Iodine (7.8 g) was filtered. Distillation of filtrate gave: 4.1 g of n-$C_5H_{11}Cl$, yield 66%, based on amyl iodide which entered the reaction. At a ratio of $C_5H_{11}I:ICl_3 = 2:1$, amyl iodide, according to GLC data, converts completely into amyl chloride. Under the same conditions, CH_2I_2 and ICl_3 taken in a ratio of 4:1 gave a mixture of CH_2Cl_2 — 10, CH_2ClI — 30, CH_2I_2 — 60% (according to GLC); the yields of CH_2Cl_2 and CH_2ClI were 34 and 50%, respectively.

CONCLUSIONS

1. Iodide trichloride reacts with acrylonitrile and methyl acrylate with the formation of adducts ClCH CHIR (R = CN, $COOCH_3$), and with 1-hexene it forms a mixture of adducts $ClCH_2$-$CHIC_4H_9$ and $ICH_2CHClC_4H_9$, with the latter compound predominating.

2. In the reaction of ICl_3 with terminal olefins, not only vicinal chloroiodides but also vicinal dichlorides are formed.

3. Iodine tricyloride is an effective agent for exchange iodine for chlorine in mono- and gem-diiodo-containing groups of aliphatic carbon chain.

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FLUORINE-CONTAINING IMINES.

COMMUNICATION 4.* SYNTHESIS AND PROPERTIES OF HEXAFLUOROACETONE N-PERFLUOROPIVALOYLIMINE

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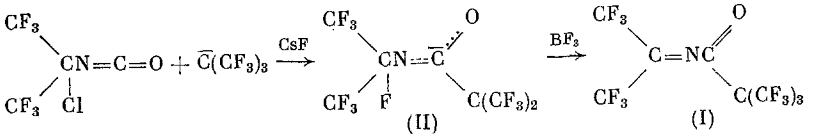
and N. P. Gambaryan

UDC 542.91:547.415.3'161:547.446

Hexafluoroacetone pivaloylimine (I) has already been obtained by isomerizing the corresponding perfluoro-α-lactam by the action of CsF, and also by condensing perfluoroisopropyl isocyanate with perfluoro-tert-butyl anion [2]. These reactions are unsuitable for the preparative synthesis of (I) because the initial reagents are not very available. At attempt to obtain acylimine (I) in analogy with the known method of synthesis of perfluoroacylimines [3] by condensing hexafluoroacetone with perfluoropivaloylamide was unsuccessful probably because of the low nucleophilicity of the latter. The perfluoro-tert-butyl substituent usually introduces certain unique features into the properties of these compounds [4, 5], and therefore it was interesting to develop a convenient method for the synthesis and detailed study of pivaloylimine (I). The condensation of the available α-chlorohexafluoroisopropyl isocyanate† with perfluoro tert-butyl anion was found to be effective



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*For communication 3, see [1].

†α-Chlorohexafluoroisopropyl isocyanate was synthesized by a method described in [5].

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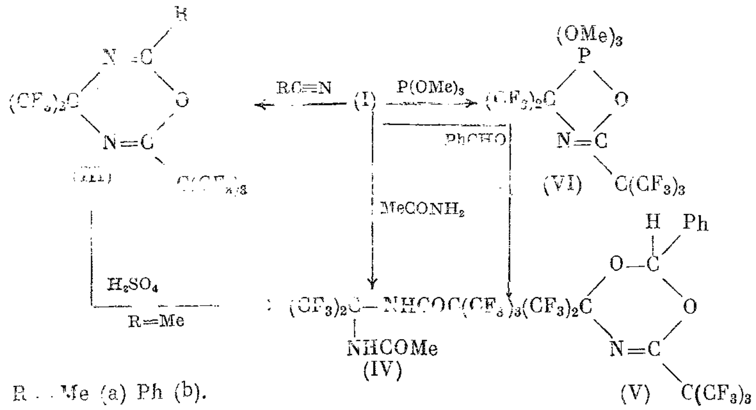
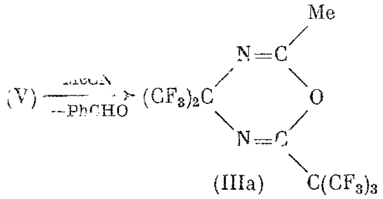
The examination of (I) showed that it enters the reactions of nucleophilic addition and also the reaction of 1,4-cycloaddition with nitriles, carbonyl compounds, and trimethyl phosphite (see [6, 7]) much more readily than hexafluoroacetone benzoylimine

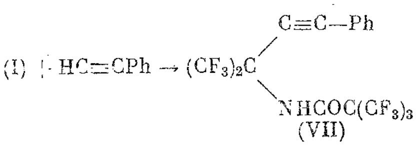


R = Me (a) Ph (b).

