The structure and CH-acidity of CF_3-substituted β-thiolactones. A theoretical study

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Ab initio calculations of the molecules of CH_3- and CF_3-substituted β-propiothiolactones and the products of their deprotonation were carried out by the restricted Hartree—Fock method with full geometry optimization using the 6-31G* basis set. Peculiarities of the geometry and electronic structure of the systems in question were established. Only 2-methyl-β-propiothiolactone forms a mesomeric stabilized carbanion in the case of proton abstraction from the α-position of thiolactone cycle. Carbanions of 3-methyl, 2-, and 3-thrifluoromethyl-β-propiothiolactones are stabilized due to the ring opening to form ketene thiolate ions. The CH-acidity of fluorine-containing β-thiolactones is much higher than that of nonfluorinated analogs (the differences in the deprotonation energies are 13.4 to 25.2 kcal mol^{-1}).

Key words: *ab initio* calculations, α- and β-methyl- and -trifluoromethyl-substituted β-propiothiolactones, CH-acidity.

β-Thiolactones have been rather poorly studied despite the fact that the first information on their synthesis appeared as long ago as 1955.[1] Trifluoromethyl-substituted β-thiolactones are unknown. Both α- and β-CF_3-substituted 3-mercaptopropane acids, which were synthesized recently,[2] can be considered as their potential precursors. However, the attempts to carry out the intramolecular dehydration of these compounds using the known procedure[3] (by the action of chlorocarbonic esters in the presence of Et_3N) failed. Oligomers of expected thiolactones were the only products in this case. Analogous results were obtained when using chlorocarbonic esters and pyridine, trifluoroacetic anhydride and pyridine, and carbodiimides as dehydrating agents. Despite the fact that thiolactonization occurs readily even at −20 °C, the oligomerization of thiolactones formed also occurs under these conditions.

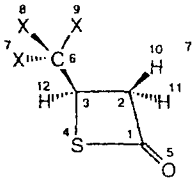
It can be assumed that such marked distinctions in the behavior of nonfluorinated and CF_3-substituted 3-mercaptopropane acids under conditions of dehydration are mainly due to a considerable effect of CF_3 groups on the CH-acidity of β-thiolactones formed. This was just the reason for performing a theoretical study of their structure and CH-acidity. Since the geometry and electronic structure of nonfluorinated β-thiolactones are not clearly understood to date, we also studied CH_3-analogs of CF_3-substituted β-propiothiolactones.

Procedure for Calculations

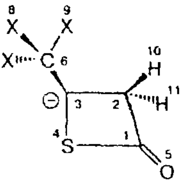
Ab initio calculations of CH_3- and CF_3-substituted β-propiothiolactones and products of their deprotonation were carried out by the restricted Hartree—Fock (RHF) method with full geometry optimization in the 6-31G* basis set using the GAMESS program[4] on a Pentium II-266 computer.

Results and Discussion

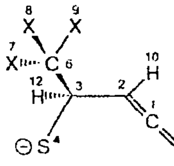
The structures of systems investigated and the numbering of the atoms used in this work are shown below. Compounds **1**, **1a**, **4**, and **4a** are neutral molecules;



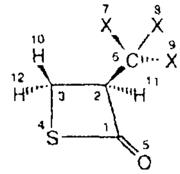
1, **1a**



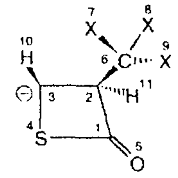
2, **2a**



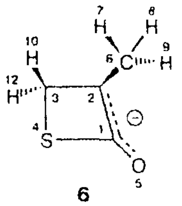
3, **3a**



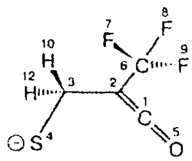
4, **4a**



5, **5a**



6



6a

X = H (**1**—**5**), F (**1a**—**5a**)

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[*] Deceased.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1719—1725, September, 1998.

