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Unexpected distinction in reactivity of pentafluorobenzenesulfonyl halides toward organolithiums and organomagnesium halides

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Abstract: $C_6F_5SO_2Cl$ reacts with organolithiums and organomagnesium halides RM (R = Me, Bu, Ph; M = Li, MgX) to give mainly C_6F_5H and C_6F_5Cl. $C_6F_5SO_2Br$ and PhMgBr form C_6F_5H and $(C_6F_5S)_2$. This is in contrast to known transformations of them which yield exclusively $C_6F_5SO_2Nu$ under the action of O- and N-nucleophiles. Alternatively, $C_6F_5SO_2F$ is converted to $C_6F_5SO_2R$ and 4-$BuC_6F_4SO_2F$ or 2-$PhC_6F_4SO_2Ph$ under the same conditions. When R = Me, minor amounts of $(C_6F_5SO_2)_2CH_2$ and 4-$C_6F_5SO_2CH_2C_6F_4SO_2F$ form in addition to $C_6F_5SO_2CH_3$.

Keywords: C-nucleophiles; organolithium; organomagnesium halides; pentafluorobenzenesulfonyl halides.

1 Introduction

The nucleophilic substitution of halogen atoms X in RSO_2X is one of the typical reactions of this class of organosulfur derivatives [1, 2]. While O- and N-nucleophiles convert RSO_2X to the corresponding sulfonates and sulfonamides, organolithiums and organomagnesium halides (C-nucleophiles) give two types of products. The reaction of aryllithium or arylmagnesium halides with arenesulfonyl fluorides leads to the formation of diarylsulfones [3–5] (Scheme 1, route a). When the nucleophile is AlkM, aryl(alkyl)sulfones are the minor admixture and major products are 1,1-bis(arylsulfonyl)alkanes [6–9] (Scheme 1, route b). Similar reactions occur between methanesulfonyl fluoride or phenylmethanesulfonyl fluoride and phenyllithium, although with the less basic PhMgBr, only the substitution of fluorine atom occurs [10] (Scheme 1, routes c and d). At low temperatures, sulfones were obtained in high yield [5] (Scheme 1, route e).

Reactions of arenesulfonyl chlorides with alkyl- and arylmagnesium bromide give mainly the corresponding sulfones, but the processes are often complicated by partial reduction of $ArSO_2Cl$ to $ArSO_2H$; formation of sulfoxides, sulfides, biaryls and alkyl or aryl chlorides; and so on. It should be noted that these data are very old and the compositions of products were not analyzed completely [11–13]. In all these cases, aryl moieties in $ArSO_2X$ were phenyl, tolyl, xylyl or naphthyl, whereas the effect of electron-withdrawing substituent(s) in aryl moiety on the reaction pathways was not investigated.

In search of the convenient synthetic routes to (arylsulfonyl)polyfluoroarenes and (alkylsulfonyl)polyfluoroarenes, we explored the interaction of $C_6F_5SO_2X$ with some organometallic compounds. Our expectations were based on the facts of the easy substitution of chlorine atom in $C_6F_5SO_2Cl$ by O- and N-nucleophiles and formation of organyl pentafluorobenzenesulfonates [14–25] and pentafluorobenzenesulfonamides [22, 26–30], respectively. Pentafluorobenzenesulfonyl fluoride was the less promising reactant: the strong electron-withdrawing effect of five fluorine atoms and SO_2F group caused the substitution of fluorine atom at C-4 carbon atom, while fluorine atom bonded to sulfur remained intact. For example, $C_6F_5SO_2F$ reacts with piperidine in ether to yield 4-piperidinotetrafluorobenzenesulfonyl fluoride [31]. The related substitution occurs with other N-nucleophiles such as aniline [32] and hexamethyldisilazane [33]. The latter forms 4-aminotetrafluorobenzenesulfonyl fluoride and $NH(4\text{-}C_6F_4SO_2F)_2$. The interaction of sodium thiosulfate and $C_6F_5SO_2F$ in DMF led to $S(4\text{-}C_6F_4SO_2F)_2$ [34].

In fact, pentafluorobenzenesulfonyl halides displayed the unpredictable reactivity toward these C-nucleophiles. Herein we present results of reactions of $C_6F_5SO_2X$ (X = F, Cl, Br) with some organolithiums and organomagnesium halides.

