

Synthesis and Cycloaddition Reactions of Ethyl 3-Aryl-2-(perfluoroalkanesulfonyl)propenoates – A Revised Stereochemistry of the Cyclopentadiene Adducts

Régis Goumont,^{*,[a]} Karine Magder,^[a] Marc Tordeux,^[a] Jérôme Marrot,^[b] François Terrier,^[a] and Claude Wakselman^{*,[a]}

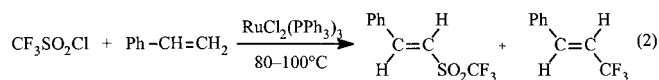
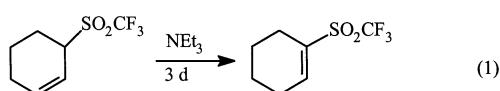
Keywords: Vinyl triflones / Vinyl nonaflones / Knoevenagel reaction / Diels–Alder reaction

Ethyl 3-aryl-2-(perfluoroalkanesulfonyl)propenoates were prepared by the Knoevenagel reaction from various aldehydes and ethyl (trifluoromethanesulfonyl)acetate or ethyl (nonafluorobutanesulfonyl)acetate. These deactivated olefins were used in Diels–Alder cycloaddition reactions with

cyclopentadiene. The reactions occurred at room temperature to give [4+2] cycloadducts as racemates. The *endo* stereochemistry of the carboxylic ester and aryl groups was unambiguously assigned by NOE experiments and X-ray analysis.

Introduction

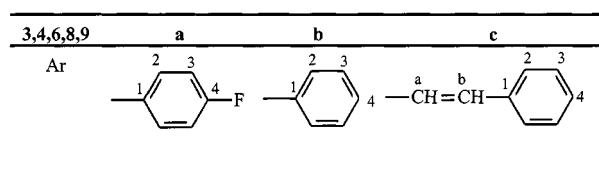
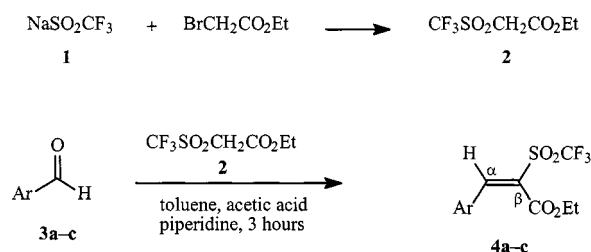
Perfluoroalkanesulfonyl groups R_FSO_2 ^[1–6] are of special interest in organic chemistry because of their manifold reactivity – they may function either as electrophiles or as nucleofugic leaving groups, carrying away the electron pair to form a sulfinate anion.^[7–8] These powerfully electron-withdrawing^[1,9–10] groups can stabilize negatively charged carbanions^{[11][12]} or activate olefins in nucleophilic addition^[1] or cycloaddition reactions.^[1,13–15] Vinyl triflones, although structurally simple, are not widely available. Some examples were prepared by isomerization of allylic triflones^[1] (migration into conjugation of the carbon–carbon double bond) (Equation 1). Condensation of styrenes with trifluoromethanesulfonyl chloride, catalysed by a ruthenium complex (Equation 2), was found to give the corresponding vinyl triflones, but only as secondary products because the reaction proceeds mainly with extrusion of sulfur dioxide.^[16]



Interestingly, the preparation of unsaturated sulfonyl esters is well known, and the Knoevenagel condensation reaction^[14–15,17–18] is the most convenient method for this

purpose. The formation of a condensation product derived from *p*-dimethylaminobenzaldehyde in acetic anhydride was described by Yagupol'skii.^[19] However, Hanack was unable to reproduce this method with other aromatic aldehydes.^[15] As a result, new reaction conditions were developed in which catalytic amounts of piperidine and acetic acid in benzene are used to prepare 3-aryl-2-(nonafluorobutanesulfonyl)propenoates.

In this paper, we report the preparation of vinyl triflones **4** by the condensation of ethyl (trifluoromethanesulfonyl)acetate (**2**)^[6,20–21] with various aldehydes **3a–d** (Schemes 1 and 2). The precursor **2** was prepared by the reaction of sodium triflinate (**1**) with ethyl bromoacetate.^[6,20–21]



Scheme 1. Knoevenagel condensations of simple aromatic aldehydes with ethyl (trifluoromethanesulfonyl) acetate

The esters **4** were used in Diels–Alder condensation reactions with cyclopentadiene (**5**). These reactions occurred smoothly within 2–5 d at room temperature in carbon tetrachloride to give the [4+2] cycloadducts **6** in fair to good yields. The structure of **6** and, thus, the presence of a

^[a] Laboratoire SIRCOB, ESA CNRS 8086, Bâtiment Lavoisier, Université de Versailles,

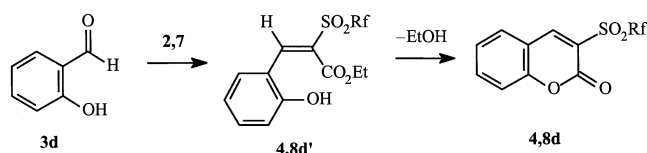
45, avenue des Etats-Unis, F-78035 Versailles Cedex, France

^[b] Institut Lavoisier, Laboratoire IREM, CNRS CO173, Université de Versailles,

45, avenue des Etats-Unis, F-78035 Versailles Cedex, France

E-mail: goumont@chimie.uvsq.fr

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Scheme 2. Knoevenagel condensation of salicylaldehyde with ethyl (trifluoromethanesulfonyl) acetate

Diels–Alder addition product, was clearly established from NMR data, especially with the aid of NOE experiments. The stereochemistry of the cycloaddition was unambiguously assigned by an X-ray analysis of **6a**. The reaction appeared to be highly stereoselective and, in all cases, only the *endo* isomer was observed and isolated.

Results and Discussion

1. Synthesis of Vinyl Triflones **4a–d**

The Knoevenagel condensation reaction between activated aldehydes **3a–d** and sulfonyl ester **2** led to the formation of only the (*E*) isomers **4a–d** in good yields. These compounds were characterized by their spectral data (Table 1).

