JOC The Journal of Organic Chemistry

Featured Article

pubs.acs.org/joc

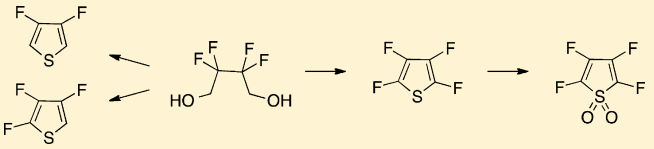
Tetrafluorothiophene *S,S*-Dioxide: A Perfluorinated Building Block

David M. Lemal,* Marc Akashi, Yan Lou, and Vivek Kumar

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, United States

Supporting Information

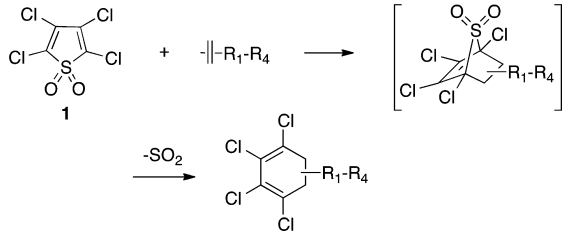
ABSTRACT: Tetrafluorothiophene *S,S*-dioxide, a highly reactive diene and dienophile, has been synthesized. A new route to 3,4-difluoro- and tetrafluorothiophene has been realized, and the previously unknown 2,3,4-trifluorothiophene has been obtained. The reactivity of tetrafluorothiophene *S*-oxide has been compared with that of the *S,S*-dioxide.



INTRODUCTION

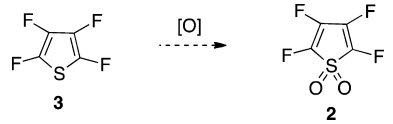
Decades ago, Raasch synthesized tetrachlorothiophene *S,S*-dioxide (**1**) and showed it to be a very reactive and versatile diene.[1] Accompanied by extrusion of sulfur dioxide, its Diels–Alder reactions result in incorporation of a tetrachlorobutadiene fragment $(CCl)_4$ into the product (shown with alkenes in Scheme 1). In the hope of being able to build a $(CF)_4$ fragment

Scheme 1



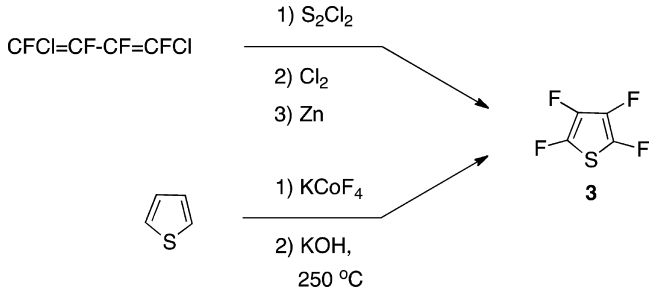
in analogous fashion into a diverse array of molecular architectures, we set out to synthesize tetrafluorothiophene *S,S*-dioxide (**2**).[2] We envisioned simply oxidizing the known tetrafluorothiophene (**3**) (Scheme 2). The first synthesis of this

Scheme 2



molecule, reported in a patent, proceeded in three steps from 1,4-dichlorotetrafluorobutadiene (Scheme 3).[3] No yields were reported for any of the steps, and the starting material also required synthesis. Later, Tatlow's group prepared **3** in two steps from the parent thiophene by fluorination followed by dehydrofluorination (Scheme 3).[4] The fluorination step required a stirred bed reactor and gave a complex mixture; both steps proceeded in low yield. For a practical route to the target molecule **2**, a more efficient synthesis of **3** was essential.

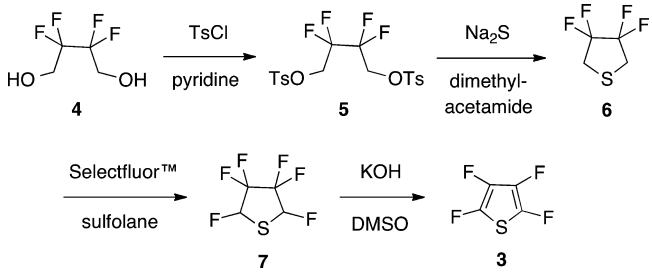
Scheme 3



RESULTS AND DISCUSSION

Synthesis of Fluorothiophenes. We carried out the four-step synthesis outlined in Scheme 4, beginning with

Scheme 4



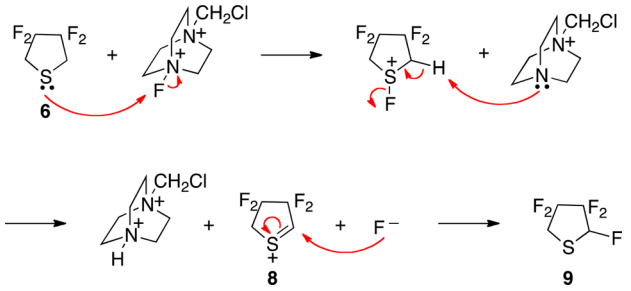
commercially available diol **4**. Ditosylate **5**[5] was cyclized to 3,3,4,4-tetrafluorothiolane (**6**) in the high boiling solvent dimethylacetamide, from which it was isolated by vacuum transfer. If sodium sulfide nonahydrate was used for this reaction, a significant amount of 3,3,4,4-tetrafluorooxolane was always formed as a byproduct, but the use of hydrate containing 60–63% of the sulfide (cheaper by far than the anhydrous salt) gave both better yields of **6** and very little of the oxolane. Fluorination of **6** with Selectfluor to afford hexafluorothiolane **7**

Received: October 24, 2013
Published: December 6, 2013

   dx.doi.org/10.1021/jo402373x | J. Org. Chem. 2013, 78, 12330–12337

was accomplished via a tandem fluoro-Pummerer rearrangement. With a single equivalent of Selectfluor the reaction yielded pentafluorothiolane **9**; the presumed mechanism for its formation is shown in Scheme 5.[6]

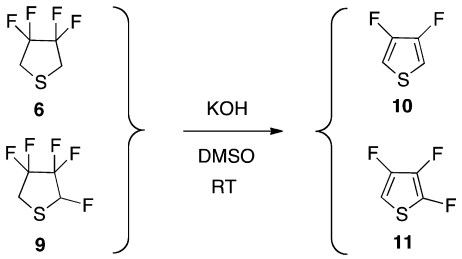
Scheme 5



The key transformation to **7** required much optimization. The solvent had to be sufficiently polar to dissolve the salt Selectfluor, yet non-nucleophilic so it would not compete with fluoride ion for the extremely electrophilic intermediate **8**. Solvents we tried that met the first criterion failed the second, with the exception of sulfolane. A further advantage of that solvent was its very high boiling point (285 °C), which again allowed isolation of the product by vacuum transfer. The cis and trans isomers of **7** were formed in the ratio 1.5:1.[7] Two-fold dehydrofluorination of the isomer mixture with potassium hydroxide in DMSO occurred smoothly at rt, and the resulting tetrafluorothiophene (**3**) was obtained in high yield and quite pure form by vacuum transfer. The overall yield of **3** was 33%.

Fluorothiophenes are of interest because of the important role thiophenes play in conducting polymers[8] and liquid crystal displays.[9] We have obtained two more starting from diol **4**: 3,4-difluorothiophene (**10**)[10] and 2,3,4-trifluorothiophene (**11**). The latter is the sole previously unknown fluorothiophene.[11] Compounds **10** and **11** are available in high yield by 2-fold dehydrofluorination of **6** and **9**, respectively (Scheme 6).