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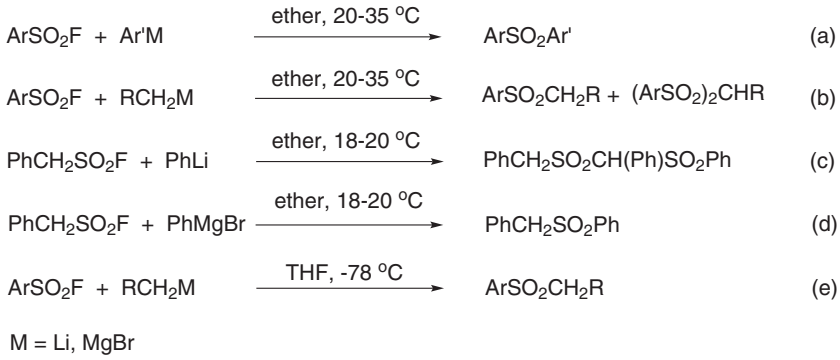


Scheme 1: Typical reactions of organosulfonyl fluorides with C-nucleophiles.

2 Results and discussion

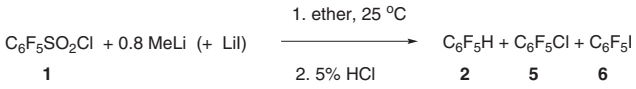
To avoid or minimize secondary processes, all reactions were performed in excess of $C_6F_5SO_2X$.

We found that the reaction of pentafluorobenzenesulfonyl chloride (**1**) with selected C-nucleophiles is completely different from the reaction with by O- and N-nucleophiles, and $C_6F_5SO_2R$ was not formed. Thus, pentafluorobenzene (**2**) was the only polyfluoroaromatic product derived from **1** and PhMgBr in ether. Similarly, a mixture of pentafluorobenzene, bromopentafluorobenzene (**3**) (ratio 27:1) and decafluorodiphenyldisulfide (**4**) (trace) was obtained from **1** and BuMgBr (Scheme 2) (here and below only polyfluoroaromatic products are presented on schemes).

The slow addition of MeLi (contained LiI) in ether to **1** and subsequent hydrolysis gave **2**, chloropentafluorobenzene (**5**) and iodopentafluorobenzene (**6**) in the ratio of 5:1:2 (^{19}F NMR). The expected $C_6F_5SO_2CH_3$ was not detected (Scheme 3).

Products **2** and **5** (2:1) were produced from **1** and BuLi. In addition, minor amounts of butylpentafluorobenzene (**7**) and 1-(1-ethoxyethyl)pentafluorobenzene (**8**) were detected by ^{19}F NMR and GS-MC analysis, whereas $C_6F_5SO_2Bu$ was not found (Scheme 4).

When pentafluorobenzenesulfonyl bromide (**9**) was combined with PhMgBr in ether, the major product was

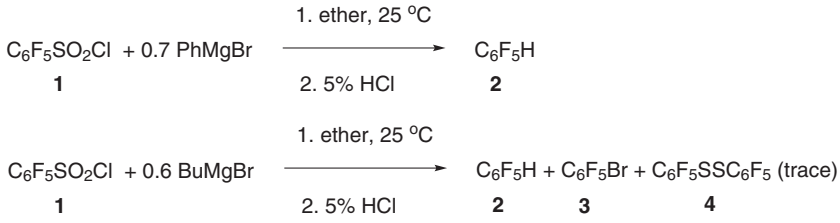


Scheme 3: Reaction of $C_6F_5SO_2Cl$ with MeLi in the presence of LiI.

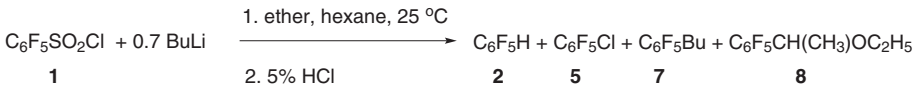
pentafluorobenzene. Unexpectedly, a significant amount of decafluorodiphenyldisulfide was also formed (ratio of **2** to **4** = 4:1), while **3** and $C_6F_5SO_2Ph$ were absent (Scheme 5).

