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# Phase-Transfer Catalysed Ion-Radical Perfluoroalkylation of Thiols

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## SUMMARY

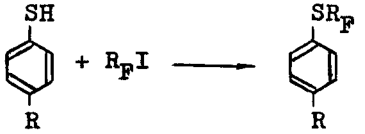
It has been shown that under conditions of phase-transfer catalysis under UV-irradiation perfluoroalkyl iodides react with aliphatic and aromatic thiols in the water-organic solvent media to form alkyl or aryl perfluoroalkyl sulfides in 60-80% yield.

## INTRODUCTION

Earlier we have shown that despite the unfavourable polarization of the carbon-iodine bond in perfluoroalkyl iodides these compounds can be successfully used in the perfluoroalkylation of aliphatic [ 1 ], aromatic [1-3 ] and heterocyclic thiols [ 4 ], seleno- [5 ] and tellurophenols [ 6 ], sulphinic and C-H acids [ 8 ]. The reaction is normally carried out in liquid ammonia or polar organic solvents. Previously prepared sodium thiophenolates are normally used for S-perfluoroalkylation in the last case. The application of dried sodium hydroxide for the preparation of the sodium thiolates in situ decreases the yields of products of the perfluoroalkylation by 15-30% depending on the solvents [ 1 ] .

It is well known [ 9 ] that alkylation of the organic compounds by alkyl iodides can be successfully and sometimes with the considerable advantage carried out under conditions of phase-transfer catalysis. It was interesting to explore the possibility of the application of phase-transfer catalysis for the ion-radical perfluoroalkylation.

We have found that in the presence of triethylbenzylammonium chloride under UV-irradiation perfluoroalkyl iodides alkylate aromatic and aliphatic thiols in the water-organic solvent media in 60-80% yield.



$R_F$=$CF_3$, R=H(1),Cl(2),$CH_3$(3), $CH_3O$(4); $R_F$=$C_3F_7$, R=H(5),Cl(6), $CH_3$(7), $CH_3OOC$(8);$R_F$=$(CF_3)_2CF$, R=Cl(9); $R_F$=n-$C_6F_{13}$,R=Cl(10)

$HSCH_2COOC_2H_5 + CF_3I \longrightarrow CF_3SCH_2COOC_2H_5$ (56%)

The reaction is carried out in a mixture of water with ether or benzene. Use of dichloromethane or chloroform is also possible, but the yields of aryl perfluoroalkyl sulfides are 20-30% lower in this case.

## RESULTS and DISCUSSION

It is found that high yields of products of perfluoroalkylation can be obtained in a wide range of concentrations of sodium hydroxide (15-30%) but for the satisfactory yields of aryl perfluoroalkyl sulfides the concentration of sodium hydroxide must not be lower than 10%. After a number of experiments it was shown that the optimal yields can be obtained with a 20-25% solution of NaOH and 30 minutes irradiation. The yields are normally higher when liquid perfluoroalkyl iodides are used. When gaseous trifluoroiodomethane is taken as the perfluoroalkylating reagent the yields of aryl trifluoromethyl sulfides are generally lower than the yields of the corresponding aryl perfluoropropyl sulfides though the reaction was run in a sealed glass tube and an excess of trifluoroiodomethane was taken.

The yields are also 25-30% lower when a branched perfluoroisopropyl iodide is employed. Similar results were previously obtained when the reaction was run in liquid ammonia [2].

Earlier we have mentioned [1], that p-nitrothiophenol did not react with trifluoroiodomethane in liquid ammonia at -30°. The formation of p-nitrophenyl trifluoromethyl sulfide was observed only after the irradiation of the reaction mixture in a sealed tube at 30-45°C. It was hoped that as

TABLE 1

The phase-transfer catalyzed perfluoroalkylation of aromatic thiols

| Thiol R | Perfluoroalkyl iodide, $R_F$ | Solvent | Product (Yield, %) |
|---|---|---|---|
| H | $CF_3$ | ether | 1(54) |
| Cl | $CF_3$ | ether | 2(61) |
| $CH_3$ | $CF_3$ | ether | 3(57) |
| $CH_3O$ | $CF_3$ | ether | 4(52) |
| H | $C_3F_7$ | ether | 5(78) |
| Cl | $C_3F_7$ | ether | 6(85) |
| Cl | $C_3F_7$ | benzene | 6(68) |
| $CH_3$ | $C_3F_7$ | ether | 7(83)[a] |
| $CH_3$ | $C_3F_7$ | benzene | 7(67) |
| $CH_3$ | $C_3F_7$ | $CH_2Cl_2$ | 7(50) |
| $CH_3$ | $C_3F_7$ | $CHCl_3$ | 7(55) |
| $CH_3OOC$ | $C_3F_7$ | ether | 8(71)[b] |
| Cl | $(CF_3)_2CF$ | ether | 9(60) |
| Cl | $C_6F_{13}$ | ether | 10(71) |

[a] B.p. 120-121° (80 torr), [b] B.p. 126-127° (21 torr)

Satisfactory microanalysis obtained for both new products: F ± 0.3%

under conditions of phase-transfer catalysis the perfluoroalkylation was carried out at positive temperatures the result of interaction of perfluoroalkyl iodides with p-nitrothiophenol would be successful. But even under these conditions the yield of p-nitrophenyl trifluoromethyl sulfide was less than 5% (by GLC) and the formation of large amounts of 4,4'-dinitrodiphenyl disulfide was observed. In contrast to p-nitrothiophenol other aromatic thiols with electron withdrawing or donating substituents react easily with perfluoroalkyl iodides under these conditions.

## Aryl perfluoroalkyl sulfides. General procedure.

To a water solution of sodium hydroxide (20-25%, 5 ml) and triethylbenzyl ammonium chloride (0.001 mol) in a Pyrex three-necked flask (or sealed tube in the case of $CF_3I$) the corresponding thiol (0.01 mol) and perfluoroalkyl iodide (0.012 mol or 0.015-0.02 mol in the case of $CF_3I$) were added. The stirred reaction mixture was exposed to a high pressure mercury lamp "PRK-4" at a distance of 25-30 cm from the flask for 30 minutes. The reaction was diluted with water and organic layer was extracted with ether. The ether solution was washed with water and dried with magnesium sulphate. The solvent was distilled, the products were purified by distillation and identified by GLC.

The yields, solvents and physical constants of the new compounds are given in Table I.

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