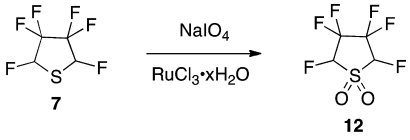
Scheme 6



Early Attempts To Prepare Tetrafluorothiophene *S,S*-Dioxide (2). Raasch successfully oxidized tetrachlorothiophene to its *S,S*-dioxide (**1**) with *m*-chloroperbenzoic acid,[1] but the expectation that tetrafluorothiophene (**3**) could be similarly oxidized to dioxide **2** was mistaken. A series of oxidizing agents either obliterated the thiophene or failed to react with it: *m*-chloroperbenzoic acid, peroxytrifluoroacetic acid, dimethyldioxirane, and sodium periodate/ruthenium(III) chloride. To circumvent this problem, we decided to reverse the order of the dehydrofluorination and oxidation steps.

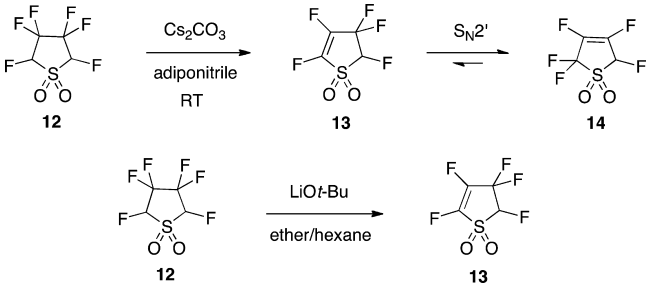
Oxidation of hexafluorothiolane **7** with peroxytrifluoroacetic acid in methylene chloride/trifluoroacetic acid at rt stopped at the monoxide stage, but sodium periodate with ruthenium III chloride catalyst smoothly transformed the thiolane into its *S,S*-dioxide **12** at rt (Scheme 7).[12] The cis/trans ratio was 1.5:1, respectively.

Scheme 7



Unfortunately, treatment of **12** with strong, hindered bases killed it without yielding a detectable amount of the thiophene dioxide. The gentler base cesium carbonate in acetonitrile or adiponitrile effected the first dehydrofluorination step at rt, affording initially thiolene **13**. This quickly isomerized almost completely to **14**, presumably via S_N2' attack by the liberated fluoride ion (Scheme 8).[13] Longer reaction time with the

Scheme 8



carbonate again resulted in decomposition. The role of fluoride ion here suggested that **2** might actually have been formed under these conditions but immediately attacked by fluoride ion to regenerate a thiolene. It seemed that if there were a way to sequester fluoride ion, the 2-fold dehydrofluorination of **12** might be accomplished successfully.

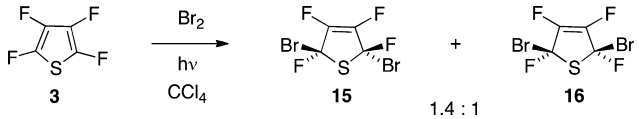
In light of the low solubility of lithium fluoride, dehydrofluorination of **12** was attempted with 1 equiv of lithium *tert*-butoxide in ether/hexane at 0 °C. In contrast to the result with cesium carbonate, the product was **13** unadulterated with **14** (Scheme 8). Thus, sequestration worked, so the reaction was repeated with 2 equiv of the hindered base. Gratifyingly, prominent signals for the desired sulfone **2** appeared in the ^{19}F NMR spectrum of the product. Signals for **13** and four new ones ascribed to an adduct of *tert*-butyl alcohol with sulfone **2** were present as well, however. Because attack of *tert*-butoxide on **2** was apparently competing effectively with its dehydrofluorination of **13**, we concluded that a more hindered lithium base was needed. Accordingly, 2-phenyl-2-propanol was converted to its lithium salt with methyllithium in ether, but this new base gave results similar to those of the *tert*-butoxide. No conditions were found that delivered sulfone **2** in acceptable yield and purity.

Protection of Tetrafluorothiophene. Clearly, the highly electrophilic sulfone had to be generated under conditions where it was safe from nucleophilic attack. We speculated that protection of the thiophene by bromine addition might be a successful tactic, as that should make possible both oxidation at sulfur and deprotection under mild conditions. Tetrafluorothiophene (**3**) was reported to react extremely slowly with bromine,[4b] but we found that addition occurs readily under

dx.doi.org/10.1021/jo402373x | J. Org. Chem. 2013, 78, 12330−12337

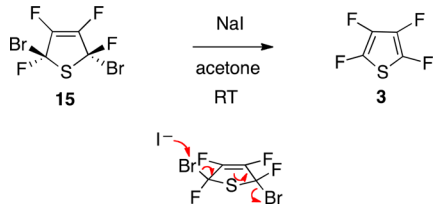
irradiation with visible light, presumably a radical chain process. Addition takes place exclusively at the 2- and 5-positions, yielding a 1.4:1 mixture of trans (**15**) and cis (**16**) isomers (Scheme 9). The basis for the configurational assignments is discussed below.

Scheme 9



Interestingly, treatment of the mixture with sodium iodide in acetone brought about highly selective reduction of the trans isomer **15** back to the thiophene (Scheme 10). Only with the

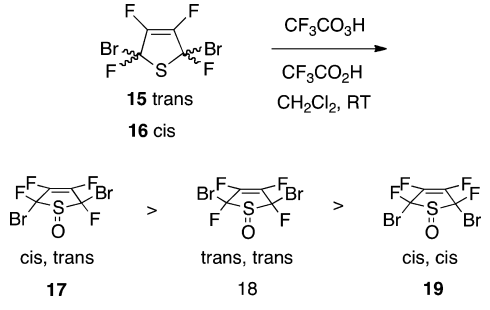
Scheme 10



trans isomer can reaction occur antarafacially on the C=C π bond, as shown. Thus, the observed selectivity supports the view that a C=C double bond has an inherent preference for reacting in transoid fashion.[14]

Synthesis and Reactivity of Tetrafluorothiophene *S*-Oxide (20). Oxidation of the dibromide mixture with peroxytrifluoroacetic acid at rt proceeded only to the sulfoxide stage despite that fact that the first oxidation step for a sulfide is usually slower than the second. Since the reagent contained considerable trifluoroacetic acid, protonation on or hydrogen bonding to the sulfoxide oxygen may have inhibited further oxidation, as both Bronsted and Lewis acids have been shown to stop oxidation of less electron-deficient thiophenes at the sulfoxide stage.[15] All three stereoisomeric sulfoxides were obtained: cis, trans (**17**); trans, trans (**18**); and cis, cis (**19**), in decreasing order of abundance (Scheme 11). The dominant

Scheme 11



isomer was easily recognized as cis, trans by ^{19}F NMR because of its lack of symmetry. Since it had to arise from the more abundant of the two dibromide isomers, that one had to have the trans configuration.

Assignment of stereochemistry to the two symmetric sulfoxide isomers derived from the cis dibromide was not obvious; it was done by a combination of equilibration and computation. Treatment of the isomer mixture with sodium bromide in DMF at rt interconverted the three, probably via a series of S_N2' transformations with bromide ion. The least abundant, present in very small amount initially, became the dominant compound, and the other symmetric isomer nearly vanished. Calculation of the free energies of the three left no doubt that the most stable isomer had the cis,cis configuration (**19**) (Figure 1).

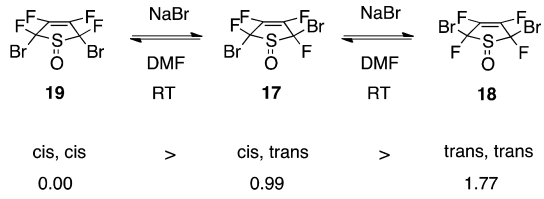
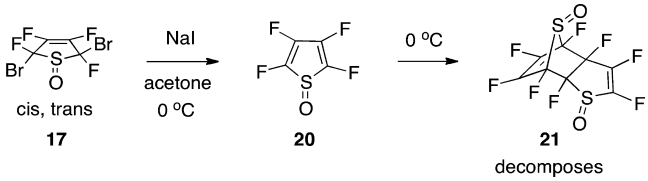


Figure 1. Equilibration of the dibromosulfoxides and computed relative energies (kcal/mol).[16]

Kinetically controlled oxidation of the cis dibromide had introduced the oxygen on the less hindered face of the molecule to afford **18**. Less repulsion between bond dipoles may help explain why **19** is the more stable of the two forms.

