

## Novel reactions of perfluoroalkylphenyl sulfides with organolithium reagents

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### Abstract

The reaction of anisole with organolithium reagents, commonly known as *ortho*-directed metallation, is of considerable synthetic utility in organic chemistry and as such has attracted considerable attention in recent years. Over the past 50 years, several mechanisms have been proposed to account for the observed regioselective metallation. For the first time, the reaction of perfluoroalkylphenyl sulfides with organolithium reagents has been investigated and found to furnish products resulting from the replacement of the perfluoroalkyl moieties with alkyl groups derived from the metallating agents. Phenyltrifluoromethyl ether, the anisole analog, failed to undergo metallation. A rationalization for the formation of unusual products via mediation of a single-electron-transfer process is presented in this paper together with the spectral data of the products.

**Keywords:** Reactions; Perfluoroalkylphenyl sulfides; Organolithium reagents; NMR spectroscopy; Mass spectrometry; Orthometallation

### 1. Introduction

Since the discovery of the *ortho*-directed metallation of aryl ethers [1], considerable interest has been evinced not only in its uses and synthetic applications [2] but also in the study of the mechanism of metallation [3]. The presence of the heteroatom containing the *ortho*-directing substituent on the aryl ring makes this process regiospecific and hence particularly useful in the introduction of functional groups. Extensive competitive metallation studies [4] have led to the following order or reactivity:  $\text{CONR}_2 > \text{SO}_2\text{NR}_2 > 2\text{-oxazolines} > \text{CH}_2\text{NR}_2 > \text{OCH}_3 > \text{NMe}_2 = \text{F}$ . Recent modifications of the metallation reaction include the use of the tricarbonyl chromium [5a] and the super-base composed of <sup>n</sup>BuLi/<sup>n</sup>BuOK [5b].

Several attempts have been made to develop synthetic strategies aimed at taking advantage of the powerful influence of the sulfur-containing heterosubstituent-directed metallations [6]. Thus, *ortho*-lithiation of alkylthioarenes has been shown to effect metallation of the side-chain prior to ring metallation [6b–d].

Also, two recent examples of the metallation of alkylthio- and arylthio-tetrahydropyrans have shown that products arise exclusively from the side-chain and aromatic ring metallations respectively [6e], while the metallation of 4-methylthiophenol in the presence of tetramethylenediamine (TMEDA) yielded both C- and S-double metallated derivatives [6f]. In continuation of our interest in the chemistry of the trifluoromethylthio group [7], the reaction of the perfluoroalkylphenyl sulfides with organolithium reagents has now been investigated. The required perfluoroalkylphenyl sulfides were synthesized by reacting the substituted iodo-benzenes with trifluoromethylthiocopper, which was itself prepared as described earlier [8].

### 2. Results and discussion

Before attempting to rationalize the unusual course of the directed metallation reaction with perfluoroalkylarene sulfides, a brief review of the mechanisms proposed to account for the observed regioselective

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metallation of the alkylarene sulfides is in order. Anisole and substituted anisoles have been the most popularly used substrates in metallation reactions, although anisole undergoes metallation very slowly at 0 °C and virtually not at all below 0 °C. This behavior of anisole at –75 °C has been attributed to electronic effects [9]. The results of the directed metallation are generally described in terms of two primary effects; namely coordination with organometallic species and inductive effects, and complexation occurring between the substituent and the lithiating agent prior to metallation. The overall effect appears to be more complex than the mere formation of the complex via coordination. The ‘proximity factor’ has been stated to play a prominent part in directed metallations [3h]. In fact, it has been suggested that the complex-induced proximity effect (CIPE) is as equally important as the classical effects [3h]. Also, the directed metallation has been reported to involve various processes such as (i) a polar ‘push-pull’ mechanism [10a], (ii) a radical pair mechanism [10b,c], (iii) the involvement of a bicyclic transition state [3f], (iv) a multi-step single-electron-transfer (SET) process involving intermediate radical anions [10d], (v) the participation of a four-membered cyclic transition state not involving the disruption of the aromatic p-orbital system [10e], etc.

