Polyfluoroalkylthiotrifluoroacetylketenes

R. N. Serdyuk, A. Yu. Sizov, and A. F. Ermolov*

Military University of Radiational, Chemical, and Biological Defense,
13 Brigadirskii per., 107005 Moscow, Russian Federation.
Fax: +7 (095) 267 5107

A procedure was developed for the synthesis of polyfluoroalkylthiotrifluoroacetylketenes, and their reactions with nucleophilic reagents were studied. The resulting compounds were demonstrated to act as heterodienes in reactions with unsaturated compounds.

Key words: polyfluoroalkanesulfenyl chlorides, sulfenylation, polyfluoroalkylthiotrifluoroacetylketenes, heterodienes.

Being highly reactive, fluorine-containing ketenes are valuable synthons allowing the introduction of fluorinated fragments into organic compounds of different classes. This is demonstrated, as an example, by numerous transformations of their best-studied representative, *viz.*, bis(trifluoromethyl)ketene (principal, although far from complete, data on its transformations were surveyed in the review[1]). The presence of additional functional groups in ketenes further extends their synthetic potential. For example, perfluoroacyl-containing ketenes do not only undergo standard transformations but also are actively involved in Diels—Alder reactions as 1,3-heterodienes.[2—5]

Only a few examples of fluoroketenes stable in individual form are known,[1—3,6—10] and they are, as a rule, prepared using special procedures. For instance, the only known representative of the ketene structural type under consideration, *viz.*, heptafluoroisopropylthioheptafluoroisobutyrylketene,[3] was synthesized in several steps starting from perfluoropropene, whereas an analogous approach was inapplicable for the preparation of other homologs.

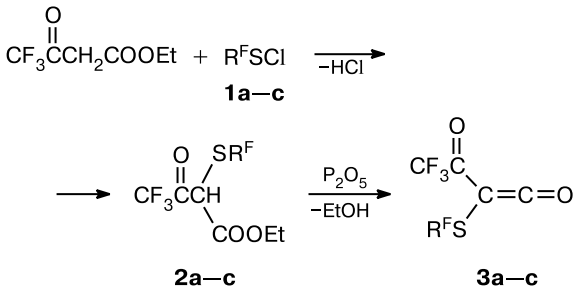
Dehydration of α-substituted α-H-polyfluorocarboxylic acids[1,6] or dealcoholysis of their esters[7—10] by P_2O_5 can, in principle, be considered as versatile procedures for the synthesis of fluoroketenes. However, their use is limited by the available assortment of the corresponding starting reagents. Consequently, the question as to the synthetic potential of these reactions is, in essence, consists in searching for new precursors of ketenes.

The present study was aimed at extending this approach to the synthesis of fluoroketenes and studying new representatives of this peculiar class of compounds.

Results and Discussion

The reactions of ethyl trifluoroacetoacetate with polyfluoroalkanesulfenyl chlorides **1a—c** (under conditions analogous to those described by us earlier for C-sulfenylation of ethyl trifluoroacetoacetate by 2-methoxycarbonyl-1,3,3,3-tetrafluoropropenesulfenyl chloride[11]) afforded ethyl 2-polyfluoroalkylthio-3-oxotrifluorobutyrates **2a—c**. The reactions of the latter compounds with P_2O_5 gave rise to polyfluoroalkylthiotrifluoroacetylketenes **3a—c** (Scheme 1).

Scheme 1



R^F = HCF_2CF_2 (**a**), Cl_2CFCF_2 (**b**), CF_3CFHCF_2 (**c**)

Dealcoholysis of sulfides **2a—c** was carried out at ~180 °C with simultaneous distillation of the resulting ketenes **3a—c**, which were prepared in 60—80% yields as pale-yellow mobile liquids slightly fuming in air.

