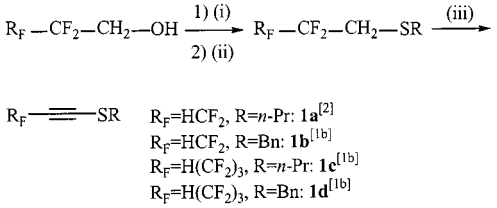
1-(Alkylsulfinyl- and -alkylsulfonyl)-2-(F-alkyl)ethynes − Applications in Cycloaddition Reactions and Synthesis of Aromatic Derivatives

Jean-Philippe Bouillon,[a] Rostyslav Musyanovich,[b] Charles Portella,*[a] and Yuriy Shermolovich*[b]

Keywords: Alkynes / Arenes / Cycloadditions / Fluoroorganic compounds / Organosulfur compounds

Syntheses and cycloaddition reactions of 1-(alkylsulfinyl- and -alkylsulfonyl)-2-(F-alkyl)ethynes are described. These alkynes are strong dienophiles and produce the corresponding F-alkylated sulfinyl- and sulfonylbenzenes in two high-yielding steps. When treated under basic conditions, the (F-alkyl)cyclohexadienyl adducts were converted into a mixture of the same aromatic compounds and the corresponding α-defluorinated derivatives, by way of a competitive oxidation/(HF) elimination on the deprotonated intermediates.

In the framework of a program on the chemistry of 1,1-dihydroperfluoroalkyl sulfides,[1] we recently reported a method for the synthesis of 1-(alkylsulfanyl)-2-(perfluoroalkyl)ethynes **1**,[1b,2] a new type of fluorine-containing alkynes[3] (Scheme 1).

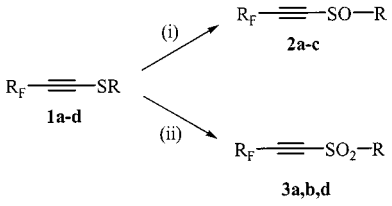


Scheme 1. (i) TsCl; (ii) RSH, KOH, DMSO; (iii) KOH, dioxane, 18-crown-6

The presence of a sulfur atom on the carbon−carbon triple bond significantly influences the chemical properties of these alkynes, modifying the regioselectivity of nucleophilic addition with respect to alkynes bearing only a perfluoroalkyl (F-alkyl)[4] group.[5] Modification of the oxidation state of the sulfur atom should also strongly influence the properties of oxidized derivatives. The ability of alkynes bearing sulfinyl[6,7] and sulfonyl[8−11] groups to take part in cycloaddition reactions with dienes is well documented. Such cycloadditions with fluorine-containing sulfinyl- and/or sulfonylalkynes would produce new cycloalkadienes, potential precursors of new polysubstituted F-alkyl aromatic derivatives. In this paper we report our study into the syntheses of 1-(alkylsulfinyl)- and 1-(alkylsulfonyl)-2-(F-alkyl)ethynes **2** and **3**, their cycloaddition reactions with 1,3-dienes, and the chemical transformations of the corresponding cycloadducts.

Results and Discussion

Similarly to the non-fluorinated series,[12] alkynes **1a−d** reacted easily with *m*-chloroperbenzoic acid, giving the corresponding sulfoxides **2a−c** or sulfones **3a**, **3b**, or **3d**, depending on the stoichiometry of the reactants (Scheme 2, Table 1).[13] Compounds **2a**, **2b**, **3a**, and **3b** are stable, yellow liquids at room temperature. They partially decompose on vacuum distillation but can be purified by silica gel chromatography. Compounds **2c** and **3d** decomposed on silica gel and were used without isolation (**2c**) or purification (**3d**) in further transformations.



Scheme 2. MCPBA, CH_2Cl_2, −15 °C to room temp.: (i) 1.35 equiv.; (ii) 2.70 equiv.

Table 1. Preparation of sulfoxides **2a−c** and sulfones **3a**, **3b**, and **3d**

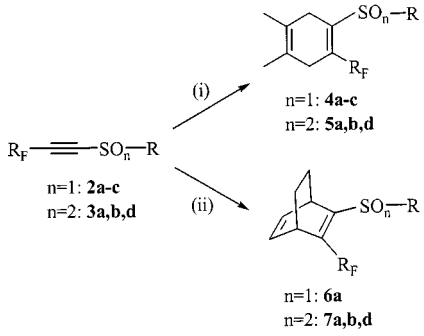
Entry	Sulfide	R_F	R	Sulfoxide or sulfone (% yield)
1	**1a**	HCF_2	*n*Pr	**2a** (76)[5]
2	**1b**	HCF_2	Bn	**2b** (87)
3	**1c**	$H(CF_2)_3$	*n*Pr	**2c** (−)[a]
4	**1a**	HCF_2	*n*Pr	**3a** (87)
5	**1b**	HCF_2	Bn	**3b** (82)
6	**1d**	$H(CF_2)_3$	Bn	**3d** (61)[b]

[a] Compound **2c** was used without isolation for further transformations. − [b] Crude compound.

