Structure Elucidation

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Preparation and Characterization of Alkenyl Aryl Tetrafluoro-λ^6-sulfanes**

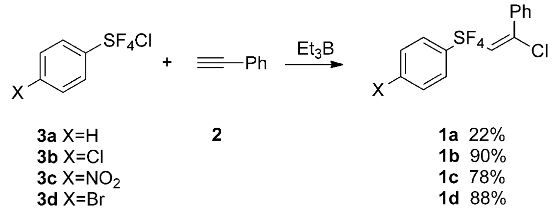
*Linbin Zhong, Paul R. Savoie, Alexander S. Filatov, and John T. Welch**

***Abstract:** Substituted alkenyl aryl tetrafluoro-λ^6-sulfanes have been prepared by the direct addition of readily accessible chlorotetrafluorosulfanyl arenes to primary alkynes. Substitution of an apical fluorine of the pentafluorosulfanyl group enables modulation of the reactivity of this little explored functional group while at the same time facilitating the direct investigation of aryl substituent effects on the aryl tetrafluorosulfanyl-substituted products.*

Substituted alkenyl aryl tetrafluoro-λ^6-sulfanes (**1**; for structure see Scheme 1) were prepared by the direct addition of chlorotetrafluorosulfanyl arenes[1] to primary alkynes. Substitution of the apical fluorine of the pentafluorosulfanyl group enables modulation of the reactivity of this functional group while facilitating the direct investigation of the aryl substituent effects on the aryl tetrafluorosulfanyl-substituted products.

In spite of the intriguing properties of hypervalent fluorinated sulfur compounds,[2] the preparation of these substances has been limited to the synthesis of molecules bearing pentafluorosulfanyl arenes.[3] However, preparations of pentafluorosulfanylated aliphatic compounds are increasingly common.[4] Investigations of tetrafluoro-λ^6-sulfanes, where the electronic effects of hypervalent fluorinated sulfur may be modulated by selective substitution, are rarer. Selective substitution can be a tool for the potential control of reactivity, but synthetic access to the substituted compounds is challenging. Diaryl tetrafluorosulfanes were prepared by fluorination of the corresponding diaryl sulfides with trifluoromethylhypofluorite[5] or fluorine.[6] Aryl trifluoromethyl tetrafluorosulfanes were prepared by direct fluorination of the corresponding aryl trifluoromethyl sulfides.[7] Trifluoromethyl tetrafluorosulfanyl chloride, prepared by oxidative fluorination of trifluoromethylsulfenyl chloride with chlorine fluoride, was used to prepare a variety of alkyl trifluoromethyl tetrafluorosulfanes.[8] Photolytic initiation was necessary to promote the reaction of the trifluoromethyl tetrafluorosulfanyl chloride with alkenes.[9] Unfortunately, systematic investigation of the influence of the carbon substituent, which is the apical substituent on sulfur, on the reactivity, structure, and bonding of the product alkenyl aryl tetrafluorosulfanes remained an elusive goal.

The addition of triethylboron to an ethereal solution of a the chlorotetrafluorosulfanyl arene **3** and alkynes **2** promotes formation of **1** in 15 minutes. The required chlorotetrafluorosulfanyl arenes **3** are easily and inexpensively prepared by a general process which is applicable to a variety of substituted chlorotetrafluorosulfanyl arenes.[1] Yields of isolated and recrystallized **1** are reported in Scheme 1. The yield (crude reaction mixture) of **1a** was excellent, but the recovery of the lower melting crystalline product was more challenging than with higher melting solids **1b–e**.



Scheme 1. Triethylboron-catalyzed addition of chlorotetrafluorosulfanyl arenes to alkynes.

The facile formation of the desired tetrafluoro-λ^6-sulfanes in good yields is supported by computations suggesting that homolytic cleavage of the S–Cl bond of **3a** requires approximately 6.7 kcal mol^{-1} less energy than homolytic cleavage of the S–Cl bond of SF_5Cl (B3LYP/6-31 + G(d,p)).[10] In contrast to the triethylboron-facilitated addition of SF_5Cl to alkenes and alkynes where a nonpolar solvent such as pentane n-pentane or trichlorofluoromethane is required to suppress ionic halofluorination,[11] the ease of homolytic S–Cl bond cleavage in **3**, presumably a consequence of the reduced electronegativity of aryl tetrafluoro-λ^6-sulfane, enables the use of ethereal solvent.