In contrast to $C_6F_5SO_2Cl$ and $C_6F_5SO_2Br$, pentafluorobenzenesulfonyl fluoride (**10**) was converted to $C_6F_5SO_2R$ using organolithiums or organomagnesium halides although this process is accompanied by parallel reactions. For instance, the addition of PhMgBr to **10** in ether at 25°C and subsequent hydrolysis gave (phenylsulfonyl) pentafluorobenzene (**11**) and, presumably, a few 1-phenylsulfonyl-2-phenyltetrafluorobenzene (**12**) (ratio 8:1). Under the same conditions, the reaction of **10** with BuMgCl gave two main products, (butylsulfonyl)pentafluorobenzene (**13**) and 4-butyltetrafluorobenzenesulfonyl fluoride (**14**) (ratio 1:1) (Scheme 6).

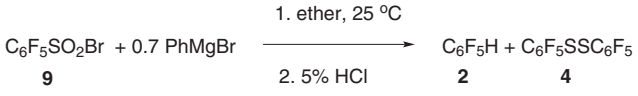
The action of MeLi on **10** also caused the substitution of fluorine bonded to sulfur by a methyl group and the formation of (methylsulfonyl)pentafluorobenzene (**15**). Unlike the above processes, the main by-products are bis(pentafluorophenylsulfonyl)methane (**16**) and 4-(pentafluorophenylsulfonylmethyl)tetrafluorobenzenesulfonyl



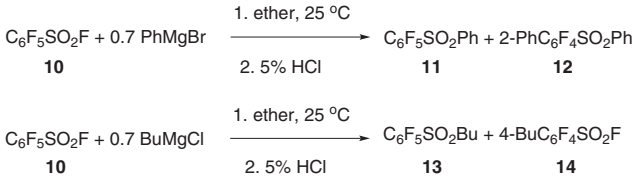
Scheme 2: Reaction of $C_6F_5SO_2Cl$ with organomagnesium bromides.



Scheme 4: Reaction of $C_6F_5SO_2Cl$ with BuLi.



Scheme 5: Reaction of $C_6F_5SO_2Br$ with phenylmagnesium bromide.



Scheme 6: Reaction of $C_6F_5SO_2F$ with organomagnesium halides.

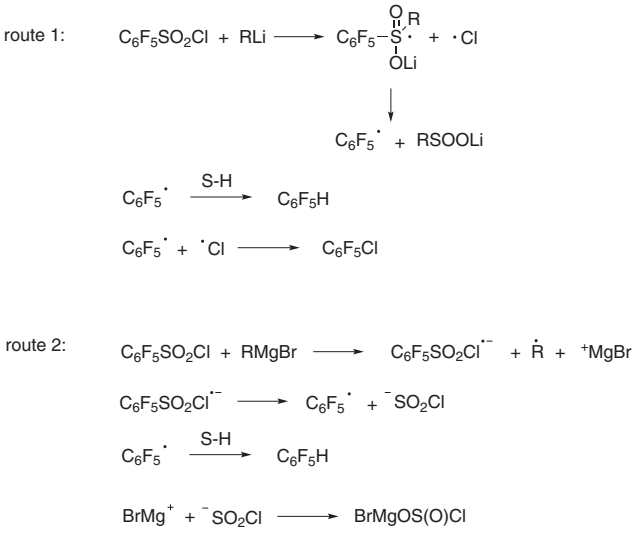
fluoride (**17**). They were formed because of the hydrogen abstraction from **15** by MeLi (Lewis base) and subsequent attack of **10** at the sulfur atom and carbon atom C-4, respectively, by the carboanion $C_6F_5SO_2CH_2^-$ (molar ratio of **15**:**16**:**17** = 5:6:1) (Scheme 7).

Comparing the reactivity of $C_6F_5SO_2F$ with $C_6F_5SO_2Cl$ and $C_6F_5SO_2Br$ reveals the following distinctions. Under the action of RMgX, pentafluorobenzenesulfonyl fluoride underwent the substitution of fluorine atom bonded to sulfur as well as of fluorine bonded to carbon atom of pentafluorophenyl moiety. The other C-nucleophile, $C_6F_5SO_2CH_2^-$, generated by hydride abstraction from the methyl group of **15** by methyllithium reacted with **10** in a similar manner. In contrast, reactions of pentafluorobenzenesulfonyl chloride (bromide) led to the other type of products. Taking into account the easy substitution of chlorine in $C_6F_5SO_2Cl$ with O- and N-nucleophiles, this reaction route was quite unexpected.

