Synthesis of β-trifluoroacetyl-substituted vinyl sulfones and vinyl sulfides

A. L. Krasovsky, V. G. Nenajdenko, and E. S. Balenkova*

M. V. Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: nen@acylium.chem.msu.ru

Oxidation of β-(trifluoroacetyl)vinyl sulfides afforded a series of the corresponding sulfones. The reactions of sulfones with various alkyl- and arylthiols were studied. These reactions provide the basis for a new procedure for the synthesis of β-(trifluoroacetyl)vinyl sulfides.

Key words: vinyl sulfides, vinyl sulfones, oxidation, nucleophilic substitution, thiols.

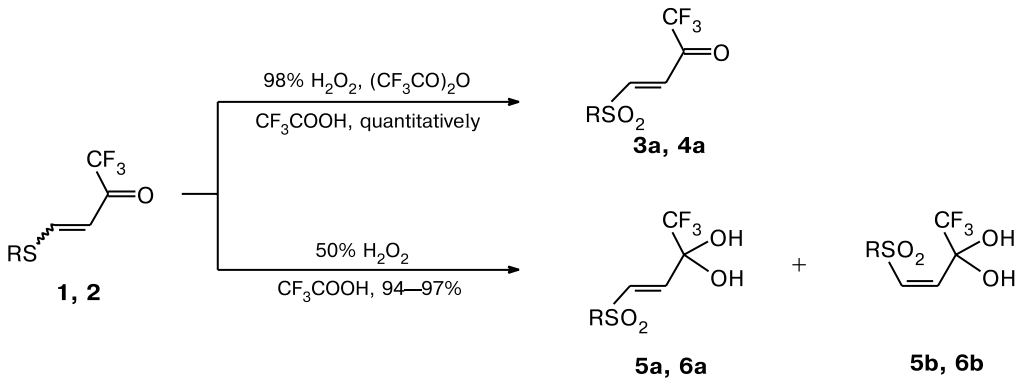
β-Acylvinyl sulfones are of considerable theoretical and practical interest.[1,2] This interest stems primarily from the fact that these compounds are active dienophiles and can serve as synthetic equivalents of vinyl ketones[3—6] and ethynyl ketones[7—12] because the sulfonyl group can readily be removed from the resulting cycloadducts. In addition, β-acylvinyl sulfones serve as active electrophiles and the sulfonyl group often acts as a good leaving group.[13—15] However, the only example of the synthesis of analogous fluorinated compounds, *viz.*, β-aryl-β-(methylsulfonyl)vinyl trifluoromethyl ketones, was reported,[16] whereas unsubstituted β-(trifluoroacetyl)vinyl sulfones have not been prepared at all.

In the present study, we developed a procedure for the synthesis of β-(trifluoroacetyl)vinyl sulfones and examined their electrophilic properties in reactions with thiols.

We used β-(trifluoroacetyl)vinyl sulfides **1** and **2** as the starting compounds, which were prepared by trifluoroacetylation according to the Hojo method from the corresponding readily available phenyl vinyl sulfide and methyl vinyl sulfide.[17] We studied oxidation of β-(trifluoroacetyl)vinyl sulfides **1** and **2** to the corresponding sulfones. Previously,[16] oxidation of analogous compounds, *viz.*, β-aryl-β-(methylthio)vinyl trifluoromethyl ketones, has been performed with the use of hydrogen peroxide in acetic acid. However, the compounds under consideration were not oxidized under these conditions at room temperature, whereas an attempt to carry out the reaction at higher temperature resulted in complete resinification of the reaction mixture. Because of this, we performed oxidation of sulfides **1** and **2** with a stronger oxidizer, *viz.*, trifluoroperacetic acid, which allows one to carry out oxidation under mild conditions. Oxidation of vinyl sulfides to sulfones under the action of trifluoroperacetic acid can be carried out both in dichloromethane[18,19] and trifluoroacetic acid.[20]

It should be noted that oxidation with trifluoroperacetic acid, which was prepared by mixing 50% hydrogen peroxide and trifluoroacetic acid (1 equiv./1 equiv.), afforded the corresponding diols **5** and **6** rather than the expected β-(trifluoroacetyl)vinyl sulfones **3** and **4** (Scheme 1).

Scheme 1



R = Ph (**1**, **3**, **5**), Me (**2**, **4**, **6**); *E*/*Z* = 7/5 (**1**), 3/1 (**2**)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1925—1930, November, 2002.

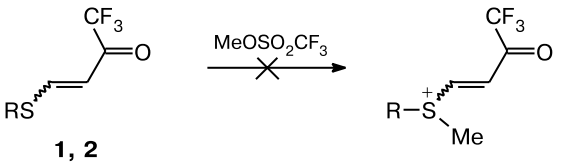
1066-5285/02/5111-2080 $27.00

Interestingly, the precursors of sulfones, *viz.*, sulfides **1** and **2**, exist exclusively as ketones. However, oxidation of these sulfides to sulfones **5** and **6** led to such an enhancement of the electron-withdrawing properties of the carbonyl group of these compounds that they form stable *gem*-diols as white crystalline compounds.

We also carried out oxidation of sulfides **1** and **2** in the absence of water. Oxidation was performed with the use of anhydrous trifluoroperacetic acid synthesized from 98% hydrogen peroxide and trifluoroacetic anhydride. The reaction was performed in anhydrous trifluoroacetic acid at −20 °C. It is particularly interesting that we obtained exclusively the *E*-isomers of ketones **3** and **4** in both reactions.

