

Preliminary note

Synthesis of perfluoroalkyl-substituted arenes by oxidative desulfurization–fluorination

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Abstract

Perfluoroalkyl-substituted arenes have been readily synthesized from 2-aryl-2-perfluoroalkyl-1,3-dithiolanes by the action of an *N*-halo imide and HF/pyridine (or HF/melamine).

Keywords: Synthesis; Perfluoroalkyl-substituted arenes; Oxidative desulfurization–fluorination

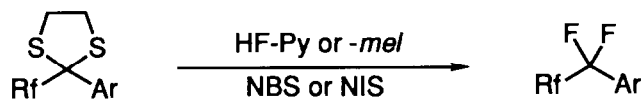
The introduction of a perfluoroalkyl group into an organic molecule brings unique properties such as high chemical and thermal stability, high gas permeability, high interfacial activity, low refractive index and low viscosity [1]. Some methods for the introduction of the perfluoroalkyl group have been reported, e.g. the coupling reaction of R_f -Mtl (Mtl=Zn or Cu) with aryl halides under sonication [2], decarbonylative substitution of perfluoroalkanoyl halide to aromatic compounds in the presence of a Ni catalyst [3] or alkylation of aromatic compounds with a perfluoroalkyl radical derived from perfluoroalkyl iodonium salt [1,4] or perfluoroalkanoyl peroxide [5]. However, yields and selectivities of these reactions are not necessarily high enough.

We have demonstrated that organosulfur compounds can be easily converted into organofluorine compounds through 'oxidative desulfurization–fluorination' (Scheme 1), which has allowed us to prepare difluoromethylene compounds [6], trifluoromethylated aromatics [7], trifluoromethyl ethers [8] and *N*-trifluoromethylamines [9]. We have further extended the

methodology to the syntheses of perfluoroalkylated aromatics and report herein the experimental details.

Aryl perfluoroalkyl ketones **1** [10], prepared from 2 mol of arylmagnesium reagents and perfluoroalkanoic acids in 58%–82% yield, were converted into the corresponding 1,3-dithiolanes **2** by means of 1,2-ethanedithiol and $BF_3 \cdot AcOH$ in refluxing $CHCl_3$ [11]. In contrast to non-fluorinated ketones, dithioacetalization did not occur at room temperature due to the high electronegativity of the perfluoroalkyl group. A dichloromethane (1 ml) solution of **2** (0.5 mmol) was added to a CH_2Cl_2 (1.5 ml) suspension of *N*-bromosuccinimide (NBS, 1.1 mmol) and a hydrogen fluoride pyridine complex (HF/py, 70:30 wt.%, 1 ml) at $-78^\circ C$, and the resulting mixture was stirred at room temperature for the period shown in Table 1. The reaction was monitored by TLC and after **2** had been consumed the reaction mixture was poured into a mixture of an aqueous solution of $NaHCO_3/NaHSO_3$ and ice and extracted with Et_2O . After work-up and purification, the perfluoroalkyl-substituted arene **3** was isolated in the yields shown in Table 1.

In addition to HF/py (runs 1, 3 and 4), a hydrogen fluoride/melamine complex (HF/mel) was also effective (runs 2, 5–7); $Bu_4NH_2F_3$ [12] was totally ineffective in contrast to its behaviour in the fluorination of non-fluorinated dithiolanes [6]. Ring halogenation took place when Ar was electron-rich, but this side reaction was suppressed by the use of *N*-iodosuccinimide (NIS) as the oxidant. Dithiolanes having a longer perfluoroalkyl group than CF_3 could be transformed more readily into

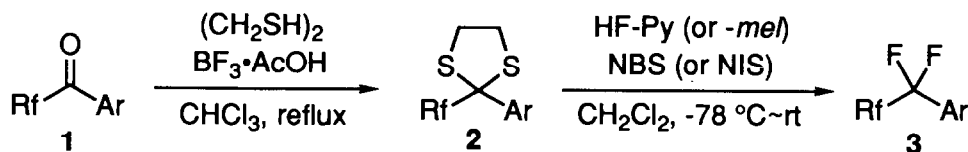


Scheme 1. Preparation of perfluoroalkylated arenes by oxidative desulfurization–fluorination.

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Table 1

Preparation of perfluoroalkylated aromatics



Run No.	Ar	R _f	2 (%)	3 (%)
1	4- ⁿ PrC ₆ H ₄	CF ₃	69	53
2				52
3	4- ⁿ BuOC ₆ H ₄	CF ₃	78	74
4	1-NaPh	CF ₃	88	98
5	4- ⁿ PrC ₆ H ₄	n-C ₃ F ₇	61	74
6				70
7	4- ⁿ BuOC ₆ H ₄	n-C ₃ F ₇	58	79

the products: the reaction was complete within 15 min with NBS (runs 5 and 7) and free from halogenation by an electron-rich substrate (run 7).

Perfluoroalkyl iodides or perfluoroalkanoyl peroxides, usually used in the perfluoroalkylation of aromatic compounds, are apparently difficult to manipulate owing to their volatility or instability. We have demonstrated herein that dithioacetals of perfluoroalkanoyl-substituted arenes are readily transformed to perfluoroalkyl-substituted arenes under extremely mild conditions. Since perfluoroalkanoylarenes are readily prepared from the corresponding perfluoroalkanoic acids under regio control, the oxidative desulfurization–fluorination reaction allows the ready introduction of the perfluoroalkyl group into aromatic compounds.

References

- [1] T. Umamoto, *Yuki Gosei Kagaku Kyokai Shi*, 41 (1983) 251, and references cited therein.
- [2] V.C.R. McLoughlin and J. Thrower, *Tetrahedron*, 25 (1969) 5921; N. Ishikawa and M. Ochiai, *Nippon Kagaku Kaishi*, (1973) 2351; N. Ishikawa and T. Kitazume, *Yuki Gosei Kagaku Kyokai Shi*, 41 (1983) 432; T. Kitazume and N. Ishikawa, *Chem. Lett.*, (1982) 137.
- [3] J.J. Drysdale and D.D. Coffman, *J. Am. Chem. Soc.*, 82 (1960) 5111.
- [4] L.M. Yagupolskii, I.I. Maletina, N.V. Kondratenko and V.V. Orda, *Synthesis*, (1978) 835; M. Yoshida, H. Amemiya, M. Kobayashi, H. Sawada, H. Hagii and K. Aoshima, *J. Chem. Soc., Chem. Commun.*, (1985) 234.
- [5] H. Sawada, M. Yoshida, H. Hagii, K. Aoshima and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 59 (1986) 215; M. Yoshida, T. Yoshida, M. Kobayashi and N. Kamigata, *J. Fluorine Chem.*, 46 (1990) 423; M. Yoshida, N. Kamigata, H. Sawada and M. Nakayama, *J. Fluorine Chem.*, 49 (1990) 1.
- [6] M. Kuroboshi and T. Hiyama, *Synlett*, (1991) 909.
- [7] M. Kuroboshi and T. Hiyama, *Chem. Lett.*, (1992) 827.
- [8] M. Kuroboshi, K. Suzuki and T. Hiyama, *Tetrahedron Lett.*, 33 (1992) 4173.
- [9] M. Kuroboshi and T. Hiyama, *Tetrahedron Lett.*, 33 (1992) 4177.
- [10] A. Moore and R. Levine, *J. Org. Chem.*, 29 (1964) 1439.
- [11] T.W. Greene, *Protective Groups in Organic Synthesis*, Wiley, New York, 1981.
- [12] P. Albert and J. Cousseau, *Bull. Soc. Chim. Fr.*, (1986) 910.