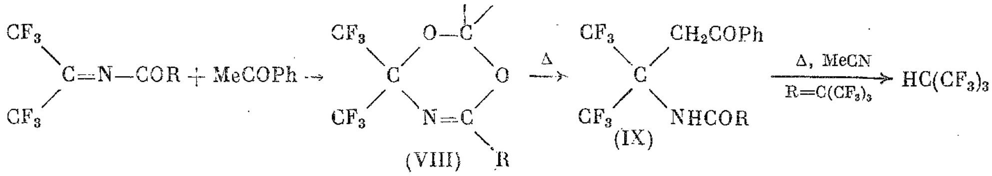
For example, the reaction of acetonitrile with hexafluoroacetone benzoylimine is completed after 12 h at 100°C [6], while with (I) it proceeds instantly and exothermally (see [8]). The oxadiazine (IIIa) thus formed is hydrolyzed into diamide (IV), which was obtained by an alternative synthesis by addition of acetamide to (I) at ∼20°C. We have already observed a reversible thermal dissociation of the cycloadducts of hexafluoroacetone benzoylimine with aldehydes, so that on heating with MeCN (100°C) they can be converted into the corresponding oxadiazines [5]. A similar "retrodissociation" takes place in the case of dioxazine (V) also but already at ∼20°C.



Compound (I) reacts with phenylacetylene in the same way as hexafluoroacetone benzoylimine [9], but under much milder conditions

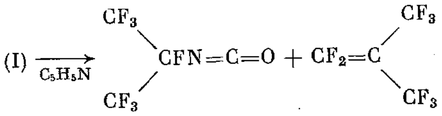


In the study of the reaction of acylimine (I) with acetophenone, we found that the primary product is dioxazine (VIIIa) (10 min at ∼20°C), which on prolonged heating converts into a thermodynamically more stable linear addition product (IXa). According to the data in [9], hexafluoroacetone benzoylimine reacts with acetophenone at 150°C as with a compound with a labile hydrogen atom. Repeated study of the reaction showed that with acetophenone, hexafluoroacetone benzoylimine gives a cycloadduct (VIIIb) also (3 months at 20°C), which on heating isomerizes into the linear product (IXb)



R = C(CF$_3$)$_3$ (a), Ph (b).

As known, the perfluoro-tert-butyl group is readily eliminated in the form of an anion [10]. Therefore, replacement of the phenyl group for perfluoro-tert-butyl group leads to a change in the properties of both acylimines and of the reaction products obtained from them. Thus, in contrast to benzoylamino ketone (IXb), perfluoropivaloylamino ketone (IXa) on prolonged heating with MeCN eliminates monohydroperfluoroisobutane. In contrast to other hexafluoroacetone acylimines, in the presence of catalytic amounts of pyridine, compound I dissociates into perfluoroisopropyl isocyanate and perfluoroisobutylene



$$(I) \xrightarrow[C_5H_5N]{} (CF_3)_2CFN{=}C{=}O + CF_2{=}C(CF_3)_2$$

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra were recorded on the Perkin–Elmer R-32 spectrometer (^{1}H, 90 MHz, ^{19}F, 84.6 MHz) with reference to CF_3COOH and TMS as external standards; the IR spectra were run on the UR-20 spectrophotometer.

α-Chlorohexafluoroisopropyl Isocyanate. A 40-g portion of α-chlorohexafluoroisobutyryl chloride was added dropwise, with ice-bath cooling and stirring, to a solution of 13 g of activated NaN_3 in 40 ml of H_2O and 75 ml of xylene. The mixture was stirred for 1 h, with cooling, and 3 h at 20°C. The xylene layer was separated, washed with water, and dried first over $MgSO_4$ and then over Na. The dry azide solution was cautiously heated to cessation of nitrogen evolution, and the isocyanate was distilled. Yield, 27 g (74%) of α-chlorohexafluoroisopropyl isocyanate, bp 52-54°C, that was identical with an authentic sample [11].

