The decrease of FT yield as temperature increases while at the same time FB yield increases may be related to partial dealkylation of FT in the presence of HCl that is formed during decomposition of DFCM at 924-1160 K. In particular, according to [4], dealkylation of toluene to benzene is the principal reaction under conditions of pulsed gas compression in a toluene—HCl mixture. By using special experiments it was shown that pyrolysis of a mixture of FT and DFCM leads to an insignificant decrease in the quantity of FT (~8% at 1194 K) and to formation of FB (Table 4).

LITERATURE CITED

1. Yu. A. Kolbanovskii, N. Ya. Chernyak, V. S. Shchipachev, et al., in: Abstracts of Proceedings, 4th All-Union Conf. on the Chemistry of Carbenes, Moscow (1987), pp. 120-121.
2. O. M. Nefedov and A. A. Ivashenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 446 (1968); USSR Inventor's Certificate No. 279,608, Byull. Izobret., No. 27 (1970).
3. O. M. Nefedov (ed.), Chemistry of Carbenes and Small-Sized Cyclic Compounds [Russian translation], Mir, Moscow (1989), pp. 69-100.
4. Yu. A. Kolbanovskii, V. S. Shchipachev, N. Ya. Chernyak, et al., Pulsed Gas Compression in Chemistry and Technology [in Russian], Nauka, Moscow (1982), p. 240.
5. V. A. Mironov, M. E. Dolgaya, S. A. Yankovskaya, and E. I. Pukhova, Izv. Vuz. Khim. Khim. Tekhnol., 26, No. 8, 923-928 (1983).

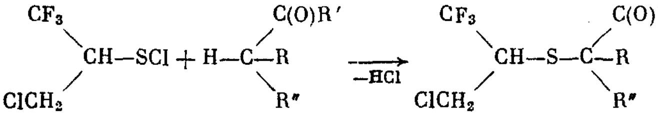
1-TRIFLUOROMETHYL-2-CHLOROETHYLTHIOLATED CARBONYL COMPOUNDS: SYNTHESIS AND PROPERTIES

A. Yu. Sizov, A. F. Kolomiets, and A. V. Fokin

UDC 542.91:547.446

1-Trifluoromethyl-2-chloroethylsulfenyl chloride thiolates enolizible ketones, forming products of mono- and disubstitution. The properties of the resultant sulfides are determined by the presence in the molecule of two acidic CH centers. Thus, bromination proceeds at the ambident center and reaction with bases leads to (1-trifluoromethylvinyl) sulfides which are able to undergo intramolecular cyclizations and Diels—Alder reactions.

1-Trifluoromethyl-2-chloroethylsulfenyl chloride (I), like trifluoromethanesulfenyl chloride [1, 2], reacts under mild conditions (—50°C) with carbonyl compounds (acetone, acetophenone, acetylacetone, acetoacetic and methylacetoacetic esters), giving products of monothiolation of (II)-(VI) in yields up to 90%.



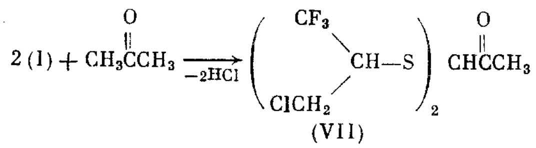
(I) (II)—(VI)

$R = R'' = H, R' = CH_3$ (II); $R = R'' = H, R' = C_6H_5$ (III); $R = H, R' = CH_3, R'' = C(O)CH_3$ (IV); $R = H, R' = CH_3, R'' = C(O)OC_2H_5$ (V); $R = R' = CH_3, R'' = C(O)OC_2H_5$ (VI).

With excess (I) under more rigid conditions (20°C) the bis-substitution product (VII) is also formed (see scheme at the top of following page).

