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3-Chloro-4-fluorothiophene-1,1-dioxide. A new synthetically useful fluorodiene

Wojciech Dmowski *, Vladimir A. Manko, Ireneusz Nowak

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

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Abstract

Simple, three step synthesis of a new fluorine containing diene, 3-chloro-4-fluorothiophene-1,1-dioxide (**4**), from commercially available 3-sulpholene (**1**) has been developed. The synthetic value of compound **4** as a Diels–Alder diene has been demonstrated by its reactions with various type of dienophiles: acetylenes, alkenes, furans, quinone and anthracene. The reactions proceed with high regioselectivity to give good yields of 3-fluoro-4-chloro substituted aromatics or cyclic chlorofluorodienes. In reactions with alkenes, immediate aromatisation often occurs. In some instances, when reacted with a diene, compound **4** behaves as a dienophile.

Keywords: Chlorofluorodienes; Chlorofluorothiophene dioxide; Cycloadditions; Chlorofluoroaromatics; Chlorofluorocyclodienes

1. Introduction

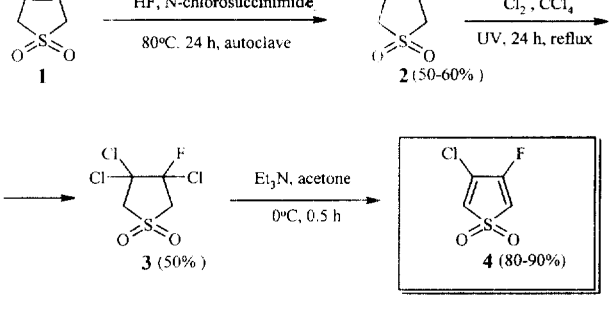
The Diels–Alder cycloaddition is one of the most fundamental and useful reactions in synthetic organic chemistry but only limited number of such reactions with fluorinated dienes have been reported till now. Highly fluorinated dienes are better known for their [2+2] reactions, rather then Diels–Alder type condensations. Exceptions are perfluorocyclopentadiene [1] and a few trifluoromethylated dienes [2] and heterocycles [3]; the latter are particularly prone to inverse-electron-demand Diels–Alder reactions with electron rich dienophiles. Dienes with low fluorine contents, such as 2-fluoro-1,3-butadiene and 2-fluoro-3-methyl-1,3-butadiene were reported to readily undergo [4+2] cycloadditions [4] but they are available only with difficulty.

On the other hand, it has been reported that di- and tetrachlorosubstituted thiophene-1,1-dioxides easily undergo cycloadditions with a variety of dienophiles, followed by loss of sulphur dioxide, to give high yields of haloaromatics and carbo- and heterocycles [5–7]. Unsubstituted thiophene dioxide is known to be very unstable so that it could not be isolated in a pure state but in a solution it readily dimerises with the liberation of SO_2, even at low temperature [8–10]. The presence of halogen atoms stabilises the thiophene dioxide molecule sufficiently to allow halosubstituted analogues to be isolated and stored but they still retain their reactivity as diene components in Diels–Alder reactions.

In the present work, we describe synthesis of the first fluorine containing thiophene dioxide, 3-chloro-4-fluorothiophene-1,1-dioxide (**4**), from the inexpensive commercially available precursor, 3-sulpholene (**1**) and demonstrate its applicability as a diene (in some instances also as a dienophile) in Diels–Alder type cycloadditions leading to chlorofluorosubstituted aromatics, heterocyclics and alicyclics.

2. Results and discussion

The synthetic route to 3-chloro-4-fluorothiophene-1,1-dioxide (**4**) is straightforward and involves three steps: chlorofluorination of 3-sulpholene (**1**) to 3-chloro-4-fluorosulpholane (**2**), photochemical chlorination of **2** to 3,3,4-trichloro-4-fluorosulpholane (**3**) and dehydro-chlorination of the latter:



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* Corresponding author.

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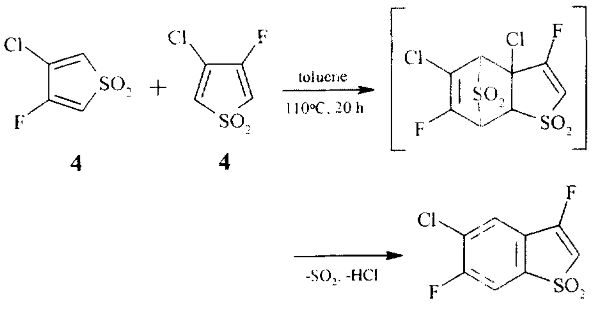
Heating of sulpholene (**1**), like many other alkenes [11], with anhydrous hydrogen fluoride and a source of halogen cation, i.e., *N*-chlorosuccinimide, resulted in a *trans*-addition of F–Cl to form *trans*-3-chloro-4-fluorosulpholane (**2**) which was easily purified from unconverted reagents simply by washing with water. Substitutive chlorinations of compound **2** to **3** proceeds in refluxing CCl_4 under efficient UV irradiation as described for the chlorination of 3,4-dichlorosulpholene [5]; trichlorofluorosulpholane **3** was separated by crystallisation from methanol. The final step, selective dehydrochlorination of **3**, was conveniently carried out in dry acetone with triethylamine as the base; the amine hydrochloride formed as the side product was removed by filtration and evaporation of the solvent, followed by recrystallisation of the residue from toluene, to give compound **4** sufficiently pure for investigation of its cycloaddition reactions. Anhydrous conditions during the dehydrohalogenation are essential for quantitative removal of solid $Et_3N \cdot HCl$.