Treatment of the sulfoxide mixture with sodium iodide in acetone at 0 °C resulted again in very selective reduction of the form with trans bromines (**17**) (Scheme 12). In the ^{19}F NMR

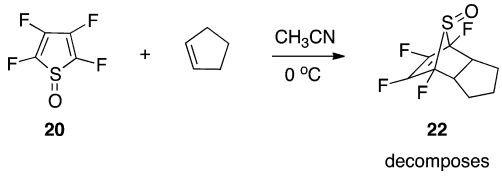
Scheme 12



spectrum a new pair of signals appeared that represented tetrafluorothiophene *S*-oxide (**20**), but they faded at 0 °C and were replaced by eight signals of roughly equal intensity signifying formation of its Diels–Alder dimer **21** (configuration at sulfur discussed below). Zinc–copper couple in acetonitrile was a better choice of reducing system because it smoothly debrominated all three sulfoxides to give **20** at 0 °C, the cis,cis isomer **19** most rapidly. We were surprised to find that the dimer **21** spontaneously decomposed upon attempting to isolate it.

Sulfoxide **20** is a highly reactive diene that can be trapped by some dienophiles before it can dimerize. Cyclopentene, for example, yielded adduct **22**, but this compound also decomposed even at 0 °C (Scheme 13). In contrast, reaction with an alkyne leads to a stable product. With phenylacetylene, the resulting adduct spontaneously extrudes sulfur monoxide with the driving force of aromatization, affording 2,3,4,5-

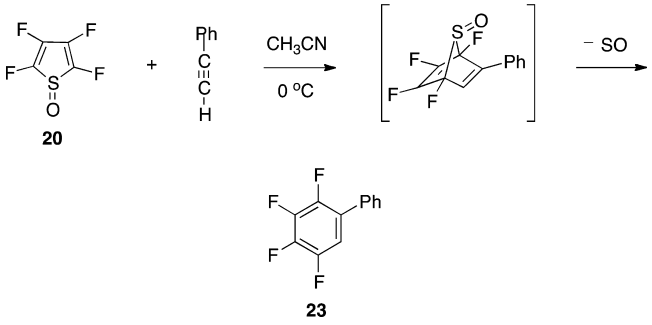
Scheme 13



dx.doi.org/10.1021/jo402373x | J. Org. Chem. 2013, 78, 12330–12337

tetrafluorobiphenyl (**23**) (Scheme 14).[17] It was apparent that the SO group was somehow responsible for the lability of the

Scheme 14



dimer and alkene adducts, and to understand this it was imperative that the configuration at sulfur in those compounds be established.

Thiophene *S*-oxides in general are reactive Diels–Alder dienes that show a marked preference for syn-facial addition, i.e., addition that orients the oxygen on the same side as the developing σ bonds.[18−21] Interaction of the sulfur lone pair with a σ^* orbital of those bonds, an example of the Cieplak effect,[22] has been invoked by a number of authors to explain this selectivity.[15a,19,23] It has also been suggested that ground-state distortion of the sulfoxide from planarity is a contributing factor.[20] Based on AM1 calculations, Werstiuk proposed that relative product stability plays a role in determining π-facial selectivity.[24] For the reaction of 2,5-dimethylthiophene *S*-oxide with maleic anhydride, he calculated a 4.15 kcal/mol lower ΔH_f for the syn-facial product than for the anti. No reason was given for the difference he found.

To help assign the configuration at sulfur of the tetrafluorothiophene *S*-oxide–cyclopentene adduct **22**, we examined the reaction of sulfoxide **20** with ethylene computationally. Finding the syn-facial adduct **25** a full 7.0 kcal/mol lower in free energy than the anti product **24** gave us an appreciation for Werstiuk's surmise, as that amount could certainly account for most of the 4.2 kcal/mol difference in transition state free energy we found for the two reaction pathways (Figure 2). Curious about whether the 7 kcal/mol results from stabilization of the favored product or destabilization of the other, we examined this question with a stripped-down model system. We calculated the energy changes arising from oxidizing sulfide **26** to oxides **27** and **28** and for

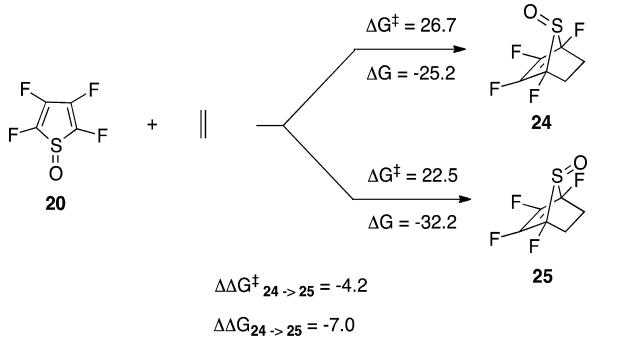


Figure 2. Comparison of computed free energy changes in the syn and anti cycloadditions of sulfoxide **20** to ethylene (kcal/mol).[16]

calibration the change from oxidizing the saturated analogue **29** to **30**. Adduct **28** was found to lie 7.38 kcal/mol lower in energy than **27**, and the (negative) ΔE for **26** → **28** was 8.66 kcal/mol greater than that for **29** → **30** (Figure 3). Thus,

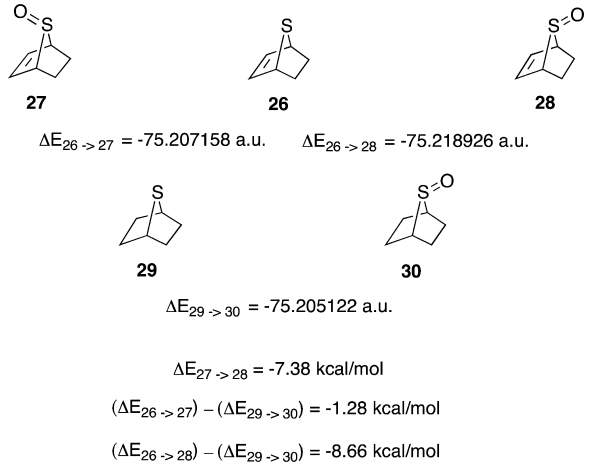
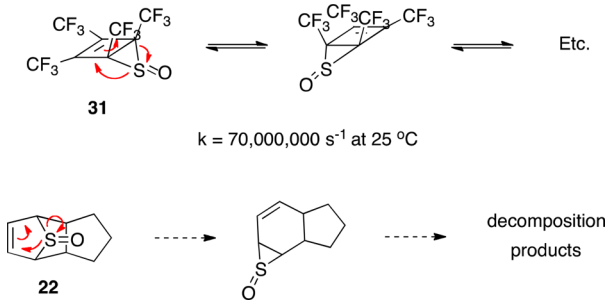


Figure 3. Computed energy differences for syn vs anti cycloaddition and for both vs a saturated reference system.[16]

stabilization of the syn-facial product is responsible for the syn/anti difference. Among the several highest occupied MOs of **28**, the C=C π bond participates only in the HOMO-2 and to a much smaller extent in the HOMO. Both lie below their anti adduct counterparts, as does the HOMO-1, but it is not obvious why. Thus, the absence of a detectable stabilizing interaction between the π bond and the sulfur leaves unresolved the interesting question of the origin of the product energy difference.

