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PERFLUOROALKYLATION OF THIOLS WITH $R_fI(Ph)OSO_2CF_3$

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Perfluoroalkylation of various thiols with perfluoroalkylphenyliodonium trifluoromethanesulfonates (FITS) under mild conditions was described.

Thermal or photochemical reaction of iodoperfluoroalkanes with dimethyl disulfide, or alkane- or arenethiols under basic conditions is known as the preparative method for perfluoroalkylthio-compounds.[1,2] A few examples of the reaction of perfluoroalkylaryliodonium chlorides or tetrafluoroborates with sodium salts of arenethiols appeared in the literatures.[3,4] There were no data about the reaction with other thiols. Recently it was reported that alkyl- or arylthiocyanates were treated with perfluoroalkyl anions to give the perfluoroalkylthio-compounds.[5] However, as the conventional methods were done under severe conditions, a new useful method of preparing the perfluoroalkylthio-compounds has been desired.

In the previous work, we reported the reaction of perfluoroalkylphenyliodonium trifluoromethanesulfonates (FITS) toward carbanions[6] and aromatic compounds,[7] affording perfluoroalkyl-compounds in moderate to high yields. In a continuation of the studies on the reactivity of FITS as a cationic perfluoroalkylating agent, we now wish to report on the reaction with thiols.

From the examination of the conditions for the reaction with an alkanethiol (Table 1), it was found that FITS could react smoothly with various thiols in methylene chloride at room temperature for a short period in the presence of pyridine or its derivative as a very weak base to give the corresponding perfluoroalkylthio-compounds in good to excellent yields and iodobenzene was liberated in an almost quantitative yield (Table 2). FITS can react with the thiols exclusively at the sulfur site even in the presence of other functional groups such as hy-

Table 1. Examination of conditions for reaction of FITS-m with alkanethiol

$$\underset{\text{FITS-m}^{8)}}{R_fI(Ph)OSO_2CF_3} \xrightarrow[\text{in } CH_2Cl_2 \text{ at r.t.}]{n\text{-}C_{12}H_{25}SH/\text{Base}} R_fSC_{12}H_{25} + PhI$$

$$(R_f = n\text{-}C_mF_{2m+1})$$

FITS-m	Alkanethiol (eq.)	Base (eq.)	Time (min)	Yield (%) $R_fSC_{12}H_{25}$	+ PhI
m=8	1.2	Pyridine (1.2)	15	82	96
8	1.2	K_2CO_3 (1.2)	15	26	89
8	1.2	CH_3COONa (1.2)	20	19	85
2	1.0	2,6-Di-t-butyl-4-methylpyridine (1.0)	20	87	100

Table 2. Reaction of FITS-m with thiols

$$\mathrm{RSH} \xrightarrow[\text{in } CH_2Cl_2 \text{ at r.t.}]{\text{FITS-m/Base}} \mathrm{R_fSR} \qquad (\mathrm{R_f{=}n\text{-}C_mF_{2m+1}})$$

Run	R_fSR[a)]	FITS-m	Base[b)] (1 eq.)	Time (min)	Yield[c)] (%)	Mp[d)] (°C)
1	$R_fSCH_2COOn\text{-}Bu$	m=3	B	10	(88)	
2	R_fSCH_2COOH	10	A	10	89	109-111
3	"	8	A	60	93	68-70
4	"	6	A	10	92	36-38
5	"	2	B	10	90	
6	$R_fSCH(CH_3)COOH$	2	B	20	(81)	
7	$R_fSCH(COOH)CH_2COOH$	8	A	40	63	136
8	$R_fSCH_2CH_2COOH$	8	A	90	83	83-84
9	$R_fSCH_2CH_2OH$	8	A	20	83	42-43
10	$R_fSCH_2CH(OH)CH_2OH$	8	A	60	83	103-105
11	$R_fSCH_2CH_2SH$ + $(R_fSCH_2\text{-})_2$	8	A	30	46 {1.3:1}	30-31 78-80
12	R_fSCH_2Ph	3	B	10	(76)	
13[e)]	R_fSPh	2	B	60	(59)	
14[f)]	$R_fSCH_2CH_2N(CH_3)_2$	8	A	120	52	

a) All products exhibited spectral data (^{1}H- and ^{19}F-NMR, IR, and Mass) and elementary analysis in accord with the assigned structures. b) A=pyridine. B=2,6-di-t-butyl-4-methylpyridine. c) Isolated yields. Values in parenthese are determined by GLC. d) Melting points of new compounds. e) Reaction temperature 0°C. f) 2-Dimethylaminoethanethiol hydrochloride and acetonitrile were used as a starting material and a solvent, respectively.

droxy, dimethylamino, carboxy, or alkoxycarbonyl groups under the mild conditions.

Thus our technique using FITS offers a promising synthetic method for a wide variety of perfluoroalkylthio-compounds. Since the perfluoroalkylthio group can be readily converted to the perfluoroalkylsulfinyl or the perfluoroalkylsulfonyl group which is the important functional group in the organic synthesis,[9,10)] it is also expected that FITS serves as a useful reagent among organic chemists.

$$\mathrm{R_fSCH_2CH_2OH} \xrightarrow[86\%]{\text{MCPBA}} \mathrm{R_fSOCH_2CH_2OH} \xrightarrow[85\%]{\text{MCPBA}} \mathrm{R_fSO_2CH_2CH_2OH}^{10)}$$

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