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ON THE INTERACTION OF PERFLUOROALKYL CARBANIONS WITH SILVER SALTS

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SUMMARY

Perfluoroalkyl derivatives of silver may be produced by reacting fluoroolefins with silver salts in the presence of alkali metal fluorides in dimethylformamide, 1,2-dimethoxyethane or acetonitrile as a solvent. ^{19}F NMR spectra and certain reactions of these compounds have been investigated.

RESULTS AND DISCUSSION

In 1968, Miller and Burnard[1] showed that an addition reaction takes place between silver fluoride and perfluoropropene, 2-chloroperfluoropropene and perfluoro-2-methyl-2-pentene with the formation of perfluoroalkyl derivatives of silver. Later, a similar addition reaction was demonstrated between silver fluoride and tetrafluoroallene[2], as well as between silver fluoride and bis(trifluoromethyl)acetylene[3]; in these cases perfluoroalkenyl derivatives of silver are formed. Pentafluorophenylsilver has been produced by the reaction of pentafluorophenyllithium with silver trifluoroacetate[4], while α-H-hexafluoroisopropylsilver has been formed through the decarboxylation of the silver salt of α-H-hexafluoroisobutyric acid in pyridine, dimethylformamide or acetonitrile as a solvent[5]. These compounds are more stable than their non-fluorinated analogues and may be employed for synthetic purposes.

Perfluoroalkyl mercurial compounds have recently been shown by us to be readily produced by the reaction of perfluoroalkyl carbanions (from fluoro-olefins and the fluoride ion) with mercury salts[6,7].

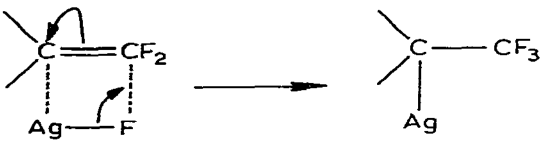
It seemed interesting to attempt to extend this reaction to the synthesis of perfluoroalkyl compounds of silver, and thus avoid the use of AgF, since many other silver salts are much easier to produce, display a higher stability towards light and are less hygroscopic. A convenient compound in this respect proved to be silver trifluoroacetate which is easily prepared by reacting silver oxide or silver carbonate with trifluoroacetic acid and is readily soluble in most organic solvents.

Perfluoroisobutene was found to react exothermally with silver trifluoroacetate in the presence of potassium fluoride in dimethylformamide, acetonitrile or 1,2-dimethoxyethane, giving perfluoro-tert-butylsilver. Perfluoropropene, trifluorochloroethene and perfluorocyclobutene have also been successfully employed in this reaction, but in these cases caesium fluoride, which has a higher solubility in organic solvents, was employed as the source of the fluoride ion. Perfluoroisopropylsilver, α-chloroperfluoroethylsilver and perfluorocyclobutylsilver have been produced in this way.

$$\left.\begin{array}{l}\mathrm{(CF_3)_2C{=}CF_2}\\ \mathrm{CF_3CF{=}CF_2}\\ \mathrm{CF_2{=}CFCl}\\ \overline{\mathrm{CF_2{-}CF{=}CF{-}CF_2}}\end{array}\right\} + \mathrm{CF_3COOAg} + \mathrm{MF} \rightarrow \left\{\begin{array}{l}\mathrm{(CF_3)_3CAg}\\ \mathrm{(CF_3)_2CFAg}\\ \mathrm{CF_3CFClAg}\\ c\text{-}\mathrm{C_4F_7Ag}\end{array}\right\} + \mathrm{CF_3COOM} \qquad \begin{array}{r}(1)\\ (2)\\ (3)\\ (4)\end{array}$$

where in eqn. (1), $M = K$; and in eqns. (2), (3) and (4), $M = Cs$.