The ^1H - and ^{13}C -NMR spectra recorded in CDCl_3 for **4a** were in agreement with the vinyl triflone structure. Besides the signals of the aromatic protons, the ^1H -NMR spectra contained triplet and quadruplet peaks ($\delta = 1.35/4.42$) typical for the ethyl group, as well as a characteristic H^a ($\delta = 7.93$) singlet which was deshielded by the electron-withdrawing ester and triflyl groups. Each carbon atom of the aromatic ring gave rise to a doublet [$\delta(\text{C}-1) = 126.72$, $^4J(\text{C}-1-\text{F}) = 3.4$ Hz; $\delta(\text{C}-2) = 133.71$, $^3J(\text{C}-2-\text{F}) = 9.3$ Hz; $\delta(\text{C}-3) = 116.68$, $^2J(\text{C}-3-\text{F}) = 22.3$ Hz; $\delta(\text{C}-4) = 165.53$, $^1J(\text{C}-4-\text{F}) = 258.0$ Hz] in the ^{13}C -NMR spectrum. The coupling between the fluorine atom and the aromatic carbon atoms made the unambiguous assignment of the other carbon resonances possible (Table 1). The

$^3J(\text{CO}-\text{H}^a)$ coupling constant of 11.3 Hz, measured in the proton-coupled ^{13}C -NMR spectra, was in agreement with a *trans* coupling and an (*E*) configuration^{[22][23]} of the $\text{C}=\text{C}$ double bond. The NMR data of **4b** were similar to that of **4a** [$\delta(\text{H}^a) = 7.97$], therefore the (*E*) configuration could also be assigned to **4b** [$^3J(\text{CO}-\text{H}^a) = 11.3$ Hz].^{[22][23]}

IR data^[24] agreed with vinylic structures [$\nu(\text{CO}) = 1729$ and 1734 cm^{-1} , for **4a** and **4b**, respectively; $\nu(\text{C}=\text{C}) = 1607$ for **4a** and $\nu(\text{C}=\text{C}) = 1612\text{ cm}^{-1}$ for **4b**]. Mass spectrometry^[24] also agreed well with the above structures. Beside base peaks ($m/z = 349$ and 331 [$\text{M} + \text{Na}]^+$ for **4a** and **4b**, respectively), the mass spectra also exhibited other peaks ($m/z = 675$ for **4a** and 639 for **4b**) corresponding to $[2\text{M} + \text{Na}]^+$.

Vinyl triflone **4c** was obtained as a pale yellow solid from *trans*-cinnamaldehyde in quantitative yield. Its ^1H -NMR spectra appeared to be similar to those of **4a** and **4b**, with two new second-order signals for the ethylenic protons H^a ($\delta = 7.42$) and H^b ($\delta = 7.96$).

Treatment of salicylaldehyde (**3d**) with ethyl (trifluoromethanesulfonyl)acetate (**2**) did not result in the expected vinyl triflone **4d'**, which was not isolable. Instead, a coumarin derivative **4d** was obtained as a pale yellow solid in 70% yield. Formation of **4d** may be explained by an intramolecular cyclization of **4d'** with concomitant elimination of an ethanol molecule (Scheme 2).^[25] The absence of the signals due to the ethyl group, in both the ^1H - and ^{13}C -NMR spectra, provide strong support for the formation of this compound. ^1H - and ^{13}C -NMR data are collected in Table 1.

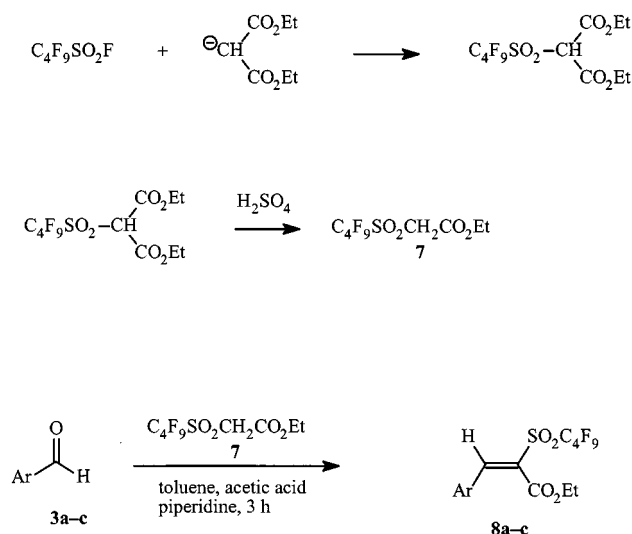
As we will describe later in this paper, these vinyl triflones reacted readily with cyclopentadiene to give cycloadducts **6a–d** with high stereoselectivity. However, the *endo* stereochemistry of these adducts contrasted with the *exo* stereochemistry of the adducts derived from vinyl nonaflones^[15] as previously reported by Hanack and co-workers. To understand and explain this difference of stereoselectivity, the vinyl nonaflones **8a–d** were prepared.

Table 1. NMR data of the vinyl triflones **4a–d**

Product	^1H NMR	^{13}C NMR	^{19}F NMR
4a	7.93 (s, 1 H, H^a), 7.64 (dd, $J = 8.5$ Hz, $J = 8.43$ Hz, 2 H, 2-H), 7.17 (dd, $J = 5.5$ Hz, $J = 8.43$ Hz, 2 H, 3-H), 4.42 (q, $J = 7$ Hz, 2 H, CH_2), 1.35 (t, $J = 7$ Hz, 3 H, CH_3)	165.53 (d, $J = 258.0$ Hz, C-4), 160.99 (CO), 151.15 (C^a), 133.71 (d, $J = 9.3$ Hz, C-2), 126.72 (d, $J = 3.4$ Hz, C-1), 126.30 (C^b), 119.75 (q, $J = 327.2$ Hz, CF_3), 116.68 (d, $J = 22.3$ Hz, C-3), 63.45 (CH_2), 13.62 (CH_3)	–75.8 (s, 3 F, SO_2CF_3), –103.3 (m, 1 F, $\text{C}_6\text{H}_4-\text{F}$)
4b	7.97 (s, 1 H, H^a), 7.56 (m, 2-H, 3 H, 4-H), 7.47 (m, 2 H, 3-H), 4.42 (q, $J = 7.2$ Hz, 2 H, CH_2), 1.34 (t, $J = 7.2$ Hz, 3 H, CH_3)	161.08 (CO), 152.77 (C^a), 133.31 (C-4), 130.88 (C-2), 130.36 (C-1), 129.19 (C-3), 126.22 (C^b), 119.75 (q, $J = 327.2$ Hz, CF_3), 63.33 (CH_2), 13.54 (CH_3)	–76.0 (s, SO_2CF_3)
4c	8.03 (d, $J = 11.4$ Hz, 1 H, H^a), 7.96 (dd, $J = 14.3$ Hz, $J = 11.4$ Hz, 1 H, H^b), 7.63–7.47 (m, 5 H, 2-H, 3-H, 4-H), 7.42 (d, $J = 14.3$ Hz, 1 H, H^a), 4.42 (q, $J = 7$ Hz, 2 H, CH_2), 1.41 (t, $J = 7$ Hz, 3 H, CH_3)	160.43 (CO), 158.73 (C^a), 154.26 (C^a), 134.57 (C-1), 131.98 (C-4), 129.25 (C-3), 129.17 (C-2), 122.57 (C^b), 122.60 (C^b), 119.67 (q, $J = 327.2$ Hz, CF_3), 62.54 (CH_2), 13.85 (CH_3)	–75.8 (s, SO_2CF_3)
4d	8.84 (s, 1 H, 4-H), 7.86 (t, $J = 7.9$ Hz, 1 H, 7-H), 7.79 (d, $J = 8.2$ Hz, 1 H, 5-H), 7.50 (d, $J = 6.7$ Hz, 1 H, 6-H), 7.49 (t, $J = 7.9$ Hz, 1 H, 8-H)	156.21 (C-9), 155.13 (C-4), 153.66 (C-2), 137.69 (C-5), 131.16 (C-7), 126.02 (C-6), 123.1 (q, $J = 324.3$ Hz, CF_3), 120.15 (C-3), 117.45 (C-8), 116.77 (C-10)	–75.7 (s, SO_2CF_3)