3-Chloro-4-fluorothiophene-1,1-dioxide (**4**) is a white solid stable up to at least 100°C; it melts at ca. 110°C with darkening indicating decomposition. Compound **4**, when heated in toluene in the absence of dienophile, dimerises with the simultaneous loss of one molecule of sulphur dioxide and one molecule of hydrogen chloride to give in one step an aromatic product, 5-chloro-3,6-difluoro-benzothiophene-1,1-dioxide (**5**):

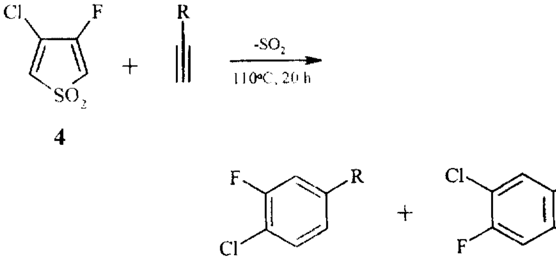


4 **4**

5 (57%)

The above reaction indicates that thiophene dioxide **4** could act either as a diene and a dienophile and suggests that the reactivity of **4** is between that of unsubstituted thiophene dioxide which dimerises spontaneously and that of tetrachloro-substituted analogues for which no such behaviour was reported. Interestingly, in this particular case, only the –C=C–Cl bond plays the role of a dienophile. Also, the cycloaddition proceeds with high regioselectivity; no 6-chloro-3,5-difluoro isomer was formed. It has been reported that the structural analog of **4**, 3,4-dichlorothiophene-1,1-dioxide, under analogous conditions gives a mixture of the dimeric and trimeric product, the latter resulting from cycloadditions to both –C=C–Cl bonds [5]. The structure of compound **5** has been shown by its ^{1}H and ^{13}C NMR data (Table 2) the most characteristic feature of which are two proton-to-fluorine couplings constants for H-4 proton ($^4J_{HF}$) and only one for H-7 proton ($^3J_{HF}$), two small carbon-to-fluorine coupling constants ($^3J_{CF}$) for C-8 carbon atom and one large coupling ($^2J_{CF}$) for C-9 carbon atom.

Annelation of alkynes with compound **4** gave reasonable yields of *ortho*-chlorofluoro aromatics **6**–**8** but usually these reactions were not fast enough to prevent concurrent self annelation leading to benzothiophene dioxide **5**. Cycloadditions of **4** to alkynes proceeded with full regioselectivity in such a way that in the resultant aromatic compounds the alkyne substituent R was always placed *para* to the chlorine atom. Thus, the reactions with phenylacetylene, 3-butyn-1-ol and propargyl bromide gave, respectively, 4-chloro-3-fluorobiphenyl (**6**), 3-(4-chloro-3-fluoro)-1-propanol (**7**) and 4-chloro-3-fluorobenzyl bromide (**8**) as the only aromatic compounds:

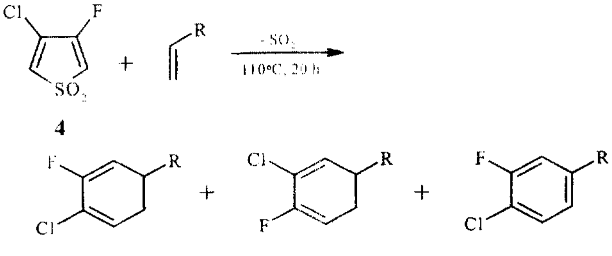


4

5

R = phenyl:	**6** (57%)	
R = CH_2CH_2OH:	**7** (38%)	11%
R = CH_2Br:	**8** (45%)	14%

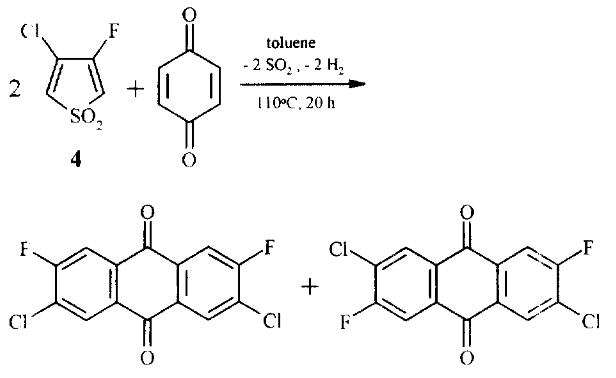
Reactions of **4** with alkenes proceeded with lower regioselectivity as compared to reactions with alkynes: thus, allyl alcohol and allyl bromide gave approximately 3:1 mixtures of isomeric cyclohexadienes **9a**, **9b** and **10a**, **10b**. In the latter case a considerable amount of aromatic compound **8** was also formed. It seems that the tendency to oxidative aromatisation of the initially formed cycloadducts increases with increased polarity of the reactant alkenes. Under standard reaction conditions methyl acrylate gave methyl 4-chloro-3-fluorobenzoate (**12**) as the main product with only a small amount of diene **11**, however, shortening the reaction time from 20 to 3.5 h resulted in the formation of isomeric dienes **11a** and **11b** as the main products. Thus, it is likely that aromatic products are formed as the result of slow thermal dehydrogenation of initially formed adducts; the rate of dehydrogenation probably increases in the presence of electron withdrawing substituents such as an ester group.



4

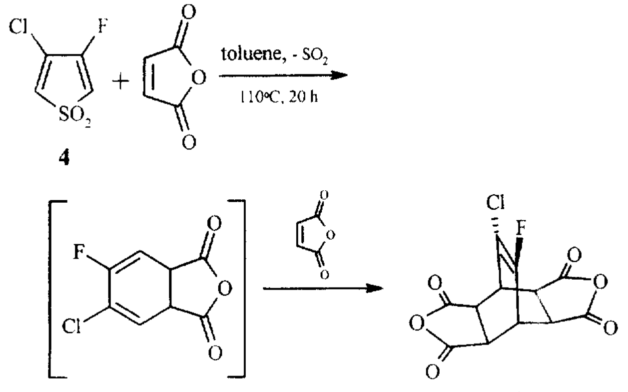
R = CH_2OH:	**9a** (60%)	**9b** (24%)	
R = CH_2Br:	**10a** (35%)	**10b** (10%)	**8** (23%)
R = CO_2CH_3	**11a** (6%)		**12** (63%)
3.5 h	**11a** (58%)	**11b** (19%)	**12** (7%)

1,4-Benzoquinone underwent double annelation with **4** to give high yield of a 1:1 mixture of isomeric dichloro-difluoroanthraquinones **13a** and **13b**. This reaction proceeded with spontaneous dehydrogenenation of the initial Diels–Alder adduct; the latter was not detected in the reaction mixture. It has been earlier suggested for the similar reaction of benzoquinone with 3,4-dichlorothiophene-1,1-dioxide that the dehydrogenation (aromatisation) mechanism involves enolisation of the adduct to hydroquinone followed by oxidation of the latter with an excess of benzoquinone [5].



