mixture was cooled and filtered. An Et_2O solution of the filtrate was washed successively with 1 N HCl (five times), saturated $NaHCO_3$, H_2O, and brine. It was then dried and concentrated, giving 2.33 g of a yellow solid, mp 79–87°. The solid was recrystallized from hexane and cyclohexane, giving 1.66 g (41%) of **16** as light yellow crystals: mp 89–92°; ir 5.76 and 5.96 (C=O), 6.14 and 6.40 μ (C=C); nmr ($CDCl_3$) δ 1.16 [s, 6, $C(CH_3)_2$], 2.46 (s, 2, 6-CH_2), 2.79 (s, 2, 8-CH_2), 6.30 (d, 1, J = 9.75 Hz, vinyl), 7.91 (d, 1, J = 9.75 Hz, vinyl).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.31; H, 6.39.

Registry No.—**3**, 20452-84-0; **4**, 3265-69-8; **5**, 33777-60-5; **6**, 606-23-5; **6a**, 1707-95-5; **7**, 20452-88-4; **9**, 33777-64-9; **10**, 33777-65-0; **11**, 33777-66-1; **12**, 33777-67-2; **12a**, 33777-68-3; **14**, 33886-29-2; **15**, 33777-69-4; **15a**, 33777-70-7; **16**, 33777-71-8; trifluoroacetic acid, 76-05-1.

Acknowledgment.—The author is indebted to Dr. Stanley C. Bell for encouragement.

α- and β-(Trifluoromethylthio)acrylic Acid Derivatives

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The product of the free-radical addition of CF_3SCl to methyl acrylate has been converted to a series of α-CF_3S-acrylic acid derivatives. The preparation of the corresponding β-CF_3S-substituted compounds began with the addition of CF_3SH to methyl propiolate. (Trifluoromethylthio)acetonitrile readily undergoes Knoevenagel reactions to yield α-CF_3S-substituted acrylonitriles.

Following the development of convenient laboratory syntheses for bis(trifluoromethylthio)mercury, trifluoromethanethiol, and trifluoromethanesulfenyl chloride, a modest number of CF_3S-substituted organic compounds have been synthesized.[1] To date no CF_3S-substituted, unsaturated acids or derivatives have been reported. This paper summarizes the results of a study of methods of preparation and the properties of CF_3S-substituted acrylic acid derivatives.

Results and Discussion

α-CF_3S-Substituted Acrylic Acid Derivatives.—For preparation of several α-CF_3S-substituted acrylic acid derivatives, the free-radical addition of trifluoromethanesulfenyl chloride (CF_3SCl) to methyl acrylate served as the starting point. When carried out with a large excess of CF_3SCl, the reaction yielded as the major product a 1:1 adduct fraction which contained about 90% methyl α-(trifluoromethylthio)-β-chloropropionate (**1**) and 10% of an isomeric material, presumably the other possible 1:1 adduct (**2**) (eq 1).

$$CF_3SCl + CH_2{=}CHCO_2CH_3 \xrightarrow{h\nu} \underset{\mathbf{1}}{ClCH_2\overset{CF_3S}{\overset{|}{C}}HCO_2CH_3} + \underset{\mathbf{2}}{CF_3SCH_2CHClCO_2CH_3} + \underset{\mathbf{3}}{ClCH_2\overset{CO_2CH_3}{\overset{|}{C}}HCH_2{-}\overset{SCF_3}{\overset{|}{C}}HCO_2CH_3} \quad (1)$$

A considerable quantity of a 2:1 adduct (**3**) was formed, which, according to gas chromatography and ^{19}F nmr spectroscopy, contained two isomers in roughly equal amounts.

The orientation of the major 1:1 adduct (**1**) was established by analysis of the ^{13}C nmr pattern.[2,3] The ^{13}C resonances of the hydrogen-bearing carbons along with the ^{13}C–H coupling constants are shown in Table I.

TABLE I

^{13}C NMR SPECTRUM OF METHYL α-(TRIFLUOROMETHYLTHIO)-β-CHLOROPROPIONATE (NEAT)

$$ClCH_2\overset{SCF_3}{\overset{|}{C}}HCO_2CH_3$$

Carbon atom	Chemical shift, ppm	Splitting pattern	J (^{13}C–H), Hz
CH_3	73.4	Quartet	149
CH	68.2	Doublet	148
CH_2	63.5	Triplet	158

Neither of the resonances for the carbons possibly containing the CF_3S group showed any spin–spin coupling clearly attributable to the presence of this group, and thus no structure assignment could be made on that basis. However, since values of J (^{13}C–H) for CH groups with chlorine substituents have been observed to be 150 Hz and higher,[4] it is concluded that the CH group, with J (^{13}C–H) of 148 Hz, cannot have the Cl, but must instead have the CF_3S group as substituent. This structure is consistent with the structures of the dehydrochlorination products from the 1:1 adduct discussed below.