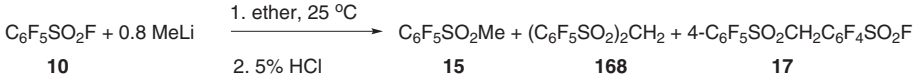
The investigation of reaction mechanisms was out of the framework of this paper, but we would like to make some suggestions. The analysis of products indicated the radical nature of processes. Thus, the reaction of $C_6F_5SO_2Cl$ with highly nucleophilic RLi always leads to C_6F_5H and C_6F_5Cl (Schemes 3 and 4). The latter product as well as C_6F_5Br was not found in reactions with the less nucleophilic RMgBr. Probably, the first process proceeds via the addition of RLi and subsequent homolytic dissociation of S–Cl and then C–S bonds. The abstraction of hydrogen atom by pentafluorophenyl radical from solvent gives C_6F_5H, and recombination with chlorine atom results in C_6F_5Cl (Scheme 8, route a). Alternatively, the redox process can be a source of pentafluorophenyl radical from $C_6F_5SO_2X$ (X = Cl, Br) and RMgBr (Scheme 8, route b).

The other remarkable peculiarity is the formation of C_6F_5I from $C_6F_5SO_2Cl$ and MeLi that contains LiI (Scheme 3) and the absence of C_6F_5I in the reaction of $C_6F_5SO_2F$ (Scheme 7). It should be noted that the closely related replacement of the SO_2Cl group by hydrogen and iodine atoms was observed in the reaction of **1** with NaI in MeCN at room temperature [35] (Scheme 9).

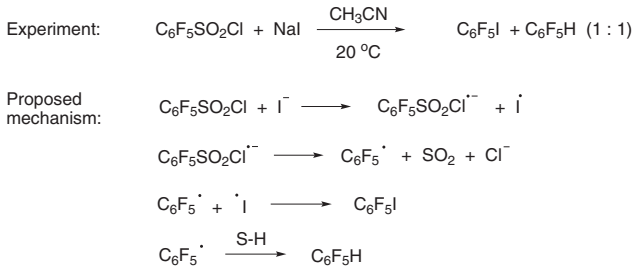
Following the author of [35], we concluded that the formation of C_6F_5I in our case also proceeded via a similar redox mechanism.



Scheme 8: Proposed routes of decomposition of $C_6F_5SO_2X$ (X = Cl, Br) under the action of C-nucleophiles.



Scheme 7: Reaction of $C_6F_5SO_2F$ with MeLi.



Scheme 9: Experimental data and the proposed route of formation of C_6F_5I from $C_6F_5SO_2Cl$ and NaI in acetonitrile [35].

3 Conclusions

1. Under the action of organolithiums or organomagnesium halides, pentafluorobenzenesulfonyl chloride (bromide) mainly forms C_6F_5H, whereas the substitution of chlorine (bromine) with the organyl rest does not occur. This distinguishes them from $ArSO_2Cl$ with the less electron-withdrawing aryl moieties (phenyl, tolyl, xylyl or naphthyl) which mainly form the corresponding diarylsulfones.
2. In contrast to $C_6F_5SO_2X$ (X = Cl, Br), $C_6F_5SO_2F$ undergoes only the nucleophilic substitution of fluorine in the pentafluorophenyl substituent as well as at the sulfur atom.
3. Increased electron-accepting character of the aryl moiety in arenesulfonyl halide facilitates redox reactions, and decreases the substitution of chlorine (bromine). On the other hand, $C_6F_5SO_2F$ reacts as its non-fluorinated analog (Scheme 1), although the parallel reaction at the C_6F_5 group also occurs.