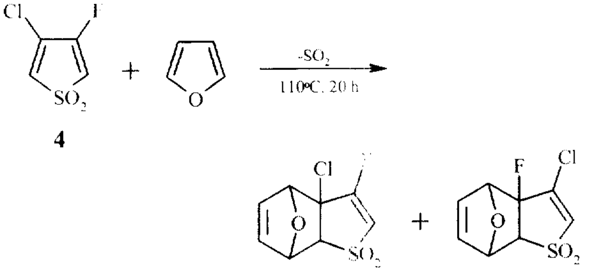
13a (1 : 1, total 86%) **13b**

Maleic anhydride reacted with **4** to give a 2:1 adduct **14** as the only isolable product; apparently the initially formed 1:1 adduct is a more reactive diene than compound **4**:

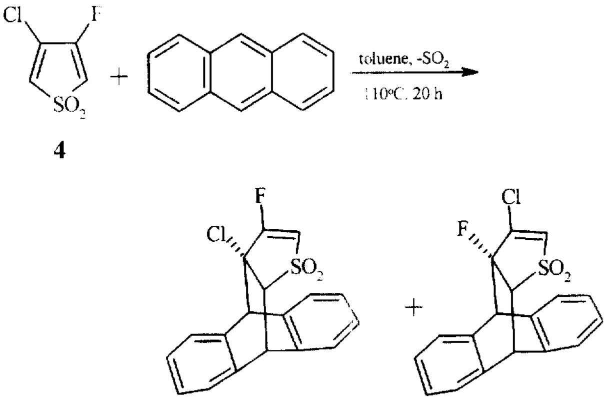


14 (45%)

In reactions with furan and anthracene, thiophene dioxide **4** behaves as a dienophile rather than as a diene: in both cases good yields of 1:1 adducts **15** and **16** were obtained. Similarly to the self-condensation of **4** leading to **5**, described above, the diene attacks predominantly the –C=C–Cl bond to give mainly isomers **15a** and **16a** with chlorine atom in a bridgehead position. Isomers **15b** and **16b** formed by annelation of the –C=C–F bond were only minor products:

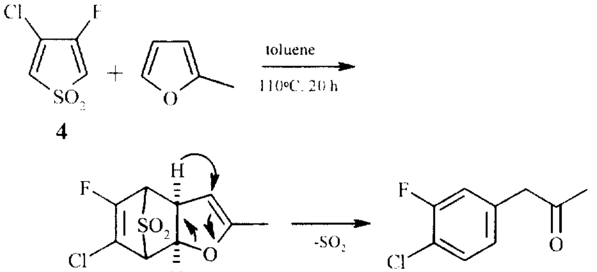


15a (60%) **15b** (4%)



16a (65%) **16b** (13%)

In contrast to furan, 2-methylfuran possesses strong dienophilic affinity towards **4**. The reaction, similarly to reactions of substituted furans with di- and tetrachloro analogues of **4** [7], proceeded with the furan ring opening and rearrangement of the primary adduct to yield methyl 3-chloro-4-fluorobenzyl ketone (**17**) almost quantitatively:



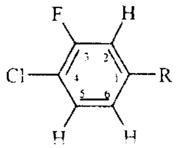
17 (90%)

Structures of aromatic compounds **6–8**, **12** and **17** have been assigned by comparison of their ^{13}C and ^{1}H NMR data (Table 1) with those reported for unsubstituted *ortho*-chlorofluorobenzene [12,13]. The ^{13}C chemical shifts and coupling constants of five aromatic carbon atoms, i.e., *ortho* to CF (C-2) and *ortho* and *meta* to CCl (C-5 and C-6), for our compounds are almost identical with those for the model compound. The only ^{13}C chemical shift which varies with the variation of a substituent R is that for a carbon atom *para* to CCl group (C-1) and, therefore, assigns the R group on this carbon atom, i.e., *para* to CCl and *ortho* to CF groups. Chemical shifts and coupling constants of aromatic protons for our compounds closely resemble those in the model compound.

Assignments of chlorine and fluorine atoms positions in the benzene ring of primary cycloadducts **9–11** have been

Table 1

^{13}C, ^{19}F and ^{1}H NMR data of chlorofluoroaromatics **6-8**, **12** and **17** and *ortho*-chlorofluorobenzene [12,13], δ (J Hz)



Compound	R = H	**6**: R = C_6H_5	**7**: R = CH_2CH_2OH	**8**: R = CH_2Br	**12**, R = CO_2CH_3	**17**: R = CH_2COCH_3
C-1 ($^3J_{CF}$)	128.8 (7.2)	141.8 (6.8)	139.7 (6.5)	139.7 (6.5)	130.4 (6.5)	134.8 (6.7)
C-2 ($^2J_{CF}$)	117.0 (20.8)	115.0 (21.7)	117.0 (20.7)	117.0 (20.7)	117.6 (22.6)	117.6 (21.1)
C-3 ($^1J_{CF}$)	158.8 (248.1)	158.3 (247.1)	157.8 (248.3)	157.7 (247.4)	157.8 (248.5)	157.9 (247.6)
C-4 ($^2J_{CF}$)	121.4 (17.5)	119.8 (17.8)	118.5 (17.6)	120.8 (17.6)	116.6 (21.7)	119.6 (17.5)
C-5 ($^3J_{CF}$)	131.2 (<0.3)	not resolved	130.3 (0.0)	130.7 (0.0)	130.7 (0.0)	130.6 (0.0)
C-6 ($^4J_{CF}$)	125.5 (4.0)	123.3 (3.6)	125.4 (3.5)	125.3 (3.6)	125.9 (3.8)	125.9 (3.6)
C-R		not resolved	38.2; 62.9	31.4	52.2; 174.2	29.5; 49.7; 204.8
F-3 ($^3J_{HF}$; $^4J_{HF}$)		115.8 (10.1; 7.5)	116.3 (9.9; 7.8)	114.9 (9.0; 7.9)	114.7 (9.3; 7.4)	115.7 (9.6; 7.7)
H-2 ($^3J_{HF}$; $^4J_{HH}$)	6.97 (9.06; 1.46)	7.2 - 7.7 multiplet complex	6.94 (10.0; 1.7)	7.19 (9.4; ~ 2)	7.80 (9.3, 1.60	6.98 (9.6; 2.0)
H-5 ($^4J_{HF}$; $^3J_{HH}$)	7.26 (7.29; 8.02)		7.22 (average 7.9)	7.36 (average 7.8)	7.48 (7.4, 8.8)	7.34 (average 7.9)
H-6 ($^3J_{HH}$; $^4J_{HH}$)	6.91 (8.02; 1.46)		6.87 (8.1; 1.7)	7.11 (7.0; ~ 2)	7.78 (8.8, 1.35)	6.94 (8.1; 2.0)
H-R			2.10 (s, OH); 2.74 and 3.74 (^3J = 6.4, CH_2CH_2)	4.42 (s, CH_2Br)	3.69 (s, CH_3)	2.19 (s, CH_3) 3.69 (s, CH_2)