Structure **3** was assigned to the 2:1 adduct on the basis of a dehydrochlorination experiment (eq 2), which produced a single, unsaturated ester in 78.5% yield (distilled). On the basis of the ^1H nmr and infrared spectra, **4** is the most likely structure for this product. The ^1H nmr pattern contains two unsplit CH_3 resonances, a CH_2 resonance split to a doublet, each com-

(1) J. F. Harris, Jr., *J. Org. Chem.*, **32**, 2063 (1967).

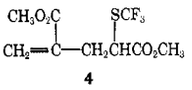
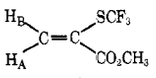
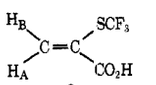
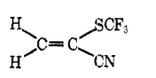
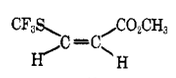
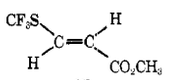
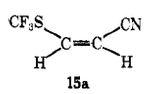
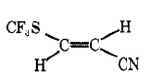
(2) Neither the ^1H nor the ^{19}F nmr pattern of the mixture of 1:1 adducts gave evidence sufficient for structure assignment.

(3) The author is indebted to Dr. G. S. Reddy of this laboratory for determination and interpretation of the ^{13}C nmr pattern of the 1:1 adduct fraction.

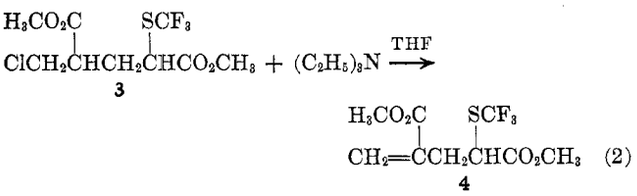
(4) For example, see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, p 195, Table 5.21.

TABLE II

^1H AND ^{19}F NMR SPECTRA OF CF_3S-ACRYLIC ACID DERIVATIVES

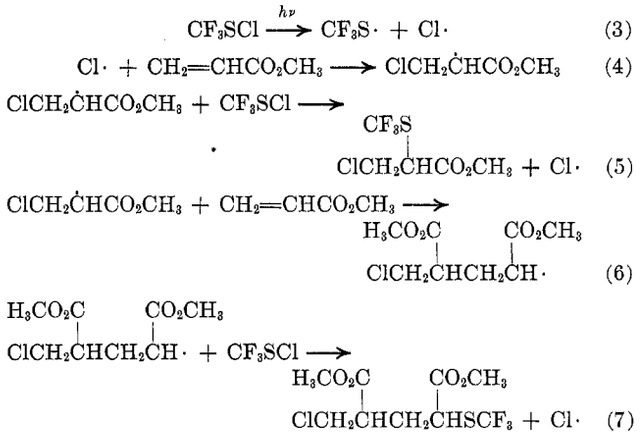
Compd	^1H, δ (ppm) from the ^1H resonance of $(CH_3)_4Si$			^{19}F, δ (ppm) from the ^{19}F resonance of Cl_3CF
	=CH	CH_3	Other	
 4	6.29 (2) J_{H-H} = 1.2 Hz 5.73 (2, 3) J_{H-H} = 1.2 Hz J_{H-H} = 1.0 Hz	3.73 (1) 3.77 (1)	2.89 (CH_2, 2 br) J_{H-H} = 7.8 Hz 4.12 (CH, 3) J_{H-H} = 7.8 Hz	−41.2 (1)
 5	6.86[a] (4) J_{H-F} = 0.9 Hz 6.32 (4) J_{H-F} = 0.8 Hz J_{H-H} = 0	3.81 (1)		−42.8 (2, 2) J = 0.8 Hz
 6	7.15 (1 broad) 6.61 (1 broad)		11.8 (OH, 1)	−42.6 (3) J = <1 Hz
 9	6.73 (5) J_{H-H} = ~0.7 Hz 6.60			−49.4 (2, 2) J = 0.8 Hz J = 0.4–0.5 Hz
 11a	7.17 (2 broad) J_{H-H} = 10 Hz 6.10 (2, 4) J_{H-F} = 1 Hz	3.76 (1)		−45.9 (2, 2) J = 1 Hz J = 0.4 Hz
 11b	7.53 (2) J_{H-H} = 15.6 Hz 6.09 (2, 4) J_{H-F} = 0.7 Hz	3.71 (1)		−42.4 (2) J = 0.7 Hz
 15a	7.27 (2) J_{H-H} = 10.2 Hz 5.76 (2, 4) J_{H-F} = 1.1 Hz			−42.1 (2) J = 1.1 Hz
 15b	7.36 (2) J_{H-H} = 16.1 Hz 5.69 (2, 4) J_{H-F} = 0.6 Hz			−42.2 (2) J = 0.6 Hz

[a] Analysis of this spectrum based on the spectra of $CF_3SCH{=}CH_2$ (ref 1) and methyl acrylate by the method of E. U. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell [*Tetrahedron*, **25**, 691 (1969)] suggests that the low-field resonance belongs to the proton cis to the carbomethoxy group, *i.e.*, H_A.



ponent of which is rather broad, a CH resonance (doublet), and two vinyl proton resonances (Table II). These vinyl protons are mutually spin coupled (J = 1.2 Hz), and the high-field one is, in addition, split to triplets, thus indicating the proximity of the CH_2 group. This pattern supports structure **4** and makes alternative structures in which the CH_2 group is not adjacent to the double bond unlikely. The logical precursor to **4** is **3**, whose two asymmetric centers account for the two components indicated by gas chromatography and ^{19}F nmr spectroscopy.