We believe that the need for a strong oxidizer, such as trifluoroperacetic acid, arises from the low nucleophilicity of the S atom in the starting sulfides **1** and **2** due to the electron-withdrawing effect of the trifluoroacetyl group. Actually, our attempt to prepare the corresponding sulfonium salt by methylation of sulfides **1** and **2** under the action of even such a strong methylating agent as methyl triflate was unsuccessful (Scheme 2).

Scheme 2



1, 2

The NMR spectroscopic studies of sulfones **5** and **6** showed that the transformations between the dipolar and ketone forms of the sulfones under consideration as well as between the *E*/*Z* isomers of the diols occur depending on the nature of the solvent used. The configurations and ratios of the sulfones obtained were determined based on the spin-spin coupling constants between the protons at the double bond found from the ^{1}H NMR spectra and taking into account the characteristic signals for the C atoms of the carbonyl group (for compounds **3** and **4**) or the *gem*-diol group (for compounds **5** and **6**) in the ^{13}C NMR spectra. Thus, the highest content of *Z*-diol **5b** was obtained in low-polarity aprotic solvents (for example, in $CDCl_3$) due, apparently, to intermolecular hydrogen bonding resulted from the low solvating ability of these solvents. In polar solvents, for example, in CD_3CN or CD_3OD, *E*-diol **5a** occurred as virtually the only isomer, which is attributed both to its higher polarity compared to **5b** and the fact that it can be solvated in CD_3OD (Table 1).

A somewhat different situation was observed for diol **6** (see Table 1). Thus, the NMR spectra recorded in $CDCl_3$ have signals corresponding to *E*-ketone **4a** along with the signals of *E*-diol **6a**. The ^{1}H NMR spectrum shows

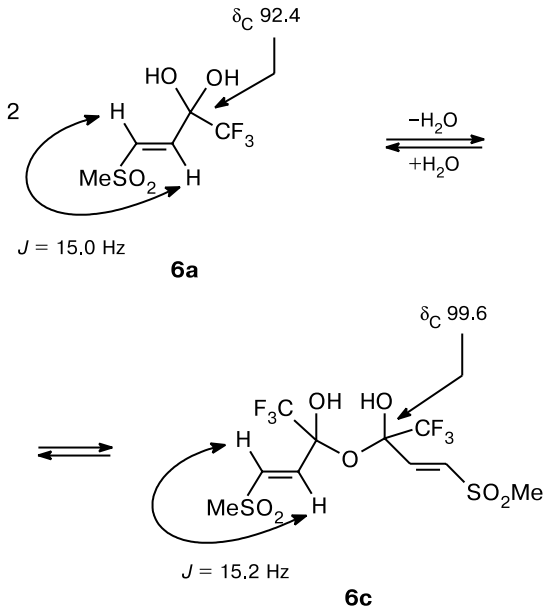
Table 1. Isomer ratios of ketones **4** and diols **5** and **6** in the oxidation products of sulfides **1** and **2** in different solvents

Sulfide	Compound	Content (%)		
		$CDCl_3$	CD_3CN	CD_3OD
1*	**5a**	75	100	100
	5b	25	—	—
2**	**4a**	33	—	—
	6a	67	33	100
	6c	—	66	—

* Compound **3a** was not detected.
** Diol **6b** was not detected.

two pairs of doublets with the constants $^3J_{H,H}$ = 15.1 and 15.4 Hz, which correspond to *trans*-diol **6a** and *trans*-ketone **4a**, respectively. The ^{13}C NMR spectrum has a quadruplet at δ 178.6 corresponding to the C atom of the carbonyl group of ketone **4a** and a quadruplet at δ 93.2 belonging to the C atom of the diol group of molecule **6a**. The ^{1}H NMR spectrum recorded in CD_3CN shows two pairs of doublets with the constants $^3J_{H,H}$ = 15.0 and 15.2 Hz. The ^{13}C NMR spectrum has two quadruplets at δ 99.6 and 92.4. We believe that the second set of signals belongs to hemihydrate **6c** (Scheme 3). Compounds containing an analogous fragment have been prepared previously[21] in our research group and their structures were unambiguously established by X-ray diffraction analysis.

Scheme 3

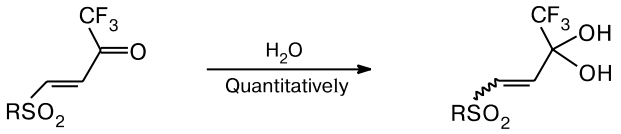


The assignment of the signals in the spectra was made based on the comparison of the corresponding signals of

E-diol **6a** in the spectrum recorded in $CDCl_3$ with those measured in CD_3CN. It should be noted that the spin-spin coupling constant for the H atoms at the double bond in *E*-hemihydrate **6c** is intermediate between the analogous constants for *E*-diol **6a** and *E*-ketone **4a**. The absence of the hemihydrate form in the case of phenylsulfonyl-substituted diol **5a** is attributable to the stronger electron-withdrawing ability of the phenylsulfonyl group compared to that of the mesyl group. The NMR spectra in CD_3OD, like those of the phenyl analog **5**, have signals corresponding only to the *E*-isomer of diol **6a**.

When studying ketones **3** and **4**, we found that they readily added a water molecule at the carbonyl group to form diols **5** and **6**, respectively, even upon storage in air* (Scheme 4). The ratios of the *E*/*Z* isomers in the diol forms of **5** and **6** are identical with those obtained from sulfides **1** and **2**.