It should be pointed out that when silver fluoride was reacted with trifluorochloroethene only a slow and incomplete reaction occurred (in a sealed ampoule), and the reaction products were not identified[1]. From this it may be deduced that the combination $CF_3COOAg + MF$ is a more effective reagent than pure silver fluoride. Indeed, a separate experiment has demonstrated that perfluoropropene is converted into perfluoroisopropylsilver more readily under these conditions than under those reported in Ref. 1. This behaviour may be explained by the fact that silver fluoride is essentially a covalent compound, although in its reactions with fluoro-olefins it behaves as a nucleophilic reagent (as may be inferred from the observed order of the reactivity of fluoro-olefins), and its addition to a double bond in the absence of external fluoride ion probably proceeds via a four-centre mechanism:



In the system fluoro-olefin + $CF_3COOAg + MF$, however, the following equilibria are set up:

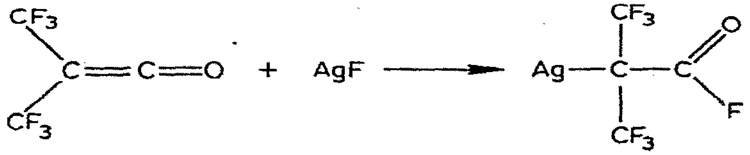
$$\begin{array}{l}{>}\mathrm{C{=}CF_2} + \mathrm{F^-} \rightleftarrows \mathrm{R_f^-}\\ \mathrm{CF_3COOAg} + \mathrm{MF} \rightleftarrows \mathrm{CF_3COOM} + \mathrm{AgF}\end{array}$$

and the formation of R_fAg occurs as a result of the interaction of the R_f^- ion with silver trifluoroacetate, or silver fluoride, or with the Ag^+ ion.

$$2\,\mathrm{R_f^-} + \begin{array}{l}\mathrm{CF_3COOAg}\\ \mathrm{AgF}\end{array} \rightarrow 2\,\mathrm{R_fAg} + \begin{array}{l}\mathrm{CF_3COO^-}\\ \mathrm{F^-}\end{array}$$

In all the cases studied, reaction occurs via the nucleophilic perfluoroalkyl carbanion R_f^-, and our results show that the introduction of catalytic amounts of caesium fluoride merely accelerates the addition of silver fluoride to perfluoropropene.

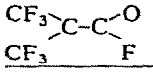
Catalysis involving the F^- ion is not necessary with strong electrophiles. Thus, bis(trifluoromethyl)ketene readily adds AgF in dimethylformamide, giving α-silverperfluoroisobutyryl fluoride. Introduction of an alkali metal fluoride into the system leads to the dimerisation of the bis(trifluoromethyl)ketene, as has been described earlier[8].



We have not attempted to isolate the silver perfluoroalkyl compounds obtained from their respective solutions, and although perfluoroisopropylsilver may be isolated as a complex with acetonitrile[1], generally this is rather difficult to accomplish since many compounds of this class are sensitive to oxygen, moisture and light. We have, in fact, concentrated our attention on a study of the ^{19}F NMR spectra of these substances. The experimental data obtained are presented in Table 1*.

TABLE 1

^{19}F NMR SPECTRA OF SOME PERFLUOROALKYL DERIVATIVES OF SILVER

R	*Conditions of measurement Solvent, temp. (°C)*	*Chemical shift (ppm)*		*Spin–spin coupling constant J (Hz)*		
		CF	*CF₃*	*F–C–Ag*	*F–C–C–Ag*	*F–F*
$(CF_3)_3C-$	CH_3CN, 34		−25			
	CH_3CN, −10				13.8	
	DMF, 34		−25.08		13.5	
$(CF_3)_2CF-$	DMF, 34	136.9	− 9.5	17.9	12.0[a]	121
				20.6[b]	13.7[b]	
CF_3CFCl-	DMF, 34	58.8	− 0.17	36.9	8.4	8.4[c]
 $(CF_3)_2C{-}C(=O)F$	DMF, 34	−95.4	−26.8			16.1

[a] ^{107}Ag. [b] ^{109}Ag. [c] "Apparent" constant (no accurate calculations were performed).

The presence of two isotopes of silver (^{107}Ag and ^{109}Ag) both with spin $=\frac{1}{2}$ governs the spin–spin coupling of these nuclei with ^{19}F nuclei. This coupling is observed at room temperature which indicates that the Ag–C bond is quite covalent. Thus, the ^{19}F signal of perfluoro-tert-butylsilver in acetonitrile at 34° is a singlet which even at −10° is converted into a doublet. In dimethylformamide, spin–spin coupling is observed at 34° and coalescence occurs only at +60°. Such a difference in the rates of anion formation is obviously related to the different solvation capacities of the two solvents. With perfluoroisopropylsilver, however, virtually no difference is observed in the spectra obtained in different solvents. In this compound, spin–spin coupling between the ^{19}F nuclei and the two silver isotopes is characterised by two different constants. It is, in fact, very difficult to achieve rapid exchange along the Ag–C bond in this compound and although the CF_3 signal ultimately changes to a doublet at +100°, this is of little value as far as resolution is concerned for the sub-