2. Synthesis of Vinyl Nonaflones 8a–d

These compounds were prepared by the Knoevenagel condensation reaction of ethyl (nonafluorobutanesulfonyl)-acetate (**7**) and the aldehydes **3a–d** (Schemes 2 and 3) by the previously established reaction conditions (catalytic amounts of piperidine and glacial acetic acid in toluene).^[15] The nonafllyl ester **7** was prepared by condensation of nonafllyl fluoride with sodium malonate, followed by a decarboxylation step.^{[19][26]} The precursor **7** could also be prepared by the reaction of nonafllylmethane with butyllithium in tetrahydrofuran, followed by the addition of diethyl carbonate.^{[26][27]}



Scheme 3. Knoevenagel condensations of aromatic aldehydes with ethyl (nonafluorobutanesulfonyl) acetate

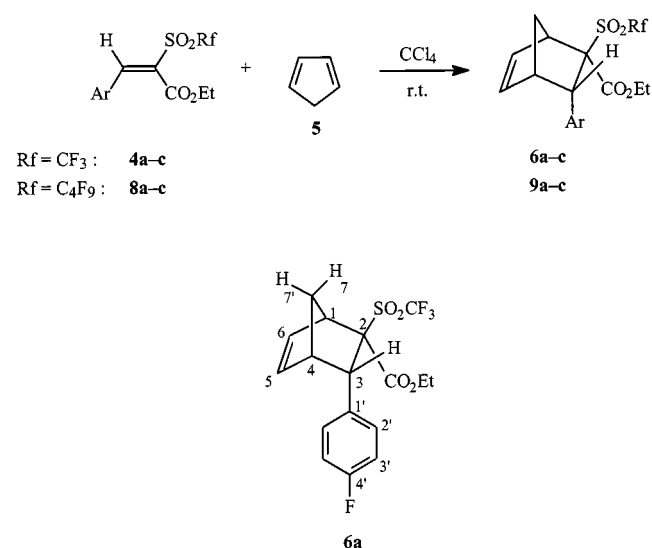
The products **8a–d** were obtained as single (*E*) isomers in fair to good yields. ¹H- and ¹³C-NMR spectra of **8a–d** were found to be very similar to those obtained for the triflones **4a–d** (Tables 1 and 2), therefore the resonances (¹H

and ¹³C) for **8a–d** were simply assigned by comparison with the data of **4a–d**. The nonaflone^[15] **8b** was previously described by Hanack, and our spectral and experimental data for this compound agree with the reported data.^[15] Finally, in the ¹⁹F-NMR spectra, four signals, which are typical for the nonafllyl group, were observed [for **8a**: δ = −81.0 (CF₃), −109.1 (CF₂–SO₂), −121.2 (CF₂–CF₂–SO₂), −126.2 (CF₂–CF₃)].

3. Preparation of the Cycloadducts

a. Reaction of Triflones 4a–d with Cyclopentadiene

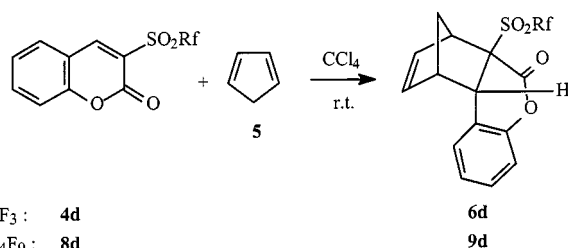
The deactivated vinyl triflones reacted as dienophiles in Diels–Alder reactions with cyclopentadiene (**5**) giving Diels–Alder cycloadducts **6a–d** in modest to good yields (Schemes 4 and 5).



Scheme 4. Diels–Alder reactions of cyclopentadiene with simple vinyl triflones and nonaflones