[a] Laboratoire "Réactions Sélectives et Applications", Associé au CNRS (UMR 6519), Université de Reims, Faculté des Sciences, B. P. 1039, 51687 Reims Cedex 2, France
[b] Institute of Organic Chemistry, NAS of Ukraine, Murmanskaya Str. 5, 02094 Kiev, Ukraine
Supporting information for this article is available on the WWW under http://www.eurjoc.com or from the author.

  1434−193X/01/1019−3625 $ 17.50+.50/0

Sulfoxides **2** and sulfones **3** reacted effectively at room temperature with 2,3-dimethylbutadiene, giving the corresponding cyclohexa-1,4-dienes **4** and **5**, respectively. Similarly, treatment with 1,3-cyclohexadiene produced bicyclo-[2.2.2]octadienes **6** and **7** (Scheme 3, Table 2). The particular substitution pattern of our alkynes enhances their dienophilic reactivity in comparison with that of 1-alkyl-2-sulfonylethyne,[9,14] 1-(F-alkyl)ethyne,[15] and even 2-F-alkynoic acids.[16] The reactivity strongly depends on the oxidation state of sulfur (**3** > **2**). When treatment of 1-(alkylsulfinyl)-2-(difluoromethyl)ethynes **2a** and **2b** was carried out under aerobic conditions, minor proportions of the cycloadducts were oxidized to the corresponding aromatic derivatives (Table 2; Entries 1, 2). The aerial oxidation was confirmed by 50% conversions of **4a** and **4b** into **8a** and **8b** after one week's exposition to air. The sulfinylcyclohexadienes **4a** and **4b** were obtained cleanly when the cycloaddition reaction was carried out under argon. It is noteworthy that this spontaneous aromatization in air occurred only with cycloadducts **4a** and **4b**. Neither sulfonylated cyclohexadienes **5** nor long F-alkyl-substituted sulfinylcyclohexadiene **4c** were modified on long exposure to air. The higher stability of these compounds probably results from a higher oxidation potential, due to the enhanced electron-withdrawing characters of the highly fluorinated substituent and/or of highly oxidized sulfur. The cycloadducts **6a** and **7a**, **7b**, and **7d**, obtained from 1,3-cyclohexadiene, are stable compounds which can be stored at room temperature for several weeks without significant transformation. It is notable that no diastereoselection occurred from the sulfinylalkyne **2a** (Table 2; Entry 7). Easy and nearly quantitative (^{19}F NMR) conversion of sulfoxides **4a** and sulfones **5a**, **5b**, and **5d** into the corresponding aromatic derivatives **8a** and **9a**, **9b**, and **9d** occurred on treatment with dichlorodicyanobenzoquinone at room temperature (Scheme 4, Table 3).



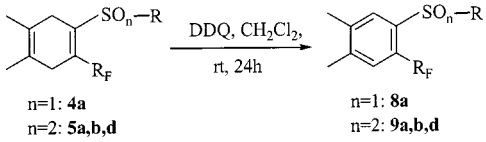
Scheme 3. Room temp., 24 h: (i) 2,3-dimethylbutadiene; (ii) 1,3-cyclohexadiene

Elimination of sulfinic acid on treatment with base is a typical transformation of sulfonylated cyclohexa-1,4-dienes, applied for the synthesis of aromatic derivatives.[9] Owing to the F-alkyl substitution, the cyclohexadienyl sulfones and sulfoxides **5** and **4** showed no elimination. When sulfoxide **4a** was treated with potassium hydroxide in dioxane, two aromatic compounds were obtained (Scheme 5, Table 4) in fair to good overall yields.

Table 2. Cycloaddition reactions with 2,3-dimethylbutadiene and 1,3-cyclohexadiene

Entry	Alkyne	Diene	*n*	R_F	R	Cycloadduct (% yield)
1	**2a**	(i)	1	HCF_2	*n*Pr	**4a** (69)[a]
2	**2b**	(i)	1	HCF_2	Bn	**4b** (60)[a]
3	**2c**	(i)	1	$H(CF_2)_3$	*n*Pr	**4c** (83)
4	**3a**	(i)	2	HCF_2	*n*Pr	**5a** (100)
5	**3b**	(i)	2	HCF_2	Bn	**5b** (97)
6	**3d**	(i)	2	$H(CF_2)_3$	Bn	**5d** (89)
7	**2a**	(ii)	1	HCF_2	*n*Pr	**6a** (68)[b]
8	**3a**	(ii)	2	HCF_2	*n*Pr	**7a** (89)
9	**3b**	(ii)	2	HCF_2	Bn	**7b** (92)
10	**3d**	(ii)	2	$H(CF_2)_3$	Bn	**7d** (89)

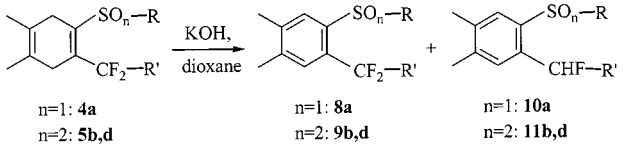
[a] Compounds **4a** and **4b** were accompanied by the corresponding aromatic products **8a** (yield: 8%) and **8b** (yield: 9%), respectively. – [b] Mixture of diastereomers (56:44).