1066-5285/98/4709-1670 $20.00

Table 1. Selected bond lengths (*d*), bond angles (ω), and torsion angles (τ) in the molecules of β-CH_3-substituted β-propiothiolactone **1**, its carbanion **2**, and ketene **3**

Bond	*d*/Å	Bond angle	ω/deg	Torsion angle	τ/deg
Structure **1**					
C(1)—C(2)	1.519	C(1)—C(2)—C(3)	95.54	C(1)—C(2)—C(3)—S(4)	0.83
C(2)—C(3)	1.547	C(2)—C(3)—S(4)	92.00	C(1)—C(2)—C(3)—C(6)	120.53
C(3)—S(4)	1.846	C(3)—S(4)—C(1)	77.26	C(1)—C(2)—C(3)—H(12)	−111.41
C(1)—S(4)	1.789	S(4)—C(1)—C(2)	95.19	C(2)—C(3)—C(6)—H(7)	−172.25
C(1)—O(5)	1.174	C(2)—C(1)—O(5)	132.97	C(2)—C(3)—C(6)—H(8)	68.37
C(2)—H(10)	1.085	C(1)—C(2)—H(10)	111.47	C(2)—C(3)—C(6)—H(9)	−51.73
C(2)—H(11)	1.084	C(1)—C(2)—H(11)	111.99	C(3)—S(4)—C(1)—O(5)	−179.03
C(3)—C(6)	1.520	C(2)—C(3)—C(6)	116.26	S(4)—C(1)—C(2)—H(10)	117.62
C(6)—H(7)	1.084	C(2)—C(3)—H(12)	111.99	S(4)—C(1)—C(2)—H(11)	−120.54
C(6)—H(8)	1.087	C(3)—C(6)—H(7)	111.14		
C(6)—H(9)	1.084	C(3)—C(6)—H(8)	109.89		
C(3)—H(12)	1.081	C(3)—C(6)—H(9)	111.20		
Structure **2**					
C(1)—C(2)	1.511	C(1)—C(2)—C(3)	98.90	C(1)—C(2)—C(3)—S(4)	9.31
C(2)—C(3)	1.551	C(2)—C(3)—S(4)	86.17	C(1)—C(2)—C(3)—C(6)	116.74
C(3)—S(4)	2.033	C(3)—S(4)—C(1)	75.36	C(2)—C(3)—C(6)—H(7)	−165.32
C(1)—S(4)	1.757	S(4)—C(1)—C(2)	98.10	C(2)—C(3)—C(6)—H(8)	78.16
C(1)—O(5)	1.195	C(2)—C(1)—O(5)	130.32	C(2)—C(3)—C(6)—H(9)	−41.54
C(2)—H(10)	1.097	C(1)—C(2)—H(10)	107.55	C(3)—S(4)—C(1)—O(5)	−170.50
C(2)—H(11)	1.091	C(1)—C(2)—H(11)	112.06	S(4)—C(1)—C(2)—H(10)	109.45
C(3)—C(6)	1.520	C(2)—C(3)—C(6)	110.83	S(4)—C(1)—C(2)—H(11)	−133.15
C(6)—H(7)	1.089	C(3)—C(6)—H(7)	111.83		
C(6)—H(8)	1.095	C(3)—C(6)—H(8)	107.63		
C(6)—H(9)	1.101	C(3)—C(6)—H(9)	116.68		
Structure **3**					
C(1)—C(2)	1.306	C(1)—C(2)—C(3)	124.29	C(1)—C(2)—C(3)—S(4)	0.09
C(2)—C(3)	1.518	C(2)—C(3)—S(4)	111.69	C(1)—C(2)—C(3)—C(6)	125.54
C(3)—S(4)	1.830	C(3)—S(4)—C(1)	56.33	C(1)—C(2)—C(3)—H(12)	−118.90
C(1)—S(4)	2.996	S(4)—C(1)—C(2)	67.69	C(2)—C(3)—C(6)—H(7)	175.84
C(1)—O(5)	1.155	C(2)—C(1)—O(5)	173.09	C(2)—C(3)—C(6)—H(8)	55.48
C(2)—H(10)	1.081	C(1)—C(2)—H(10)	114.07	C(2)—C(3)—C(6)—H(9)	−65.08
C(3)—C(6)	1.533	C(2)—C(3)—C(6)	109.47	C(3)—S(4)—C(1)—O(5)	−179.74
C(6)—H(7)	1.085	C(2)—C(3)—H(12)	106.84	S(4)—C(1)—C(2)—H(10)	179.59
C(6)—H(8)	1.095	C(3)—C(6)—H(7)	110.03		
C(6)—H(9)	1.085	C(3)—C(6)—H(8)	111.91		
C(3)—H(12)	1.089	C(3)—C(6)—H(9)	110.16		

compounds **2**, **2a**, **5**, and **5a** are carbanions formed as a result of abstraction of a proton from β-positions of neutral molecules; thiolate-anions of ketenes **3**, **3a**, and **6a** are products of the ring opening of α-carbanions of β-CH_3-substituted β-propiothiolactones and those of the ring opening of α- and β-CF_3-substituted β-propiothiolactones; and structure **6** is a mesomeric carbanion of α-CH_3-substituted β-propiothiolactone.