The orientation of the major 1:1 and 2:1 adducts just discussed suggests that the principal adding species in the radical-chain addition of CF_3SCl to methyl acrylate is the chlorine atom which adds to the CH_2 carbon, the usual site of radical attack in methyl acrylate. The resulting radical apparently either chain transfers by attacking the sulfur atom of the sulfenyl chloride to give the major 1:1 adduct obtained, or else adds to another molecule of methyl acrylate to produce a radical which leads by chain transfer to the 2:1 adduct. The main steps assumed in this process are shown in eq 3–7.



This reaction is wholly analogous to previously studied examples of free-radical additions of CF_3SCl to unsymmetrical double bonds.[5]

Dehydrochlorination of the 1:1 adduct fraction was easily achieved by treatment with triethylamine in anhydrous ether, and methyl α-(trifluoromethylthio)-acrylate (**5**) was obtained in over 60% yield (eq 8). The proof of structure for **5** is based primarily upon spectral evidence. Thus the ^1H nmr pattern (Table II)

(5) J. F. Harris, Jr., *J. Amer. Chem. Soc.*, **84**, 3148 (1962).

$$\mathrm{ClCH_2CHCO_2CH_3} + (\mathrm{C_2H_5})_3\mathrm{N} \longrightarrow \underset{\mathbf{5}}{\mathrm{CH_2{=}CCO_2CH_3}} \quad (8)$$

indicates two vinyl protons each spin coupled to the CF_3 group by 8–9 Hz but apparently not coupled to one another, consistent with their being on the same carbon atom. This pattern is clearly different from those of the isomeric *cis*- and *trans*-methyl β-(trifluoromethylthio)acrylates discussed later in this paper. Further support for structure **5** is seen in the infrared spectrum, which contains a =CH stretch band at 3106 cm^{-1} in the region consistent for a $R_2C{=}CH_2$ type structure.[6] The C=C stretch band occurs at 1603 cm^{-1}. After several days at room temperature, **5** polymerized to a solid polymer.

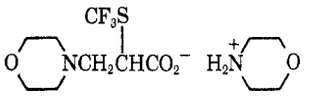
Treatment of the CF_3SCl–methyl acrylate 1:1 adduct fraction with dilute aqueous HCl at reflux also resulted in dehydrochlorination, giving a small amount of **5**, α-(trifluoromethylthio)acrylic acid (**6**) (32%), and a high-boiling fraction containing (trifluoromethylthio)-hydroxypropionic acid (**7**) (eq 9). The vinyl proton

$$\mathrm{ClCH_2CHCO_2CH_3} + \mathrm{H_2O} \xrightarrow{\mathrm{HCl}} \underset{\mathbf{5}}{\mathrm{CH_2{=}CCO_2CH_3}} + \underset{\mathbf{6}}{\mathrm{CH_2{=}CCO_2H}} + \underset{\mathbf{7}}{\mathrm{HOCH_2CHCO_2H}} \quad (9)$$

portion of the ^1H nmr spectrum of the acid **6** (Table II) is similar to that of the ester **5** and indicates that the product is indeed the α-CF_3S acid. On the basis of elemental analysis and the infrared spectrum, it was concluded that the high-boiling fraction is a CF_3S-substituted hydroxypropionic acid. The infrared spectrum contains a broad band in the 3330 cm^{-1} region (OH), a broad band at 2632 cm^{-1} (acid OH), bands at 2967 and 2899 cm^{-1} (saturated CH), and a carbonyl band at 1733 cm^{-1} as well as bands in the 1110–1250 cm^{-1} region (CF). There was no indication of carbon–carbon unsaturation. The ^{19}F nmr spectrum contains two resonances in a ratio of 85:15, thus indicating the presence of two CF_3S-containing compounds in the fraction. The 85% peak is unsplit and is no help in structure assignment. The 15% peak is split to a triplet (J = 0.7 Hz), suggesting that the minor component is probably α-hydroxy-β-(trifluoromethylthio)-propionic acid. The major component is thus presumed to be β-hydroxy-α-(trifluoromethylthio)propionic acid (**7**), although admittedly other isomeric structures are possible.

It is not clear from the experiment just described whether the hydroxy acids arise from a substitution reaction on the saturated ester (or acid), or whether there is first a dehydrochlorination followed by addition of the elements of water. Addition of water to the double bond was observed in an experiment in which the ester **5** was heated with dilute HCl giving the unsaturated acid **6** and the hydroxy acid **7** as major products. Another addition to the double bond occurred when the acid **6** was treated with excess morpholine. Although not proved, the structure of the product, isolated as the morpholine salt, was assumed to be **8**.

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 34.