4 Experimental section

The NMR spectra were recorded on a Bruker Avance 300 (^{1}H at 300.13 MHz, ^{19}F at 282.40 MHz) spectrometer. The chemical shifts were referenced to TMS (^{1}H), CCl_3F [^{19}F, with C_6F_6 as secondary reference ($\delta = -162.9$ ppm)]. A Hewlett-Packard 1800A (with HP-5MS column) instrument was used for gas chromatography-mass spectrometry (GC-MS) analysis. BuLi (2.4 M solution in hexanes) (Sigma-Aldrich) was used as supplied. Solutions of C_4H_9MgCl, C_4H_9MgBr and C_6H_5MgBr in ether were prepared from chlorobutane, bromobutane and bromobenzene and Mg, respectively. CH_3Li was prepared from methyl iodide and lithium. Ether was distilled over $LiAlH_4$ and stored over sodium. (Phenylsulfonyl)pentafluorobenzene [36], and pentafluorobenzenesulfonyl halides $C_6F_5SO_2F$ [37], $C_6F_5SO_2Cl$ [38] and $C_6F_5SO_2Br$ [39, 40] were prepared by the reported procedures. The known compounds **13** [36], **15** [21], **2** [12], **3**, **5**, **6** [41], **4** [42], **8** [43] and **16** [44] were identified by ^{19}F NMR spectroscopy and GC-MS data. The preparation of **14** will be reported in a forthcoming publication. The constitution of **12** (minor component) was deduced from the ^{1}H, ^{19}F NMR spectra and GC-MS data of its mixture with **13**. Yields of products were determined by ^{19}F NMR spectroscopy using C_6H_5F as a quantitative internal reference. For reliable identification, compound **7** was prepared separately by the modified procedure given in [45].

4.1 Preparation of butylpentafluorobenzene 7

A solution of 2.4 M butyllithium in hexanes (5 mL, 12 mmol) was added dropwise to a cold (0–3°C) solution of C_6F_6 (5.2 g, 29 mmol) in ether (30 mL) within 1 h. The reaction solution was stirred at 20–25°C for 1 h and poured into 5% HCl. The organic phase was washed with brine and dried with $MgSO_4$. Volatiles were removed under reduced pressure and the residue was distilled to give **7** (1.45 g, 55%), b.p. 170–172°C (lit. [46]: b.p. 54–55°C/2 Torr, 174–175°C/760 Torr).

4.1.1 Butylpentafluorobenzene 7

^{1}H NMR (CCl_4): $\delta = 2.71$ (t, $^3J(H^1,H^2) = 7.5$ Hz, 2H, H^1), 1.58 (tt, $^3J(H^2,H^1) = 7.5$ Hz, $^3J(H^2,H^3) = 7.5$ Hz, 2H, H^2), 1.39 (tq, $^3J(H^3,H^2) = 7.5$ Hz, $^3J(H^3,H^4) = 7.2$ Hz, 2H, H^3), 0.97 (t, $^3J(H^4,H^3) = 7.2$ Hz, 3H, H^4). – ^{19}F NMR (CCl_4): $\delta = -145.7$ (m, 2F, $F^{2,6}$), –159.1 (t, $^3J(F^4,F^{3,5}) = 20$ Hz, 1F, F^4), –164.0 (m, 2F, $F^{3,5}$) [lit. [46]: ^{19}F NMR ([D_6]acetone): $\delta = -145.4$ (2F), –158.2 (1F), –169.6 (2F)].

4.2 Reaction of $C_6F_5SO_2Cl$ with phenylmagnesium bromide

A two-necked flask equipped with a magnetic stir bar, rubber septum and reflux condenser topped with an adapter for inlet/outlet argon and connected with a bubbler was flushed with dry argon and charged with $C_6F_5SO_2Cl$ (803 mg, 3.01 mmol) in ether (5 mL). A solution of 0.68 M PhMgBr in ether (3 mL, 2.04 mmol) was added with a syringe within 15 min. The reaction mixture was stirred for 1 h and quenched with 5% HCl (2 mL). The organic phase was decanted and dried with $MgSO_4$. The solution contained $C_6F_5SO_2Cl$ (1.78 mmol) and C_6F_5H (1.06 mmol). In addition, C_6H_6, C_6H_5Cl, and $C_6H_5C_6H_5$ (3:12:1) were found (GC-MS).

4.3 Reaction of $C_6F_5SO_2Cl$ with butylmagnesium bromide

A solution of 0.32 M BuMgBr in ether (2.6 mL, 0.84 mmol) was added within 40 min with a syringe to a stirred solution of $C_6F_5SO_2Cl$ (319 mg, 1.20 mmol) in ether (3 mL). The reaction mixture was left overnight and quenched with 5% HCl (2 mL). The organic phase was decanted and dried with $MgSO_4$. The solution contained $C_6F_5SO_2Cl$ (0.16 mmol), C_6F_5H (0.81 mmol), C_6F_5Br (0.03 mmol) and traces of $C_6F_5SSC_6F_5$ (^{19}F NMR). In addition, BuCl, BuBr and C_8H_{18} were found (GC-MS).