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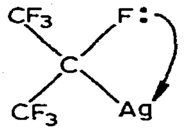
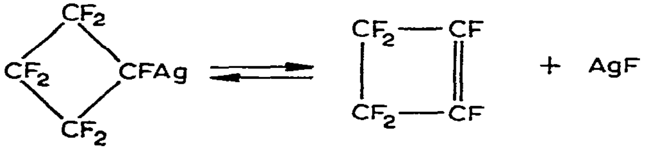
* Spectra were recorded on an R-20 Hitachi–Perkin–Elmer apparatus; working frequency, 56.46 MHz. Temperature dependences were studied using a spectrometer Model PR-2305 produced in the Soviet Union; working frequency of the apparatus, 56.46 MHz. Chemical shifts are given relative to CF_3COOH as the external standard.

stance begins to decompose at this temperature. The low mobility of the perfluoroisopropyl group attached to the silver atom may be attributed to the interaction of the unshared pair of electrons of the fluorine atom attached to the α-carbon atom with the vacant orbitals of silver (α-coordination). This conclusion is in fair agreement with results obtained earlier. Thus, in the case of α-H-perfluoroisopropylsilver, $(CF_3)_2CHAg$, where such interaction is impossible, rapid anion exchange occurs and spin–spin coupling between ^{19}F and silver nuclei may be readily observed at temperatures as low as −40° (in dimethylformamide)[5]. α-Coordination between a fluorine atom and a metal atom was reported earlier for perfluoroalkyl derivatives of mercury[9] and cadmium[10].



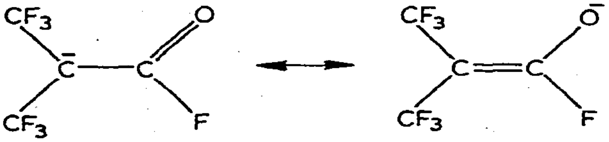
Although the spectrum of the perfluorocyclobutyl group is rather complicated that of perfluorocyclobutylsilver is even more complex due to fluorine–silver spin–spin coupling. In addition, with this latter compound there is the possibility of an equilibrium of the type:



being set up. Because of this, in addition to signals corresponding to perfluorocyclobutylsilver being present the spectrum also contains those of perfluorocyclobutene. On cooling, the spectrum is transformed, but its characteristics have not been studied in greater detail.

In the spectrum of α-chloroperfluoroethylsilver two signals are observed: a broadened CF_3 triplet and a doublet of CF quadruplets. On cooling, the CF_3 signal is converted into a strong triplet, and this on heating changes into a doublet (at +70°). Thus, at +70° rapid exchange along the Ag–C bond is attained in this compound.

With α-silverperfluoroisobutyryl fluoride, signals corresponding to the anion are observed in the spectrum at +34°; spin–spin coupling involving silver nuclei is however apparently absent. On decreasing the temperature, a broadened signal is observed which is not resolved above −110°. In this case the high mobility of the anion is due to its resonance stabilisation, *viz*:



Although it is not possible to arrest the exchange until the onset of spin–spin coupling with the silver atom, the fact that the signal broadens is indicative of the slowing down of the process.

