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β-Trifluoroacetylvinyl phenyl sulfoxide—synthesis, Diels–Alder reaction and computational study

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The Diels–Alder reaction of sulfoxide **2** with 1,3-dienes in CH_2Cl_2 afforded the corresponding CF_3-containing mono- and polycycloadducts. In the case of the reaction of sulfoxide **2** and sulfonium salt **10** with cyclopentadiene, a mixture of four diastereomers was formed. The rotational potential energy surface (PES) of reagents **2**, **10** was calculated and gave three minimum energy conformations with S=O, Ph or the lone pair synperiplanar to the carbon–carbon double bond.

Introduction

Substituted α,β-unsaturated sulfoxides have received considerable attention as dienophiles and also as Michael acceptors.[1] Substituted phenyl vinyl sulfoxides can effectively function as the corresponding acetylene equivalents in Diels–Alder reactions.[2,3] Besides, it is known that incorporation of a fluorine atom or CF_3 group into a bioactive molecule leads to increased lipid solubility and thereby enhances the rate of absorption and transport of that substance *in vivo*.[4] β-Trifluoroacetylvinyl sulfoxides are expected to be good dienophiles and promising building blocks for the construction of novel CF_3-containing compounds, but their synthesis and reactivity in Diels–Alder cycloadditions have not been described previously in the literature.

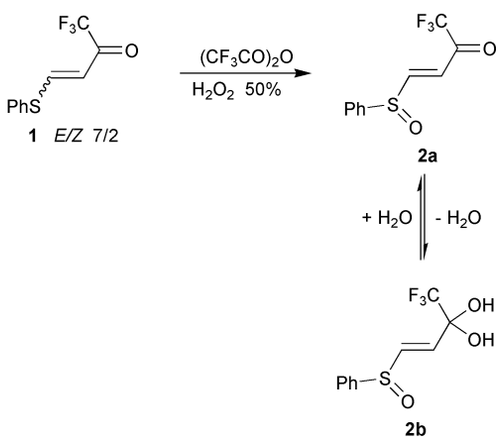
Results and discussion

At the present time many methods for the oxidation of acyl substituted vinyl sulfides to the corresponding sulfoxides are available in the literature.[5–11] In recent work [12] we have prepared some trifluoroacetylvinyl sulfones by oxidation of the readily available sulfides. We have found that these alkenes are very reactive electrophiles,[13,14] and dienophiles.[12] In the course of these investigations we devised a method for the synthesis of the corresponding sulfinyl analogues.

We preferred to use trifluoroperacetic acid as oxidant, because of the high reactivity of this reagent and the simple experimental setup. Oxidation of sulfide **1** was carried out in trifluoroacetic acid using 50% hydrogen peroxide. We found that the preparation of sulfoxide **2** demands accurately measured, stoichiometric quantities of hydrogen peroxide (Scheme 1).

The structure of **2** was established by NMR spectroscopy and X-ray crystallography (Fig. 1). It is interesting that in the crystal, sulfoxide **2** exists in the diol form **2b** exclusively, but in CH_2Cl_2 solution spontaneous elimination of water was observed leading to the keto-form (*E*)-1,1,1-trifluoro-4-(phenylsulfinyl)but-3-en-2-one **2a**. In all cases only the (*E*)-isomers of sulfoxides **2** were obtained; we believe that acidic isomerization of enones **2** to the more stable (*E*)-isomers occurred during reaction. The same effect takes place in the case of the sulfone analogues.[12]

Sulfoxide **2a** crystallised in the centrosymmetric group *C*2/*c*. The crystal cell contains both enantiomers. Molecules



Scheme 1

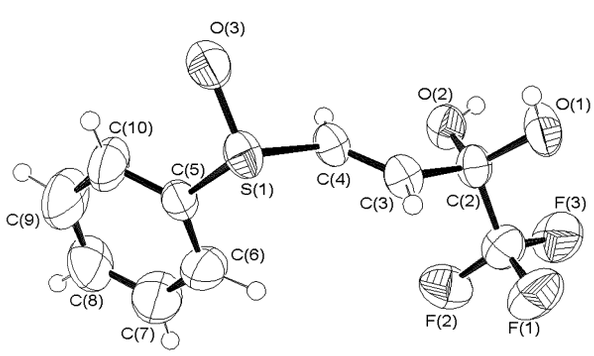


Fig. 1 Molecular structure of **2b**.

are joined in dimers by hydrogen bonds O_1–H ··· O_3'=S_1' between the hydroxy and sulfinyl groups. The other hydroxy group (O_2–H) is bonded to the sulfinyl group of the molecule displaced by $(0,\frac{1}{2},0)$, forming a stack of molecules of the same sulfoxide moiety configuration, which is symmetric about the 2-fold symmetry axis parallel to the *y*-axis of the cell.

We now report the investigation of the reactivity of vinyl sulfoxide **2** in the reaction with 1,3-dienes. We found that sulfoxide **2** is a highly active dienophile. Its reactions with cyclic and linear dienes proceed easily even at 0 °C in absolute CH_2Cl_2 to form cycloadducts **5**–**9** in excellent yield.