Table 2
^{1}H, ^{19}F and ^{13}C NMR data of the cycloaddition products **5**, **9-11** and **13-16**

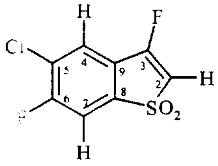
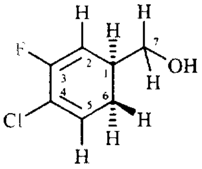
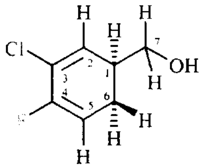
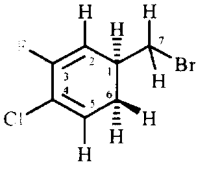
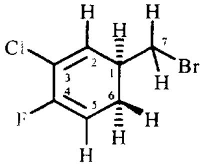
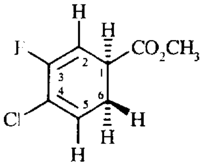
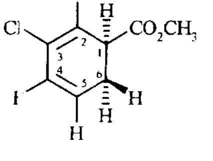
Compound	Nucleus: δ (mutiplicity, J Hz)
 **5**	H-2: 6.44 (dd, $^3J_{HF} = 2.3$, $J = 0.5$) H-4: 7.86 (dd, $^4J_{HF} = 6.0$ and 2.6) H-7: 7.34 (d, $^3J_{HF} = 7.4$) F-3: 121.8 (dd, $^4J_{HF} = 2.6$, $^3J_{HF} = 2.3$) F-6: 104.0 dd, $^3J_{HF} = 7.4$, $^4J_{HF} = 6.0$) C-2: 110.1 (d, $^2J_{CF} = 37.7$); C-3: 161.8 (dd, $^1J_{CF} = 272.8$, $^5J_{CF} = 2.1$); C-4: 110.3 (s); C-5: 125.9 (d, $^2J_{CF} = 19.7$) C-6: 160.8 (d, $^1J_{CF} = 275.5$); C-7: 127.9 (d, $^2J_{CF} = 28.7$) C-8: 135.6 (dd, $^3J_{CF} = 4.3$ and 3.1) C-9: 127.7 (d, $^2J_{CF} = 28.8$)
 **9a**	H-1 and OH: 2.7 (broad, very complex, 2H) H-2: 5.33 (dd, $^3J_{HF} = 12.0$, $^3J_{HH} = 4.3$) H-5: 5.96 (dt, $^4J_{HF} = 7.9$, $^3J_{HH} = 4.5$) H-6: 2.3-2.4 (complex AB, 2H) H-7: 3.56 and 3.59 (AB, $J_{AB} < 0.7$) F-3: 120.2 (ddd, $^3J_{HF} = 12.0$, $^4J_{HF} = 7.9$, $^5J_{HF} = 4.9$) C-1: 35.1 (d, $^3J_{CF} = 4.7$); C-2: 103.9 (d, $^2J_{CF} = 15.9$) C-3: 152.9 (d, $^1J_{CF} = 252.3$); C-4: 122.3 (d, $^2J_{CF} = 30.6$) C-5: 126.1 (s); C-6: 26.3 (s); C-7: 64.3 (d, $^4J_{CF} = 3.2$)
 **9b**	H-1,OH and H-6: overlapped by signals of isomer **9a** H-2: 5.94 (dd, $^4J_{HF} = 11.0$, $^3J_{HH} = 4.4$) H-5: 5.34 (dt, $^3J_{HF} = 11.5$, $^3J_{HH} = 4.7$) H-7: 3.59 and 3.62 (AB, $J_{AB} = 0.9$) F-4: 122.8 (td, $^3J_{HF} \approx {}^3J_{HF} \approx 11$, $^5J_{HF} \approx 5$) C-1: 37.8 (s); C-2: 125.8 (s); C-3: 123.8 (d, $^2J_{CF} = \text{ca. } 30$) C-4: 151.9 (d, $^1J_{CF} = 249.6$); C-5: 101.9 (d, $^2J_{CF} = 17.0$) C-6: 23.2 (d, $^3J_{CF} = 5.1$); C-7: 63.9 (s)
 **10a**	H-1: 2.78 (broad, very complex) H-2: 5.38 (dd, $^3J_{HF} = 11.7$, $^3J_{HH} = 4.8$) H-5: 5.97 (dt, $^4J_{HF} = 7.8$, $^3J_{HH} = 4.8$) H-6: 2.4-2.5 (complex AB, 2H) H-7: 3.33 and 3.36 (AB, $J_{AB} = 0.75$) F-3: 119.2 (ddd, $^3J_{HF} = 11.7_{0}$, $^4J_{HF} = 7.8$, $^5J_{HF} = 4.7$) C-1: 35.0 (d, $^3J_{CF} = 5.3$); C-2: 105.2 (d, $^2J_{CF} = 17.3$) C-3: 154.1 (d, $^1J_{CF} = 255.5$); C-4: 123.1 (d, $^2J_{CF} = 30.4$) C-5: 126.3 (s); C-6: 28.3 (s); C-7: 34.9 (d, $^4J_{CF} = 4.5$)
 **10b**	H-1 and H-6: overlapped by signals of isomer **10a** H-2: 5.945(dd, $^4J_{HF} = 7.5$, $^3J_{HH} = 5.5$) H-5: overlaped by the signal of isomer **10a** H-7: 3.36 and 3.39 (AB, $J_{AB} = 2.5$) F-4: 122.4 (ddd, $^3J_{HF} \approx 12.5$; $^4J_{HF} \approx 7.5$, $^5J_{HF} = 5.3$) C-1: 37.4 (s); C-2: 126.0 (d, $^3J_{CF} = 3.5$); C-3: not found C-4: 152.7 (d, $^1J_{CF} = 251.8$); C-5: 102.2 (d, $^2J_{CF} = 17.0$) C-6: 25.2 (d, $^3J_{CF} = 5.3$); C-7: 34.3 (s)
 **11a**	H-1: 3.35-3.55 (complex) H-2: 5.54 (dd, $^3J_{HF} = 11.5$, $^3J_{HH} = 4.3$) H-5: 6.02 (dt, $^4J_{HF} = 7.8$, $^3J_{HH} = 4.8$) H-6: 2.5-2.8 (complex AB, 2H); CH_3: 3.74 (s) F-3: 119.8 (ddd, $^3J_{HF} = 11.5$, $^4J_{HF} = 7.8$, $^5J_{HF} = 5.0$) C-1: 38.0 (d, $^3J_{CF} = 5.9$); C-2: 101.5 (d, $^2J_{CF} = 20.5$) C-3: 152.7 (d, $^1J_{CF} = 252.6$); C-4: 122.6 (d, $^2J_{CF} = 30.3$) C-5: 126.0 (s); C-6: 26.2 (s); CO_2: 172.2 (d, $^4J_{CF} = 3.2$); CH_3: 52.5 (s)
 **11b**	H-1: overlapped by the signal of isomer **11a** H-2: 6.12 (dd, $^4J_{HF} = 7.5$, $^3J_{HH} = 4.2$) H-5: 5.42 (dt, $^3J_{HF} = 11.8$, $^3J_{HH} = 4.8$) H-6: overlapped by the signal of isomer **11a** F-3: 122.2 (complex multiplet) C-1: 40.5(s); C-2: 124.0 (s); C-3: 122.8 (d, $^2J_{CF} = 34.1$) C-4: 152.0 (d, $^1J_{CF} = 251$); C-5: 102.2 (d, $^2J_{CF} = 17.6$) C-6: 23.3 (s); CO_2: 172.0 (s); CH_3: 52.5 (s)