Table 2. NMR data for the vinyl nonaflones **8a–d**

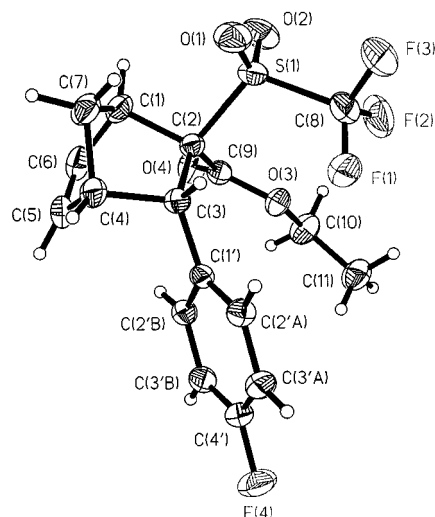
Product	¹ H NMR	¹³ C NMR	¹⁹ F NMR
8a	7.97 (s, 1 H, H ^a), 7.63 (dd, <i>J</i> = 8.6 Hz, <i>J</i> = 5.5 Hz, 2 H, 2-H), 7.18 ("t", <i>J</i> = 8.4 Hz, 2 H, 3-H), 4.42 (q, <i>J</i> = 7 Hz, 2 H, CH ₂), 1.35 (t, <i>J</i> = 7 Hz, 3 H, CH ₃)	165.57 (d, <i>J</i> = 257.7 Hz, C-4), 161.0 (CO), 151.94 (C ^a), 133.68 (d, <i>J</i> = 9.6 Hz, C-2), 127.41 (C ^b), 126.73 (d, <i>J</i> = 3.4 Hz, C-1), 116.73 (d, <i>J</i> = 22 Hz, C-3), 63.46 (CH ₂), 13.63 (CH ₃)	−126.2 (m, 2 F, CF ₂ CF ₃), −121.2 (m, 2 F, CF ₂ CF ₂ –SO ₂), −109.1 (m, 2 F, CF ₂ –SO ₂), −103.2 (s, 1 H, C ₆ H ₄ –F), −81.0 (m, 3 F, CF ₃)
8b	7.91 (s, 1 H, H ^a), 7.5 (m, 5 H, 2-H, 3-H, 4-H), 4.42 (q, <i>J</i> = 7 Hz, 2 H, CH ₂), 1.34 (t, <i>J</i> = 7.3 Hz, 3 H, CH ₃)	161.09 (CO), 153.25 (C ^a), 133.35 (C-4), 130.86 (C-2), 130.43 (C-1), 129.20 (C-3), 127.77 (C ^b), 63.28 (CH ₂), 13.39 (CH ₃)	−126.2 (m, 2 F, CF ₂ CF ₃), −121.3 (m, 2 F, CF ₂ CF ₂ –SO ₂), −109.3 (m, 2 F, CF ₂ –SO ₂), −81.2 (m, 3 F, CF ₃)
8c	8.02 (d, <i>J</i> = 11.4 Hz, 1 H, H ^a), 7.99 (dd, <i>J</i> = 11.4 Hz, <i>J</i> = 14.3 Hz, 1 H, H ^b), 7.43 (d, <i>J</i> = 16.5 Hz, 1 H, H ^a), 7.64–7.47 (2 m, 2 H, 3 H, 2-H, 3-H, 4-H), 4.42 (q, <i>J</i> = 7.3 Hz, 2 H, CH ₂), 1.41 (t, <i>J</i> = 7 Hz, 3 H, CH ₃)	160.44 (CO), 159.27 (C ^a), 154.47 (C ^a), 134.52 (C-1), 132.02 (C-4), 129.23 (C-3), 129.18 (C-2), 123.63 (C ^b), 122.54 (C ^b), 62.52 (CH ₂), 13.84 (CH ₃)	−126.2 (m, 2 F, CF ₂ CF ₃), −121.2 (m, 2 F, CF ₂ CF ₂ –SO ₂), −108.8 (m, 2 F, CF ₂ –SO ₂), −81.2 (m, 3 F, CF ₃)
8d	8.82 (s, 1 H, 4-H), 7.86 (t, <i>J</i> = 8.5 Hz, 1 H, 7-H), 7.78 (d, <i>J</i> = 8.1 Hz, 1 H, 5-H), 7.50 (d, <i>J</i> = 6.6 Hz, 1 H, 6-H), 7.49 (t, <i>J</i> = 8.1 Hz, 1 H, 8-H)	156.34 (C-9), 155.50 (C-4), 153.49 (C-2), 137.77 (C-5), 131.25 (C-7), 126.0 (C-6), 121.06 (C-3), 117.46 (C ₈), 116.81 (C-10)	−126.1 (m, 2 F, CF ₂ CF ₃), −121.4 (m, 2 F, CF ₂ CF ₂ –SO ₂), −109.7 (m, 2 F, CF ₂ –SO ₂), −81.0 (m, 3 F, CF ₃)



Scheme 5. Diels–Alder reactions of cyclopentadiene with cyclic unsaturated triflones and nonaflones

Adduct **6a** was obtained as a yellow solid in 45% yield. It was structurally analysed by X-ray crystallography, and as shown by its ORTEP view (Figure 1), an *endo* cycloadduct resulted from the condensation reaction, i.e., the aromatic ring and the ester group are located “under” the norbornene skeleton.

The Diels–Alder reaction was clearly indicated by the spectral data (Table 3), especially by the disappearance of the signal from the deshielded proton H^a in the ¹H-NMR spectra. Concomitantly, in the ¹H-NMR spectra of **6a**, resonances appeared for two ethylenic protons in the form of two doublets of doublets (δ = 6.67, 6.55) of an ABX₃ system characteristic for an ethyl group. The asymmetric carbon atom C-2 causes the two protons of the ester function

Figure 1. ORTEP view of adduct **6a**

to appear diastereotopic. The signals of protons 7-H and 7'-H of the methylene bridge were two doublets [*J*(7-H–7'-H) = 9.6 Hz] at δ = 2.46 and 1.63. Finally, three other broad signals (δ = 4.18, 3.88, 3.12) may be attributed to protons 1-H, 3-H and 4-H.

Two-dimensional homonuclear chemical shift correlation (COSY) showed that there is a three-bond coupling be-