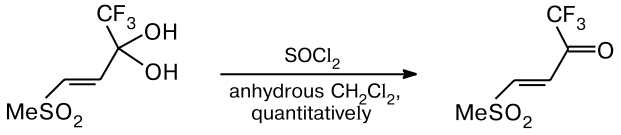
Scheme 4



3a, 4a **5, 6**

Diol **6a** can be readily subjected to the reverse transformation under the action of thionyl chloride in anhydrous CH_2Cl_2 at room temperature (Scheme 5). This reaction afforded *E*-ketone **4a** as the only product.

Scheme 5



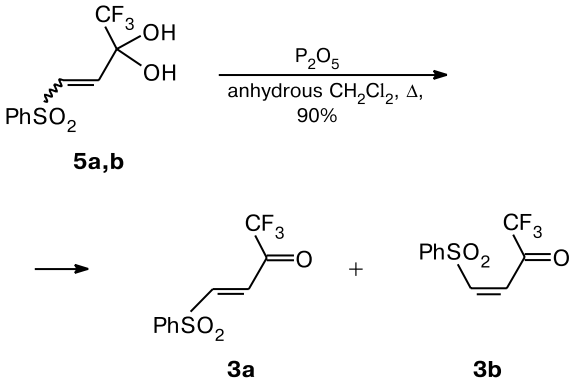
6a **4a**

Dehydration of diol **5** proceeded on refluxing over P_2O_5 in anhydrous CH_2Cl_2 (Scheme 6). Interestingly, the *E*/*Z*-isomer ratio of ketones **3a**/**3b** is identical with that for the starting diol **5**.

Previously, using the reactions with the C-, N-nucleophiles and dienes as examples, we have demonstrated that sulfones **5** and **6** belong to a new class of active dienophiles[22] and electrophiles.[23,24] In this connection, in the present study, we examined also the reactions of sulfones **5** and **6** with S-nucleophiles, *viz.*, thiols. These reactions will enable one to synthesize various β-(trifluoroacetyl)vinyl sulfides. We used a number of solvents (CH_2Cl_2, H_2O, EtOH, and MeCN). It appeared that the highest yields were achieved in MeCN, the reaction proceeding readily even with the less reactive diol forms of sulfones **5** and **6**. In most cases, the yield of the target product was virtually independent of which diol (**5** or **6**) was added (Scheme 7). The *E*/*Z*-isomer ratio in the resulting β-(trifluoroacetyl)vinyl sulfides **1** and **7—10** is independent of the *E*/*Z*-isomer ratio in the starting sulfones **5** and **6** and is determined, apparently, exclusively by the structure of the substituent R´.

* Hydration did not allow us to obtain reliable data from elemental analysis of ketones **3a** and **4a**.

Scheme 6

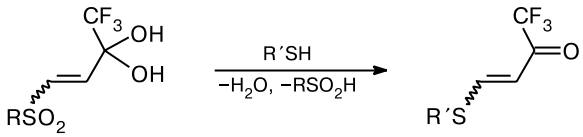


5a,b

3a **3b**

5a/**5b** = **3a**/**3b** = 3/1

Scheme 7



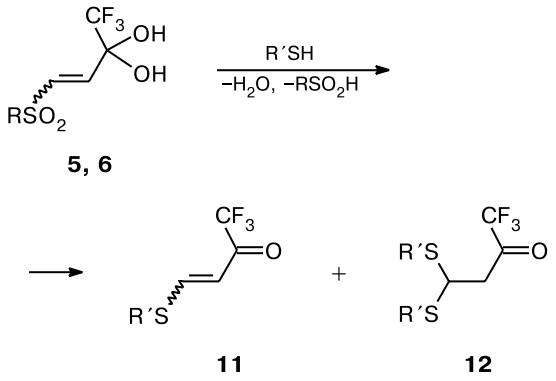
5, 6 **1, 7—10**

Compound	R´	*E*/*Z*	Yield from different diols (%)	
			5	**6**
1	Ph	7/5	90	86
7	Et	3/2	87	84
8	4-MeC_6H_4	2/1	89	86
9	1-Naphthyl	7/3	80	82
10	4-$NO_2C_6H_4$	0/1	76	—

In the case of poorly reactive *p*-nitrothiophenol, diol **5** is the reagent of choice because the reaction with diol **6** proceeded very slowly resulting finally in resinification of the reaction mixture. It should be emphasized that vinyl sulfide **10** was produced as the only *Z* isomer, whereas sulfides **1** and **7—9** were obtained as mixtures of the *E*/*Z* isomers, which is attributable to the fact that compound **10** has the stronger hypervalent bond between the S atom and the O atom of the carbonyl group.[25]

The reactions of *p*-methoxythiophenol with diols **5** and **6** also gave interesting results (Scheme 8). The reaction with the use of 1 equiv. of *p*-methoxythiophenol afforded a poorly separable mixture of mono- and diadducts, whereas the reaction with the use of 2.2 equiv. of *p*-methoxythiophenol gave stable diadduct **12** in quantitative yield. Apparently, this fact is attributed to the high nucleophilicity of *p*-methoxythiophenol resulting in the addition of the thiol at the double bond of unsaturated ketone **11** to form diadduct **12**.