Table 2 (*continued*)

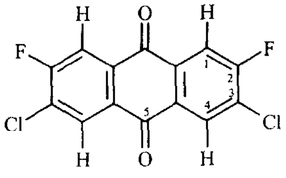
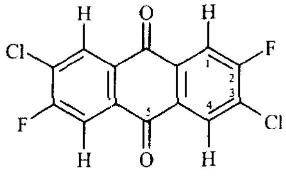
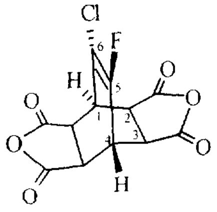
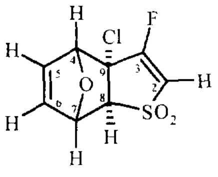
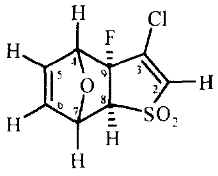
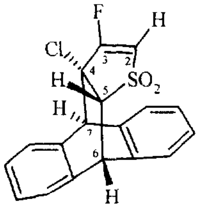
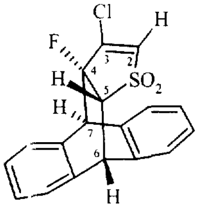
Compound	Nucleus: δ (mutiplicity, J Hz)
 **13a**	H-1: 8.028 (d, $J_{HF} = 8.6$) H-4: 8.63 (d, $^{4}J_{HF} = 6.9$) F: 103.2 (dd, $^{3}J_{HF} = 8.6$, $^{4}J_{HF} = 6.9$)
 **13b**	H-1: 8.034 (d, $J_{HF} = 8.6$) H-4: 8.68 (d, $^{4}J_{HF} = 7.0$) F: 103.8 (dd, $^{3}J_{HF} = 8.6$, $^{4}J_{HF} = 7.0$)
 **14**	H-1: 3.74 (s); H-2 and H-3: 3.82 (s) H-4: 3.50 (d, $^{3}J_{HF} = 13.1$) F-5: 105.4 (d, $^{3}J_{HF} = 13.1$) C-1: 43.8 (s); C-2: 45.1 (s); C-3: 44.9 (d, $^{3}J_{CF} = 1.9$) C-4: 39.4 (d, $^{2}J_{CF} = 20.7$); C-5: 154.5 (d, $^{1}J_{CF} = 286.6$) C-6: 106.8 (d, $^{2}J_{CF} = 8.0$); CO: 171.0 (s) and 171.3 (s)
 **15a**	H-2: 6.41 (dd, $^{3}J_{HF} = 1.9$, $^{4}J_{HH} \sim 1$) H-4: 5.57 (broad s) H-5 and H-6: 6.67 and 6.70 (AB, $J_{AB} = 1.5$) H-7: 5.24 (broad s); H-8: 3.54 (t, $J \sim 1$) F-3: 112.0 (d, $^{3}J_{HF} \approx 2$) C-2: 114.7 (d, $^{2}J_{CF} = 13.3$); C-3: 164.6 (d, $^{1}J_{CF} = 295.6$) C-4: 73.6 (d, $^{3}J_{CF} = 1.6$); C-5 and C-6: 135.4 and 136.4 (s) C-7: 81.2 (s); C-8: 133.8 (d, $^{3}J_{CF} = 3.5$) C-9: 69.3 (d, $^{2}J_{CF} = 25.0$)
 **15b**	H-2: not found; H-4: 5.54 (broad s) H-5 and H-6: 6.76 and 6.78 (AB, $J_{AB} = 1.8$) H-7: 5.10 (broad s); H-8: 3.40 (dd, $^{3}J_{HF} = 11.5$, $J \sim 1$) F-9: 159.3 (d, $^{3}J_{HF} = 11.5$)
 **16a**	H-2: 5.98 (dd, $^{3}J_{HF} = 2.4$, $J_{HH} = 1.0$) H-5: 4.89 (t, $^{4}J_{HF} = 2.4$); H-6: 3.94 (m); H-7: 4.75 (s) H-Ar: 7.17-7.50 (complex) F-3: 115.0 (d, $^{3}J_{HF} = 2.4$) C-2: 114.2 (d, $^{2}J_{CF} = 12.3$); C-3: 116.0 (d, $^{1}J_{CF} = 295.6$) C-4: 70.5 (d, $^{2}J_{CF} = 22.9$); C-5: 75.2 (s); C-6: 45.1 (s) C-7: 52.9 (s); C-Ar: 124.1; 124.4; 126.9; 127.4; 127.8; 127.9; 128.0; 135.9; 137.8; 137.9; 138.8

