4.58 (t, 2H, J=7.5 Hz, CH_2), 7.36-8.21 (m, 4H, C_6H_4), 12.94 (s, 1H, enolic OH); IR (KBr) 3340-2200 (br), 1700, 1555, 1345, 1210, 760 cm^{-1}; MS m/e 260 (M^+, 51.8), 218 (100), 172 (20), 160 (9.5), 145 (11.4), 90 (15.6). **9c**: ^{1}H-NMR (DMSO-d_6) δ 1.35-1.81 (m, 10H, $5CH_2$), 5.40 (m, 1H, CH), 7.43-8.24 (m, 4H, C_6H_4), 12.85 (s, 1H, enolic OH); IR (KBr) 3600-2400 (br), 1720, 1540, 1350, 1330, 1190, 1140, 760 cm^{-1}; MS m/e 300 (M^+, 8.9), 218 (100), 172 (14.4), 160 (9.0), 145 (11.7), 90 (16.6), 82 (19.6), 41 (46.2). **9d**: ^{1}H-NMR (DMSO-d_6) δ 7.33-8.28 (m, 9H, $C_6H_4+C_6H_5$), 12.80 (s, 1H, enolic OH); IR (KBr) 3600-2400 (br), 1690, 1640, 1540, 1345, 1320, 1180, 770 cm^{-1}; MS m/e 295 ($M+1$, 18), 294 (M^+, 94), 236 (15), 208 (6), 135 (3), 106 (12), 77 (23), 76 (6), 65 (5), 58 (2).

A Novel Synthesis of 1H, 1H-Perfluoroalkyl Aromatics *via* Reduction of Perfluoroalkylated Dithioketals[1]

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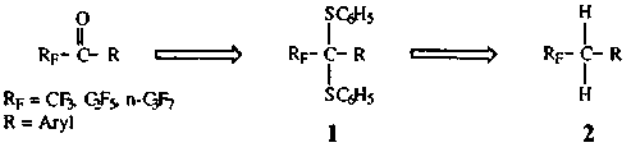
The introduction of a perfluoroalkyl functionality into organic compounds is an important subject in organofluorine chemistry because the resultant molecules exhibit unique properties in the areas of agrochemicals and pharmaceuticals and material.[2] Numerous methods for the perfluoroalkylation of organic compounds have been intensively developed during the last two decades and a couple of reviews has been reported in recent years.[3] In particular, trifluoromethyl functionality in aromatic compounds has attracted much attention mainly due to the profound enhancement in biological activities as compared to those of nonfluorinated aromatics.[4] However, it has been well known that perfluoroalkyl-functionalized aromatic compounds are very slowly metabolized in biological systems because of high stability of a perfluoroalkyl group connected directly to an aromatic ring.[5] Therefore, it has been suggested that introduction of 1H, 1H-perfluoroalkyl functionality into aromatic compounds, in which a methylene unit links a perfluoroalkyl group to the aromatic ring, may overcome the drawback of perfluoroalkyl-functionalized aromatic compounds. Although the methods for the preparation of perfluoroalkylated aromatic compounds has been well established,[3b] there are only limited reports on the synthesis of 1H, 1H-perfluoroalkylated aromatic compounds. Most of these methods[6] have disadvantages such as low yields, vigorous reaction conditions, the use of toxic reagents, multistep procedure and lack of generality. As part of our continuing studies on the chemistry and application of 1,1-bis(phenylthio)perfluoroalkyl aromatic compounds **1**,[7] we now describe a general approach for the preparation of 1H, 1H-perfluoroalkylated aromatic compounds **2**.



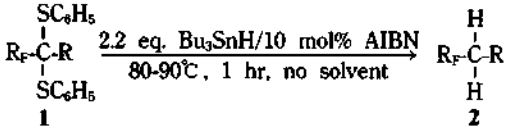
Recently, we developed a general and efficient method for the synthesis of **1** from the reaction of aryl perfluoroalkyl ketones with thiophenol at −78℃ in the presence of aluminum chloride.[8] Therefore, desulfurization of **1** would be a promising pathway for the synthesis of **2** because Clemmensen reduction of aryl perfluoroalkyl ketones failed to provide **2**.[9] Although only one successful example for the synthesis of **2** from aryl perfluoroalkyl ketones has been reported by DePuy and Schultz,[6f] this example shows multistep procedure and relatively low yield.