The results of calculation of the geometry of CH_3- and CF_3-substituted β-propiothiolactones, corresponding carbanions, and products of their transformations are listed in Tables 1—4.

The calculated total energies and energies of deprotonation of α- and β-CH_3- and CF_3-substituted β-propiothiolactones are listed in Table 5. The Mulliken effective charges on the atoms of CH_3- and CF_3-substituted β-propiothiolactones, their carbanions, and products of their transformation are presented in Tables 6 and 7; the dipole moments (μ) for compounds **1**, **1a**, **4**, and **4a** and the populations of d-orbitals of sulfur atoms (Nd_S) are also given therein.

The fact that attempts to obtain CF_3-substituted β-thiolactones by intramolecular cyclocondensation of CF_3-substituted 3-mercaptopropane acids failed appeared to be unexpected in the light of available information on the syntheses of β-thiolactones and their oxygen analogs (β-lactones). In fact, nonfluorinated 3-mercaptopropane acids, in contrast to 3-hydroxypropane derivatives, are readily cyclized into β-thiolactones.[1,3,5] This is explained by a lesser ring strain in β-thiolactones compared to that in β-lactones.[6] At the same time, CF_3-substituted 3-hydroxypropane acids are also readily cyclized into β-lactones,[7] which is due to the known capability of CF_3 groups to stabilize small cycles. Therefore, it was natural to expect that CF_3 groups in α- or β-positions of 3-mercaptopropane acid must, on the one hand, favor

Table 2. Selected bond lengths (*d*), bond angles (ω), and torsion angles (τ) in the molecules of β-CF_3-substituted β-propiothiolactone **1a**, its carbanion **2a**, and ketene **3a**

Bond	*d*/Å	Bond angle	ω/deg	Torsion angle	τ/deg
			Structure **1a**		
C(1)—C(2)	1.520	C(1)—C(2)—C(3)	94.78	C(1)—C(2)—C(3)—S(4)	0.44
C(2)—C(3)	1.544	C(2)—C(3)—S(4)	93.06	C(1)—C(2)—C(3)—C(6)	120.15
C(3)—S(4)	1.829	C(3)—S(4)—C(1)	76.95	C(1)—C(2)—C(3)—H(12)	−115.45
C(1)—S(4)	1.796	S(4)—C(1)—C(2)	95.21	C(2)—C(3)—C(6)—F(7)	−171.06
C(1)—O(5)	1.171	C(2)—C(1)—O(5)	133.18	C(2)—C(3)—C(6)—F(8)	69.85
C(2)—H(10)	1.083	C(1)—C(2)—H(10)	111.95	C(2)—C(3)—C(6)—F(9)	−49.68
C(2)—H(11)	1.083	C(1)—C(2)—H(11)	112.05	C(3)—S(4)—C(1)—O(5)	−178.74
C(3)—C(6)	1.509	C(2)—C(3)—C(6)	114.90	S(4)—C(1)—C(2)—H(10)	118.41
C(6)—F(7)	1.320	C(2)—C(3)—H(12)	113.91	S(4)—C(1)—C(2)—H(11)	−118.93
C(6)—F(8)	1.325	C(3)—C(6)—F(7)	111.31		
C(6)—F(9)	1.319	C(3)—C(6)—F(8)	109.68		
C(3)—H(12)	1.079	C(3)—C(6)—F(9)	112.68		
			Structure **2a**		
C(1)—C(2)	1.517	C(1)—C(2)—C(3)	96.47	C(1)—C(2)—C(3)—S(4)	5.17
C(2)—C(3)	1.544	C(2)—C(3)—S(4)	90.12	C(1)—C(2)—C(3)—C(6)	117.86
C(3)—S(4)	1.884	C(3)—S(4)—C(1)	77.37	C(2)—C(3)—C(6)—F(7)	−166.92
C(1)—S(4)	1.767	S(4)—C(1)—C(2)	95.61	C(2)—C(3)—C(6)—F(8)	73.61
C(1)—O(5)	1.190	C(2)—C(1)—O(5)	132.21	C(2)—C(3)—C(6)—F(9)	−45.15
C(2)—H(10)	1.091	C(1)—C(2)—H(10)	109.40	C(3)—S(4)—C(1)—O(5)	−172.56
C(2)—H(11)	1.089	C(1)—C(2)—H(11)	111.19	S(4)—C(1)—C(2)—H(10)	115.04
C(3)—C(6)	1.469	C(2)—C(3)—C(6)	112.39	S(4)—C(1)—C(2)—H(11)	−126.38
C(6)—F(7)	1.339	C(3)—C(6)—F(7)	113.36		
C(6)—F(8)	1.346	C(3)—C(6)—F(8)	110.81		
C(6)—F(9)	1.366	C(3)—C(6)—F(9)	118.75		
			Structure **3a**		
C(1)—C(2)	1.309	C(1)—C(2)—C(3)	122.79	C(1)—C(2)—C(3)—S(4)	−0.17
C(2)—C(3)	1.511	C(2)—C(3)—S(4)	112.45	C(1)—C(2)—C(3)—C(6)	126.54
C(3)—S(4)	1.825	C(3)—S(4)—C(1)	56.18	C(1)—C(2)—C(3)—H(12)	−121.89
C(1)—S(4)	2.975	S(4)—C(1)—C(2)	68.57	C(2)—C(3)—C(6)—F(7)	171.86
C(1)—O(5)	1.151	C(2)—C(1)—O(5)	172.77	C(2)—C(3)—C(6)—F(8)	54.53
C(2)—H(10)	1.077	C(1)—C(2)—H(10)	114.81	C(2)—C(3)—C(6)—F(9)	−64.65
C(3)—C(6)	1.516	C(2)—C(3)—C(6)	108.49	C(3)—S(4)—C(1)—O(5)	−179.51
C(6)—F(7)	1.326	C(2)—C(3)—H(12)	108.19	S(4)—C(1)—C(2)—H(10)	−179.22
C(6)—F(8)	1.352	C(3)—C(6)—F(7)	112.85		
C(6)—F(9)	1.322	C(3)—C(6)—F(8)	110.67		
C(3)—H(12)	1.087	C(3)—C(6)—F(9)	114.87		