In any event, it seems clear that the cyclopentene adduct **22** has the syn-facial configuration at sulfur, but the question remains as to why the compound is so labile. A discovery made in our laboratory in the 1970s may be relevant. We synthesized Dewar thiophene *S*-oxide **31** and found that it undergoes degenerate allylic rearrangement at an enormous rate (Scheme 15).[25] There is a close correspondence in geometry between **22**

Scheme 15



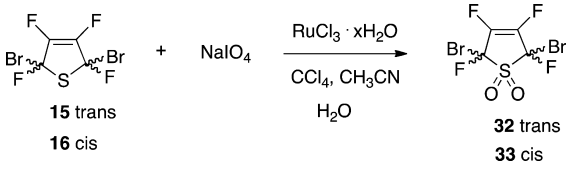
and **31**, which have their sulfur atom similarly positioned to react with the π bond, and both have their oxygen on the opposite face of the sulfur. We suggest that the decomposition of the dimer and alkene adducts of tetrafluorothiophene *S*-oxide (**20**) begins with allylic rearrangement, as illustrated with adduct **22** in Scheme 15.[26]

Synthesis of Tetrafluorothiophene *S,S*-Dioxide (2). Tetrafluorothiophene *S*-oxide (**20**) is a very reactive Diels–

dx.doi.org/10.1021/jo402373x | J. Org. Chem. 2013, 78, 12330−12337

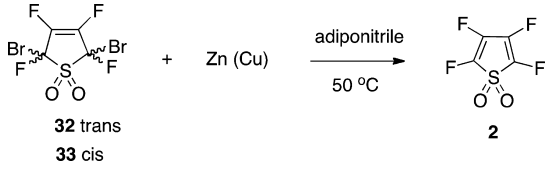
Alder diene, but its usefulness in synthesis is severely limited by both its rapid dimerization and the self-destruction of its alkene adducts. It was therefore essential to obtain the original synthetic target, dioxide **2**, and that meant completing oxidation of *trans*- and *cis*-2,5-dibromotetrafluorothiol-3-ene (**15** and **16**) to their dioxides (**32** and **33**). Sodium periodate with ruthenium chloride as catalyst, a very effective combination for oxidation of electron-deficient sulfides,[12] accomplished this transformation at rt in good yield (Scheme 16).

Scheme 16



Zinc/copper couple in acetonitrile smoothly reduces this mixture of isomeric sulfones at rt to the elusive **2**. To avoid aqueous workup of this highly reactive electrophile, a solvent was needed from which **2** could be obtained directly. As the sulfone is somewhat volatile, the need was for a high-boiling solvent that, like acetonitrile, was dipolar aprotic but not so nucleophilic that it would destroy the product. Adiponitrile met these criteria nicely, with a dielectric constant of 30,[27] a dipole moment of 3.9,[28] and a boiling point of 295 °C. The reduction proceeded in good yield at 50 °C in this underutilized dipolar aprotic solvent, and **2** was obtained as a mobile liquid in fairly pure form simply by vacuum transfer (Scheme 17).

Scheme 17



Synthesis of **2** has been completed in seven steps in 18% overall yield: tosylation of diol **4**, cyclization to thiolane **6**, tandem fluoro-Pummerer rearrangement giving **7**, dehydrofluorination to thiophene **3**, bromination affording **15** and **16**, oxidation to **32** and **33**, and debromination to yield **2**. No chromatography or recrystallization is required.

In sharp contrast to the monoxide **20** that dimerizes readily at 0 °C, dioxide **2** survives in solution for many hours at 100 °C.[29] Neither frontier orbital energies (Figure 4) nor their shapes contribute much to an understanding of this striking difference, a problem for the future. The dioxide's reluctance to dimerize is most fortunate, as that allows it to function as a highly versatile diene and dienophile, capable of reacting with alkenes and alkynes across the polarity spectrum. A foray into its cycloaddition chemistry will be reported elsewhere.

EXPERIMENTAL SECTION

NMR spectra were measured on 300 and 500 MHz spectrometers. ^{19}F NMR spectra were referenced to internal chlorotrifluoromethane, as ^{1}H and ^{13}C NMR spectra were referenced to TMS. Electrospray mass spectra were obtained with a q-TOF detector (Harvard FAS System). Preparative GC was carried out on a 1/4″ x 10′ column packed with 10% OV-101 on Chromosorb W AW-DMCS.

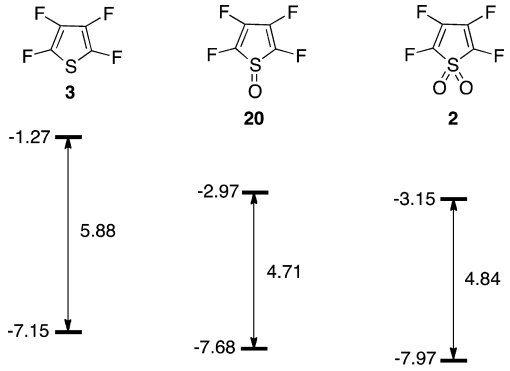


Figure 4. Frontier orbital energies for tetrafluorothiophene and its oxides (eV).

2,2,3,3-Tetrafluoro-1,4-di(tosyloxy)butane (4).[5] Into a 1 L round-bottom flask were placed 37.50 g (0.231 mol) of 2,2,3,3-tetrafluorobutane-1,4-diol, 107 g (0.561 mol) of tosyl chloride, and 400 mL of pyridine. The flask was immersed in a bath at ∼55 °C for 24 h. Contents were poured into a 2 L Erlenmeyer flask cooled in ice, and 400 mL of water was added with good swirling. Product was collected by filtration, washed with water, and then dissolved in 550 mL of CH_2Cl_2. A wash with 360 mL of 5% H_2SO_4 in two portions followed, and the organic phase was dried over Na_2SO_4. Solvent was removed by rotary evaporation, leaving a white solid, 104.0 g (0.221 mol, 96% yield). Mp: 90.5−91.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.79 (d, J = 7.8 Hz, 4H), 7.38 (d, J = 7.8 Hz, 4H), 4.36 (m, 4H), 2.47 (s, 6H). ^{19}F NMR ($CDCl_3$): δ −121.1 (s, 4F). ^{13}C NMR ($CDCl_3$): δ 146.2, 131.8, 130.4, 128.2, 114.1 (tt, J = 256, 33 Hz), 64.0 (t, J = 28 Hz), 21.9. Anal. Calcd for $C_{18}H_{18}F_4O_6S_2$: C, 45.95; H, 3.86; S, 13.63. Found: C, 45.94; H, 4.05; S, 13.60.

3,3,4,4-Tetrafluorothiolane (6). A 1 L round-bottom flask was charged with 50.00 g (0.106 mol) of the ditosylate, 20.7 g of sodium sulfide hydrate (Acros, 60−63% Na_2S, ∼0.16 mol,), and 225 mL of dimethylacetamide. The mixture was purged (two aspirator/N_2 cycles), placed in a bath at 70 °C, and magnetically stirred for 8 h. The flask was fitted with a reflux condenser that was connected via a large liquid N_2-cooled U-trap to a mechanical pump. Pressure was controlled with a nitrogen bleed and measured with a digital manometer. Vacuum transfer was carried out, finally down to a pressure of 12 Torr at 70 °C for 0.5 h. Product was pipetted out of the trap into a 50 mL pear-shaped flask. To facilitate separation of the thiolane from accompanying water, a drop of red food coloring was added, then the colorless lower layer was carefully removed by pipet. Wt.: 13.54 g. Concentrated H_2SO_4 (4 mL) was added to sequester the very small amount of water present, and the thiolane was short-path distilled to free it of dimethylacetamide. The colorless distillate weighed 12.60 g (74% yield). It contained 1.3 mol % of 3,3,4,4-tetrafluorooxolane[30] [^{19}F NMR ($CDCl_3$): δ −123.8 (s, 4F)]. Thiolane bp: 100 °C. ^{19}F NMR ($CDCl_3$): δ −120.3 (s, 4F). ^{1}H NMR ($CDCl_3$): δ 3.22 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 119.4 (tt, J = 262, 29 Hz), 30.0 (m). A sample was prepared for microanalysis by GC: inj 120 °C, col 90 °C, det 160 °C. Anal. Calcd for $C_4H_4F_4S$: C, 30.00; H, 2.52; F, 47.46. Found: C, 29.75; H, 2.39; F, 47.19.