Bauer and Schleyer in a recent paper have provided convincing evidence for the formation of a 1:1 complex between the RLi and anisole, although the complex itself failed to undergo metallation [3g]. The evidence for complex formation supports a 50-year old suggestion of Roberts and Curtain [3a]. Further, based on semi-empirical MNDO theoretical calculations, direct interaction between CH<sub>3</sub>O and Li has been implied. A similar formation of the alkylaryl ether–<sup>n</sup>BuLi complex had been reported earlier [11]. This complex formation has also been questioned [10e]. There is growing evidence for the participation of the single-electron-transfer (SET) mechanism in the so-called ‘nucleophilic reactions’ of organolithium compounds [12a–d]. The multi-step SET mechanism proposed by Grayhill and Shirley [11] to explain the products formed stands unsupported by evidence. According to the most recent communication on this subject, the *ortho*-metallation has been described to occur “via a simple overriding base metal hydrogen exchange with acidic protons” and without the involvement of coordination [9]. In summary, the mechanism of directed metallation is rather complex and as yet not clearly defined.

The results of the present study are briefly summarized in Fig. 1. The required perfluoroalkyl phenyl sulfides were synthesized in good yields [Eq. (1) >75%]. The exposure of a solution of thiophenol (3) and 2-iodo-perfluoropropane in dry acetonitrile and triethylamine to UV light furnished excellent yields of perfluoroisopropylphenyl sulfide [4, Eq. (2)]. The treatment of 3-

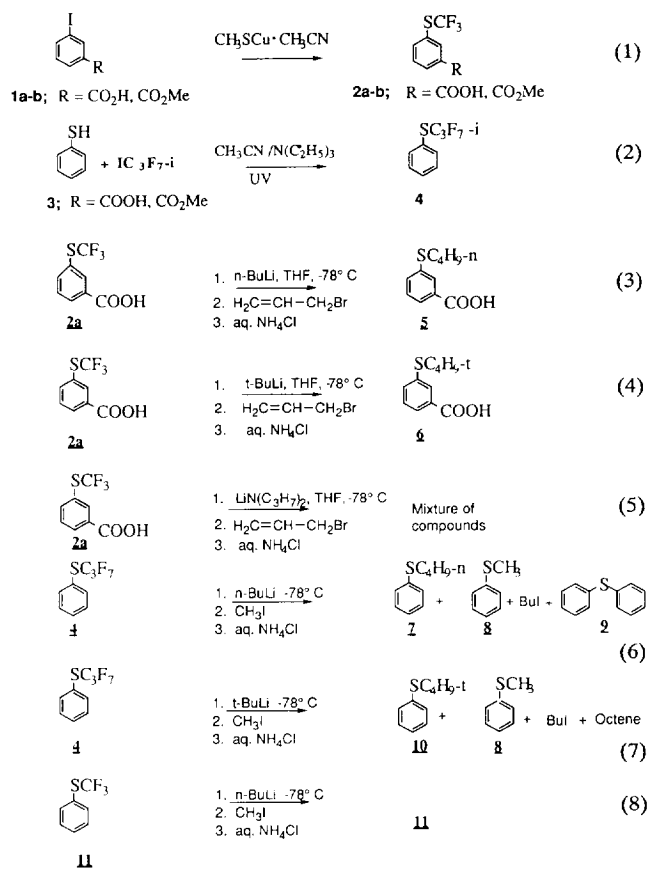


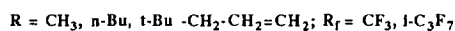
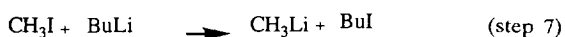
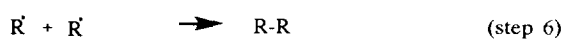
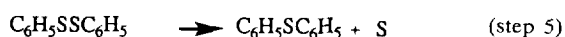
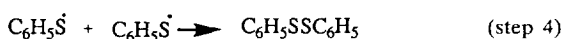
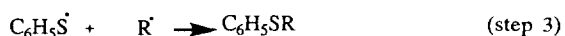
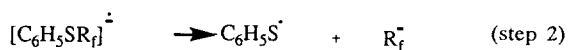
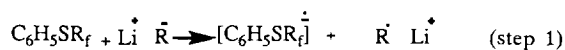
Fig. 1.

