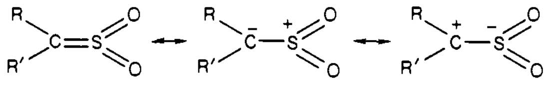
Bis(trifluoromethyl)sulfene: Generation and Cycloaddition Reactions†

Bruce E. Smart* and William J. Middleton§

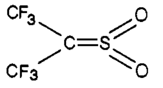
Contribution No. 4289, Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898. *Received January 8, 1987*

Abstract: Bis(trifluoromethyl)sulfene (**2**) was generated in solution by treating $[(CH_3)_2N]_3S^{+}\,{}^{-}C(CF_3)_2SO_2F$ with silicon tetrafluoride or boron trifluoride. (The $TAS^{+}\,{}^{-}C(CF_3)_2SO_2F$ salt was obtained in quantitative yield from tris(dimethylamino)sulfonium (TAS) trimethyldifluorosiliconate and 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane 1,1-dioxide.) Although **2** is unstable toward rearrangement to $CF_2{=}C(CF_3)SO_2F$ and has escaped detection, it was trapped by monolefins, dienes, and anthracenes to give cycloadducts in moderate to good yields. Moderately electron-rich terminal olefins reacted regiospecifically with **2** to give [2 + 2] cycloadducts, and dienes gave either [2 + 2] or [4 + 2] cycloadducts. The X-ray crystal structures of two [2 + 2] cycloadducts show that the thietane 1,1-dioxide ring can be either puckered or planar depending upon the cis-2,4 ring substituents. 2-*tert*-Butyl- and 9-methylanthracene reacted with **2** to afford cycloadducts wherein the sulfene has added across the 9,10-position of the anthracene, whereas 9,10-dimethylanthracene reacted with loss of sulfur dioxide to afford exclusively 7,7-bis(trifluoromethyl)dibenzonorbornadiene. An electron-transfer mechanism is postulated to account for these results.

Sulfenes are molecules of the formula $RR'C{=}SO_2$, which can be thought of as sulfonyl analogues of ketenes. They were first proposed as reactive intermediates by Wedekind and Schenk in 1911, and their existence is now firmly established. Despite numerous attempts to electronically or sterically stabilize sulfenes, no stable monomeric sulfene has yet been isolated.[1,2] The usual strategy to electronically stabilize a sulfene, which was first suggested by Paquette and co-workers[3] in analogy to the stabilization of sulfur, nitrogen, and phosphorus ylides, is to delocalize the negative charge on the carbon atom of its dipolar ylide hybrid **1b**. The regioselectivity of sulfene reactions indeed shows that the sulfur atom is electrophilic, and thus the dipolar character of a sulfene presumably is best represented by **1b** rather than by **1c**.



1a **1b** **1c**



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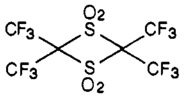
Since it is well known that the electron-withdrawing trifluoromethyl group often confers unusual thermal stabilities to heterocumulenes, such as in the cases of $(CF_3)_2C{=}C{=}O$[4] and $(CF_3)_2C{=}C{=}S$,[5] it seemed plausible to expect that bis(trifluoromethyl)sulfene (**2**) would be especially stabilized electronically and perhaps even long-lived under ambient conditions. This expectation was heightened by the recent reports by Sundermeyer and co-workers on the synthesis, isolation, and remarkable thermal stability of the related bis(trifluoromethyl)sulfine, $(CF_3)_2C{=}SO$.[6]

Although the formal dimer **3**[6] and trimer **4**[7] of bis(trifluoromethyl)sulfene are known, there have been no reports on the synthesis or trapping of this sulfene. There is, however, circumstantial evidence for the intermediacy of **2** in the thermochemistry of certain tetrakis(trifluoromethyl)-1,3-dithietane oxides. For example, pyrolysis of **5** at 500 °C gives a 1:1 mixture of $(CF_3)_2C{=}SO$ and $CF_2{=}C(CF_3)SO_2F$, and pyrolysis of **3** at 530 °C gives a 6:1 mixture of $(CF_3)_2C{=}C(CF_3)_2$ and $CF_2{=}C(CF_3)SO_2F$.[6b] It is postulated that the sulfonyl fluoride is a product of isomerization of **2**.

In this paper we report a mild procedure for generating bis(trifluoromethyl)sulfene (**2**) in solution at ambient or low temperatures, and we describe our attempts to spectroscopically detect the sulfene and to trap it in situ with olefins, dienes, and anthracenes.



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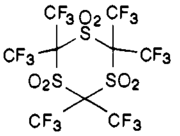

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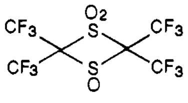

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Results

Generation and Fate of Bis(trifluoromethyl)sulfene. The most common procedure to generate a sulfene involves the dehydrohalogenation of a sulfonyl halide with base, usually triethylamine.[1] Although the presence of the amine and its hydrohalide salt can complicate the chemistry of the sulfene,[1,8] the dehydrofluorination of the known[7c] sulfonyl fluoride $(CF_3)_2CHSO_2F$ in principle would be the simplest method to generate bis(trifluoromethyl)sulfene. It has been reported, however, that $(CF_3)_2CHSO_2F$ reacts reversibly with tertiary amines to give unstable salts, which thermally revert to the sulfonyl fluoride and amine.[7c,9] Our approach to generating bis(trifluoromethyl)sulfene required a stable salt of ${}^{-}C(CF_3)_2SO_2F$ from which fluoride ion could be abstracted from the sulfonyl fluoride group by a reagent with high fluoride ion affinity. We have exploited the unique ability of the tris(dimethylamino)sulfonium (TAS) cation to stabilize fluorinated

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§ Present address: Ursinus College, Collegeville, PA 19426.

[1] For reviews of the synthesis and properties of sulfenes see: (a) King, J. F. *Acc. Chem. Res.* **1975**, *8*, 10. (b) Opitz, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 107.

[2] The only physical evidence for a sulfene is the IR spectrum of the parent sulfene $CH_2{=}SO_2$ at −196 °C in the presence of HCl and other pyrolysis products. At −155 °C, the sulfene and HCl react to give CH_3SO_2Cl.[1a]

[3] Paquette, L. A.; Freeman, J. P.; Houser, R. W. *J. Org. Chem.* **1969**, *34*, 2901.

[4] England, D. C.; Krespan, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 5582.

[5] Raasch, M. S. *J. Org. Chem.* **1972**, *37*, 1347.

[6] (a) Elsasser, A.; Sundermeyer, W. *Chem. Ber.* **1985**, *118*, 4553. (b) Elsasser, A.; Sundermeyer, W.; Stephenson, D. S. *Chem. Ber.* **1985**, *118*, 116. (c) Elsasser A.; Sundermeyer, W. *Tetrahedron Lett.* **1983**, *24*, 2141.

[7] (a) Sokol'skii, G. A.; Pavlov, V. M.; Golovkin, V. M.; Gorelov, V. F.; Knunyants, I. L. *Khim. Geterotsikl. Soedin.* (*Engl. Trans.*) **1974**, 34. (b) Sokol'skii, G. A.; Pavlov, V. M.; Ezhov, V. V.; Knunyants, I. L. *Khim. Geterotsikl. Soedin.* (*Engl. Trans.*) **1974**, 37. (c) Eleev, A. F.; Sokol'skii, A. F.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* (*Engl. Trans.*) **1977**, 1444.

[8] (a) Block, E.; Aslam, M. *Tetrahedron Lett.* **1982**, *23*, 4203. (b) Block, E.; Wall, A. *Tetrahedron Lett.* **1985**, *26*, 1425. (c) Grossert, J. S.; Bharadwaj, M. M. *J. Chem. Soc., Chem. Commun.* **1974**, 144.

[9] The $(C_2H_5)_3NH^{+}\,{}^{-}C(CF_3)_2SO_2F$ salt is stable only below −30 °C, and the pyridinium salt is marginally stable at 20 °C; see ref 7c.

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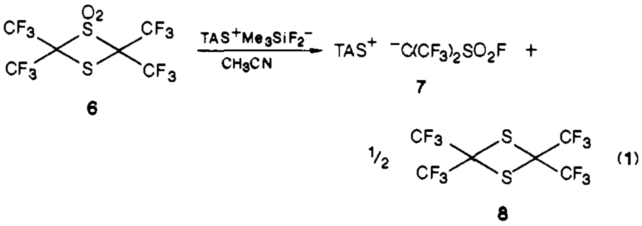
anions[10] for the synthesis of such a salt.

Tris(dimethylamino)sulfonium (TAS) trimethyldifluorosiliconate[11] reacted rapidly with 2,2,4,4-tetrakis(trifluoromethyl)dithietane 1,1-dioxide (**6**)[6b,12] in CH_3CN at 25 °C to afford $TAS^{+}\,{}^{-}C(CF_3)_2SO_2F$ (**7**) and tetrakis(trifluoromethyl)-1,3-dithietane (**8**) (eq 1). The salt **7** was isolated in quantitative yield by evaporating the reaction mixture to dryness.[13] (With 0.5 equiv of **6** and 1 equiv of $TAS^{+}Me_3SiF_2^{-}$, a 1:1 mixture of **7** and $TAS^{+}(CF_3)_2CFS^{-}$ resulted.)[14] The salt **7** is stable up to its melting point (215–219 °C) and can be stored indefinitely at room temperature without noticeable decomposition. Unlike other TAS salts of perfluorinated anions,[10] **7** is only slightly hygroscopic and can be handled briefly in air without any decomposition.



The salt **7** in anhydrous CH_2Cl_2 or CH_3CN at 0–25 °C reacted exothermically with BF_3, BF_3 etherate, or SiF_4 to give $TAS^{+}BF_4^{-}$ or $TAS^{+}SiF_5^{-}$ and $CF_2{=}C(CF_3)SO_2F$ (**9**) as the principal products (eq 2) along with small, variable amounts of $(CF_3)_2CHSO_2F$.[15] The reaction between **7** and SiF_4 in CH_2Cl_2 at 0 °C, for example, afforded a 10:1 mixture of **9**:$(CF_3)_2CHSO_2F$ by ^{19}F NMR, and pure **9** was isolated in 58% yield. The $(CF_3)_2CHSO_2F$ byproduct likely resulted from a reaction between **7** and adventitious HF in the reaction mixture. This reaction was confirmed independently (see Experimental Section). The sulfonyl fluoride **9** is very unstable hydrolytically, and water converts it to $CF_3CH_2SO_2F$.

$$\mathbf{7} + SiF_4 \rightarrow \underset{\mathbf{2}}{[(CF_3)_2C{=}SO_2]} \rightarrow \underset{\mathbf{9}}{CF_2{=}C(CF_3)SO_2F} + TAS^{+}SiF_5^{-} \quad (2)$$

Several reactions between **7** and SiF_4 in CH_2Cl_2 or CH_2Cl_2/CH_3CN mixtures were run at various temperatures down to −78 °C and monitored by ^{19}F NMR spectroscopy. The products **9**, $(CF_3)_2CHSO_2F$, and $TAS^{+}SiF_5^{-}$ plus unreacted **7** in each case accounted for >95% of the fluorinated species present. The absence of any singlet resonances in the ^{19}F NMR spectra of the reaction mixtures (besides that for SiF_5^{-}) precluded the presence of either bis(trifluoromethyl)sulfene (**2**) or its dimer **3** and trimer **4**. Any sulfene that was generated thus must rapidly rearrange to **9** at or above −78 °C.

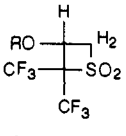
These results alone, of course, do not establish that **2** was produced initially in the reactions between **7** and SiF_4 or BF_3. It is equally plausible that the Lewis acids could have abstracted fluoride ion from a CF_3 group rather than from the SO_2F group in $^{-}C(CF_3)_2SO_2F$ to directly give **9**. This possibility, however, was ruled out by the following results which show that **2** can be very efficiently intercepted.

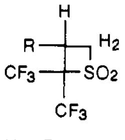
Table I. [2 + 2] Cycloadditions of Bis(trifluoromethyl)sulfene[a] with Olefins

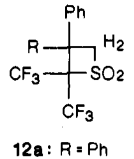
olefin	7/olefin ratio	cycloadduct (% yield)[b]
$ROCH{=}CH_2$	0.5	**10a** (33)
(R = CH_3; C_2H_5;		**10b** (44)
n-C_4H_9)		**10c** (41)
$PhSCH{=}CH_2$	1.1	**11a** (49)
CH_3O-1,4-c-C_6H_4-$CH{=}CH_2$	1.0	**11b** (90)
$Ph_2C{=}CH_2$	1.1	**12a** (34)
$PhC(CH_3){=}CH_2$	1.2	**12b** (69)

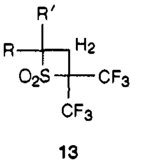
[a] From **7** and SiF_4 in CH_3CN at 0–25 °C. [b] Isolated, unoptimized yield of analytically pure product.