3,4-Difluorothiophene (10).[3] Into a 25 mL round-bottom flask were placed 905 mg (5.66 mmol) of 3,3,4,4-tetrafluorothiolane and 7 mL of DMSO. Powdered 85% KOH, 1.8 g, (27 mmol) was added, and the mixture was stirred at rt for 1 h. The thiophene was isolated by vacuum transfer to a liquid N_2-cooled U-trap, finally to ∼3 Torr and 70 °C for 10 min. The liquid in the trap after thawing was pipetted into a 5 mL round-bottom flask, and the water droplet on the bottom was dyed with a drop of red food coloring to facilitate its separation from the product. Careful pipetting removed the thiophene: 560 mg (82% yield). A little tetrafluorooxolane (1.8 mol %) was present. ^{1}H NMR ($CDCl_3$): δ 6.71 (s, 2H). ^{19}F NMR ($CDCl_3$): δ −139.1 (s, 2F). ^{13}C NMR ($CDCl_3$): δ 145.8 ($^{1}J_{CF}$ = 261 Hz), 103.4.

dx.doi.org/10.1021/jo402373x | J. Org. Chem. 2013, 78, 12330−12337

2,3,3,4,4-Pentafluorothiolane (9). To a 50 mL round-bottom flask were added 1.50 g (9.38 mmol) of 3,3,4,4-tetrafluorothiolane, 15 mL of sulfolane, and 3.70 g (10.4 mmol) of powdered Selectfluor. The mixture was stirred in a bath at ∼60 °C for 2.5 h. Vacuum transfer was carried out, finally to 70 °C for several minutes at full oil pump vacuum. After thawing, the cloudy material in the trap was transferred into a 5 mL round-bottom flask by pipet, with warming using a heat gun. It set to a cloudy, colorless, waxy solid, 1.238 g (74% yield). ^{19}F NMR ($CDCl_3$): δ −111.8 (dm, J = ∼243 Hz, 1F), −121.8 (d, J = ∼243 Hz, 1F), −124.9 (d, J = ∼252 Hz, 1F), −127.3 (dm, J = ∼252 Hz, 1F), −162.8 (dm, J = 56 Hz, 1F). Two mol % of tetrafluorooxolane was present plus an additional impurity signal of about the same area. A sample was purified by GC: inj 120 °C, col 97 °C, det 160 °C. The waxy solid had an ill-defined melting range, but it became a clear liquid at 28 °C. ^{1}H NMR ($CDCl_3$): δ 5.92 (d, J = 56 Hz, 1H), 3.40 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 118.7 (tm, $^1J_{CF}$ = 263 Hz), 116.1 (tm, $^1J_{CF}$ = 267 Hz), 93.0 (dddd, J = 236, 39, 22, 2.3 Hz), 31.2 (t, J = 27 Hz). HRMS, APCI: calcd for $C_4H_4F_5S^+$ 178.9948, found 178.9946.

2,3,4-Trifluorothiophene (11). Into a 25 mL round-bottom flask were placed 944 mg (5.30 mmol) of 2,3,3,4,4-pentafluorothiolane and 6 mL of DMSO. Powdered 85% KOH, 1.9 g (29 mmol), was introduced, and the mixture warmed considerably. It was stirred for 45 min and then subjected to vacuum transfer. The pressure was lowered to ∼3 Torr and the temperature raised to 60 °C for 10 min. Product was pipetted from the U-trap into a small pear-shaped flask, and the large drop of water on the bottom was dyed by addition of a bit of red food coloring. Careful pipetting isolated the colorless thiophene layer. Weight: 582 mg (80% yield). There was 2.3 mol % of tetrafluorooxolane in the product. A sample was purified by GC: inj 120 °C, col 84 °C, det 160 °C. ^{19}F NMR ($CDCl_3$): δ −133.1 (s, 1F), −148.3 (s, 1F), −156.0 (s, 1F). ^{1}H NMR ($CDCl_3$): δ 6.10 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 145.1 (ddd, J = 287, 10.6, 6.9 Hz), 142.8 (dd, J = 262, 16.6 Hz), 129.8 (ddd, J = 260, 22, 7.6 Hz), 88.6 (dd, J = 17.0, 2.8 Hz). MS: m/z 138 (M^+), 118 (M^+ − HF), 107 (M^+ − CF, base), 93 (M^+ − CHS). HRMS, APCI: calcd for $C_4HF_3S^+$ 137.9746, found 137.9741.

***cis*- and *trans*-2,3,3,4,4,5-Hexafluorothiolane (7).** Into a 200 mL round-bottom flask were placed 8.00 g (50.0 mmol) of 3,3,4,4-tetrafluorothiolane and 65 mL of sulfolane. Selectfluor (15.0 g, 42.3 mmol) was added as a powder in portions through flexible tubing from a 50 mL round-bottom flask while the reaction flask was contained in a cool water bath and vigorously stirred. Stirring was continued for 25 min after addition was complete, and then another 24.0 g (67.7 mmol) of Selectfluor was added all at once (total, 39.0 g, 110 mmol). The flask was mounted in a bath at 65 °C and stirred for 4 h. ^{19}F NMR revealed that reaction was complete, so the mixture was subjected to vacuum transfer into a liquid N_2-cooled U-trap at ∼0.1 Torr. The bath temperature was gradually raised to 120 °C and maintained there for several minutes. After thawing, the product was transferred by pipet with the help of a heat gun into a 10 mL round-bottom flask (7.92 g) and short-path distilled without water in the condenser. Fraction 1: 80−97 °C, 0.522 g of mobile, pale yellow oil; fraction 2: 97−105 °C, 5.793 g that set to a nearly colorless, waxy solid. The first fraction was mostly the desired thiolane but contaminated with impurities. Fraction 2 constituted a 59% yield of thiolane isomers in the ratio 1.3: 1 (cis: trans). In other runs the ratio was nearly 1.5:1. A sample dissolved in ether was purified by GC: inj 140 °C, col 75 °C, det 160 °C), and a portion of it was sublimed at 46 °C and 3−4 Torr. ^{19}F NMR ($CDCl_3$): cis, δ −120.2, −123.0 (ABq, J = 255 Hz, 4F); −163.6 (d, J_{HF} = 51 Hz, 2F); trans, δ −121.3 (d, J = 255 Hz, 2F), −134.1 (d, J = 255 Hz, 2F), −161.1 (d, J_{HF} = 50 Hz, 2F). ^{1}H NMR ($CDCl_3$): both isomers, δ 6.09 (dm, J_{HF} (apparent) = 56 Hz due to nonidentical δs, 2H). ^{13}C NMR ($CDCl_3$): cis, δ 115.4 (tm, $^1J_{CF}$ = 271 Hz), 94.3 (dm, $^1J_{CF}$ = 244 Hz); trans, δ 114.7 (tm, $^1J_{CF}$ ∼260 Hz), 91.3 (dm, $^1J_{CF}$ = 239 Hz). Anal. Calcd for $C_4H_2F_6S$: C, 24.49; H, 1.03; S, 16.35. Found: C, 24.31; H, 0.91; S, 16.13.

Tetrafluorothiophene (3).[4] To a 200 mL round-bottom flask was added 5.02 g (25.6 mmol) of hexafluorothiolane and 55 mL of DMSO. The flask was placed in a water bath at rt, and 7.5 g of powdered KOH (large excess) was introduced. The resulting dark brown slurry was stirred for 2.5 h at rt and then subjected to vacuum transfer to a liquid N_2-cooled trap at pressures down to 3 Torr at 45 °C. After thawing, the trap contained colorless, mobile liquid that was removed by pipet, leaving a very small amount of water as droplets on the walls of the trap (3.24 g, 20.8 mmol, 81% yield). ^{19}F NMR ($CDCl_3$): δ −155.6 (t, J = 12.0 Hz, 2F), −164.5 (t, J = 12.0 Hz, 2F). ^{13}C NMR ($CDCl_3$): δ 134.2 ($^1J_{CF}$ = 291 Hz), 127.0 ($^1J_{CF}$ = 263 Hz).