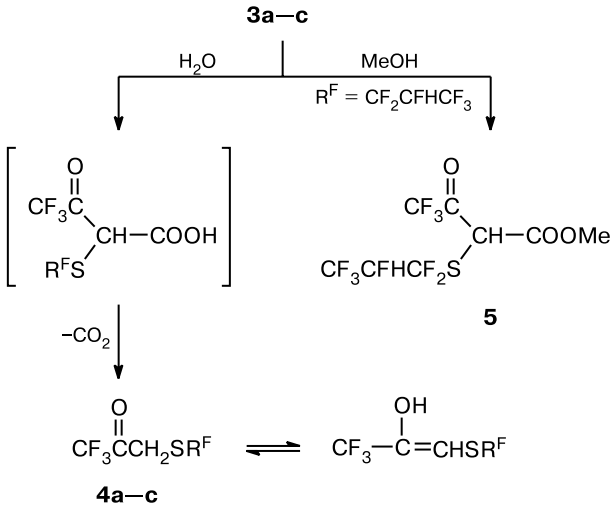
The chemical properties of ketenes **3a—c** are determined by the presence of the highly reactive C=C=O group and the conjugated carbonyl group of the acyl fragment. Thus, these compounds readily added water and methanol at the C=C bond to form 1,1,1-trifluoro-2-polyfluoroalkylthioacetones **4a—c** or methyl ester **5**, respectively (Scheme 2). Apparently, unstable carboxylic acids are direct precursors of ketones **4a—c**.

We examined the ability of ketenes to acylate aromatic compounds, which has been found earlier,[2,3] using the reaction of ketene **3c** with *N*,*N*-dimethylaniline as an

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1758—1762, August, 2003.

1066-5285/03/5208-1854 $25.00

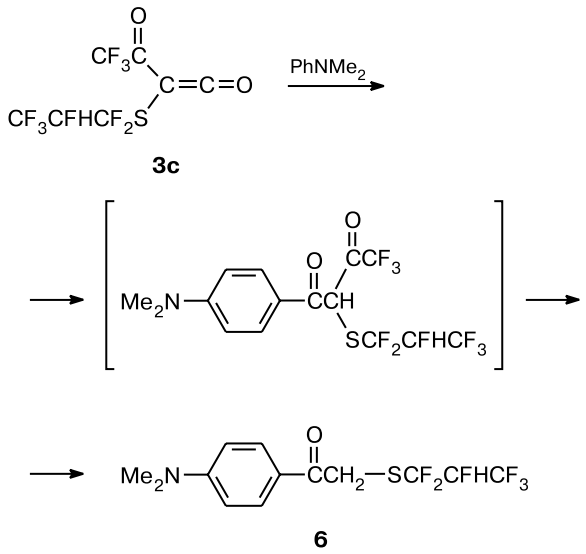
Scheme 2



R^F = HCF_2CF_2 (**a**), Cl_2CFCF_2 (**b**), CF_2CFHCF_3 (**c**)

example. It appeared that this reaction was accompanied by detrifluoroacetylation to give sulfide **6** (Scheme 3).

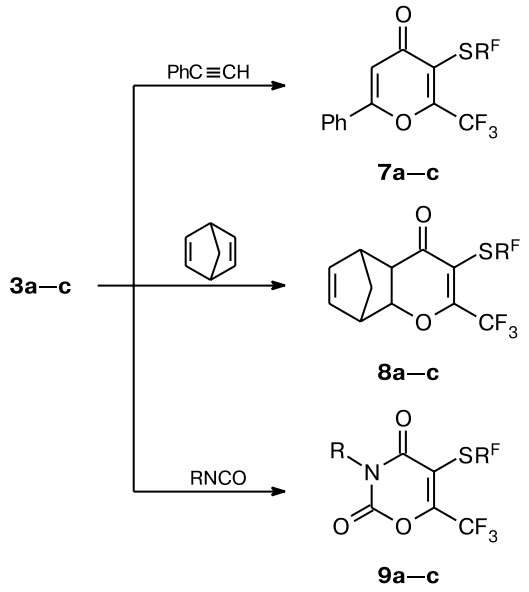
Scheme 3



The characteristic feature of ketenes **3a—c** is their ability to react with unsaturated compounds according to the heterodiene synthesis scheme.[2–5] For example, these compounds are involved in Diels—Alder reactions with phenylacetylene, norbornadiene, and isocyanates (PrNCO and PhNCO) to form heterocyclic products **7—9**, respectively (Scheme 4).

These reactions were carried out with slight cooling in the absence of solvents. Compounds **7—9** are colorless solids, whose structures were established by ^1H and

Scheme 4



R = Pr (**9a**), Ph (**9b,c**)

^{19}F NMR spectroscopy. Products **8a** and **8c** were prepared as mixtures of *endo* and *exo* isomers, whereas **8b** was synthesized in individual form. Based on the published data,[12] it can be assumed that the *exo* isomers are the major products in mixtures of **8a,c**. Compound **8b** has an analogous structure.

