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An improved synthesis of perfluoroalkyl aldehydes from the reaction of perfluoroalkyl iodides with dimethylformamide

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Abstract

The reactivity of perfluoroalkyl iodide in the presence of a zinc–copper metal couple and a radical initiator in DMF, has been investigated. This led to the formation of a mixture of *N*,*N*-dimethyl perfluoroalkylamide and perfluoroalkyl aldehyde. After studying the influence of different reaction parameters, the perfluoroalkyl aldehyde formation has been optimized to high yield (over 90%).

Introduction

Perfluorinated aldehydes are of potential interest as suitable precursors for chemical products containing a linear perfluorinated chain, useful, for example, as surface-active agents.

The following are among the various currently known access routes to perfluorinated aldehydes: (i) the reaction of perfluorobutyronitrile with a magnesium compound such as isopropylmagnesium bromide, leading to the formation of perfluorobutyraldehyde in 37% yield [1]; (ii) the ozonolysis of compounds of the type $CF_3(CF_2)_nCH{=}CHR$ to give aldehydes of the type $CF_3(CF_2)_nCHO$ directly in 25% yield [2]; (iii) the preparation of perfluorobenzaldehyde in 40% yield by the reaction of perfluorophenyl-lithium with *N*-methylformamide [3] or in 63% yield by the reaction of perfluorophenylmagnesium chloride with *N*-methylformanilide [4]; and (iv) the reaction of tetrafluoroethylene with $(CF_3)_3C–CH(NMe_2)_2$ leading, after hydrolysis, to the aldehyde $(CF_3)_3C–CF_2–CHO$ [5].

Recently, the synthesis of another type of polyfluoroalkyl aldehyde has been performed in this laboratory, involving reaction of perfluoroalkyl iodide with vinyl acetate in the presence of azobisisobutyronitrile and leading, after hydrolysis, to the aldehyde R_FCH_2CHO in 85% yield [6].

We have also searched for a new synthetic method for these perfluorinated aldehydes, since none of the reactions mentioned above were satisfactory (low yield, too drastic experimental conditions). In 1988, we described and

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patented a new perfluoroalkyl aldehyde synthesis, involving the functionalization of perfluoroalkyl iodides [7]. This method is reported in more detail in this paper.

In previous work, it was shown that perfluoroalkyl iodides R_FI ($R_F=C_nF_{2n+1}$) reacted with a zinc–copper metal couple, leading to the formation of the corresponding perfluoro-organozinc derivatives. The results obtained proved that the reactivity of the organometallic intermediates depended on the solvent used for the reaction. Indeed, it was known that these perfluoro-organozinc compounds, prepared in diethyl ether or dioxan as solvents, were solvated in these media and for this reason were not very reactive [8], whereas these derivatives when obtained in dissociating solvents were adsorbed on the metallic surface and were therefore very reactive either with different substrates, such as SO_2 or CO_2 for example, in the case of reactions performed in DMF or DMSO [9], or with the solvent being used for the reaction, such as alkyl carbonates [10] and alkyl phosphates [11].

Hence, the reactivity of R_FI was investigated in the presence of a zinc–copper metal couple and a radical initiator in DMF as the solvent. Surprisingly, this reaction led to the formation of *N*,*N*-dimethylperfluoroalkylamide and a perfluoroalkyl aldehyde, involving a *C*-alkylation of the DMF. After studying the influence of different parameters such as the kind of radical initiator employed, the reaction time (R_FI addition time), the temperature and the molar ratio of DMF relative to R_FI, *N*,*N*-dimethylperfluoroalkylamide formation has been suppressed and perfluoroalkyl aldehyde synthesis has been optimized to over 90% yield.

The influence of the radical initiator on the reaction mechanism has been studied and discussed.

Results

The dropwise addition of a perfluoroalkyl iodide R_FI (I) at room temperature in the presence of a zinc–copper metal couple and a radical activator or initiator (concentration, *c*. 0.03 mol per mol R_FI) such as ethyl chloroformate (V), azobisisobutyronitrile (VI) or 3,3′-azobis(3-cyanovaleric) acid (VII), to *N*,*N*-dimethylformamide (VIII) as the solvent, leads mainly to the formation of the *C*-alkylation products of DMF, i.e. perfluoroalkyl aldehyde R_FCHO (II) and *N*,*N*-dimethylperfluoroalkylamide $R_FCON(CH_3)_2$ (III), and to the formation of by-products, perfluorohydroalkane (IV) and perfluoroalkenes. No reaction occurred unless zinc in a stoichiometric amount and a radical initiator were both present in the medium (Scheme 1).