Scheme 4

Table 3. Treatment of cyclohexa-1,4-dienes **4a**, **5a**, **5b**, and **5d** with DDQ

Entry	Cycloadduct	*n*	R_F	R	Aromatic product (% yield)
1	**4a**	1	HCF_2	*n*Pr	**8a** (71)
2	**5a**	2	HCF_2	*n*Pr	**9a** (85)
3	**5b**	2	HCF_2	Bn	**9b** (85)
4	**5d**	2	$H(CF_2)_3$	Bn	**9d** (51)



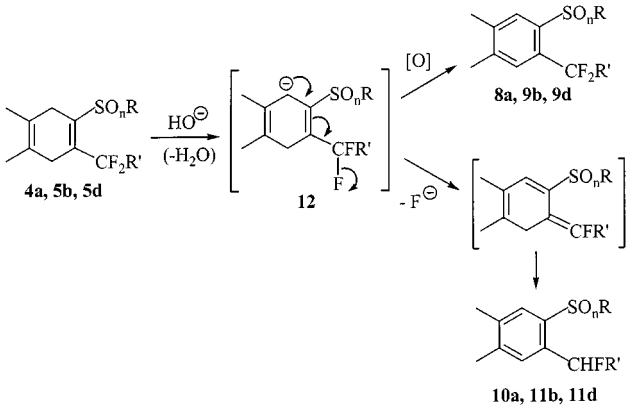
Scheme 5

Table 4. Treatment of cyclohexa-1,4-dienes **4a**, **5b**, and **5d** with KOH

Entry	Cycloadduct	*n*	R′	R	Products (% yield)	
1	**4a**	1	H	*n*Pr	**8a** (35)	**10a** (41)
2	**5b**	2	H	Bn	**9b** (30)	**11b** (20)
3	**5d**	2	$H(CF_2)_2$	Bn	**9d** (35)	**11d** (30)

The production of the (difluoromethyl)aryl sulfoxide **8a** corresponds, at least formally, to a simple oxidative aromatization. The new (fluoromethyl)aryl sulfoxide **10a** is the result of an HF elimination, which can easily be explained as shown in Scheme 6. Performance of the reaction under argon did not prevent the formation of **8a**, but other unidenti-

fied products appeared. This seems to indicate that **8a** is the result of oxidation of the intermediate anion **12** by oxygen or, under anaerobic conditions, by the sulfoxide itself (Scheme 6).



Scheme 6.

Very similar results were observed when the cyclohexadienyl sulfones **5b** and **5d** were treated with KOH under the same conditions, giving the (F-alkyl)aryl sulfones **9b** and **9d** and the corresponding α-defluorinated aryl sulfones **11b** and **11d** (Scheme 5, Table 4). Neither the degree of fluorination nor the oxidation state of the sulfur atom seems to have any significant influence on the basic reactivity of the cycloadducts **4a**, **5b**, and **5d**.

Summary

1-(Alkylsulfanyl)-2-(F-alkyl)alkynes, easily prepared from 1,1-dihydro-F-alkanols, were converted into the corresponding sulfoxides and sulfones, which proved to be strong dienophiles. Their [4+2] cycloadditions with dienes permitted an effective two-step synthesis of 1-(alkylsulfinyl- and -sulfonyl)-2-(F-alkyl)benzenes. Under basic conditions, partial HF elimination resulted in the corresponding α-defluorinated aromatic derivatives.

Experimental Section

General Remarks:[17] The syntheses of sulfides **1a**−**d** have been described previously.[1b,2]

Synthesis of Sulfoxides 2 and Sulfones 3. − General Procedure: The appropriate quantity (for the preparation of sulfoxides: 0.027 mol, 1.35 equiv.; for the preparation of sulfones: 0.054 mol, 2.70 equiv.) of *m*-chloroperbenzoic acid (Janssen Chimica, technical quality, 75%) was added at −15 °C to a solution of acetylenic sulfide (0.02 mol) in dichloromethane (30 mL). The reaction mixture was stirred for 0.5 h at −15 °C and then for 24 h at room temperature. *m*-Chlorobenzoic acid was filtered off, and the filtrate was concentrated in vacuo (15−20 mbar) to approximately half of its original volume, and then cooled to −15 °C. An additional quantity of *m*-chlorobenzoic acid was filtered off, and the filtrate was again concentrated in vacuo (15−20 mbar). The sulfoxides and the sulfones were generally purified by chromatography on silica gel (petroleum ether/ethyl acetate, 70:30). The sulfone **3b** was recrystallized from dichloromethane. The sulfoxide **2c** and the sulfone **3d** were used without additional purification. Compound **2a** was described previously.[5]

1-(Benzylsulfinyl)-3,3-difluoropropyne (2b): Yield: 87%. Oil. − ^{1}H NMR: δ = 4.42 (m, 2 H, CH_2), 6.29 (t, 1 H, $^2J_{H,F}$ = 53.4 Hz, CHF_2), 7.3−7.5 (m, 5 H, Ph). − ^{13}C NMR: δ = 61.9 (s, CH_2), 84.8 (t, $^3J_{C,F}$ = 8.2 Hz, CSO), 91.6 (t, $^2J_{C,F}$ = 36.4 Hz, *C*CHF_2), 102.7 (t, $^1J_{C,F}$ = 237.1 Hz, CHF_2), 127.6 (s, C_4 Ph), 128.8 (s, 2 × CH Ph), 129.1 (s, CH Ph), 130.4 (s, 2 × CH Ph). − ^{19}F NMR: δ = −110.1 (d, $^2J_{H,F}$ = 53.4 Hz, CHF_2). − IR (film): $\tilde{\nu}$ = 3018, 2203, 1366, 1216, 1116, 1064 cm^{-1}. − MS; *m*/*z*: 214 [M$^+$], 181, 139, 123. − $C_{10}H_8F_2OS$ (214.2): calcd. C 56.07, H 3.76; found C 56.42, H 3.62.