Therefore, the procedure developed for the synthesis of polyfluoroalkylthiotrifluoroacetylketenes is more versatile than the method described earlier.[3] Evidently, the new method can be extended to the synthesis of a broad spectrum of compounds of this type by varying the length and structure of fluorinated fragments in both the starting sulfenyl chlorides and β-ketoesters.

Experimental

The ^{19}F NMR spectra were recorded on a Bruker AC-200F spectrometer operating at 188.31 MHz. The ^1H NMR spectra were measured on a Bruker AC-300SF instrument operating at 300.13 MHz. The chemical shifts are given in the δ scale relative to CF_3COOH (^{19}F, external standard) and Me_4Si (^1H, internal standard). The NMR spectra of compounds **3a—c** were recorded for samples sealed in a glass insert in the absence of a solvent. The spectra of the other compounds were measured in solutions in DMSO-d_6 or $CDCl_3$. The IR spectra (ν/cm^{-1}) were recorded on a Perkin-Elmer 1720X instrument. The physical and spectroscopic characteristics and data from elemental analysis of the compounds are given in Table 1.

Ethyl 3,3,3-trifluoroacetoacetate was prepared according to a known procedure.[13] 2,2-Dichlorotrifluoroethanesulfenyl chloride (**1b**) was synthesized according to a procedure described earlier.[14]

Table 1. Yield, properties, spectroscopic characteristics, and data from elemental analysis of the compounds synthesized

Compound	Yield (%)	B.p./°C (*p*/Torr) [M.p./°C]	Found / Calculated (%)		Molecular formula	^{19}F NMR	^{1}H NMR
			C	H		(δ, *J*/Hz)*	
1a	87	55—56 (*cf.* lit. data[15])	14.02 14.24	0.50 0.59	C_2HClF_4S	−55.20 (dt, 2 F, CF_2H, $J_{F,F}$ = 10, $J_{H,F}$ = 53); −19.9 (dt, 2 F, CF_2S, $J_{F,F}$ = 10, $J_{H,F}$ = 4)	6.10 (dm, CH, $J_{H,F}$ = 53)
1c	34	74—75	16.14 16.48	0.41 0.46	C_3HClF_6S	−125.00 (dm, 1 F, CFH, $J_{H,F}$ = 43); −14.00 (m, 2 F, CF_2S); 1.50 (m, 3 F, CF_3)	4.90 (dm, CH, $J_{H,F}$ = 43)