Olefin Reactions. Moderately electron-rich olefins trapped bis(trifluoromethyl)sulfene that was generated in situ from **7** and SiF_4 to give [2 + 2] cycloadducts **10–12** (Table I). The reactions were conducted by simply bubbling SiF_4 into a solution of the olefin derivative and **7** in anhydrous CH_3CN at 0–25 °C. (Since the olefins were more compatible with SiF_4 than with BF_3, the results cited here and in the following sections apply to SiF_4 only.) A slight molar excess of **7** over the olefin derivative was used, except for the vinyl ethers which were employed in a twofold excess because of their susceptibility to electrophilic polymerization. In each reaction, only one cycloadduct was detected by GLPC and NMR analyses.









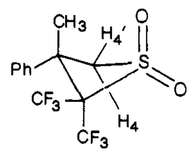
10a: R = CH_3
10b: R = C_2H_5
10c: R = n-C_4H_9

11a: R = SPh
11b: R = C_6H_5-OCH_3

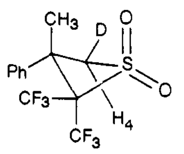
12a: R = Ph
12b: R = CH_3

13

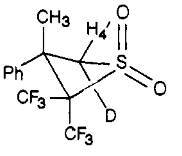
The structures of the cycloadducts were readily established by ^{1}H and ^{19}F NMR spectroscopy. The chemical shifts of the geminal methylene protons in **10–12** appear at 4.06–5.28 ppm downfield from Me_4Si, which compare to the δ 4.09 value for the protons adjacent to the SO_2 group in thietane 1,1-dioxide itself,[16] but are clearly too far downfield from the ring protons in the opposite regioisomer **13** (the β-protons in thietane 1,1-dioxide appear at δ 2.14).[16] Also, the $^{2}J_{HH'}$ couplings of 13.6–13.7 Hz, which were resolved in **10a**, **10b**, and **12b**, are in better agreement for protons α rather than β to the SO_2 group ($^{2}J_{\alpha} = 14 \pm 0.5$, $^{2}J_{\beta} = 12 \pm 0.5$ Hz for thietane 1,1-dioxides).[16] The structure of **12b** was confirmed by X-ray diffraction analysis (see below).



12b



12c



12d

To check the stereospecificity of sulfene cycloaddition, an 85:15 mixture of (E)-:(Z)-α-methyl-β-deuteriostyrene was prepared[17] and used to trap **2**. An 85:15 (±2%) mixture of **12c**:**12d** (73% isolated yield) was obtained by ^{1}H and ^{2}H analyses. These analyses were particularly easy because the chemical shifts of the geminal protons H_4,$H_{4'}$ in **12a** differ by 1.05 ppm ($J_{H4,H4'} = 13.6$ Hz), wherein H_4 cis to the phenyl group is significantly deshielded (**12b**: δ $H_4 = 5.11$, $H_{4'} = 4.06$; **12c**: δ H = 5.06; **12d**: δ H = 3.99 ppm downfield from Me_4Si). Thus the [2 + 2] cycloaddition of **2** to α-methylstyrene is both regiospecific and stereospecific. By contrast, its cycloaddition to (E)-β-deuterio-p-methoxystyrene (eq 3) is not stereospecific. A twofold excess of this olefin with

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(10) (a) Smart, B. E.; Middleton, W. J.; Farnham, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 4905. (b) Farnham, W. B.; Middleton, W. J.; Fultz, W. C.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 3125. (c) Farnham, W. B.; Middleton, W. J.; Calabrese, J. C.; Dixon, D. A.; Smart, B. E. *J. Am. Chem. Soc.* **1985**, *107*, 4565.

(11) (a) Middleton, W. J. *Org. Synth.* **1985**, *64*, 221. (b) Middleton, W. J. (to Du Pont) US Patent 3 940 402.

(12) Carboni, R. A.; Kauer, J. C. (to Du Pont) US Patent 3 058 993.

(13) If desired, the volatiles can be collected and fractionated to recover **8** in >90% yields for recycle.

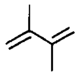
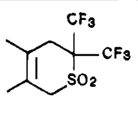
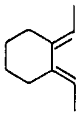
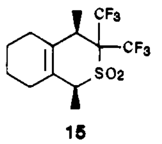
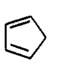
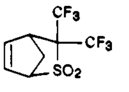
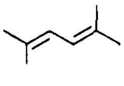
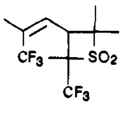
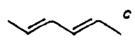
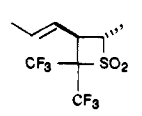
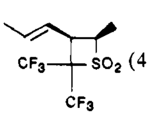
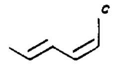
(14) The $TAS^{+}(CF_3)_2CFS^{-}$ salt can be made cleanly by reacting **8** with 2 equiv of $TAS^{+}Me_3SiF_2^{-}$. It was isolated as a pale orange glass: ^{19}F NMR (CD_3CN) δ −75.8 (d, 6 F, J = 20 Hz), −118.0 (septet, 1 F, J = 20 Hz).

(15) The TAS salt products have been made independently by reacting $TAS^{+}Me_3SiF_2^{-}$ with BF_3 etherate and SiF_4, respectively. $TAS^{+}BF_4^{-}$: mp 251–253 °C; ^{1}H NMR ($CDCl_3$) δ 2.80 (s); ^{19}F NMR ($CDCl_3$) δ −152.51 (s, ^{10}B), −152.57 (s, ^{11}B). $TAS^{+}SiF_5^{-}$: mp 258–260 °C; ^{1}H NMR (CD_3CN) δ 2.88 (s); ^{19}F NMR (CD_3CN) δ −135.56 (s). The $2TAS^{+}SiF_6^{2-}$ salt, which was prepared from 2 equiv of $TAS^{+}Me_3SiF_2^{-}$ and SiF_4 (W. B. Farnham), was not detected in the reactions between **7** and SiF_4. ($2TAS^{+}SiF_6^{2-}$: mp 133 °C; ^{19}F NMR (CD_3CN) δ −124 ($J_{Si-F} = 111$ Hz.)

(16) Cistaro, C.; Fronza, G.; Mondelli, R.; Bradamante, S.; Pagani, G. A. *J. Magn. Reson.* **1974**, *15*, 367.

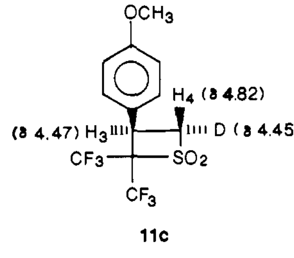
(17) (a) Davis, R. R.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 2252. (b) McKinney, M. A.; Nagarajan, S. C. *J. Org. Chem.* **1979**, *44*, 2233.

Table II. Cycloadditions of Bis(trifluoromethyl)sulfene[a] with Dienes

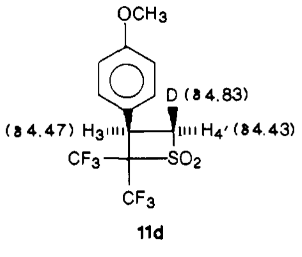
diene	7/diene ratio	cycloadduct (% yield)[b]	
	0.5	 **14**	(41)
	1.0	 **15**	(81)
	0.5	 **16**	(71)
	0.6	 **17**	(83)
[c]	1.1	 **18** +  **19**	(43) (96.1:3.9)[d]
[c]	1.1	**18** + **19** (40)	(12.7:87.3)[d]

[a] From 7 and SiF_4 in CH_3CN at 0–25 °C. [b] Isolated, unoptimized yield of analytically pure product. [c] Diene isomerized during reaction; see text. [d] Ratio of **18**:**19** in crude product mixture by GLPC.

2 gave a mixture of ca. 80% **11c** and 20% **11d** by ^1H and ^2H NMR analyses. The stereochemical integrity of the olefin after reaction could not be determined, however, since the excess olefin had completely polymerized under the reaction conditions.

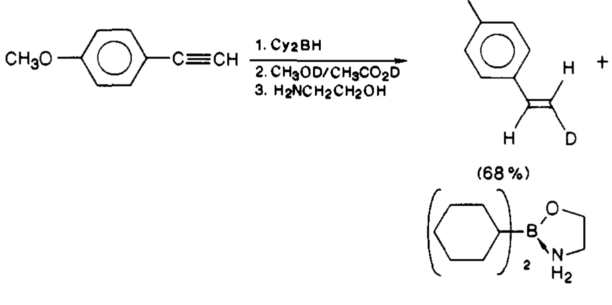


11c



11d

Moderately electron-poor olefins such as vinyl acetate, methyl vinyl ketone, ethyl acrylate, or acrylonitrile did not trap **2**. Aqueous workup of their reaction mixtures afforded $CF_3CH_2SO_2F$ and minor amounts of $(CF_3)_2CHSO_2F$, but no other fluorinated organic products. *cis*- or *trans*-stilbene neither trapped **2** nor isomerized under the reaction conditions. Cyclohexene, 1-phenylcyclohexene, and, more surprisingly, (*E*)-β-methylstyrene did not trap **2**.

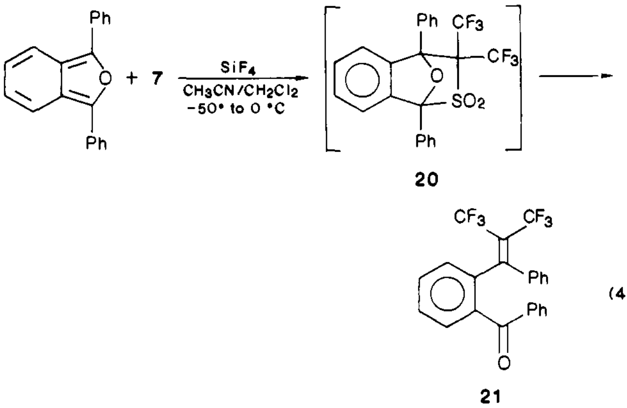


(3)

Diene Reactions. Several dienes efficiently trapped **2** to give cycloadducts (Table II). Notably, in each reaction either [2 + 2] cycloadduct(s) or a [4 + 2] cycloadduct was produced, but in no case were both [2 + 2] and [4 + 2] cycloadducts observed.

The reactions with (*E,E*)- and (*E,Z*)-2,4-hexadiene each gave two adducts that proved to be the isomers **18** and **19**. When a solution of **7** and isomerically pure (*E,E*)-2,4-hexadiene (1:1 molar ratio) was treated with SiF_4, **18** and **19** were produced in a ratio of 96.1:3.9 by GLPC. An identical reaction with (*E,Z*)-2,4-hexadiene (99.7% (*E,Z*), 0.3% (*E,E*)) also gave **18** and **19**, but in the ratio of 12.7:87.3. The respective reactions were repeated with a 2:1 molar ratio of diene:**7**, and both the products and unreacted dienes were analyzed by GLPC. The (*E,E*)-2,4-hexadiene similarly gave a 95.5:4.5 mixture of **18**:**19** and a 94.0:6.0 mixture of unreacted (*E,E*):(*E,Z*) dienes. The (*E,Z*)-2,4-hexadiene gave an 88.0:12.0 mixture of **19**:**18** and an 82.2:17.8 mixture of unreacted (*E,Z*):(*E,E*) dienes. Both **18** and **19** were stable to the reaction conditions (SiF_4, CH_3CN at 25 °C). Moreover, the (*E,E*)-2,4-hexadiene in CH_3CN was *not* isomerized by SiF_4, and the (*E,Z*)-2,4-hexadiene was isomerized to the extent of only about 1% under the same conditions.

Phenyl substituents at the terminal positions of the dienes markedly decreased their reactivities toward **2**. For example, in contrast to (*E,E*)-2,4-hexadiene and 1,2-(*E,E*)-bis(ethylidene)cyclohexane,[18] 1,4-diphenylbutadiene and 1,2-(*E,E*)-bis(benzylidene)cyclohexane[18] failed to trap **2**. 1,3-Diphenylisobenzofuran, however, trapped **2** at 0 °C to give only **21** in 67% isolated yield (eq 4). None of the expected [4 + 2] cycloadduct **20** was detected in reactions that were run at temperatures as low as −50 °C where **21** was still produced.[19]



(4)

The assignments of structures **14**–**17** by ^1H and ^{19}F NMR spectroscopy were straightforward. A single-crystal X-ray diffraction structure for **17** also was obtained (see below). The assignments of structures **18** and **19** were more involved, however. The ^1H, ^{19}F, and ^{13}C NMR data for **18** and **19** are summarized in Table III. Decoupling experiments were required to determine the ^1H chemical shifts and coupling constants unambiguously. The relatively large 15 Hz coupling constant for the vinyl protons H_6,H_7 in the adducts is consistent with trans but not cis vinyl proton stereochemistry ($^3J_{trans}$ = 12–18 Hz, $^3J_{cis}$ = 6–12 Hz for vinyl protons). This immediately rules out the [4 + 2] cycloadducts **22** and the [2 + 2] cycloadducts **23**. The over 7 ppm difference in chemical shifts of C_5 and C_8 in the methyl groups also argues against **22**. The strongly deshielded H_4 methine proton resonances in the cycloadducts (δ 4.50 and 4.80, respectively) precludes **24** as possible product structures (cf. δ 2.65 for the methine proton in 3-methylthietane 1,1-dioxide).[20] Obviously then, the major product from (*E,E*)-2,4-hexadiene must be the trans isomer **18**, and that from (*E,Z*)-2,4-hexadiene the cis isomer **19**.

