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# REACTIONS OF PERFLUOROALKYLCALCIUM DERIVATIVES WITH KETONES AND ALDEHYDES

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## Summary

Perfluoroalkyl iodides, $R_FI$, react in ethers with aldehydes and ketones in the presence of calcium to give the alcohols $R_FC(OH)R1R2$. The best yields (20—70%) were obtained with Ca/Hg amalgam in THF as solvent at −20 to −40°C. The new alcohols were characterized by $^1H$ and $^{19}F$ NMR and mass spectrometry. The results are interpreted in terms of the intermediate formation of an organocalcium species.

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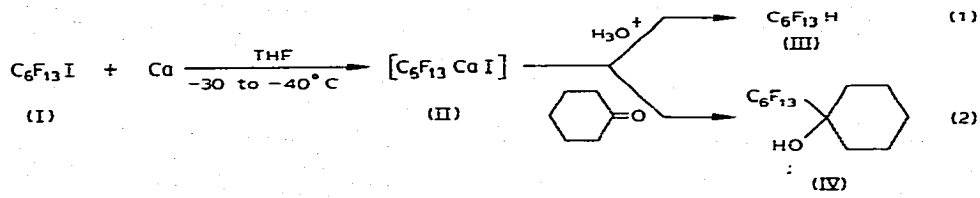
The relative paucity of methods available for the selective introduction of a perfluoroalkyl chain into a molecule has stimulated investigations of perfluoroalkyl organometallic compounds. Among these are the Grignard and the copper(I) derivatives. The former are obtained by an exchange reaction [1]; their use in synthesis mainly involves addition to carbonyl compounds, but remains very limited, probably on account of the relative difficulty of their preparation. The copper(I) derivatives do not react with carbonyl compounds, but couple with aromatic halides [2], and add to various unsaturated substrates [3—5].

As a part of our efforts to devise more efficient selective methods of perfluoroalkylating, we investigated the reaction of perfluoroalkyl iodides with carbonyl compounds in the presence of calcium, a reaction which is presumed to proceed through a perfluoroalkylcalcium intermediate [6].

## Results and discussion

The perfluoroalkyl iodides referred to below as F-alkyl iodides, and denoted by $R_FI$, were found to react with finely divided metallic calcium in basic solvents such as tetrahydrofuran (THF), dioxan or diethylether. When the mixture was quenched with dilute HCl after various reaction times (1, 2, 4, 8, 16 h), increasing quantities of $R_FH$ (up to ca. 80% after 16 h for $R_F = C_6F_{13}$) were obtained, while the addition of cyclohexanone to the reaction mixture gave the alcohol $(CH_2)_5C(OH)R_F$ in ca. 35% yield after 15 h, along with some $R_FH$. The

nature of the products which were isolated in reactions 1 and 2 supports the formation of an organocalcium intermediate.




*(a) Optimisation of the reaction.* The reaction with cyclohexanone was used to optimise the experimental conditions: the solvent, reaction temperature, physical state of the metal and order of addition of the reactants were varied.

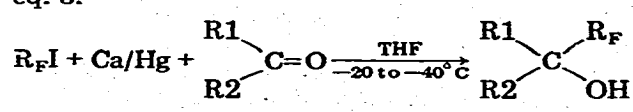
The most satisfactory solvent tested was THF. In dioxan or diethyl ether, induction periods varying from 30 min to 1 h were observed. In non-polar solvents such as benzene no reaction occurred even at room temperature; in this case, the reaction started after addition of THF (ca. 2/3 by vol.). A reaction was also not observed in more basic solvents such as triethylamine, ethylenediamine or tetramethylethylenediamine, perhaps because of the formation of charge transfer complexes between $R_FI$ and the solvent [7].

When the reaction was carried out in THF containing cyclohexanone at room temperature, calcium was readily consumed (90—95% after 2 h), but only $R_FH$ and no alcohol was formed. The best yields of the expected condensation product were obtained between −20 and −40°C.

The importance of the purity and physical state of the metal in the initial stage of formation of alkylcalcium compounds has already been recognized, and various methods have been proposed to make the calcium more reactive [8]. With F-alkyl iodides, and finely divided, highly-pure calcium raspings ($\phi$ 0.3 mm), etching of the metal was observed after an induction period of ca. 30 min at −20°C. After completion of the reaction large quantities of III were produced along with 20 to 30% of IV. In contrast, the reaction started immediately at −20°C when a calcium/mercury amalgam was used; it then proceeded smoothly, and the yield of IV was increased to 58%.

The timing of the addition of the carbonyl compound is also important: better yield were obtained when the reaction of I with calcium took place in the presence of the carbonyl compound (Barbier method), an observation which parallels that of Chastrette for the hydrocarbon series [9].