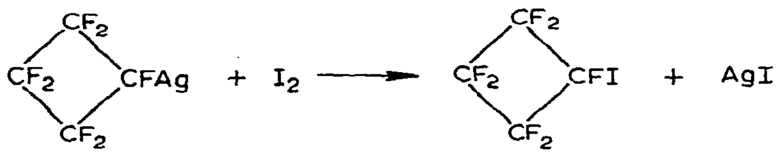
It is also pertinent to mention one other peculiarity observed in the ^{19}F NMR spectra of perfluoroalkyl derivatives of silver. Under certain conditions (depending on the temperature and the solvent) additional signals may be observed in the spectra of these compounds. Thus, the spectrum of perfluoro-tert-butylsilver in dimethylformamide consists of a somewhat broadened doublet exhibiting different intensities for the signals. On cooling, this spectrum is converted into one exhibiting two symmetrical doublets. On solution in 1,2-dimethoxyethane, the spectrum of this compound exhibits spin–spin coupling between the fluorine nuclei and ^{107}Ag and ^{109}Ag nuclei, but, in addition to these signals, a broadened doublet is also present. The characteristics of the spectrum are as follows: (*a*) $\delta(CF_3)$ 24.77 ppm; $J(^{19}F\text{–}C\text{–}C\text{–}^{107,109}Ag)$ 12.4 and 14.3 Hz. and (*b*) $\delta(CF_3)$ 24.68 ppm; $J(^{19}F\text{–}C\text{–}C\text{–}^{107,109}Ag)$ 14.5 Hz. On addition of 2,2′-bipyridine, the spectrum is converted into one containing a system two doublets: (*a*) $\delta(CF_3)$ 24.93 ppm; $J(^{19}F\text{–}C\text{–}C\text{–}^{107,109}Ag)$ 13.7 Hz. and (*b*) $\delta(CF_3)$ 26.32 ppm; $J(^{19}F\text{–}C\text{–}C\text{–}^{107,109}Ag)$ 16.6 Hz. It is suggested that this phenomenon may be attributed to the presence of complexes formed between the silver perfluoroalkyl derivatives and molecules of the solvent. For instance, it is probable that complexes with different numbers of solvent molecules exist in the solution. Silver nitrate is known to exist in acetonitrile solution as two solvates in equilibrium with each other[11]:

$$Ag^+ \xrightleftharpoons{CH_3CN} [AgNCCH_3]^+ \xrightleftharpoons{CH_3CN} [Ag(NCCH_3)_2]^+$$

and it has been shown recently that silver salts in different solvents are capable of giving complexes with dimethylformamide of the type $Ag(DMF)_n^+$ [12].

In addition to the ^{19}F NMR spectra, we have also studied a number of reactions involving the perfluoroalkyl derivatives of silver. All these compounds react readily with iodine, giving perfluoroalkyl iodides:

$$(CF_3)_2CFAg + I_2 \longrightarrow (CF_3)_2CFI + AgI$$



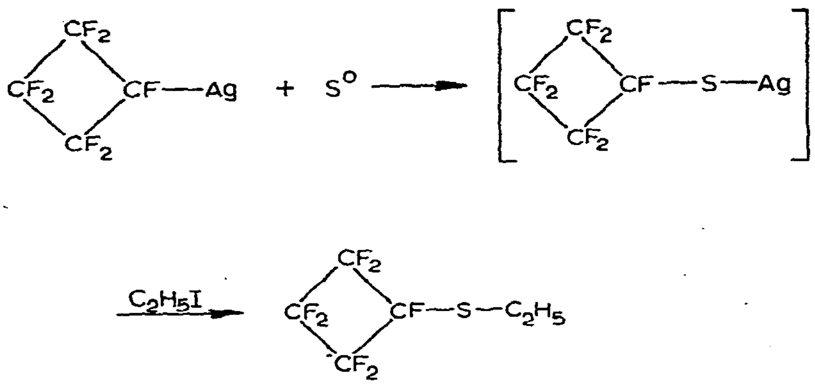
$$CF_3CFClAg + I_2 \longrightarrow CF_3CFClI + AgI$$

Perfluoro-tert-butylsilver reacts with elemental sulphur; the resulting perfluoro-tert-butylthiosilver may be regarded as a convenient source of the perfluoro-tert-butylthio-group, as has been shown by its reaction with allyl iodide:

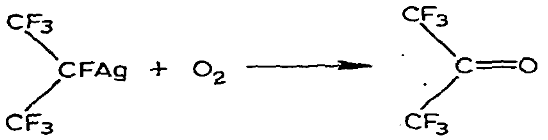
$$(CF_3)_3CAg + S^0 \rightarrow (CF_3)_3CSAg$$

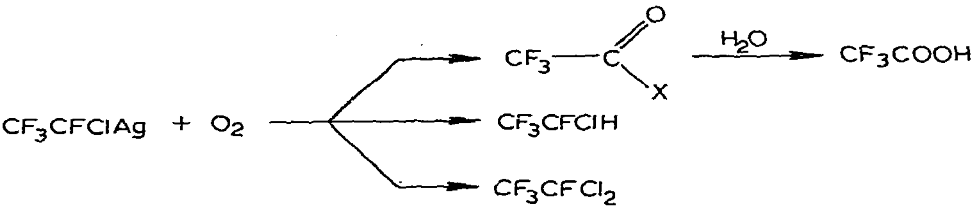
$$(CF_3)_3CSAg + CH_2{=}CH\text{–}CH_2I \rightarrow (CF_3)_3C\text{–}S\text{–}CH_2\text{–}CH{=}CH_2$$