2a	61	95—96 (19)	30.46 30.38	2.25 2.22	$C_8H_7F_7O_3S$	—	1.30 (t, 3 H, Me, *J* = 7); 4.06 (s, 1 H, CH); 4.20 (q, 2 H, CH_2, *J* = 7); 6.42 (tm, 1 H, CHF, *J* = 53)
2b	71	64—65 (3)	26.29 26.16	1.59 1.63	$C_8H_6Cl_2F_6O_3S$	—	1.25 (t, 3 H, Me, *J* = 7); 4.10 (s, 1 H, CH); 4.21 (q, 2 H, CH_2, *J* = 7)
2c	63	91—92 (12)	29.98 29.51	1.88 1.91	$C_9H_7F_9O_3S$		1.27 (t, 3 H, Me, *J* = 7); 4.12 (s, 1 H, CH); 4.20 (q, 2 H, CH_2, *J* = 7); 6.00 (dm, 1 H, CHF, *J* = 40)
3a	79	144—145	26.52 26.67	0.40 0.37	$C_6HF_7O_2S$	−56.0 (m, 2 F, CF_2H); −18.4 (m, 2 F, CF_2S); 0.8 (s, 3 F, CF_3)	—
3b	61	83—84 (24)	22.61 22.43	—	$C_6Cl_2F_6O_2S$	−9.0 (d, 2 F, CF_2S); 1.6 (s, 3 F, CF_3, *J* = 15); 6.4 (t, F, $CFCl_2$, *J* = 15)	
3c	67	98—100 (85)	26.41 26.25	0.35 0.31	$C_7HF_9O_2S$	−129.5 (m, F, CFH); −12.5 and −8.0 (AB system, both d, 2 F, CF_2S, *J* = 225); 0.9 (s, 3 F, CF_3); 2.0 (m, 3 F, CF_3)	—
4a	53	130—132	24.75 24.59	1.20 1.23	$C_5H_3F_7OS$	Keto form: −57.0 (m, 2 F, CF_2H); −14.0 (m, 2 F, CF_2S); 0.1 (s, 3 F, CF_3) Enol form: −54.2 (m, 2 F, CF_2H); −13.6 (m, 2 F, CF_2S); −7.3 (s, 3 F, CF_3) Ketone—enol ratio 3 : 1	Keto form: 4.08 (s, 2 H, CH_2); 5.87 (tm, H, CHF_2, *J* = 53) Enol form: 3.32 (s, H, CH); 6.02 (tm, H, CHF_2, *J* = 53) Ketone—enol ratio 3 : 1
4b	65	112—114 (90)	20.26 20.34	0.72 0.68	$C_5H_2Cl_2F_6OS$	Keto form: −6.0 (d, 2 F, CF_2S, *J* = 12.5); 0.5 (s, 3 F, CF_3); 7.6 (t, F, $CFCl_2$, *J* = 12.5) Enol form: −7.2 (s, 3 F, CF_3); −4.9 (d, 2 F, CF_2S, *J* = 12.5); 8.1 (t, F, $CFCl_2$, *J* = 12.5) Ketone—enol ratio 2 : 1	Keto form: 4.11 (s, 2 H, CH_2). Enol form: 2.80 (br.s, $OH+H_2O$); 3.39 (s, H, CH) Ketone—enol ratio 2 : 1
4c	64	84—86 (90)	24.55 24.49	1.04 1.02	$C_6H_3F_9OS$	Keto form: −130.3 (m, F, CFH); −6.5 (m, 2 F, CF_2S); −2.7 (s, 3 F, CF_3); 0.4 (m, 3 F, CF_3) Enol form: −129.5 (m, F, CFH); −11.5 (m, 2 F, CF_2S); −10.5 (s, 3 F, CF_3); 0.6 (m, 3 F, CF_3) Ketone—enol ratio 3 : 1	Keto form: 4.10 (s, 2 H, CH_2); 4.98 (d. sept, H, CHF, *J* = 4.3 and 41) Enol form: 3.38 (s, H, CH); 5.03 (m, H, CHF) Ketone—enol ratio 3 : 1