Influence of the nature of the radical initiator

The influence of the specific radical activator **V** or initiator **VI** or **VII** on the reaction has been investigated. The results obtained are reported in Table 1 and show that the DMF *C*-alkylation products depend on the nature of the radical activator or initiators. The best results were obtained when the reactions were carried out in the presence of radical initiators **VI** or **VII**.

R_FI (I)

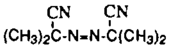
R_FCHO (II)

$R_FCON(CH_3)_2$ (III)

R_FH (IV)

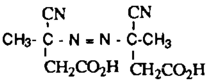
$R_F = C_nF_{2n+1}$, $n = 4,6,8$

$ClCO_2Et$ (V)



$(CH_3)_2\overset{CN}{C}\text{-}N{=}N\text{-}\overset{CN}{C}(CH_3)_2$

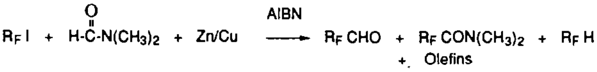
(VI)



$CH_3\text{-}\underset{CH_2CO_2H}{\overset{CN}{C}}\text{-}N{=}N\text{-}\underset{CH_2CO_2H}{\overset{CN}{C}}\text{-}CH_3$

(VII)

$H\text{-}CON(CH_3)_2$ (VIII)



$$R_FI + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}N(CH_3)_2 + Zn/Cu \xrightarrow{AIBN} R_FCHO + R_FCON(CH_3)_2 + R_FH + \text{Olefins}$$

Scheme 1.

TABLE 1

Influence of radical activator or initiator[a] on the reaction

Radical activator or radical initiator	Yield of perfluoroalkyl compounds (%)		
	R_FCHO (II)	$R_FCON(CH_3)_2$ (III)	R_FH (IV) + perfluoro-olefins
V	30	30	40
VI	40	40	20
VII	40	40	20

[a] Concentration, *c.* 0.03 mol per mol R_FI.

Influence of the rate of addition of perfluoroalkyl iodide (I)

In order to increase the yield of perfluoroalkyl aldehyde (**II**) and thus try to suppress the formation of *N,N*-dimethylperfluoroalkylamide (**III**), the perfluoroalkyl iodide R_FI (**I**) was added quickly, instead of dropwise, to the medium (*c.* 8 min per 0.1 mol of **I**). The results obtained show that in the presence of **VI** or **VII** R_FCHO and $R_FCON(CH_3)_2$ were obtained in 60% and 20% yield, respectively.

Influence of temperature on the reaction

The influence of the temperature on the formation of **II** and **III** has been investigated. Perfluoroalkyl iodide R_FI was added quickly and reactions were performed in the presence of a zinc–copper metal couple and radical initiator **VI** or **VII** in DMF (**VIII**). The results obtained are given in Table 2.

These results reveal that it is possible to increase the yield of aldehyde **II** to 70% when the reaction is performed at 0 °C or slightly below.

Influence of the molar ratio of DMF to R_FI on the reaction

The influence of the molar ratio of DMF and R_FI (**I**) has also been investigated. The perfluoroalkyl iodide R_FI was added quickly to the medium.

TABLE 2

Influence of the temperature on the reaction

Temperature (°C)	Yield of perfluoroalkyl compounds (%)		
	R_FCHO (II)	$R_FCON(CH_3)_2$ (III)	R_FH (IV) + perfluoro-olefins
70	40	20	40
45	40	20	40
25	60	20	20
<0	70	20	10

TABLE 3

Influence of the molar ratio of DMF (VIII) to R_FI (I) on the reaction

DMF(VIII)/R_FI(I)	Yield of perfluoroalkyl compounds (%)		
	R_FCHO (II)	$R_FCON(CH_3)_2$ (III)	R_FH (IV) + perfluoro-olefins
4:1	70	20	10
2:1	>90	–	<10
1:1[a]	–	–	–

[a] No reaction occurred when the DMF/R_FI mole ratio was 1:1.

Reactions were performed at 0 °C or slightly below, in the presence of a zinc–copper metal couple and radical initiator **VI** or **VII** in DMF (**VIII**).

The results obtained by variation of the molar ratio of DMF (**VIII**) to R_FI (**I**) are reported in Table 3.