Perfluorocyclobutylsilver also reacts with sulphur in a similar manner:



The attempted oxidation of perfluoro-tert-butylsilver with oxygen was not successful despite the fact that perfluoroisopropylsilver and α-chloroperfluoroethylsilver are readily oxidised by this method. With perfluoroisopropylsilver, hexafluoroacetone was obtained and with α-chloroperfluoroethylsilver the product was a mixture from which, after treatment with water, trifluoroacetic acid was obtained.



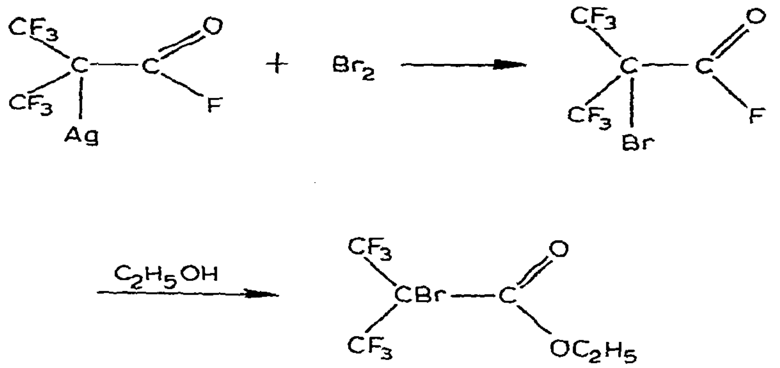


The formation of 1-H-1-chloroperfluoroethane, which occurs despite thorough drying of the oxygen used in the reaction, may be explained by the decomposition of the organosilver compound leading to the formation of the free radical $CF_3CFCl\cdot$. This radical is also, possibly, the precursor of 1,1-dichloroperfluoroethane, but it should be mentioned that the formation of the last-mentioned compound has also been observed in the reaction between caesium fluoride and trifluorochloroethene in dimethylformamide.

$$CF_2{=}CFCl + CsF \rightarrow CF_3CFCl_2 + \text{oligomers (b.p. up to } 150^\circ)$$

The structure of the α-silverperfluoroisobutyryl fluoride obtained from bis-

(trifluoromethyl)ketene has been confirmed by its transformation into the ethyl ester of α-bromoperfluoroisobutyric acid.



EXPERIMENTAL

Perfluoro-tert-butylsilver

Into a three-neck flask equipped with a gas inlet, a stirrer and a reflux condenser, and cooled at −78°, was placed 40 ml of acetonitrile, 10 g (45.5 mmoles) of silver trifluoroacetate and 5 g (86 mmoles) of freshly calcined finely divided potassium fluoride. Into this mixture 10.5 g (52 mmoles) of perfluoroisobutene were introduced with vigorous stirring. A weak exothermic reaction occurred. In the ^{19}F NMR spectrum of the resulting solution only the signal of perfluoro-tert-butylsilver was observed; signals corresponding to perfluoroisobutene were absent*.

Perfluoro-tert-butylthiosilver

Finely divided sulphur (6 g) was slowly added to a solution of perfluoro-tert-butylsilver prepared as described above. On completion of the resulting exothermic reaction, the mixture was heated at 50° for 1 h after which the volatile portion was vacuum distilled and the residue recrystallised from methanol. As a result of this treatment 5.3 g of perfluoro-tert-butylthiosilver were obtained (32% yield based on the amount of perfluoroisobutene used), in the form of colourless crystals stable in air and decomposing at 80°. (Found: C, 13.82; S, 8.90. C_4F_9SAg calcd.: C, 13.38; S, 8.93%.) ^{19}F NMR spectrum: singlet at −10.7 ppm.