(trifluoromethylthio)benzoic acid (2a) with <sup>n</sup>BuLi at –78 °C for 30 min, followed by electrophilic quenching with allyl bromide and stirring for additional 30 min at –78 °C, decomposition of the reaction mixture with saturated aq. NH<sub>4</sub>Cl and the usual work-up gave the product which was identified by GC–MS and NMR data as 3-(n-butylthio)benzoic acid [5, Eq. (3)]. A similar treatment of 2a with <sup>t</sup>BuLi furnished 3-(t-butylthio)benzoic acid [6, Eq. (4)]. A similar product profile was noted in the reaction of 2b with organolithium reagents. Use of lithium diisopropylamide (LDA) as the metallating agent yielded a very complex mixture which was not further analyzed [Eq. (5)]. The reaction of perfluoroisopropylphenyl sulfide (4) with <sup>n</sup>BuLi, followed by quenching with CH<sub>3</sub>I and work-up, resulted in the characterization of n-butylphenyl sulfide (7), methylphenyl sulfide (8), phenyl sulfide (9) and n-butyl iodide [Eq. (6)], the last being formed from a simple exchange with CH<sub>3</sub>I and the metallating agent. A similar treatment of 4 with <sup>t</sup>BuLi gave 8, t-butylphenyl sulfide (10), 4-octene and butyl iodide [Eq. (7)].

In all the cases we have examined, the major product(s) of the reaction, other than the recovered starting materials, have turned out to be compounds in which the perfluoroalkyl groups have been replaced by the alkyl moieties derived from the respective me-

tallating agents. The products derived from the  $R_f$  groups attached to the sulfur atom were gases and hence not detected. The yields of the various products arising from the metallation reaction are given in the Experimental section. However, it is interesting to note that compounds **8** and **10** were formed in significant amounts [Eq. (7)]. These results are in complete contrast with the products of the reaction of the organolithium reagents with alkylarene sulfides, the primary process in this case being the metallation of the alkyl side-chain [13]. Moderate yields of the products are obtained by the direct dimetallation of the alkylphenyl sulfides with a two-fold excess of the metallating agent [13b,c] and/or in the presence of the so-called super bases [13d].

The results described in Fig. 1 can be rationalized by invoking the participation of the SET process in the directed metallation reactions (Scheme 1). The process begins with the transfer of an electron from the organolithium reagent to the substrates (namely the  $ArSR_f$  derivatives) to form the radical anion (step 1), which subsequently collapses to form the phenylthiyl radical (step 2). The phenylthiyl radical then reacts with the alkyl radical formed earlier (step 1) to give the alkyl phenyl sulfide (step 3). Characterization of *n*- and *t*-butylphenyl sulfides (**7** and **10**) and *m*-(*n*- and *t*-butylthio)benzoic acids (**5** and **6**) as well as methylphenyl sulfide (**8**) strongly supports this contention. The dimerization of the phenylthiyl radical formed earlier (step 2) to phenyl disulfide (step 4), followed by the extrusion of sulfur, would then give rise to phenyl sulfide (**9**, step 5). The origin of 4-octene which was detected among the reaction products [Eq. (7)] must be due to the dimerization of the butyl radical (formed in step 1) to octane, followed by the abstraction and loss of hydrogen. These are standard reactions arising from the free-radical reactions (cf. Ref. [7], and references cited therein). Step 7 explains the formation of butyl iodide.



Scheme 1. Reactions of perfluoroalkylphenyl sulfides with organolithium reagents.