Table 3. NMR data for the adducts **6a–d**

Product	¹ H NMR	¹³ C NMR	¹⁹ F NMR
6a	7.08 (dd, <i>J</i> = 5.2 Hz, 2 H, 2'-H), 6.94 (m, 3 H, 3'-H), 6.67 (dd, <i>J</i> = 5.5 Hz, <i>J</i> = 3.7 Hz, 1 H, 6-H), 6.55 (dd, <i>J</i> = 5.5 Hz, <i>J</i> = 3.3 Hz, 1 H, 5-H), 4.18 (d, <i>J</i> = 2.9 Hz, 1 H, 3-H), 3.88 (m, 1 H, 1-H), 3.86 (ABX ₃ , 2 H, CH ₂), 3.12 (m, 1 H, 4-H), 2.46 (d, <i>J</i> = 9.6 Hz, 1 H, 7-H), 1.63 (dt, <i>J</i> = 9.6 Hz, <i>J</i> = 1.9 Hz, 1 H, 7'-H), 0.84 (t, <i>J</i> = 7.3 Hz, 3 H, CH ₃)	164.16 (CO), 162.09 (d, <i>J</i> = 247.0 Hz, C-4'), 138.81 (C-5), 138.67 (C-6), 134.26 (d, <i>J</i> = 3.4 Hz, C-1'), 130.55 (d, <i>J</i> = 13.9 Hz, C-2'), 120.47 (q, <i>J</i> = 332.3 Hz, CF ₃), 114.77 (d, <i>J</i> = 20.9 Hz, C-3'), 86.61 (C-2), 62.75 (CH ₂), 52.23 (C-3), 51.23 (C-1), 49.19 (C-4), 48.10 (C-7), 12.80 (CH ₃)	–70.0 (s, 3 F, SO ₂ CF ₃), –115.4 (m, 1 F, C ₆ H ₄ –F)
6b	7.25 (m, 3 H, 3'-H,4'-H), 7.10 (dd, 2 H, 2'-H), 6.74 (dd, <i>J</i> = 5.3 Hz, <i>J</i> = 3.3 Hz, 1 H, 6-H), 6.58 (dd, <i>J</i> = 5.3 Hz, <i>J</i> = 3.0 Hz, 1 H, 5-H), 4.17 (d, <i>J</i> = 2.6 Hz, 1 H, 3-H), 3.88 (m, 1 H, 1-H), 3.82 (ABX ₃ , <i>J</i> = 7.2 Hz, 2 H, CH ₂), 3.14 (m, 1 H, 4-H), 2.48 (d, <i>J</i> = 9.5 Hz, 1 H, 7-H), 1.63 (dt, <i>J</i> = 9.5 Hz, <i>J</i> = 1.7 Hz, 1 H, 7'-H), 0.75 (t, <i>J</i> = 7.2 Hz, 3 H, CH ₃)	164.29 (CO), 139.01 (C-2'), 138.61 (C-1'), 138.40 (C-4'), 128.96 (C-3'), 127.94 (C-5), 127.38 (C-6), 120.52 (q, <i>J</i> = 332.3 Hz, CF ₃), 87.06 (C-2), 62.62 (CH ₂), 53.59 (C-3), 51.25 (C-1), 49.34 (C-4), 48.13 (C-7), 12.62 (CH ₃)	–69.9 (s, SO ₂ CF ₃)
6c	7.34–7.25 (m, 5 H, 2'-H, 3'-H,4'-H), 6.54 (dd, <i>J</i> = 5.5 Hz, <i>J</i> = 2.9 Hz, 1 H, 6-H), 6.53 (d, <i>J</i> = 15.3 Hz, 1 H, H ^a), 6.41 (dd, <i>J</i> = 5.5 Hz, <i>J</i> = 3.3 Hz, 1 H, 5-H), 5.74 (dd, <i>J</i> = 15.3 Hz, <i>J</i> = 9.8 Hz, 1 H, H ^a), 4.20 (ABX ₃ , 2 H, CH ₂), 3.91 (m, 1 H, 1-H), 3.84 (dd, <i>J</i> = 9.5 Hz, <i>J</i> = 2.6 Hz, 1 H, 3-H), 3.06 (m, 1 H, 4-H), 2.36 (d, <i>J</i> = 9.5 Hz, 1 H, 7-H), 1.58 (dt, <i>J</i> = 9.5 Hz, <i>J</i> = 1.7 Hz, 1 H, 7'-H), 1.21 (t, <i>J</i> = 7.2 Hz, 3 H, CH ₃)	163.81 (CO), 128.58 (C-2'), 136.87 (C-1'), 131.58 (Cb), 128.78 (Ca), 127.55 (C-4'), 126.29 (C-3'), 140.12 (C-5), 137.67 (C-6), 120.88 (q, <i>J</i> = 331.4 Hz, CF ₃), 83.12 (C-2), 62.82 (CH ₂), 51.91 (C-3), 50.86 (C-1), 49.40 (C-4), 46.28 (C-7), 13.61 (CH ₃)	–71.1 (s, SO ₂ CF ₃)
6d	7.17–7.34 (m, 3 H, 2'-H, 3'-H,4'-H), 6.99 (d, <i>J</i> = 8.1 Hz, 1 H, 5'-H), 6.30 (dd, <i>J</i> = 5.5 Hz, <i>J</i> = 3.3 Hz, 1 H, 6-H), 6.22 (dd, <i>J</i> = 5.5 Hz, <i>J</i> = 2.9 Hz, 1 H, 5-H), 4.30 (d, <i>J</i> = 3.3 Hz, 1 H, 3-H), 4.21 (s, 1 H, 1-H), 3.52 (s, 1 H, 4-H), 2.33 (d, <i>J</i> = 9.9 Hz, 1 H, 7-H), 1.70 (d, <i>J</i> = 9.6 Hz, 1 H, 7'-H)	159.59 (C-9), 153.59 (C-1'), 141.15 (C-5), 136.34 (C-6), 129.10 (C-2'), 128.19 (C-4'), 125.46 (C-3'), 120.04 (q, <i>J</i> = 320.1 Hz, CF ₃), 119.65 (C-6'), 117.17 (C-5'), 74.78 (C-2), 53.76 (C-1), 51.23 (C-4), 45.92 (C-7), 44.44 (C-3)	–71.4 (s, SO ₂ CF ₃)

tween the two ethylenic protons and the signals at $\delta = 3.88$ and 3.12 , which are obviously the two bridgehead protons 1-H and 4-H. The signal at $\delta = 4.18$, corresponding to 3-H, exhibited a three-bond coupling response with the signal at $\delta = 3.12$ which may be attributed to 4-H. Finally, the chemical shifts of the two ethylenic protons could be readily assigned to be $\delta(6\text{-H}) = 6.67$ and $\delta(5\text{-H}) = 6.55$. NOE experiments allowed us to confirm the *endo* stereochemistry and to discriminate between the two bridge protons 7-H and 7'-H. Saturation of 3-H showed a positive response with 2'-H ($\delta = 7.07$), 4-H ($\delta = 3.12$) and 7-H ($\delta = 2.46$). Saturation of 7-H gave two positive NOEs, with 7'-H ($\delta = 1.63$) and 3-H ($\delta = 4.18$); saturation of 2'-H resulted in responses from 5-H ($\delta = 6.55$) and 3-H ($\delta = 4.18$) (Figure 2). These NOE results are in agreement with the distances between these atoms measured by X-ray crystallography: $d[\text{H}(7)\text{--H}(3)] = 2.409 \text{ \AA}$, $d[\text{H}(3)\text{--H}(4)] = 2.385 \text{ \AA}$,

$d[\text{H}(3)\text{--H}(2')] = 2.225 \text{ \AA}$, $d[\text{H}(7)\text{--H}(7')] = 1.684 \text{ \AA}$ and $d[\text{H}(5)\text{--H}(2')] = 2.593 \text{ \AA}$. The resonances of the carbon atoms (Table 3) were assigned unambiguously on the basis of two NMR experiments, *J* modulation and two-dimensional heteronuclear chemical shift correlation (HETCOR). IR data and MS experiments^[24] also confirmed that vinyl triflone **4a** underwent addition with one equiv. of cyclopentadiene.

The ^1H - and ^{13}C -NMR data of **6b** resemble those of **6a**. Assignments were made by comparison and only the complex second-order signals of the protons of the aromatic ring could not be accurately assigned. NOE experiments confirmed the *endo* stereochemistry: Saturation of 3-H resulted in a positive response from 4-H ($\delta = 3.14$) and 7-H ($\delta = 2.48$); saturation of 5-H caused a positive NOE with 2'-H ($\delta = 7.10$).