***cis*- and *trans*-2,3,3,4,4,5-Hexafluorothiolane *S*,*S*-Dioxide (12).** A 200 mL round-bottom flask was charged with hexafluorothiolane (4.42 g, 22.6 mmol), CCl_4 (45 mL), CH_3CN (45 mL), H_2O (90 mL), and $NaIO_4$ (13.0 g, 60.8 mmol). Several milligrams of $RuCl_3 \cdot xH_2O$ was added, and the mixture was vigorously stirred at rt for 22 h. The reaction mixture was partitioned between 160 mL of ether and 160 mL of water; the ether layer was washed with 20 mL of saturated $NaHCO_3$ solution and then 50 mL of brine. After drying over Na_2SO_4, the nearly colorless ether solution was passed through a silica gel pad several mm thick on a 30 mL sintered glass funnel, and followed with an ether wash. Rotary evaporation left partially crystalline, pale yellow sulfone as a 1.5: 1 (cis: trans) mixture of isomers, 4.00 g, 17.5 mmol (78% yield). Product from another run was short-path distilled, bp ∼146 °C, to give a white solid. A sample of this sublimed at 55 °C and 23 Torr afforded a waxy solid. ^{19}F NMR ($CDCl_3$): cis, δ −120.9 (d, J = 280 Hz, 2F), −130.0 (d, J = 280 Hz, 2F), −190.2 (d, J_{HF} = 50 Hz, 2F); trans, −119.3 (d, J = 274 Hz, 2F), −132.5 (d, J = 274 Hz, 2F), −182.7 (d, J_{HF} = 50 Hz, 2F). ^{1}H NMR ($CDCl_3$): cis, δ 5.59 (dm, J_{HF} = 50 Hz, 2H); trans, δ 5.52 (dm, J_{HF} = 50 Hz, 2H). ^{13}C NMR ($CDCl_3$): cis, δ 111.5 (tm, $^1J_{CF}$ ∼ 273 Hz), 96.1 (dm, $^1J_{CF}$ = 251 Hz); trans, δ 111.5 (tm, $^1J_{CF}$ ∼ 273 Hz), 95.3 (dm, $^1J_{CF}$ = 251 Hz). Anal. Calcd for $C_4H_2F_6O_2S$: C, 21.06; H, 0.88; S, 14.06. Found: C, 21.16; H, 0.92; S, 13.90.

2,3,4,4,5-Pentafluorothiol-2-ene *S*,*S*-Dioxide (13). Into a small side arm flask fitted with septum were placed hexafluorothiolane dioxide (300 mg, 1.32 mmol) and 3 mL of ether. The flask was cooled in an ice bath under N_2, and LiO*t*-Bu, 1 M in hexane (1.5 mL, 1.5 mmol) was added via syringe with vigorous stirring during 10 min. The bath was removed after another 5 min; 15 min later a ^{19}F spectrum showed that reaction was complete, giving the title sulfone plus tetrafluorothiophene *S*,*S*-dioxide in a 5: 1 ratio. Water (5 mL) was added, and after shaking and layer separation the aqueous phase was extracted with ether (2 × 5 mL). The combined ether solution was dried over Na_2SO_4 and then evaporated. The residue was chromatographed on silica gel (4 g) with 30% CH_2Cl_2 as eluent, giving 41 mg of colorless oil (15% yield). ^{19}F NMR ($CDCl_3$): δ −101.3 (dm, J = 266 Hz, 1F), −113.5 (dm, J = 266 Hz, 1F), −147.5 (s, 1F), −150.2 (narrow m, 1F), −185.0 (d, J_{HF} = 50 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ 5.66 (dm, J_{HF} = 50 HZ, 1H). ^{13}C NMR ($CDCl_3$): δ 145.0 ($^1J_{CF}$ = 327 Hz), 138.5 ($^1J_{CF}$ = 308 Hz), 109.6 ($^1J_{CF}$ = 259 Hz), 95.9 ($^1J_{CF}$ = 251 Hz). Since a little water was detected in the NMR solution, it was dried over Na_2SO_4, evaporated, and sent for microanalysis. Anal. Calcd for $C_4HF_5O_2S$: C, 23.09; H, 0.48; S, 15.41. Found: C, 22.99; H, 0.50; S, 15.14.

Because the isolated yield was so low in this experiment, owing perhaps to volatility, the reaction was repeated as above to determine the yield by NMR. Carefully measured hexafluorobenzene was introduced as an area standard after a little dilute HCl had been added to ensure that no base remained to attack it. Integration of the ^{19}F spectrum of the ether solution, taken with a 6 s delay between pulses to prevent differential relaxation, revealed that the thiol-2-ene dioxide was present in 70% yield. There was also 11% of tetrafluorothiophene *S*,*S*-dioxide.

2,2,3,4,5-Pentafluorothiol-3-ene *S*,*S*-Dioxide (14). Into a 10 mL round-bottom flask were placed hexafluorothiolane dioxide (440 mg, 1.93 mmol), adiponitrile (4 mL), and Cs_2CO_3. (695 mg, 2.13 mmol). Mixture was stirred vigorously at RT for ∼75 min, then subjected to vacuum transfer into a small liquid N_2-cooled U-trap. At full oil pump vacuum, the temperature was raised to 100 °C during ∼20 min; solvent was refluxing by the end. After thawing, the trap was washed down with a little CH_2Cl_2 which was transferred to a graduated test tube (∼0.3 mL). The solution was diluted to 1 mL with

dx.doi.org/10.1021/jo402373x | J. Org. Chem. 2013, 78, 12330−12337

pentane and chromatographed on 5 g of silica gel with 30% CH_2Cl_2 in pentane as eluent. The yield of thiol-3-ene dioxide was ~120 mg (30%). ^{19}F NMR ($CDCl_3$): δ −95.8 (d, J = 218 Hz, 1F), −111.6 (dd, J = 218, 12.6 Hz, 1F), −134.5 (narrow m, 1F), −148.7 (d, J = 37 Hz, 1F), −169.2 (dd, J = 56, 25 Hz, 1F). ^1H NMR ($CDCl_3$): δ 5.97 (dm, J = 56 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 140.7 ($^1J_{CF}$ = 295 Hz), 137.3 ($^1J_{CF}$ = 300 Hz), 113.8 ($^1J_{CF}$ = 290 Hz), 92.3 ($^1J_{CF}$ = 239 Hz). Anal. Calcd for $C_4HF_5O_2S$: C, 23.09; H, 0.48; S, 15.41. Found: C, 22.99; H, 0.48; S, 15.19.

***trans-* and *cis*-2,5-Dibromo-2,3,4,5-tetrafluorothiol-3-ene (15 and 16).** Into a 250 mL round-bottom flask were placed tetrafluorothiophene (3.08 g, 19.7 mmol), CH_2Cl_2 (55 mL), and Br_2 (3.5 g, 21.9 mmol). The flask was mounted in a large crystallizing dish which was filled continuously to overflowing with cold water that was caught in a basin with a drain. The solution was irradiated for 5.5 h with a 120 W tungsten spot lamp that was mounted directly underneath the water bath. Evaporation of the solvent left 5.88 g of the dibromides as oil containing some crystals (94% yield). The trans/cis ratio was 1.4:1. A sample was chromatographed with pentane as eluent on silica gel to obtain the isomer mixture as analytically pure, colorless oil. ^{19}F NMR ($CDCl_3$): trans, δ −75.8 (m, 2F), −140.7 (m, 2F); cis, δ −64.0 (m, 2F), −140.4 (m, 2F). ^{13}C NMR ($CDCl_3$): trans, δ 137.8 ($^1J_{CF}$ ~ 290 Hz), 93.6 ($^1J_{CF}$ ~ 290 Hz); cis, δ 138.0 ($^1J_{CF}$ ~ 290 Hz), 93.1 ($^1J_{CF}$ ~ 290 Hz). Anal. Calcd for $C_4Br_2F_4S$: C, 15.21; H, 0.00; Br, 50.59; F, 24.06. Found: C, 15.22; H, 0.00; Br, 50.30; F, 23.80.