Table 2 (*continued*)

Compound	Nucleus: δ (mutiplicity J Hz)
 **16b**	H-2: 6.25 (t, $^4J_{HH} \approx 1.0$); H-5: 4.84 (d, $^3J_{HH} = 6.1$) H-6: 3.46(s); H-7: 3.74 (ddd, $^3J_{HF} = 21.6$, $J_{HH} = 2.6$ and 0.8); H-Ar: 7.17-7.50 (complex) F-3: 139.5 (dd, $^3J_{HF} = 21.6$ and 6.1) C-2: 114.5 (s); C-3: 144.8 (d, $^2J_{CF} = 24.0$) C-4: 102.8 (d, $^1J_{CF} = 210$); C-5: 69.7 (d, $^2J_{CF} = 20.4$) C-6: 44.8 (s); C-7: 50.[illegible] (d, $^2J_{CF} = 25.3$); C-Ar: 124.0; 124.9; 126.7; 127.2; 127.5; 127.7; 134.5 (d, $^3J_{CF} = 4.2$); 136.0 (d, $^3J_{CF} \approx 8$); 136.8; 137.4; 137.9

made on the basis of relative magnitudes of the $^3J_{HH}$ and $^4J_{HH}$ coupling constants and multiplicities of the H-2 and H-5 protons (dd and dt, respectively) as well as on the appearance of $^3J_{CF}$ couplings for C-1 in the isomers **a** and for C-6 in the isomers **b** (Table 2).

Molecular compositions of all products **5–17** have been confirmed by precise masses of their molecular ions in the HRMS (Table 3).

In conclusion, 3-chloro-4-fluorothiophene-1,1-dioxide (**4**) is a new fluorinated Diels–Alder reaction component with numerous potential applications, both as a diene and a dienophile, which provide an easy access to a variety of chlorofluoroaromatics and chlorofluorocarbocyclics.

3. Experimental details

Melting points were determined in capillaries and are uncorrected. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded in CDCl$_3$ or acetone-d_6, as indicated, with a Varian Gemini 200 spectrometer at 200, 188 and 50 MHz, respectively. Chemical shifts are quoted in ppm relative to internal TMS for protons and carbon nuclei (positive downfield) and relative to internal CFCl$_3$ for fluorine nuclei (positive upfield). GC–MS analyses were performed with a Hewlett-Packard 5890 apparatus (70 eV) using a 30 m capillary column coated with a HP5 oil. High resolution mass spectra were obtained with an AMD-604 spectrometer.

3.1. Trans-3-chloro-4-fluorosulpholane (2)

Sulpholene (**1**) (24 g, 0.2 mol) and *N*-chlorosuccinimide (30 g, 0.225 mol) were placed in a 200 ml stainless steel autoclave equipped with a needle valve, the autoclave was immersed in a dry ice–acetone bath then anhydrous hydrogen fluoride (42 g, 2.1 mol) was condensed into it. After warming up to ambient temperature, the autoclave was placed in an rocking furnace and heated at 75–80°C for approximately 24 h. While the autoclave was still hot, the excess of HF was gently released by stepwise opening of the valve, then the valve was closed, connected by a flexible tube with a water container (ca. 200 ml) and then, after cooling the autoclave to ca. 5°C, opening the valve caused sucking of water into the autoclave. After opening, the contents of the autoclave were transferred into a polyethylene container, the water layer was decanted and the remaining solid material was washed once with cold water (removal of unreacted substrates and succinimide), filtered, dried at room temperature and finally recrystallised from ethanol to give pure *trans*-3-chloro-4-fluorosulpholane (**2**) (17.5 g, 0.1 mol) as colourless crystals. Yield: 50.7%. M.p. 136–138°C. Analysis: Found: C, 28.05; H, 3.75; Cl, 20.7; F, 10.9; S, 18.5%. $C_4H_6ClFO_2S$ requires: C, 27.8; H, 3.5; Cl, 20.5; F, 11.0; S, 18.6%. ^{1}H NMR (acetone-d_6): ABM and ABMX systems: δ 3.55 (dd, $^2J_{HH} = 14.6$ Hz, $^3J_{HH} = 3.84$ Hz, 1H, 2-CH$_2$); 3.82 (dd, $^2J_{HH} = 14.6$ Hz, $^3J_{HH} =$ ca. 5.5 Hz, 1H, 2-CH$_2$); 3.54 (ddm, $^2J_{HH} = 14.95$ Hz, $^3J_{HF} = 21.0$ Hz, 1H, 5-CH$_2$); 3.79 (dddd, $^2J_{HH} = 14.95$ Hz, $^3J_{HF} = 31.5$ Hz, $^3J_{HH} = 5.2$ Hz, $^4J = 0.6$ Hz, 1H, 5-CH$_2$); 5.63 (dm, $^2J_{HF} = 48.4$ Hz, 1H, CHF); 5.05 (complex, 1H, CHCl) ppm. ^{19}F NMR (acetone-d_6) δ: 171.1 (dddd, $^2J_{FH} = 48.4$ Hz, $^3J_{FH} = 31.5$ Hz, $^3J_{FH} = 21.0$ Hz, $^3J_{FH} = 10.4$ Hz, CHF) ppm. ^{13}C NMR (acetone-d_6) δ: 55.7 (d, $^2J_{CF} = 22.0$ Hz, C-5); 55.8 (d, $^2J_{CF} = 29.6$ Hz, C-3); 57.6 (s, C-2); 93.7 (d, $^1J_{CF} = 186$ Hz, C-4) ppm. MS m/z [relative intensity, ion]: 174, 172 [2,6%, M$^+$]; 137 [1,(M − Cl)$^+$]; 109, 107 [3, 9, (M − SO$_2$H)$^+$]; 64, 62 [30, 90, $C_2H_3Cl^+$]; 44 [100, C_2HF^+].