Scheme 8



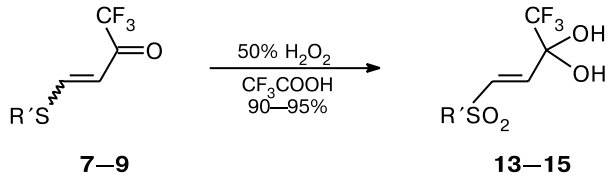
R′ = 4-$MeOC_6H_4$

It should be noted that the main procedure for the synthesis of unsaturated β-(trifluoroacetyl)vinyl sulfides involves trifluoroacetylation of the corresponding vinyl sulfides.[17,26,27] Therefore, the development of a procedure for the synthesis of β-(trifluoroacetyl)vinyl sulfides directly from thiols is an important synthetic problem, which allows one to circumvent laborious steps of the pre-preparation of vinyl sulfides followed by trifluoroacylation. This method made it possible to synthesize for the first time (*p*-nitrophenylthio)vinyl trifluoromethyl ketone (**10**). Our attempts to perform trifluoroacetylation of *p*-nitrophenyl vinyl sulfide failed due to the low reactivity of this substrate.

Therefore, we devised a new one-step procedure for the synthesis of β-(trifluoroacetyl)vinyl sulfides from thiols, the thiol molecule remaining intact in the course of the reaction. The latter fact enables one to perform the reactions with optically active thiols.

We also studied oxidation of the resulting β-(trifluoroacetyl)vinyl sulfides **7—10** to the corresponding sulfones (Scheme 9). Sulfides **7—9** containing electron-donating substituents were oxidized to sulfones **13—15** in good yields. It should be noted that all these sulfones, like sulfones **5** and **6**, occurred in the dipole form. However, attempts to oxidize electron-withdrawing sulfide **10** both in aqueous and non-aqueous conditions led to complete resinification of the reaction mixture.

Scheme 9



7—9 **13—15**

R′ = Et (**7**, **13**), 4-MeC_6H_4 (**8**, **14**), 1-Naphthyl (**9**, **15**)

To summarize, we developed a procedure for the synthesis of new promising electro- and dienophiles **3—6**. We investigated the reactions of diols **5** and **6** with different thiols and devised a new procedure for the synthesis of β-(trifluoroacetyl)vinyl sulfides. The resulting sulfides were successfully oxidized to the corresponding sulfones.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. The IR spectra were measured on a UR-20 spectrometer in Nujol mulls. The TLC analysis was carried out on Silufol UV-254 plates; visualization was carried out in an acidified solution of $KMnO_4$ and with iodine vapor.

Synthesis of phenyl β-(trifluoroacetyl)vinyl sulfone (3a) and methyl β-(trifluoroacetyl)vinyl sulfone (4a) from the corresponding sulfides 1 and 2. Sulfide **1** or **2** (0.02 mol) was placed in a round-bottom three-neck flask and cooled to −10 °C. Then CF_3COOH (15 mL) was added and the reaction solution was cooled to −30 °C. A mixture of 98% H_2O_2 (0.045 mol) and $(CF_3CO)_2O$ (0.05 mol) was slowly added dropwise with vigorous stirring, the temperature being maintained at no higher than −30 °C. Then the reaction mixture was kept at −30 °C for 3 h and slowly warmed to ~20 °C, after which CF_3COOH was distilled off *in vacuo* (10 Torr). The product (oily white crystals) was dried *in vacuo* (0.1 Torr).

Sulfone 3a. The yield was 96%, m.p. 74—78 °C. ^1H NMR ($CDCl_3$), δ: 7.75 (m, 2 H, Ph); 7.48 (m, 1 H, Ph); 7.44 (d, 1 H, C(4)H, J = 15.3 Hz); 7.36 (m, 2 H, Ph); 7.18 (d, 1 H, C(3)H, J = 15.3 Hz). ^{13}C NMR, δ: 178.5 (C=O); 146.5, 136.8, 134.7, 129.5, 129.2, 126.9, 115.1 (q, CF_3, J = 290.0 Hz).

Sulfone 4a. The yield was 97%, m.p. 56—58 °C. The ^1H and ^{13}C NMR spectra are given below.

Synthesis of 1,1,1-trifluoro-4-(*R*-sulfonyl)but-3-ene-2,2-diols 5, 6, and 13—15. The corresponding sulfide **1**, **2**, or **7—9** (10 mmol) was placed in a round-bottom one-neck flask and cooled to −20 °C. Then CF_3COOH (20 mL) was added. The reaction mixture was cooled to −30 °C and a mixture of 50% H_2O_2 (30 mmol) and CF_3COOH (10 mL) was slowly added dropwise with vigorous stirring. The reaction mixture was kept at −20 °C for 3 h and slowly warmed to ~20 °C. Then CF_3COOH was distilled off under weak vacuum. Benzene was added to the product and the reaction mixture was refluxed with azeotropic distillation with CF_3OOH. The procedure was repeated three times. The resulting white crystals were washed with benzene.

1,1,1-Trifluoro-4-(phenylsulfonyl)but-3-ene-2,2-diol (5). The yield was 94%, m.p. 155—158 °C. Found (%): C, 42.31; H, 3.36.