4.4 Reaction of $C_6F_5SO_2Cl$ with methyllithium

A solution of 0.92 M methyllithium in ether (1.1 mL, 1.01 mmol) was added dropwise within 25 min with a syringe to a stirred solution of $C_6F_5SO_2Cl$ (311 mg, 1.16 mmol) in ether (3 mL) to give a brown suspension. It was stirred for 1 h and quenched with 5% HCl (1 mL). The brown organic phase was decanted and dried with $MgSO_4$. According to the ^{19}F NMR spectrum, the solution contained C_6F_5Cl (0.13 mmol), C_6F_5H (0.60 mmol) and C_6F_5I (0.26 mmol).

4.5 Reaction of $C_6F_5SO_2Cl$ with butyllithium

A solution of 2.4 M butyllithium (1 mL, 2.4 mmol) was added dropwise within 30 min with a syringe to a stirred solution of $C_6F_5SO_2Cl$ (854 mg, 3.2 mmol) in ether (3 mL) to give a white suspension. It was stirred overnight and treated with 5% HCl (3 mL). The organic phase was decanted, washed with brine and dried with $MgSO_4$. According to the ^{19}F NMR spectrum, the solution contained $C_6F_5SO_2Cl$ (0.45 mmol), C_6F_5Cl (0.78 mmol), C_6F_5H (1.57 mmol), C_6F_5Bu and $C_6F_5CH(CH_3)OC_2H_5$ (traces). In addition, BuCl and $BuSO_2Cl$ (1:2) were detected by GC-MS.

4.6 Reaction of $C_6F_5SO_2Br$ with phenylmagnesium bromide

A solution of 0.68 M PhMgBr in ether (1 mL, 0.68 mmol) was added within 15 min with a syringe to a stirred solution of $C_6F_5SO_2Br$ (318 mg, 1.02 mmol) in ether (5 mL). Initially, the colorless solution became yellow and turbid, but within several minutes it became transparent again. After 1 h, the yellow solution was poured into 5% HCl (2 mL). The organic phase was decanted and dried with $MgSO_4$. The solution contained $C_6F_5SO_2Br$ (0.31mmol), C_6F_5H (0.53 mmol) and $(C_6F_5S)_2$ (0.13 mmol) (^{19}F NMR). In addition, C_6H_6, C_6H_5Br and $C_6H_5C_6H_5$ (6:8:1) were found (GC-MS).

It should be noted that $C_6F_5SO_2Br$ decomposes under the conditions of the GC-MS analysis. Thus, The GC-MS analysis of a mixture of $C_6F_5SO_2Br$ and $C_6F_5CF_3$ (quantitative internal reference; molar ratio of 1:1.3; ^{19}F NMR) showed the presence of C_6F_5Br, C_6F_5H and $C_6F_5CF_3$ (molar ratio of 0.5:0.5:1.3), while $C_6F_5SO_2Br$ was not found.

4.7 Reaction of $C_6F_5SO_2F$ with phenylmagnesium bromide

A solution of 0.68 M PhMgBr in ether (1 mL, 0.68 mmol) was added within 10 min to $C_6F_5SO_2F$ (266 mg, 1.06 mmol) in ether (5 mL). The reaction mixture was stirred for 1 h and washed with 5% HCl (2 mL). The organic phase was decanted and dried with $MgSO_4$.

The solution contained $C_6F_5SO_2F$ (0.69 mmol), $C_6F_5SO_2Ph$ (0.24 mmol) and 2-$PhC_6F_4SO_2Ph$ (0.03 mmol) (^{19}F NMR). The solution was evaporated *in vacuo* and the residue (a mixture of **11** and **12**) was dissolved in CCl_4.

4.7.1 (Phenylsulfonyl)pentafluorobenzene 11 (mixture with 12)

^1H NMR (CCl_4): $\delta = 8.00$ (d $^3J(H^2,H^3) = 8.0$ Hz, 2H, $H^{2,6}$), 7.65 (t $^3J(H^4,H^{3,5}) = 7.5$ Hz, 1H, H^4), 7.57 (t $^3J(H^3,H^{2,4}) = 7.6$ Hz, 2H, $H^{3,5}$). – ^{19}F NMR (CCl_4): $\delta = -136.7$ (m, 2F,$F^{2,6}$), –146.4 (tt, $^3J(F^4,F^{3,5}) = 21$ Hz, $^4J(F^4,F^{2,6}) = 7$ Hz, 1F, F^4), –159.9 (m, 2F, $F^{3,5}$). – ^{19}F NMR (ether): $\delta = -135.9$ (m, 2F, $F^{2,6}$), –145.9 (tt, $^3J(F^4,F^{3,5}) = 21$ Hz, $^4J(F^4,F^{2,6}) = 7$ Hz, 1F, F^4), –159.6 (m, 2F, $F^{3,5}$). – GC-MS: $m/z = 308$.