*(b) Reactions with carbonyl compounds.* All the reactions, the results of which are summarized in Table 1, were performed by the procedure established for cyclohexanone. In most cases the only product of the reaction was the alcohol resulting from addition of the F-alkyl group to the carbonyl group, according to eq. 3.




(3)

Along with these alcohols, small amounts of diols were isolated as side products in the case of the easily enolisable acetone (28%) or 2-butanone (10%).

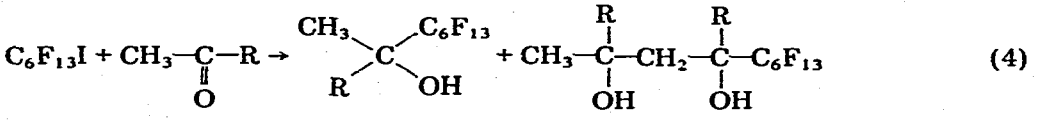
TABLE 1

REACTION OF IODO-PERFLUOROALKANES WITH KETONES AND ALDEHYDES IN THE PRESENCE OF CALCIUM

| Carbonyl compound | Exp. conditions | | Products | No. | Yields (%) |
|---|---|---|---|---|---|
| | time (h) | temperature (°C) | | | |
| cyclo-$C_6H_{10}O$ | 8 | —20 | cyclo-$C_6H_{10}(OH)C_6F_{13}$ | IV | 58 |
| $CH_3C(O)CH_3$ | 20 | —40 | $(CH_3)_2C(OH)C_6F_{13}$ | V | 37 |
| | | | $(CH_3)_2C(OH)CH_2C(CH_3)(OH)C_6F_{13}$ | VI | 28 |
| $CH_3C(O)C_2H_5$ | 18 | —30 | $CH_3C(OH)C_2H_5C_6F_{13}$ | VII | 29 |
| | | | $CH_3C(OH)C_2H_5CH_2C(OH)C_2H_5C_6F_{13}$ | VIII | 10 |
| $C_2H_5C(O)C_2H_5$ | 8 | —40 | $(C_2H_5)_2C(OH)C_6F_{13}$ | IX | 66 |
| $[(CH_3)_2CH]_2C(O)$ | 18 | —40 | $C_{12}F_{26}$ | X | 31 |
| | | | $[(CH_3)_2CH]_2C(OH)C_6F_{13}$ | XI | 40 |
| $C_4H_9C(O)C_4H_9$ | 15 | —30 | $(C_4H_9)_2C(OH)C_6F_{13}$ | XII | 22 |
| $CH_3C(O)C_6H_5$ | 22 | —35 | $CH_3C(OH)C_6H_5C_6F_{13}$ | XIII | 30 [a] |
| $C_6H_5CHO$ | (a) $C_2F_5I$ 20 | —40 | $C_6H_5CH(OH)C_2F_5$ | XIV | 69 |
| | (b) $C_6F_{13}I$ 20 | —40 | $C_6H_5CH(OH)C_6F_{13}$ | XV | 56 |
| o-$OHC_6H_4CHO$ | 20 | —40 | o-$OHC_6H_4CH(OH)C_6F_{13}$ | XVI | 21 |

[a] Estimated by GLC.

They probably result from the addition of the organometallic species to a ketol (eq. 4).



$$C_6F_{13}I + CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-R \rightarrow \begin{matrix} CH_3 \\ R \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} C_6F_{13} \\ OH \end{matrix} + CH_3-\overset{\displaystyle R}{\overset{|}{C}}(OH)-CH_2-\overset{\displaystyle R}{\overset{|}{C}}(OH)-C_6F_{13} \qquad (4)$$

(R = $CH_3$, $C_2H_5$)

This type of product was previously observed to predominate in the reaction between methylcalcium iodide and acetone, which gives mesityl oxide in 95% yield [10], but this observation has recently been disputed [11]. The nature of the ketolisation agent (calcium salts or organometallic compound itself) has not been elucidated.

The reaction with diisopropylketone afforded the expected alcohol $(i\text{-}C_3H_7)_2C(OH)C_6F_{13}$ (40%), but it was accompanied by the formation of $C_{12}F_{26}$ (30%), a compound likely to arise from free radical decomposition of the organometallic species. The formation of radicals would not be surprising in reactions involving hindered substrates, as was shown with Grignard reagents in the hydrocarbon series [12].

Acetophenone gave about 30% of the alcohol $C_6H_5C(CH_3)OHC_6F_{13}$ (estimated by VPC), along with some fluorine-containing polymeric substances. The alcohol could not be satisfactorily freed from acetophenone, and was characterized by its spectra only.