The directed metallation of alkylarene ethers and thioethers takes an altogether different course when perfluoroalkyl moieties are attached to the heteroatom. Anisole has been the most popular substrate in the study of the directed metallation reactions. When the  $CH_3$  attached to the heteroatom of anisole is changed to  $CF_3$ , the directed metallation fails [Eq. (8)]. Just as the oxygen in alkyl arene ethers, the sulfur atom in alkylphenyl sulfides is a  $\pi$ -electron donor to the aromatic ring. However, in contrast to the alkyl groups, the perfluoroalkyl moieties are highly electronegative groups. Consequently, they dramatically reduce the electron-donating ability of the heteroatom and thereby modify the normal course of the metallation process. In contrast with the above observation on the metallation of  $ArSR_f$ , the side-chain of the alkylarene sulfides is first metallated. The facile cleavage of the  $S-R_f$  bond during the metallation process suggests that this bond is weakened by the highly electronegative perfluoroalkyl moiety attached to the sulfur atom.

The mass spectrum of **2a** shows an  $M+1$  peak ( $m/e=233$ , CI, 100%) as being the most prominent, followed by the  $M^+$  peak. Among other usual peaks are  $M-OH$  ( $m/e=205$ ) and  $M-SCF_3$  ( $m/e=121$ ). The molecular ion ( $m/e=211$ , CI) in the spectrum of **5** is the most prominent peak. Other peaks representing the loss of  $OH$  ( $m/e=193$ ),  $C_2H_5$  ( $m/e=181$ ),  $C_3H_7$  ( $m/e=167$ ),  $C_4H_9$  ( $m/e=153$ ) and  $SC_4H_9$  ( $m/e=121$ ) are also observed. The mass spectral behavior of **6** is slightly different from that of **5**, although the  $M+1$  peak is the most prominent. Also seen in its mass spectrum are peaks corresponding to the loss of  $-OH$ ,  $-C_4H_9$  and  $-SC_4H_9$  moieties. The mass spectra of alkyl aryl sulfides are characterized by the presence of peaks corresponding to the cleavage of the carbon-sulfur bond, skeletal rearrangement and extrusion of sulfur [14]. A prominent peak with  $m/e=123$  in the mass spectrum of **7** is due to the loss of  $C_3H_7$  from the parent ion. However, the most prominent peak of **7** appears at  $m/e=110$  and is due to  $M-C_4H_9$ . Its overall fragmentation pattern is very similar to that of pentylphenyl sulfide [14b]. Compound **10** exhibits a fragmentation behavior similar to that of **7**. The fragmentation of phenyl sulfide (**9**) is straightforward and has been discussed earlier [14b,15].

### 3. Experimental details

The reactions were carried out in a flame-dried, argon gas-purged 10 or 25 ml three-necked flask equipped with a magnetic stirrer, a gas inlet, a pressure equalizing dropping funnel and a reflux condenser carrying a Dry Ice and acetone trap. The temperature of the coolant passing through the condenser was maintained at  $-20^\circ\text{C}$ . All solvents were dry and freshly

distilled prior to use. All reactions were carried out by adding stoichiometric amount of the alkyl lithium reagent to the substrate cooled to  $-78^{\circ}\text{C}$ . The reactions were terminated by the addition of moist ether and aqueous ammonium chloride, followed by extraction with ether. After drying over sodium sulfate, the solvent was evaporated under reduced pressure and the residue flash distilled and analyzed by GC–MS methods. Mass spectra were obtained on a Finnigan Model 5100 GC–MS instrument equipped with a silica  $25\text{ m} \times 0.31\text{ mm}$  i.d. SE-54 capillary column (J & W Scientific, Rancho Cordova, CA). Routine GC analyses were accomplished with a Hewlett Packard 5890A gas chromatograph equipped with a J & W Scientific  $30\text{ m} \times 0.53\text{ mm}$  i.d. DB-5 column (J & W Scientific, Folsom, CA). The NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ ) were recorded in  $\text{CDCl}_3$  with TMS as the internal standard on a Varian VXR-400S spectrometer at 100 MHz and 376 HMz, respectively. The external reference for  $^{19}\text{F}$  NMR was  $\text{CCl}_3\text{F}$ .