To functionalize the alkenyl aryl tetrafluorosulfanes, Suzuki coupling of the boronic acids **4** with **1d** formed **1e–g**, in good yields, and is consistent with coupling of pentafluorosulfany-substituted arenes (Scheme 2).[12] In contrast to the reaction of pentafluorosulfanyl aryl bromide, addition to **1** required a significantly higher reaction temperature of 120 °C, as opposed to room temperature. A variety of solvent systems and temperatures were examined to determine the optimum reaction conditions for coupling reactions of **1**. Reactions in 1,4-dioxane, over a range of temperatures from room temperature to 100 °C with either potassium carbonate or potassium acetate are slower than those in THF. Use of acetone or DMF leads to decomposition. Even on heating at 120 °C for 96 hours with potassium acetate, the yields of the

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[*] L. Zhong, P. R. Savoie, A. S. Filatov, Prof. J. T. Welch
Department of Chemistry, University at Albany, SUNY
1400 Washington Ave, Albany, NY 12222 (USA)
E-mail: Jwelch@albany.edu

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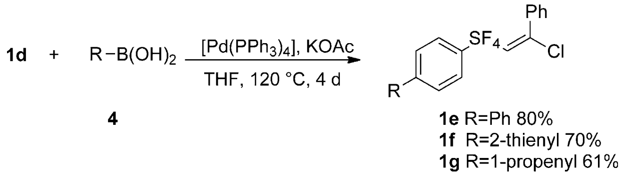


Scheme 2. Stability of aryl tetrafluoro-λ^6-sulfanes under Suzuki coupling conditions.

coupling reactions of **1d** demonstrated the robustness of the tetrafluoro-λ^6-sulfane nuclei of **1d**–**g**.

The influence of arene substituents correlates with the ^{13}C NMR chemical shifts of **1a**–**e**.[13] In **1a**–**e**, the ^{13}C chemical shift of the resonance attributed to C4 (see Figure 1 for numbering; $\delta = 158.3$–163.7 ppm) correlates weakly with increasing σ values,[14] however a better correlation is found with the computed NMR shielding tensors (B3LYP, 6-31G (d), $r^2 = 0.9545$). Consistent with the Spiesecke–Schneider relationship,[15] these shifts may be a barometer of charge density, with an increase in σ leading to lower-field chemical shifts for C4. However, the ^{13}C chemical shift of C5, located at the opposite apical position of sulfur, decreases from $\delta = 144.7$ to δ 142.5 with increasing σ ($r^2 = 0.9826$). Correlation of C5 chemical shifts with the shielding tensors is worse ($r^2 = 0.8056$). The decrease in C5 chemical shift with strongly electron-withdrawing *p*-substituents was unanticipated. For comparison, in styrene, the corresponding Cα chemical shifts decrease, but only slightly, from $\delta = 135.8$ to δ 135.0. The decrease in chemical shift at C5 on introduction of electronegative substituents suggests an increase in charge density, and is consistent with the contribution of ionization of the C5−S bond to the Rundle–Pimentel–Coulson[16]/charge-shift[17] description of bonding at sulfur. Four-bond carbon–fluorine coupling constants ($^4J_{C,F}$), typically 1.8 Hz, are observed in the spectra of **1**. In contrast, with benzotrifluoride, $^4J_{C,F}$ couplings are not detected,[18] but $^5J_{C,F}$ values (1.11 Hz) are reported.[18b]

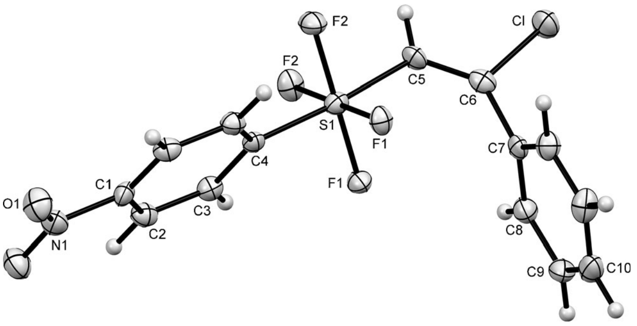


Figure 1. Molecular structure of **1c**. Thermal ellipsoids are shown at 50% probability.