The secondary alcohols resulting from the reactions of aldehydes could be isolated only in the case of aromatic aldehydes ($C_6H_5CHO$ and o-$OHC_6H_4CHO$);

TABLE 2

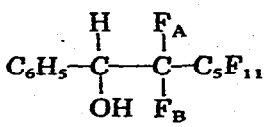
PROTON MAGNETIC RESONANCE DATA FOR ALCOHOLS IV–XVI [a]

| Compound (No.) | Chemical shifts and coupling constants | | | | Solvent |
|---|---|---|---|---|---|
| cyclo-$C_{10}H_{10}(OH)C_6F_{13}$ (IV) | $\delta(CH_2)$ | 1.75 [b] | | | $CCl_3F$ |
| | $\delta(OH)$ | 2.30 | | | |
| $(CH_3)_2C(OH)C_6F_{13}$ (V) | $\delta(CH_3)$ | 1.45s | | | $CCl_4$ |
| | $\delta(OH)$ | 2.45 | | | |
| $(CH_3)_2C(OH)CH_AH_BC(OH)(CH_3)C_6F_{13}$ (VI) | $\delta(CH_A)$ | 2.17 | $\delta(CH_B)$ | 1.6 | $CCl_3F$ |
| | | | $^2J(H_A-H_B)$ | 15 Hz | |
| | $\delta(CH_3)_X$ | 1.45s, 1.32s | $\delta(CH_3)_Y$ | 1.55s | |
| $(CH_3CH_2)(CH_3)C(OH)C_6F_{13}$ (VII) | $\delta(CH_3)$ | 1.05s | $\delta(CH_3CH_2)$ | 1.8q | $CCl_4$ |
| | $\delta(CH_3CH_2)$ | 1.61t | $\delta(OH)$ | 2.76s | |
| $(CH_3)(C_2H_5)C(OH)CH_2(C_2H_5)C(OH)C_6F_{13}$ (VIII) | | [c] | | | $CCl_4$ |
| $(C_2H_5)_2C(OH)C_6F_{13}$ (IX) | $\delta(CH_2)$ | 1.85q | $\delta(OH)$ | 2.75s | $CCl_4$ |
| | $\delta(CH_3)$ | 1.03t | $^3J(H-H)$ | 7.5Hz | |
| $(i\text{-}C_3H_7)_2C(OH)C_6F_{13}$ (XI) | $\delta(CH_3)$ | 1.1d | $^3J(H-H)$ | 7.5Hz | $CCl_4$ |
| | $\delta(CH)$ | 2.45spt | $\delta(OH)$ | 2.75s | |
| $(n\text{-}C_4H_9)_2C(OH)C_6F_{13}$ (XII) | | [c] | | | $CCl_4$ |
| $CH_3C(OH)C_6H_5C_6F_{13}$ (XIII) | $\delta(CH_3)$ | 1.75s | $\delta(C_6H_5)$ | 7.0 [b] | $CCl_4$ |
| | $\delta(OH)$ | 2.52s | | | |
| $C_6H_5CH(OH)CF_AF_BCF_3$ (XIV) | $\delta(CH)$ | 4.9dd | | | $CCl_4$ |
| | $^3J(H-F_A)$ | 10Hz | $^3J(H-F_B)$ | 14Hz | |
| $C_6H_5CH(OH)CF_AF_BC_5F_{11}$ (XV) | $\delta(CH)$ | 5.2dd | $\delta(OH)$ | 2.8s | $CCl_3F$ |
| | $^3J(H-F_A)$ | 6.5Hz | $^3J(H-F_B)$ | 17.5Hz | |
| $o\text{-}OHC_6H_4CH(OH)CF_AF_BC_5F_{11}$ (XVI) | $\delta(CH)$ | 5.25dd | $\delta(OH)$ | 3.8s | $CCl_3F$ |
| | $^3J(H-F_A)$ | 7Hz | $^3J(H-F_B)$ | 17Hz | |

[a] s = singlet; d = doublet; t = triplet; q = quartet; spt = septulet. δ are given in ppm downfield from TMS as internal standard. Errors are 0.2 ppm for chemical shifts and 0.5 Hz for coupling constants. [b] Broad signal. [c] Complex spectrum.

the aliphatic aldehydes we tested ($C_2H_5CHO$, $C_3H_7CHO$ and $CH_3CH{=}CHCHO$) gave high boiling mixtures.

*(c) Spectral characteristics.* The F-alkylated alcohols were characterized through NMR ($^1H$ and $^{19}F$ NMR, Tables 2 and 3), IR, and mass spectrometry and elemental analysis. The proton NMR spectra are consistent with the proposed structures. The benzylic proton in alcohols XIV, XV and XVI consist of doublets of doublets showing the two neighboring fluorine atoms to be anisochronous, thus for example in XV:



$^3J(H-F_A)$ 6.5 Hz
$^3J(H-F_B)$ 17.5 Hz

Variable temperature NMR measurements show that the two distinct coupling constants are preserved up to 110°C; thus they originate in the diastereotopic character of the two fluorine atoms rather than an intramolecular hydrogen bond. This conclusion is further supported by the observation of a single sharp absorption band at 3620 $cm^{-1}$ in the IR, assignable to a free $\nu$(OH) vibration.