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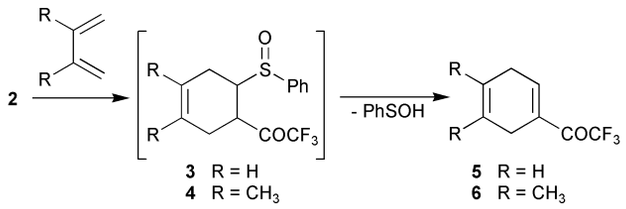
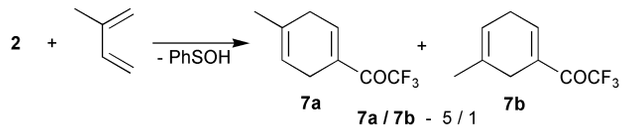
We started our investigation with interaction of the sulfoxide **2** with linear dienes. Reaction of buta-1,3-diene and 2,3-dimethylbuta-1,3-diene with the sulfoxide **2** results in the formation of cycloadducts **3**, **4** which are very unstable giving, after spontaneous elimination of the sulfinyl group, the corresponding α,β-unsaturated trifluoromethyl ketones **5**, **6** (Scheme 2).



Scheme 2

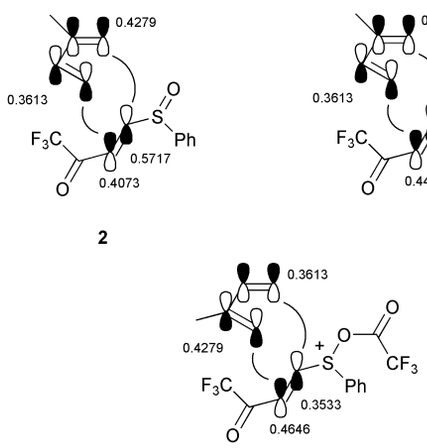
To study the regiochemistry of the cycloaddition we investigated the reaction of sulfoxide **2** with isoprene. We found that a mixture of the two possible cycloadducts **7a** and **7b** is formed (Scheme 3). The regioisomer with *para*-situated substituents is



Scheme 3

formed predominantly **7a/7b** (by NMR 5 : 1, crude; 4 : 1, after purification).

We have observed similar regiochemistry in the reaction of isoprene with sulfone analogs of **2**, which also give **7a** : **7b** in a 2 : 1 ratio.[12] The increase in regioselectivity in the case of sulfoxide **2** can be explained using the values of the LUMO atomic contributions at the HF/6-31G* level. The preferential formation of the *para*-$COCF_3$-isomers in the case of reaction with isoprene is in good agreement with "large–large" molecular orbital overlap in the transition state (Scheme 4). In the

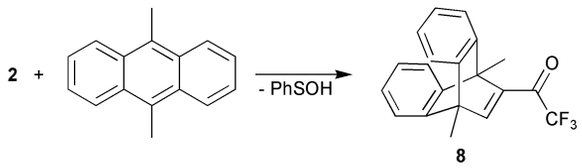


Scheme 4

case of sulfoxide **2** a greater difference compared with the sulfone analogues between the LUMO orbital coefficients at the carbon atoms of the double bond is observed (Scheme 4).

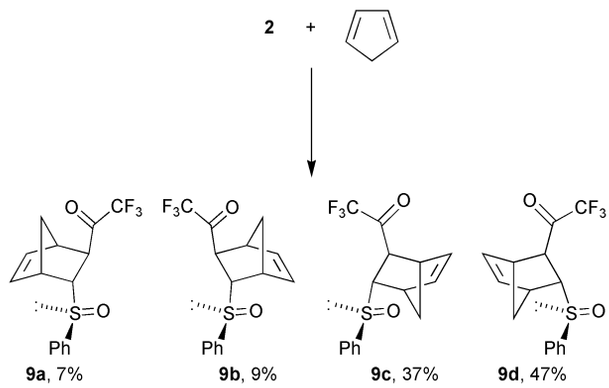
In the case of reaction with 9,10-dimethylanthracene prolonged reflux in CH_2Cl_2 is required. Unfortunately the yield of the target product **8** was lower at 63% (Scheme 5). We believe that this is connected with the low stability of the sulfoxide **2** at higher temperatures.

It is worth noting that the reaction of α,β-unsaturated



Scheme 5

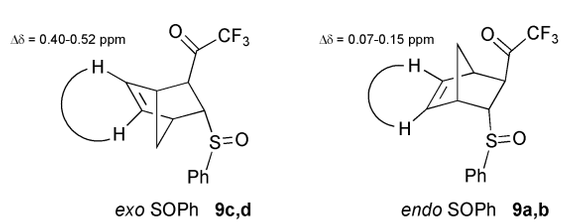
racemic sulfoxides with cyclic dienes have been reported and low stereoselectivity was obtained as a rule.[15,16] The stereochemistry of addition of sulfinyl dienophiles has been examined from a computational point of view,[17] but the matter is still controversial.[18] Low stereoselectivity is observed in the case of the reaction of sulfoxide **2** with cyclopentadiene: a mixture of four isomers was isolated, and the individual stereoisomers were not separated (Scheme 6). In this case elimination of



Scheme 6

the sulfinyl group did not take place. Cycloadducts **9c**,**d** having an *endo*-oriented $COCF_3$ group were predominant (ratios of stereoisomers **9a**–**d** before and after purification are equivalent).