It is possible to obtain the perfluoroalkyl aldehyde R_FCHO in >90% yield and to avoid the formation of perfluoroalkylamide when the molar ratio of DMF to R_FI is 2:1.

Discussion

The reaction was performed under heterogeneous conditions and for this reason it was difficult to investigate the mechanism.

Before discussing the reaction process, it is important to point out the following experimental observations: (i) no reaction occurred unless zinc in a stoichiometric amount together with a radical initiator were both present; (ii) the reaction became very exothermic after an induction time of 5 min and then required cooling down to about 0 °C; and (iii) the formation of the aldehyde was favoured by rapid addition of R_FI to the medium and a molar ratio of DMF to R_FI of 2.

According to all these observations it is possible to advance two ways to explain the formation of the *C*-alkylation compounds of DMF, both requiring the use of zinc and a radical initiator.

The first route (Scheme 2) suggests a two-step process, involving firstly the formation of a perfluoro-organozinc iodide/DMF complex, $R_FZnI(DMF)_2$, as an intermediate. Lang *et al.* have described a similar complex, $R_FZnCl(DMF)_2$ ($R_F = CF_3(CF_2)_nCCl_2$) [12]. This would entail an organized structure for the medium, as reported with many organometallic compounds [13], and hence complexation by DMF molecules leading to the formation of a four-membered transition state stabilized by electrostatic interactions.

At this point, it is important to note that the observed induction time could be explained in such a process by the time required for complex formation. Moreover, the exothermicity of complex formation would be sufficient to initiate decomposition of the radical initiator and hence the subsequent radical process.

Electron transfer either from the radical thus formed to the carbonyl bond of DMF (Scheme 2, path A) or from the carbonyl bond to the radical (Scheme 2, path B) (initiated by the introduction of the radical initiator into the medium) subsequently induces homolytic cleavage of the C–Zn bond. The perfluoroalkyl radical would then react exclusively with the nearest atom of DMF, i.e. the carbonyl carbon atom*, leading to the formation of the intermediate $R_FCHN(CH_3)_2O^-ZnI^+$ (**IX**), which via a classical elimination process could give either the perfluoroalkyl aldehyde or the *N,N*-dimethylperfluoroalkylamide. The radical initiator would be regenerated leading to a continuing radical process.

The second proposal (Scheme 3) consists of a radical mechanism involving firstly, an electron-transfer reaction initiated by the zinc and/or the radical initiator on the R_FI, leading to the formation of the corresponding perfluoroalkyl radical, $R_F^{\bullet}$, and secondly the reaction of the perfluoroalkyl radical on the carbon atom of DMF, probably on its tautomeric form stabilized by zinc, resulting in the formation of another radical as shown in Scheme 3. This radical could then react with another R_FI molecule leading to the formation of: (i) another perfluoroalkyl radical, suitable for process re-initiation; (ii) the corresponding iodide addition compound **X**. This bipolar neutral tetracoordinated perfluoroalkyl intermediate would afford, via a classical elimination process, the perfluoroalkyl aldehyde and the *N,N*-dimethylperfluoroalkylamide (Scheme 3).

It is important to point out that in this process the leaving groups, IH for perfluoroalkylamide formation and $I–N(CH_3)_2$ for the perfluoroalkyl aldehyde, are more suitable than those in the previous mechanism. These