Hexafluoroacetone N-Perfluoropivaloylimine (I). Perfluoroisobutylene (8.8 g) was passed, with ice-bath cooling and stirring, through a suspension of 13.5 g of freshly calcined CsF in 50 ml of absolute diglyme, and at the same time 10 g of α-chlorohexafluoroisopropyl isocyanate was added dropwise. The mixture was left to stand for 20 h at 20°C, and the precipitate was filtered without access of moisture, and to the filtrate (a solution of anion (II), according to ^{19}F NMR data) 6.5 g of BF_3 etherate were added dropwise, with ice-bath cooling and stirring. After 2 h, volatile products were distilled into a trap (–78°C), the lower layer was separated and distilled. Yield, 10.2 g (56%) of (I), bp 99-101°C, which was identical with an authentic sample.

4H,1,3,5-Oxadiazines (III). An excess of MeCN was added, with stirring, to 1.75 g of (I). At the end of the exothermal reaction, the MeCN was distilled. By distillation of the residue, 1.4 g (72%) of 2-methyl-4,4-bis(trifluoromethyl)-6-perfluoro-tert-butyl-4H,1,3,5-oxadiazine (IIIa), bp 75°C (50 mm), was obtained. Found: C 26.15; H 0.65; F 62.75; N 6.36%. $C_{10}H_3F_{15}N_2O$. Calculated: C 26.54; H 0.66; F 63.05; N 6.19%. IR spectrum (ν, cm^{-1}): 1670, 1695 1760 (C=N). PMR spectrum: 1.9 s (CH_3). ^{19}F NMR spectrum: 2.4 s ($(CF_3)_2C$), –13.9 s ($(CCF_3)_3C$).

Compound (IIIa) was obtained from 2-phenyl-4,4-bis(trifluoromethyl)-6-perfluoro-4H,1,3,5-dioxazine (V) in an excess of MeCN after 4 days at 20°C (according to ^{19}F NMR).

Under similar conditions, from 0.5 g of (I) and 0.12 g of PhCN after 2 days at 20°C, 0.45 g (72%) of (IIIb), mp 65-67°C (from hexane, sublimation), was obtained. Found: F 55.50; N 5.96%. $C_{15}H_5F_{15}N_2O$. Calculated: F 55.44; N 5.44%. IR spectrum (ν, cm^{-1}): 1610, 1660, 1740, (C=N). ^{19}F spectrum (in CCl_4): –0.2 s ($(CF_3)_2C$, –16.0 s ($(CF_3)_3C$).

N-Acetyl-N'-Perfluoropivaloyl-2,2-diaminohexafluoropropane (IV). a) A 0.2-g portion of (IIIa) was dissolved in 1 ml of concentrated H_2SO_4, and after 15 min, the mixture was poured into ice. In the precipitate 0.12 g (57.5%) of (IV), mp 106-108°C (from hexane), were obtained. Found: C 25.49; H 1.34: N 5.77%. $C_{10}H_5F_{15}N_2O_2$. Calculated: C 25.53; H 1.06; N 5.95%. IR spectrum (ν, cm^{-1}): 1580, 1690, 1720, 1765 (C=O), 3240-3350, 3470 (NH). ^{19}F NMR spectrum (in dioxane): –3.3 s ($(CF_3)_2C$), –14.9 s ($(CF_3)_3C$).

b) A 0.2-g portion of (I) was added to a mixture of 0.03 g of acetamide in 1 ml of absolute ether, and the mixture was left to stand at 20°C to dissolution of the precipitate. After distillation of ether, 0.1 g (43.5%) of (IV), mp 106-108°C (from aqueous EtOH), was obtained.

2-Phenyl-4,4-bis-(trifluoromethyl)-6-perfluoro-tert-butyl-1,3,5-dioxazine (V). A solution of 0.39 g of benzaldehyde in 1 ml of absolute ether was added to a solution of 1.5 g of (I) in 1 ml of ether. Two hours after the end of the exothermal reaction, ether was distilled off. Yield, 1.5 g (79%) of (V), bp 75-78°C (10 mm). Found: C 34.99; H 1.34; N 2.29%. $C_{15}H_6F_{15}NO_2$. Calculated: C 34.81; H 1.16; N 2.70%. IR spectrum (ν, cm^{-1}) 1695 (C=H). PMR spectrum: 6.1 s (CH), 6.7-7.4 m (C_6H_5). ^{19}F NMR spectrum: 2.3 q (CF_3), –0.5 q (CF_3), –14.1 s ($(CF_3)_3C$), $J_{CF_3-CF_3} = 9.4$ Hz.

