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SYNTHESIS AND CHEMICAL TRANSFORMATIONS OF PERFLUOROALKYLIMIDOYL IODIDES

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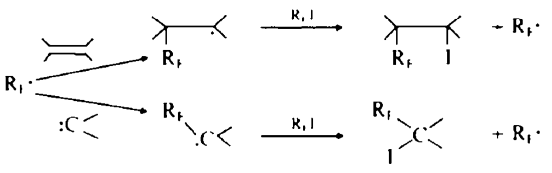
Abstract The addition of perfluoroalkyliodides $CF_3(CF_2)_nI$ (n = 3, 5, 7) to isocyanides **2** produces perfluoroalkylimidoyl iodides **3** under thermal conditions when the isocyanide nitrogen substituent is n-butyl or cyclohexyl, but fails when it is t-butyl or 2,6-dimethylphenyl. The same reaction can be induced at room temperature by the addition of a decimolar quantity of copper powder. This type of metal-catalyzed condensation is general for all perfluoroalkyliodides and isocyanides studied. The perfluoroalkylimidoyliodides **3** have been transformed into a variety of perfluorocarboxylic acid derivatives (amides, amidines, imidates, imidoylfluorides) and perfluoroalkylamines.

Study of the chemistry of perfluoroalkyliodides R_FI $[R_F = CF_3(CF_2)_n]$ has revealed a facile homolytic cleavage of the carbon iodine bond by heat or UV irradiation[1] and numerous additions of these iodides to double bonds have been described.[2] It has been demonstrated that these condensations proceed by a radical chain mechanism. The possibility of the reaction of electrophilic perfluoroalkyl radicals with divalent carbon atoms, has also been taken into consideration (Scheme 1), however, with the exception

$R_FI \rightarrow R_F\cdot + I\cdot$



of diazomethane itself, attempts to perform such condensations with carbenes and diazocompounds have failed. Insertion of one or two methylene groups into the carbon–iodine bond of R_FI was observed using this reagent.[3,4] However, some of the numerous α-additions to isocyanides were thought to be free radical in nature.[5] Several possible products could be formed in these condensations, including compounds having a carbon nitrogen double bond and nitriles produced by a collapse of the imidoyl radical intermediate.[5]

Herein, we describe the clean formation of perfluoroalkylimidoyl iodides **3** by thermal addition of R_FI **1** to isocyanides **2**, and their chemical transformations. We have also observed catalysis of this α-addition by copper powder (preliminary communication, Ref. 6).

Examination by ^{19}F NMR of the crude products showed only the formation of a single new fluorinated compound. After isolation, it was assigned structure **3** on the basis of spectroscopic data. The IR absorption at about 1690 cm^{-1} was in agreement with a carbon nitrogen double bond. ^1H NMR spectra showed only the signals of the alkyl or aryl group R. ^{19}F NMR spectra were in agreement with a perfluoroalkyl chain; the chemical shift of the CF_2 signal α to the functional group was approximately 110 ppm to high field of fluorotrichloromethane. To our knowledge the perfluoroalkyl imidoyliodides **3** and their derivatives (**4** → **8**) are new compounds.

Thermal reactions

The thermal α-addition was performed under the usual conditions for the addition of R_FI to double bonds. An equimolar mixture of **1** and **2** was heated for 24 h in an inert solvent (e.g. benzene) in the presence of azabisisobutyronitrile (AIBN) which acted as a radical initiator. Compounds **3** were obtained in 60 to 80% yields from various R_FI ($R_F = C_4F_9, C_6F_{13}, C_8F_{17}$) and isocyanides when substituted by a primary or secondary alkyl group (R = n-butyl, cyclohexyl) (Table 1). However, under these conditions, the condensation failed when the substituent was a tertiary

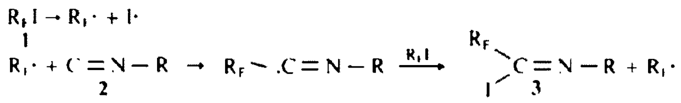
Table 1. N-alkyl perfluoroalkylimidoyl iodides produced by thermal condensation.