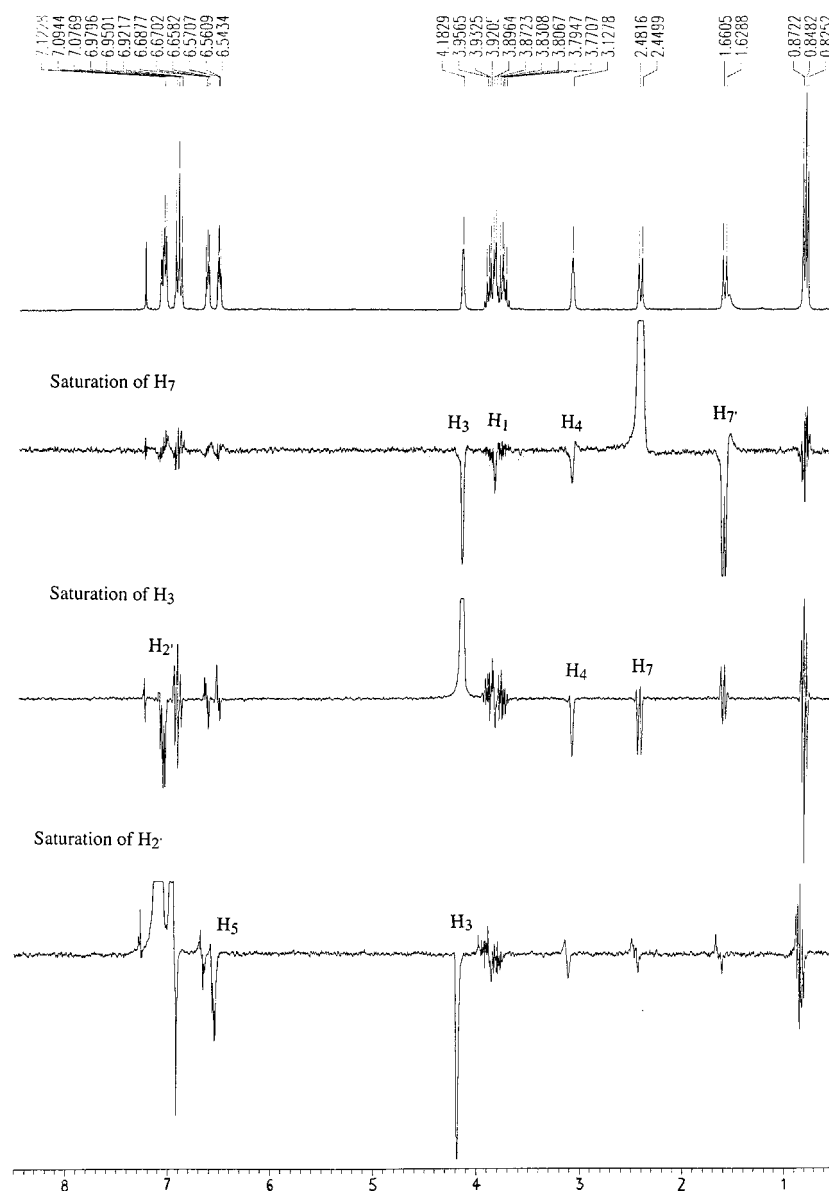


Figure 2. NOE spectra of adduct **6a** in CDCl_3

Cycloadduct **6c** was obtained as an oil in quantitative yield upon treatment of **4c** with cyclopentadiene. The ^1H -NMR spectra appeared to be similar to those of **6a** and **6b**, and contained signals for two new ethylenic protons H^a ($\delta = 5.74$) and H^b ($\delta = 6.53$) as a doublet of doublets [$^3J(\text{H}-\text{H}^a) = 9.8$ Hz and $^3J(\text{H}^a-\text{H}^b) = 15.2$ Hz] and a doublet [$^3J(\text{H}^a-\text{H}^b) = 15.2$ Hz], respectively.

Treatment of **4d** with cyclopentadiene **5** led, after purification, to a 50% yield of adduct **6d**. Detailed NMR analysis in CDCl_3 solution (Table 3), including NOE experiments, identified the stereochemistry as *endo*. Saturation of 3-H resulted in a positive NOE with the bridge proton 7-H ($\delta = 2.33$) and saturation of 2'-H gave rise to two positive responses, with 3-H ($\delta = 4.30$) and 4-H ($\delta = 3.52$).

b. Reaction of Nonaflones **8a–d** with Cyclopentadiene

As described by Hanack,^[15] vinyl nonaflones reacted with dienes like cyclopentadiene to give cycloadducts **9a–d** (Schemes 4 and 5). These adducts^[15] were obtained in good yields, but they appeared to be somewhat less stable than **6a–d**. However, their spectral data (Table 4) agree well with the data collected for compounds **6a–d**. NOE experiments were carried out, showing that the stereochemistry of adducts **8a–d** is *endo*. Moreover, saturation of 3-H showed in all cases a positive NOE with the bridge proton 7-H.

Comparison of the cyclopentadiene adducts **6a–d** and **9a–d** showed that the triflone derivatives are clearly more stable than the nonaflones ones. This higher stability allowed us to study the structure of **6a** in great detail by NMR and X-ray analysis. Both methods showed that Diels–Alder cycloaddition resulted in *endo* isomers of **6a–d**. The NMR data of compounds **6a–d** and **9a–d** are also very similar. It can therefore be concluded that the stereochemistry of the nonaflones derivatives **9a–d** is also *endo*, whereas they were previously considered to be *exo* cycloadducts.^[15] Addition of (*E*)-**4a–d** or (*E*)-**8a–d** to cyclopentadiene involves secondary orbital interactions with the aromatic ring and the ester group. That no trace of the *exo* diastereoisomer could be detected in the present study may be due to the larger steric constraints of the nonafluorobutanesulfonyl or trifluoromethanesulfonyl group in the *exo* approach.

Conclusion

We have shown that vinyl triflones may be prepared easily and in good yields by the Knoevenagel condensation reaction. These esters may be dealkylated/decarboxylated by anhydrous lithium iodide in dimethylformamide to produce a new series of vinyl triflones. Alternatively, these compounds may be used in the Michael condensation reaction^[1] be-

