; N 4.13. Infrared spectrum: ν_{max} 1670 cm^{-1} (C=N).

With β-Nitroperfluoronitrosoethane. Similar to the preceding experiment, 4.3 g of the nitroso compound was added to 3.36 g of diethyl phosphite, after which the mixture was allowed to stand overnight and then vacuum-distilled. We obtained 5.6 g (73%) of the adduct (Xc), bp 68-70° (7 mm); n_D^{20} 1.3681. After redistillation, bp 46-47° (2 mm); n_D^{20} 1.3680; d_4^{20} 1.3342. Found%: C 22.82; H 3.69; F 23.76; N 8.85. $C_6H_{11}F_4N_2O_6P$. Calculated%: C 22.94; H 3.53; F 24.19; N 8.92. Infrared spectrum: ν_{max} 1610 (NO_2), 1705 (C=N) cm^{-1}.

Triethoxyphosphazoperfluorotert-butyl (XI). To a solution of 8.8 g of triethyl phosphite in 30 ml of absolute ether, contained in a two-necked flask fitted with a reflux condenser and cooled to -78°, was gradually added 6.6 g of tert-nitrosoperfluoroisobutane through the gas-inlet tube, and the mixture was allowed to stand overnight. Then the ether was distilled off, while the unreacted triethyl phosphite was vacuum-distilled through a short column (5-7 theoretical plates), after which the residue was cooled and poured into a small amount of water, followed by separation of the lower layer, which was washed again with water and then distilled. We obtained 7.2 g (70.6%) of (XI), bp 70-71° (6.5 mm); n_D^{20} 1.3540; d_4^{20} 1.3582. Found%: C 29.95; H 3.92; F 42.91; N 3.69; P 7.80. $C_{10}H_{15}F_9NO_3P$. Calculated%: C 30.08; H 3.79; F 42.84; N 3.51; P 7.77.

Perfluorotert-butylamide of Diethylphosphoric Acid (XII). Through a solution of 2.45 g of (XI) in 5 ml of ether was passed a stream of dry hydrogen chloride at 0° for 1 h, after which the solution was allowed to stand for 2 days at 0°. The ether was distilled off, while the residue was vacuum-distilled. We obtained 1.60 g (69%) of (XII), bp 105-106° (8 mm); mp 31.5-32°. Found%: C 25.71; H 3.24; F 45.63; N 4.10; P 7.68. $C_8H_{11}NO_3P$. Calculated%: C 25.89; H 2.98; F 46.07; N 3.77; P 8.34. Infrared spectrum: ν_{max} 2940 (III), 2990, 3130 (III) cm^{-1}.

Triphenylphosphazoperfluorotert-butyl (XIII). To a solution of 21.6 g of triphenylphosphine in 50 ml of absolute ether in a flask, fitted with a reflux condenser and cooled to -78°, was gradually added 8.2 g of tert-nitrosoperfluoroisobutane (at such a rate that the ether boiled gently). The mixture was allowed to stand overnight, the triphenylphosphine was filtered (5.5 g), and the ether was distilled from the filtrate. The residue was dissolved in chloroform, bromine was added until a distinct color appeared, and the chloroform was distilled off. The obtained residue was treated with 20 ml of water, after which the mixture was heated under reflux for 15 min, cooled, 30 ml of ether was added, the mixture was stirred well, and the precipitate was filtered and washed several times with ether. We obtained an additional 6.7 g of triphenylphosphine oxide. The ether was distilled from the filtrate, and the residue was recrystallized from methanol. We obtained 12.2 g (74.8%) of (XIII), which after a double recrystallization from methanol had mp 146-147.5°. Found%: C 53.17; H 3.28; F 34.28; N 2.99; P 6.21. $C_{22}H_{15}F_9NP$. Calculated%: C 53.32; H 3.06; F 34.51; N 2.83; P 6.26.

Reaction of 2-Nitrosoperfluoropropane with Triphenylphosphine. In the same manner as the preceding, 4.8 g of 2-nitrosoperfluoropropane was added to a solution of 8 g of triphenylphosphine in 30 ml of absolute ether. The mixture was allowed to stand overnight, the ether was distilled off, and the residue was treated with a little water, after which conc. H_2SO_4 was added and 3.05 g (70%) of perfluoroacetone was distilled off, bp 68-70° (literature data [15]: bp 69-71°). The compound was identified by the GLC method.

The infrared spectra were taken on a UR-10 instrument, while the F^{19} NMR spectra were taken on an NMR-100 JEOL instrument, with an operating frequency of 94 MHz.

Analysis and identification by the GLC method were carried out on an instrument equipped with a heat-conductivity detector. The carrier gas was helium, and the packing was Rheoplex-400 (20%) deposited on celite. The oximes and their ethyl ethers were also chromatographed on diatomaceous brick, impregnated with 20% thiokol.

CONCLUSIONS

1. Depending on the structure of the perfluoronitrosoalkanes, their reaction with triethyl phosphite leads to obtaining fluorine-containing phosphazo compounds, the ethyl ethers of oximes of perfluoro ketones, and the oxides of perfluoronitriles.

2. Some new examples of a chemical analogy between the perfluoronitrosoalkanes and perfluoro ketones were discovered.

3. The obtained results are in agreement with the concept that the phosphite initially attacks the nitrogen atom of the nitroso group.

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