4.7.2 1-Phenylsulfonyl-2-phenyltetrafluorobenzene 12 (mixture with 11)

^1H NMR (CCl_4): $\delta = 8.00$ (d $^3J(H^2,H^3) = 8.0$ Hz, 2H, $H^{2,6}$), 7.64 (t $^3J(H^4,H^{3,5}) = 7.6$ Hz, 1H, H^4), 7.59 (t $^3J(H^3,H^{2,4}) = 6.9$ Hz, 2H, $H^{3,5}$) ($SO_2C_6H_5$), 7.6–7.4 (5H, C_6H_5). – ^{19}F NMR (CCl_4): $\delta = -132.5$ (ddd, $^3J(F^6,F^5) = 22$ Hz, $^4J(F^6,F^4) = 11$ Hz, $^5J(F^6,F^3) = 11$ Hz, 1F, F^6), –135.9 (ddd, $^3J(F^3,F^4) = 23$ Hz, $^4J(F^3,F^5) = 3$ Hz, $^5J(F^3,F^6) = 11$ Hz, 1F, F^3), –148.1 (ddd, $^3J(F^4,F^3) = 20$ Hz, $^3J(F^4,F^5) = 23$ Hz, $^5J(F^4,F^6) = 11$ Hz, 1F,F^4), –154.5 (ddd, $^3J(F^5,F^4) = 20$ Hz, $^4J(F^5,F^6) = 23$ Hz, $^5J(F^5,F^3) = 3$ Hz, 1F,F^5). – ^{19}F NMR (ether): $\delta = -131.5$ (ddd, $^3J(F^6,F^5) = 22$ Hz, $^4J(F^6,F^4) = 11$ Hz, $^5J(F^6,F^3) = 11$ Hz, 1F, F^6), –135.0 (ddd, $^3J(F^3,F^4) = 23$ Hz, $^4J(F^3,F^5) = 3$ Hz, $^5J(F^3,F^6) = 11$ Hz, 1F, F^3),

–147.9 (ddd, $^3J(F^4,F^3)=20$ Hz, $^3J(F^4,F^5)=23$ Hz, $^5J(F^4,F^6)=11$ Hz, 1F, F^4), –154.2 (ddd, $^3J(F^5,F^4)=20$ Hz, $^4J(F^5,F^6)=23$ Hz, $^5J(F^5,F^3)=3$ Hz, 1F, F^5). – GC-MS: $m/z=366$.

4.8 Reaction of $C_6F_5SO_2F$ with butylmagnesium chloride

A solution of 0.37 M BuMgCl in ether (2 mL, 0.74 mmol) was added to a stirred solution of $C_6F_5SO_2F$ (257 mg, 1.0 mmol) in ether (3 mL). The suspension formed was stirred for 1 h, treated with 5% HCl (1 mL). The organic phase was decanted and dried with $MgSO_4$. The solution contained $C_6F_5SO_2F$ (0.75 mmol), $C_6F_5SO_2Bu$ (0.06 mmol) and 4-$BuC_6F_4SO_2F$ (0.07 mmol) (^{19}F NMR). The solution was evaporated under reduced pressure and the residue (a mixture of **13** and **14**) was dissolved in CCl_4.

4.8.1 (Butylsulfonyl)pentafluorobenzene 13 (mixture with 14)

^{1}H NMR (CCl_4): $\delta=3.24$ (t, $^3J(H^1,H^2)=7$ Hz, 2H, SCH_2), 1.7–1.6 (m, 4H, $2CH_2$), 1.05 (t, $^3J(H^4,H^3)=7$ Hz, 3H, CH_3). – ^{19}F NMR (CCl_4): $\delta=-136.9$ (m, 2F,$F^{2,6}$), –145.3 (tt, $^3J(F^4,F^{3,5})=20$ Hz, $^4J(F^4,F^{2,6})=7$ Hz, 1F, F^4), –159.3 (m, 2F, $F^{3,5}$). – ^{19}F NMR (ether): $\delta=-136.0$ (m, 2F, $F^{2,6}$), –145.8 (tt, $^3J(F^4,F^{3,5})=21$ Hz, $^4J(F^4,F^{2,6})=7$ Hz, 1F, F^4), –159.5 (m, 2F, $F^{3,5}$). – GC-MS: $m/z=288$.