On the basis solely of the NMR data, it would be difficult to assign the correct stereochemistry of the cycloadducts unambig-

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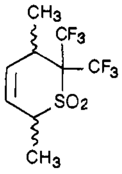
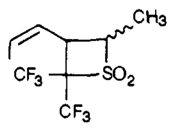
[18] (a) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. (b) Nugent, W. A. *Org. Synth.*, submitted for publication.

[19] A similar result has been reported for the reaction between 1,3-diphenylisobenzofuran and sulfene itself; see ref 8a.

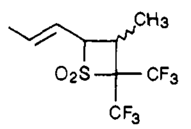
[20] Siegl, W. O.; Johnson, C. R. *J. Org. Chem.* **1970**, *35*, 3657.



22

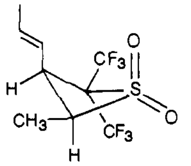


23



24

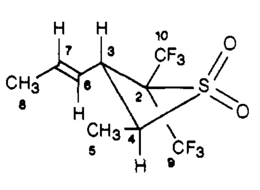
uously. The nearly identical ${}^3J_{H3H4}$ values for **18** and **19** clearly do not distinguish the cis from the trans isomer. The ${}^1H$ NMR data a posteriori do reveal some interesting features that prove to be consistent with the structure assignments, provided that differences in the thietane 1,1-dioxide ring conformations are taken into account. The significant difference (0.49 ppm) in chemical shifts for H_3 in **18** and **19** is notable and might be taken to indicate that H_3 is pseudo-axial in **18** and pseudo-equatorial in **19** (The S=O bond shields groups that lie directly behind it along the S=O bond axis).[16,20-23] That is, the preferred conformation for **18** would be that shown in Table III, and it would be **19′** for the cis isomer. The magnitude of ${}^3J_{trans}$ in **18** (11.1 Hz) indeed is comparable to reported values for ${}^3J_{2ax3ax}$ couplings (11.9–12.5 Hz), but not ${}^3J_{2eq3eq}$ couplings (3.2–3.9 Hz), in other thietane 1,1-dioxides.[16,21,24] Thus, the preferred conformation for **18** which is displayed in Table III is the correct one. The assignment of **19′** for the preferred conformation of the cis isomer is questionable, however. Significantly, the chemical shift of H_3 in the cis product (3.62 ppm) is nearly identical with that for H_3 (3.69 ppm) in **17**, whose ring is planar rather than puckered in the solid state (see below). If the ring in **19** is also planar and remains so in solution, the reason for the relative downfield shift of H_3 in **19** vs. **18** becomes clear, that is, the effect of flattening the thietane 1,1-dioxide ring is to move H_3 away from the shielding zone of the S=O group. The magnitude of ${}^3J_{cis}$ in **19** (11 Hz) also is somewhat larger than the ${}^3J_{2ax3eq}$ values which have been reported for puckered thietane 1,1-dioxide derivatives (7.5–9.2 Hz)[21,24] but is reasonable for a planar structure where the HCCH dihedral angle ≅0°.[25] For these reasons, the cis product is assigned the planar structure **19** that is shown in Table III.



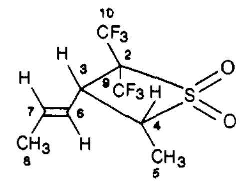
19′

Anthracene Reactions (Table IV). 2-*tert*-Butylanthracene trapped **2**, both in the dark and in diffuse laboratory light, to give approximately a 2:1 mixture of the [4 + 2] cycloadducts **25a** and **25b**,[26] whose structures could not be differentiated unambiguously by NMR. Anthracene itself gave little or no reaction, apparently because of its low solubility in the reaction medium. 9-Methylanthracene gave a single [4 + 2] cycloadduct under the same reaction conditions, which proved to be **26** by X-ray single-crystal analysis. 9,10-Dimethylanthracene unexpectedly gave **28** but none of **27**. Since both **25** and **26** were stable to the reaction conditions, it seemed unlikely that **27** could be an intermediate to **28**. To substantiate this, **27** was prepared from **26** (eq 5) and its structure was confirmed by X-ray analysis. Indeed, **27** was stable both to the reaction conditions and to prolonged reflux in CH_3CN. Thus, product **28** definitely did not arise by loss of SO_2 from the potential intermediate **27**.

Table III. NMR Data for [2 + 2] Cycloadducts **18** and **19**



18



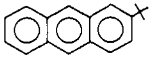
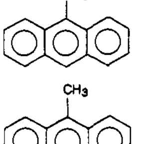
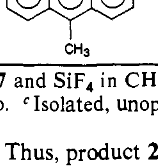
19

nucleus	chemical shift (ppm)[a] 18	chemical shift (ppm)[a] 19
H_3	3.125	3.616
H_4	4.50	4.81
H_5	1.534	1.477
H_6	5.42	5.64
H_7	5.86	5.05
H_8	1.78	1.789
C_2	86.327	88.05
C_3	39.625	34.85
C_4	78.442	77.36
C_5	10.947	9.39
C_6	119.549	118.15
C_7	135.717	135.717
C_8	17.992	17.97
C_9[b]	121.4	121.62
C_{10}[b]	120.4	120.40
F_9[b]	−61.92	−60.52
F_{10}[b]	−63.35	−67.04

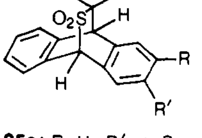
nuclei	coupling constant (Hz) 18	coupling constant (Hz) 19
H_3, H_4	11.1	10.95
H_3, H_6	9.6	8.5
H_4, H_5	6.7	7.47
H_6, H_7	15.04	15.07
H_6, H_8	~2	1.6
H_7, H_8	6.54	6.55
F_9, F_{10}	9.3	10.35
C_9, F_9[b]	283.2	283.6
C_{10}, F_{10}[b]	284.8	284.1
C_2, $F_{9,10}$	26.9	24.9

[a] ${}^1H$ (360 mHz) and ${}^{13}C$ (46 mHz) shifts downfield from Me_4Si; ${}^{19}F$ (188 mHz) shifts downfield from $CFCl_3$. [b] C_9, C_{10} and F_9, F_{10} nuclei not differentiable.

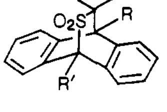
Table IV. Cycloadditions of Bis(trifluoromethyl)sulfene[a] with Substituted Anthracenes

anthracene[b]	product (% yield)[c]
	**25a** + **25b** [2:1] (50)
	**26** (79)
	**28** (83)

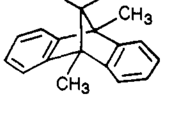
[a] From **7** and SiF_4 in CH_3CN/CH_2Cl_2 at 25 °C. [b] **7**/anthracene in 1.2/1 ratio. [c] Isolated, unoptimized yield of analytically pure product.



25a: R = H; R′ = *t*-Bu
25b: R = *t*-Bu; R′ = H



26: R = CH_3; R′ = H
27: R, R′ = CH_3



28

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(21) Dobson, R. M.; Jancis, E. H.; Klose, G. *J. Org. Chem.* **1970**, *35*, 2520.

(22) Cooper, R. D. G.; DeMarco, P. V.; Cheng, J. C.; Jones, N. D. *J. Am. Chem. Soc.* **1969**, *91*, 1408.

(23) Siegel, W. O.; Johnson, C. R. *Tetrahedron* **1971**, *27*, 341.

(24) Cistaro, C.; Fronza, G.; Mondelli, R. *Tetrahedron Lett.* **1973**, 189.

(25) From the approximate Barfield–Karplus equation that was derived for *cis*-2,4-diphenylthietane 1,1-dioxide,[21] ${}^3J_{H,H'} = 9.9 \cos^2 \phi - 0.9 \cos \phi + 2.2$, the calculated value for ${}^3J_{H,H'}$ is 11.2 Hz when the dihedral angle $\phi = 0°$.

(26) The formal adduct between **2** and anthracene, **25** (R, R′ = H), is known. It was prepared by oxidation of the anthracene/hexafluorothioacetone cycloadduct; see ref 6b.

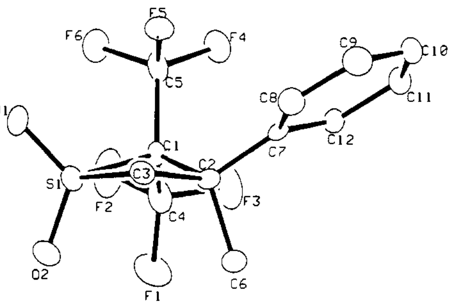


Figure 1. X-ray crystal structure of **12b** (hydrogen atoms removed for clarity). Featured bond angles (deg), bond lengths (Å), and bond angles between planes (deg): $\angle O_1S_1O_2$ = 118.4 (3), $\angle C_1S_1C_3$ = 80.0 (3), $\angle S_1C_1C_2$ = 87.3 (4), $\angle S_1C_3C_2$ = 92.5 (5), $\angle C_1C_2C_3$ = 94.8 (5), $\angle C_4C_1C_5$ = 109.7 (6), $S_1–O_1$ = 1.409 (5), $S_1–O_2$ = 1.420 (6), $S_1–C_1$ = 1.854 (7), $S_1–C_3$ = 1.759 (8), $C_1–C_2$ = 1.612 (10), $C_2–C_3$ = 1.557 (10), $\angle C_1S_1C_3/C_1C_2C_3$ = 154.5.

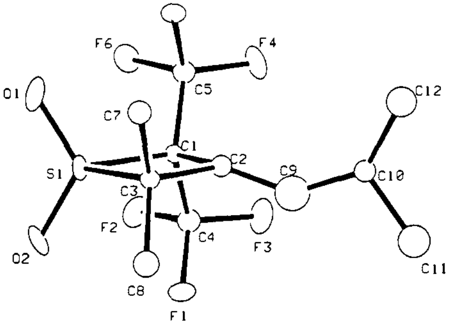


Figure 2. X-ray crystal structure of **17** (hydrogen atoms removed for clarity). Featured bond angles (deg), bond lengths (Å), and bond angles between planes (deg): $\angle O_1S_1O_2$ = 119.1 (6), $\angle C_1S_1C_3$ = 82.1 (6), $\angle S_1C_1C_2$ = 87.9 (8), $\angle S_1C_3C_2$ = 89.5 (9), $\angle C_1C_2C_3$ = 101 (1), $\angle C_4C_1C_5$ = 111 (1), $S_1–O_1$ = 1.416 (9), $S_1–O_2$ = 1.443 (11), $S_1–C_1$ = 1.844 (11), $S_1–C_3$ = 1.832 (13), $C_1–C_2$ = 1.588 (16), $C_2–C_3$ = 1.550 (16), $\angle C_1S_1C_3/C_1C_2C_3$ = 179.9.

Table V. Comparative Bond Angles in Puckered Thietane 1,1-Dioxides

	angle (deg)				
	29[a]	**30**[b]	**31**[c]	**32**[d]	**12b**[e]
∠OSO	118.1	119.6	117.6	117.2	118.4 (3)
∠CSC	80.9	81.6	80.2	77.6	80.0 (3)
∠CCC	99.1	99.3	97.2	95.3	94.8 (5)
∠SCC[f]	87.3	86.6	89.1	88.8	89.9 (5)
∠CSC/CCC	154.9	154.5	157.5	148.7	154.5

[a] Andretti, G. D.; Cavalca, L.; Sgarabotto, P. *Gazz. Chim. Ital.* **1971**, *101*, 442. [b] Andretti, G. D.; Bocelli, G.; Sgarabotto, P. *Gazz. Chim. Ital.* **1974**, *104*, 1207. [c] Ziegler, M. L.; Weiss, J.; Schildknecht, H.; Grund, N.; Sasse, H. E. *Liebigs Ann. Chem.* **1973**, *10*, 1702. [d] Kumakura, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2164. [e] This work. [f] Average value.