The $^{19}F$ NMR data call for two remarks concerning the chemical shifts of the

TABLE 3

$^{19}F$ NMR CHEMICAL SHIFTS FOR ALCOHOLS IV–XVI [a]

| Compound | $CF_2$ (α) | $CF_2$ (β) | $CF_2$ (γ) | $CF_2$ (δ) | $CF_2$ (ε) | $CF_3$ | Solvent |
|---|---|---|---|---|---|---|---|
| cyclo-$C_6H_{10}(OH)C_6F_{13}$ (IV) | 117.0 | 119.5 | (120.0 [†] | 121.6 [†]) | 124.1 | 80.0 | $CCl_3F$ |
| $(CH_3)_2C(OH)C_6F_{13}$ (V) | 117.9 | 120.4 | 121.2 | 121.2 | 125.0 | 80.4 | $CCl_4$ |
| $(CH_3)_2C(OH)CH_2C(OH)CH_3C_6F_{13}$ (VI) | 116.2 | 119.5 | (119.5 | 120.4 [†]) | 124.0 | 80.4 | $CCl_3F$ |
| $(CH_3)(C_2H_5)C(OH)C_6F_{13}$ (VII) | 116.6 | 118.3 | (119.5 [†] | 120.4 [†]) | 124.1 | 80.8 | $CCl_4$ |
| $(CH_3)(C_2H_5)C(OH)CH_2(C_2H_5)C(OH)C_6F_{13}$ (VIII) | 116.2 | 117.9 | (120.8 | 121.6 [†]) | 124.5 | 81.6 | $CCl_4$ |
| $(C_2H_5)_2C(OH)C_6F_{13}$ (IX) | 115.8 | 117.9 | 120.8 | 120.8 | 124.5 | 80.4 | $CCl_3F$ |
| $(i\text{-}C_3H_7)_2C(OH)C_6F_{13}$ (XI) | 108.0 | 117.1 | 120.5 | 120.5 | 124.5 | 80.5 | $CCl_4$ |
| $(n\text{-}C_4H_9)_2C(OH)C_6F_{13}$ (XII) | 115.8 | 117.9 | (120.0 [†] | 120.8 [†]) | 124.5 | 80.4 | $CCl_4$ |
| $CH_3C(OH)C_6H_5F_{13}$ (XIII) | 116.5 | 118.5 | (122.0 [†] | 123.0 [†]) | 126.2 | 80.5 | $CCl_4$ |
| $C_6H_5CH(OH)CF_AF_BCF_3$ (XIV) | $F_A$ 119.4 [b] | | | | | 80.4 | $CCl_4$ |
| | $F_B$ 126.8 [b] | | | | | | |
| $C_6H_5CH(OH)CF_AF_BC_5F_{11}$ (XV) | $F_A$ 116.0 [c] | 118.3 | 121.2 | 121.2 | 125.0 | 80.8 | $CCl_3F$ |
| | $F_B$ 124.7 [c] | | | | | | |
| $o\text{-}OHC_6H_4CH(OH)CF_AF_BC_5F_{11}$ (XVI) | $F_A$ 116.3 [d] | 122.5 | 122.5 | 122.5 | 126.2 | 80.8 | $CCl_3F$ |
| | $F_B$ 124.5 [d] | | | | | | |

[a] Measured positively upfield from $CCl_3F$ as internal referrence. $\Delta\delta = 1$ ppm. [†] = unassigned signals. [b] $^2J(F-F)$ 287 Hz. [c] $^2J(F-F)$ 308 Hz. [d] $^2J(F-F)$ 300 Hz.

$CF_2(\alpha)$ group in the F-alkylated alcohols. This group shows a resonance at 116—118 ppm for all the tertiary alcohols except $(i\text{-}C_3H_7)_2C(OH)C_6F_{13}$ (XI), where it was found at 108 ppm. Steric hindrance around the two fluorine atoms, which is greater in the present case, was previously reported to be responsible for deshielding effects in fluorinated aliphatic compounds [13]. With the secondary alcohols, the $CF_2(\alpha)$ shows an AB system due to the fact that the fluorine atoms are diastereotopic. The differences in values of the chemical shifts ($\Delta\delta \sim 8$—10 ppm) and coupling constants $^2J(F_A—F_B) \simeq 280$—300 Hz are consistent with previous measurements made on similar compounds [14].