3.2. 3,3,4-Trichloro-4-fluorosulpholane (3)

A solution of *trans*-3-chloro-4-fluorosulpholane (**2**) (21.7 g, 0.126 mol) in CCl$_4$ (700 ml) was placed in a 1000 ml photochemical reactor fitted with an internal UV lamp, reflux condenser, capillary gas inlet and a magnetic stirring bar. The solution was irradiated and stirred for 24 h while a slow stream of dry chlorine was continuously introduced to the bottom of the reactor. The reaction temperature was maintained autothermally at gentle boiling. After completion of

Table 3
Physical properties, isolation methods, MS and HRMS data and isolated yields of the cycloaddition products **5**–**17**

Compound number	Melting point (°C)	Isolation method	MS (70 eV) m/z (relative intensity, ion^a)	HRMS found (calcd. for M^+)^a	Yield (%)
5	153–155	cc (hex/CH_2Cl_2) and cr (MeOH)	236 [45, M^+]; 207 [100, $(M-CHO)^+$]	235.94812 (235.95104)	57
6	54–56	s (40°, 1 Torr)	206 [100, M^+]; 170 [30, $(M-HCl)^+$]	206.02996 (206.02986)	57
7	Oil	cc (hexane)	174 [40, M^+]; 143 [100, $(M-CH_3OH)^+$]	174.02249 (174.02476)	58
8	Oil	cc (hexane)	222 [20, M^+]; 143 [100, $(M-Br)^+$];107 [18, $(M-Br{-}HCl)^+$]	221.92463 (221.92472)	38
9a + 9b	Oil	cc (hex/CH_2Cl_2)	162 [20, M^+]; 131 [70, $(M-CH_2OH)^+$]; 95 [100, $C_6H_4F)^+$]	162.02462 (162.02477)	84
10a + 10b	Oil	cc (hexane)	224 [50, M^+]; 145 [100, $(M-Br)^+$]; 131 [80, $(M-CH_2Br)^+$]	223.94012 (223.94037)	45
11a + 11b	oil	cc (hexane)	190 [60, M^+]; 131 [100, $(M-CH_3O)^+$]	190.01889 (190.01968)	84
12	oil	cc (hexane)	188 [35, M^+]; 157 [100, $(M-CH_3O)^+$] 129 [40, $(M-CO_2CH_3)^+$]	188.00340 (188.00404)	63
13a + 13b	>250	s (160°, 1 Torr)	312 [100, M^+]: 284 [55, $(M-CO)^+$]; 256 [45, $(M-2CO)^+$] 221 [25, $(M-2CO{-}Cl)^+$]; 186 [55, $(M-2CO{-}2Cl)^+$]	311.95524 (311.95564)	86
14	>250	cr (MeOH)	300 [20, M^+]; 228 [15, $(M-C_2O_3)^+$] 130 [100, $C_6H_4ClF^+$]	Analysis: Found: C, 47.8; H, 2.0; Cl, 11.6; F, 6.3%. Calc. for $C_{12}H_6ClFO_6$: C, 47.9; H, 2.0; Cl, 11.8; F, 6.3%	45
15a + 15b	152–154	cc (hexane) and cr (MeOH)	200 [5, $(M-HCl)^+$]; 68 [100, $C_4H_4O^+$]	$(M-HCl)^+$: 199.99026 (199.99434)	64
16a + 16b	226–234	cc (hex/CH_2Cl_2) and cr (MeOH)	346 [5, M^+];310 [28, $(M-HCl)^+$] 246 [30, $(M-SO_2{-}HCl)^+$]; 262 [12, $(M-SO_2{-}HF)^+$] 202 [30, $C_{16}H_{10}{}^+$]; 178 [100, $C_{14}H_{10}{}^+$]	346.02044 (346.02305)	78
17	Oil	cc (hexane)	186 [15, M^+]; 143 [20, $(M-CH_3CO)^+$]; 107 [15, $M-CH_3CO{-}HCl)^+$]; 43 [100, CH_3CO^+]	186.02465 (186.02477)	90

^{a} ^{35}Cl and ^{79}Br ions only.
cc-Column chromatography.
cr-Crystallisation.
s-Sublimation.

the reaction, the solution (together with partially deposited product) was evaporated to dryness and the solid residue was recrystallised from methanol to give 3,3,4-trichloro-4-fluorosulpholane (**3**) as colourless crystals. Yield: 15.2 g (0.063 mol, 50%). M.p. 141–142°C. Analysis: Found: C, 19.9; H, 1.9; Cl, 43.8; F, 7.8; S, 13.0%. $C_4H_4Cl_3FO_2S$ requires: C, 19.89; H, 1.67; Cl, 44.04; F, 7.87; S, 13.28%. ^{1}H NMR (500 MHz, acetone-d_6): AB and ABX systems: δ 4.32 (ddd, $^2J_{HH}=14.6$ Hz, $^4J_{HF}=2.9$ Hz, $^4J_{HH}=0.75$ Hz, 1H, 2-CH_2); 4.63 (dt, $^2J_{HH}=14.6$ Hz, $^4J_{HH}=0.9$ Hz, 1H, 2-CH_2); 4.38 (ddd, $^2J_{HH}=14.8$ Hz, $^3J_{HF}=30.3$ Hz, $^4J_{HH}=0.9$ Hz, 1H, 5-CH_2) 4.52 (td, $^2J_{HH}={}^3J_{HF}=14.8$ Hz, $^4J_{HH}=0.75$ Hz, 1H, 5-CH_2) ppm. ^{19}F NMR (acetone-d_6) δ: 104.1 (ddd, $^3J_{FH}=30.3$ Hz, $^3J_{FH}=14.8$ Hz, $^4J_{FH}=2.0$ Hz) ppm. ^{13}C NMR (acetone-d_6) δ: 62.5 (d, $^2J_{CF}=24.1$ Hz, C-5); 76.2 (s, C-2); 86.7 (d, $^2J_{CF}=28.0$ Hz, C-3); 113.3 (d, $^1J_{CF}=253$ Hz, C-4) ppm. M.S m/z [relative intensity, ion]: 246, 244, 242, 240 [<1%, M^+]; 209, 207, 205 [<1, $(M-Cl)^+$]; 182, 180, 178, 176 [max 2%, $(M-SO_2)^+$], 145, 143, 141 [3, 30, 48, $(M-SO_2Cl)^+$]; 131, 129, 127 [3, 35, 52, $C_3H_2Cl_2F^+$]; 107, 105 [8, 24, $C_4H_3ClF^+$]; 100, 98, 96 [10, 60, 100, $(CH_2{=}CCl_2)^+$]; 87, 85 [6, 18, CF_2Cl^+]; 82, 80 [10, 30, $(CH_2{=}CFCl)^+$].