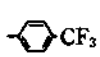
Compound **1a** was easily reduced by treatment with 2.2 equiv. of Bu_3SnH and 10 mol% AIBN without solvent at 80-90℃ for 1 hour and gave excellent yield of **2a**. The use of 1.1 equiv. of Bu_3SnH in this reaction resulted in the formation of 1-phenylthio-2,2,2-trifluoroethylbenzene **4a** in 82% yield. Product **2a** was easily isolated by flash distillation after reaction was finished, followed by simple distillation. Several substituents on the benzene ring did not interfere desulfurization of **1a** and provided excellent yields of **2**. Also, 1,1-bis(phenylthio)-trifluoroethylthiophene **1j** was easily reduced to give the corresponding product **2j**. Similar reduction of pentafluoroethyl and heptafluoropropyl substituted compounds **1k** and **1l** under the same reaction condition afforded the corresponding products **2k** and **2l** in 96% and 90% yields, respectively. All results are summarized in Table 1.

In a typical experimental procedure, a 50 m*l* two-necked round bottomed flask equipped with a septum, magnetic stir bar and a nitrogen inlet was charged with 1,1-bis(phenylthio)-trifluoroethylbenzene (4.70 g, 12.5 mmol),[8] tributyltin hydride (7.62 m*l*, 27.5 mmol) and AIBN (0.20 g). The mixture was heated at 80-90℃ (oil bath temperature) for 1 hour and then cooled to room temperature. Flash distillation of the mixture, followed by simple redistillation provided 1.60 g (80% yield) of 2,2,2-trifluoroethylbenzene **2a**. bp. 123-125℃; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 3.31 (q, J=10.6 Hz, 2H); ^{19}F NMR (80 MHz, $CDCl_3$) δ −50.32 (t, J=10.9 Hz); MS, m/e (relative intensity) 160 (M^+, 87.6), 91 (100); IR (neat) 3005, 2900, 1490, 1425, 1350, 1250, 1200, 1130, 1090, 1065, 905, 750, 690, 660 cm^{-1}.

Initially, we began our studies by examing the desulfurization of **1** under a couple of conditions which has been employed in the desulfurization of nonfluorinated dithioacetals or dithioketals. When **1a** reacted with a large excess of Raney Ni (20 equiv.) in acetone at reflux temperature for 2 hours, unexpected 2,2-difluoro-1-phenylthiostyrene **3a** which would be very useful synthetic intermediate was obtained in 63% yield and 1-phenylthio-2,2,2-trifluoroethylbenzene **4a** was obtained in 10% yield. No 1H,1H-trifluoroethylbenzene **2a** was detected. This result indicates that β-defluorination after insertion of Ni into carbon-sulfur bond may occur much faster than reduction. Similarly, treatment of **1a** with a mixture of 2 equiv. of $TiCl_4$ and 4 equiv. of $LiAlH_4$

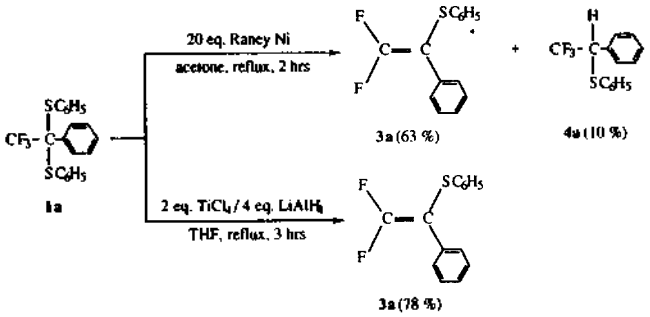
Table 1. Preparation of 1H, 1H-perfluoroalkyl Aromatic Compounds **2**



Compound No.	R	R_F	**2**, yield (%)[a]
1a		CF_3	80
1b		CF_3	84
1c		CF_3	82
1d		CF_3	83
1e		CF_3	84
1f		CF_3	73
1g		CF_3	92
1h		CF_3	85
1i		CF_3	87
1j		CF_3	78
1k		CF_3CF_2	96
1l		$CF_3CF_2CF_2$	90

[a]Isolated yields.

in THF at reflux temperature for 3 hours afforded only **3a** in 78% yield. In this reaction products **2a** and **4a** were not detected.



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A Facile Synthesis of 5(4H)-Oxazolones

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5(4H)-Oxazolones which are considered anhydrides of *N*-acyl-α-amino acids have been employed as intermediates[1] for various organic synthesis, especially in the filed of α-amino acid, peptide and penicillin chemistry. Recently, Saegusa[2] reported a new ring opening polymerization of 5(4H)-oxazolone and its derivatives to synthesize various poly (*N*-formyl-α-peptides) in order to develop stimuli sensitive polymers and reemphasized their application as valuable monomers in polymer chemistry.

Unsaturated 5(4H)-oxazolones were synthesized by the condensation of benzaldehyde with hippuric acid in the presence of an acetic anhydride by Plöchl[3] in 1883. Mohr and coworkers[3] prepared several saturated 5(4H)-oxazolones by the reaction using an acetic anhydride and *N*-acyl-α-amino acids. In general, 5(4H)-oxazolones have been prepared by cyclization of *N*-acyl-α-amino acids treated with an excess acetic