The mass spectra of compounds IV—XVI show patterns characteristic of perfluorinated derivatives [15]. Thus, the easy loss of fluorine atoms under the electronic impact leads to low abundance of the parent ion $M^+$, while the systematic fragmentation of the perfluoroalkyl chain gives fragments with *m/e*: $50\,n + 19 = (nCF_2 + F)$; $50\,n + 31 = (nCF_2 + CF)$; $50\,n + 43 = (nCF_2 + C_2F)$ with decreasing intensity as $n$ increases. Characteristic of the perfluoroalkylated alcohols [16] is the loss of a water molecule, and of a neutral alkyl (compounds V, VI and VII) or perfluoroalkyl fragment [the ion $(M - R_F)^+$ is sometimes the most important]. Intensities and tentative assignments of the main fragments observed for each compound are given in the Experimental section.

## Experimental

*General.* THF freed from peroxides was distilled over sodium under dry nitrogen. The 1-iodo F-alcanes were freed from trace amounts of dissolved iodine by filtration over alumina. Calcium powder ($\phi$ 0.3 mm quality NB; Mg < 0.7%) was kindly provided by Planet—Wattohm and used as such. All operations were carried out under argon.

The $^1H$ and $^{19}F$ NMR spectra were recorded on a JEOL C-60 HL instrument at 60 MHz and 56.4 MHz. Infrared measurements were run on a Perkin—Elmer 577 spectrometer and mass spectra on a JEOL D 100 instrument. VPC analyses were performed on a Carlo—Erba Fractovap 2400 chromatograph equipped with a 2 m × 2 mm column packed with 10% QFI on Chromosorb W 80—100 mesh.

*Calcium amalgam.* Calcium powder (1.1 g, $2.75 \times 10^{-2}$ g at.) is degassed in vacuo in a 100 ml two-necked Pyrex flask; 46.2 g of Hg is then added and the mixture is heated until the calcium completely dissolves (ca. 350—400°C [17]. The hot liquid amalgam is slowly agitated and allowed to solidify. It forms a mirror ca. 2 mm thick on the walls of the flask after solidification. No attack on the glass was observed under these conditions.

*General procedure for the reaction of the F-alkyl iodide with carbonyl compounds in the presence of the Ca/Hg amalgam.* The reaction vessel containing the Ca/Hg mirror is cooled to —20 to —40°C and the solution of the carbonyl compound (25 mmol in 50 ml THF) is added. The 1-iodo F-alcane (25 mmol) is added dropwise with stirring during 1 to 2 h. After ca. 30 min the solution rapidly turns dark-brown, and a light-grey precipitate appears. The mixture is stirred at this temperature for periods varying from 8 to 20 hours (see Table 1), after which the reaction is quenched by addition of 20 ml of HCl 6 *N*. Mercury is then separated (>99.5% recovery). The organic layer is washed repeatedly with

water to remove the THF, the diluted with diethyl ether and dried over molecular sieves. The solvent is evaporated and the products are isolated by distillation or column chromatography (neutral alumina of activity II—III; elution by pentane/ethyl acetate 95 : 5 v/v).

*Reaction with cyclohexanone.* Cyclo-$C_6H_{10}(OH)C_6F_{13}$ (IV), purified by chromatography, was isolated in 58% yield (b.p. 222°C; found: C, 33.66; H, 3.08; F, 57.84%. $C_{12}H_{11}F_{13}O$ (mol.wt.) calcd.: C, 34.45; H, 2.63; F, 59.09%). Mass spectrum of IV: *m/e* 418 ($C_{12}H_{11}F_{13}O^+$; 3.0%); 399 ($C_{12}H_{11}F_{12}O^+$; 20.0%); 368 ($C_{11}H_{11}F_{11}O^+$; 10.6%); 149 ($C_7H_{11}F_2O^+$; 4.5%); 131 ($C_7H_9F_2^+$, $C_3F_5^+$(?); 53.0%); 119 ($C_2F_5^+$; 33.3%); 99 ($C_6H_{11}O^+$; 90.9%); 81 ($C_6H_{10}^+$; 100%); 79 ($C_6H_7^+$; 30.3%); 77 ($C_6H_5^+$; 18.2%); 69 ($CF_3^+$; 83.3%).