8

Application of the traditional sequence for converting acids to nitriles gave very small amounts of α-(trifluoromethylthio)acrylonitrile (**9**) (eq 10).

$$\mathrm{CH_2{=}CCO_2H} \xrightarrow[3.\ P_2O_5]{1.\ SOCl_2\ 2.\ NH_3} \underset{\mathbf{9}}{\mathrm{CH_2{=}CCN}} \quad (10)$$

Somewhat higher yields were obtained from a two-step process starting with acrylamide and CF_3SCl (eq 11). The structure assigned to this nitrile (**9**) is

$$\mathrm{CF_3SCl} + \mathrm{CH_2{=}CHCNH_2} \xrightarrow{\text{acetonitrile}} [\mathrm{ClCH_2CHCONH_2}] \xrightarrow{P_2O_5} \underset{\mathbf{9}}{\mathrm{CH_2{=}CCN}} \quad (11)$$

based primarily upon the similarity of the vinyl proton portion of the ^1H nmr pattern to that of the other compounds in the α-CF_3S series (Table II).

Another entry into the synthesis of α-CF_3S-substituted acrylonitrile derivatives is *via* Knoevenagel reactions of aldehydes and ketones with (trifluoromethylthio)acetonitrile (**10**) (prepared according to eq 12). The reaction appears to be rather general, and

$$\mathrm{CF_3SCl} + \mathrm{CH_2{=}C{=}O} \longrightarrow \mathrm{CF_3SCH_2CCl} \xrightarrow[2.\ P_2O_5]{1.\ NH_3} \underset{\mathbf{10}}{\mathrm{CF_3SCH_2CN}} \quad (12)$$

examples were carried out with aldehydes and ketones containing both aromatic and aliphatic substituents (eq 13) (Tables III–V).[7]

$$\mathrm{R(R')C{=}O} + \mathrm{CF_3SCH_2CN} \longrightarrow \mathrm{R(R')C{=}C}\begin{matrix}\mathrm{SCF_3}\\ \diagdown\\ \diagup\\ \mathrm{CN}\end{matrix} \quad (13)$$

As with other Knoevenagel reactions, those examples with hydrocarbon aromatic aldehydes were most rapid and went in highest yield.[8] In the reactions with aliphatic ketones and pentafluorobenzaldehyde,[9] relatively large amounts of catalyst were used in order to achieve substantial reactions. In all cases, the expected α-CF_3S acrylonitrile was obtained as the major product, but sometimes minor yields of higher boiling, unidentified compounds were also noted (Table III). The elemental analyses and infrared, ^1H, and ^{19}F nmr spectra from all of the major products were consistent with the assigned acrylonitrile structure (Tables IV and V). In those reactions with unsymmetrical carbonyl compounds, both the cis and trans isomers of the ex-

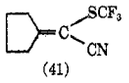
(7) Knoevenagel reactions involving sulfonyl-substituted acetonitriles and aryl- or alkylthioacetic acids and -acetamides as the active methylene component are well known, but the reactions reported in this paper are apparently the first employing an acetonitrile with a thiyl substituent: G. Jones, "The Knoevenagel Reaction," in "Organic Reactions," Vol. 15, Wiley, New York, N. Y., 1967.

(8) G. Jones, "The Knoevenagel Reaction," in "Organic Reactions," Vol. 15, Wiley, New York, N. Y., 1967.

(9) The lower reactivity of pentafluorobenzaldehyde compared with benzaldehyde in Knoevenagel reactions has been noted previously: N. G. Ivanova, V. A. Barkhash, and N. N. Vorozhtsov, *J. Gen. Chem. USSR*, **39**, 1317 (1969).

TABLE III

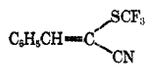
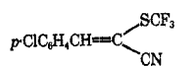
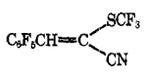
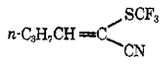
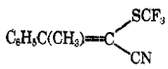
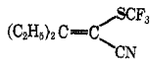
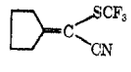
KNOEVENAGEL REACTIONS OF ALDEHYDES AND KETONES WITH CF_3SCH_2CN

Aldehyde or ketone, g (mol)	CF_3SCH_2CN, g (mol)	Piperidine, ml	Benzene, ml	Reflux time, hr	Product (yield of distilled product, %)	Comments
C_6H_5CHO 16.0 (0.151)	20 (0.142)	3	145	1/2	$C_6H_5CH=C(SCF_3)CN$ (83)	The ^{19}F nmr spectrum of crude product indicated two isomers in a ratio of 90.1:8.6.
p-ClC_6H_4CHO 20 (0.142)	20 (0.142)	3	145	1 1/2	p-$ClC_6H_4CH=C(SCF_3)CN$ (68)	
C_6F_5CHO 17 (0.0866)	10 (0.0707)	5[a]	70	7 2/3	$C_6F_5CH=C(SCF_3)CN$ (63)	The ^{19}F nmr spectrum of the distilled product indicated two isomers in a ratio of 79:21.
n-C_3H_7CHO 6 (0.0831)	10 (0.0707)	1.5	70	2	$C_3H_7CH=C(SCF_3)CN$ (45)	Gc before distillation showed 83.9% expected product (two isomers – ratio 71:29) and 16.1% of higher retention time materials.
$C_6H_5C(=O)CH_3$ 9.1 (0.0757)	10 (0.0707)	5.5[a]	70	25 1/4	$C_6H_5C(CH_3)=C(SCF_3)CN$ (34)	Gc before distillation indicated two isomers in a ratio of 41:59.
$C_2H_5C(=O)C_2H_5$ 10 (0.116)	10 (0.0707)	5.0[a]	70	22 1/2	$(C_2H_5)_2C=C(SCF_3)CN$ (34)	Gc before distillation showed 76.8% expected product plus two other materials.
 10 (0.119)	10 (0.0707)	1.5	70	21 1/3	 (41)	Gc before distillation showed 91% expected product plus 9% of an unknown material at longer retention time.

