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Convenient Synthesis of N-Containing Perfluoroalkyl Iodides

Haruhiko FUKAYA,* Takashi ABE, and Eiji HAYASHI
Government Industrial Research Institute, Nagoya,
Hirate-cho, Kita-ku, Nagoya 462

Some new nitrogen-containing perfluoroalkyl iodides were synthesized directly by the reaction of corresponding perfluoroacid fluorides with lithium iodide in high yield.

The development of synthetic routes to perfluoroalkyl iodides has been the subject of considerable synthetic activities, because they are one of the key precursors in organofluorine chemistry.[1] Perfluoroalkyl iodides have generally been prepared either by the reaction of perfluoroolefins with "iodine fluoride"[2] or by the pyrolytic reaction of metal salts of perfluorocarboxylic acids in the presence of iodine.[3] The method involving the reaction of perfluoroacid chlorides with KI has also been reported.[4] However, the synthesis of perfluoroalkyl iodides containing a nitrogen atom have not been succeeded.[5]

We have found the new convenient method for the preparation of perfluoroalkyl iodides which consists of the direct conversion of acid fluoride into iodide by the reaction with lithium iodide. Furthermore, this method could be successfully applied to the syntheses of N-containing perfluoroalkyl iodides with high yield. The requisite perfluoroacid fluorides, which contain a perfluorodialkylamino group, are easily available, for example, as the products of electrochemical fluorination of appropriate starting materials.[6]

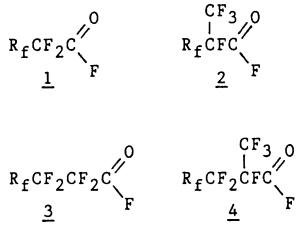
Typical experimental procedures are as follows: A mixture of lithium iodide (16.7 mmol) and perfluoro(2-(N,N-dimethylamino)propionyl fluoride) (2a, 13.9 mmol) was heated at 180 °C for 6.5 h in a pyrex tube (13 mmϕ X 180 mm). The iodides were separated by trap-to-trap distillation using consecutive traps cooled at -78 °C and -196 °C, respectively. The compounds retained at the -78 °C trap (5.59 g) consisted mainly of iodides and small quantities of unreacted 2a. The crude iodide, faint purple-colored, were further purified by preparative gas chromatography, and the structure of the products were determined by IR, ^{19}F-NMR, Mass spectra, and elemental analysis. The results of the reaction of various N-containing perfluoroacid fluorides (1 - 4) including those of trifluoroacetyl

fluoride and pentafluoropropionyl fluoride are summarized in Table 1. This reaction is considered to be proceeded via perfluoroacid iodides as an intermediate, followed by subsequent splitting of CO by a radical process. Table 1 shows that the yields of iodides are in the order of 3 > 4 > 1 > 2, which is strongly related with the degree of steric hindrance by the perfluorodialkylamino group toward the carbonyl carbon atom.

Table 1. Syntheses of perfluoroalkyl iodides[a)]

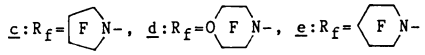
Acid fluoride	(mmol)	LiI (mmol)	Time h	Conv. %	Yield %
CF_3COF	0.77	10.1	7.0	100	73
CF_3CF_2COF	0.69	10.2	7.0	100	87
1a	26.4	30.1	6.5	67	66
1d	12.9	15.0	6.5	100	69
1e	6.39	11.0	6.5	100	59
2a	13.9	16.7	6.5	75	61
2c	8.55	14.0	6.5	100	54
2d	8.07	13.6	6.5	100	50
2e	9.19	12.2	6.5	75	59
3a	12.5	25.1	6.5	100	90
3b	8.19	12.5	6.5	53	72
3c	11.4	13.8	5.5	100	73
3d	12.0	13.4	6.5	100	86
4b	7.89	11.4	6.5	100	63
4c	9.07	12.2	6.5	100	67
4d	9.11	12.0	6.5	100	76

a) At 180 °C.



1 2 3 4

a:$R_f=(CF_3)_2N-$, b:$R_f=(C_2F_5)_2N-$,



The incorporation of the N-atom in the perfluoroalkyl skeleton results in the weakness of the C-F bond at the α-carbon usually.[7)] So, new iodides (3b, 4b) are considered to be the prospective materials for making soft type (degradable) fluorosurfactants instead of the ordinary (hard type) one[8)] in connection with the recent global environmental problem.[9)]

Furthermore, this procedure can be extended to the syntheses of the iodides having another functional group, e.g. $I(CF_2)_2SO_2F$ and $I(CF_2)_3COF$. Studies on chemistry using new iodides are now in progress.

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