### 3.1. Syntheses of the substrates

The trifluoromethylthiocopper–acetonitrile adduct was prepared from bis(trifluoromethyl)disulfide as described elsewhere [8].

3-(Trifluoromethylthio)benzoic acid (**2a**): A mixture of trifluoromethylthiocopper (2.07 g, 10.07 mmol) and *m*-iodobenzoic acid (0.5 g, 2.02 mmol) was heated in dry DMF at  $115\text{--}120^{\circ}\text{C}$  for 4 h. The reaction mixture was cooled, treated with water, extracted with ether and the ether solution dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure on a Rotoevaporator and the residue purified by chromatography over a silica column. Elution was carried out using a diethyl ether/petroleum ether (1:9) mixture to yield 0.295 g of a light yellow colored solid [66%, **2a**, Eq. (1)].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 8.42 (bs, 1H); 8.25 (dd,  $J=8.1, 1.2$  Hz, 1H); 7.91 (bd, 1H); 7.57 (dd,  $J=8.8$  Hz, 1H) ppm.  $^{19}\text{F}$  NMR  $\delta$ :  $-43.51$  ppm. MS *m/e* (CI, isobutane): 223 ( $\text{M}+\text{H}$ , 100%); 222 ( $\text{M}^+$ , 32.5%); 205 ( $\text{M}-\text{OH}$ ); 121 ( $\text{M}-\text{SCF}_3$ ).

Methyl 3-(trifluoromethylthio)benzoate (**2b**): This compound was similarly prepared in 90% yield from trifluoromethylthiocopper and methyl *m*-iodobenzoate [**2b**, Eq. (1)]. MS *m/e* (CI, isobutane): 237 ( $\text{M}^+$ ).

Phenylperfluoroisopropyl sulfide (**4**): To a solution of thiophenol in freshly distilled dry acetonitrile and dry triethylamine, cooled in an ice bath, was added dropwise, with stirring, a solution containing a stoichiometric quantity of perfluoroisopropyl iodide in dry acetonitrile under an argon atmosphere. After addition was complete, the reaction mixture was exposed to UV light for 15 min and stirred for 15 min under laboratory lighting conditions. The process was repeated twice. The reaction mixture was then stirred for an additional

hour, treated with water and extracted with diethyl ether. The ether extract was dried over sodium sulfate, concentrated on a Rotoevaporator under slightly reduced pressure and the residue distilled at  $80\text{--}82^{\circ}\text{C}/54\text{ mmHg}$  to yield the desired product [Eq. (2)] in 88% yield and 99.2% purity (GLC) [16] (b.p.  $85\text{--}86^{\circ}\text{C}/56\text{ mmHg}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.41 (m, *meta* protons, 2H); 7.51 (m, *para* proton, 1H) ppm.  $^{13}\text{C}$  NMR  $\delta$ : 120.3 [q,  $J=288$  Hz,  $(\text{CF}_3)_2$ ]; 98.2 [d,  $J=299$  Hz, septet  $J=30.5$  Hz; (CF)]; 120 (C–S); 137.6 (*o*-carbons); 129.3 (*m*-carbons); 131.2 (*p*-carbon) ppm.  $^{19}\text{F}$  NMR  $\delta$ :  $-73.01$  [d,  $J=11.3$  Hz,  $(\text{CF}_3)_2$ ]; and  $-156.25$  [septet,  $J=11.3$  Hz, (CF)] ppm. GC–MS *m/e*: 278 ( $\text{M}^+$ ); 259 ( $\text{M}-\text{F}$ ); 239 (259–HF); 209 ( $\text{M}-\text{CF}_3$ ); 201 ( $\text{M}-\text{SC}_3\text{F}_7$ ); 189 (209–HF); 170 (190–F); 109 (100%,  $\text{C}_6\text{H}_5\text{S}$ ); 77 ( $\text{C}_6\text{H}_5$ ); 69 ( $\text{CF}_3$ ); 45 (CSH).