2,2,2-Trimethoxy-3,3-bis(trifluoromethyl)-5-perfluoro-tert-butyl-1,4,2-oxaazaphospholine (VI). A 1.03-g portion of trimethyl phosphite was added dropwise, with cooling and stirring, to 3.5 g of (I). Two hours after the end of the exothermal reaction, 4.1 g (91%) of (VI), mp 43-45°C (from hexane), were obtained. Found: C 24.27; H 1.78; F 52.98; N 2.60; P 5.77%. $C_{11}H_9F_{15}NO_4P$. Calculated: C 24.67; H 1.68; F 53.27; N 2.61; P 5.79%. IR spectrum (ν, cm^{-1}): 1650 (C=N). PMR spectrum (in CCl_4): 3.8 d (CH_3O), $J_{CH_3-P} = 13$ Hz. ^{19}F NMR spectrum (in CCl_4) -11.8 d ($(CF_3)_2C$), -15.6 s ($(CF_3)_3C$); $J_{CF_3-P} = 4.7$ Hz.

Phenyl[α-(perfluoropivaloylamino)hexafluoroisopropyl]acetylene (VII). A 0.3-g portion of phenylacetylene was added to 1.2 g of (I), and 1 h after the end of the exothermal reaction, 0.82 g (55%) of (VII), bp 65°C (2 mm), were obtained. Found: C 37.35; H 1.19; F 55.54; N 3.49%. $C_{16}H_6F_{15}NO$. Calculated: C 37.45; H 1.17; F 55.54; N 2.73%. IR spectrum (ν, cm^{-1}): 1550, 1765 (C=O), 2260 (C≡C), 3470 (NH). PMR spectrum: 6.7 br. s. (NH), 7.0-7.4 (C_6H_5). ^{19}F NMR spectrum: -1.8 s ($(CF_3)_2C$), -14.1 s ($(CF_3)_3C$).

ω-[α-(Perfluoropivaloylamino)hexafluoroisopropyl]acetophenone (VIII). A 0.55-g portion of acetophenone was added to 2.4 g of (I). Ten minutes after the end of the exothermal reaction, the mixture contained 80% of (VIIIa). [PMR spectrum: 2.3 s (CH_3), 7.0-7.8 m (C_6H_5). ^{19}F NMR spectrum: 0.9 m ($(CF_3)_2C$), -14.8 s ($(CF_3)_3C$)]. The mixture was heated for 70 h at 140°C. By distillation, 1.52 g (62%) of acylamino ketone (IXa), bp 100-103°C (1 mm), were obtained. Found: C 36.59; H 1.48; F 53.74; N 2.67%. $C_{16}H_8F_{15}N_2O_2$. Calculated: C 36.15; H 1.50; F 53.67; N 2.63%. IR spectrum (ν, cm^{-1}): 1540, 1690, 1760 (C=O), 3250 (NH). PMR spectrum: 3.7 s (CH_2), 7.2-7.9 m (C_6H_5), 9.0 s (NH). ^{19}F NMR spectrum: -5.1 s ($(CF_3)_2C$), -14.2 s ($(CF_3)_3C$). When (IXa) was heated with MeCN (80 h, 120°C), $(CF_3)_3CH$ is eliminated (according to ^{19}F NMR spectrum).

Reaction of Hexafluoroacetone Benzoylimine with Acetophenone. A mixture of equimolar amounts of hexafluoroacetone benzoylimine and acetophenone was left to stand at 20°C; after 3 months the reaction mixture contained 23% of the initial reagents and 75% of (VIIIb) (^{19}F NMR spectrum: 0.1 q (CF_3), 1.5 q (CF_3), $J_{F-F} = 10.5$ Hz). After heating for 43 h at 120°C, the dioxazine (VIIIb) isomerizes completely into ω-[α-(benzoylamino)hexafluoroisopropyl]acetophenone (IXb) (^{19}F NMR spectrum: -6.0 s ($(CF_3)_2C$)), and the crystals that separate, mp 110-112°C, are identical to an authentic sample [9].