3,3-Difluoro-1-(propylsulfonyl)propyne (3a): Yield: 87%. − ^{1}H NMR: δ = 1.13 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H), 1.9−2.1 (m, 2 H, CH_2), 3.25 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 6.34 (t, 1 H, $^2J_{H,F}$ = 53.4 Hz, CHF_2). − ^{13}C NMR: δ = 12.8 (s, CH_3), 15.5 (s, CH_2), 56.0 (s, CH_2), 80.4 (t, $^3J_{C,F}$ = 7.8 Hz, CSO_2), 81.7 (t, $^2J_{C,F}$ = 36.0 Hz, *C*CF_2 H), 102.7 (t, $^1J_{C,F}$ = 238.0 Hz, CHF_2). − ^{19}F NMR: δ = −111.6 (d, $^2J_{H,F}$ = 53.4 Hz, CHF_2). − IR (film): $\tilde{\nu}$ = 2961, 2857, 2230, 1462, 1410, 1283, 1110 cm^{-1}. − MS; *m*/*z*: 182 [M$^+$], 162, 107, 43.

Synthesis of Cyclohexa-1,4-dienes 4 and 5 and Bicyclo[2.2.2]octa-2,5-dienes 6 and 7. − General Procedure: A mixture of sulfoxides **2** or sulfones **3** (0.010 mol) and 2,3-dimethylbutadiene or 1,3-cyclohexadiene (0.012 mol, 1.2 equiv.) was stirred for 24 h at room temperature. The excess of diene was evaporated in vacuo (15−20 mbar) and the cycloadducts were purified by chromatography on silica gel (petroleum ether/ethyl acetate, 85:15) or by recrystallization from petroleum ether.

1-(Difluoromethyl)-4,5-dimethyl-2-(propylsulfinyl)cyclohexa-1,4-diene (4a): Yield: 69%. Oil. − ^{1}H NMR: δ = 1.08 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2), 1.6−1.9 (m, 2 H), 1.70 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 2.5−2.7 (m, 1 H), 2.8−3.1 (m, 4 H), 3.1−3.3 (m, 1 H), 6.81 (t, 1 H, $^2J_{H,F}$ = 57.2 Hz, CHF_2). − ^{13}C NMR: δ = 12.8 (s, CH_3), 16.2 (s, CH_2), 17.6 (s, CH_3), 17.8 (s, CH_3), 26.4 (s, CH_2), 30.1 (d, $^3J_{C,F}$ = 3.9 Hz, CH_2), 53.5 (s, CH_2), 109.5 (dd, $^1J_{C,F}$ = 237.1, 234.8 Hz, CHF_2), 121.3 (s, 2 × *C*-CH_3), 134.1 (dd, $^2J_{C,F}$ = 25.8, 21.1 Hz, *C*CHF_2), 142.4 (dd, $^3J_{C,F}$ = 9.4, 7.0 Hz, CSO). − ^{19}F NMR: δ = −114.2 (dd, 1 F, $^2J_{F,F}$ = 316.7, $^2J_{H,F}$ = 57.2 Hz, CHF_AF_B), −120.3 (dd, 1 F, $^2J_{F,F}$ = 316.7, $^2J_{H,F}$ = 57.2 Hz, CHF_AF_B). − $C_{12}H_{18}F_2OS$ (248.3): calcd. C 58.03, H 7.30; found C 57.87, H 6.94.

1-(Benzylsulfonyl)-2-(difluoromethyl)-4,5-dimethylcyclohexa-1,4-diene (5b): Yield: 97%. White solid; m.p. 153−155 °C. − ^{1}H NMR: δ = 1.58 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 2.80 (m, 2 H, CH_2), 2.92 (m, 2 H, CH_2), 4.25 (s, 2 H, CH_2), 6.96 (t, 1 H, $^2J_{H,F}$ = 53.4 Hz, CHF_2), 7.25−7.34 (m, 2H Ph), 7.35−7.40 (m, 3H Ph). − ^{13}C NMR: δ = 17.8 (s, 2 × CH_3), 30.8 (t, $^3J_{C,F}$ = 3.9 Hz, CH_2), 34.7 (s, CH_2), 61.4 (s, CH_2), 109.5 (t, $^1J_{C,F}$ = 236.3 Hz, CHF_2), 121.2 (s, *C*CH_3), 121.3 (s, *C*CH_3), 127.1 (s, C_4 Ph), 128.9 (s, 2 × CH Ph), 129.3 (s, CH Ph), 130.8 (s, 2 × CH Ph), 136.6 (t, $^3J_{C,F}$ = 7.5 Hz, CSO_2), 141.6 (t, $^2J_{C,F}$ = 25.6 Hz, *C*CHF_2). − ^{19}F NMR: δ = −120.4 (d, $^2J_{H,F}$ = 53.4 Hz, CHF_2). − IR (KBr): $\tilde{\nu}$ = 3072, 2971, 2921, 2868, 1495, 1457, 1380, 1302, 1147, 1106 cm^{-1}. − MS; *m*/*z*: 292 [M$^+$ − HF], 201, 181, 137, 109, 91. − $C_{16}H_{18}F_2O_2S$ (312.4): calcd. C 61.52, H 5.81; found C 61.46, H 5.44.