R_F	R	Yield %	B.p. °C at torr	IR	NMR $^{19}F^a$
C_4F_9	nbutyl	64	82/23	1695	109
C_4F_9	cyclohexyl	61	102/23	1690	110
C_6F_{13}	nbutyl	80	60/0.5	1685	109
C_6F_{13}	cyclohexyl	61	70/0.1	1685	109
C_8F_{17}	nbutyl	72	72/0.5	1685	109
C_8F_{17}	cyclohexyl	80	107/0.3	1685	110

^{a}Chemical shift of the CF_2 signals α to the functional group.

alkyl or an aromatic group (R=t-butyl; 2,6-dimethylphenyl).

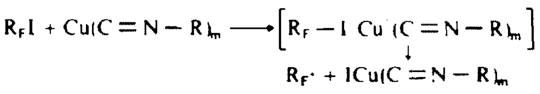
The observation that the reaction is catalysed by AIBN and inhibited by the addition of diphenyl picrylhydrazyl is consistent with the operation of a chain radical mechanism (Scheme 2). Blum and Roberts recently reported that the ESR signal obtained when trifluoromethyl radical was generated in the presence of t-butylisocyanide, was not in agreement with a trifluoromethyl imidoyl σ-radical structure. Indeed, we did not observe the formation of **3** from R_fI and this tertiary alkyl isocyanide. However, **3** was formed when trifluoromethyl iodide was heated with n-butylisocyanide.



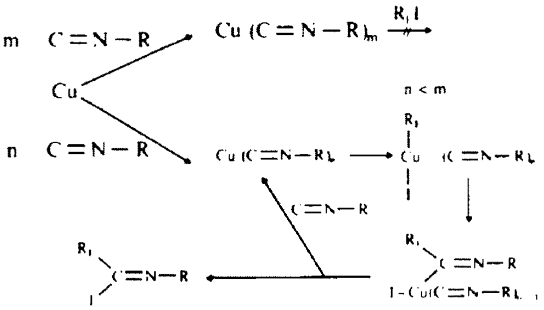
Copper catalyzed reactions

Perfluoroalkylimidoyl iodides **3** could also be obtained by adding a decimolar quantity of copper powder to a mixture of **1** and **2** at room temperature. After a short while, an exothermic reaction occurred. Filtration of the unchanged copper gave **3** in 70–90% yield from various R_FI (C_4F_9, C_6F_{13}, C_8F_{17}) and primary, secondary and even tertiary alkylisocyanides (R=n-butyl, cyclohexyl, t-butyl). **3** was obtained in 30% yield with benzyl isocyanide. In the case of 2,6-dimethylphenyl isocyanide, the mixture had to be heated in refluxing benzene. The adduct **3** (R_F=C_6F_{13}) was obtained under these conditions in 52% yield (Table II). So, it appeared that the less reactive aromatic and tertiary alkyl isocyanides, while inert under thermal conditions, were able to add R_fI in the presence of copper powder.

We observed that the metal catalyzed reaction was not inhibited by diphenylpicrylhydrazyl. This observation, although not in agreement with a radical chain process, could not exclude a cage mechanism. The formation of perfluoroalkyl radicals by the interaction of R_fI with a copper isocyanide complex (Scheme 3) might be envisaged, as the existence of isocyanide complexes of metals included in Groups Ib and IIb of the Periodic Table and their derivatives has been proved by Saegusa *et al.*[8] Recently, a one electron-transfer process between such a copper complex and an alkyl halide was involved in the mechanism of the formation of Wurtz coupling products.[9] However, this mechanism hardly explained why aromatic and tertiaryalkyl isocyanides could add perfluoroalkyl radicals but not radicals obtained by thermal fragmentation of R_fI. Moreover, neither copper iodide nor R_f. R_f compounds were detected in the reaction.



$$R_FI + Cu(C{\equiv}N-R)_m \longrightarrow \left[R_F-I\ Cu\ (C{\equiv}N-R)_m\right] \downarrow R_F\cdot + ICu(C{\equiv}N-R)_m$$