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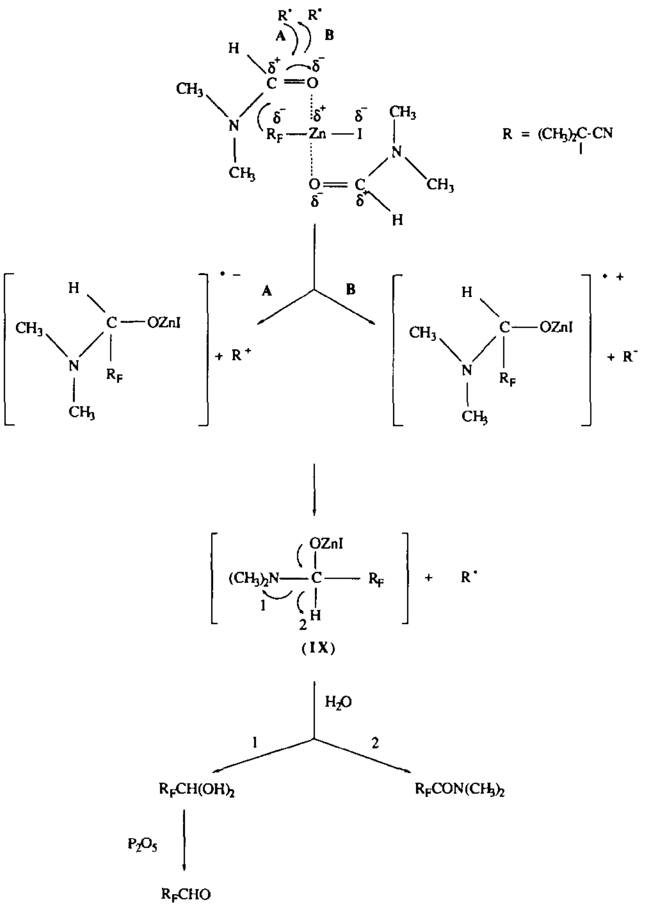
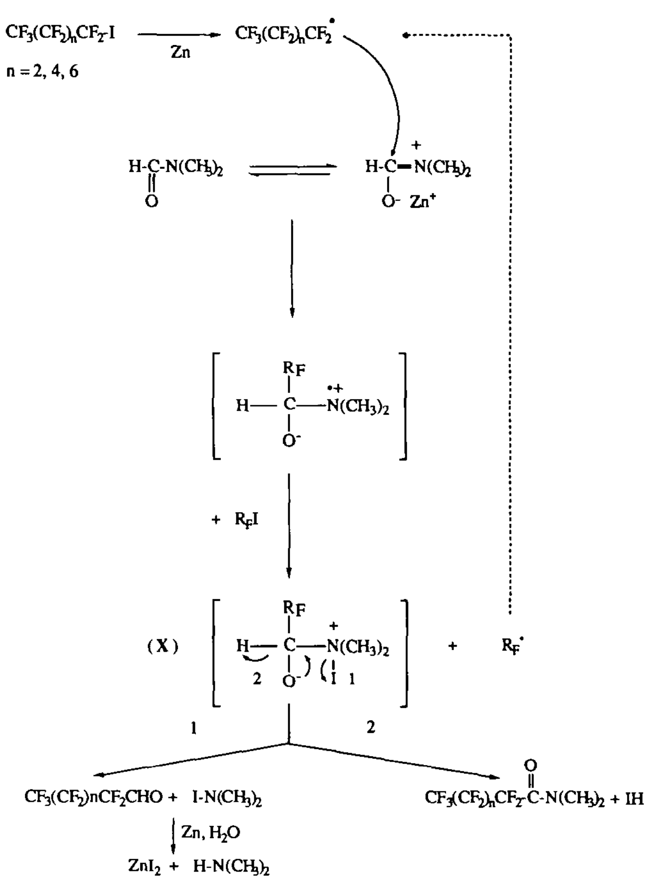
*The formation of an organized structure in the medium would explain the reactivity of the perfluoroalkyl radical $R_F^{\bullet}$ with the carbon atom of DMF instead of the oxygen atom as in previous work, where the perfluoroalkyl radicals $R_F^{\bullet}$ (produced by electrochemical reduction of the corresponding perfluoroalkyl iodides) reacted exclusively with the oxygen atom of DMF [14]. Moreover, Kobrina has demonstrated the electrophilicity of these perfluoroalkyl radicals and thus their reactivity towards the carbonyl oxygens [16].



Scheme 2.

neutral compounds are unstable and probably react with zinc to give zinc salts via an exothermic process.

In this discussion, two reaction mechanisms have been advanced involving either an intermediary perfluoro-organozinc iodide/DMF complex (Scheme 2) or perfluoroalkyl radicals (Scheme 3). The first proposal would explain the formation of the *C*-alkylation compounds of DMF, especially perfluoroalkyl aldehyde, based on the usual reactivity of intermediate **IX** and the nature of the leaving group $-N(CH_3)_2$ compared to H–, although both are not really likely. Moreover, the formation of the aldehyde is favoured by a molar ratio DMF to R_FI of 2, as required by complex formation in this proposal. This observation could be related to the existence of a perfluoro-organozinc iodide/ DMF complex. The second mechanism involving the formation of a bipolar neutral tetracoordinated perfluoroalkyl intermediate is also interesting because of the nature of the leaving groups, especially in the case of *N*,*N*-dimethylperfluoroalkylamide formation.