[a] Addition of an initial 1.5 ml of piperidine resulted in the separation of very little water after 1 hr or more of reflux. Additional piperidine was added, usually in 1.5-ml increments, until the totals shown were obtained.

TABLE IV

PRODUCTS FROM KNOEVENAGEL REACTIONS OF CF_3SCH_2CN

Structure	Registry no.	Bp, °C (mm)	Molecular formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Fluorine, % Calcd	Fluorine, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Sulfur, % Calcd	Sulfur, % Found
	7437-06-0	69 (0.15)	$C_{10}H_6F_3NS$					24.9	25.1			14.0	13.6
	7437-05-9	102 (0.4) 108 (0.5)	$C_{10}H_5ClF_3NS$							5.3	5.7	12.2	12.4
	34033-90-4	67–71 (0.1)	$C_{10}HF_3NS$	37.6	38.2 38.0	0.3	0.7 0.5	47.6	47.0 47.4			10.0	10.3 10.1
	34033-91-3	69–80 (16)	$C_7H_6F_3NS$	43.1	43.3 43.1	4.1	4.3 4.3	29.2	29.1 29.1			16.4	16.8 16.8
	34033-92-6	81 (0.2) 94 (0.45)	$C_{11}H_6F_3NS$	54.3	54.3 54.1	3.3	3.7 3.8	23.4	23.5 23.3				
	34033-93-7	61 (1.75)	$C_8H_{10}F_3NS$	46.0	45.8 45.5	4.8	4.9 4.7					15.3	15.6 15.7
	4033-94-8	40 (0.025)	$C_8H_6F_3NS$	46.4	46.4 46.5	3.9	4.2 4.0	27.5	26.8 27.0				

pected products were detected by gas chromatography and the nmr spectra, but in no case could a specific assignment be made on the basis of the spectra obtained. The proportion of the two isomers varied from 91:9 with benzaldehyde to 41:59 with acetophenone.

β-CF_3S-Substituted Acrylic Acid Derivatives.—A route to β-CF_3S acrylic acid derivatives was provided by the uv-catalyzed addition of CF_3SH to methyl propiolate, which yielded methyl β-(trifluoromethylthio)acrylate (**11**) in over 50% yield (eq 14). This process gave both the cis and trans isomers (ratio 77.5:22.5), which were isolated by preparative-scale

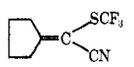
$$CF_3SH + HC{\equiv}CCO_2CH_3 \xrightarrow{h\nu} \underset{\mathbf{11}}{CF_3SCH{=}CHCO_2CH_3} \quad (14)$$

gas chromatography. Structures were assigned on the basis of the ^1H nmr spectra, each of which contained in addition to a CH_3 resonance two coupled vinyl proton resonances: J = 10 (77.5% isomer) and 15.6 Hz (22.5% isomer). Since trans H–H coupling is almost always greater than cis H–H coupling[10] in such struc-

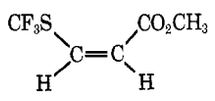
(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 238.