*Reaction with acetone.* Distillation gave $(CH_3)_2C(OH)C_6F_{13}$ (V) (37%, b.p. 47°C/15 mmHg, m.p. 38—40°C; found: C, 28.88; H, 1.75; F, 65.24. $C_9H_7F_{13}O$ (mol.wt. 378) calcd.: C, 28.57; H, 1.85; F, 65.34%); and $(CH_3)_2C(OH)CH_2C(OH)(CH_3)C_6F_{13}$ (VI) (28%, b.p. 130—134°C/0.05 mmHg; found: C, 32.98, H, 2.93; F, 56.08. $C_{12}H_{13}F_{13}O_2$ (mol.wt. 436) calcd.: C, 33.03; H, 2.98; F, 56.65%). Mass spectrum of V: *m/e* 377 ($C_9H_6F_{13}O^+$; 2.8%); 363 ($C_8H_4F_{13}O^+$; 100%); 343 ($C_8H_3F_{12}O^+$; 12.9%); 319 ($C_6F_{13}^+$; 11.4%); 219 ($C_4F_9^+$; 11.4%); 181 ($C_4F_7^+$; 12.9%); 169 ($C_3F_7^+$; 17.1%); 131 ($C_3F_5^+$; 47.1%); 119 ($C_2F_5^+$; 32.8%); 100 ($C_2F_4^+$; 31.4%); 93 ($C_3F_3^+$; 21.4%); 69 ($CF_3^+$; 82.8%); 59 ($C_3H_7O^+$; 78.5%); 43 ($C_2F^+$; $C_2H_3O^+$ (?); 74.2%). Mass spectrum of VI: *m/e* 437 ($C_{12}H_{14}F_{13}O^+$; 4.4%); 421 ($C_{11}H_{10}F_{13}O_2^+$; 100%); 419 ($C_{11}H_8F_{13}O_2^+$; 83.3%); 403 ($C_{11}H_8F_{13}O^+$; 32.2%); 401 ($C_{11}H_6F_{13}O^+$; 58.9%); 363 ($C_8H_4F_{13}O^+$; 10%); 343 ($C_8H_3F_{13}O^+$; 3.3%); 341 ($C_8HF_{12}O^+$; 2.2%); 319 ($C_6F_{13}^+$; 3.3%); 231 ($C_5F_9^+$; 2.2%); 181 ($C_4F_7^+$; 3.3%); 169 ($C_3F_7^+$; 6.7%); 131 ($C_3F_5^+$; 21.1%); 119 ($C_2F_5^+$; 17.8%); 69 ($CF_3^+$; 72.2%); 61 ($C_4H_8O^+$; 28.9%).

*Reaction with 2-butanone.* Column chromatography gave $C_2H_5C(OH)(CH_3)C_6F_{13}$ (VII) (29%, b.p. 176°C; found: C, 30.66; H, 2.31; F, 62.24%. $C_{10}H_9F_{13}O$ (mol.wt. 392) calcd.: C, 30.61; H, 2.30; F, 63.01%); from $C_2H_5C(OH)(CH_3)CH_2C(OH)(C_2H_5)C_6F_{13}$ (VIII) (10%, found: C, 36.60; H, 3.10; F, 53.00. $C_{14}H_{17}F_{13}O_2$ (mol.wt. 464) calcd.: C, 36.21; H, 3.66; F, 53.23%). Mass spectrum of VII: *m/e* 392 ($C_{10}H_9F_{13}O^+$; 0.4%); 377 ($C_9H_6F_{13}O^+$; 19.2%); 363 ($C_8H_4F_{13}O^+$; 100%); 343 ($C_8H_3F_{12}O^+$; 8.5%); 309 ($C_8H_4F_{11}^+$; 12.0%); 262 ($C_6H_4F_9O^+$; 5.4%); 181 ($C_4F_7^+$; 4.8%); 169 ($C_3F_7^+$; 7.9%); 131 ($C_3F_5^+$; 18.0%); 119 ($C_2F_5^+$; 14.4%); 100 ($C_2F_4^+$; 14.1%); 73 ($C_5H_9O^+$; 58.2%); 69 ($CF_3^+$; 32.1%); 55 ($C_4H_7^+$; 44.1%); 43 ($C_2H_3O^+$; $C_2F^+$ (?); 88.3%). Mass spectrum of VIII: *m/e* 449 ($C_{13}H_{14}F_{13}O_2^+$; 6.8%); 435 ($C_{12}H_{12}F_{13}O_2^+$; 21.6%); 417 ($C_{12}H_{10}F_{13}O^+$; 19.3%); 399 ($C_{12}H_8F_{13}^+$; 8.0%); 397 ($C_{12}H_6F_{13}^+$; 10.2%); 377 ($C_{12}H_5F_{12}^+$; 6.8%); 231 ($C_5F_9^+$; 2.3%); 181 ($C_4F_7^+$; 3.4%); 169 ($C_3F_7^+$; 5.7%); 145 ($C_8H_{17}O_2^+$; 6.8%); 131 ($C_3F_5^+$; 11.4%); 127 ($C_8H_{15}O^+$; 18.2%); 119 ($C_2F_5^+$; 11.4%); 100 ($C_2F_4^+$; 8.0%); 73 ($C_4H_9O^+$; 36.4%); 69 ($CF_3^+$; 38.6%); 43 ($C_2H_3O^+$; $C_2F^+$ (?); 100%).