4.8.2 4-Butyltetrafluorobenzenesulfonyl fluoride 14 (mixture with 13)

^{1}H NMR (CCl_4): $\delta=2.93$ (t, $^3J(H^1,H^2)=7$ Hz, 2H, CH_2), 1.4–1.5 (m, 4H, $2CH_2$), 1.05 (t, $^3J(H^4,H^3)=7$ Hz, 3H, CH_3). – ^{19}F NMR (CCl_4): $\delta=72.3$ (t, $^4J(SO_2F,F^{2,6})=15$ Hz, 1F, SO_2F), –136.1 (m, 2F, $F^{2,6}$), –140.9 (m, 2F, $F^{3,5}$). – ^{19}F NMR (ether): $\delta=73.7$ (t, $^4J(SO_2F,F^{2,6})=15$ Hz, 1F, SO_2F), –135.4 (m, 2F, $F^{2,6}$), –140.2 (m, 2F, $F^{3,5}$). – GC-MS: $m/z=288$.

4.9 Reaction of $C_6F_5SO_2F$ with methyllithium

A solution of 0.92 M MeLi in ether (2 mL, 1.84 mmol) was added with a syringe within 20 min to a stirred solution of $C_6F_5SO_2F$ (588 mg, 2.35 mmol) in ether (5 mL). After 1.5 h, the reaction mixture was treated with 5% HCl (1.5 mL). The organic phase was decanted and dried with $MgSO_4$. The solution contained $C_6F_5SO_2F$ (1.03 mmol), $C_6F_5SO_2CH_3$ (0.42 mmol), $(C_6F_5SO_2)_2CH_2$ (0.50 mmol) and, presumably, 4-$C_6F_5SO_2CH_2C_6F_4SO_2F$ (0.08 mmol) (^{19}F NMR).

4.9.1 (Methylsulfonyl)pentafluorobenzene 15

^{1}H NMR (acetone): $\delta=3.33$ (s, 3H, CH_3). – ^{19}F NMR (ether): $\delta=-137.2$ (m, 2F, $F^{2,6}$), –146.3 (tt, $^3J(F^4,F^{3,5})=21$ Hz, $^4J(F^4,F^{2,6})=7$ Hz, 1F, F^4), –160.0 (m, 2F, $F^{3,5}$) (lit. [21]: ^{1}H NMR (DMSO): $\delta=3.51$ (s, 3H, CH_3); ^{19}F NMR (DMSO): $\delta=-137.56$ (2F), –145.51 (1F), –159.4 (2F)).

4.9.2 Bis(pentafluorophenylsulfonyl)methane 16

^{1}H NMR (acetone): $\delta=5.70$ (s, 2H, CH_2) (lit. [44]: ^{1}H NMR ($CDCl_3$): $\delta=6.08$ (s)). – ^{19}F NMR (acetone): $\delta=-134.5$ (m, 4F, $F^{2,6}$), –142.4 (tt, $^3J(F^4,F^{3,5})=20$ Hz, $^4J(F^4,F^{2,6})=9$ Hz, 2F, F^4), –159.4 (m, 4F, $F^{3,5}$).

4.9.3 4-(Pentafluorophenylsulfonylmethyl)-tetrafluorobenzenesulfonyl fluoride 17

^{1}H NMR (acetone): $\delta=5.20$ (s, 2H, CH_2). – ^{19}F NMR (acetone): $\delta=74.0$ (t, $^4J(SO_2F,F^{2,6})=13$ Hz, 1F, SO_2F), –133.9 (m, 2F, $F^{2,6}$), –135.5 (m, 2F, $F^{3,5}$) ($C_6F_4SO_2F$), –135.4 (m, 2F, $F^{2,6}$), –143.0 (tt, $^3J(F^4,F^{3,5})=21$ Hz, $^4J(F^4,F^{2,6})=8$ Hz, 1F, F^4), –159.4 (m, 2F, $F^{3,5}$) ($C_6F_5SO_2CH_2$).

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