Allyl perfluoro-tert-butyl sulphide

To a mixture consisting of 40 ml of dry dimethylformamide, 10 g (45.5 mmoles) of silver trifluoroacetate and 5 g (86 mmoles) of potassium fluoride were added 10.5 g (52 mmoles) of perfluoroisobutene, followed by 6 g of finely divided sulphur and 7.8 g (46.5 mmoles) of allyl iodide in succession with vigorous stirring. The mixture was stirred for 1 h then poured into dilute hydrochloric acid, the lower layer separated, dried over calcium chloride and distilled. The resulting product consisted of 6.1 g (46.2% yield based on the amount of perfluoroisobutene) of allyl perfluoro-tert-butyl sulphide, b.p. 113–115°. (Found: C, 28.51; H, 1.72; F, 58.15; S, 10.39. C_7-

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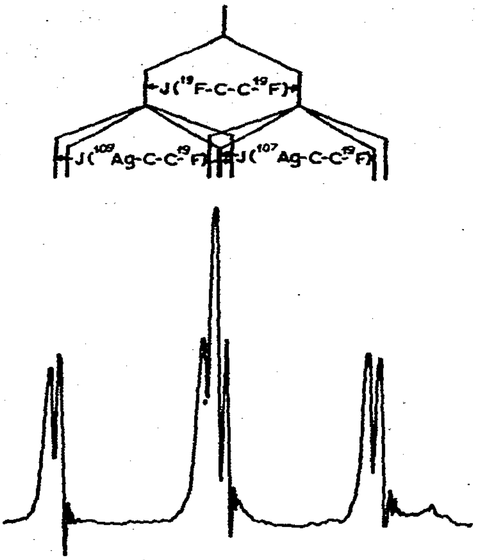
* In addition, of course, to the signal of CF_3COO^- in each case.



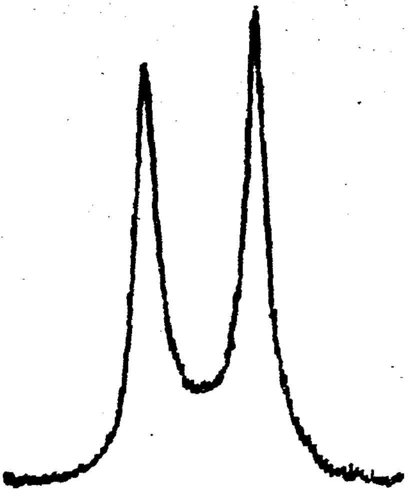


Fig. 1. ^{19}F NMR spectrum of perfluoroisopropylsilver in acetonitrile (CF_3 group).

Fig. 2. ^{19}F NMR spectrum of perfluoro-tert-butylsilver in 1,2-dimethylformamide.

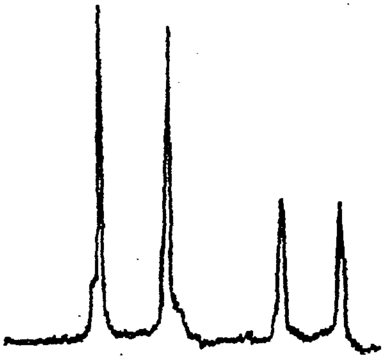


Fig. 3. ^{19}F NMR spectrum of perfluoro-tert-butylsilver in 1,2-dimethoxyethane.

Fig. 4. ^{19}F NMR spectrum of perfluoro-tert-butylsilver in 1,2-dimethoxyethane+2,2'-bipyridine.

H_5F_9S calcd.: C, 28.77; H, 1.72; F, 58.53; S, 10.97%.) ^{19}F NMR spectrum: singlet at −11.9 ppm. ^1H NMR spectrum: characteristic of a five-spin allyl system, containing two groups of signals with centres at δ 3.2 ppm (CH_2) and 4.5–6 ppm (vinyl group). (Here and subsequently the external standard was TMS).

Perfluoroisopropylsilver

As in the preparation of perfluoro-tert-butylsilver, the preparation involved the introduction of 4.5 g (30 mmoles) of perfluoropropene into a mixture consisting of 30 ml of dimethylformamide, 6.6 g (30 mmoles) of silver trifluoroacetate and 9.1 g (60 mmoles) of caesium fluoride, the mixture being vigorously stirred during the introduction. The resulting reaction was weakly exothermal and involved the complete consumption of the perfluoropropene as demonstrated by the absence of all signals other than those of perfluoroisopropylsilver from the ^{19}F NMR spectrum.