5	73	95—97 (25)	27.46 27.27	1.50 1.42	$C_8H_5F_9O_3S$	—	3.58 (s, 3 H, CH_3); 4.02 (s, 1 H, CH); 5.80 (dm, 1 H, CHF, J = 50)
6	42	[63—64]	45.41 45.22	3.72 3.77	$C_{13}H_{13}NF_6OS$	—	3.07 (s, 6 H, 2 Me); 4.40 (s, 2 H, CH_2); 5.05 (d sept, 1 H, CHF, J = 4 and 54); 6.78 and 7.87 (both d, 2 H each, C_6H_4, J = 8)
7a	62	[54—55]	45.34 45.16	1.96 1.88	$C_{14}H_7F_7O_2S$	−55.2 (m, 2 F, CF_2H); −29.5 and −24.4 (AB system, both d, 2 F, CF_2S, J = 200); 5.25 (s, 3 F, CF_3)	6.70 (tm, 1 H, CF_2H, J = 53); 7.58 and 7.82 (both m, 3 H and 2 H, Ph); 7.65 (s, 1 H, CH)
7b	58	[79—80]	39.91 39.72	1.40 1.42	$C_{14}H_6Cl_2F_6O_2S$	−2.2 (m, 2 F, CF_2S); 7.2 (s, 3 F, CF_3); 9.4 (t, 1 F, $CFCl_2$, J = 13.9)	7.32 (s, 1 H, CH); 7.60 and 7.95 (both m, 3 H and 2 H, Ph)
7c	70	[91—92]	42.54 42.65	1.66 1.65	$C_{15}H_7F_9O_2S$	−96.7 (m, 1 F, CFH); −4.9 (m, 2 F, CF_2S); 1.3 (m, 3 F, CF_3); 4.6 (s, 3 F, CF_3)	6.15 (m, 1 H, CHF); 7.54 and 7.80 (both m, 3 H and 2 H, Ph); 7.60 (s, 1 H, CH)
8a	41	[101—102]	43.17 43.09	2.55 2.49	$C_{13}H_8F_7O_2S$	*exo*-**7a**: −56.1 (m, 2 F, CF_2H); −31.0 (m, 2 F, CF_2S); 5.3 (s, 3 F, CF_3) *endo*-**7a**: −55.1 (m, 2 F, CF_2H); −13.7 (m., 2 F, CF_2S); 3.2 (s, 3 F, CF_3) Ratio *exo*-**7a**/*endo*-**7a** = 6 : 1	*exo*-**7a**: 1.55 (m, 2 H, CH_2); 2.96 (d, 1 H, J = 7.5); 3.23 (s, 1 H); 3.61 (s, 1 H); 3.95 (d, 1 H, J = 7.5); 6.31 (m, 1 H); 6.50 (m, 1 H); 6.85 (tt, 1 H, HCF_2, J = 54, J = 3) *endo*-**7a**: 1.70 (m, 2 H, CH_2); 3.03 (d, 1 H, J = 7.4); 3.35 and 3.82 (both s, 1 H each); 4.48 (d, 1 H, J = 7.4); 6.25 and 6.49 (both m, 1 H each); 6.70 (tm, 1 H, HCF_2, J = 54). Ratio *exo*-**7a**/*endo*-**7a** = 6 : 1
8b	52	[121—123]	37.54 37.77	1.96 1.94	$C_{13}H_8Cl_2F_6O_2S$	−21.6 and −19.0 (AB system, both d, 2 F, CF_2S, J = 190); 4.9 (s, 3 F, CF_3); 5.8 (m, 1 F, $CFCl_2$)	1.60 (m, 2 H, CH_2); 3.08 (d, 1 H, CH, J = 8); 3.27 (s, 1 H, CH); 3.65 (s, 1 H, CH); 3.98 (d, 1 H, CH, J = 8); 6.30 and 6.5 (both m, 1 H each, 2 CH=)
8c	51	[98—99]	40.92 40.78	2.25 2.18	$C_{14}H_9F_9O_2S$	−133.4 (m, 1 F, CFH); −30.7 (m, 2 F, CF_2S); 1.4 (m, 3 F, CF_3); 4.0 (m, 3 F, CF_3)	*exo*-**7c**: 1.70 (m, 2 H, CH_2); 3.03 (m, 1 H, CH); 3.48 (m, 2 H, 2CH); 3.78 (m, 1 H, CH); 5.40 (m, 1 H, CHF); 6.31 and 6.55 (both m, 1 H each, 2CH=). *endo*-**7c**: 1.70 (m, 2 H, CH_2); 3.35 (m, 1 H, CH); 3.60 (m, 1 H, CH); 3.94 (m, 1 H, CH); 4.12 (m, 1 H, CH); 5.40 (m, 1 H, CHF); 6.27 (m, 2 H, 2CH=). Ratio *exo*-**7c**/*endo*-**7c** = 5 : 1
9a	67	[40—41]	33.69 33.80	2.23 2.25	$C_{10}H_8F_7NO_3S$	−54.7 (dt, 2 F, CF_2H, J = 53.5 and 9.5); −12.9 (m, 2 F, CF_2S); 13.0 (s, 3 F, CF_3)	1.00 (m, 3 H, Me); 1.73 (m, 2 H, CH_2); 3.85 (m, 2 H, NCH_2); 6.08 (tt, 1 H, CF_2H, J = 53.5, J = 3.0)
9b	75	[156—157]	35.58 35.45	1.17 1.14	$C_{13}H_5Cl_2F_6NO_3S$	−3.0 (m, 2 F, CF_2S); 7.8 (t, 1 F, $CFCl_2$, J = 13); 13.2 (s, 3 F, CF_3)	7.30 and 7.55 (both m, 2 H and 3 H, 5 H, Ph)
9c	68	[126—127]	38.50 38.27	1.42 1.37	$C_{14}H_6F_9NO_3S$	−127.5 (m, 1 F, CFH); −6.08 and −4.33 (AB system, both d, 2 F, CF_2S, J = 220); 4.0 and 13.3 (both s, 3 F each, CF_3)	5.25 (d. sept, 1 H, CHF, J = 40, J = 4); 7.28 and 7.59 (both m, 2 H and 3 H, 5 H, Ph)