The stereochemistry of compounds **9a**–**d** was established by a detailed analysis of the ^{1}H-NMR spectra, as described below. Bicyclic products **9a**–**d** with *trans*-arranged $COCF_3$ and SOPh groups have $^3J_{Hexo\text{-}Hendo}$ in the range 4.4–4.6 Hz, but in the case of *cis*-cycloadducts ^3J = 9–10 Hz is observed.[19] If the $COCF_3$ group is *endo*-arranged a significant difference between the signals of the CH-5 and CH-6 protons in the ^{1}H-NMR spectra is observed. In contrast the compounds with the $COCF_3$ group in the *exo*-position have similar shifts of the CH-5 and CH-6 protons in the ^{1}H-NMR spectra (Scheme 7). Previously we



Scheme 7

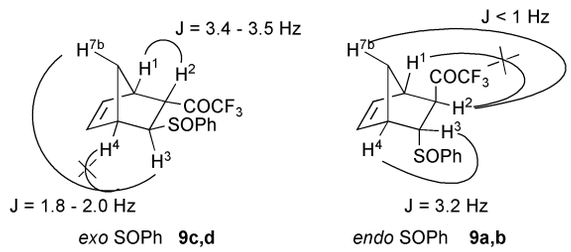
observed the same effect in cycloadducts with the sulfone analogues.[12]

The coupling constants between H-3 and H-7b in the *endo*-$COCF_3$ oriented cycloadducts **9c**,**d** are found to be 1.8–2.0 Hz, but in adducts **9a**,**b** only broadening of the corresponding signals of H-2 and H-7b takes place. In both cases coupling between the *endo*-oriented and bridgehead protons (H-2/H-1 for **9a**,**b** and H-3/H-4 for **9c**,**d**) was very small (Scheme 8). Similar dependences for the structurally related sulfoxides have been described in the literature.[12,20]

According to the literature data for analogous sulfoxides,[21,22–24] the proton which is close to the oxygen of the

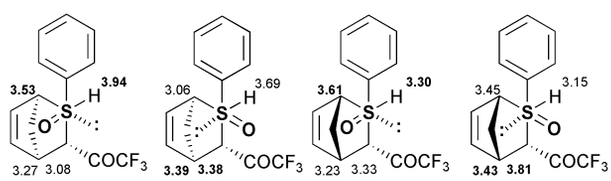
Table 1 ^{1}H-NMR assignments for cycloadducts **9a–d**

H	*endo* SOPh **9a**	*endo* SOPh **9b**	*exo* SOPh **9c**	*exo* SOPh **9d**
1	3.27	3.39	3.23	3.43
2	3.08	3.38	3.33	3.81
$J_{H2(H3)H7b}$/Hz	<1.0	<1.0	1.8	2.0
3	3.94	3.69	3.30	3.15
4	3.53	3.06	3.61	3.45
J_{H3H4}/Hz	3.2	3.2	3.4	3.5
5/6	6.41/6.33	6.57/6.42	6.27/5.87	6.40/5.88
$\Delta\delta$ (6 − 5)	0.08	0.15	0.40	0.52
7a	1.49	1.94	2.01	2.18
7b	1.61	1.44	1.65	1.55
$\Delta\delta$ (7a − 7b)	−0.12	0.50	0.36	0.63



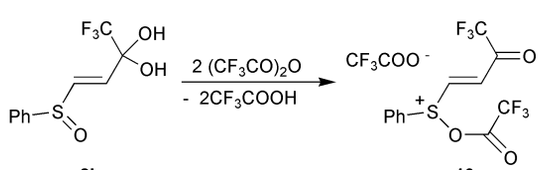
Scheme 8

sulfoxide moiety is shifted downfield, while the proton which is close to the lone pair of the sulfoxide is shifted upfield. On the basis of these data a correlation between signals in the ^{1}H-NMR spectra and structure was achieved (Scheme 9, Table 1).



Scheme 9

In order to improve the stereoselectivity of the cycloaddition of sulfoxide **2** we investigated the reaction of sulfoxide **10** activated by trifluoroacetic acid anhydride (TFAA) with isoprene and cyclopentadiene. Reaction of sulfoxide **2** with TFAA proceeds at room temperature in absolute methylene chloride to form sulfonium salt **10** quantitatively (Scheme 10). The



Scheme 10

structure of **10** was determined from its ^{1}H-NMR and ^{13}C-NMR spectra.