Perfluoroisopropyl iodide

To the solution of perfluoroisopropylsilver, prepared as described above, 7.6 g (30 mmoles) of finely divided iodine was added with vigorous stirring. The mixture was further stirred for 1 h, the resulting product plus the solvent vacuum distilled into a trap cooled at $-78°$, the contents of the trap poured into dilute hydrochloric acid, the lower layer separated and distilled over concentrated sulphuric acid. The resulting product consisted of 3.7 g of perfluoroisopropyl iodide (42% yield based on the amount of perfluoropropene), b.p. 41°. Lit.[13]: b.p. 41.2°. ^{19}F NMR spectrum: doublet, -2 (CF_3); heptet, 70.8 ppm (CF): $J(^{19}F\text{–}C\text{–}^{19}F)$ 14.2 Hz.

Oxidation of perfluoroisopropylsilver

Perfluoroisopropylsilver was prepared from 11 g (50 mmoles) of silver trifluoroacetate, 7.6 g (50 mmoles) of caesium fluoride and 7.5 g (50 mmoles) of perfluoropropene in 40 ml of acetonitrile. When heating of the reaction mixture had been completed, oxygen was added with vigorous stirring and resulted in an exothermal reaction. On completion of this reaction, the resulting mixture was decomposed by the addition of dilute hydrochloric acid and was extracted several times with ether. The ethereal extract was dried over calcium chloride and the solvent was distilled off by heating on a water bath. Distillation of the residue gave a fraction boiling over the temperature range of 90–110° (the ^{19}F NMR spectrum exhibited a singlet at 5.43 ppm) which was identified as the "hydrate" of hexafluoroacetone; on treatment with concentrated sulphuric acid, this material gave 3.8 g of hexafluoroacetone (43% yield based on the amount of perfluoropropene), which was identified as an adduct with aniline, m.p. 64–66°. Lit.[14]: m.p. 64–66°. Mixing with a standard specimen gave no depression of the melting point.

Perfluorocyclobutylsilver

Using a procedure similar to that used for the preparation of perfluoro-tert-butylsilver, perfluorocyclobutylsilver was produced from the reaction of 6.2 g (28 mmoles) of silver trifluoroacetate and 4.5 g (29.5 mmoles) of perfluorocyclobutene in 40 ml of acetonitrile. The reaction was weakly exothermic.

Perfluorocyclobutyl iodide

To the solution of perfluorocyclobutylsilver obtained as described above, 7.1 g (28 mmoles) of finely divided iodine was added with vigorous stirring. The mixture was further stirred for 1 h and the resulting perfluorocyclobutyl iodide separated by a similar procedure to that used in the preparation of perfluoroisopropyl iodide. In this way 3.3 g of product was obtained (38% yield based on the amount of perfluorocyclobutene), b.p. 42°. The substance was identified by a GLC method, employing a standard specimen prepared by reacting perfluorocyclobutene with I_2+IF_5. (Found: C, 16.07; F, 42.54. C_4F_7I calcd.: C, 15.60; F, 43.19%.)

Ethyl perfluorocyclobutyl sulphide

To a mixture consisting of 8 g (36.4 mmoles) of silver trifluoroacetate, 5.7 g

(37.5 mmoles) of caesium fluoride and 30 ml of dimethylformamide, 4.5 g (28 mmoles) of perfluorocyclobutene were initially added followed by 3 g of finely divided sulphur with vigorous stirring. The mixture was heated at 60° for 30 min when 6.25 g (40 mmoles) of ethyl iodide were added and the resulting mixture heated for 2 h at 75°. The reaction products together with a portion of the solvent were distilled under moderate vacuum into a trap cooled at −78°. The contents of the trap were poured into dilute hydrochloric acid, the lower layer separated, dried over calcium chloride and distilled. In addition to ethyltrifluoroacetate, 1.45 g of ethyl perfluorocyclobutyl sulphide were obtained (21.4% yield based on the amount of perfluorocyclobutene), b.p. 104°. (Found: C, 29.49; H, 2.02; S, 13.11. $C_6H_5F_7S$ calcd.: C, 29.76; H, 2.08; S, 13.24%.) ^{19}F NMR spectrum: group of signals characteristic of the perfluorocyclobutyl system. ^1H NMR spectrum: triplet, 11.5; quartet, 27.2 ppm; $J(^1H\text{–}C\text{–}^1H)$ 7.35 Hz. Mass spectrum (*m/e* ratio): 242, *M*; 227, $M\text{–}CH_3$; 213, $M\text{–}C_2H_5$; 142, $M-C_2F_4$; 114, $M-(C_2F_4+C_2H_4)$; 69, CF_3; 29, C_2H_5.