the formation of β-thiolactone cycle, and, on the other hand, increase its stability.

The expected high CH-acidity of CF_3-substituted β-thiolactones (since they are synthesized in the presence of bases) can have a negative effect on their stability. It is known that carbanions of small heterocycles including thietanes are capable of ring opening[8] and that CF_3 groups, as has been shown previously,[9,10] sharply increase the acidity of the C—H bond adjacent to these groups and stabilize carbanions. For β-thiolactones, high acidity of the C—H bond could be expected only in α-position to the carbonyl group. The deprotonation of such a system should result in mesomeric carbanions, which are highly stable in the case of fluoro derivatives, as was shown taking 2-hydrohexafluoroisobutyrates as an example.[11] Moreover, the formation of such carbanions is accompanied by a considerable rehybridization of molecular orbitals, which results in an appreciable decrease in the kinetic CH-acidity in aprotic media,[12] particularly, with decreasing basicity of the deprotonating agent.

In the reaction under consideration the nature and basicity of dehydrating agents have no effect on the general character of the process. Hence, the final result of this reaction is due to the totality of factors and, primarily, to the specificity of the effect of CF_3 groups on the β-thiolactone cycle. These peculiarities should be revealed when analyzing the results of calculations listed in Tables 1—7.

As follows from the data in Tables 1—4, the molecules of thiolactones **1**, **4**, **1a**, and **4a** have nearly planar structures; the carbonyl group and the C(2) and C(3) atoms lie in the same plane, whereas the S atom slightly deviates from this plane. The deviation of the

Table 3. Selected bond lengths (*d*), bond angles (ω), and torsion angles (τ) in the molecules of α-CH_3-substituted β-propiothiolactone **4** and its carbanions **5**, **6**