Scheme 3.

Hence, these two proposed mechanisms are both adequate to explain the formation of *C*-alkylation compounds of DMF, although they are not entirely satisfactory and additional information is required to fully understand the mechanism.

Experimental

Reagent quality DMF was used without further purification. The starting materials, R_FI and the radical initiators were supplied by the Atochem Co. All reactions were carried out under atmospheric pressure. Yields refer to isolated compounds.

Microanalyses were obtained using a DIONEX 2001 element analyzer. Mass spectra were recorded on a JEOL JMS D 100 spectrometer. NMR spectra were obtained using a Varian EM 390 spectrometer (^1H at 90 MHz, internal standard Me_4Si; ^{19}F at 84.7 MHz, internal standard $CFCl_3$). IR spectra were recorded on a Perkin-Elmer 1420 spectrometer.

General procedure for the synthesis of perfluoroalkyl aldehydes

The Zn–Cu couple was prepared by the addition of Zn powder (6.5 g, 0.1 mol) in small portions to a vigorously stirred solution of $(AcO)_2Cu$ (0.2 g, 0.001 mol) in hot AcOH. After a rapid exothermic reaction, the mixture was cooled and the AcOH evaporated *in vacuo*. The freshly prepared couple was dispersed in DMF (15 ml) and then azobisisobutyronitrile or 3,3′-azobis(3-cyanovaleric) acid (0.5 g, 3 mmol) was added.

Synthesis of perfluoropentanal

To this stirred and cooled (alcohol bath) solution was rapidly added perfluorobutyl iodide C_4F_9I (34.6 g, 0.1 mol). After *c.* 8 min, the addition was complete. The perfluoro-organic portion was removed by phase separation, treated with water and filtered (for reprocessing the zinc salts). Distillation of the filtrate under reduced pressure (133 Pa) gave 26.5 g of a mixture containing 70 mol% of perfluoropentanal C_4F_9CHO (i.e. 23.6 g) and 30 mol% of dimethylformamide (i.e. 2.9 g), corresponding to a 95% yield of perfluoropentanal based on the initial perfluorobutyl iodide employed. The molar percentages were determined by ^1H NMR spectral integration.

Perfluoropentanal was obtained in its hydrated form $C_4F_9CH(OH)_2$, free from dimethylformamide, by sublimation. Distillation of the white powder thus obtained from fresh P_2O_5 under reduced pressure gave C_4F_9CHO (22.8 g) in 92% yield. This method was suitable for iodide reprocessing.

To a suspension of 2,4-dinitrophenylhydrazine (0.25 g) in MeOH (5 ml) was added conc. H_2SO_4 (0.4–0.5 ml). The warm solution was filtered, a solution of the aldehyde (0.5 g) in a small volume of chloroform was added and after 10 min the corresponding solid hydrazone was collected, washed with a little aq. MeOH and recrystallized from EtOH.

C_4H_9CHO: b.p. 122 °C. ^1H NMR δ: 9.8 (t, 1H, $J(CH–CF_2) = 1$ Hz, $C\mathit{H}O$) ppm. ^{19}F NMR δ: 81.8 (t, 3F, $C\mathit{F}_3$); 123.1 (t, 2F, $C\mathit{F}_2CHO$) ppm. IR (cm^{-1}): 1100–1300 ($\nu_{C–F}$); 1730 ($\nu_{C=O}$). Mass spectrum *m/z*: 248 (0.86, M^+); 247 [0.2, $(M-H)$]; 229 [0.68, $(M-F)$]; 219 (0.4, C_4F_9); 181 (0.5, C_4F_7); 169 (0.6, C_3F_7); 100 (0.4, C_2F_4); 69 (0.6, CF_3). Analysis: $C_{11}H_5F_9N_4O_4$ requires: C, 30.85; F, 39.93; H, 1.18%. Found: C, 30.80; F, 39.87; H, 1.20%.

Synthesis of perfluoroheptanal

Perfluorohexyl iodide (34.6 g, 0.1 mol) was converted, according to the previous procedure, into perfluoroheptanal (31.3 g) in 90% yield.