1-(Benzylsulfonyl)-2-(1′,1′,2′,2′,3′,3′-hexafluoropropyl)-4,5-dimethylcyclohexa-1,4-diene (5d): Yield: 89%. White solid; m.p.

75−77 °C. − ^{1}H NMR: δ = 1.45 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 2.58 (m, 2 H, CH_2), 2.98 (t, $^4J_{H,F}$ = 7.6 Hz, 2 H, CH_2), 4.41 (s, 2 H, CH_2), 6.38 (tt, 1 H, $^2J_{H,F}$ = 51.8, $^3J_{H,F}$ = 5.7 Hz, CHF_2), 7.3−7.5 (m, 5 H, Ph). − ^{13}C NMR: δ = 17.3 (s, CH_3), 17.5 (s, CH_3), 34.7 (m, CH_2), 37.1 (s, CH_2), 62.8 (s, CH_2), 107.7 (tt, $^1J_{C,F}$ = 252.0, $^2J_{C,F}$ = 29.5 Hz, CHF_2), 111.2 (tm, $^1J_{C,F}$ = 253.5 Hz, CF_2), 115.7 (tt, $^1J_{C,F}$ = 255.9, $^2J_{C,F}$ = 30.5 Hz, CF_2C), 120.3 (s, CCH_3), 122.2 (s, CCH_3), 126.8 (s, quat. C Ph), 128.9 (s, 2 × CH Ph), 129.2 (s, CH Ph), 131.0 (s, 2 × CH Ph), 135.2 (t, $^2J_{C,F}$ = 23.4 Hz, CCF_2), 143.5 (m, CSO_2). − ^{19}F NMR: δ = −105.0 (m, 2 F, CF_2), −126.8 (td, $^3J_{F,F}$ = 8.0, $^3J_{H,F}$ = 6.5 Hz, CF_2), −138.9 (dtt, $^2J_{H,F}$ = 51.8, $^3J_{F,F}$ = 8.7, $^4J_{F,F}$ = 4.4 Hz, CHF_2). − IR (KBr): ṽ = 2924, 2863, 1495, 1456, 1320, 1202, 1151, 1123 cm^{-1}. − MS; *m*/*z*: 412 [M$^+$], 395, 321, 303, 181, 155. − $C_{18}H_{18}F_6O_2S$ (412.4): calcd. C 52.43, H 4.40; found C 52.24, H 4.06.

2-(Difluoromethyl)-3-(propylsulfinyl)bicyclo[2.2.2]octa-2,5-diene (6a): Yield: 68%. Oil. Mixture of diastereomers (56:44). − **Major Diastereomer:** ^{1}H NMR: δ = 1.08 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.4−1.6 (m, 4 H), 1.6−1.8 (m, 2 H), 2.7−2.9 (m, 2 H), 4.06 (m, 1 H, CH), 4.13 (m, 1 H, CH), 6.3−6.5 (m, 2 H, 2 × =CH), 6.93 (t, 1 H, $^2J_{H,F}$ = 55.7 Hz, CHF_2). − ^{13}C NMR: δ = 13.0 (s, CH_3), 15.7 (s, CH_2), 24.8 (s, CH_2), 25.5 (s, CH_2), 34.6 (s, CH), 36.2 (s, CH), 53.7 (s, CH_2), 108.7 (t, $^1J_{C,F}$ = 232.4 Hz, CHF_2), 133.1 (s, CH), 134.5 (s, CH), 143.9 (t, $^2J_{C,F}$ = 25.8 Hz, $CCHF_2$), 148.3 (t, $^3J_{C,F}$ = 9.4 Hz, CSO). − ^{19}F NMR: δ = −113.8 (dd, $^2J_{F,F}$ = 321.2, $^2J_{H,F}$ = 54.9 Hz, $CH\mathit{F_A}F_B$), −116.8 (dd, $^2J_{F,F}$ = 321.2, $^2J_{H,F}$ = 54.9 Hz, $CHF_A\mathit{F_B}$). − IR (film): ṽ = 2967, 2878, 1649, 1603, 1464, 1368, 1238, 1101. − MS; *m*/*z*: 246 [M$^+$], 219, 202, 175, 156, 137. − **Minor Diastereomer:** Selected data: ^{1}H NMR: δ = 1.01 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 4.27 (m, 1 H), 6.69 (t, 1 H, $^2J_{H,F}$ = 54.9 Hz, CHF_2). − ^{13}C NMR: δ = 24.9 (s, CH_2), 25.3 (s, CH_2), 33.8 (s, CH), 36.5 (s, CH), 54.0 (s, CH_2), 109.2 (t, $^1J_{C,F}$ = 232.4 Hz, CHF_2). − ^{19}F NMR: δ = −114.1 (dd, $^2J_{F,F}$ = 322.4, $^2J_{H,F}$ = 57.2 Hz, $CH\mathit{F_A}F_B$), −116.2 (dd, $^2J_{F,F}$ = 322.4, $^2J_{H,F}$ = 57.2 Hz, $CHF_A\mathit{F_B}$).