Bond	*d*/Å	Bond angle	ω/deg	Torsion angle	τ/deg
Structure **4**					
C(1)—C(2)	1.525	C(1)—C(2)—C(3)	94.56	C(1)—C(2)—C(3)—S(4)	−2.93
C(2)—C(3)	1.547	C(2)—C(3)—S(4)	92.91	S(4)—C(1)—C(2)—C(6)	125.50
C(3)—S(4)	1.834	C(3)—S(4)—C(1)	77.01	C(1)—C(2)—C(3)—H(12)	−119.74
C(1)—S(4)	1.791	S(4)—C(1)—C(2)	95.39	C(1)—C(2)—C(6)—H(7)	−57.24
C(1)—O(5)	1.174	C(2)—C(1)—O(5)	132.57	C(1)—C(2)—C(6)—H(8)	−177.42
C(3)—H(10)	1.080	C(1)—C(2)—H(11)	108.58	C(1)—C(2)—C(6)—H(9)	62.67
C(2)—H(11)	1.086	C(2)—C(3)—H(10)	113.91	C(3)—S(4)—C(1)—O(5)	176.52
C(2)—C(6)	1.525	C(1)—C(2)—C(6)	114.22	C(1)—C(2)—C(3)—H(10)	112.67
C(6)—H(7)	1.085	C(2)—C(3)—H(12)	114.85	S(4)—C(1)—C(2)—H(11)	−111.25
C(6)—H(8)	1.085	C(2)—C(6)—H(7)	111.06		
C(6)—H(9)	1.084	C(2)—C(6)—H(8)	110.55		
C(3)—H(12)	1.080	C(2)—C(6)—H(9)	110.25		
Structure **5**					
C(1)—C(2)	1.518	C(1)—C(2)—C(3)	99.50	C(1)—C(2)—C(3)—S(4)	−3.24
C(2)—C(3)	1.562	C(2)—C(3)—S(4)	86.16	S(4)—C(1)—C(2)—C(6)	129.19
C(3)—S(4)	2.021	C(3)—S(4)—C(1)	76.57	C(1)—C(2)—C(6)—H(7)	−56.53
C(1)—S(4)	1.759	S(4)—C(1)—C(2)	97.60	C(1)—C(2)—C(6)—H(8)	−175.54
C(1)—O(5)	1.195	C(2)—C(1)—O(5)	130.32	C(1)—C(2)—C(6)—H(9)	63.97
C(3)—H(10)	1.098	C(2)—C(3)—H(10)	105.29	C(3)—S(4)—C(1)—O(5)	177.64
C(2)—H(11)	1.094	C(1)—C(2)—H(11)	106.91	C(1)—C(2)—C(3)—H(10)	95.31
C(2)—C(6)	1.528	C(1)—C(2)—C(6)	113.44	S(4)—C(1)—C(2)—H(11)	−111.75
C(6)—H(7)	1.087	C(2)—C(6)—H(7)	110.72		
C(6)—H(8)	1.088	C(2)—C(6)—H(8)	110.27		
C(6)—H(9)	1.088	C(2)—C(6)—H(9)	111.71		
Structure **6**					
C(1)—C(2)	1.361	C(1)—C(2)—C(3)	104.08	C(1)—C(2)—C(3)—S(4)	−0.09
C(2)—C(3)	1.500	C(2)—C(3)—S(4)	92.36	S(4)—C(1)—C(2)—C(6)	179.83
C(3)—S(4)	1.836	C(3)—S(4)—C(1)	72.56	C(1)—C(2)—C(3)—H(12)	115.73
C(1)—S(4)	1.975	S(4)—C(1)—C(2)	91.01	C(1)—C(2)—C(6)—H(7)	−119.10
C(1)—O(5)	1.206	C(2)—C(1)—O(5)	142.57	C(1)—C(2)—C(6)—H(8)	119.95
C(3)—H(10)	1.091	C(2)—C(3)—H(10)	116.20	C(1)—C(2)—C(6)—H(9)	0.41
C(2)—C(6)	1.498	C(1)—C(2)—C(6)	127.46	C(3)—S(4)—C(1)—O(5)	179.87
C(6)—H(7)	1.095	C(2)—C(3)—H(12)	116.15	C(1)—C(2)—C(3)—H(10)	−116.01
C(6)—H(8)	1.095	C(2)—C(6)—H(7)	113.26		
C(6)—H(9)	1.087	C(2)—C(6)—H(8)	113.27		
C(3)—H(12)	1.091	C(2)—C(6)—H(9)	109.53		

S atom from the plane in β-substituted thiolactones **1** and **1a** is small (0.83° and 0.44°, respectively), while that in α-derivatives **4** and **4a** is equal to 2.9° and 4.7°, respectively. Interior bond angles at the C atoms of the cycle vary from 92° to 95.5°, and those at the S atom vary from 76° to 77.5°, fluorine-containing thiolactones **1a** and **4a** having some more equalized interior bond angles at the C atoms than their nonfluorinated analogs **1** and **4**, respectively.

The C—C bond lengths in the β-thiolactone cycle are either equal to the sum of covalent atomic radii[13] (the C(2)—C(3) bond) or larger than it (the C(1)—C(2) bond). The lengthening of the C(1)—C(2) bond is maximum if the C(2) atom has a substituent. The lengths of S—C bonds (especially the S—C(O) bond) also exceed the sum of covalent radii. The CF_3 group bonded to the C(3) atom favors a larger lengthening of the S—C(O) bond.