We found that sulfonium salt **10** is a highly reactive dienophile. Its reactions with isoprene proceed at −10 °C in absolute CH_2Cl_2 during 10 min. However, as in the case of reaction with non-activated sulfoxides, a mixture of the two regioisomers **7a** and **7b** was formed. The regioisomer with *meta*-situated substituents is formed predominantly: **7a** : **7b** = 1 : 1.5. The opposite regioselectivity to the sulfoxide **2** can be explained using the values of the LUMO atomic contributions at the HF/6-31G* level (Scheme 4, Table 4).

In the case of reaction of sulfonium salts **10** with cyclopentadiene the mixture of four cycloadducts **9a–d** was formed (Table 2).

Table 2 Yields and diastereomeric ratio cycloadducts **9a–d** in reaction with **2** and **10**

Entry	Diastereomeric ratio **9a**	**9b**	**9c**	**9d**	Yield (%)
2	7	9	37	47	72
10	19	19	31	31	85

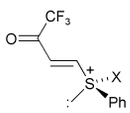
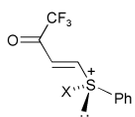
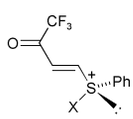
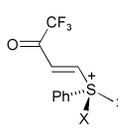
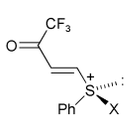
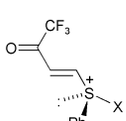
An increase in the *endo*-SOPh cycloadducts **9a**,**b** and the levelling of the ratio of each diastereomer pair **9a**–**b** and **9c**–**d** was observed in comparison of the reaction of sulfonium salts **10** with the reaction of sulfoxide **2**.

For the understanding of the stereochemistry of cycloaddition it is important to know the conformations of reagents **2**, **10**, and how these conformations can be "held in place" (importance of rotational barriers). Methyl vinyl sulfoxide has been computed by Kahn and Hehre[25] who showed that conformation with a C=C–S=O dihedral angle of approximately 0° represents the global minimum on the rotational potential energy surface (PES). Later Tietze[26] also calculated some vinyl sulfoxides with electron-withdrawing substituents (CN, COOR, COOH) in the α-position and their complexes with Lewis acids. However, no computational study of vinyl sulfoxides with β-electron-withdrawing substituents has been described in the literature previously.

The rotational potential energy surface (PES) of sulfoxide **2** and sulfonium salt **10** was calculated by means of the density functional theory (DFT) methods using the TAINA program.[27] The density functional PBE96[28] and the triple-ζ valence-split basis set augmented with polarization functions (TZVP) of Schäfer *et al.*[29] were used for the DFT calculations. Our calculation of sulfoxide **2** and sulfonium salt **10** showed conformation **2c** to be global, with the S=O bond almost syncoplanar to the carbon–carbon double bond, and **2a**,**e** to be local minima on the rotational potential energy surface (PES) (Table 3). The energy difference between the minima and the height of the rotational barrier was calculated to be 5.6 and 6.4 kcal mol^{-1} and the relative energy differences between **2c** and **2a**,**e** were 2.5 and 4.4 kcal mol^{-1}. Conformer **2c** has a C=C–S=O dihedral angle of −10°. The sulfonium salt **10** displays a different energy profile, where **10a** (C=C–S=O dihedral angle −120°, lone pair is syncoplanar to the C=C bond) is the global minimum and **10c**,**e** are 0.5 and 0.9 kcal mol^{-1} higher in energy (Fig. 2). We supposed that this is a consequence of the repulsion between the trifluoroacetyl group and the (*Z*)-hydrogen.

Calculations showed that in all cases low rotation barriers were observed between the rotamers **2a**–**c**–**e** and **10a**–**c**–**e**. Though the energy difference between the observed conformers would give a moderate conformational preference for these compounds, the experimental results show all of the conformers to be considered as reactive and even the NMR spectra show a unique conformer in the solution. Therefore on the basis of these DFT calculations one could predict the low diastereoselectivity in the Diels–Alder reaction, where a mixture of

Table 3 Dihedral angle and relative energy of sulfoxide **2** and sulfonium salt **10**

Compound	Sulfoxide **2**, X = O^-		Sulfonium salt **10**, X = $OCOCF_3$	
	Dihedral angle/°	rel *E*/kcal mol^{-1}	Dihedral angle/°	rel *E*/kcal mol^{-1}
a 	−135	2.54	−120	0
b 	−75	5.40	−65	1.37
c 	−10	0	−20	0.52
d 	60	6.42	45	5.60
e 	140	4.39	140	0.87
f 	165	4.58	180	1.68