*Reaction with 3-pentanone.* Chromatographic purification gave $(C_2H_5)_2C(OH)C_6F_{13}$ (IX) (66%, b.p, 198°C; found: C, 32.96; H, 2.61; F, 60.04. $C_{11}H_{11}F_{13}O$ (mol.wt. 406) calcd.: C, 34.29; H, 2.64; F, 59.23%). Mass spectrum of IX: *m/e* 377 ($C_9H_6F_{13}O^+$; 100%); 319 ($C_6F_{13}^+$; 7.3%); 309 ($C_8H_5F_{10}O^+$; 23.4%); 169 ($C_3F_7^+$; 5.6%); 131 ($C_3F_5^+$; 12.7%); 119 ($C_2F_5^+$; 11.3%); 93 ($C_3F_3^+$; 9.9%); 87 ($C_5H_{11}O^+$; 67.6%); 69 ($CF_3^+$; 36.6%); 57 ($C_4H_9^+$; 74.6%).

*Reaction with diisopropylketone.* Fractional distillation gave $C_{12}F_{26}$ (X) (31%, b.p. 54—60°C/13 mmHg; found: C, 22.73; F, 76.35. $C_{12}F_{26}$ (mol.wt. 638)

calcd.: C, 22.57; F, 77.43%); and $[(CH_3)_2CH]_2C(OH)C_6F_{13}$ (XI) (40%, b.p. 86—92°C/13 mmHg; found: C, 35.18; H, 3.31; F, 57.29. $C_{13}H_{15}F_{13}O$ (mol.wt. 434) calcd.: C, 35.94; H, 3.46; F, 56.91%). Mass spectrum of X: *m/e* 581 ($C_{12}F_{23}^+$; 16.2%); 481 ($C_{10}F_{19}^+$; 10.8%) 431 ($C_8F_{15}^+$; 27.0%); 381 ($C_8F_{15}^+$; 20.3%); 331 ($C_7F_{13}^+$; 75.7%); 293 ($C_7F_{11}^+$; 5.4%); 281 ($C_6F_{11}^+$; 72.9%); 243 ($C_6F_9^+$; 10.8%); 231 ($C_5F_9^+$; 45.9%); 219 ($C_4F_9^+$; 16.2%); 193 ($C_5F_7^+$; 27.0%); 181 ($C_4F_7^+$; 48.6%); 169 ($C_3F_7^+$; 35.1%); 143 ($C_4F_5^+$; 21.6%); 131 ($C_3F_5^+$; 51.3%); 119 ($C_2F_5^+$; 45.9%); 100 ($C_2F_4^+$; 16.2%); 93 ($C_3F_3^+$; 20.3%); 69 ($CF_3^+$; 100%). Mass spectrum of XI: *m/e* 434 ($C_{13}H_{15}F_{13}O^+$; 0.4%); 391 ($C_{10}H_8F_{13}O^+$; 89.4%); 373 ($C_{10}H_6F_{13}^+$; 5.3%); 327 ($C_{11}H_7F_8O^+$; 1.6%); 323 ($C_9H_6F_{11}^+$; 2.1%); 281 ($C_6F_{11}^+$; 1.6%); 231 ($C_5F_9^+$; 1.6%); 219 ($C_4F_9^+$; 1.1%); 181 ($C_4F_7^+$; 2.1%); 169 ($C_3F_7^+$; 3.2%); 131 ($C_3F_5^+$; 10.1%); 121 ($C_5H_7F_2O^+$; 3.2%); 119 ($C_2F_5^+$; 8.0%); 115 ($C_7H_{15}O^+$; 10.6%); 107 ($C_4H_5F_2O^+$; 5.8%); 71 ($C_4H_7O^+$; 15.4%); 69 ($CF_3^+$; 23.4%); 43 ($C_2F^+$; 100%).

*Reaction with acetophenone.* The alcohol $C_6H_5C(OH)(CH_3)C_6F_{13}$ (XIII) could not be obtained free from acetophenone. It was identified by NMR spectroscopy and its yield (ca. 30%) was estimated by GLC.

*Reaction with benzaldehyde.* (a) $C_2F_5I$. Column chromatography gave $C_6H_5CHOHC_2F_5$ (XIV) (69%, b.p. 214°C; found: C, 47.43; H, 2.65; F, 41.76. $C_9H_7F_5O$ (mol.wt. 226) calcd.: C, 47.79; H, 3.10; F, 42.04%). Mass spectrum of XIV: *m/e* 226 ($C_9H_7F_5O^+$; 13.3%); 209 ($C_9H_6F_5^+$; 2.5%); 190 ($C_9H_6F_4^+$; 5.9%); 169 ($C_9H_7F_2O^+$; 3.6%); 159 ($C_8H_6F_3^+$; 14.7%); 140 ($C_8H_6F_2^+$; 12.3%); 127 ($C_8H_5F_2^+$; 13.4%); 119 ($C_2F_5^+$; 15.5%); 107 ($C_7H_7O^+$; 100%); 79 ($C_6H_7^+$; 76.6%); 77 ($C_6H_5^+$; 48.2%); 69 ($CF_3^+$; 12.5%); 51 ($C_4H_3^+$; 21.6%).