2-(Difluoromethyl)-3-(propylsulfonyl)bicyclo[2.2.2]octa-2,5-diene (7a): Yield: 89%. Oil. − ^{1}H NMR: δ = 1.03 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.4−1.9 (m, 6 H), 2.95 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 4.14 (m, 1 H), 4.24 (m, 1 H), 6.4−6.5 (m, 2 H, 2 × =CH), 7.27 (t, 1 H, $^2J_{H,F}$ = 55.5 Hz, CHF_2). − ^{13}C NMR: δ = 12.8 (s, CH_3), 15.8 (s, CH_2), 24.2 (s, CH_2), 24.9 (s, CH_2), 36.6 (s, CH), 39.1 (s, CH), 55.7 (s, CH_2), 108.3 (t, $^1J_{C,F}$ = 232.4 Hz, CHF_2), 133.0 (s, =CH), 133.9 (s, =CH), 144.0 (t, $^3J_{C,F}$ = 9.4 Hz, CSO_2), 149.2 (t, $^2J_{C,F}$ = 27.0 Hz, $CCHF_2$). − ^{19}F NMR: δ = −117.7 (d, $^2J_{H,F}$ = 55.5 Hz, CHF_2). − IR (film): ṽ = 2948, 2880, 1651, 1605, 1367, 1309, 1237, 1138, 1022 cm^{-1}. − MS; *m*/*z*: 262 [M$^+$], 234, 192, 172, 155, 127, 108.

Oxidation of Cyclohexa-1,4-dienes with DDQ. − General Procedure: A mixture of cyclohexa-1,4-dienes **4a**, **5a**, **5b**, or **5d** (0.015 mol) and DDQ (0.015 mol, 1 equiv.) in dichloromethane (15 mL) was stirred for 24 h at room temperature. The precipitate of dichlorodicyanohydroquinone was filtered off on Celite and the resulting solution was concentrated in vacuo (15−20 mbar). The aromatic compounds **8a**, **9a**, **9b**, or **9d** were purified by chromatography on silica gel (petroleum ether/ethyl acetate, 90:10) and then recrystallized from petroleum ether or petroleum ether/dichloromethane (80:20).

1-(Difluoromethyl)-4,5-dimethyl-2-(propylsulfinyl)benzene (8a): Yield: 71%. White solid; m.p. 63−64 °C (petroleum ether). − ^{1}H NMR: δ = 1.05 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.80 (m, 2 H, CH_2), 2.34 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.78 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 6.89 (t, 1 H, $^2J_{H,F}$ = 55.3 Hz, CHF_2), 7.40 (s, 1 H, =CH), 7.80 (s, 1 H, =CH). − ^{13}C NMR: δ = 13.1 (s, CH_3), 16.5 (s, CH_2), 19.6 (s, CH_3), 19.8 (s, CH_3), 59.7 (s, CH_2), 112.2 (t, $^1J_{C,F}$ = 239.5 Hz, CHF_2), 125.5 (s, =CH), 127.2 (t, $^3J_{C,F}$ = 7.0 Hz, =CH), 128.4 (t, $^2J_{C,F}$ = 23.5 Hz, CCF_2 × H), 140.0 (m, CSO), 140.5 (s, CCH_3), 141.2 (s, CCH_3). − ^{19}F NMR: δ = −102.4 (dd, 1 F, $^2J_{F,F}$ = 299.5, $^2J_{H,F}$ = 55.3 Hz, $CH\mathit{F_A}F_B$), −114.8 (dd, 1 F, $^2J_{F,F}$ = 299.5, $^2J_{H,F}$ = 55.3 Hz, $CHF_A\mathit{F_B}$). − IR (KBr): ṽ = 3019, 2977, 1605, 1491, 1427, 1267, 1202, 1092 cm^{-1}. − MS; *m*/*z*: 246 [M$^+$], 204, 184, 165, 123. − $C_{12}H_{16}F_2OS$ (246.3): calcd. C 58.51, H 6.55; found C 58.71, H 6.40.