3.3 3-Chloro-4-fluorothiophene-1,1-dioxide (4)

Anhydrous triethylamine (35 g, 0.35 mol) was added dropwise to a stirred solution of sulpholane **3** (35 g, 0.145 mol) in anhydrous acetone (200 ml) at 0°C. The stirring was continued for half an hour then the precipitate of $Et_3N\cdot HCl$ was filtered off, washed with acetone, and the combined acetone solutions were evaporated on a rotary evaporator. Recrystallisation of the solid residue from toluene gave 3-chloro-4-fluorothiophene-1,1-dioxide (**4**) as yellowish crystals. Yield: 21.5 g (0.127 mol, 88%). M.p. 109–111°C (slight decomposition). The analytical sample was obtained after chromatography on silica-gel using CH_2Cl_2 as an eluent. Analysis: Found: C, 28.50; H, 1.20; Cl, 21.03; F, 11.27; S, 19.02%. $C_4H_2ClFO_2S$ requires: C, 28.3; H, 1.1; Cl, 21.2; F, 11.2; S, 18.9%. ^{1}H NMR (acetone-d_6) δ: 7.00 (dd, $^4J_{HH}=3.0$ and 0.8 Hz, 2-CH); 7.44 (dd, $^3J_{HF}=4.3$ Hz, $^4J_{HH}=3.0$ Hz, 5-CH) ppm. ^{19}F NMR (acetone-d_6) δ:122.6 (d, $^3J_{FH}=4.3$ Hz) ppm. ^{13}C NMR (acetone-d_6) δ:158.4 (d, $^1J_{CF}=291$ Hz, C-4); 132.8 (d, $^2J_{CF}=32.8$ Hz, C-3); 131.4 (s, C-2, nondecoupled spectrum: $^1J_{CH}=201$ Hz); 110.7 (d, $^2J_{CF}=13.4$ Hz, C-5, nondecoupled spectrum: $^1J_{CH}=199.7$ Hz) ppm. M.S m/z [relative intensity, ion]: 170, 168 [12, 36, M^+]; 141, 139 [10, 30, $(M-CHO)^+$]; 122, 120 [33, 100, $(M-SO)^+$]; 113, 111 [13, 40, $C_2HClFO_2^+$]; 93, 91 [13, 40, C_3HClF^+]; 69 [70, $(M-SO_2Cl)^+$]; 57 [35, $C_3H_2F^+$], 50 [38, $C_4H_2^+$]. HRMS: Found: 167.94470. $C_4H_2Cl^{35}FSO_2$ requires: 167.94478.

3.4. 3,5-Difluoro-6-chlorothianaphthene-1,1-dioxide (5)

Thiophene dioxide **4** (1 g, 6 mmol) in toluene (20 ml) was heated in a sealed ampoule at 100°C for 20 h after which time the solvent was removed under reduced pressure and the oily residue was chromatographed on silica-gel with *n*-hexane/CH_2Cl_2 (9:1). The solid product obtained was recrystallised from methanol to give compound **5** (0.4 g, 57%) as colourless crystals. Spectral and physical properties are listed in Tables 2 and 3.

*3.5. Cycloaddition reactions of compound **4**. General procedure*

Thiophene dioxide **4** (1 g, 6 mmol) and an excess of freshly distilled dienophile (20 ml) (in cases of solid reagents toluene was added as a solvent) were sealed in a glass tube and heated on an oil bath at 100–110°C for 20 h. After completion of the reaction an excess of the dienophile and the solvent were removed on a rotary evaporator and the residue was subjected to column chromatography on silica gel using *n*-hexane or *n*-hexane/CH_2Cl_2 (9:1) as the eluent. Solid products were additionally purified by crystallisation or vacuum sublimation. Yields, isolation methods, physical properties, MS and HRMS data for the adducts are given in Table 3. ^{1}H, ^{19}F and ^{13}C NMR data for aromatic products **6–8**, **12** and **17** are listed in Table 1 and for products **5**, **9–11** and **13–16** in Table 2.

References

[1] R.E. Banks, Fluorocarbons and Their Derivatives, MacDonald Technical and Scientific, London, 1970, pp. 51–52.

[2] T. Nagai, Y. Nasu, T. Shimada, H. Shoda, M. Koyama, A. Ando, T. Miki, H. Kumadaki, J. Fluorine Chem. 57 (1992) 245.

[3] B.E. Smart, in: M. Hudlický, A. Pavlath (Eds.), Chemistry of Organic Fluorine Compounds: II. A Critical Review, ACS Monograph 187, ACS, Washington, DC, 1995, pp. 832–833.

[4] A.A. Petrov, A.V. Tumanova, Zh. Obshch. Khim., 26 (1956) 2744, 2991, 2995.

[5] H. Bluestone, R. Bimber, R. Berkey, Z. Mandel, J. Org. Chem. 26 (1961) 346.

[6] M.S. Raash, J. Org. Chem. 45 (1980) 856.

[7] M.S. Raash, J. Org. Chem. 45 (1980) 867.

[8] W.J. Bailey, E.W. Cummins, J. Am. Chem. Soc. 76 (1954) 1932.

[9] W.J. Bailey, E.W. Cummins, J. Am. Chem. Soc. 76 (1954) 1936.

[10] W.J. Bailey, E.W. Cummins, J. Am. Chem. Soc. 76 (1954) 1940.

[11] W.A. Sheppard, C.M. Sharts, Organic Fluorine Chemistry, Chap. 5.2G, W.A. Benjamin, New York, 1969, pp. 127–132.

[12] W.S. Brey, L.W. Jaques, H.J. Jakobsen, Org. Magn. Res. 12 (1979) 243.

[13] J.E. Loemker, J.M. Read, J.H. Goldstein, J. Phys. Chem. 72 (1968) 991.