$C_{10}H_9F_3O_4S$. Calculated (%): C, 42.56; H, 3.21. ^{1}H NMR ($CDCl_3$) of a mixture of the *E*/*Z* isomers (75/25), δ: 7.94 (m, 2 H, Ph, *E* + *Z*); 7.76 (m, 1 H, Ph, *E* + *Z*); 7.67 (m, 2 H, Ph, *E* + *Z*); 7.54 (d, 1 H, C(4)H, *E*, *J* = 15.3 Hz); 7.32 (d, 1 H, C(3)H, *E*, *J* = 15.3 Hz); 6.85 (d, 1 H, C(4)H, *Z*, *J* = 11.3 Hz); 6.75 (d, 1 H, C(3)H, *Z*, *J* = 11.3 Hz). ^{13}C NMR, δ: 138.5, 137.9, 137.6, 135.7, 134.3, 143.2, 129.5, 127.8, 127.7, 127.6, 121.8 (q, CF_3, *Z*, *J* = 289.9 Hz); 121.8 (q, CF_3, *E*, *J* = 290.0 Hz); 98.2 (q, C(2), *E*, *J* = 32.1 Hz); 91.4 (q, C(2), *Z*, *J* = 33.8 Hz). IR, ν/cm^{-1}: 1670 (C=C); 3150 (OH).

1,1,1-Trifluoro-4-(methylsulfonyl)but-3-ene-2,2-diol (6). The yield was 97%, m.p. 93—94 °C. Found (%): C, 26.34; H, 3.42. $C_5H_7F_3O_4S$. Calculated (%): C, 27.28; H, 3.20. A mixture of **6a**/**4a** (67/33). ^{1}H NMR ($CDCl_3$), δ: 7.61 (d, 1 H, C(4)H, **4a**, *J* = 15.4 Hz); 7.36 (d, 1 H, C(3)H, **4a**, *J* = 15.4 Hz); 7.09 (d, 1 H, C(4)H, **6a**, *J* = 15.1 Hz); 6.74 (d, 1 H, C(3)H, **6a**, *J* = 15.1 Hz); 3.11 (s, 3 H, **4a**, Me); 3.01 (s, 3 H, **6a**, Me). ^{13}C NMR, δ: 178.6 (q, C(2), **4a**, *J* = 38.6 Hz); 145.4, 137.5, 137.5, 129.1, 121.8 (q, CF_3, **6a**, *J* = 287.3 Hz); 115.0 (q, CF_3, **4a**, *J* = 289.9 Hz); 93.2 (q, C(2), **6a**, *J* = 33.3 Hz); 42.5 and 42.3 (both s, Me). A mixture of diol **6a**/hemihydrate **6c** (33/66). ^{1}H NMR (CD_3CN), δ: 7.10 (d, 1 H, C(4)H, **6c**, *J* = 15.2 Hz); 7.07 (d, 1 H, C(4)H, **6a**, *J* = 15.0 Hz); 6.72 (d, 1 H, C(3)H, **6a**, *J* = 15.0 Hz); 6.68 (d, 1 H, C(3)H, **6c**, *J* = 15.2 Hz); 2.99 and 2.97 (both s, 3 H each, Me). ^{13}C NMR, δ: 139.6, 138.9, 136.8, 136.8, 123.5 (q, CF_3, **6a**, *J* = 287.2 Hz); 122.4 (q, CF_3, **6c,** *J* = 287.5 Hz); 99.6 (q, C(2), **6c**, *J* = 32.1 Hz); 92.4 (q, C(2), **6a**, *J* = 33.0 Hz); 42.6 (s, **6a**, Me); 42.6 (s, **6c**, Me). IR, ν/cm^{-1}: 1675 (C=C); 3150 (OH).

4-Ethylsulfonyl-1,1,1-trifluorobut-3-ene-2,2-diol (13). The yield was 94%, white crystals, m.p. 120—123 °C. Found (%): C, 30.53; H, 3.72. $C_6H_9F_3O_4S$. Calculated (%): C, 30.77; H, 3.87. A mixture of diol **13a**/hemihydrate **13c** (38/62). ^{1}H NMR (CD_3CN), δ: 7.02 (d, 1 H, C(4)H, **13c**, *J* = 15.2 Hz); 6.97 (d, 1 H, C(4)H, **13a**, *J* = 14.9 Hz); 6.71 (d, 1 H, C(3)H, **13a**, *J* = 14.9 Hz); 6.69 (d, 1 H, C(3)H, **13c**, *J* = 15.3 Hz); 3.09 (m, 2 H, CH_2, **13a** + **13c**); 1.24 (m, 3 H, Me, **13a** + **13c**). ^{13}C NMR, δ: 141.2, 138.5, 136.7, 134.6, 124.0 (q, CF_3, **13a**, *J* = 287.6 Hz); 123.1 (q, CF_3, **13c**, *J* = 287.6 Hz); 99.4 (q, C(2), **13c**, *J* = 32.6 Hz); 92.4 (q, C(2), **13a**, *J* = 32.5 Hz); 49.0 (s, CH_2); 7.2 (s, Me). IR, ν/cm^{-1}: 1670 (C=C); 3150—3170 (OH).