1-(Benzylsulfonyl)-2-(difluoromethyl)-4,5-dimethylbenzene (9b): Yield: 85%. White solid; m.p. 118−119 °C (petroleum ether/dichloromethane, 80:20). − ^{1}H NMR: δ = 2.22 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 4.38 (s, 2 H, CH_2), 7.1−7.2 (m, 2 H Ph), 7.2−7.3 (m, 3 H Ph), 7.38 (t, 1 H, $^2J_{H,F}$ = 53.4 Hz, CHF_2), 7.36 (s, 1 H, =CH), 7.59 (s, 1 H, =CH). − ^{13}C NMR: δ = 19.2 (s, CH_3), 19.9 (s, CH_3), 63.6 (s, CH_2), 111.1 (t, $^1J_{C,F}$ = 238.2 Hz, CHF_2), 127.5 (s, quat. C Ph), 127.6 (t, $^3J_{C,F}$ = 7.0 Hz, =CH), 128.5 (s, 2 × CH Ph), 128.8 (s, CH Ph), 130.8 (s, 2 × CH Ph), 131.0 (t, $^2J_{C,F}$ = 22.5 Hz, $CCHF_2$), 132.4 (s, =CH), 132.7 (t, $^3J_{C,F}$ = 5.1 Hz, CSO_2), 140.0 (s, CCH_3), 143.9 (s, CCH_3). − ^{19}F NMR: δ = −112.8 (d, 2 F, $^2J_{H,F}$ = 53.4 Hz, CHF_2). − IR (KBr): ṽ = 3073, 2940, 1604, 1495, 1380, 1290, 1088 cm^{-1}. − GC MS; *m*/*z*: 310 [M$^+$], 195, 105, 91, 65. − $C_{16}H_{16}F_2O_2S$ (311.4): calcd. C 61.72, H 5.18; found C 61.33, H 4.90.

Treatment of Cyclohexa-1,4-dienes with KOH. − General Procedure: A mixture of cyclohexa-1,4-dienes **4a**, **5b**, or **5d** (0.01 mol) and KOH (0.02 mol, 2 equiv.) in dioxane (25 mL) was stirred for 24 h at room temperature (for cyclohexa-1,4-diene **5d**: at −110 °C, for 10 min). The solid was filtered off and the filtrate was concentrated in vacuo (15−20 mbar). Diethyl ether (20 mL) was added to the resulting mixture and the solution was then washed with water (2 × 10 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuo (15−20 mbar). The residues were purified by chromatography on silica gel (petroleum ether/ethyl acetate, 90:10) to give the difluoromethyl derivatives **8a** (yield: 35%), **9b** (yield: 30%), and **9d** (yield: 35%) and the fluoromethyl derivatives **10a**, **11b**, and **11d**. Analytical samples of compounds **10a**, **11b**, and **11d** were obtained by recrystallization from petroleum ether.

1-(Fluoromethyl)-4,5-dimethyl-2-(propylsulfinyl)benzene (10a): Yield: 41%. White solid; m.p. 125−126 °C. − ^{1}H NMR: δ = 1.06 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.7−2.0 (m, 2 H, CH_2), 2.33 (s, 3 H, CH_3), 2.36 (d, $^6J_{C,F}$ = 2.3 Hz, 3 H, CH_3), 2.80 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 5.31 (dd, 1 H, $^2J_{H,F}$ = 49.6, $^2J_{H,H}$ = 10.9 Hz, $CH\mathit{_A}H_BF$), 5.55 (dd, 1 H, $^2J_{H,F}$ = 49.6, $^2J_{H,H}$ = 10.9 Hz, $CH_A\mathit{H_B}F$), 7.78 (s, 1 H, =CH), 7.19 (d, $^4J_{H,F}$ = 1.5 Hz, 1 H, =CH). − ^{13}C NMR: δ = 13.1 (s, CH_3), 16.3 (s, CH_2), 19.4 (s, CH_3), 19.6 (s, CH_3), 59.6 (s, CH_2), 81.0 (d, $^1J_{C,F}$ = 166.7 Hz, CH_2F), 125.3 (s, =CH), 129.8 (d, $^2J_{C,F}$ = 16.4 Hz, CCH_2F), 131.3 (d, $^3J_{C,F}$ = 7.0 Hz, =CH), 139.6 (d, $^3J_{C,F}$ = 5.5 Hz, CSO), 140.0 (s, CCH_3), 141.0 (s, CCH_3). − ^{19}F NMR: δ = −197.4 (t, 1F, $^2J_{H,F}$ = 49.6 Hz, CH_2F). − IR (film): ṽ = 2967, 2876, 1607, 1455, 1385, 1252, 1065 cm^{-1}. − MS; *m*/*z*: 228 [M$^+$], 209, 184, 166, 137, 105. − HRMS: calcd. for $C_{12}H_{17}FOS$ 228.0979; found 228.0985.

1-(Benzylsulfonyl)-2-(fluoromethyl)-4,5-dimethylbenzene (11b): Yield: 20%. White solid; m.p. 120−122 °C. − ^{1}H NMR: δ = 2.23 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 4.37 (s, 2 H, CH_2), 5.48 (d, $^2J_{H,F}$ = 47.5 Hz, 2 H, CH_2F), 7.07−7.13 (m, 2H Ph), 7.22−7.31 (m, 3H Ph), 7.32 (s, 1 H, =CH), 7.46 (s, 1 H, =CH). − ^{13}C NMR: δ = 19.2 (s, CH_3), 19.8 (s, CH_3), 63.4 (d, $^5J_{C,F}$ = 3.0 Hz, CH_2),