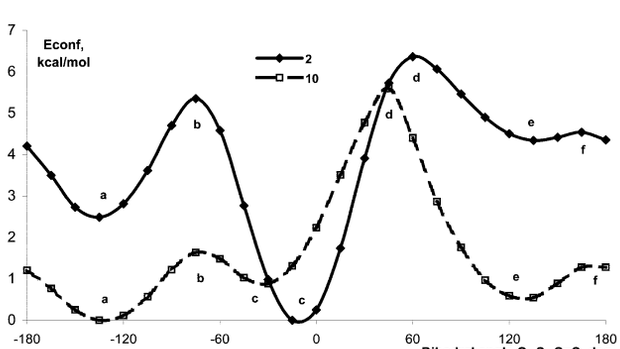


Fig. 2 Rotational PES of sulfoxide **2** and sulfonium salt **10**.

diastereomers in approximately equal quantities would be formed, taking into account the assumption of the higher reactivity of the conformationally strained rotamers of the structures investigated due to the generally reduced LUMO–HOMO gap in these structures. This would result in greater electrophilicity of the higher energy rotamers.[30] The rotational barriers in **10** are generally lower than in **2**. This seemed to be the additional explanation of the lower stereoselectivity of the cation **10** additions. Experimental data confirm our calculations and are in a good agreement with literature calculations[26] and with experiments of Kagan and Ronan.[31]

In order to describe the conformational features of the sulfonium salt **10** in detail we performed a two-dimensional conformational search of the molecule. Since the conformation of the trifluoroacetoxy substituent was invariable in the course of the internal rotation of the trifluoroacetylvinyl substituent when the 1D-search was performed (the S–O–C=O dihedral angle varied from 86 to 91 degrees), two other bonds of the sulfur atom were chosen to perform the 2D investigation. The values of the dihedral angles were varied from 0 to 180 degrees for the phenyl substituent (T_1) and from −180 to 180 degrees for the trifluoroacetylvinyl fragment (T_2), using a step of 15 degrees in both cases (25 and 13 points respectively). Other internal coordinates are optimized using the PBE96/TZVP approximation. The resulted PES surface is shown in Fig. 3.

Considering the most stable conformer found at (T_1 = 45°, T_2= −135°), one may observe two other minima interconverting by changing the O=S–C=C dihedral angle: at (T_1 = 60°, T_2 = −45°) with a relative energy of 0.97 kcal mol^{-1} and at (T_1 = 60°, T_1 = 135°) with a conformational energy of 0.67 kcal mol^{-1}. The energies of the transition states in the course of the internal rotation between these conformers are relatively small (1.75 kcal mol^{-1} and 1.29 kcal mol^{-1}) and show that no clear conformational preference exists for the trifluoroacetylvinyl group orientation in the cation structure. The barrier to phenyl rotation found at (T_1 = 0, T_2 = −150°) is only 4.14 kcal mol^{-1} higher than the most stable form of the molecule. This conformational lability obviously results in a lack of selectivity in the cycloaddition reactions.

Frontier molecular orbital theory is one of the most successful approaches in the prediction of the regio- and *endo–exo* selectivity for Diels–Alder reactions. We have calculated the LUMO energy and atomic orbital contributions of reagents **2**,**10** in the most stable conformation at the HF/6-31G* level. There is a dramatic difference between the LUMO energies of sulfoxide **2** and sulfonium salt **10**. The presence of the positive charge in the sulfonium salt **10** results in a significant decrease in the LUMO energy, therefore reagent **10** is a much more electron-deficient and reactive dienophile (Table 4). Moreover the absolute values of the LUMO atomic contributions of **2**/**10** really predict the opposite regioselectivity of the reaction with isoprene in the case of salt **10** compared to the sulfoxide **2**.

The stereoselectivity of the reactions of **2**, **10** with cyclopentadiene is in good agreement with the LUMO orbital