1,1,1-Trifluoro-4-(4-methylphenylsulfonyl)but-3-ene-2,2-diol (14). The yield was 91%, white crystals, m.p. 137—140 °C. Found (%): C, 44.41; H, 3.87. $C_{11}H_{11}F_3O_4S$. Calculated (%): C, 44.59; H, 3.73. ^{1}H NMR (CD_3CN), δ: 7.79 (d, 2 H, Ph, *J* = 8.1 Hz); 7.45 (m, 2 H, Ph, *J* = 8.1 Hz); 7.02 (d, 1 H, C(4)H, *J* = 14.9 Hz); 6.75 (d, 1 H, C(3)H, *J* = 14.9 Hz); 2.44 (s, 3 H, Me). ^{13}C NMR, δ: 146.5, 138.8, 137.5, 137.2, 131.1, 128.8, 123.4 (q, CF_3, *J* = 287.6 Hz); 92.2 (q, C(2), *J* = 32.6 Hz); 21.6. IR, ν/cm^{-1}: 1675 (C=C); 3150—3170 (OH).

1,1,1-Trifluoro-4-(1-naphthyl)but-3-ene-2,2-diol (15). The yield was 81%, white crystals, m.p. 150—153 °C. Found (%): C, 50.39; H, 3.58. $C_{14}H_{11}F_3O_4S$. Calculated (%): C, 50.60; H, 3.34. ^{1}H NMR (CD_3CN), δ: 7.80—7.45 (m, 2 H, Naphth); 7.03 (d, 1 H, C(4)H, *J* = 15.0 Hz); 6.75 (d, 1 H, C(3)H, *J* = 15.0 Hz). ^{13}C NMR, δ: 146.5, 140.2, 138.8, 138.6, 137.6, 137.5, 137.2, 137.0, 136.9, 136.6, 131.1, 128.8, 123.2 (q, CF_3, *J* = 287.6 Hz); 92.1 (q, C(2), *J* = 32.5 Hz). IR, ν/cm^{-1}: 1665 (C=C); 3150—3170 (OH).

Dehydration of diol 5. A mixture of diol **5** (10 mmol) and dry CH_2Cl_2 (20 mL) was placed in a round-bottom one-neck flask. Then an excess of P_2O_5 (5 equiv.) was added. The reaction mixture was refluxed with stirring for 30 min, cooled to ~20 °C, and filtered. The filtrate was concentrated *in vacuo* (20 Torr).

Ketone 3. The yield was 90%, white crystals rapidly deliquesce in air, m.p. 64—70 °C. A mixture of **3a**/**3b** (3/1) (the spectrum of sulfone **3a** is given above). ^{1}H NMR ($CDCl_3$), δ: 7.94 (m, 2 H, **3b**, Ph); 7.72 (m, 1 H, **3b**, Ph); 7.60 (m, 2 H, **3b**, Ph); 7.03 and 6.96 (both d, 1 H each, C(4)H, **3b**, *J* = 11.6 Hz). ^{13}C NMR, δ: 179.0 (C=O); 178.8 (C=O); 146.5, 142.5, 141.0, 140.0, 139.7, 139.6, 135.6, 135.8, 130.8, 130.2, 129.0, 129.0, 116.0 (q, CF_3, **3b**, *J* = 290.5 Hz); 115.1 (q, CF_3, **3a**, *J* = 290.3 Hz).

Dehydration of diol 6. Diol **6** (10 mmol) and dry CH_2Cl_2 (20 mL) were placed in a round-bottom one-neck flask. Then $SOCl_2$ (30 mmol) was added to the reaction mixture. The mixture was kept for ~10 h and then concentrated *in vacuo*. The yield of ketone **4a** was 99%, white crystals, m.p. 56—58 °C.

Synthesis of sulfides 1 and 7—10. A solution of diol **5** or **6** (0.005 mol) in MeCN (20 mL) was placed in a flask and a solution of thiol (0.005 mol) in a minimum amount of MeCN (the reaction with *p*-nitrothiophenol was carried out with refluxing) was added. The course of the reaction was monitored by TLC. The product was isolated by chromatography.

Phenyl β-(trifluoroacetyl)vinyl sulfide (1). A mixture of the *E*/*Z* isomers (7/5). The yield from sulfone **5** was 90% and the yield from sulfone **6** was 86%. The NMR spectra correspond to the data published in the literature.[17]

Ethyl β-(trifluoroacetyl)vinyl sulfide (7). The yield from sulfone **5** was 87% and the yield from sulfone **6** was 84%, oil. Found (%): C, 39.01; H, 3.70. $C_6H_7F_3OS$. Calculated (%): C, 39.13; H, 3.83. A mixture of the *E*/*Z* isomers (3/2). ^{1}H NMR ($CDCl_3$), δ: 8.21 (d, 1 H, C(4)H, *E*, *J* = 15.0 Hz); 7.76 (d, 1 H, C(4)H, *Z*, *J* = 9.9 Hz); 6.57 (d, 1 H, C(3)H, *Z*, *J* = 9.9 Hz); 6.37 (d, 1 H, C(3)H, *E*, *J* = 15.0 Hz); 2.92 (m, 2 H, CH_2, *E* + *Z*); 1.38 (m, 3 H, Me, *E* + *Z*). ^{13}C NMR, δ: 178.4 (q, C=O, *Z*, *J* = 34.8 Hz); 177.2 (q, C=O, *E*, *J* = 34.9 Hz); 161.9, 157.4, 117.2 (q, CF_3, *E*, *J* = 290.0 Hz); 116.9 (q, CF_3, *Z*, *J* = 290.0 Hz); 113.5, 112.5, 31.4, 27.0, 15.2, 13.5. IR, ν/cm^{-1}: 1690 (C=O).