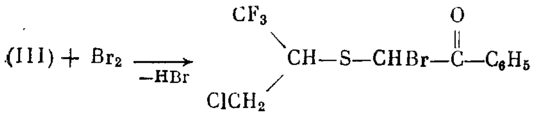
The obtained sulfides of β-dicarbonyl compounds (IV) and (V), unlike (II), (III), and (VII, exist mostly in the enol form (IR, PMR). Their PMR spectra have a signal at 13-18 ppm (OH) and in the IR spectra the OH absorption band lies in the region of 2990-3000 cm^{-1}.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 676-681, March, 1991. Original article submitted January 15, 1990.



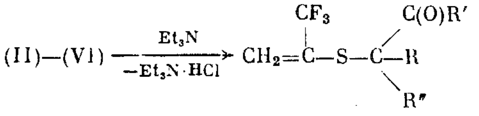
(VII)

The properties of sulfides (II)-(VII) are determined by the presence in the molecule of two acidic CH centers. Their halogenation proceeds exclusively at the ambident center. For example, by bromination of (III) sulfide (VIII) is obtained in high yield.



(VIII)

Reaction of sulfides (II)-(VI) with nucleophilic agents (Et_3N, alkalis, alcoholates) leads to trifluoroisopropenyl sulfides (IX)-(XIII)

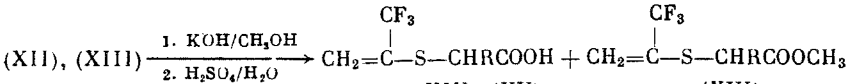


(IX)—(XIII)

$R = R'' = H$, $R' = CH_3$ (IX), C_6H_5 (X); $R = H$, $R' = CH_3$, $R'' = C(O)CH_3$ (XI), $C(O)OC_2H_5$ (XII); $R = R' = CH_3$, $R'' = C(O)OC_2H_5$ (XIII).

Trifluoroisopropenyl sulfides (XI) and (XII) exist analogously to (IV) and (V) in the enol form.

Reaction of sulfides (V) and (VI) with alkalis is accompanied by deacetylation. As a result, trifluoroisopropenyl sulfides (XII) and (XIII) yield acids (XIV) and (XV) [sometimes contaminated with ester (XVI)]

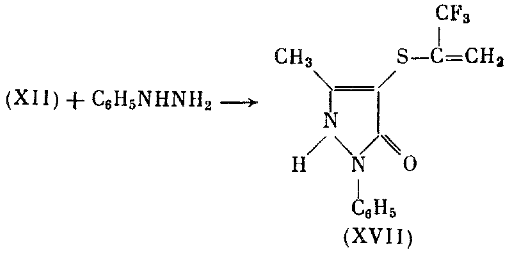


$$\text{(XII), (XIII)} \xrightarrow[\text{2. } H_2SO_4/H_2O]{\text{1. } KOH/CH_3OH} CH_2{=}\overset{CF_3}{\overset{|}{C}}{-}S{-}CHRCOOH + CH_2{=}\overset{CF_3}{\overset{|}{C}}{-}S{-}CHRCOOCH_3$$

(XIV), (XV) (XVI)

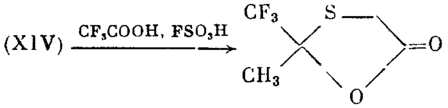
$R = H$ (XIV), (XVI), CH_3 (XV).

Reaction of trifluoroisopropenyl sulfide (XII) with phenylhydrazine leads exclusively to pyrazolone (XVII), i.e., the vinylthio group in this case is not touched



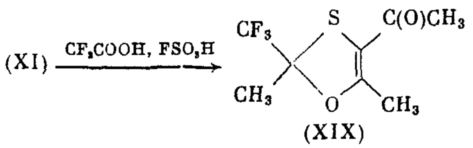
(XVII)

Heating of acid (XIV) in CF_3COOH with catalysis by fluorosulfonic acid is accompanied by lactonization and formation in preparative yield of the corresponding octathiolanone (XVIII)



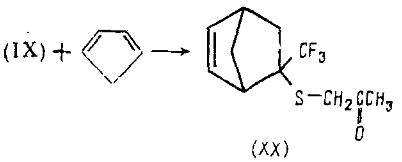
(XVIII)

Under more rigid conditions (100°C) intramolecular cyclization of trifluoroisopropenyl sulfide (XI) occurs. In this case, the reaction is complicated by resinification of the reaction mixture (product yield does not exceed 30%)



(XIX)

Trifluoroisopropenyl sulfides (IX)-(XIII) at 100-130°C enter into the Diels–Alder reaction. For example, sulfide (X) undergoes [4 + 2]-cycloaddition with cyclopentadiene in 82% yield to form a mixture of endo- and exo-isomers in a ratio of 7:4.