Table 4. NMR data for the adducts **9a–d**

Product	^1H NMR	^{13}C NMR	^{19}F NMR
9a	7.10 (dd, $J = 7.9$ Hz, $J = 5.3$ Hz, 2 H, 2'-H), 6.95 ("t", $J = 8.7$ Hz, 2 H, 3'-H), 6.68 (dd, $J = 5.3$ Hz, $J = 3.2$ Hz, 1 H, 6-H), 6.54 (dd, $J = 5.3$ Hz, $J = 3.4$ Hz, 1 H, 5-H), 4.18 (m, 1 H, 3-H), 3.87 (m, 1 H, 1-H), 3.86 (ABX ₃ , 2 H, $J = 10.8$ Hz, CH ₂), 3.10 (m, 1 H, 4-H), 2.48 (d, $J = 9.5$ Hz, 1 H, 7-H), 1.65 (d, $J = 9.5$ Hz, 1 H, 7'-H), 0.85 (t, $J = 6.9$ Hz, 3 H, CH ₃)	164.12 (CO), 162.11 (d, $J = 246.9$ Hz, C-4'), 138.88 (C-6), 138.65 (C-5), 134.24 (d, $J = 3.3$ Hz, C-1'), 130.61 (d, $J = 8.2$ Hz, C-2'), 114.78 (d, $J = 21.3$ Hz, C-3'), 89.23 (C-2), 62.67 (CH ₂), 53.0 (C-3), 51.66 (C-1), 48.95 (C-4), 48.20 (C-7), 12.83 (CH ₃)	–126.1 (m, 2 F, CF ₂ CF ₃), –121.3 (m, 2 F, CF ₂ CF ₂ –SO ₂), –115.4 (s, 1 F, C ₆ H ₄ –F), –105.3 (m, 2 F, CF ₂ SO ₂), –81.1 (m, 3 F, CF ₃)
9b	7.31 (m, 1 H, 4'-H), 7.26 (m, 2 H, 3'-H), 7.13 (m, 2 H, 2'-H), 6.69 (m, 1 H, 6-H), 6.56 (m, 1 H, 5-H), 4.17 (m, 1 H, 3-H), 3.89 (m, 1 H, 1-H), 3.8 (ABX ₃ , 2 H, $J = 11.8$ Hz, CH ₂), 3.13 (m, 1 H, 4-H), 2.5 (d, $J = 9.6$ Hz, 1 H, 7-H), 1.65 (d, $J = 9.5$ Hz, 1 H, 7'-H), 0.77 (t, $J = 7.2$ Hz, 3 H, CH ₃)	164.27 (CO), 138.87 (C-2'), 138.59 (C-4'), 138.52 (C-1'), 129.01 (C-3'), 127.94 (C-5), 127.38 (C-6), 89.68 (C-2), 62.55 (CH ₂), 53.81 (C-3), 51.70 (C-1), 49.06 (C-4), 48.24 (C-7), 12.67 (CH ₃)	–126.1 (m, 2 F, CF ₂ CF ₃), –121.4 (m, 2 F, CF ₂ CF ₂ –SO ₂), –103.3 (m, 2 F, CF ₂ –SO ₂), –81.1 (m, 3 F, CF ₃)
9c	7.33–7.30 (m, 5 H, 2'-H, 3'-H, 4'-H), 6.56 (dd, $J = 5.6$ Hz, $J = 3.3$ Hz, 1 H, 5-H), 6.53 (d, $J = 15.4$ Hz, 1 H, H ^b), 6.39 (d, $J = 5.6$ Hz, 1 H, 6-H), 5.78 (dd, $J = 15.8$ Hz, $J = 9.8$ Hz, 1 H, H ^a), 4.20 (ABX ₃ , $J = 11.2$ Hz, 2 H, CH ₂), 3.96 (m, 1 H, 1-H), 3.85 (d, $J = 9.8$ Hz, 1 H, 3-H), 3.06 (m, 1 H, 4-H), 2.36 (d, $J = 9.8$ Hz, 1 H, 7-H), 1.57 (dd, $J = 9.5$ Hz, $J = 1$ Hz, 1 H, 7'-H), 1.22 (t, $J = 7.2$ Hz, 3 H, CH ₃)	163.66 (CO), 140.57 (C-5), 137.38 (C-6), 136.94 (C-1'), 132.24 (C ^b), 129.22 (C ^a), 128.55 (C-2'), 127.48 (C-4'), 126.27 (C-3'), 85.52 (C-2), 62.7 (CH ₂), 52.01 (C-1), 51.58 (C-4), 49.47 (C-3), 46.22 (C-7), 13.63 (CH ₃)	–126.2 (m, 2 F, CF ₂ CF ₃), –121.6 (m, 2 F, CF ₂ CF ₂ –SO ₂), –108.9 (m, 2 F, CF ₂ –SO ₂), –81.9 (m, 3 F, CF ₃)
9d	7.32 (dd, $J = 7.6$ Hz, $J = 1$ Hz, 1 H, 2'-H), 7.26 (t, $J = 7.7$ Hz, 1 H, 4'-H), 7.19 (t, $J = 7.6$ Hz, 1 H, 3'-H), 6.97 (dd, $J = 8.1$ Hz, $J = 1.5$ Hz, 1 H, 5'-H), 6.28 (dd, $J = 5.6$ Hz, $J = 2.9$ Hz, 1 H, 6-H), 6.23 (dd, $J = 5.6$ Hz, $J = 3$ Hz, 1 H, 5-H), 4.30 (m, 1 H, 1-H), 4.27 (d, $J = 3.6$ Hz, 1 H, 3-H), 3.51 (m, 1 H, 4-H), 2.33 (d, $J = 9.8$ Hz, 1 H, 7-H), 1.66 (dt, $J = 9.8$ Hz, $J = 1.4$ Hz, 1 H, 7'-H)	159.12 (CO), 148.61 (C-1'), 141.75 (C-5), 135.93 (C-6), 129.01 (C-2'), 128.03 (C-4'), 125.42 (C-3'), 119.90 (C-6'), 117.02 (C-5'), 75.80 (C-2), 54.93 (C-1), 51.81 (C-4), 46.12 (C-7), 44.74 (C-3)	–126.3 (m, 2 F, CF ₂ CF ₃), –121.3 (m, 2 F, CF ₂ CF ₂ –SO ₂), –107.1 (m, 2 F, CF ₂ –SO ₂), –81.2 (m, 3 F, CF ₃)

cause conjugate additions to vinyl triflones are favourable reactions, proceeding with a variety of common nucleophiles under mild conditions. In this paper, it was shown that vinyl triflones are active dienophiles in Diels–Alder cycloaddition reactions. This reaction occurred highly stereoselectively and led to the formation of only the *endo* isomer.

Experimental Section

Melting points were determined with a Reichert microscope (hot-stage type) and are uncorrected. — ^1H -, ^{13}C - and ^{19}F -NMR spectra were recorded with a Bruker AC300 instrument; internal standards were tetramethylsilane (TMS) for ^1H and ^{13}C NMR, and CFCl_3 for ^{19}F NMR; ^1H -, ^{13}C - and ^{19}F -NMR spectra were recorded at 300 MHz, 75.5 MHz and 282.3 MHz, respectively. Chemical shifts are reported in parts per million (ppm) and coupling constants J in Hertz (Hz). — Column chromatography was performed with Merck silica gel (70–230 mesh) using various ratios of ethyl acetate/pentane as eluent. TLC was carried out on Merck 60F-254 precoated silica gel plates (0.25 mm). — Sodium trifluoromethanesulfonate (**1**),^[21] ethyl (trifluoromethanesulfonyl)acetate (**2**),^[20] ethyl (nonafluorobutanesulfonyl)acetate^{[19][26]} (**7**) were prepared according to standard procedures. Cyclopentadiene (**5**) was obtained by heating bicyclopentadiene and was used without further purification. Aldehydes **3a–d** were freshly distilled before use. When needed, reactions were carried out under argon and dry conditions.