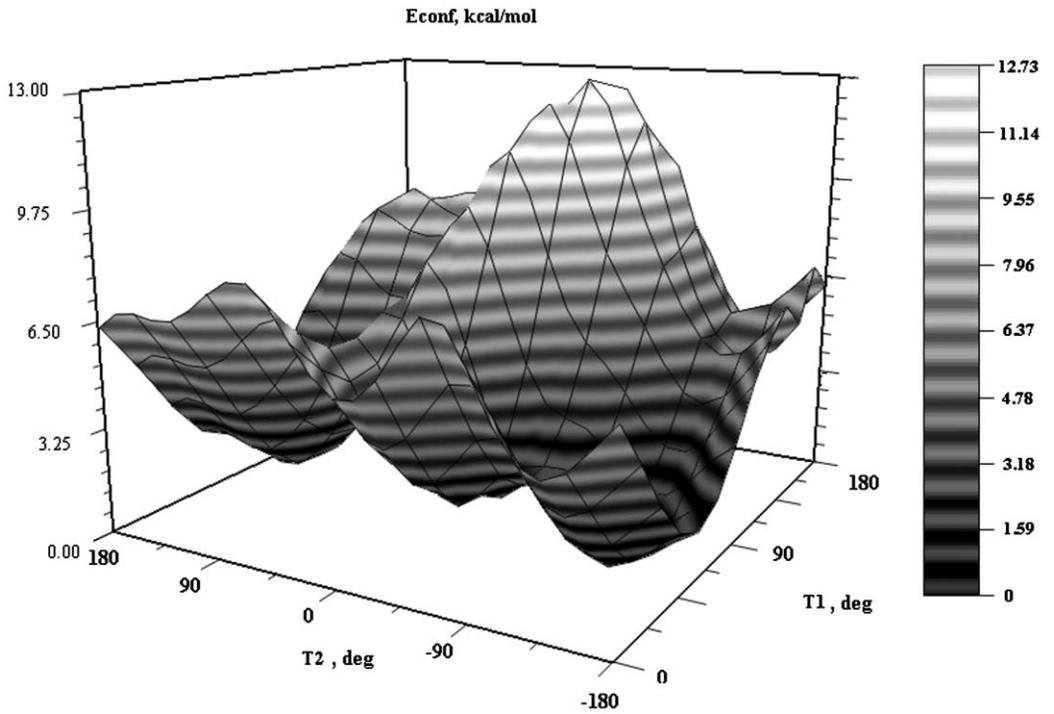


Fig. 3 Two-dimensional rotational PES of cation **10**.

Table 4 The absolute values of LUMO atomic contributions

LUMO	**2c**	**10a**
O (1)	0.4202	0.2782
C (2)	0.4105	0.2132
C (3)	0.4073	0.4646
C (4)	0.5717	0.3533
S (5)	0.2754	0.6042
O (6)	0.0690	0.4649
E/eV	1.45	−3.56

coefficients calculated. We have found that the reaction with cyclopentadiene is *endo*-$COCF_3$ selective. We suppose that the *endo*-$COCF_3$ selectivity is connected with the secondary *p*-orbital interaction between the π-system of the dienes and the π-system of the carbonyl groups of the reagents **2**, **10**. Having greater LUMO coefficients at the carbonyl group than at the sulfinyl group in sulfoxide **2**, secondary *p*-orbital interactions in the transition state are more probable between the C(2) carbon of the reagents and the π-system of the diene resulting in preferable *endo*-$COCF_3$ stereochemistry. In the case of sulfonium salt **10** LUMO coefficients at the sulfinyl group are much higher leading to an increase in the proportion of *endo*-SOPh cycloadducts **9a**,**b**, but *endo*-$COCF_3$ cycloadducts are also formed predominantly.

We also investigated the possibility of sulfinyl group removal from bicyclic cycloadduct **9**. But our attempts to prepare the corresponding diene from cyclopentadiene derivatives **9** were unsuccessful, probably due to the instability of the forming diene connected with its high strain and the basic reaction conditions. We also attempted to carry out this reaction under thermal conditions, but no target product was observed.

In conclusion, we have prepared a novel dienophile—(*E*)-1,1,1-trifluoro-4-(phenylsulfinyl)but-3-en-2-one **2**—and investigated its reactivity in Diels–Alder reactions. The reaction of the sulfoxide **2** with dienes is rather convenient for the one-step preparation of trifluoroacetyl substituted derivatives of cyclohexa-1,4-diene **5**–**7**, and polycyclic adducts **8**, **9**. We show that sulfonium salt **10** prepared easily from sulfoxide **2** by reaction with TFAA is a highly reactive dienophile. The DFT calculation of the rotational potential energy surface of reagents **2**, **10**, the two-dimensional search of conformational space of **10** and *ab initio* calculations of LUMO energy are in a good agreement with experimental results.

Experimental

General procedures

All solvents used were dried and distilled according to standard procedures. Silica gel Merck 60 and Merck $60F_{254}$ plates were used for conventional and analytical (TLC) chromatography, respectively. Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on a Varian VXR-400 and Bruker AM 400C spectrometers with TMS as an internal standard. *J* values are given in Hz. The IR spectra were obtained with UR-20 spectrometer.

Crystal structure determination of sulfoxide 2 †

Crystal data. A crystal of **2** was prepared by the solvent evaporation from the acetonitrile solution. Formula unit $C_{10}H_9F_3O_3S$, M = 266.23; monoclinic, a = 19.913(4) Å, b = 5.138(1) Å, c = 22.413(4) Å, β = 90.92(3)°, cell volume V = 2292.8(8) Å^3 space group $C2/c$, Z = 8, T = 293K. From the 1181 unique reflections of 1219 collected (R_{int} = 0.0415) the final structure was refined using the full-matrix least-square method to the final values R_f = 0.0318, wR_f = 0.0890.

Preparation of sulfoxide 2

To a solution of vinyl sulfide **1** (10 mmol) in TFA (15 ml) a mixture of 50% H_2O_2 (10 mmol) and TFA (10 ml) was added at −20 °C. The mixture was stirred at −20 °C for three hours. Removal of the solvent under reduced pressure at 0 °C afforded products. The white solid was washed with benzene (2 × 5 ml) and dried in air.

† CCDC reference number 161707. See http://www.rsc.org/suppdata/p1/b2/b202583c/ for crystallographic files in .cif or other electronic format.