TABLE V

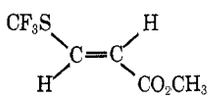
SPECTRAL CHARACTERIZATION OF PRODUCTS FROM KNOEVENAGEL REACTIONS OF CF_3SCH_2CN

Compd	Infrared, cm^{-1}	^1H nmr (ppm from TMSI)	^{19}F nmr (ppm from ^{19}F resonance of Cl_3CF)
$C_6H_5CH{=}C(SCF_3)(CN)$	1592, 1570, 1531, 1499 (C=C) 3058 and 3096 (=CH) 2222 (-C≡N) 1105 and 762 (-SCF_3) 688 and 742 (monosubstituted aromatic)	Complicated pattern in vinyl and aromatic proton region at 7.4–8.0	$2CF_3$'s Major −43.2 (1) Minor −41.3 (1)
$C_6F_5CH{=}C(SCF_3)(CN)$	1658, 1600, 1524, 1504 (C=C) 3058 (=CH) 2257 (-C≡N) 762 (-SCF_3) Strong absorption at 1100 region (-CF)	Single resonance in vinyl region at 7.67 (4, broad), J = 1.2 Hz	$2CF_3$'s Major −42.4 (1) Minor −40.9 (3) J = 3 Hz Three groups of aromatic CF centered at −138.0, −148.6, −161.0
$n\text{-}C_3H_7CH{=}C(SCF_3)(CN)$		Overlapping CH_2's at 2.58 and 1.63 Overlapping CH_3's at 1.0 2 vinyl H's major, 7.18 (3) J = 7.8 Hz minor, 7.28 (3) J = 7.6 Hz	$2CF_3$'s Major −43.8 (1) Minor −42.2 (1)
$C_6H_5C(CH_3){=}C(SCF_3)(CN)$	1592, 1570, 1497 (C=C) 2967, 2874 (-CH) 3086 (=CH) 706 (monosubstituted aromatic) 2227 (-C≡N) 1374 (-CCH_3) 1101, 765 (-SCF_3)	Aromatic protons at 7.0–7.6 Two CH_3's at *ca.* 2.58 separated by 2 Hz Both unsplit, but smaller one is broad	$2CF_3$'s Major −42.5 (4) J = 0.5 Hz Minor −42.4 (1)
$(C_2H_5)_2C{=}C(SCF_3)(CN)$	1590 (C=C) 3003, 2976, 2907 (-CH) 2232 (-C≡N) 1110, 762 (-SCF_3)	At 220 Mcps two triplets (CH_3's) at 1.12 and 1.22 (J = 7.5 Hz) Two superimposed quadruplets (CH_2's) at 2.65 J = 7.5 Hz	CF_3 −43.1 (1)
	1616 (C=C) 2994, 2907 (-CH) 2227 (-C≡N) 1107, 762 (-SCF_3)	Two multisplit CH_2 resonances at 1.90 and 2.78	CF_3 −42.9 (1)

tures, it is concluded that the more prevalent isomer obtained in this reaction is methyl-*cis*-β-(trifluoromethylthio)acrylate (**11a**). Support for this assignment is seen in the infrared spectrum of the trans isomer, which contains a band at 949 cm^{-1}, a frequency consistent with the C–H out-of-plane bending frequency often observed in trans-disubstituted olefins.[11] The predominance of the cis adduct is consistent with several previously studied free-radical additions of thiols to acetylenes.[12]

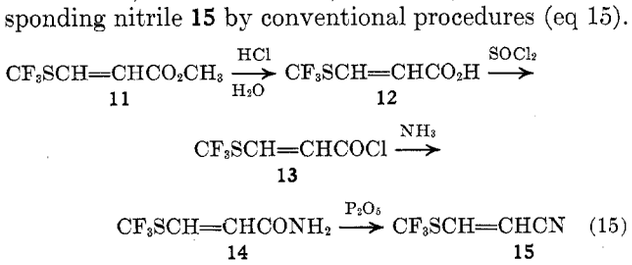


11a



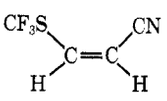
11b

From the ester mixture (**11a** and **11b**) were obtained the acid **12**, acid chloride **13**, amide **14**, and the corresponding nitrile **15** by conventional procedures (eq 15).

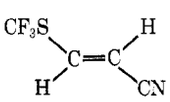


(15)

The nitrile mixture contained two isomers (ratio 72:28), and the ^1H nmr patterns (Table II) show that, as in the case of the esters, the cis isomer (**15a**) predominates.



15a



15b

Experimental Section

Reaction of Trifluoromethanesulfenyl Chloride with Methyl Acrylate.—Into a quartz tube (12 × 1.5 in.) fitted with a dropping funnel, a gas inlet tube, a magnetic stirrer, and a Dry Ice condenser, was added 92 g (0.673 mol) of liquid CF_3SCl.[13] Freshly distilled methyl acrylate (7 ml) was added, and the mixture was irradiated with a low-pressure mercury resonance lamp for 0.5 hr. This procedure was repeated four times, *i.e.*, until a total of 35 ml (0.388 mol) of methyl acrylate had been added. After the last addition, the mixture was irradiated for 1 hr. The excess CF_3SCl was distilled off, and then the residue was fractionated through a small spinning-band still. There was obtained 40 g (46%) of a 1:1 adduct fraction distilling at 66–72° (25 mm), $n^{25}D$ 1.4152, and 11.83 g (19%) of a 2:1 adduct fraction distilling at 70–72° (0.20 mm), $n^{25}D$ 1.4385. ^{19}F nmr spectra indicated that each fraction contained two major components in ratios of 90:10 (1:1 adduct fraction) and 55:45 (2:1 adduct fraction).

Anal. Calcd for 1:1 adduct $C_5H_6ClF_3O_2S$: C, 27.0; H, 2.7; S, 14.4. Found: C, 27.6; H, 3.1; S, 14.2. Calcd for 2:1 adduct $C_9H_{12}ClF_3O_4S$: C, 35.0; H, 3.9; S, 10.4. Found: C, 35.2; H, 4.2; S, 10.6.

Dehydrochlorination of the 2:1 Methyl Acrylate–CF_3SCl

(11) C. N. R. Rao, "Chemical Application of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 152, 153.

(12) The cis adduct arises from a two-step, overall trans addition, and this appears to be the preferred stereochemistry of radical thiol additions to acetylenes: O. Simamura, "The Stereochemistry of Cyclohexyl and Vinylic Radicals," in "Topics in Stereochemistry," Vol. 4, E. L. Eliel and N. L. Allinger, Ed., Wiley, New York, N. Y., 1969, pp 23–25.