4-Methylphenyl β-(trifluoroacetyl)vinyl sulfide (8). The yield from sulfone **5** was 89% and the yield from sulfone **6** was 86%, m.p. 73—75 °C. Found (%): C, 53.44; H, 3.77. $C_{11}H_9F_3OS$. Calculated (%): C, 53.65; H, 3.68. A mixture of the *E*/*Z* isomers (2/1). ^{1}H NMR ($CDCl_3$), δ: 8.15 (d, 1 H, C(4)H, *E*, *J* = 14.9 Hz); 7.75 (d, 1 H, C(4)H, *Z*, *J* = 9.8 Hz); 7.27 (m, 2 H, Ph, *E* + *Z*); 7.16 (d, 2 H, Ph, *E*, *J* = 7.9 Hz); 7.11 (d, 2 H, Ph, *Z*, *J* = 7.9 Hz); 6.50 (d, 1 H, C(3)H, *Z*, *J* = 9.8 Hz); 6.09 (d, 1 H, C(3)H, *E*, *J* = 14.9 Hz); 2.29 (s, 3 H, Me, *E*); 2.26 (s, 3 H, Me, *Z*). ^{13}C NMR, δ: 179.4 (q, C=O, *Z*, *J* = 35.1 Hz); 177.5 (q, C=O, *E*, *J* = 35.1 Hz); 162.4, 158.2, 141.5, 140.3, 133.8, 132.5, 131.7, 131.5, 131.0, 125.8, 116.9 (q, CF_3, *E*, *J* = 290.0 Hz); 116.6 (q, CF_3, *Z*, *J* = 290.0 Hz); 114.4, 112.1, 21.3, 21.1. IR, ν/cm^{-1}: 1695 (C=O).

1-Naphthyl β-(trifluoroacetyl)vinyl sulfide (9). The yield from sulfone **5** was 80% and the yield from sulfone **6** was 82%, m.p. 80—82 °C. Found (%): C, 59.133; H, 3.48. $C_{14}H_9F_3OS$. Calculated (%): C, 59.57; H, 3.21. A mixture of the *E*/*Z* isomers (7/3). ^{1}H NMR ($CDCl_3$), δ: 8.16 (d, 1 H, C(4)H, *E*, *J* = 14.9 Hz); 7.77 (d, 1 H, C(4)H, *Z*, *J* = 9.8 Hz); 7.55—7.10 (m, 7 H, Ph, *E* + *Z*); 6.53 (d, 1 H, C(3)H, *Z*, *J* = 9.8 Hz); 6.10 (d, 1 H, C(3)H, *E*, *J* = 14.9 Hz). ^{13}C NMR, δ: 179.3 (q, C=O, *Z*, *J* = 35.1 Hz); 177.4 (C=O, *E*, *J* = 35.1 Hz); 160.6, 157.0, 133.1, 132.9, 132.8, 132.7,

132.1, 129.9, 129.8, 129.6, 129.6, 129.3, 129.2, 129.2, 129.1, 129.0, 129.9, 129.8, 129.6, 125.9, 125.7, 125.4, 116.8 (q, CF_3, *E*, *J* = 290.1 Hz); 116.4 (q, CF_3, *Z*, *J* = 290.1 Hz); 114.4, 112.0. IR, ν/cm^{-1}: 1680 (C=O).

4-Nitrophenyl β-(trifluoroacetyl)vinyl sulfide (10). The yield from sulfone **5** was 76%, m.p. 113—115 °C. Found (%): C, 43.15; H, 2.31. $C_{10}H_6F_3NO_3S$. Calculated (%): C, 43.33; H, 2.18. ^{1}H NMR (CD_3CN), δ: 8.27 (d, 1 H, Ph, *J* = 9.0 Hz); 8.19 (d, 2 H, C(4)H, *J* = 10.0 Hz); 7.79 (d, (2 H, Ph, *J* = 8.0 Hz); 6.87 (d, 1 H, C(3)H, *J* = 10.0 Hz). ^{13}C NMR, δ: 178.7 (C=O, *J* = 35.3 Hz); 158.2, 143.7, 133.1, 131.5, 125.3, 116.4 (q, CF_3, *J* = 290.2 Hz); 114.2. IR, ν/cm^{-1}: 1685 (C=O).

Reaction of methoxythiophenol with diols 5 and 6. A solution of diol **5** or **6** (0.005 mol) in MeCN (20 mL) was placed in a flask and a solution of *p*-methoxythiophenol in MeCN (0.005 or 0.011 mol) was added. The course of the reaction was monitored by TLC. The product was isolated by chromatography.

4-Methoxyphenyl β-(trifluoroacetyl)vinyl sulfide (11) was prepared only as a mixture with compound **12** although 1 equiv. of thiol was used; the total yield was 88%, oil. A mixture of the *E*/*Z* isomers (2/1). ^{1}H NMR ($CDCl_3$), δ: 8.24 (d, 1 H, C(4)H, *E*, *J* = 14.9 Hz); 7.79 (d, 1 H, C(4)H, *Z*, *J* = 9.9 Hz); 7.40 (m, 2 H, Ph, *E* + *Z*); 6.98 (d, 2 H, Ph, *E*, *J* = 8.9 Hz); 6.92 (d, 2 H, Ph, *Z*, *J* = 8.7 Hz); 6.58 (d, 1 H, C(3)H, *Z*, *J* = 9.9 Hz); 6.10 (d, 1 H, C(3)H, *E*, *J* = 14.9 Hz); 3.85 (s, 3 H, Me, *E*); 3.78 (s, 3 H, Me, *Z*). ^{13}C NMR, δ: 179.0 (q, C=O, *Z*, *J* = 35.1 Hz); 177.7 (q, C=O, *E*, *J* = 35.1 Hz); 160.8, 158.1, 140.9, 140.4, 134.2, 132.8, 131.6, 131.5, 131.2, 125.1, 116.8 (q, CF_3, *E*, *J* = 290.1 Hz); 116.2 (q, CF_3, *Z*, *J* = 290.0 Hz); 114.8, 112.2, 55.3, 55.0.