### 3.2. Metallation experiments

Reaction of 3-(trifluoromethylthio)benzoic acid (**2a**) with  $^n\text{BuLi}$ : To a solution of **2a** (0.105 g, 0.473 mmol) in dry THF (5 ml) cooled to  $-78^{\circ}\text{C}$  was added a 1.5 M solution of  $^n\text{BuLi}$  (0.7 ml) dropwise under an argon atmosphere with stirring. Stirring was continued for 25 min after addition was complete and then allyl bromide (0.063 g, 0.52 mmol) in dry THF was added dropwise to the cold reaction mixture. The mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h, then allowed to warm slowly to ambient temperature over 45 min and the reaction mixture stirred at room temperature for an additional 45 min. The reaction mixture was quenched with a saturated solution of ammonium chloride, extracted with diethyl ether, dried with anhydrous sodium sulfate, concentrated and purified via silica gel column chromatography. GC–MS analysis of the purified material showed 3-(*n*-butylthio)benzoic acid (62%) [Eq. (3)].

Reaction of 3-(trifluoromethylthio)benzoic acid (**2a**) with  $^t\text{BuLi}$ : The reaction of **1** with  $^t\text{BuLi}$  was carried out in exactly the same manner as described above. The yield of the product was 52%. The results are shown in Eq. (4).

Reaction of phenylperfluoroisopropyl sulfide (**4**) with  $^n\text{BuLi}$ : To a solution of **4** (101 mg) in dry pentane (2 ml) cooled to  $-78^{\circ}\text{C}$  was added dropwise a solution of 1.5 M  $^n\text{BuLi}$  in pentane under argon with stirring. After addition, the mixture was stirred for 35 min and then treated with a stoichiometric amount of  $\text{CH}_3\text{I}$  in dry pentane (1 ml). The mixture was stirred for 1 h at  $-78^{\circ}\text{C}$  and allowed to warm to room temperature when it was stirred for an additional 30 min. The reaction mixture was processed as before. GC–MS analysis of the product showed it consisted of *n*-butyl iodide (9.6%,  $\text{M}^+=184$ ), methylphenyl sulfide (0.9%,  $\text{M}^+=124$ ), diphenyl sulfide (0.3%,  $\text{M}^+=186$ ), *n*-butylphenyl sulfide (6.5%,  $\text{M}^+=166$ ) and starting material ( $\text{M}^+=278$ ) [Eq. (6)]. Also identified were *n*-octanol

(2.1%) and dodecanol (0.4%) by matching their mass spectra with authentic spectra from the catalog.

$C_4H_9I$ : 184 ( $M^+$ ); 155 ( $M-C_2H_5$ ); 128 (I); 127 (I); 57 ( $C_4H_9$ , 100%); 41 ( $C_3H_5$ ).

$C_6H_5SCH_3$  (8): 124 ( $M^+$ , 100%); 109 ( $M-CH_3$ ); 91 ( $C_7H_7$ ); 78 ( $C_6H_6$ ); 45 (CSH).

$C_6H_5SC_4H_9-n$  (7): 166 ( $M^+$ ); 149 ( $M-CH_3$ ); 137 ( $M-C_2H_5$ ); 123 ( $M-C_3H_7$ ); 110 ( $M-C_4H_8$  or  $C_6H_5SH$ , 100%); 77 ( $C_6H_5$ ); 45 (CSH).

$C_6H_5SC_6H_5$  (9): 186 ( $M^+$ , 100%); 109 ( $C_6H_5S$ ); 77 ( $C_6H_5$ ).

Reaction of phenylperfluoroisopropyl sulfide (4) with  $^tBuLi$ : Reaction of 4 with  $^tBuLi$  was carried out essentially in the same way as with  $^nBuLi$ . GC-MS analysis of the product showed the presence of t-butyl iodide (0.6%), t-butylphenyl sulfide (10, 77.8%,  $M^+ = 166$ ), methylphenyl sulfide (8, 21.5%,  $M^+ = 124$ ), octene (0.3%,  $M^+ = 112$ ) with the remainder being the starting material [4, Eq. (7)]. The yields were comparable to those obtained from the reaction of  $^nBuLi$  with 4.

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