Neither 9-phenylanthracene nor 9,10-diphenylanthracene trapped **2**, and the latter did not quench the reaction of 9-methylanthracene with **2**. (The cycloadduct **26** was still formed when a mixture of 9,10-diphenylanthracene (2–3 eq), 9-methylanthracene (1 eq), and **7** (1 eq) in CH_3CN/CH_2Cl_2 was treated with SiF_4.) Anthracenes substituted with electron-withdrawing groups (CN, CHO, Br, Cl) at the 9- or 9,10-positions failed to intercept bis(trifluoromethyl)sulfene.

$$\mathbf{26} \xrightarrow[\text{2. } CH_3I]{\text{1. } n\text{-BuLi/THF, } -70\ ^\circ C} \mathbf{27} \tag{5}$$

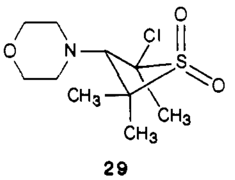
X-ray Crystal Structures. Suitable crystals of **12b** and **17** were obtained for X-ray diffraction analysis. Their structures and selected geometry parameters are given in Figures 1 and 2. The conformations of the thietane 1,1-dioxide rings in **12b** and **17** markedly differ. The ring is puckered 25.5° in **12** but is planar, or very nearly so, in **17**. (The unit cell of **17** contains four independent pairs of molecules whose bond lengths and angles slightly differ. The $C_1S_1C_3/C_1C_2C_3$ dihedral angles are 179.9, 177.3, 175.2, and 170.2° for the four independent molecules.)

Table VI. Comparative Bond Angles in Slightly Puckered Thietane 1,1-Dioxides and **17**

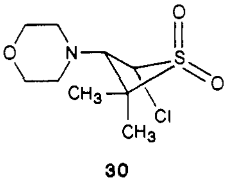
	angle (deg)			
	33a[a]	**33b**[b]	**33c**[c]	**17**[d]
∠OSO	116.2	117.9	117.5	119.6 (6)
∠CSC	82.2	81.5	82.4	82.1 (6)
∠CCC	101.3	99.1	99.1	101.0 (10)
∠SCC	87.9	89.3	88.8	88.7 (9)[e]
∠CSC/CCC	171.0	170.6	173.2	179.9

[a] Chiang, J. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 737. [b] Andretti, G. D.; Bocelli, G.; Sgarabotto, P. *Cryst. Struct. Commun.* **1973**, *2*, 323. [c] Andretti, G. D.; Bocelli, P.; Sgarabotto, P. *Cryst. Struct. Commun.* **1973**, *3*, 499. [d] This work. [e] Average value.

The shape of the ring in **12b** is remarkably similar to that of other significantly puckered thietane 1,1-dioxides **29–32**, despite the quite different ring substituents (Table V). A comparison of **12b** to **29–31**, which all have nearly the same angles of ring pucker, reveals that only ∠CCC in **12b** is slightly outside the range of bond angles in **29–31**. Likewise, the ring in **17** is very similar in shape to the rings in 3-substituted thietane 1,1-dioxides (**33a–c**), which are only slightly bent (Table VI). Except for the larger ∠CSC/CCC in **17** (and its somewhat larger ∠OSO), the rings in **17** and **33a–c** have essentially the same shape within experimental uncertainty.



29



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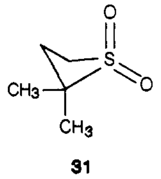
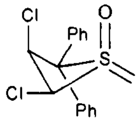
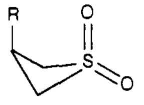


31



32



33a: R=Br
33b: R=Cl
33c: R=OH

From the previously known thietane 1,1-dioxide structures, it had been observed that the degree of ring pucker was smaller when there were no α-ring substituents (α-hydrogens only).[27] This trend obviously does not hold in the case of **17**. It is likely that steric interactions between the CF_3 and CH_3 groups at C_2 and C_4 have an important effect on conformation. In a bent conformation there is appreciable steric repulsion between the pseudo-axial CF_3 and CH_3 groups. Flattening the ring increases the $CF_3 \cdots CH_3$ nonbonded distance and, consequently, diminishes this steric repulsion. In **12b**, however, the steric effect is smaller since only CF_3 and H groups are involved, and apparently it is not sufficient to overcome the proclivity of the ring to pucker.

It may seem inconsistent that **29** and **30**, which have pseudo-axial $CH_3 \cdots CH_3$ and $CH_3 \cdots Cl$ interactions, respectively, still prefer to have puckered ring conformations. In these cases, the repulsive interaction between the eclipsed morpholino and CH_3 or Cl groups that would arise upon flattening the ring seemingly dominates any relief of these pseudo-axial interactions. For **17**, the relief of the $CF_3 \cdots CH_3$ steric interaction must predominate owing to the relatively large steric bulk of the CF_3 group.[28] (The isopropylidene

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(27) Footnote *b*, Table V.

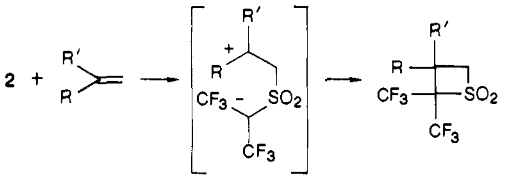
(28) The CF_3 group is sterically much larger than Cl or the CH_3 group and is at least as large as the $(CH_3)_2CH$ group, judging from the relative modified Taft steric parameters ($E_s°(CF_3) = -2.40$, $E_s°(i\text{-Pr}) = -1.71$),[29] Charton's steric parameters ($\nu(CF_3) = 0.91$, ν(i-Pr = 0.76),[30] *A* values ($A(CF_3) \cong 2.1$, $A(i\text{-Pr}) \cong 2.2$),[31] and rotational barriers in biphenyl derivatives.[32]

(29) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.

(30) Gallo, R. *Prog. Phys. Org. Chem.* **1983**, *10*, 115.

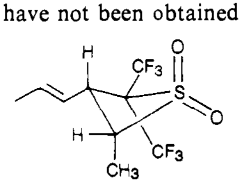
(31) Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.

Scheme I



group in **17** is nearly perpendicular to the planar ring and is rotated away from the neighboring CF_3 groups to minimize the eclipsing interaction.)

The experimental results for **17** imply that **19** also should prefer to have a planar ring rather than a puckered one (**19''**) to minimize the $CF_3 \cdots CH_3$ interactions. A bent structure would be acceptable, however, if the preferred conformation was **19'**, but the solution NMR data are more consistent with the planar structure (see above). Perhaps an unfavorable 1,3-interaction between the propenyl group and the S=O bond inhibits the molecule from adopting conformation **19'**. Unfortunately, these predictions about the preferred conformations of **18** and **19** remain unconfirmed since crystals of the pure compounds that are suitable for X-ray diffraction analysis have not been obtained to date.



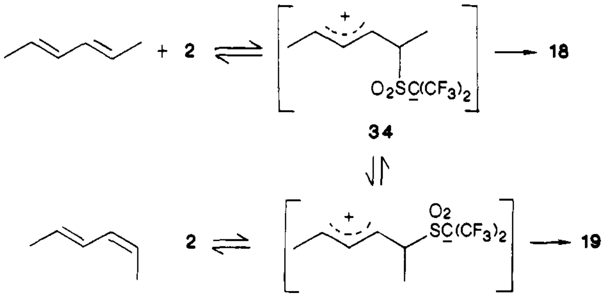
19''

Discussion

The trapping experiments with olefins, dienes, and anthracenes to give cycloadducts in isolated yields of over 80% in some cases clearly demonstrate that bis(trifluoromethyl)sulfene (**2**) is generated in situ from **7** and SiF_4. The sulfene, however, is too short-lived to be detected. It neither dimerizes nor oligomerizes but simply rearranges to its isomer **9**.[33] Sundermeyer and coworkers[6b] therefore were correct to postulate **2** as an intermediate in the pyrolyses of **3** and **5**.

The attempt to stabilize a sulfene by introducing electron-withdrawing CF_3 groups obviously failed. Although its thermodynamic stability is difficult to assess,[34] **2** is a highly reactive species kinetically. The fact that it is trapped by diverse compounds having only moderately electron-rich double bonds, whereas sulfenes ordinarily can be intercepted by only very electron-rich olefins such as enamines or ketene acetals and aminals, suggests that **2** may have special reactivity.[35] Experiments that actually compare the reactivity of **2** with that of other sulfenes generated under identical reaction conditions have not been performed, however.[37]

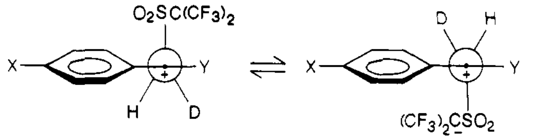
Scheme II



34

35

The regiospecificity of the [2 + 2] cycloadditions to olefins confirms that **2** has dipolar character **1b**. Its cycloadditions, like those of several other dipolarophiles,[38] most likely proceed via zwitterionic intermediates (Scheme I). The finding that 1,1-diphenylethylene and α-methylstyrene intercept **2**, but 1,2-diphenylethylenes and (*E*)-β-methylstyrene do not, is reminiscent of the sensitivity to olefin structure that is seen in the stepwise cycloadditions of tetracyanoethylene (TCNE) to olefins, which involve zwitterionic intermediates. For instance, α-methoxystyrene adds TCNE some 10^4 times faster than β-methoxystyrene.[39] Moreover, the unreactivity of **2** toward ethyl acrylate and acrylonitrile argues against a biradical mechanism. The stereospecific cycloaddition of **2** to α-methylstyrene might appear to be inconsistent with a stepwise mechanism. Retention of olefin configuration, however, does not necessarily rule out a two-step process involving zwitterionic intermediates.[38] If the rate of cyclization is fast relative to bond rotation in the zwitterionic intermediate, the two-step process can be stereospecific. This is reasonable for the isomeric (*E*)-(*Z*)-α-methyl-β-deuteriostyrene cycloadditions since bond rotation in the zwitterion intermediates shown below (X = H; Y = CH_3) would require and unfavorable eclipsing interaction between the bulky $SO_2C(CF_3)_2$ group and the adjacent methyl or phenyl groups. The observed nonstereospecific addition of **2** to (*E*)-β-deuterio-*p*-methoxystyrene implies that bond rotation can compete with cyclization if the process permits the $SO_2C(CF_3)_2$ group to rotate past an adjacent hydrogen (X = OCH_3; Y = H). A similar example (cf. zwitterions **34** and **35**) is discussed below.



The cycloadditions of **2** to dienes have some intriguing mechanistic implications. In many respects the behavior of **2** parallels that of TCNE, but there are peculiar differences. Like TCNE, **2** adds to cisoid fixed dienes and 2,3-dimethylbutadiene to give

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[32] Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* **1980**, *102*, 5618.

[33] The rearrangement of **2** to **9** could be a concerted intramolecular [1,3] sigmatropic process, an intermolecular process, a fluoride ion catalyzed reaction, or an SiF_5^- promoted process ($2 + SiF_5^- \rightleftharpoons {}^-C(CF_3)_2SO_2F + SiF_4 \rightarrow 9 + SiF_5^-$). We cannot distinguish among these possibilities under our reaction conditions.

[34] The calculated ΔEs of −8.4 and −26.6 kcal/mol respectively for the two reactions below unexpectedly indicate that CF_3 substituents thermodynamically destabilize the sulfene. The total energies of the reactants and products were calculated with a (9,5)/[3,2] double-ζ basis set augmented by polarization functions on C, O, and S (D. A. Dixon, B. E. Smart, unpublished results).

$$2 + CF_2H_2 \rightarrow CH_2{=}SO_2 + CF_3CF_2CF_3$$
$$2 + CH_4 \rightarrow CH_2{=}SO_2 + CF_3CH_2CF_3$$

[35] An enhanced reactivity of **2** actually was anticipated several years ago by the work of Snyder (Snyder, J. P. *J. Org. Chem.* **1973**, *38*, 3965). From MO-SCF-CNDO calculations on $CH_2{=}SO_2$ and $(CN)_2C{=}SO_2$, it was shown that electron-withdrawing cyano groups increase the electrophilicity of sulfur and decrease the HOMO-LUMO energy gap in the sulfene. Hence, it was predicted that $(CN)_2C{=}SO_2$ would be kinetically more reactive than $CH_2{=}SO_2$, at least toward dimerization or oligomerization. The trifluoromethyl substituents should similarly increase the electrophilicity at sulfur in **2**[36] and enhance its kinetic reactivity. The finding that "free" $CH_2{=}SO_2$ does not dimerize or oligomerize,[8a] however, casts doubt on the validity of the calculations and predictions. (The formation of dimers or oligomers is presumably due to reactions of tertiary amine/sulfene adducts rather than the free sulfenes.[8])

[36] From Mulliken population analyses using a polarized double-ζ basis set, the SO_2 group charge is +0.34 e in **2** and +0.16 e in $CH_2{=}SO_2$.[34]

[37] Previous attempts to intercept sulfenes by cycloadditions to ethyl vinyl ether, 1,1-bis(4-methoxyphenyl)ethylene, 4-tolylthioethylene, and anthracene were unsuccessful,[1b] but in these cases the sulfenes were generated in situ from a tertiary amine and alkanesulfonyl halide. It is now known that the chemistry of sulfenes that are generated under these conditions is dominated by amine-sulfene complexes which can form at a rate faster than that for sulfene trapping.[8] A striking example is the finding that cyclopentadiene, which gives little or no cycloadduct with sulfene produced in situ from mesyl chloride/triethylamine, efficiently traps sulfenes in the absence of tertiary amines.[8a,b] Any comparisons of the chemistry of **2** with that of sulfenes generated in the presence of amines therefore could be misleading. We thank the referees for their comments on this point.