(13) CF_3SCl (bp 0°) is highly toxic and should be handled only in an efficient hood.

Adduct.—A mixture of 30 g (0.0970 mol) of the 2:1 methyl acrylate–CF_3SCl adduct, 10 g (0.0987 mol) of triethylamine, and 100 ml of tetrahydrofuran was refluxed for a period of 20 hr. A gas chromatogram indicated that a very small amount of starting material remained and that essentially a single product was present. The mixture was filtered and the triethylamine hydrochloride was rinsed and dried on the filter, yield 12.03 g (90%). Distillation of the filtrate through a small Vigreux still yielded 20.78 g (78.4%) of dimethyl α-methylene-α'-(trifluoromethylthio)glutarate distilling at 52° (0.10 mm), $n^{25}D$ 1.4301 (>97% pure by gas chromatography).

Anal. Calcd for $C_9H_{11}F_3O_4S$: C, 39.7; H, 4.1; F, 20.9. Found: C, 39.9; H, 4.1; F, 21.6, 21.3.

The infrared spectrum contains bands at 2994, 2959, and 2849 (saturated CH), 1742 and 1721 (>C=O), 1656 (-C=C-), *ca.* 1110 (broad) (CF), 756 (-SCF_3), and 954 cm^{-1} (CH_2=C<). The ^1H and ^{19}F nmr spectra are tabulated in Table II.

Reaction of Methyl α-(Trifluoromethylthio)-β-chloropropionate with Triethylamine. Preparation of Methyl α-(Trifluoromethylthio)acrylate.—To a solution of 10 g (0.045 mol) of the 1:1 methyl acrylate–CF_3SCl adduct fraction in 75 ml of anhydrous ether was added 6.2 ml of triethylamine. After the resulting mixture was stirred for 0.5 hr, it was filtered and the solid was rinsed on the filter with anhydrous ether. Distillation of the ether solution through a small Vigreux still yielded 6.0 g. (72%) of methyl α-(trifluoromethylthio)acrylate as a colorless liquid distilling at 58–60° (42 mm), $n^{25}D$ 1.4067.

Anal. Calcd for $C_5H_5F_3O_2S$: C, 32.3; H, 2.7; F, 30.6. Found: C, 32.7; H, 2.8; F, 30.3.

Hydrolysis of Methyl α-(Trifluoromethylthio)-β-chloropropionate.—A mixture of 45 g (0.202 mol) of the 1:1 methyl acrylate–CF_3SCl adduct, 60 ml of concentrated HCl, and 300 ml of distilled water was refluxed for 15 hr. The mixture was cooled in an ice–water bath, and the organic layer was separated. Following three extractions of the aqueous layer with 100 ml of ether, the extracts and the organic layer were combined, dried over anhydrous magnesium sulfate, and distilled through a small spinning-band still. After a fraction containing some methyl α-(trifluoromethylthio)acrylate was obtained, 11.04 g (32%) of colorless α-(trifluoromethylthio)acrylic acid distilled at 68–72° (2.00 mm), $n^{25}D$ 1.4213–1.4240.

Anal. Calcd for $C_4H_3F_3O_2S$: F, 33.1; S, 18.6. Found: F, 33.2; S, 17.7.

In addition there was obtained 7.62 g (20%) of a viscous fraction distilling at 97.5–99° (0.025 mm) which contained isomers of (trifluoromethylthio)hydroxypropionic acid. A ^{19}F nmr indicated the presence of two CF_3S-containing materials in a ratio of 85:15.

Anal. Calcd for $C_4H_5F_3O_3S$: C, 25.2; H, 2.6; F, 30.0. Found: C, 25.8, 25.9; H, 2.7, 2.6; F, 30.7, 30.7.

Hydrolysis of Methyl α-(Trifluoromethylthio)acrylate.—A mixture of 11.86 g (0.0636 mol) of methyl α-(trifluoromethylthio)acrylate, 100 ml of distilled water, and 23 ml of concentrated HCl was refluxed for a period of 15 hr. The mixture was cooled, the organic layer was separated, and the aqueous layer was extracted twice with 50 ml of ether. The combined extracts and organic layer were dried over anhydrous magnesium sulfate and distilled through a small Vigreux still. There was obtained 3.62 g (33%) of α-(trifluoromethylthio)acrylic acid as a colorless liquid distilling at 64–69° (1.0 mm), $n^{25}D$ 1.4207, and 3.90 g (32%) of (trifluoromethylthio)-hydroxypropionic acid(s) as a viscous, colorless liquid distilling at 102° (0.7 mm), $n^{25}D$ 1.4284.

Reaction of α-(Trifluoromethylthio)acrylic Acid with Morpholine.—To a stirred solution of 2.0 g (0.01163 mol) of α-(trifluoromethylthio)acrylic acid in 20 ml of anhydrous ether was slowly added 2.20 g (0.0252 mol) of morpholine in 10 ml of ether. After the mixture had stood for 1 hr, it was filtered to remove the product presumed to be morpholinium β-*N*-morpholino-α-(trifluoromethylthio)propionate, yield 3.07 (76%), mp 95°.