81.7 (d, $^1J_{C,F}$ = 165.4 Hz, CH_2F), 127.9 (s, quat. C Ph), 128.5 (s, 2 × CH Ph), 128.8 (s, CH Ph), 130.6 (d, $^3J_{C,F}$ = 10.8 Hz, =CH), 130.9 (s, 2 × CH Ph), 132.2 (s, =CH), 133.9 (d, $^2J_{C,F}$ = 16.7 Hz, CCH_2F), 137.95 (s, CCH_3), 137.99 (s, CCH_3), 143.8 (m, CSO_2). − ^{19}F NMR: δ = −209.7 (t, 1 F, $^2J_{H,F}$ = 47.5 Hz, CH_2F). − IR (KBr): ṽ = 3068, 2982, 2925, 1603, 1495, 1314, 1254, 1120 cm^{-1}. − MS; *m*/*z*: 292 [M^+], 228, 193, 137, 115, 109. − $C_{16}H_{17}FO_2S$ (292.4): calcd. C 65.73, H 5.86; found C 65.77, H 5.73.

Supporting Information: Spectroscopic data for compounds **2c**, **3b**, **3d**, **4b**, **4c**, **5a**, **7b**, **7d**, **8b**, **9a**, **9d**, and **11d** are available; see footnote on page 1.

Acknowledgments

We thank H. Bailla and S. Lanthony for NMR spectra and microanalyses. The CNRS (associate position to Yu. G. S.) and INTAS (fellowship to R. M.), and Network 95−005 are gratefully acknowledged.

[1] [1a] C. Portella, Yu. G. Shermolovich, O. Tschenn, *Bull. Soc. Chim. Fr.* **1997**, *134*, 697−702. − [1b] V. M. Timoshenko, V. V. Listvan, E. B. Rusanov, Yu. G. Shermolovich, L. N. Markovsky, *Zhur. Org. Khim.* **1997**, *33*, 70−76.

[2] Yu. G. Shermolovich, V. M. Timoshenko, R. Ya. Musyanovich, M. J. Povolotsky, V. V. Pirozhenko, L. N. Markovsky, *Heteroatom Chem.* **1998**, *9*, 151−154.

[3] Only two representatives of this type of compounds was described early: [3a]A. L. Braga, J. V. Comasseto, N. Petragnani, *Tetrahedron Lett.* **1984**, *25*, 1111−1114. − [3b] A. L. Belferman, V. U. Shevchuk, I. D. Kushina, M. M. Gilburd, B. G. Sirvatka, *J. Gen. Chem. USSR* **1967**, *37*, 1970−1974.

[4] We use the terminology "F-alkyl" to describe both perfluoroalkyl and polyfluoroalkyl groups.

[5] Yu. G. Shermolovich, R. Ya. Musyanovich, V. M. Timoshenko, L. N. Markovsky, *Heteroatom Chem.* **2000**, *11*, 383−386.

[6] W. E. Parham, R. F. Motter, G. L. O. Mayo, *J. Am. Chem. Soc.* **1959**, *81*, 3386−3389.

[7] [7a]K. Maignan, F. Belkasmioni, *Bull. Soc. Chim. Fr.* **1989**, *126*, 695−698. − [7b] A. W. M. Lee, W. H. Chan, M. S. Wong, *J. Chem. Soc., Chem. Commun.* **1988**, 1585−1586.

[8] M. Shen, A. G. Schultz, *Tetrahedron Lett.* **1981**, *22*, 3347−3350.

[9] O. De Lucchi, G. Licini, L. Pasquato, M. Senta, *Tetrahedron Lett.* **1988**, *29*, 831−834.

[10] T. G. Back, R. J. Bethell, M. Parvez, J. A. Taylor, D. Wehrli, *J. Org. Chem.* **1999**, *64*, 7426−7432.

[11] C. Zhang, C. J. Ballay II, M. L. Trudell, *J. Chem. Soc., Perkin Trans. 1* **1999**, 675−676.

[12] W. E. Truce, L. D. Markley, *J. Org. Chem.* **1970**, *35*, 3275−3281.

[13] Only one example of the synthesis of 1-(phenylsulfonyl)-2-(trifluoromethyl)acetylene by dehydrobromination of the corresponding ethylene was described previously: H.-C. Ming, H. Feng, J. Biao, X. Yuangoo, *J. Fluorine Chem.* **1994**, *66*, 215−218.

[14] D. L. J. Clive, R. J. Bergstra, *J. Org. Chem.* **1990**, *55*, 1786−1792.

[15] [15a] G. Pawlowski, M. Hanack, *Synth. Commun.* **1981**, *11*, 351−364. − [15b] E. S. Turbanova, N. A. Orlova, V. B. Lebedev, *Zhur. Org. Khim.* **1979**, *15*, 1155−1159.

[16] [16a] M. Kuwabara, K. Fukunishi, M. Nomura, H. Yamanaka, *J. Fluorine Chem.* **1988**, *41*, 227−240. − [16b] M. Kuwabara, A. Murakami, K. Fukunishi, M. Nomura, H. Yamanaka, *J. Fluorine Chem.* **1989**, *42*, 105−118.

[17] J.-P. Bouillon, B. Didier, B. Dondy, P. Doussot, R. Plantier-Royon, C. Portella, *Eur. J. Org. Chem.* **2001**, 187−192.

Received March 7, 2001
[O01116]