An alternative mechanism (Scheme 4) deserves comment. Oxidative addition of R_FI on to the copper complex may be followed by perfluoroalkyl group and iodine group migrations from the metal to one of the isocyanide ligands leading to the imidoyl iodide **3**. However, we noticed that a preformed complex obtained by heating copper powder and isocyanides[8] did not react with R_fI. Perhaps, the number m of ligands in the preformed complex at the equilibrium

Table 2. Copper catalyzed condensation of $C_6F_{13}I$ to isocyanides

Isocyanide **2**	% molar of **2**[a]	Methanol	Yield of **3**[b]	B.p.	NMR ^{19}F[c]	IR
cyclohexyl	1.2	A	87	70/0.1	109	1685
nbutyl	1.3	A	90	60/0.5	109	1685
tbutyl	1.5	A	70	61/0.8	108	1703
benzyl	2	B	32	92/0.2	109	1680
2,6-dimethylphenyl	1	C	52	85/0.5	109	1680

[a] Molar equivalents isocyanide iodotridecafluorohexane.

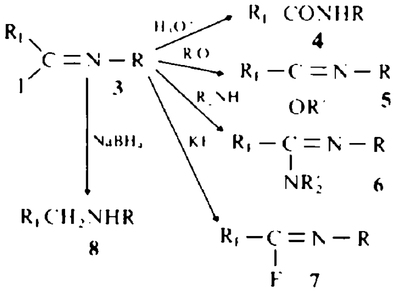
[b] Yield of imidoyliodide form iodotridecafluorohexane.

[c] Chemical shift of the CF_2 signals α to the functional group.

was higher than the number n of these ligands in the complex which was formed *in situ* during the reaction. In other words, a small number of isocyanide ligands around the metal might allow the oxidative addition of R_fI which would not be able to displace a ligand in the preformed complex. From a synthetic point of view, the addition order of reagents was crucial in inducing the reaction: the metal had to be added in a mixture of **1** and **2**. Apart from copper, silver powder induced a very slow reaction with cyclohexylisocyanide. We observed that Zn, $ZnCl_2$, $CdCl_2$, Cu_2O and $CdCl_2$ did not catalyze the R_fI addition. It was reported that, in the case of a platinum isocyanide complex, the trifluoromethyliodide addition occurred on the metal and not on the ligand.[10]

Chemical transformations of the adducts

Imidoylhalides bearing an electronegative substituent like an ester group, are not very reactive.[11] Indeed hydrolysis of **3** into amide **4** does not occur under mild conditions; it is necessary to perform this transformation at reflux in a strong acidic medium. However, it is possible to replace the iodine atom of **3** by other groups (Scheme 5). Nucleophilic substitution by alcoholates occurs at room temperature and produces imidates **5**. Attack by amines leads to amidines **6**. Halogen exchange by potassium fluoride gives the imidoylfluoride **7**. Reduction of **3** with sodium borohydride leads to amines **8**. These nucleophilic substitutions occur probably by an addition elimination mechanism.[12]



It appears that perfluoroalkylimidoyl iodides, easily obtained from R_fI and isocyanides, can be transformed into a variety of perfluorocarboxylic acid derivatives which are potential tensioactive agents.[13]

EXPERIMENTAL

^{1}H and ^{19}F NMR spectra were recorded in deuterochloroform on a Jeol C60HL instrument. The chemical shift values δ are in ppm relative to tetramethylsilane (for ^{1}H NMR spectra) or fluorotrichloromethane (for ^{19}F spectra). IR spectra were recorded in tetrachloromethane with a Perkin Elmer 167 spectrometer. Microanalysis of the products were in agreement with the proposed structures (the limits of accepted errors are ±0.3% for C, N and ±0.2% for H). N-butyl and benzyl isocyanides were purchased by Aldrich; t-butyl, cyclohexyl, 2,6-dimethylphenyl isocyanide by Fluka; Copper powder by Koch light. Perfluoroalkyl iodides were furnished by P.C.U.K.