(XX)

EXPERIMENTAL

NMR spectra (^{1}H, ^{19}F, and ^{13}C) were taken on a Bruker WR-200SY spectrometer with working frequencies of 200, 188, and 50 mHz, respectively. Chemical shifts (δ, ppm) were determined relative to TMS (internal standard) and CF_3COOH (external standard) for 10% solutions in $CDCl_3$, CD_3CN, or CD_3COCD_3. IR spectra (ν, cm^{-1}) were recorded on a UR-20 spectrometer. The R_f values of the obtained compounds are shown for Silufol UV-254 plates run in acetone–CCl_4.

Reactions of 1-Trifluoromethyl-2-chloroethylsulfenyl Chloride (I) with Ketones (typical experiment). To 0.1 mole of ketone with stirring and cooling to –50°C, 0.1 mole of sulfenyl chloride (I) was added. The mixture was slowly (10-12 h) heated to 20°C, kept at this temperature until completion of HCl evolution (1-2 h), and fractionated. By this method there were obtained: (1-trifluoromethyl-2-chloroethylthio)acetone (II), (1-trifluoromethyl-2-chloroethylthio)acetone (III), 3-(1-trifluoromethyl-2-chloroethylthio)-2,4-pentandione (IV), the ethyl ester of 2-(1-trifluoromethyl-2-chloroethylthio)acetoacetic acid (V), the ethyl ester of 2-methyl-2-(1-trifluoromethyl-2-chloroethylthio)acetoacetic acid (VI).

TABLE 1. NMR Spectra of Compounds (II)-(XX) ($CDCl_3$, δ, ppm, J, Hz)

Compound	^{19}F NMR spectrum δ (J_{H-F})	^{1}H NMR spectrum δ (J)
(II)	–8,5 d (7,3)	3,88 dd (1H, 4,6 and 11,6), 3,65 dd (1H, 7,3 and 11,6), 3,50 m (1H), 3,43 d (2H, 4,0), 2,31 s (3H)
(III) *	–9,7 d (8,7)	8,06 m (2H), 7,60 m (3H), 4,44 s (2H), 4,08 m (3H)
(IV)	–9.2 d (7,7)	17.31 s (1H), 3,87 dd (1H, 4.6 and 12,3), 3.60 dd (1H, 7,7 and 12,3), 3,24 dp (1H. 4,6 and 7,7), 2,47 s (6H)
(V)	–9,3 d (7,3)	13,65 s (1H), 4,30 q (2H, 7.0), 3,80 m (2H), 3,43 m (1H), 2,39 s (3H), 1,37 t (3H, 7,0)
(VI)	–9,8 dd (8,4 and 23,0)	3.90 m (3H), 3.65 m (2H), 1,98 s and 1,95 s (3H, 2 : 3), 1,44 s 1.39 s (3H, 3 : 2), 0,90 q (3H, 7,2)
(VII)	–8,7 m	4,84 m (1H), 3,83 m (6H), 2,41 s (3H)
(VIII) *	–9,7 d (9,0)	8.11 m (2H), 7.65 m (3H), 7,26 d (1H, 14,2), 4,40 m (1H), 4.19 dd (2H, 5,0 and 11,0)
(IX)	–11.97 s	5,58 s (1H), 5,07 s (1H), 2,76 s (2H), 1,61 s (3H)
(X) *	–12,2 s	8.10 m (2H), 7,65 m (3H), 6,15 s (1H), 5,85 s (1H), 4,65 s (2H)
(XI)	–12.5 s	17.25 s (1H). 5.85 s (1H), 5,18 s (1H), 2,35 s (6H)
(XII)	–12,3 s	13,82 s (1H), 5,80 s (1H), 5,30 s (1H), 4.29 q (2H, 7,0). 2,35 s (3H). 1,35 t (3H, 7,0)
(XIII) **	–11,82 s	6.55 s (1H), 6.08 s (1H). 4.24 q (2H, 7,0), 2,28 s (3H). 1,61 s (3H), 1.25 t (3H, 7,0)
(XIV)	–11.6 s	9,14 s (1H), 6,20 s (1H), 5.85 s (1H), 3,60 s (2H)
(XV)	–11,55 s	9,15 s (1H), 5.73 s (1H), 5,43 s (1H), 3.42 q (1H, 7,0), 1,11 d (3H. 7,0)
(XVI)	–11.5 s	6,13 s (1H). 5,80 s (1H). 3,77 s (3H), 3,55 s (2H)
(XVII) **	–13,3 s	7,69 m (2H), 7,47 m (2H), 7,30 m (1H), 5,92 s (1H), 5.28 s (1H), 2,21 s (3H)
(XVIII)	2,2 s	3.38 dd (2H. 17,0 and 38,0), 1.85 s (3H)
(XIX)	6.6 s	2.28 s (3H). 2.27 s (3H), 1,91 s (3H)
(XX)	–13,6 s and –11.7 s (7 : 4)	6.30–5.92 m (2H). 3,50 m (2H), 3,00 m (2H), 2,28 s and 2,24 s (3H. 7 : 4), 1,90–1,10 m (4H)