* The spectra of compounds **2a—c**, **5, 7a—c,** and **8a,b** were recorded in a 3 : 7 DMSO-d_6—CCl_4 mixture. The spectra of compounds **1a—c**, **4a—c, 6, 8c,** and **9a—c** were measured in $CDCl_3$. The spectra of compounds **3a—c** were recorded without a solvent.

1,1,2,2-Tetrafluoroethanesulfenyl chloride (1a). An excess of dry chlorine was bubbled through benzyl 1,1,2,2-tetrafluoroethylsulfide at 20 °C until absorption ceased. The resulting mixture was fractionated.

1,1,2,3,3,3-Hexafluoropropanesulfenyl chloride (1c) was prepared analogously by chlorination of a mixture of products of the addition and substitution of benzylthiol and perfluoropropene.[15]

Ethyl 4,4,4-trifluoro-3-oxo-2-(1,1,2,2-tetrafluoroethylthio)butanoate (2a). A mixture of ethyl trifluoroacetoacetate (9.2 g, 0.05 mol) and 1,1,2,2-tetrafluoroethanesulfenyl chloride (10.1 g, 0.06 mol) was heated to 70 °C, kept at 70 °C until liberation of HCl ceased (20 h), and distilled *in vacuo*.

Ethyl 2-(2,2-dichloro-1,1,2-trifluoroethylthio)-4,4,4-trifluoro-3-oxobutanoate (**2b**) and ethyl 4,4,4-trifluoro-2-(1,1,2,3,3,3-hexafluoropropylthio)-3-oxobutanoate (**2c**) were prepared analogously.

(1,1,2,2-Tetrafluoroethylthio)trifluoroacetylketene (3a). A mixture of ester **2a** (6.3 g, 20 mmol) and P_2O_5 (14.2 g, 100 mmol) was stirred by shaking and heated to 180 °C with a gas burner, the products that distilled being collected. The resulting distillate was distilled once again. IR, ν/cm^{-1}: 2155 (C=C=O), 1790 (C=O).

Compounds **3b** and **3c** were prepared analogously.

(2,2-Dichloro-1,1,2-trifluoroethylthio)trifluoroacetylketene (3b). IR, ν/cm^{-1}: 2160 (C=C=O), 1780 (C=O).

(1,1,2,3,3,3-Hexafluoropropylthio)trifluoroacetylketene (3c). IR, ν/cm^{-1}: 2155 (C=C=O), 1785 (C=O).

1,1,1-Trifluoro-3-(1,1,2,2-tetrafluoroethylthio)propan-2-one (4a). Water (2 mL) was added dropwise with stirring to ketene **3a** (2.7 g, 10 mmol) at 15—20 °C; the reaction was accompanied by liberation of a gas (CO_2). The reaction mixture was kept at this temperature for 3 h, heated at 80 °C for 1 h, and distilled over P_2O_5.

3-(2,2-Dichloro-1,1,2-trifluoroethylthio)-1,1,1-trifluoropropan-2-one (4b) and **1,1,1-trifluoro-3-(1,1,2,3,3,3-hexafluoropropylthio)propan-2-one (4c)** were prepared analogously.

Methyl 4,4,4-trifluoro-2-(1,1,2,3,3,3-hexafluoropropylthio)-3-oxobutanoate (5). Anhydrous MeOH (3 mL) was added with stirring to ketene **3c** (3.2 g, 10 mmol) at 5—10 °C. The reaction mixture was kept at 20 °C for 24 h, washed with water, extracted with Et_2O, dried over $CaCl_2$, and distilled.

4-(*N*,*N*-Dimethylamino)phenyl 1,1,2,3,3,3-hexafluoropropylthiomethyl ketone (6). Ketene **3c** (1.6 g, 5 mmol) was added with stirring to a solution of *N*,*N*-dimethylaniline (0.6 g, 5 mmol) in Et_2O (10 mL). The reaction mixture was kept at 20 °C for 24 h. The solvent was removed *in vacuo* and the residue was recrystallized from hexane.

Reactions of ketenes 3a—c with unsaturated compounds (general procedure). Ketene **3a—c** (10 mmol) was added with stirring to the corresponding unsaturated compound (10 mmol) at 5—10 °C. The reaction mixture was slowly warmed to 20 °C and kept for 20 h. The reaction products were recrystallized from hexane (**7a—c** and **9a—c**) or a 1 : 1 hexane—Et_2O mixture (**8a—c**).