All exocyclic bonds are shortened as compared to the sum of covalent atomic radii. The length of the C=O bond is close to that of the analogous bond in the CO_2 molecule.[13] The C—H bond lengths in thiolactones are the same as those in ethylene; in this case, the C—H bonds at the geminal CF_3 groups and S atom are most shortened as well as the C—H bonds adjacent to C=O and CF_3 groups (they are intermediate between the lengths of C—H bonds in ethylene and acetylene). The C—CF_3 bonds are also shortened, and their lengths are equal to the half-sum of the lengths of the C(sp^2)—C(sp^3) and C(sp^3)—C(sp^3) bonds. The s-character of C—CH_3 bonds is also appreciably increased. The C—F bonds in trifluoromethyl groups are also substantially shortened and their lengths are close to those of C—F bonds in CF_4 and to those of C—H bonds in methyl groups.

Table 4. Selected bond lengths (*d*), bond angles (ω), and torsion angles (τ) in the molecules of α-CF_3-substituted β-propiothiolactone **4a**, carbanion **5a**, and ketene **6a**

Bond	*d*/Å	Bond angle	ω/deg	Torsion angle	τ/deg
Structure **4a**					
C(1)—C(2)	1.532	C(1)—C(2)—C(3)	94.79	C(1)—C(2)—C(3)—S(4)	−4.70
C(2)—C(3)	1.543	C(2)—C(3)—S(4)	92.51	S(4)—C(1)—C(2)—C(6)	126.17
C(3)—S(4)	1.833	C(3)—S(4)—C(1)	77.49	C(1)—C(2)—C(3)—H(12)	−121.65
C(1)—S(4)	1.783	S(4)—C(1)—C(2)	94.87	C(1)—C(2)—C(6)—F(7)	−52.87
C(1)—O(5)	1.171	C(2)—C(1)—O(5)	132.41	C(1)—C(2)—C(6)—F(8)	−172.17
C(3)—H(10)	1.079	C(1)—C(2)—H(11)	110.06	C(1)—C(2)—C(6)—F(9)	67.89
C(2)—H(11)	1.083	C(2)—C(3)—H(10)	113.99	C(3)—S(4)—C(1)—O(5)	176.14
C(2)—C(6)	1.509	C(1)—C(2)—C(6)	115.13	C(1)—C(2)—C(3)—H(10)	110.72
C(6)—F(7)	1.322	C(2)—C(3)—H(12)	114.32	S(4)—C(1)—C(2)—H(11)	−111.69
C(6)—F(8)	1.323	C(2)—C(6)—F(7)	111.46		
C(6)—F(9)	1.316	C(2)—C(6)—F(8)	110.39		
C(3)—H(12)	1.078	C(2)—C(6)—F(9)	111.44		
Structure **5a**					
C(1)—C(2)	1.526	C(1)—C(2)—C(3)	98.15	C(1)—C(2)—C(3)—S(4)	−8.09
C(2)—C(3)	1.557	C(2)—C(3)—S(4)	87.06	S(4)—C(1)—C(2)—C(6)	130.66
C(3)—S(4)	1.971	C(3)—S(4)—C(1)	77.25	C(1)—C(2)—C(6)—F(7)	−52.22
C(1)—S(4)	1.750	S(4)—C(1)—C(2)	96.45	C(1)—C(2)—C(6)—F(8)	−173.42
C(1)—O(5)	1.191	C(2)—C(1)—O(5)	130.77	C(1)—C(2)—C(6)—F(9)	68.26
C(3)—H(10)	1.091	C(2)—C(3)—H(10)	107.07	C(3)—S(4)—C(1)—O(5)	171.69
C(2)—H(11)	1.091	C(1)—C(2)—H(11)	108.24	C(1)—C(2)—C(3)—H(10)	−110.78
C(2)—C(6)	1.505	C(1)—C(2)—C(6)	114.11	S(4)—C(1)—C(2)—H(11)	−112.14
C(6)—F(7)	1.323	C(2)—C(6)—F(7)	113.71		
C(6)—F(8)	1.332	C(2)—C(6)—F(8)	111.69		
C(6)—F(9)	1.338	C(2)—C(6)—F(9)	112.15		
Structure **6a**					
C(1)—C(2)	1.318	C(1)—C(2)—C(3)	121.15	C(1)—C(2)—C(3)—S(4)	−1.24
C(2)—C(3)	1.518	C(2)—C(3)—S(4)	111.04	S(4)—C(1)—C(2)—C(6)	178.63
C(3)—S(4)	1.827	C(3)—S(4)—C(1)	57.52	C(1)—C(2)—C(3)—H(12)	121.03
C(1)—S(4)	2.914	S(4)—C(1)—C(2)	70.28	C(1)—C(2)—C(6)—F(7)	−116.64
C(1)—O(5)	1.144	C(2)—C(1)—O(5)	173.74	C(1)—C(2)—C(6)—F(8)	124.20
C(3)—H(10)	1.087	C(2)—C(3)—H(10)	108.25	C(1)—C(2)—C(6)—F(9)	3.78
C(2)—C(6)	1.480	C(1)—C(2)—C(6)	116.50	C(3)—S(4)—C(1)—O(5)	−178.89
C(6)—F(7)	1.335	C(2)—C(3)—H(12)	108.37	C(1)—C(2)—C(3)—H(10)	−123.44
C(6)—F(8)	1.333	C(2)—C(6)—F(7)	113.24		
C(6)—F(9)	1.335	C(2)—C(6)—F(8)	112.91		
C(3)—H(12)	1.087	C(2)—C(6)—F(9)	112.65		