Reaction of Imine (I) with Pyridine. In the presence of a catalytic amount of pyridine, after 10 days at 20°C, imine (I) decomposes almost completely into perfluoroisopropyl isocyanate, perfluoroisobutylene, and $(CF_3)_3CH$ (according to ^{19}F NMR).

CONCLUSIONS

1. Hexafluoroacetone N-perfluoropivaloylimine was obtained by condensation of α-chloroperfluoroisopropyl isocyanate with perfluoro-tert-butyl anion. The compound readily adds nucleophiles, and enters into 1,4-cycloaddition reactions with nitriles, carbonyl compounds, and trimethyl phosphite.

2. Cycloadducts of hexafluoroacetone acylimines with acetophenone isomerize on heating into linear ketoamides.

3. By the action of pyridine, hexafluoroacetone perfluoropivaloylimine splits into perfluoroisopropyl isocyanate and perfluoroisobutylene.

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EXCHANGE OF HALOGEN FOR FLUORINE IN REACTIONS OF VICINAL DIHALOPOLYFLUOROALKANES WITH CESIUM FLUORIDE

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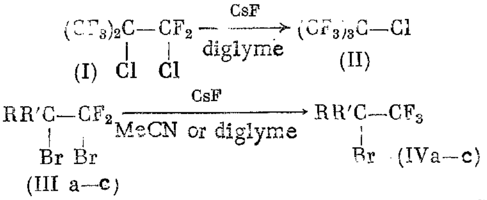
In contrast to perfluoroalkyl halides, vicinal dihalopolyfluoroalkanes readily enter halogenophilic type reactions with nucleophilic reagents, which lead to dehalogenation [1-4] or exchange of halogen for the nucleophile residue according to the elimination—addition mechanism. The last case was studied in detail with respect to the reaction of 1,2-dibromotetrafluoroethane with C-, O-, S, and Se-nucleophiles [4-7].

We found that under relatively mild conditions, certain vicinal dihalopolyfluoroalkanes and related compounds react with CsF also in aprotic dipolar solvents (MeCN, diglyme), and give products of the exchange of one of the halogens for fluorine. Thus, from dichloride (I) we can obtain monochloride (II), and from dibromides (III), monobromides (IV).

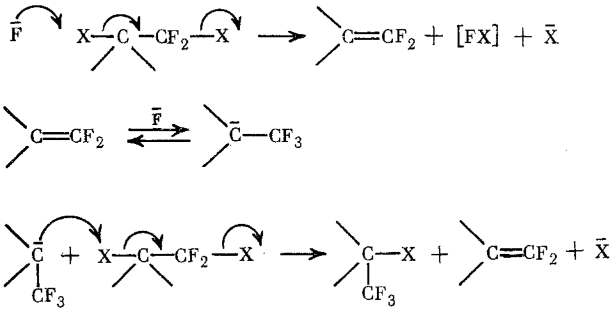


$$\underset{\text{(I)}}{(CF_3)_2\underset{Cl}{C}-\underset{Cl}{CF_2}} \xrightarrow[\text{diglyme}]{CsF} \underset{\text{(II)}}{(CF_3)_3C-Cl}$$

$$\underset{\text{(III a—c)}}{RR'\underset{Br}{C}-\underset{Br}{CF_2}} \xrightarrow[\text{MeCN or diglyme}]{CsF} \underset{\text{(IVa—c)}}{RR'\underset{Br}{C}-CF_3}$$

$R = F$, $R' = CO_2Et$ (a); $R = CF_3$, $R' = CC_2Et$ (b); $R = CF_3$, $R' = C_6H_4F$ (c).

These reactions are well described by an ionic elimination—addition chain mechanism [6], assuming that the role of the nucleophile at the initiation stage is played by anion $\bar{F}$, and the fluorocarbanion (V) participates in the chain propagation



This mechanism explains the main feature of the exchange reactions studied, namely, their selectivity. In this respect the result of the reaction of CsF with 1-iodo-1,2-dichlorotrifluoroethane (VI) is especially representative. Of the three halogens available in compound (VI), only the chlorine attached to the CF_2Cl group is exchanged, which leads to iodide (VIII). In accordance with the accepted mechanism, iodide (VIII) is the only product also in the reaction of CsF with 1-iodo-2,2-dichlorotrifluoroethane (VII)

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