Thermal condensation

0.04 mole of perfluoroalkyl iodide, 0.04 mole of isocyanide and 0.1 g of azobisisobutyronitrile in 20 ml of benzene were heated to reflux during 24 h. The imidoylhalide was distilled (bulb to bulb) under vacuum (1 torr), then redistilled with a 15 cm Vigreux column. Physical constants are recorded in Table 1.

Copper catalyzed condensation

The experiments are described in the case of iodotridecafluorohexane. Physical characteristics are reported in Table 2.

Method A. 0.01 Mole of iodotridecafluorohexane was mixed with the isocyanide equivalent, listed in Table 2. 0.01 mole of copper powder is added and the mixture, shaken for ten seconds. After a few minutes, an exothermic reaction occurred. The copper was filtered off two hours later, and the product was distilled under vacuum.

Method B. As in method A, but just before the copper filtration, ethyl ether added (a copper isocyanide complex separated). The ether was removed after filtration. After distillation of the product there is a spontaneous loss of iodine; nevertheless, NMR and IR characteristics are in agreement with the imidoyliodide structure (in this case radical addition takes place also, with a similar poor yield).

Method C. 13.5 g of iodotridecafluorohexane, 3.93 g of 2,6-dimethylphenylisocyanide, 0.18 g of copper in 10 ml of benzene were refluxed for three hours. After filtration and removal of benzene the product is distillated bulb to bulb and then sublimed at 60° 0.5 torr (F 45).

Chemical transformations

N-Alkyl perfluorocarboxylic acid amides **4**. 0.01 M of the imidoyl iodide is refluxed for 12 h in 10 ml of 20% sulphuric acid solution in water. After extraction with diethyl ether and washing with a solution of sodium thiosulphate, the amide is either distilled or sublimed (60 at 0.5 torr). Physical constants are reported in Table 3.

Ethyl N-butyl tridecafluoroheptanimidate **5**. 5.3 g of N-butyl tridecafluoroheptanoic imidoyliodide were shaken at room temperature with 0.4 g of sodium hydroxyde in 10 ml of ethanol for 2 h. After distillation 3.4 g of ethyl N-butyltridecafluoroheptanimidate were obtained. Yield 75%; b.p. 60 0.5 torr IR 1697 cm^{-1} ØF 117 ppm^a.

N_2 butyl, N_1,N_1 diethyl tridecafluoroheptanimidine **6**. 5.6 g of Nbutyl tridecafluoroheptanoic imidoyliodide was heated to reflux with 10 ml of diethylamine for 2 h. 4 g of N_2 butyl N_1, N_1-diethyl tridecafluoroheptanamidine **6** were distilled. Yield 80%; b.p. 79° at 0.5 torr. IR 1645 cm^{-1} ØF 112 ppm.

N-butyl heptadecafluorononanoic imidoyl fluoride **7**. 12.6 g of N-butyl heptadecafluoronoic imidoyl iodide were heated for 3 h with 5 g potassium fluoride in 10 ml of N-

Table 3. N-Alky. perfluoro carboxylic acid amides **4**

R_f	R	Yield	B.p. or m.p.	IR	^{19}F NMR^a
C_4F_9	n-butyl	81	68 at 0.3 torr	3460, 1730	125
C_6F_{13}	cyclohexyl	77	68	3440, 1725	125
C_8F_{17}	n-butyl	82	59 60	3450, 1730	127

^{a}Chemical shift of the CF_2 signals α to the functional group methylpyrrolidone. After filtration, two layers separated. The lower layer was distilled to obtain 8.8 g of N-butyl heptadecafluorononanoic imidoyl fluoride 7. Yield 85%; b.p. 90° at 25 torr; IR 1742 cm^{-1} ØF 122 ppm, ØFF C=N 50 ppm.

N-butyl N(1-tridecafluorohexyl) methyl amine **8**. 0.38 g of sodium borohydride was added to 5.3 g of N-butyl tridecafluoroheptanoic imidoyl iodide in 10 ml of absolute ethanol. The mixture is shaken for two hours. Then, 4 g of N-butyl N (tridecafluorohexyl) methylamine **8** are distilled. Yield 90%; b.p. 70° at 15 torr; ØF 123 ppm.

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