Thus, the stabilization of β-thiolactone cycle is provided by a specific differentiation of molecular orbitals formed by the carbon skeleton and determines the formation of interior and exterior bonds. The interior bonds of the cycle have an appreciably increased p-character

Table 5. Calculated total energies (E_{tot}/au) and deprotonation energies (E_{dep}/kcal mol^{-1}) of CH_3- and CF_3-substituted β-propiothiolactones

Structure	E_{tot}	E_{dep}	Structure	E_{tot}	E_{dep}
1	−627.3292	—	**1a**	−923.9128	—
2	−626.6681	414.6	**2a**	−923.2920	389.4
3	−626.7320	374.6	**3a**	−923.3369	361.2
4	−627.3295	—	**4a**	−923.9099	—
5	−626.6685	414.6	**5a**	−923.2710	400.7
6	−626.7208	381.8	**6a**	−923.3305	363.4

Table 6. Mulliken effective charges (*q*/au) on the atoms of CH_3-substituted β-propiothiolactones and products of their deprotonation **1—6**

Atom	**1**	**2**	**3**	**4**	**5**	**6**
C(1)	0.364	0.353	0.566	0.364	0.338	0.360
C(2)	−0.394	−0.369	−0.371	−0.234	−0.214	−0.124
C(3)	−0.350	−0.289	−0.219	−0.503	−0.476	−0.442
S(4)	0.144	−0.204	−0.708	0.144	−0.198	−0.211
O(5)	−0.486	−0.593	−0.507	−0.487	−0.590	−0.701
C(6)	−0.472	−0.443	−0.430	−0.482	−0.465	−0.478
H(7)	0.173	0.097	0.082	0.178	0.133	0.103
H(8)	0.182	0.113	0.144	0.177	0.140	0.103
H(9)	0.180	0.081	0.149	0.197	0.135	0.155
H(10)	0.221	0.118	0.161	0.212	0.058	0.118
H(11)	0.223	0.136	—	0.222	0.139	—
H(12)	0.214	—	0.134	0.212	—	0.118

Note. For structures **1** and **4**, μ = 3.65 and 4.12 D, and Nd_S = 0.107 and 0.108, respectively.

Table 7. Mulliken effective charges (*q*/au) on the atoms of CF_3-substituted β-propiothiolactones and products of their deprotonation **1a—6a**

Atom	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**
C(1)	0.376	0.352	0.589	0.365	0.348	0.577
C(2)	−0.410	−0.405	−0.397	−0.393	−0.402	−0.340
C(3)	−0.506	−0.476	−0.380	−0.511	−0.491	−0.382
S(4)	0.202	−0.037	−0.642	0.189	−0.115	−0.689
O(5)	−0.472	−0.573	−0.489	−0.461	−0.562	−0.455
C(6)	1.141	1.072	1.119	1.146	1.141	1.143
F(7)	−0.356	−0.408	−0.380	−0.358	−0.371	−0.381
F(8)	−0.362	−0.414	−0.419	−0.363	−0.391	−0.381
F(9)	−0.353	−0.431	−0.367	−0.345	−0.395	−0.391
H(10)	0.251	0.163	0.195	0.240	0.071	0.150
H(11)	0.240	0.157	—	0.264	0.167	—
H(12)	0.250	—	0.171	0.227	—	0.149

Note. For structures **1a** and **4a**, μ = 2.72 and 3.65 D, and Nd_S = 0.109 and 0.110, respectively.

and the exterior bonds have a drastically increased s-character. The strained state of the S atom (the C(1)—S(4)—C(3) angle is equal to ~77°) is stabilized due to the participation of d-orbitals, which is evidenced by their high population. The nature of the substituents and their positions in the cycle affect the parameters of interior bonds. On the whole, the CF_3 groups favor weakening of the C(1)—C(2) bond while the methyl groups affect the C(3)—S(4) bond in the same way.