[38] (a) Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171. (b) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117. (c) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.

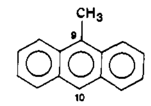
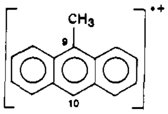
[39] Steiner, G.; Huisgen, R. *Tetrahedron Lett.* **1973**, 3763.

exclusively [4 + 2] cycloadducts, presumably in a concerted fashion.[8a,b,40] With 1,1-disubstituted 1,3-dienes and some (*Z*)-1-substituted dienes where the cisoid conformation is relatively disfavored, TCNE reacts to give preferentially [2 + 2] cycloadducts via zwitterionic intermediates.[40a,41] (The kinetic [2 + 2] products then can rearrange in a stepwise ionic process to the thermodynamically favored [4 + 2] adducts.) The sulfene **2** indeed reacts like TCNE with 2,5-dimethyl-2,4-hexadiene[40c] to give only a [2 + 2] cycloadduct, but it also gives exclusively [2 + 2] cycloadducts with (*E*,*Z*)-2,4-hexadiene, whereas TCNE reportedly gives only a [4 + 2] cycloadduct with this diene.[40a,b] The reason for this difference is unclear. One possibility is that the [4 + 2] product from TCNE and (*E*,*Z*)-2,4-hexadiene is actually the thermodynamic and not the kinetic one, and [2 + 2] cycloadditions in fact are kinetically favored for both **2** and TCNE.[42]

Even more surprising is the exclusive [2 + 2] cycloaddition of **2** to (*E*,*E*)-2,4-hexadiene. With this diene in particular and with (*E*)-1-substituted dienes in general, TCNE reacts only in a [4 + 2] manner.[40,41] In fact, TCNE reacts over 10^4 times faster with (*E*,*E*)- than with (*E*,*Z*)-2,4-hexadiene, and it even reacts marginally faster with (*E*,*E*)-2,4-hexadiene than with 2,3-dimethylbutadiene (in CH_2Cl_2).[40a,b] The exclusive [2 + 2] addition of **2** to (*E*,*E*)-2,4-hexadiene vs. its exclusive [4 + 2] addition to 2,3-dimethylbutadiene marks a striking contrast in the behavior of the sulfene and TCNE. Clearly, additional experiments that probe the effects of diene substituents on the mode of cycloaddition, the relative reactivities of dienes toward **2**, and the importance of solvent effects[43] are needed to further elucidate the unusual cycloaddition chemistry of **2**.

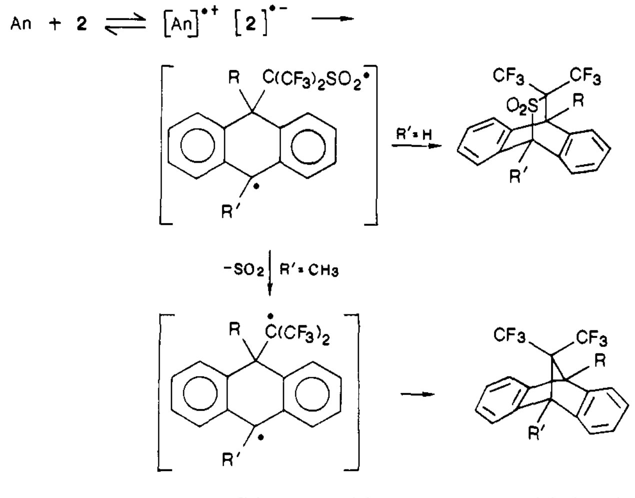
Although the factors that underlie the control of [2 + 2] vs. [4 + 2] cycloaddition of **2** to dienes have not been resolved, the results with the 2,4-hexadienes clearly establish a zwitterionic mechanism for the [2 + 2] cycloadditions. The nonstereospecificity of the cycloadditions coupled with the observed isomerization of the dienes, but only in the presence of **2**, are classic evidence[38] for the process illustrated in Scheme II.

Table VII. PRDDO[a] Orbital Coefficients, Atom Charges, and Unpaired Spin Densities at C_9 and C_{10} in 9-Methylanthracene and Its Radical Cation[b]

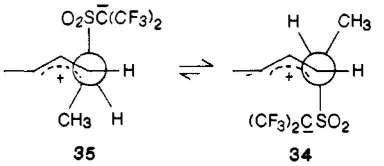
		
c_9[c]	0.41	0.26
c_{10}	−0.42	−0.49
q_9[d]	0.05	0.22
q_{10}	−0.07	−0.03
ρ_9[e]		0.25
ρ_{10}		0.60

[a] For descriptions of the PRDDO method, see: (a) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569. (b) Halgren, T. A.; Kleier, D. A.; Hall, J. H., Jr.; Brown, L. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6569. (c) Dixon, D. A.; Kleier, D. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 5681. [b] Experimental input geometry, except for standard values of $r(C-H)_{aromatic}$ = 1.05 Å, $r(H_2C-H)$ = 1.09 Å, and ∠(HCH) = 109.5°, from: Bart, J. C. J.; Schmidt, G. M. J. *Isr. J. Chem.* **1971**, *9*, 429. [c] HOMO coefficients. [d] Atom charge in e. [e] p_z unpaired spin density.

Scheme III



The partial loss of stereochemistry of the dienes requires not only that the zwitterionic intermediates **34** and **35** be sufficiently long-lived to undergo C–C bond rotation but also that they be formed reversibly. The control experiments, however, show that cyclization of the zwitterions to **18** or **19** is irreversible. From the limited experimental data, nothing quantitative can be said about the relative rates of the individual steps in Scheme II, but some qualitative conclusions can be drawn. The absence of products **23** indicates that **2** adds much faster to a (*Z*)-substituted double bond[44] and thus **2** presumably reacts faster with the (*E*,*Z*)-2,4-hexadiene isomer. (The (*E*,*Z*)-hexadiene represents a model for the intramolecular competitive addition of **2** to a (*Z*)- vs. (*E*)-alkene. A bona fide competition experiment with (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene has not been run and any interpretation of the results will be complicated by the concomitant isomerization of the dienes.) The finding that the (*E*,*Z*)-diene isomerizes to the extent of about 18%, but only 6% of the (*E*,*E*)-diene isomerizes under identical reaction conditions, implies that the ratio of $k_{rotation}/k_{cyclization}$ is greater for zwitterion **35** than for **34**. (The extent of isomerization of the dienes is well short of the equilibrium ratio of about 2 (*E*,*E*):1 (*E*,*Z*),[47] which means that the combined rates of the equilibrium steps in Scheme II cannot be fast relative to $k_{cyclization}$.) Since from simple steric considerations it is reasonable to expect $k_r(\mathbf{35})/k_r(\mathbf{34}) > 1$, it follows that $k_c(\mathbf{35})/k_c(\mathbf{34}) \leq 1$.



35 **34**

In contrast to the olefin and diene cycloadditions, the results of the anthracene reactions (Table IV) cannot be adequately explained by either the usual stepwise, zwitterionic mechanism or a concerted mechanism. Any plausible mechanism has to account for not only the effect of 9,10-dimethyl substitution on

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[40] (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. (b) Rucker, C.; Lang, D.; Sauer, J.; Friege, H.; Sustmann, R. *Chem. Ber.* **1980**, *113*, 1663. (c) Bartlett, P. D. *Q. Rev. Chem. Soc.* **1973**, *24*, 473.

[41] Kataoka, F.; Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1980**, *102*, 711.

[42] The literature on the subject of kinetic vs. thermodynamic product control in the reactions of TCNE with (*Z*)-1-substituted 1,3-dienes is not particularly illuminating. For instance, 4-methyl-1,3-pentadiene and (*Z*)-1-cyclopropylbutadiene react at roughly comparable rates in THF (ϵ = 7.58) to give 86:14 and 95:5 ratios of [2 + 2] to [4 + 2] cycloadducts, respectively.[41] However, (*Z*)-1-methylbutadiene, (*Z*)-1-phenylbutadiene, and (*E*,*Z*)-2,4-hexadiene react with TCNE in CH_2Cl_2 (ϵ = 9.08) respectively about 470, 60, and 9 times slower than 4-methyl-1,3-pentadiene, but (*Z*)-1-methylbutadiene and (*E*,*Z*)-2,4-hexadiene are reported not to give any [2 + 2] cycloadducts, whereas (*Z*)-1-phenylbutadiene gives almost 60% [2 + 2] cycloadduct.[40a,b] The apparent unpredictability of [2 + 2] vs. [4 + 2] product formation in the reactions of TCNE with (*Z*)-1-substituted 1,3-dienes is unsettling and suggests that a more careful examination of kinetic vs. thermodynamic product control with the slower reacting dienes is called for.

[43] Huisgen, R. *Pure Appl. Chem.* **1980**, *52*, 2283.

[44] This also contrasts with TCNE cycloadditions. For example, (*E*)–(*Z*) isomeric enol ethers do not differ greatly in their reactivities toward TCNE.[38b,39] The isomeric thioenol ethers display larger differences in reactivity, and the (*E*)-isomers are always more reactive.[45] The selectivity of **2** is more akin to that seen in ketene [2 + 2] cycloadditions.[46]

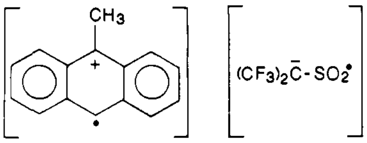
[45] Graf, H.; Huisgen, R. *J. Org. Chem.* **1979**, *44*, 2594.

[46] Ghosez, L.; O'Donnell In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2, p 79.

[47] (a) Döring, V. C. C.-E.; Hauthal, H. G. *J. Prakt. Chem.* **1964**, *24*, 27. (b) Petrova-Kuminskaya, S. V.; Baranov, O. M.; Roganov, G. N.; Kabo, G. Ya. *Neftekimica* **1983**, *23*, 489.

the course of reaction but also the regiospecific addition to 9-methylanthracene. The formation of **28** from 9,10-dimethylanthracene without the intermediacy of **27** immediately rules out a concerted addition. Also from the nearly identical HOMO coefficients and only slightly different, small atom charges that are calculated for C_9 and C_{10} in 9-methylanthracene (Table VII), a concerted addition is not expected to be regiospecific. From the regiochemistry of the [2 + 2] cycloadditions to olefins and dienes, a normal two-step reaction between **2** and the anthracene derivatives that involves zwitterion intermediates likewise should proceed by initial attack at the electrophilic sulfur atom in **2**. (The unreactivity of anthracenes substituted with electron-withdrawing groups argues against initial bond formation at the carbanionic carbon in **2**.) This mode of addition would give the correct regiospecificity for addition to 9-methylanthracene, but it would not account for the facile loss of SO_2 in the reaction with 9,10-dimethylanthracene. A mechanism that does account for all of the experimental results is given in Scheme III.

The key steps of the proposed mechanism are an initial electron transfer from the anthracene derivative (An) to **2** to form an anthracene radical cation ($An^{\bullet+}$), sulfene radical anion pair, followed by combination of the radical ions to produce a biradical intermediate. The fate of the biradical critically depends upon the substituent R′. When R′ = H, the biradical couples to give a [4 + 2] cycloadduct, but when R′ = CH_3 the biradical is more stable and sufficiently longer lived to lose SO_2 prior to intramolecular coupling. This mechanism is especially appealing because it also readily explains the regiospecific addition of **2** to 9-methylanthracene. Unlike in the neutral molecule, the orbital coefficients and atom charges at C_9 and C_{10} are quite different in the 9-methylanthracene radical cation (Table VII), wherein electronically the radical ion principally has the character of resonance hybrid **36**. Charge-annihilation coupling of the radical ion pair thus strongly favors C–C bond formation at C_9 bearing the methyl substituent to produce a relatively short-lived biradical (i.e., R′ = H) that couples before loss of SO_2.