The aryl substituent effect can also be assessed by scrutiny of the data from single-crystal X-ray diffraction studies of **1a**–**e** (Table 1). The C4-S-C5 bond angle shows a systematic distortion from linearity with compression of the C4-S-C5 bond angle from 178.1° to 175.33° and increasing σ values.

Table 1: Selected distances and angles, from single-crystal X-ray structural studies, and ^{13}C chemical shifts and σ values for **1a**–**e**.

	1a	**1b**	**1c**	**1d**	**1e**
Distances[a]					
C4−S	1.81(2)	1.8196(17)	1.814 (4)	1.822(4)	1.818(2)
S−C5	1.811(2)	1.8057(18)	1.813 (4)	1.798(4)	1.805(2)
S−F difference[b]	0.0148	0.012	0.0237	0.028	0.003
Angles[c]					
C4-S-C5	176.91(10)	175.75(8)	175.33(17)	175.4(2)	178.1(1)
^{13}C NMR shifts[d]					
C4	160.2	158.3	163.7	158.9	159.4
C5	144.67	144.32	142.55	143.6	144.7
σ[e]	0.0	0.23	0.78	0.23	−0.01

[a] In Å. [b] Maximum variation in S−F bond lengths. [c] In degrees. [d] δ [ppm]. [e] See Ref. [15].

This substituent effect on sulfur geometry is consistent with the increased significance of an ionic resonance form to the C4-S-C5 bonding and the consequent distortion of geometry around sulfur. The ionic resonance form would also be predicted to result in the S−F1 bonds *syn* to the alkene being shortened relative to the *anti* S−F2 bonds, as was found.[19]

In addition to elucidating structural trends in aryl tetrafluorosulfanyl compounds, X-ray data revealed the manifold potential of this novel class of materials. Especially interesting was the crystallization of **1d** and **1c** in a polar, non-centrosymmetric space group, as shown in Figures 2 and Figure 3, respectively. Not only do crystals of **1d** form assemblages with oriented dipoles, but the columnar assemblies interact to form two-dimensional sheets. The columns are associated by interaction of the bromine of the bromoaryl tetrafluorosulfanyl group with the arene of a neighboring column. (Figure 2)

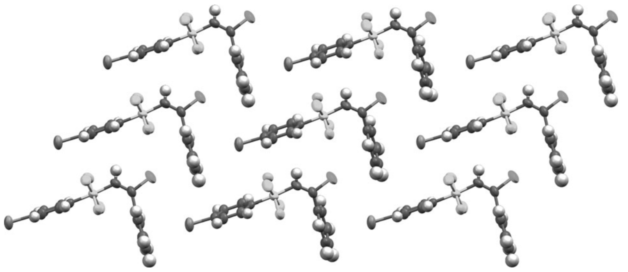


Figure 2. Packing of **1d** illustrates alignment of molecular dipoles with infinite columns of molecules apparently organized by a favorable bromine–arene interaction.

The structure of **1c** differs from that of **1d** in that substitution of the nitro group for bromine disrupts the interactions between pairs of columns with the resultant elements of the columnar pair having classic edge–π interactions, yet no obvious interaction with a neighboring assembly (Figure 3). The compounds **1c** [space group *Ima*2) and **1d** (space group *Pna*2(1)] both crystallize in the *mm*2 point group, and therefore crystals of both **1c** and **1d** could be