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*Spectra obtained in acetone-d_6.

**Spectra obtained in acetonitrile-d_3.

TABLE 2. Characteristics of Compounds (II)-(XX)

Compound	Bp, °C (p, mm Hg), MP,* °C	n_D^{25}	R_f ($CCl_4:CH_3\overset{\overset{O}{\|}}{C}CH_3$)	Yield, %	IR spectrum, (ν, cm⁻¹)	Found/Calculated, %			Empirical formula
						C	H	S	
(II)	97(9)	1,4420	–	86	1720 (C=O)	$\frac{32,73}{32.65}$	$\frac{3.67}{3,63}$	$\frac{14.60}{14,51}$	$C_6H_8ClF_3OS$
(III)	29 *	–	0,62 (10 : 1)	70	1680 (C=O)	$\frac{46,55}{46,73}$	$\frac{3,58}{3,54}$	$\frac{11.25}{11,33}$	$C_{11}H_{10}ClF_3OS$
(IV)	75(1)	1,4845	–	89	2900 (OH), 1595	$\frac{36,46}{36.57}$	$\frac{3.77}{3,81}$	$\frac{12,11}{12.19}$	$C_8H_{10}ClF_3O_2S$
(V)	87(1)	1,4638	–	87	3000 (OH), 1600	$\frac{36,81}{36.92}$	$\frac{4,08}{4,10}$	$\frac{10.99}{10,94}$	$C_9H_{12}ClF_3O_3S$
(VI)	96–97(1)	1,4462	–	88	1730 (C=O), 1720 (C=O)	$\frac{39,27}{39.15}$	$\frac{4,62}{4.57}$	$\frac{10,37}{10,44}$	$C_{10}H_{14}ClF_3O_3S$
(VII)	110(1)	1,4625	–	55	1720 (C=O)	$\frac{28,41}{28.20}$	$\frac{2,70}{2.61}$	$\frac{16,59}{16,71}$	$C_9H_{10}Cl_2F_6OS_2$
(VIII)	56–57 *	–	0,66 (10 : 1)	75	1680 (C=O)	$\frac{36,62}{36,51}$	$\frac{2,51}{2,49}$	$\frac{8.80}{8,85}$	$C_{11}H_9BrClF_3OS$
(IX)	78–80(15)	1,4250	–	84	1720 (C=O), 1620 (C=C)	$\frac{39,30}{39,13}$	$\frac{3,83}{3,80}$	$\frac{17,32}{17,39}$	$C_6H_7F_3OS$
(X)	58–59 *	–	0,60 (10 : 1)	78	1680 (C=O) 1620 (C=C)	$\frac{53,58}{53,66}$	$\frac{3,66}{3,65}$	$\frac{13,11}{13,01}$	$C_{11}H_9F_3OS$
(XI)	65(7)	1,4610	–	83	3000 (OH), 1620 (C=C), 1600	$\frac{42,57}{42.48}$	$\frac{3.95}{3.98}$	$\frac{14.09}{14.16}$	$C_8H_9F_3O_2S$
(XII)	85(7)	1,4497	–	84	3000 (OH), 1620 (C=C), 1600	$\frac{42,32}{42,19}$	$\frac{4,24}{4.29}$	$\frac{12,37}{12.50}$	$C_9H_{11}F_3O_3S$