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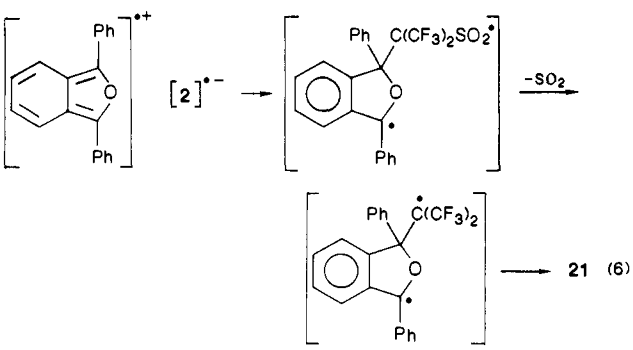
Electron-transfer mechanisms are rather uncommon for nonphotochemical dipolar cycloadditions, but they have been postulated for some [2 + 2] and [6 + 2] cycloadditions of TCNE to cyclopropane systems[48,49] and for certain special cases of spontaneous addition and polymerization reactions of alkenes.[50] Single electron transfer, however, can be thermodynamically favorable whenever particularly strong donor and acceptor molecules are involved.[48,51] Although we have no information on the electron affinity of **2** and no direct evidence for the formation of either charge-transfer complexes or radical ions in the reactions between **2** and the anthracenes, we have demonstrated a single electron-transfer reaction with **2**. We found that *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine in CH_3CN did not react with either **7** or SiF_4 individually, but in combination with both **7** and SiF_4 an intense color characteristic of Würsters' Blue was instantaneously produced. The ESR spectrum of the reaction mixture was identical with that reported for the perchlorate salt of the *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine radical cation.[52] (This was the only paramagnetic species observed at temperatures down to −50 °C. The fate of the short-lived sulfene radical anion has not been established.)

The ability of an anthracene derivative to participate in an electron-transfer reaction with **2** naturally will depend upon the ionization potential (IP) of the donor anthracene. The fact that 9-methyl- (IP = 7.26 eV),[53] 9,10-dimethyl- (IP = 7.23 eV), and 2-*tert*-butylanthracene (IP 2-methylanthracene = 7.26 eV) successfully trap **2**, but that 9-chloro- (IP = 7.45 eV), 9-bromo- (IP = 7.48 eV), and 9-cyanoanthracene (IP = 7.85 eV) do not, indicates that the IP of the donor anthracene necessarily must be less than about 7.3 eV. This, however, is not a sufficient condition as evidenced by the failure of 9-phenylanthracene (IP = 7.27 eV) and 9,10-diphenylanthracene to intercept **2**. This is particularly surprising, considering that the 9-phenyl- and 9,10-diphenylanthracene radical cations are much more stable in solution than their corresponding methyl analogues.[54] Perhaps the phenyl groups which lie out of the plane of the anthracene ring sterically inhibit addition of the sulfene radical anion.[55] Notably, the phenylanthracenes in competition experiments did not quench the addition of **2** to 9-methylanthracene. This implies that any initial electron transfer involving the phenylanthracene is reversible.

The possibility that the cycloadditions of **2** to olefins and dienes (Tables I and II) involve one-electron transfer also was considered, but this is unlikely since the IPs of these dipolarophiles are all above 7.65 eV.[56] The result with 1,3-diphenylisobenzofuran, however, strongly suggests electron-transfer chemistry (eq 6).



Conclusion

The present study shows that bis(trifluoromethyl)sulfene is a highly reactive, dipolar sulfene that exhibits a rich variety of cycloaddition chemistry. It can undergo concerted, stepwise zwitterionic, or electron-transfer reactions. Its reactivity toward and mode of addition to dipolarophiles can be dramatically affected by subtle structural or substituent changes, for reasons that are not fully understood. We intend to continue our experimental and theoretical studies of bis(trifluoromethyl)sulfene and to extend our investigations to other fluorinated sulfenes.

Experimental Section

^1H NMR spectra were recorded at 80.0 MHz on an IBM NR 80 spectrometer or at 361.0 MHz on a Nicolet NT WB-360 spectrometer. ^{19}F NMR spectra were taken on a Varian XL-100 or a Nicolet 200 spectrometer operating at 94.1 and 188.2 MHz, respectively. ^{13}C and ^2H spectra were recorded at 75.6 and 46 MHz, respectively, on a Nicolet NT 300 spectrometer. The NMR solvent was $CDCl_3$, unless noted otherwise. ^1H, ^2H, and ^{13}C chemical shifts are reported in ppm downfield from Me_4Si and ^{19}F chemical shifts in ppm downfield from $CFCl_3$. IR spectra were taken on a Nicolet 7199 spectrophotometer.

All solvents were dried by conventional means, redistilled, and stored over 4-Å molecular sieves. Unless noted otherwise, the olefin derivatives,

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(48) Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659.

(49) Nishida, N.; Murakami, M.; Mizuno, T.; Tsuji, T.; Oda, H.; Shimizu, N. *J. Org. Chem.* **1984**, *49*, 3428.

(50) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.

(51) (a) Houk, K. N. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2, Chapter 4. (b) Kosower, E. M. *Prog. Phys. Org. Chem.* **1965**, *3*, 81.

(52) Bolton, J. R.; Carrington, A.; dos-Santos Viega, J. *Mol. Phys.* **1962**, *5*, 615.

(53) Mielert, A.; Braig, C.; Suaer, J.; Martelli, J.; Sustmann, R. *Liebigs Ann. Chem.* **1980**, 954.

(54) Adams, R. N. *Acc. Chem. Res.* **1965**, *2*, 175.

(55) Phenyl substituents at the 9- or 9,10-positions of anthracene also markedly reduce reactivity in thermal [4 + 2] cycloadditions and photodimerizations; see, for example ref 53 and Davidson (Davidson, R. S. *Prog. Phys. Org. Chem.* **1983**, *19*, 1).

(56) Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements* 1971–1981; U. S. Government Printing Office: Washington, DC, 1982; NSRDS-NBS 71.

dienes, and anthracenes were commercial samples, which were redistilled or recrystallized prior to use. All melting points and boiling points are uncorrected.

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane 1,1-Dioxide (6). A mixture of 182.0 g (0.5 mol) of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**8**),[57] 210 mL of fuming nitric acid, and 120.0 g of chromium trioxide was stirred and refluxed for 15 h. The dark mixture was cooled to room temperature and poured onto ice. The solid which precipitated was collected, washed with water, and recrystallized from methanol. The white crystalline product was dried in a vacuum desiccator over concentrated sulfuric acid to give 156.7 g (79%) of **6**: mp 35–36 °C [lit.[6b,12] mp 35 °C].

Tris(dimethylamino)sulfonium Salt of 2,2,2-Trifluoro-1-(trifluoromethyl)ethanesulfonyl Fluoride (7). To a solution of 82.0 g (0.30 mol) of tris(dimethylamino)sulfonium trimethyldifluorosiliconate[11] in 150 mL of acetonitrile was added in portions 131.8 g (0.33 mol) of **6**. The solution was stirred for 1 h and then evaporated to dryness under reduced pressure to give 119.1 g (99.9%) of **7** as a white crystalline solid: mp 215–219 °C dec; IR (KBr) 2940, 2850 (CH); 1380 cm^{-1} (SO_2); ^{1}H NMR δ 2.88 (s); ^{19}F NMR δ 74.1 (septet, 1 F, J = 11.1 Hz), −48.3 (d, 6 F, J = 11.1 Hz). Anal. Calcd for $C_9H_{18}F_7N_3O_2S_2$: C, 27.20; H, 4.56; F, 33.47; N, 10.57. Found: C, 27.58; H, 4.70; F, 33.28; N, 10.59.

2,2,2-Trifluoro-1-(trifluoromethyl)ethanesulfonyl Fluoride. A solution of 28.0 g (0.071 mol) of **7** in 75 mL of benzonitrile was added slowly to a solution of 2.83 g (0.14 mol) of hydrogen fluoride in 25 mL of benzonitrile. The mixture was stirred for 2 h, and the volatiles which boiled below benzonitrile were removed under reduced pressure. The collected volatiles were fractionated to afford 6.6 g (40%) of **8**: bp 80–81 °C; ^{1}H NMR δ 4.82 (septet of d, J = 7, 1 Hz); ^{19}F NMR δ 66.0 (septet of d, 1 F, J = 11, 2 Hz), −62.9 (d of d, 6 F, J = 11, 7 Hz). Anal. Calcd for $C_3HF_7O_2S$: C, 15.39; H, 0.43; F, 56.81. Found: C, 15.39; H, 0.44; F, 56.53.

1,2,2-Trifluoro-1-(trifluoromethyl)ethanesulfonyl Fluoride (9). Silicon tetrafluoride was slowly bubbled into a solution of 15.9 g (0.04 mol) of **7** in 50 mL of CH_2Cl_2 chilled in an ice bath. The flow of silicon tetrafluoride was discontinued when the mild exotherm subsided. The solution was stirred at room temperature for 30 min. ^{19}F NMR analysis indicated a product mixture of **9**/$(CF_3)_2CHSO_2F$ in the ratio of ca. 10:1. The mixture was fractionated on a spinning band column to give 5.0 g (58%) of **9**:[6b] bp 71–73 °C; ^{19}F NMR: δ 72.33 (q of d of d, 1 F, J = 6.9, 6.0, 13.9 Hz), −45.98, −48.20 (AB m of m, 2 F, J_{AB} = 51.2 Hz, A: q of d, J = 9.3, 6.0 Hz; B: q of d, J = 22.3, 13.9 Hz), −57.70 (d of d of d, 3 F, J = 22.3, 9.3, 6.9 Hz).

2,2,2-Trifluoroethanesulfonyl Fluoride. A solution of 4.9 g (0.023 mol) of **9** in 25 mL of CH_3CN was added to 50 mL of ice water, and the mixture was vigorously stirred for 30 min. The oil which separated was drawn off and distilled to give 2.7 g (70%) of $CF_3CH_2SO_2F$: bp 100–101 °C; ^{1}H NMR δ 4.23 (d of q, J = 8, 4 Hz); ^{19}F NMR δ 64.0 (t of d (quintet), 1 F, J = 8, 8 Hz), −61.6 (q of t, 3 F, J = 8, 4 Hz). Anal. Calcd for $C_2H_2F_4O_2S$: C, 14.46; H, 1.22; F, 45.76. Found: C, 14.54; H, 1.28; F, 45.26.

Bis(trifluoromethyl)sulfene in Situ Trapping. General Procedure. All reactions were conducted in an atmosphere of dry nitrogen. The salt **7** and the olefin or diene trapping agent were dissolved in anhydrous acetonitrile. A mixture of anhydrous acetonitrile and CH_2Cl_2 was used as the solvent for the anthracene trapping agents to maintain homogeneity. The molar ratio of **7** to trapping agent was 1–1.2, except for the trapping agents that were especially susceptible to electrophilic polymerization, and in those cases the molar ratio was ca. 0.5. Silicon tetrafluoride was slowly bubbled into the stirred solution of **7** and the trapping agent at 0–25 °C. The reactions were mildly exothermic, and the silicon tetrafluoride addition was discontinued when the exotherm subsided. The reaction mixture was stirred for another 0.5–1 h and then poured into ice water. The mixture was extracted with ether, and the ethereal extract was dried ($MgSO_4$) and concentrated. The crude product mixture was analyzed by ^{19}F NMR, and in some cases by GLPC, prior to purification. Only a single cycloadduct (>98%) was detected, except for the reactions with (*E*,*E*)- and (*E*,*Z*)-2,4-hexadienes.

2,2-Bis(trifluoromethyl)-3-methoxy-1-thietane 1,1-Dioxide (10a). From 0.084 mol of **7** and 0.168 mol of methyl vinyl ether in 100 mL of CH_3CN (33% yield): bp 64–66 °C (0.5 mm); ^{1}H NMR δ 3.50 (s, 3 H), 4.43, 4.55 (AB m of m, 2 H, J_{AB} = 13.6 Hz, A: d, J = 7.7 Hz, B: d, J = 8.8 Hz), 4.63 (d of d, 1 H, J = 7.7, 8.8 Hz); ^{19}F NMR δ −62.3 (q, 3 F, J = 9 Hz), −65.2 (q, 3 F, J = 9 Hz). Anal. Calcd for $C_6H_6F_6O_3S$: C, 26.48; H, 2.22; F, 41.89. Found: C, 26.25; H, 2.38; F, 41.83.

2,2-Bis(trifluoromethyl)-3-ethoxy-1-thietane 1,1-Dioxide (10b). From 0.063 mol of **7** and 0.126 mol of ethyl vinyl ether in 75 mL of CH_3CN (44% yield): bp 85 °C (0.8 mm); mp 52–54 °C; ^{1}H NMR δ 1.26 (t, 3 H, J = 7 Hz), 3.62, 3.70 (AB m of m, 2 H, J_{AB} = 8.8 Hz, A: q, J = 7.0 Hz; B: q, J = 7.0 Hz), 4.46, 4.53 (AB m of m, 2 H, J_{AB} = 13.7 Hz, A: d, J = 8.0 Hz, B: d, J = 8.9 Hz), 4.75 (d of d, 1 H, J = 8.9, 8.0 Hz); ^{19}F NMR δ −62.5 (q, 3 F, J = 9 Hz), −65.1 (q, 3 F, J = 9 Hz). Anal. Calcd for $C_7H_8F_6O_3S$: C, 29.38; H, 2.82; F, 39.83. Found: C, 29.33; H, 2.84; F, 39.53.