α-Chloroperfluoroethylsilver

A solution of α-chloroperfluoroethylsilver was obtained by the same procedure as that used for perfluoro-tert-butylsilver but employing 9 g (41 mmoles) of silver trifluoroacetate, 10 g (66 mmoles) of caesium fluoride, 4.5 g (39 mmoles) of trifluorochloroethene and 40 ml of dimethylformamide. The reaction was weakly exothermic. Only signals corresponding to α-chloroperfluoroethylsilver were observed in the ^{19}F NMR spectrum of the solution.

α-Chloroperfluoroethyl iodide

To a solution of α-chloroperfluoroethylsilver obtained as above were added 16 g (59 mmoles) of finely divided iodine with vigorous stirring. α-Chloroperfluoroethyl iodide was separated and purified by the method described above for perfluoroisopropyl iodide, and 4.4 g of the product was obtained (45% yield based on the amount of trifluorochloroethene), b.p. 56°. ^{19}F NMR spectrum: doublet, 4.3 ppm (CF_3); quartet, chemical shift coinciding with that of the standard (CF); $J(^{19}F\text{–}C\text{–}^{19}F)$ 10 Hz. Mass spectrum: 262, *M*; 243, $M-F$; 227, $M-Cl$; 208, C_2F_3I; 193, CFClI; 158, CFI; 135, C_2F_4Cl; 126, I; 116, C_2F_3Cl; 100, C_2F_4; 69, CF_3; 66, CFCl.

Oxidation of α-chloroperfluoroethylsilver

α-Chloroperfluoroethylsilver was obtained as described above for perfluoro-tert-butylsilver using 8.25 g (66 mmoles) of silver fluoride, 2 g (13 mmoles) of caesium fluoride and 7.5 g (65 mmoles) of trifluorochloroethene in 40 ml of dimethylformamide. After heating, the reaction flask was connected to a trap cooled at −78°, and, while the contents of the flask were stirred, oxygen was bubbled through until the exothermal reaction had ceased. The reaction mixture was then decomposed by the addition of water and extracted several times with ether. The ethereal layer was dried over calcium chloride, the ether distilled off and the residue fractionated. The fraction with b.p. 102–104° (1.2 g)—hydrous trifluoricacetic acid—was separated. ^{19}F NMR spectrum: singlet at −0.7 ppm. The substance was identified as $CF_3COOC_2H_5$ by the GLC method. The trap connected to the distillation apparatus contained 2.3 g of a substance which was identified by GLC/mass spectrometry (on a Varian CH-8 chromatograph–mass-spectrometer) as a mixture consisting of 1,1-dichloroperfluoroethane and 1-H-1-chloroperfluoroethane in a 6.5/1 ratio.

α-Silverperfluoroisobutyryl fluoride

The compound was obtained by the same procedure as that used in the case of perfluoro-tert-butylsilver, employing 3 g (16.9 mmoles) of bis(trifluoromethyl)-ketene and 2.14 g (16.9 mmoles) of silver fluoride in 40 ml of dimethylformamide.

Ethyl ester of α-bromoperfluoroisobutyric acid

To the solution of α-silverperfluoroisobutyryl fluoride obtained as above, 2.85 g (18 mmoles) of bromine and 2.71 g (59 mmoles) of ethanol were added in succession with vigorous stirring. The reaction mass was stirred for 2 h, then poured into dilute hydrochloric acid, the lower layer separated, dried over calcium chloride, and vacuum distilled. From this process 1.3 g of the ethyl ester of α-bromoperfluoroisobutyric acid were obtained [36.2% yield based on amount of bis(trifluoromethyl)ketene], b.p. 64–66°/66 mmHg. Lit.[15]: b.p. 63–66°/66 mmHg. ^{19}F NMR spectrum: singlet at −10.3 ppm. Mass spectrum (for ^{79}Br): 302, *M*; 257, $(CF_3)_2CBrCO$; 229, $(CF_3)_2CBr$; 210; $CF_3(CF_2)CBr$; 129, CF_2Br; 69, CF_3; 45, C_2H_5O; C_2H_5; 15, CH_3.

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