General Procedures

Preparation of Ethyl 3-Aryl-2-(trifluoromethane)sulfonylpropenoates 4a–d and Ethyl 3-Aryl-2-(nonafluorobutane)sulfonylpropenoates 8a–d: 1 equiv. of ethyl (trifluoromethanesulfonyl)acetate (**2**) or ethyl (nonafluorobutanesulfonyl)acetate (**7**) and 1 equiv. of aldehyde **3a–d** were dissolved in toluene (20 mL). Then, piperidine (0.05 mL) and glacial acetic acid (0.1 mL) were added. The mixture was refluxed for 3–4 h with a water trap (Dean–Stark), until no further water separated. The solvent was removed under reduced pressure and the residue was taken up in Et_2O . The Et_2O was washed with HCl (50 mL, 5%), then washed several times with water, followed by drying (MgSO_4). The solvent was evaporated and the residue was purified by recrystallization from pentane/ethyl acetate or by column chromatography.

Compound, yield, mp: **4a**, 54%, 63°C; **4b**, 50%, oil; **4c**, 100%, 54°C; **4d**, 70%, 154°C; **8a**, 40%, 74°C; **8b**, 80%, oil; **8c**, 40%, 37°C; **8d**, 57%, 143–145°C.

Diels–Alder Cycloadducts 6a–d and 9a–d: A solution of 1 equiv. of **4a–d/8a–d** and 10 equiv. of cyclopentadiene (**5**) in CCl_4 (20 mL) was stirred at room temperature for 5–7 d; the disappearance of the starting olefins was monitored by TLC. The solvent was evaporated under reduced pressure. The oily residue was purified by column chromatography using a linear ethyl acetate gradient in pentane.

Compound, yield, mp: **6a**, 30%, 124°C; **6b**, 30%, 93°C; **6c**, 100%, oil; **6d**, 50%, oil; **9a**, 38%, oil; **9b**, 70%, oil; **9c**, 50%, oil; **9d**, 40%, 150–152°C.

Structure Determination: The data were collected up to $2\theta = 60^\circ$ with a Siemens SMART three-circle diffractometer equipped with a two-dimensional CCD detector. The exposure time was 10 s per frame. A total of 11425 reflections corresponding to the whole reciprocal space were collected, of which 4461 were unique ($R_{\text{int}} = 0.0214$) with $I > 2\sigma(I)$. The data (Table 5) were corrected for ab-

Table 5. Crystal and structure refinement data for the adduct **6a**

	6a
Empirical formula	$\text{C}_{17}\text{H}_{16}\text{F}_4\text{O}_4\text{S}$
Molecular mass	392.36
Crystal system	monoclinic
Space group	$P2_1/c$
Z	4
a [Å]	11.0910(3)
b [Å]	9.3056(3)
c [Å]	16.8955(5)
β [°]	98.9070(10)
V [Å ³]	1722.73(9)
Crystal size [mm]	$0.18 \times 0.54 \times 0.78$
T [K]	296(2)
Goodness-of-fit on F^2	1.059

sorption by the SADABS^[28] program specific to the CCD detector. The structure was solved by direct methods with SHELX-TL^[29] and the hydrogen atoms were located by the use of geometrical constraints. Refinement (300 parameters) was performed by full-matrix least-squares analysis of SHELX-TL up to $R_1(F_o) = 0.0503$ and $wR_2(F_o^2) = 0.1063$. Crystallographic data for the structure **6a** reported in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114256. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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- J. B. Hendrickson, D. D. Sternbarch, K. W. Bair, *Acc. Chem. Res.* **1977**, *10*, 306.
- J. B. Hendrickson, P. L. Skipper, *Tetrahedron* **1976**, *32*, 1627.
- K. Laping, M. Hanack, *Tetrahedron Lett.* **1979**, 1309.
- F. Massa, M. Hanack, L. R. Subramanian, *J. Fluorine Chem.* **1982**, *19*, 601.
- M. Hanack, B. Wilhelm, L. R. Subramanian, *Synthesis* **1988**, 592.
- R. Goumont, N. Faucher, G. Moutiers, M. Tordeux, C. Wakselman, *Synthesis* **1997**, 691.
- S. Patai, Z. Rappoport, C. Stirling in *The Chemistry of Sulfones and Sulfoxides*, John Wiley and Sons, New York, **1988**, p.1 and 483.
- N. S. Simpkins in *Sulfones in Organic Synthesis*, Pergamon, Oxford, **1993**, chapter 3, p.100 and references cited therein.
- F. G. Bordwell, N. R. Vanier, W. S. Matthews, J. B. Hendrickson, P. L. Skipper, *J. Am. Chem. Soc.* **1975**, *97*, 7160.
- T. Gramstad, R. N. Haszeldine, *J. Chem. Soc.* **1957**, 4069.
- F. Terrier, E. Kizilian, R. Goumont, N. Faucher, C. Wakselman, *J. Am. Chem. Soc.* **1998**, *120*, 9496.
- R. Goumont, M. Tordeux, C. Béguin, M. Gromova, F. Terrier, manuscript in preparation.
- Y. Koteswar Rao, M. Nagarajan, *Synthesis* **1984**, 757.
- M. Hanack, G. Bailer, J. Hackenberg, L. R. Subramanian, *Synthesis* **1991**, 1205.
- O. Menke, E. Steinhuber, A. G. Martinez, L. R. Subramanian, M. Hanack, *Synthesis* **1994**, 1291.
- N. Kamigata, T. Fukushima, Y. Terakawa, M. Yoshida, H. Sawada, *J. Chem. Soc., Perkin Trans. 1* **1991**, 627.
- S. Z. Zhu, *Synthesis* **1994**, 261.
- D. A. R. Happer, B. E. Steenson, *Synthesis* **1980**, 806.
- V. I. Ogoiko, V. P. Nazaretyan, A. Y. Ilchenko, L. M. Yagupol'skii, *J. Org. Chem. USSR, Int. Ed. Engl.* **1980**, 1200.

- [20] F. Eugene, B. Langlois, E. Laurent, *J. Fluorine Chem.* **1994**, 66, 301.
- [21] M. Tordeux, B. Langlois, C. Wakselman, *J. Org. Chem.* **1989**, 54, 2452.
- [22] L. F. Tietze, U. Beifuss in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford **1992**, vol. 2, p. 341.
- [23] U. Vogeli, W von Philipsborn, *Org. Magn. Res.* **1975**, 7, 617.
- [24] Details on the IR and MS data, together with the various data obtained for our compounds, are available as Supporting Information (Tables S₁–S₃).
- [25] F. Bigi, L. Chesini, R. Maggi, G. Sartori, *J. Org. Chem.* **1999**, 64, 1033 and references therein.
- [26] C. Harzdorf, J. N. Meussdoerffer, H. Niedeprüm, M. Wechsberg, *Liebigs Ann. Chem.* **1973**, 33.
- [27] R. J. Koshar, R. A. Mitsch, *J. Org. Chem.* **1973**, 38, 3358.
- [28] G. Sheldrick, *SADABS Programm: Siemens Area Detector Absorption Corrections*, unpublished.
- [29] *SHELX-TL: Structure Analysis Program 5.04*, Siemens Industrial Automation, Inc., Madison, WI, **1995**.

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