2,2-Bis(trifluoromethyl)-3-(*n*-butoxy)-1-thietane 1,1-Dioxide (10c). From 0.039 mol of **7** and 0.078 mol of *n*-butyl vinyl ether in 50 mL of CH_3CN (41% yield): bp 83–85 °C (0.7 mm); ^{1}H NMR δ 0.90 (t, 3 H, J = 7 Hz), 1.45 (m, 4 H), 3.56 (m, 2 H), 4.46 (m, 3 H); ^{19}F NMR δ −62.2 (q, 3 F, J = 9.5 Hz), −65.1 (q, 3 F, J = 9.5 Hz). Anal. Calcd for $C_9H_{12}F_6O_3S$: C, 34.40; H, 3.85; F, 36.28. Found: C, 34.34; H, 3.68; F, 36.42.

2,2-Bis(trifluoromethyl)-3-(phenylthio)-1-thietane 1,1-Dioxide (11a). From 0.0416 mol of **7** and 0.0378 mol of phenyl vinyl sulfide in 50 mL of CH_3CN (49% yield): bp 119–121 °C (0.7 mm); ^{1}H NMR δ 4.39–4.52 (m, 3 H), 7.38–7.52 (m, 5 H); ^{19}F NMR δ −62.2 (q, 3 F, J = 9.5 Hz), −65.3 (q, 3 F, J = 9.5 Hz). Anal. Calcd for $C_{11}H_8F_6O_2S_2$: C, 37.71; H, 2.30; F, 32.54. Found: C, 37.94; H, 2.28; F, 32.72.

2,2-Bis(trifluoromethyl)-3-(4-methoxyphenyl)-1-thietane 1,1-Dioxide (11b). From 0.058 mol of **7** and 0.057 mol of 4-vinylanisole in 75 mL of CH_3CN (90% yield): mp 108–110 °C (from hexane–ether); ^{1}H NMR δ 3.83 (s, 3 H), 4.43 (m, 1 H), 4.47 (m, 1 H), 4.83 (m, 1 H), 6.93, 7.22 (AA′BB′m, 4 H, J_{AB} = 8.7 Hz); ^{19}F NMR δ −62.0 (q, 3 F, J = 9.5 Hz), −65.1 (q, 3 F, J = 9.5 Hz). Anal. Calcd for $C_{12}H_{10}F_6O_3S$: C, 41.38; H, 2.89; F, 32.73. Found: C, 41.60; H, 3.06; F, 32.62.

A similar reaction with 3.88 g (29.0 mmol) of (*E*)-β-deuterio-*p*-methoxystyrene ((*E*)-(2-deuterioethenyl)-4-methoxybenzene, see below) and 5.70 g (14.3 mmol) of **7** in 35 mL of CH_3CN at 0 °C afforded a mixture of 80% **11c** and 20% **11d** (±2%) by ^{1}H NMR (77% **11c** and 23% **11d** by ^{2}H NMR (±5%)) in 81% isolated yield: ^{1}H NMR (**11c**) δ 3.83 (s, 3 H), 4.47, 4.82 (ABm, 2 H, J_{AB} = 11.3 Hz), 6.93, 7.22 (AA′BB′m, 4 H, J_{AB} = 8.7 Hz); ^{2}H NMR ($CHCl_3$) δ 4.45 (s); ^{1}H NMR (**11d**) δ 3.83 (s, 3 H), 4.43, 4.47 (ABm, 2 H, $J_{AB} \cong$ 11.3 Hz), 6.93, 7.22 (AA′BB′m, 4 H, J_{AB} = 8.7 Hz); ^{2}H NMR ($CHCl_3$) δ 4.83 (s). During the addition of SiF_4 to the olefin and **7**, a white, tacky polymer separated from the reaction mixture. No unreacted starting olefin was detected by NMR or GLPC in the crude product mixture.

2,2-Bis(trifluoromethyl)-3,3-diphenyl-1-thietane 1,1-Dioxide (12a). From 0.053 mol of **7** and 0.049 mol of 1,1-diphenylethylene in 75 mL of CH_3CN (34% yield): mp 173–175 °C (ether triturate); IR (KBr) 3030 (=CH), 2960 (CH), 1600, 1580, 1500 (C=C), 1360, 1190 (SO_2), 1300–1200 cm^{-1} (CF); ^{1}H NMR δ 5.28 (s, 2 H), 7.35 (m, 10 H); ^{19}F NMR δ −58.7 (s). Anal. Calcd for $C_{17}H_{12}F_6O_2S$: C, 51.78; H, 3.07; F, 28.91. Found: C, 51.40; H, 2.88; F, 29.11.

2,2-Bis(trifluoromethyl)-3-methyl-3-phenyl-1-thietane 1,1-Dioxide (12b). From 0.02 mol of **7** and 0.017 mol of α-methylstyrene in 30 mL of CH_3CN (69% yield): mp 89–91 °C (from hexane); ^{1}H NMR δ 1.99 (q, 3 H, $J \cong$ 2 Hz), 4.06, 5.11 (ABm, 2 H, J_{AB} = 13.6 Hz), 7.25 (m, 2 H), 7.39 (m, 3 H); ^{19}F NMR δ −59.48 (q of q, 3 F, J = 10.7, 2.0 Hz), −60.73 (q, 3 F, J = 10.7 Hz); ^{13}C NMR δ 29.99 (CH_3), 41.01 (C), 73.32 (CH_2), 89.4 (C, $^2J_{CF}$ = 24.9 Hz), 120.67 (CF_3, $^1J_{CF}$ = 283.3 Hz), 121.46 (CF_3, $^1J_{CF}$ = 286.3 Hz), 126 (br, *o*-CH), 128.94 (*m*-CH), 128.45 (*p*-CH), 137.74 (ipso-C). Anal. Calcd for $C_{12}H_{10}F_6O_2S$: C, 43.38, H, 3.03; F, 34.31. Found: C, 43.42; H, 3.16; F, 34.28.

The above reaction was repeated with a mixture of 85% (*E*)-β-deuterio-α-methylstyrene and 15% (*Z*)-β-deuterio-α-methylstyrene[16] to give a mixture of 85% **12c** and 15% **12d** (±2%) by ^{1}H NMR (73% yield): mp 88–90 °C; ^{1}H NMR (**12c**) δ 5.06 (s, 1 H), ^{2}H NMR ($CHCl_3$) δ 4.06 (br s); ^{1}H NMR (**12d**) δ 3.99 (s, 1 H), ^{2}H NMR ($CHCl_3$) δ 5.04 (br s).

2,2-Bis(trifluoromethyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran 1,1-Dioxide (14). From 0.076 mol of **7** and 0.152 mol of 2,3-dimethylbutadiene in 75 mL of CH_3CN (41% yield): bp 107–108 °C (2 mm); ^{1}H NMR δ 1.85 (s, 6 H), 3.06 (s, 2 H), 3.76 (s, 2 H); ^{19}F NMR δ −65.6 (s). Anal. Calcd for $C_9H_{10}F_6O_2S$: C, 36.49; H, 3.40; F, 38.48. Found: C, 36.62; H, 3.34; F, 38.67.

3,3-Bis(trifluoromethyl)-3,4,5,6,7,8-hexahydro-*cis*-1,4-dimethyl-2,1-benzothiopyran 2,2-Dioxide (15). From 0.011 mol of **7** and 0.011 mol of 1,2-(*E*,*E*)-bis(ethylidene)cyclohexane[18] in 30 mL of CH_3CN (81% yield): mp 70–71 °C (hexane triturate); ^{1}H NMR δ 1.57 (overlapping m, 10 H), 2.07 (m, 4 H), 3.33 (q, 1 H, $J \cong$ 2.5 Hz), 3.93 (q, 1 H, $J \cong$ 3 Hz); ^{19}F NMR δ −58.99 (q, 3 F, J = 10.4 Hz), −62.65 (q, 3 F, J = 10.4 Hz). Anal. Calcd for $C_{13}H_{16}F_6O_2S$: C, 44.57; H, 4.60; F, 32.54. Found: C, 44.66; H, 4.59; F, 32.54.

3,3-Bis(trifluoromethyl)-2-thiabicyclo[2.2.1]hept-5-ene 2,2-Dioxide (16). From 0.064 mol of **7** and 0.128 mol of cyclopentadiene in 75 mL of CH_3CN (71% yield): mp 149–151 °C (from ether); ^{1}H NMR δ 2.47, 2.97 (ABm of m, 2 H, J_{AB} = 12 Hz), 3.70 (br s, 1 H), 4.18 (s, 1 H), 6.55 (m, 2 H); ^{19}F NMR δ −59.9 (q of d, 3 F, J = 12.3, $\cong$ 2 Hz), −63.6 (q,

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(57) Van Der Puy, M.; Anello, L. G. *Org. Synth.* **1985**, *63*, 154.

3 F, J = 12.3 Hz). Anal. Calcd for $C_8H_6F_6O_2S$: C, 34.29; H, 2.16; F, 40.69. Found: C, 34.52; H, 2.39; F, 40.49.

2,2-Bis(trifluoromethyl)-3-[2-methyl-1-propenyl]-4,4-dimethyl-1-thietane 1,1-Dioxide (17). From 0.018 mol of **7** and 0.031 mol of 2,5-dimethyl-2,4-hexadiene in 20 mL of CH_3CN (83% yield): mp 71–73 °C (petroleum ether triturate); ^{1}H NMR δ 1.60 (s, 3 H), 1.65 (s, 3 H), 1.72 (s, 3 H), 1.87 (s, 3 H), 3.69 (d, 1 H, J = 10.2 Hz), 5.20 (d, 1 H, J = 10.2 Hz); ^{19}F NMR δ –60.48 (q, 3 F, J = 10.2 Hz), –65.68 (q, 3 F, J = 10.2 Hz); ^{13}C NMR δ 18.10 (CH_3), 18.24 (CH_3), 24.79 (CH_3), 26.40 (CH_3), 37.56 (CH), 85.89 (C), 87.4 (C, $^2J_{CF}$ = 26.7 Hz), 110.96 (=C-H), 120.98 (CF_3, $^1J_{CF}$ = 284.0 Hz), 121.31 (CF_3, $^1J_{CF}$ = 283.3 Hz), 143.74 (=C(CH_3)$_2$). Anal. Calcd for $C_{11}H_{14}F_6O_2S$: C, 40.74; H, 4.35; F, 35.15; S, 9.89. Found: C, 40.28; H, 4.36; F, 35.23; S, 9.95.

2,2-Bis(trifluoromethyl)-*trans*-3-(1-(*E*)-propenyl)-4-methyl-1-thietane 1,1-Dioxide (18) and 2,2-Bis(trifluoromethyl)-*cis*-3-(1-(*E*)-propenyl)-4-methyl-1-thietane 1,1-Dioxide (19). Silicon tetrafluoride was slowly bubbled into a solution of 74.1 g (0.186 mol) of **7** and 14.1 g (0.171 mol) of (*E*,*E*)-2,4-hexadiene (95.5% pure, 0.0% (*E*,*Z*)-isomer by GLPC: 25-m fused silica 43 capillary column, 30 °C) in 125 mL of CH_3CN chilled in an ice bath. The silicon tetrafluoride flow was discontinued when the mild exotherm subsided (ca. 30 min). The reaction mixture was allowed to warm to room temperature, stirred 30 min, and then poured into 500 mL of ice water. The mixture was extracted with ether, and the ethereal extracts were washed with brine and dried ($MgSO_4$). The solution was concentrated to 46.1 g of yellow liquid which contained a mixture of 96.1% **18** and 3.9% **19** by GLPC (10 ft × 18 in. 5% SP-1000 on 80/1000 Chromosorb MR 30067 column, 140 °C). The crude product was fractionated to give 20.6 g (43%) of a 95.2/4.8 mixture of **18**/**19** by GLPC: bp 52–54 °C (0.1 mm); mp 55–58 °C. Anal. Calcd for $C_9H_{10}F_6O_2S$: C, 36.49; H, 3.40; F, 38.48. Found: C, 36.50; H, 3.18; F, 38.64. A sample once recrystallized from hexane gave a 97.3/2.7 mixture of **18**/**19**: mp 58–59 °C (see Table III for NMR data).

The reaction was repeated with 0.05 mol of diene and 0.025 mol of **7** in 35 mL of CH_3CN. GLPC analyses of the crude product mixture showed a 94.0/6.0 ratio of unreacted (*E*,*E*)-/(*E*,*Z*)-dienes and a 95.5/4.5 ratio of **18**/**19**.