(*E*)-1,1,1-Trifluoro-4-(phenylsulfinyl)but-3-ene-2,2-diol (2). Yield 76%, white solid, mp 156–158 °C. Found C, 45.02; H, 3.53. Calc for $C_{10}H_9F_3O_3S$ C, 45.11; H, 3.41%; ν_{max}(Nujol)/cm^{-1} 1675 (C=C), 3180 (OH). Sulfoxide **2** exist in keto-form in $CDCl_3$. δ_H (400 MHz, $CDCl_3$) 7.94 (2 H, m, Ph), 7.79 (1 H, d, *J* 15.3, CH=), 7.76 (1 H, m, Ph), 7.67 (2 H, m, Ph), 7.34 (1 H, d, *J* 15.3, CH=). δ_C (100 MHz, $CDCl_3$) 177.6 (*J* 37.8), 137.9, 135.7, 129.5, 127.8, 127.7, 127.6, 121.8 (*J* 289.9).

Preparation of Diels–Alder cycloadducts 4–9

To a solution of vinyl sulfoxide **2** (1 mmol) in CH_2Cl_2 (5 ml) the corresponding diene (2 mmol) was added. The mixture was stirred at room temperature (in the case of the reaction with anthracene reactions were carried out at 40 °C with stirring). Removal of the solvent under reduced pressure afforded products, which were purified by column chromatography over silica gel using hexane as eluent.

1-Cyclohexa-1,4-dien-1-yl-2,2,2-trifluoroethanone (5). Yield 81%. The ^{1}H and ^{13}C NMR data of **5** were in agreement with the literature.[12]

1-(4,5-Dimethylcyclohexa-1,4-dien-1-yl)-2,2,2-trifluoroethanone (6). Yield 85%. The ^{1}H and ^{13}C NMR data of **6** were in agreement with the literature.[12]

The reaction of **2** with isoprene gave a mixture of regioisomers **7a/7b** (by NMR 5 : 1, crude; 4 : 1 after purification by chromatography), yield 80%, colourless oil. The ^{1}H and ^{13}C NMR data of **7a/7b** were in agreement with the literature.[12]

1-[1,8-Dimethyltetracyclo[6.6.2.0.^{2,7}.0^{9,14}]hexadeca-2,4,6,9,11,13,15-heptaen-15-yl]-2,2,2-trifluoroethan-1-one (8). Yield 63%. The ^{1}H and ^{13}C NMR data of **8** were in agreement with the literature.[12]

The reaction of **2** with cyclopentadiene gave a mixture of stereoisomers 1-[3-*endo*-(phenylsulfinyl)bicyclo[2.2.1]hept-5-en-2-*exo*-yl]-2,2,2-trifluoroethanones (**9a/9b**) and 1-[3-*exo*-(phenylsulfinyl)bicyclo[2.2.1]hept-5-en-2-*endo*-yl]-2,2,2-trifluoroethanone (**9c/9d**) (by NMR 7 : 9 : 37 : 47 after purification by chromatography), yield 72%, colourless oil; Found for mixture of isomers: C, 57.14; H, 4.01. Calc for $C_{15}H_{13}F_3O_3S$ C, 57.32; H, 4.17 %; ν_{max}(Nujol)/cm^{-1} 1760–1770 (C=O).

(9a). δ_H (400 MHz, $CDCl_3$) 7.68–7.46 (5 H, m, Ph), 6.41 (1 H, dd, *J* 3.5, *J* 5.3, CH=), 6.33 (1 H, dd, *J* 3.0, *J* 5.3, CH=), 3.94 (1 H, dd, *J* 3.2, *J* 4.4, CH-SOPh), 3.53 (1 H, br s, CH), 3.27 (1 H, br s, CH), 3.08 (1 H, br d, *J* 4.4, CH-COCF$_3$), 1.61 (1 H, ddd, *J* 9.6, *J* 1.4, *J* 1.4, CH-7b), 1.49 (1 H, br d, *J* 9.6, CH-7a).

(9b). δ_H (400 MHz, $CDCl_3$) 7.68–7.46 (5 H, m, Ph), 6.57 (1 H, dd, *J* 3.0, *J* 5.6, CH=), 6.42 (1 H, dd, *J* 3.1, *J* 5.6, CH=), 3.69 (1 H, dd, *J* 3.2, *J* 4.4, CH-SOPh), 3.39 (1 H, br s, CH), 3.38 (1 H, br d, *J* 4.4, CH-COCF$_3$), 3.06 (1 H, br s, CH), 1.94 (1 H, br d, *J* 9.2, CH-7a), 1.44 (1 H, ddd, *J* 9.2, 1.5, *J* 1.4, CH-7b).

(9c). δ_H (400 MHz, $CDCl_3$) 7.68–7.46 (5 H, m, Ph), 6.27 (1 H, dd, *J* 3.5, *J* 5.6, CH=), 5.87 (1 H, dd, *J* 3.3, *J* 5.6, CH=), 3.61 (1 H, br s, CH), 3.33 (1 H, dd, *J* 4.5, *J* 3.4, CH-COCF$_3$), 3.30 (1 H, br d, *J* 4.5, CH-SOPh), 3.23 (1 H, br s, CH), 2.01 (1 H, br d, *J* 9.4, CH-7a), 1.65 (1 H, ddd, *J* 9.4, *J* 1.8, *J* 1.4, CH-7b).