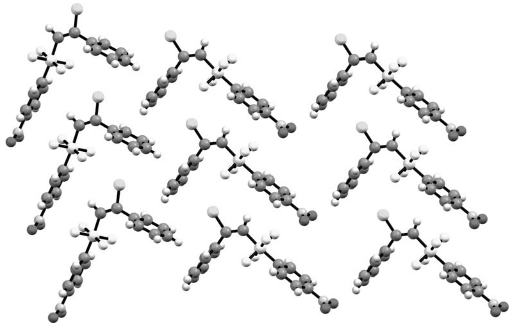
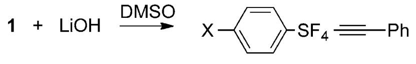


Figure 3. Packing of **1c** illustrates alignment of molecular dipoles with discretely separate infinite columns of molecular pairs enforced by the nitro group.

anticipated to exhibit piezoelectric behavior as well as be polar and possess pyroelectric properties. Such pyroelectric properties are intriguing in the design of new ferroelectric materials.[20] In the parent structure **1a**, as well as in **1b** and **1e**, conventional π–π stacking leads to alternate dipolar orientations of the columnar assemblies in centrosymmetric crystals.

The alkenyl aryl tetrafluoro-λ^6-sulfanes **1** discussed above can also undergo additional transformations without decomposition of the tetrafluorosulfanyl group. Dehydrochlorination with lithium hydroxide formed the alkynyl aryl tetrafluoro-λ^6-sulfanes **6** in excellent yields (Scheme 3).



6a X = H 97%
6b X = Cl 98%
6c X = NO$_2$ 81%

Scheme 3. Dehydrochlorination of **1** to form the acetylenes **6**. DMSO = dimethylsulfoxide

Table 2: Selected distances and angles, from single-crystal X-ray structural studies, and ^{13}C chemical shifts for **6a–c**

	6a	**6b**	**6c**
Distances[a]			
C4–S	1.809 (3)	1.8137 (15)	1.820 (3)
S–C5	1.731 (4)	1.7445 (16)	1.736 (3)
S–F difference[b]	0.0043	0.0087	0.0091
Angles[c]			
C4-S-C5	179.40 (16)	178.81 (7)	179.69 (14)
^{13}C NMR shifts[d]			
C4	159.6	157.6	163.1
C5	95.5	95.1	94.3

[a] In Å. [b] Maximum variation in S–F bond lengths. [c] In degrees. [d] δ [ppm].

In contrast to the carbon–fluorine coupling observed for **1**, the $^5J_{C,F}$ couplings in **6** were observed to aryl carbon atoms of the aryl acetylide portion of **6** where $^5J_{C,F} = 1.7$ Hz. This is in sharp contrast to **1** where only $^4J_{C,F}$ coupling can be detected. X-ray structural data shows that the deviation from linearity of the C4-S-C5 angle of **6** is greatest with *p*-chloro substitution, thus decreasing from 179.7° to 178.8° (Table 2). However with the more potent electron-withdrawing nitro group the C4-S-C5 alignment was closer to being collinear, thus suggesting the effect of the shortening of S–C5 bond in **6a–c** relative to the S–C5 bond in **1a–c** dominates structural considerations. The C4–S bond lengths of **6** were observed to strongly correlate with substituents ($r^2 = 0.978$). The stronger electron-withdrawing groups are associated with a lengthening of the C4–S bond. This finding is consistent with an increase in the ionic character of the C4–S bond.[17]

In summary, it was found that replacement of the apical fluorine of a pentafluorosulfanyl group by a substituted arene can modify the reactivity of the corresponding sulfanyl chloride and the organic compounds into which the arene tetrafluorosulfanyl group is introduced. Arene substituents influence the structural and spectroscopic properties, which are predictors of the reactivity of both the reactants and the addition products, with strongly electron-donating groups not leading to isolable products. The effects are consistent with contemporary understanding of the bonding of fluorinated hypervalent sulfur. Manipulation of these structures can lead not only to the formation of intriguing polar crystals with potential utility in sensors, but also to control of the reactivity of the adducts in further synthetic transformations. Future experiments will be devoted to expanding the scope of reactions of arene tetrafluorosulfanyl chlorides with substituted alkynes and alkenes.

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