The above reactions were repeated with the (*E*,*Z*)-2,4-hexadiene (98.5% pure, 0.3% (*E*,*E*)-diene by GLPC). The crude reaction mixture from 0.098 mol of **7** and 0.090 mol of diene contained a 87.3/12.7 mixture of **19**/**18** by GLPC, which was distilled to give 10.5 g (40%) of a 94.8/5.2 mixture of **19**/**18**: bp 66–67 °C (0.3 mm); mp 37–39 °C. Anal. Found: C, 36.61; H, 3.48; F, 38.64. A sample once recrystallized from hexane contained a 96.0/4.0 ratio of **19**/**18**: mp 37–39 °C (see Table III for NMR data).

The reaction with 0.05 mol of (*E*,*Z*)-diene and 0.025 mol of **7** in 35 mL of CH_3CN gave an 82.2/17.8 mixture of unreacted (*E*,*Z*)-/(*E*,*E*)-dienes and an 88.0/12.0 mixture of **19**/**18** by GLPC.

3-[2-Benzoylphenyl]-1,1,1-trifluoro-2-(trifluoromethyl)-3-phenylpropene (21). From 18 mmol of **7** and 9 mmol of 2,5-diphenyl-3,4-benzofuran in 20 mL of CH_3CN and 25 mL of CH_2Cl_2 (67% yield by column chromatography on 20-28 Fisher silica gel, grade 12, with 2:3 CH_2Cl_2/petroleum ether eluent): viscous oil; IR (neat) 3060 (CH), 1665 (C=O), 1630 (C=C(CF_3)$_2$), 1600, 1580, 1490 (C=C), 1350–1150 cm^{-1} (CF); ^{1}H NMR δ 7.12 (s, 5 H), 7.38 (m, 9 H); ^{19}F NMR δ –55.79 (q, 3 F, J = 8.5 Hz), –56.73 (q, 3 F, J = 8.5 Hz). Anal. Calcd for $C_{23}H_{14}F_6O$: C, 65.71; H, 3.36; F, 27.12. Found: C, 65.46; H, 3.46; F, 27.04.

2- and 3-*tert*-Butyl-9,10-dihydro-12,12-bis(trifluoromethyl)-9,10-(epithiomethano)anthracene 11,11-Dioxide (25a and 25b). From 3.8 mmol of 2-*tert*-butylanthracene and 7.5 mmol of **7** in 10 mL of 1:1 CH_3CN/CH_2Cl_2 (50% yield based on 20% recovered starting anthracene by column chromatography on Fisher 20-28 mesh silica gel, grade 12; starting material eluted with 1:4 CH_2Cl_2/petroleum ether; product eluted with 1:1 CH_2Cl_2/petroleum ether): semisolid (ca. 2:1 mixture of isomers by ^{19}F NMR); ^{1}H NMR δ 1.28 (s, 9 H), 4.95 (s, 1 H), 5.43 (s, 1 H), 7.1 (m, 7 H); ^{19}F NMR δ –61.06 (s, ~3 F), –61.10 (s, ~6 F); mass spectrum, *m*/*e* 433.0720 (M – CH_3, calcd 433.0696), 384.1309 (M – SO_2, calcd 384.1313), 369.1088 (M – CH_3, SO_2; calcd 369.1078), 315.1360 (M – SO_2, CF_3; calcd 315.1361), 285.0875 (M – SO_2, 2CH_3, CF_3; calcd 285.0891). Anal. Calcd for $C_{21}H_{18}F_6O_2S$: C, 56.25; H, 4.05; S, 7.15. Found: C, 55.63; H, 4.13; S, 7.87.

12,12-Bis(trifluoromethyl)-10-methyl-9,10-dihydro-9,10-(epithiomethyl)anthracene 11,11-Dioxide (26). From 0.046 mol of **7** and 0.038 mol of 9-methylanthracene in 60 mL of 2:1 CH_3CN/CH_2Cl_2 (79% yield by column chromatography on Fisher 20-28 mesh silica gel, grade 12, 1:1 CH_2Cl_2/petroleum ether eluent): mp 190–191 °C dec; ^{1}H NMR δ 2.33 (s, 3 H), 5.43 (s, 1 H), 7.43 (m, 8 H); ^{19}F NMR δ –56.92 (s). Anal. Calcd for $C_{18}H_{12}F_6O_2S$: C, 53.20; H, 2.98; S, 7.89. Found: C, 53.03; H, 2.86; S, 7.90.

11,11-Bis(trifluoromethyl)-9,10-dimethyl-9,10-dihydro-9,10-(methano)anthracene (28). From 5.57 mmol of **7** and 4.80 mmol of 9,10-dimethylanthracene in 15 mL of CH_3CN and 40 mL of CH_2Cl_2 (83% yield): mp 194–195 °C (ether triturate); ^{1}H NMR δ 2.33 (s, 6 H), 7.47 (m, 8 H); ^{19}F NMR δ –57.4 (s); mass spectrum, *m*/*e* 356.0991 (M, calcd 356.0999), 341.0762 (M – CH_3, calcd 341.0765), 287.1049 (M – CF_3, calcd 287.1048), 206.1086 (M – 2CF_3, calcd 206.1095), 191.0853 (M – CH_3, 2CF_3; calcd 191.0860). Anal. Calcd for $C_{19}H_{14}F_6$: C, 64.08; H, 3.96; F, 32.01. Found: C, 64.97; H, 3.46; F, 32.52.

12,12-Bis(trifluoromethyl)-9,10-dimethyl-9,10-dihydro-9,10-(epithiomethyl)anthracene 11,11-Dioxide (27). To a solution of 2.03 g (5 mmol) of **26** in 50 mL of dry tetrahydrofuran chilled to –78 °C was added dropwise 3.8 mL of 1.6 M butyllithium in hexane at such a rate so as to keep the temperature of the reaction mixture below –70 °C. The resulting pale yellow solution was stirred 30 min and then 0.95 g (7 mmol) of methyl iodide in 5 mL of dry tetrahydrofuran was added dropwise while keeping the reaction mixture below –70 °C. After being stirred for 15 min, the mixture was allowed to warm to room temperature and stirred an additional 30 min. The mixture was concentrated to an oil which was dissolved in 50 mL of CH_2Cl_2, washed with water, and filtered. The filtrate was warmed, hexane was added to the cloud point, and the mixture was allowed to stand overnight. The mixture was then chilled in a dry-ice bath and filtered to afford 1.57 g (75%) of **27**: mp 207 °C dec; ^{1}H NMR δ 2.33 (s, 3 H), 2.35 (s, 3 H), 7.45 (m, 4 H), 7.58, 7.65 (AB m of m, 4 H); ^{19}F NMR δ –56.30 (s). Anal. Calcd for $C_{19}H_{14}F_6O_2S$: C, 54.28; H, 3.36; F, 27.12. Found: C, 54.23; H, 3.42; F, 27.12.

(*E*)-(2-Deuterioethenyl)-4-methoxybenzene.[58] Borane–dimethyl sulfide complex (4.43 mL, 44.3 mmol) was added dropwise over 10 min to 8.86 mL (88.6 mmol) of dry cyclohexene in 45 mL of dry diethyl ether chilled to 0 °C. After the mixture was stirred for 3 h at 0 °C, a solution of 5.85 g (44.3 mmol) of 4-methoxyphenylacetylene[59] in 12 mL of diethyl ether was added dropwise. The mixture was stirred at 0 °C until the solid dicyclohexylborane had completely dissolved (ca. 18 h). Then 2 mL (50 mmol) of methanol-d_1 (99.5% d_1) was added, followed by 0.13 mL (2.2 mmol) of acetic acid-d_1 (98% d_1). The mixture was warmed to room temperature, stirred for 2 h, and rechilled to 0 °C. Ethanolamine (3.0 mL, 50 mmol) was added and the mixture was stirred for 30 min at 0 °C. The white dicyclohexylborane–ethanolamine complex which precipitated was removed by filtration and washed with pentane (2 × 20 mL). The filtrates were combined and washed with water and brine and dried ($MgSO_4$). The filtrate mixture was concentrated, and the residual oil was fractionated to give 4.1 g (68%) of isomerically pure (*E*)-(2-deuterioethenyl)-4-methoxybenzene (97.5% d_1): bp 40–42 °C (0.5 mm); ^{1}H NMR δ 3.74 (s, 3 H), 5.57 (d, 1 H, J = 17.6 Hz), 6.63 (d, 1 H, J = 17.6 Hz), 6.82, 7.31 (AA′BB′m, 4 H, J_{AB} = 8.7 Hz); ^{2}H NMR ($CHCl_3$) δ 5.00 (s).

X-ray Data. Crystals of **12b** were grown by slow evaporation from a petroleum ether solution, and those of **17** were obtained from diethyl ether/pentane. Large crystals of **12b** (0.33 × 0.40 × 0.44 mm) and **17** (0.35 × 0.25 × 0.30 mm) were coated with vaseline and positioned in glass capillaries. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer, graphite monochromator. For **12b**, the intensities of 3546 independent reflections were measured in the range 1.6° ≤ 2θ ≤ 55.0° with Mo Kα radiation, using the ω-scan method (1145 unique reflections were obtained). The crystal temperature was held at –75 °C. For **17**, 8711 independent reflections were measured on the crystal held at –35 °C in the range 5.2° ≤ 2θ ≤ 120.0° with Cu Kα radiation (3664 unique reflections were obtained).

The structures were solved by direct methods (MULTAN), with full-matrix, least-squares refinement on F (the solution of **17** was complicated by the presence of four independent molecules in the unit cell). The atomic scattering factors, including anomalous terms for S, were taken from the "International Tables for X-ray Chrystallography", Vol. IV. All hydrogen atoms were fixed in idealized positions. For **12b**, all non-hydrogen atoms were refined anisotropically. For **17**, S, F, and O were refined anisotropically and C isotropically.

For **12b**: orthorhombic; space group *Pbca* (No. 61); a = 9.328 (5) Å, b = 25.961 (18) Å, c = 10.880 (8) Å, V = 2634.8 Å^3, Z = 8. Final R = 0.066, R_w = 0.068 for 190 independent variables. For **17**: triclinic; space group $P\bar{1}$ (No. 2); a = 12.503 (6) Å, b = 13.693 (4) Å, c = 17.955 (8) Å, V = 2824.6 Å^3, Z = 8. Final R = 0.096, R_w = 0.108 with 501 independent variables.

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Supplementary Material Available: Crystal structure analysis and tables of atomic coordinates, bond distances and bond angles, thermal parameters, and structure amplitudes for compounds **12b**, **17**, **26**, and **27** (25 pages). Ordering information is given on any current masthead page.

Dianions and Dications Derived from Bridged [4*n* + 2]Annulenes. Paratropism as a Function of Ring Size, Conformation, and Configuration

Klaus Müllen,* Thomas Meul, Peter Schade, Hans Schmickler, and Emanuel Vogel

Contribution from the Department of Organic Chemistry, University of Mainz, D-6500 Mainz, FRG, and the Department of Organic Chemistry, University of Köln, D-5000 Köln, FRG.

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Abstract: Reduction and oxidation of bridged annulenes afford dianion and dication salts which are characterized by spectroscopic and chemical means. A broad series of title compounds is included in order to systematically vary the size, conformation, and configuration of the perimeters. These structural features markedly affect the observed paratropism of the $(4n)\pi$-ions, which is discussed in terms of the HOMO/LUMO gap and the degree of π-bond fixation. Paratropic annulene ions thus appear as most sensitive probes of bond theory. Information on the π-charge distribution in the dianions and dications comes from ^{13}C NMR studies and quenching experiments, the latter leading to useful synthetic applications.

1. Introduction

The bridging of annulenes[1-8] causes a perturbation of the π-bonding and gives rise to deviations from the expected properties of an ideal D_{nh} perimeter. For the purpose of chemical and spectroscopic considerations the inductive, hyperconjugative, and homoconjugative effects of the bridging must be worked out separately.[9-20] On the other hand, the introduction of saturated bridging groups offers the advantage that the π-perimeters are fixed within a particular ring configuration and ring conformation[21] and that one can construct homologous series of increasing ring size. These structural features allow one to assess electronic effects in a clear-cut way.

Knowledge of the frontier orbitals of a π-system is essential for an understanding of the prevailing bonding situation.[22] The creation of new frontier orbitals in annulenes upon going to the corresponding radical anions and radical cations has therefore proven a useful technique.[23,24] The spin density distribution which is inferred from ESR hyperfine coupling constants sensitively reflects the electronic effects of the bridging groups and the deviation of the perimeter from planarity.[18]

Further reduction (oxidation) toward the corresponding dianions (dications), although raising serious experimental difficulties, constitutes another promising approach:[25] (i) the creation of diamagnetic species brings into play NMR spectroscopy, which has proven the most significant method in the annulene field[26-28] (this is because the fundamental alternative of π-bond delocalization vs. π-bond localization[29-34] can be described via a number

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