(XIII)	53–55(1)	1,4349	–	83	1730 (C=O), 1725 (C=O), 1620(C=C)	$\frac{44,51}{44,44}$	$\frac{4.75}{4.81}$	$\frac{11.80}{11.85}$	$C_{10}H_{13}F_3O_3S$
(XIV)	108(7)	1,4371	–	57	1740 (C=O), 1620 (C=C)	$\frac{32,41}{32,26}$	$\frac{2,65}{2,69}$	$\frac{17.12}{17,20}$	$C_5H_5F_3O_2S$
(XV)	72–73(1)	1,4278	–	52	1720 (C=O), 1620 (C=C)	$\frac{35,89}{36,00}$	$\frac{3.47}{3,50}$	$\frac{16.08}{16,00}$	$C_6H_7F_3O_2S$
(XVI)	67–69(7)	1,4205	–	17	1750 (C=O), 1620 (C=C)	$\frac{35.85}{36,00}$	$\frac{3,42}{3,50}$	$\frac{15,96}{16.00}$	$C_6H_7F_3O_2S$
(XVII)	172–173 *	–	0,56 (3 : 1)	69	–	$\frac{52,12}{52.00}$	$\frac{3,60}{3,67}$	$\frac{10.59}{10,67}$	$C_{13}H_{11}F_3N_2OS$
(XVIII)	51(7)	1,4103	–	86	1750 (C=O)	$\frac{32.32}{32,26}$	$\frac{2,73}{2,69}$	$\frac{17,12}{17,20}$	$C_5H_5F_3O_2S$
(XIX)	70–71(7)	1,4550	–	28	1730 (C=O), 1610 (C=C)	$\frac{42,59}{42.48}$	$\frac{3,94}{3.98}$	$\frac{14.05}{14.16}$	$C_8H_9F_3OS$
(XX)	78(1)	1,4842	–	82	1725 and 1720 (C=O)	$\frac{52,68}{52.80}$	$\frac{5,11}{5.20}$	$\frac{12.72}{12.80}$	$C_{11}H_{13}F_3OS$

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*Footnote omitted in Russian original – Editor.

Bis-(1-Trifluoromethyl-2-chloroethylthio)acetone (VII). To 0.6 g (0.01 mole) of acetone with stirring and cooling to −50°C 4.0 g (0.02 mole) of sulfenyl chloride (I) was added. The mixture was slowly heated to 20°C, kept at this temperature for 200 h, and fractionated. There was obtained 4.2 g of compound (VII).

1-Bromo-1-(1-trifluoromethyl-2-chloroethylthio)acetophenone (VIII). To a solution of 2.8 g (0.01 mole) of sulfide (III) in 10 ml of CCl_4 at 10°C a solution of 1.6 g (0.01 mole) of bromine in 10 ml of CCl_4 was added. The mixture was heated to 20°C and kept at this temperature for 20 h. The solvent was removed under vacuum and the residue was recrystallized from hexane. There was obtained 2.7 g of sulfide (VIII).