The charge distribution in the cycle of CH_3- and CF_3-substituted β-propiothiolactones is of the same type (see Tables 6 and 7). The electron density in the cycle is mostly localized on the C(2) and C(3) atoms, whereas its deficiency is observed on the C(1) and S(4) atoms. Thus, the β-thiolactone cycle is bipolar. Fluorine-containing β-thiolactones are characterized by a more pronounced bipolarity and increased symmetry of charge distribution irrespective of the position of CF_3 group in the cycle, whereas in the case of methyl group the charge distribution between the atoms of the C(2)—C(3) bond changes sharply.

The charge distributions between the substituents in CH_3- and CF_3-derivatives of β-propiothiolactones differ substantially. The excess electron density on the O atom of the carbonyl group is independent of the type and position of the substituent in the cycle; however, its deficiency on the H atoms of the cycle of fluorine-containing β-thiolactones is much larger. Moreover, the electron density in large excess is localized on the C atom of the methyl group bonded to the cycle, whereas its deficiency is observed on the C atom of the CF_3 group. It appreciably affects the dipole moment: the compensation effects of the substituents in fluorine-containing β-thiolactones decrease the total polarity of the molecules, whereas the electronic effects in the cycle nonfluorinated analogs increase it.

The considered peculiarities of the geometry and electronic structure of CH_3- and CF_3-substituted β-propiothiolactones make it possible to suggest that on the whole the CF_3 group, irrespective of its position in the cycle, has a stronger stabilizing effect on the strained β-thiolactone cycle than the methyl group. At the same time, it is to a considerable extent due to the more substantial rearrangement of the sp^2 hybrid state of the C atom of carbonyl group, which can be responsible for higher sensitivity of fluorine-containing β-thiolactones towards nucleophilic agents, *i.e.*, the enhanced reactivity of these compounds as acylating agents. To a certain extent such a conclusion is confirmed by the results of studying the deprotonation products of thiolactones under investigation.

Abstraction of the proton bonded to the C(3) atom of the cycle of thiolactones **1**, **4**, **1a**, and **4a** results in stable carbanions **2**, **5**, **2a**, and **5a**. Stabilization of the carbanions is reached due to delocalization of the electron density in the cycle, which favors a substantial rehybridization of the orbitals. On the whole, the p-character of endocyclic bonds (except for the S(4)—C(1) bond) and C=O bond increases; the C—H bonds are lengthened. Simultaneously, the s-character of the bond of the cycle with the methyl group increases to a certain extent and particularly the s-character of the bond of the cycle with the CF_3 group increases appreciably. The compensation effects of the CF_3 group favor much smaller changes in geometric parameters of the cycle than in the case of nonfluorinated analogs.

Abstraction of the proton bonded to the C(2) atom of the cycle of thiolactones **1**, **4**, **1a**, and **4a** results in more pronounced changes. Only 2-methyl-β-propiothiolactone yields a mesomeric stabilized carbanion **6** whose structure is close to that of enolate anion; its formation is accompanied by a drastic shortening of the C(1)—C(2), C(2)—C(3), and C(2)—CH_3 bonds and by a great lengthening of the S—C(O) and C(1)—O bonds. Analogous carbanions **1**, **1a**, and **4a** do not exist because of the ring opening at the S—C(O) bond with the formation of thiolate ions of **3**, **3a**, and **6a**.

Judging by the deprotonation energies (see Table 5), the C—H bonds adjacent to the carbonyl group are the most acidic in thiolactones **1**, **1a**, **4**, and **4a**; fluorine-containing thiolactones are much more stronger CH-acids than nonfluorinated analogs (the differences in deprotonation energies are 13.4 to 25.2 kcal mol^{-1}). It was unusual that the S atom and methyl or trifluoromethyl group in geminal positions affect the increase in the CH-acidity of distant methylene group much more strongly than those in vicinal positions. At the same time, the differences in CH-acidity for 2- and 3-CF_3-substituted β-propiothiolactones are much smaller than those for an analogous pair of nonfluorinated analogs (the differences in deprotonation energies are equal to 2 and 6 kcal mol^{-1}, respectively).

The results of our study make it possible to suggest that the problems of obtaining β-thiolactones from 2- and 3-trifluoromethyl-3-mercaptopropane acids are due to both the higher reactivity of end products towards nucleophiles and their much higher CH-acidity as compared to that of nonfluorinated analogs.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32884).

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Received February 16, 1998