(b) $C_6F_{13}I$. The same procedure gave $C_6H_5CHOHC_6F_{13}$ (XV) (56%, m.p. 52—54°C; found: C, 37.01; H, 1.58; F, 57.18. $C_{13}H_7F_{13}O$ (mol.wt. 426) calcd.: C, 36.62; H, 1.64; F, 57.98%). Mass spectrum of XV: *m/e* 426 ($C_{13}H_7F_{13}O^+$; 4.9%); 407 ($C_{13}H_7F_{12}O^+$; 6.7%); 387 ($C_{13}H_6F_{11}O^+$; 5.3%); 269 ($C_5F_{11}^+$; 1.8%); 231 ($C_5F_9^+$; 2.8%); 169 ($C_3F_7^+$; 9.2%); 131 ($C_3F_5^+$; 16.0%); 119 ($C_2F_5^+$; 16.0%); 107 ($C_7H_7O^+$; 100%); 100 ($C_2F_4^+$; 9.6%); 79 ($C_6H_7^+$; 53.2%); 77 ($C_6H_5^+$; 33.3%); 69 ($CF_3^+$; 23.4%); 58.3* (107 → 79).

*Reaction with salicylaldehyde.* The residue was purified by sublimation, to give pure *o*-$OHC_6H_4CHOCH_6F_{13}$ (XVI) (21%, m.p. 75—79°C; found: C, 35.29; H, 1.61; F, 56.52. $C_{13}H_7F_{13}O_2$ (mol.wt. 442) calcd.: C, 35.29; H, 1.58; F, 55.88%). Mass spectrum of XVI: *m/e* 442 ($C_{13}H_7F_{13}O_2^+$; 18.5%); 426 ($C_{13}H_7F_{13}O^+$; 40.0%); 405 ($C_{13}H_5F_{12}O^+$; 9.2%); 385 ($C_{13}H_7F_{10}O_2^+$; 6.2%); 123 ($C_7H_7O_2^+$; 100%); 119 ($C_2F_5^+$, 16.9%); 95 ($C_6H_7O^+$; 92.3%); 77 ($C_6H_5^+$; 84.6%); 69 ($CF_3^+$; 20.0%); 73.4* (123 → 95); 62.4* (95 → 77).

## References


1 C.F. Smith, E.J. Soloski and C. Tamborski, J. Fluorine Chem., 4 (1974) 33.
2 V.C.R. McLoughlin and J. Thrower, Tetrahedron, 25 (1969) 5921.
3 P.L. Coe and N.E. Milner, J. Organometal. Chem., (a) 39 (1972) 395; (b) 70 (1974) 147.
4 G. Santini, M. Le Blanc and J.G. Riess, Tetrahedron, 29 (1973) 2411.
5 M. Le Blanc, G. Santini, J. Guion and J.G. Riess, Tetrahedron, 29 (1973) 3195.
6 G. Santini, M. Le Blanc and J.G. Riess, J. Chem. Soc. Chem. Commun., (1975) 678.
7 A. Mishra, Austr. J. Chem., 24 (1971) 2493.
8 (a) M. Chastrette and R. Gauthier, Bull. Soc. Chim. Fr., (1973) 753; (b) N. Kawabata, A. Matsumura and S. Yamashita, Tetrahedron, 29 (1973) 1069 and references cited.
9 M. Chastrette and R. Gauthier, J. Organometal. Chem., 66 (1974) 219.

10 A.V. Bogatskii, T.K. Chumachenko, A.E. Kozhukhova and M.V. Grenaderova, Zh. Obshch. Khim., 42 (1972) 403; Chem. Abstr., 77 (1972) 19706w.
11 N. Kawabata, H. Nakamura and S. Yamashita, J. Org. Chem., 38 (1973) 3043.
12 M.S. Karasch, R. Morrison and W.H. Merry, J. Amer. Chem. Soc., 66 (1944) 368.
13 G.V.D. Tiers, J. Amer. Chem. Soc. 78 (1956) 2914.
14 T. Nguyen and C. Wakselman, J. Fluorine Chem., 6 (1975) 311.
15 J.L. Cotter, Org. Mass spectrom., 7 (1973) 11.
16 E.R. McCarthy, J. Org. Chem., 31 (1966) 2042.
17 P. Pascal, Nouveau Traité de Chimie Minérale, tome IV, p. 290, Masson, Paris, 1958.