***cis,trans*-; *trans,trans*-; *and cis,cis*-2,5-Dibromo-2,3,4,5-tetrafluorothiol-3-ene *S*-Oxide (17−19).** Into a 25 mL round-bottom flask was placed 1.808 g (5.72 mmol) of the dibromothiolene mixture, and 9 mL (9 mmol) of 1 M CF_3CO_3H in CF_3CO_2H/CH_2Cl_2 was added. The solution became warm, and after 6.5 h at rt the oxidation was complete. The mixture was transferred with 10 mL of CH_2Cl_2 to a 125 mL Erlenmeyer flask, cooled in ice, and made alkaline with ice-cold 10% Na_2CO_3 solution (35 mL). Layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined extract was dried over Na_2SO_4, filtered, and evaporated to leave 1.804 g of colorless oil (95% yield). The order of abundance of the S-oxide isomers was cis, trans > trans, trans > cis, cis. A sample of the mixture was chromatographed on silica gel with 5% CH_2Cl_2/hexanes as eluent. ^{19}F NMR ($CDCl_3$): cis, trans, δ −106.1 (m, 1F), −109.8 (m, 1F), −135.6 (m, 1F), −137.2 (dd, J = 23, 10 Hz, 1F); trans, trans, δ −99.3 (d, J = 20 Hz, 2F), −140.2 (d, J = 20 Hz, 2F); cis cis, δ −112.6 (d, J = 20 Hz, 2F), −139.0 (d, J = 20 Hz, 2F). ^{13}C NMR ($CDCl_3$, ^{19}F decoupled): cis, trans, δ 139.5, 137.9, 110.4, 95.6 or 95.3; trans, trans, δ 140.1, 95.6 or 95.3; cis, cis, δ 137.4, 109.4. Anal. Calcd for $C_4Br_2F_4OS$: C, 14.47; H, 0.00; Br, 48.15. Found: C, 14.42; H, 0.00; Br, 48.31.

Tetrafluorothiophene *S*-Oxide (20): Generation and Trapping. *Thiophene Oxide and Its Dimer.* Into a 25 mL round-bottom flask were placed 326 mg (0.982 mmol) of the dibromothiolene oxides and 5 mL of CH_3CN. The solution was purged three times (aspirator, N_2) and cooled in an ice bath. Purging was repeated after 468 mg of zinc−copper couple was added. The slurry was vigorously stirred at 0 °C for 4 h, whereupon the ^{19}F spectrum revealed that reaction was complete, yielding the S-oxide, a larger quantity of its Diels−Alder dimer (**21**), and a small amount of the over-reduction product tetrafluorothiophene. The dimer decomposed during an attempt to isolate it. ^{19}F NMR (CH_3CN): S-oxide, δ −144.5 (s, 2F), −160.4 (s, 2F); dimer, δ −129.4 (s, 1F), −135.1 (d, J = 25 Hz), −144.0 (s, 1F), −153.8 (s, 1F), −177.3 (s, 1F), −182.4 (s, 1F), −195.9 (s, 1F), −200.5 (s, 1F); thiophene, δ −156.5 (t, J = 12.4 Hz, 2F), −164.7 (t, J = 12.4 Hz, 2F).

*Cyclopentene Adduct (**22**).* Into a 5 mL round-bottom flask were placed 101 mg (0.304 mmol) of the dibromothiolene oxides, 40 μL (31 mg, 0.39 mmol) of cyclopentene, and 2 mL of CH_3CN. Purged as above, the solution was cooled in ice, treated with 145 mg of Zn(Cu), purged again, and stirred for 1.5 h. NMR showed that reaction was complete and the product was quite clean cyclopentene Diels−Alder adduct. ^{19}F NMR (CH_3CN): δ −154.7 (s, 2F), −184.5 (s, 2F). The adduct gradually decomposed spontaneously at 0 °C.

*2,3,4,5-Tetrafluorobiphenyl (**23**).* Into a 10 mL round-bottom flask were placed 158 mg (0.476 mmol) of the dibromothiolene oxides, 143 mg (1.40 mmol) of phenylacetylene, and 3 mL of CH_3CN. Purged as above, the mixture was cooled in an ice bath, treated with 237 mg of Zn(Cu), purged again, and stirred for 6 h. The reaction was very sluggish, so additional Zn(Cu) was added in two portions during the next 10 h (total 732 mg), still at 0 °C. After another 14 h at RT reaction was essentially complete. The reaction mixture was filtered through Celite, which was then washed with 5 mL of CH_2Cl_2. Filtrate was evaporated to a wet brown solid that was chromatographed on 3 g of silica gel with hexanes as eluent, giving 44 mg of the biphenyl (41% yield). Mp: 65−66 °C (lit.[17a] mp 61−62 °C). ^{19}F NMR (1: 1 CCl_4/$CDCl_3$ for lit. comparison): 4.8, 6.8, 18.1, and 22.2 ppm relative to hexafluorobenzene (lit.[17a] 4.7, 6.7, 18.3, and 22.4 ppm).

***trans*- and *cis*-2,5-Dibromo-2,3,4,5-tetrafluorothiol-3-ene *S,S*-Dioxide (32, 33).** A 250 mL round-bottom flask was charged with 7.10 g (22.5 mmol) of dibromothiolenes, 35 mL of CCl_4, 35 mL of CH_3CN, 70 mL of H_2O, and 12.5 g (58.5 mmol) of $NaIO_4$. A few milligrams of $RuCl_3{\cdot}xH_2O$ was added, and the mixture was vigorously stirred for 23 h at rt. ^{19}F NMR showed that reaction was complete. The mixture was partitioned between 270 mL of ether and an equal amount of water. The ether phase was washed with saturated $NaHCO_3$ solution (30 mL) and 80 mL of brine; it was dried over Na_2SO_4. After filtration, it was concentrated to ~35 mL and then passed through a silica gel plug followed by an ether wash. Evaporation left 6.01 g of light brown oil (77% yield), with a trans/cis ratio of 1.4:1. A sample was chromatographed on silica gel with 3% CH_2Cl_2 in pentane to give the isomer mixture as a colorless oil. ^{19}F NMR ($CDCl_3$): trans, δ −110.0 (d, J = 25 Hz, 2F), −142.6 (d, J = 25 Hz, 2F); cis, δ −91.6 (d, J = 25 Hz, 2F), −139.6 (d, J = 25 Hz, 2F). ^{13}C NMR ($CDCl_3$): trans, δ 137.9 ($^1J_{CF}$ = 296 Hz), 97.1 ($^1J_{CF}$ = 304 Hz); cis, δ 138.5 ($^1J_{CF}$ = 293 Hz), 98.0 ($^1J_{CF}$ = 304 Hz). Anal. Calcd for $C_4Br_2F_4O_2S$: C, 13.81; H, 0.00; F, 21.84. Found: C, 13.88; H, 0.00; F, 21.66.