(9d). δ_H (400 MHz, $CDCl_3$) 7.68–7.46 (5 H, m, Ph), 6.40 (1 H, dd, *J* 3.5, *J* 5.5, CH=), 5.88 (1 H, dd, *J* 3.3, *J* 5.5, CH=), 3.81 (1 H, dd, *J* 4.4, *J* 3.5, CH-COCF$_3$), 3.45 (1 H, br s, CH), 3.43 (1 H, br s, CH), 3.15 (1 H, br d, *J* 4.4, CH-SOPh), 2.18 (1 H, br d, *J* 9.6, CH-7a), 1.55 (1 H, ddd, *J* 9.6, *J* 2.0, *J* 1.4, CH-7b).

For mixture of isomers δ_C (100 MHz, $CDCl_3$) 189.4 (*J* 34.8), 189.2 (*J* 34.7), 188.6 (*J* 34.8), 188.5 (*J* 34.6), 138.9, 138.7, 138.5, 138.1, 135.6, 135.5, 135.5, 135.1, 134.7, 134.4, 134.4, 134.2, 134.0, 133.9, 132.6, 132.5, 129.4, 129.3, 129.0, 128.9, 127.9, 127.8, 127.6, 127.5, 115.4 (*J* 292.0), 115.2 (*J* 292.3), 115.0 (*J* 292.2), 114.9 (*J* 292.3), 66.2, 66.0, 65.5, 64.7, 49.3, 49.0, 48.9, 48.9, 48.7, 48.1, 47.9, 47.1, 47.0, 46.7, 46.6, 46.4, 44.9, 44.8, 44.7, 44.5.

Preparation of sulfonium salt 10

Compound **10** could not be purified for analysis, and slowly decomposed at room temperature. It was stored in the freezer until it was used. To a solution of vinyl sulfoxide **2** (0.1 mmol) in $CDCl_3$ (0.5 ml) in an NMR tube TFAA (0.2 mmol) was added. The mixture was stirred for 1 min at room temperature and NMR spectra were taken (CF_3CO_2H is a by-product that is seen in the ^{1}H and ^{13}C NMR).

Phenyl[(trifluoroacetyl)oxy][(1*E*)-4,4,4-trifluoro-3-oxobut-1-enyl]sulfonium trifluoroacetate (10). δ_H (400 MHz, $CDCl_3$) 12.3 (2 H, s, CF_3COOH), 8.55 (1 H, d, *J* 14.4, CH=), 8.20 (2 H, m, Ph), 7.93 (3 H, m, Ph), 7.81 (1 H, d, *J* 14.4, CH=). δ_C (100 MHz, $CDCl_3$) 177.6 (*J* 37.8), 166.0 (*J* 27.2), 164.5 (*J* 40.2), 160.3 (*J* 42.3), 148.1, 139.5, 135.6, 130.7, 129.0, 128.4, 121.6 (*J* 289.9), 118.9 (*J* 290.1), 115.6 (*J* 287.3), 115.4 (*J* 288.0).

Reaction of sulfonium salt 10 with isoprene and cyclopentadiene

To a solution of vinyl sulfoxide **2** (1 mmol) in absolute CH_2Cl_2 (5 ml) TFAA (2 mmol) was added. The mixture was stirred at room temperature 10 min. Then cyclopentadiene (3 mmol) or isoprene (3 mmol) was added dropwise during 10 min at −10 °C in the case of isoprene and −35 °C in the case of cyclopentadiene. The temperature of the reaction mixture was slowly increased to 20 °C. Removal of the solvent under reduced pressure afforded products, which were purified by column chromatography over silica gel using hexane as eluent.

The reaction of **10** with isoprene gave a mixture of regioisomers **7a/7b** (by NMR 1 : 1.5, crude; 1 : 1.3 after purification by chromatography), yield 67%, colourless oil.

The reaction of **10** with cyclopentadiene gave a mixture of stereoisomers 1-[3-*endo*-(phenylsulfinyl)bicyclo[2.2.1]-hept-5-en-2-*exo*-yl]-2,2,2-trifluoroethanones (**9a/9b**) and 1-[3-*exo*-(phenylsulfinyl)bicyclo[2.2.1]hept-5-en-2-*endo*-yl]-2,2,2-trifluoroethanone (**9c/9d**) (by NMR 19 : 19 : 31 : 31 after purification by chromatography), after purification, yield 85%, colourless oil; Found for mixture of isomers: C, 57.19; H, 4.06. Calc for $C_{15}H_{13}F_3O_3S$ C, 57.32; H, 4.17 %; ν_{max}(Nujol)/cm^{-1} 1760–1770 (C=O).

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