Dehydrochlorination of 1-Trifluoromethyl-2-chloroethyl Sulfides (typical experiment). To a solution of 0.01 mole of sulfide (II)-(VI) in 25 ml of ether at 20°C a solution of 0.01 mole of Et_3N in 15 ml of ether was added dropwise. The mixture was kept until completion of the reaction (30 h), the residue was filtered off, the solvent removed under vacuum, and the residue was fractionated. By this method there were obtained: (1-trifluoromethylvinylthio)acetone (IX), (1-trifluoromethylvinylthio)acetophenone (X), 3-(1-trifluoromethylvinylthio)-2,4-pentandione (XI), the ethyl ester of 2-(1-trifluoromethylvinylthio)acetoacetic acid (XII), and the ethyl ester of 2-methyl-2-(1-trifluoromethylvinylthio)acetoacetic acid (XIII).

Decomposition of Ethyl Esters (XII) and (XIII) (typical experiment). To a solution of 0.04 mole of KOH in 20 ml of methanol 0.04 mole of sulfide (XII) or (XIII) was added. The mixture was kept for 30 h at 20°C and poured into a cold solution (0°C) of 3 ml concentrated H_2SO_4 in 150 ml H_2O. The precipitated oil was extracted with ether, dried with $MgSO_4$, and fractionated. By this method there were obtained: 2-(1-trifluoromethylvinylthio)acetic acid (XIV), 2-(1-trifluoromethylvinylthio)propionic acid (XV), and the methyl ester of 2-(1-trifluoromethylvinylthio)acetic acid (XVI).

1-Phenyl-3-methyl-4-(1-trifluoromethylvinylthio)pyrazol-5-one (XVII). To a solution of 5.1 g (0.02 mole) of sulfide (XII) in 20 ml of AcOH 2.2 g (0.02 mole) of phenylhydrazine was slowly added dropwise. The mixture was kept for 1 h at 20°C and heated at 50°C for another 3 h. The precipitated crystals were filtered off and recrystallized from AcOEt. There was obtained 4.1 g of pyrazolone (XVII).

2-Methyl-2-trifluoromethyl-1,3-oxathiolan-5-one (XVIII). To a solution of 3.7 g (0.02 mole) of acid (XIV) in 10 ml of CF_3COOH 2 drops of fluorosulfonic acid was added. The mixture was heated at 70°C for 3 h, poured into water (0°C), extracted with CH_2Cl_2, dried with $MgSO_4$, and fractionated. There was obtained 3.2 g of oxathiolanone (XVIII). ^{13}C NMR spectrum: 171.67 s (C=O); 125.46 q (CF_3, J = 283.19 Hz); 86.23 q ($-\overset{|}{\underset{|}{C}}-$, J = 33.20 Hz); 32.66 s (CH_2); 22.27 s (CH_3).

2,5-Dimethyl-2-trifluoromethyl-4-acetyl-1,3-oxathiol (XIX). To a solution of 4.5 g (0.02 mole) of sulfide (XI) in 10 ml of CF_3COOH 2 drops of fluorosulfonic acid was added. The mixture was heated in a sealed glass ampul for 30 h at 100°C. Then the ampul was opened, the contents poured into water (0°C), extracted with ether, dried with $MgSO_4$, and fractionated. There was obtained 1.26 g of oxathiol (XIX).

2-(Propyl-2-onethio)-2-trifluoromethylbicyclo[2.2.1]-hept-5-ene (XX). A mixture of 3.7 g (0.02 mole) of sulfide (IX) and 1.4 g (0.021 mole) of cyclopentadiene was heated in a sealed glass ampul for 3 h at 130°C. The ampul was opened and the contents were fractionated. There was obtained 4.15 g of compound (XX) as a mixture of endo and exo isomers (7:4).

Yield, properties, and analysis results for compounds (II)-(XX) are shown in Tables 1 and 2.

LITERATURE CITED

1. H. Bayreuther and A. Haas, Chem. Ber., 106, 1418 (1973).
2. A. Kolasa, J. Fluorine Chem., 36, 29 (1987).