$C_6F_{13}CHO$: b.p. 132 °C. ^1H NMR δ: 9.57 (t, 1H, $J(CH–CF_2) = 1$ Hz, $C\mathit{H}O$) ppm. ^{19}F NMR δ: 81.9 (t, 3F, $C\mathit{F}_3$); 122.6 (t, 2F, $C\mathit{F}_2CHO$) ppm. IR (cm^{-1}): 1100–1300 ($\nu_{C–F}$); 1730 ($\nu_{C=O}$). Mass spectrum *m/z*: 348 (0.9, M^+); 347 [0.4, $(M-H)$]; 329 [0.5, $(M-F)$]; 319 (0.6, C_6F_{13}); 219 (0.4, C_4F_9); 169 (0.6, C_3F_7); 100 (0.9, C_2F_4); 69 (0.2, CF_3). Analysis: $C_{13}H_5F_{13}N_4O_4$ requires: C, 29.56; F, 46.76; H, 0.95%. Found: C, 29.62; F, 46.69; H, 0.98%.

Synthesis of perfluorononanal

Perfluoro-octyl iodide (54.6 g, 0.1 mol), treated as above, led to the formation of perfluorononanal (38.05 g) in 85% yield.

$C_8F_{17}CHO$: b.p. 138 °C. ^1H NMR δ: 9.6 (t, 1H, $J(CH\text{–}CF_2) = 1$ Hz, CHO) ppm. ^{19}F NMR δ: 81.9 (t, 3F, CF_3); 121.8 (t, 2F, CF_2CHO) ppm. IR (cm^{-1}): 1100–1300 ($\nu_{C\text{–}F}$); 1730 ($\nu_{C=O}$). Mass spectrum *m/z*: 448 (0.6, M^+); 447 [0.3, (M − H)]; 429 ([0.4, (M − F)]; 419 (0.8, C_8F_{17}); 369 (0.5, C_7F_{15}); 319 (0.3, C_6F_{13}); 269 (0.6, C_5F_{11}); 169 (0.5, C_3F_7); 100 (0.3, C_2F_4); 69 (0.7, CF_3). Analysis: $C_{15}H_5F_{17}N_4O_4$ requires: C, 28.67; F, 51.42; H, 0.80%. Found: C, 28.74; F, 51.37; H, 0.82%.

Example of the synthesis of N,N-*dimethylperfluoroheptylamide*

To a freshly prepared zinc–copper metal couple, as above, dispersed in DMF (30 ml) was added azobisisobutyronitrile (0.5 g, 3 mmol). Perfluorohexyl iodide $C_6F_{13}I$ (34.6 g, 0.1 mol) was then added rapidly with stirring and the mixture cooled (alcohol bath). After *c.* 8 min, the addition was complete. The lower portion was then removed by phase separation and the upper portion containing *N,N*-dimethylperfluoroheptylamide in DMF solution was collected. Distillation of the solution gave 7.8 g of *N,N*-dimethylperfluoroheptylamide as a gummy residue in 20% yield.

$C_6F_{13}CON(CH_3)_2$: b.p. 185 °C. ^1H NMR δ: 3.12 [d, 6H, $J(H\text{–}H) = 8$ Hz, $N(CH_3)_2$] ppm. ^{19}F NMR δ: 81.5 (t, 3F, CF_3); 120.2 (t, 2F, CF_2CO) ppm. Mass spectrum *m/z*: 391 (0.8, M^+); 341 [0.4, M − (F–O–CH_3)]; 291 [0.6, M − (CF_3–O–CH_3)]; 319 (0.8, C_6F_{13}); 219 (0.6, C_4F_9); 169 (0.5, C_3F_7); 72 [0.6, $CON(CH_3)_2$]; 69 (0.4, CF_3); 44 [0.6, $N(CH_3)_2$]. Analysis: $C_9H_6F_{13}NO$ requires: C, 27.63; F, 63.15; H, 1.55%. Found: C, 27.67; F, 63.26; H, 1.58%.

Conclusion

In this paper, a new method of synthesizing perfluoroalkyl aldehyde R_FCHO, involving reaction of perfluoroalkyl iodides R_FI in the presence of a zinc–copper metal couple and a radical initiator in DMF, is reported. This reaction leads to the formation of a mixture of perfluoroalkyl aldehydes, R_FCHO, and *N,N*-dimethylperfluoroalkylamides, $R_FCON(CH_3)_2$. Aldehyde synthesis has been optimized to 90% yield in terms of radical initiator, rate of addition of R_FI, temperature and ratio of DMF to R_FI.

There is good evidence that double activation involving the use of a zinc–copper metal couple and radical initiator is required for the reaction to proceed.

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