1,1-Bis(4-methoxyphenylthio)-2-(trifluoroacetyl)ethane (12). The yield was 90%, m.p. 122—125°C. Found (%): C, 53.55; H, 4.40. $C_{18}H_{17}F_3O_3S_2$. Calculated (%): C, 53.72; H, 4.26. ^{1}H NMR ($CDCl_3$), δ: 7.43 and 7.87 (both d, 4 H each, Ph, *J* = 8.6 Hz); 4.57 (t, 1 H, C(3)H, *J* = 6.7 Hz); 3.81 (s, 6 H, Me); 3.09 (d, 1 H, C(2)H, *J* = 6.7 Hz). ^{13}C NMR, δ: 184.5 (q, C=O, *J* = 37.0); 160.5, 136.5, 136.3, 116.0 (q, CF_3, *J* = 290.6 Hz); 114.7, 55.3, 53.8, 36.2. IR, ν/cm^{-1}: 1690 (C=O).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 00-03-32760a and 00-03-32763a).

References

1. R. V. C. Carr and L. A. Paquette, *J. Am. Chem. Soc.*, 1980, **102**, 853.
2. N. S. Simpkins, *Tetrahedron*, 1990, **46**, 6951; O. De Lucchi and L. Pasquato, *Tetrahedron*, 1988, **44**, 6755.
3. B. M. Trost, H. C. Arndt, P. E. Strege, and T. R. Verhoeven, *Tetrahedron Lett.*, 1976, 3477.
4. L. A. Paquette, R. V. C. Carr, M. C. Boehm, and R. Gleiter, *J. Am. Chem. Soc.*, 1980, **102**, 1186.
5. L. A. Paquette and R. V. C. Carr, *J. Am. Chem. Soc.*, 1980, **102**, 7553.
6. O. De Lucchi and L. Pasquato, *Gazz. Chim. Ital.*, 1984, **114**, 349.
7. L. A. Paquette and R. V. Williams, *Tetrahedron Lett.*, 1981, **22**, 4643.
8. R. V. C. Carr, R. V. Williams, and L. A. Paquette, *J. Org. Chem.,* 1983, **48**, 4976.
9. O. De Lucchi, V. Lucchini, L. Pasquato, and G. Modena, *J. Org. Chem.*, 1984, **49**, 596.
10. U. Azzena, S. Cossu, O. De Lucchi, and G. Melloni, *Tetrahedron Lett.*, 1989, **30**, 1845.
11. N. Ono, A. Kamimura, and A. Kaji, *Tetrahedron Lett.*, 1986, **27**, 1595.
12. N. Ono, A. Kamimura, and A. Kaji, *J. Org. Chem.*, 1988, **53**, 251.
13. H. Kenji, Y. Mitsuaki, O. Satoru, and K. Ken, *J. Am. Chem. Soc.*, 1984, **106**, 6735.
14. T. A. Bryson, R. E. Dardis, and R. B. Gammill, *Tetrahedron Lett.*, 1978, **8**, 743.
15. H. N. Unn and S. Lars, *J. Chem. Soc., Perkin Trans. 1*, 1999, **21**, 3085.
16. V. G. Nenajdenko and E. S. Balenkova, *Tetrahedron.*, 1994, **50**, 12407.
17. M. Hojo, R. Masuda, and Y. Kamitori, *Tetrahedron Lett.*, 1976, **13**, 1009.
18. N. P. Petukhova, N. E. Dontsova, O. M. Sazonova, and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2654 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 2376 (Engl. Transl.)].
19. N. P. Petukhova, N. E. Dontsova, and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2327 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31** (Engl. Transl.)].
20. C. G. Venier, T. G. Squires, and Y. J. Chen, *J. Org. Chem.*, 1982, **47**, 3773.
21. V. G. Nenaidenko, A. V. Sanin, A. V. Churakov, J. A. K. Howard, and E. S. Balenkova, *Khim. Geterotsikl. Soedin.*, 1999, 618 [*Chem. Heterocycl. Compd.,* 1999 (Engl. Transl.)].
22. A. L. Krasovsky, V. G. Nenajdenko, and E. S. Balenkova, *Tetrahedron*, 2001, **57**, 201.
23. V. G. Nenajdenko, A. L. Krasovsky, M. L. Lebedev, and E. S. Balenkova, *Synlett*, 1997, **12**, 1349.
24. A. L. Krasovskii, V. G. Nenaidenko, and E. S. Balenkova, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1329 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1395].
25. K. M. Gough and J. Millington, *Can. J. Chem.*, 1995, **73**, 1287.
26. T. Moriguchi, T. Endo, and T. Takata, *J. Org. Chem.*, 1995, **60**, 3523.
27. M. Hojo, R. Masuda, Y. Kamitori, and E. Okada, *J. Org. Chem.*, 1991, **56**, 1975.

Received February 1, 2002;
in revised form March 15, 2002