Tetrafluorothiophene *S,S*-Dioxide (2). To a 50 mL round-bottom flask were added 1.128 g (3.24 mmol) of the dibromothiolene dioxides and 5 mL of adiponitrile. After a triple purge (aspirator, N_2), 1.0 g of zinc−copper couple was introduced and purging was repeated. Flask was placed in a bath at 50 °C and stirred for 75 min. Product was collected by vacuum transfer to a liquid N_2-cooled U-trap, finally at full oil pump vacuum and ~80 °C. After thawing, the trap afforded 443 mg of colorless, mobile liquid (73% yield). The sulfone decomposed on silica gel, but could be distilled via kugelrohr (aspirator, < 70 °C). ^{19}F NMR ($CDCl_3$): δ −151.7 (s, 2F), −162.7 (s, 2F). ^{13}C NMR ($CDCl_3$): δ 134.1 (dm, $^1J_{CF}$ = 298 Hz), 133.4 (dm, $^1J_{CF}$ = 331 Hz). HRMS, APCI: calcd for $C_4F_4O_2S^+$ 188.9628, found 188.9632.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H, ^{19}F, and ^{13}C NMR spectra; energies and Cartesian coordinates for structures in Figures 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: david.m.lemal@dartmouth.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation for support of this work (Grant No. CHE-0653935). We are grateful for mass spectra obtained by Sunya Trauger of the Harvard Small Molecule Mass Spectrometry Facility. D.M.L. is pleased to acknowledge a helpful discussion with Eric Block (SUNY Albany).

REFERENCES

(1) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 856.
(2) Thrasher's group has synthesized 3,4-difluorothiophene *S*,*S*-dioxide: Nowak, I.; Rogers, L. M.; Rogers, R. D.; Thrasher, J. S. *J. Fluorine Chem.* **1999**, *93*, 27.
(3) Ilgenfritz, E. M.; Ruh, R. P., U.S. Pat. 2,932,651, 1960.
(4) (a) Burdon, J.; Campbell, J. G.; Parsons, I. W.; Tatlow, J. C. *Chem. Commun.* **1969**, 27. (b) Burdon, J.; Campbell, J. G.; Parsons, I. W.; Tatlow, J. C. *J. Chem. Soc. C* **1971**, 352.
(5) Ball, T. F.; Henrie, R. N., II. *Org. Prep. Proc. Int.* **1989**, *21*, 245.
(6) Review: Hugenberg, V.; Haufe, G. *J. Fluorine Chem.* **2012**, *143*, 238.
(7) The major isomer had a somewhat higher boiling point and longer GC retention time than the minor isomer. It was assigned the cis configuration because the calculated dipole moment of that isomer (2.90 D) is significantly higher than that of the trans form (2.02 D). ^{19}F NMR provided evidence supporting this assignment. Calculated structures for both isomers have strongly twisted rings, relieving eclipsing between C_3 and C_4 (ref 16). The twist renders inequivalent the members of each pair of geminal fluorines at those carbons. Time averaging eliminates this effect in the cis isomer, but not the trans, in which one of the two twisted conformers is preferred over the other. Therefore, a larger chemical shift difference between the geminal fluorines is expected for the trans isomer (barring a strongly countervailing influence of substituents at C_2 and C_5). That difference for the minor isomer is 12.8 ppm, but only 2.8 for the major one, consistent with the conclusion that the latter is cis.
(8) (a) Jameh-Bozorghi, S.; Il Beigi, H. S. *J. Fluorine Chem.* **2011**, *132*, 190. (b) Sakamoto, Y.; Komatsu, S.; Suzuki, T. *J. Am. Chem. Soc.* **2001**, *123*, 4643.
(9) (a) Kawabata, K.; Goto, H. *Materials* **2009**, *2*, 22. (b) Funahashi, M.; Hanna, J.-I. *Adv. Mater.* **2005**, *17*, 594. (c) Zhang, H.; Shiino, S.; Shishido, A.; Kanazawa, A.; Tsutsumi, O.; Shiono, T.; Ikeda, T. *Adv. Mater.* **2000**, *12*, 1336. (d) Knawby, D. M.; Swager, T. M. *Chem. Mater.* **1997**, *9*, 535.
(10) (a) Christiansen, H.; Gronowitz, S.; Rodmar, B.; Rodmar, S.; Rosén, U.; Sharma, M. K. *Ark. Kemi* **1969**, *30*, 561. (b) See also ref 8b.
(11) The other partially fluorinated thiophenes are discussed in ref 10a and: Rodmar, S.; Rodmar, B.; Sharma, M. K.; Gronowitz, S.; Christiansen, H.; Rosén, U. *Acta Chem. Scand.* **1968**, *22*, 907.
(12) Su, W. *Tetrahedron Lett.* **1994**, *35*, 4955.
(13) Calculations (ref 16) found **14** to be more stable than **13** in both the gas phase and polar solution and even more stable than unobserved isomer 2,3,4,5,5- pentafluorothiol-2-ene *S*,*S*-dioxide that could arise by prototropic rearrangement of **14** in the basic medium.
(14) The S_N2' reaction is a good testing ground for the question of facial preference of the C═C π bond. In a recent computational study of this reaction, Streitwieser et al. found syn (suprafacial) stereochemistry in cases where the attacking reagent was an ion pair and therefore able to react via a cyclic transition state. However, when the attacking species was a lone nucleophile, reaction took place in anti (antarafacial) mode, consistent with an inherent preference for that stereochemistry. Streitwieser, A.; Jayasree, E. G.; Hasanayn, F.; Leung, S. S.-H. *J. Org. Chem.* **2008**, *73*, 9426.
(15) (a) Li, Y.; Thiemann, T.; Sawada, T.; Mataka, S.; Tashiro, M. *J. Org. Chem.* **1997**, *62*, 7926. (b) Li, Y.; Matsuda, M.; Thiemann, T.; Sawada, T.; Mataka, S.; Tashiro, M. *Synlett* **1996**, 461. (c) Pouzet, P.; Erdelmeier, I.; Ginderow, D.; Mornon, J.-P.; Dansette, P. M.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1995**, 473. (d) Pouzet, P.; Erdelmeier, I.; Ginderow, D.; Mornon, J.-P.; Dansette, P. M.; Mansuy, D. *J. Heterocycl. Chem.* **1997**, *34*, 1567.
(16) All calculations were carried out at the B3LYP/6-311**+ level of theory. *Jaguar, version 7.0*, Schrodinger, LLC, New York, 2007.
(17) (a) Bogachev, A. A.; Kobrina, L. S. *Russ. J. Org. Chem.* **1997**, *33*, 681. (b) Wei, Y.; Kan, J.; Wang, M.; Su, W.; Hong, M. *Org. Lett.* **2009**, *11*, 3346.
(18) Nakayama, J. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1.
(19) Nakayama, J. *Sulfur Rep.* **2000**, *22*, 123.
(20) Furukawa, N.; Zhang, S.-Z.; Horn, E.; Takahashi, O.; Sato, S. *Heterocycles* **1998**, *47*, 793.
(21) Nakayama, J.; Sugihara, Y. *Sulfur Rep.* **1997**, *19*, 349.
(22) (a) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540. (b) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447.
(23) Naperstkow, A. M.; Macaulay, J. B.; Newlands, M. J.; Fallis, A. G. *Tetrahedron Lett.* **1989**, *30*, 5077.
(24) Werstiuk, N. H.; Ma, J. *Can. J. Chem.* **1994**, *72*, 2493.
(25) (a) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325. (b) Bushweller, C. H.; Ross, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 629.
(26) Apparently, the fluorine substituents are responsible for the lability of alkene adducts of **20**, as other thiophene *S*-oxide adducts with alkenes are stable (refs 15, 18−21, and 23).
(27) Abu-Lebdeh, Y.; Davidson, I. *J. Electrochem. Soc.* **2009**, *156*, A60.
(28) Sengupta, K.; Roy, S. K.; Roy, S. B. *Indian J. Phys.* **1977**, *51B*, 34.
(29) Tetrachlorothiophene *S*,*S*-dioxide dimerizes very slowly in refluxing 1,2- dichloroethane.
(30) Henne, A. L.; Richter, S. B. *J. Am. Chem. Soc.* **1952**, *74*, 5420.