This method was used for the synthesis of 6-phenyl-3-(1,1,2,2-tetrafluoroethylthio)-2-trifluoromethyl-4*H*-pyran-4-one (**7a**), 3-(2,2-dichloro-1,1,2-trifluoroethylthio)-6-phenyl-2-trifluoromethyl-4*H*-pyran-4-one (**7b**), 3-(1,1,2,3,3,3-hexafluoropropylthio)-6-phenyl-2-trifluoromethyl-4*H*-pyran-4-one (**7c**), 6-oxo-5-(1,1,2,2-tetrafluoroethylthio)-4-trifluoromethyl-3-oxatricyclo[6.2.1.0^{2,7}]deca-4,9-diene (**8a**), 5-(2,2-dichloro-2,1,2-trifluoroethylthio)-6-oxo-4-trifluoromethyl-3-oxatricyclo[6.2.1.0^{2,7}]deca-4,9-diene (**8b**), 5-(1,1,2,3,3,3-hexafluoropropylthio)-6-oxo-4-trifluoromethyl-3-oxatricyclo[6.2.1.0^{2,7}]deca-4,9-diene (**8c**), 3-propyl-5-(1,1,2,2-tetrafluoroethylthio)-6-trifluoromethyl-3*H*-1,3-oxazine-2,4-dione (**9a**), 5-(2,2-dichloro-1,1,2-trifluoroethylthio)-3-phenyl-6-trifluoromethyl-3*H*-1,3-oxazine-2,4-dione (**9b**), and 5-(1,1,2,3,3,3-hexafluoropropylthio)-3-phenyl-6-trifluoromethyl-3*H*-1,3-oxazine-2,4-dione (**9c**).

References

1. Yu. A. Cheburkov and I. L. Knunyants, *Fluor. Chem. Rev.*, 1967, **1**, 107.
2. D. C. England, *J. Org. Chem.*, 1981, **46**, 147.
3. D. C. England, *J. Org. Chem.*, 1981, **46**, 153.
4. J. Boivin, L. E. Kaim, and S. Z. Zard, *Tetrahedron*, 1995, **51**, 2585.
5. Y. Morita, R. Kamakura, M. Takeda, and Y. Yamamoto, *Chem. Commun.*, 1997, 359.
6. A. Haas, M. Lieb, and H.-W. Praas, *J. Fluor. Chem.*, 1989, **44**, 329.
7. C. G. Krespan, *J. Fluor. Chem.*, 1976, **8**, 105.
8. L. Yu. Kryukova, L. N. Kryukov, V. L. Isaev, R. N. Sterlin, and I. L. Knunyants, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1977, 230 [*Mendeleev Chem. J.*, 1977 (Engl. Transl.)].
9. A. F. Eleev, S. I. Pletnev, G. A. Sokol´skii, and I. L. Knunyants, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1978, 229 [*Mendeleev Chem. J.*, 1978 (Engl. Transl.)].
10. L. Yu. Kryukova, L. N. Kryukov, A. F. Ermolov, V. L. Isaev, R. N. Sterlin, and I. L. Knunyants, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1979, 297 [*Mendeleev Chem. J.*, 1979 (Engl. Transl.)]
11. A. N. Kovregin, A. Yu. Sizov, A. F. Ermolov, and A. F. Kolomiets, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1770 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1749].
12. N. V. Vasil´ev, A. E. Patalakha, and A. V. Buzaev, *Fizicheskie i khimicheskie svoistva norbornadiena i ego proizvodnykh*, *Itogi nauki i tekhniki, Organicheskaya khimiya* [*Physical and Chemical Properties of Norbornadiene and Its Derivatives. Advances in Science and Technology: Organic Chemistry*], VINITI, Moscow, 1992, **23**, 176 (in Russian).
13. J. Burdon and V. McLoughlin, *Tetrahedron*, 1964, **20**, 2163.
14. A. V. Fokin, S. N. Shkurak, A. F. Kolomiets, and F. M. Mukhametshin, *Zh. Org. Khim.*, 1985, **21**, 1835 [*J. Org. Chem. USSR*, 1985, **21** (Engl. Transl.)].
15. R. A. Bekker and V. Ya. Popkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1898 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1725 (Engl. Transl.)].

Received November 14, 2002;
in revised form December 25, 2002