Anal. Calcd for $C_{12}H_{21}F_3N_2O_4S$: C, 41.6; H, 6.1; F, 16.4; S, 9.3. Found: C, 41.5; H, 5.8; F, 16.7; S, 9.4.

Conversion of α-(Trifluoromethylthio)acrylic Acid to α-(Trifluoromethylthio)acrylonitrile.—A mixture of 9.0 g (0.0756 mol) of thionyl chloride and 11.09 g (0.0644 mol) of α-(trifluoromethylthio)acrylic acid was stirred at room temperature for 1.5 hr and then at gentle reflux for 6.5 hr. Distillation through a small spinning-band still gave 4.48 g (36%) of α-(trifluoromethylthio)acrylyl chloride distilling at 50–52° (40 mm).

Anhydrous ammonia was passed through 3.56 g (0.019 mol) of this acid chloride in 30 ml of anhydrous ether until there was no further precipitation. The mixture was filtered, the residue was rinsed with ether, and the filtrate and rinsings were combined and evaporated to dryness. The resulting gummy residue was mixed with several grams of anhydrous phosphorus pentoxide and placed in a flask heated by an oil bath and connected through two acetone–Dry Ice cooled traps to the water pump. The system was evacuated, and the oil bath was heated to 160° during 3.5 hr and maintained at 150–160° for 5 hr. There collected in the receiver 0.25 g of colorless liquid, $n^{25}D$ 1.3990. The infrared spectrum contained bands at 3125 and 3021 (=CH), 2232 (conjugated C≡N), 1600 (conjugated C=C), and 758 cm^{-1} (CF_3S).

Preparation of α-(Trifluoromethylthio)acrylonitrile from CF_3SCl and Acrylamide.—Trifluoromethanesulfenyl chloride was passed into a stirred solution of 100 g (1.41 mol) of acrylamide in 500 ml of acetonitrile until 272 g (1.99 mol) of CF_3SCl had been absorbed. The resulting mixture was allowed to stir for a short time, and then the excess reactants were removed *in vacuo* on the oil pump. The liquid residue (267 g) was mixed as well as possible with 430 g of phosphorus pentoxide in a 2-l. flask fitted with an oil bath and a short-path stillhead whose receiver was connected to a water aspirator through two Dry Ice–acetone cooled traps. The flask was also fitted with a paddle stirrer which was manipulated by hand to periodically mix the components as well as possible. The system was evacuated and the oil bath was warmed slowly to 150°. Material began to distill at *ca.* 100°. The oil bath was maintained at 150–180° for 3 hr, whereupon the system was evacuated with an oil pump for an additional few minutes. Distillation of the combined distillate and trap contents through a small spinning-band still gave 10.97 g of a fraction boiling at 44–73° (43 mm), $n^{24}D$ 1.3999. Careful redistillation of this fraction yielded pure α-(trifluoromethylthio)acrylonitrile distilling at 44° (37 mm), $n^{25}D$ 1.3977.

Anal. Calcd for $C_4H_2F_3NS$: F, 37.2; N, 9.1; S, 20.9. Found: F, 37.3; N, 9.3; S, 21.1.

Preparation of (Trifluoromethylthio)acetonitrile. A. Preparation of (Trifluoromethylthio)acetyl Chloride.—Into a solution of 35 g (0.256 mol) of CF_3SCl in 200 ml of anhydrous ether contained in a flask fitted with a magnetic stirrer, an acetone–Dry Ice filled reflux condenser, and a gas addition tube, was passed ketene until the characteristic yellow color of the sulfenyl chloride was gone. After the mixture had stood for 18 hr, it was distilled through a small spinning-band still. There was thus obtained 31.20 g (68%) of (trifluoromethylthio)acetyl chloride distilling at 56° (90 mm), $n^{25}D$ 1.4040–1.4083.

Anal. Calcd for $C_3H_2ClF_3OS$: F, 31.9; S, 18.0. Found: F, 30.7; S, 17.5.

B. Preparation of (Trifluoromethylthio)acetamide.—Ammonia was passed through a stirred and cooled solution of 25 g (0.140 mol) of (trifluoromethylthio)acetyl chloride in 200 ml of anhydrous ether until there was no further reaction. The mixture was warmed to room temperature and then filtered. Upon evaporation of the filtrate *in vacuo*, there was obtained a liquid residue which crystallized when pentane was added, yield 21.05 g (94%), mp 84.5–86.5°. After one recrystallization from benzene, (trifluoromethylthio)acetamide was obtained as colorless plates melting at 88–89°.

Anal. Calcd for $C_3H_4F_3NOS$: C, 22.6; H, 2.5; S, 20.1. Found: C, 22.8; H, 2.6; S, 20.3.

C. Dehydration of (Trifluoromethylthio)acetamide.—A mixture of 10 g (0.0628 mol) of (trifluoromethylthio)acetamide and 10 g (0.0705 mol) of anhydrous P_2O_5 was shaken in a flask until thoroughly mixed. The flask was then fitted with a small still whose receiver was connected through an acetone–Dry Ice cooled trap to a water aspirator. The system was evacuated and then the flask was heated with an oil bath at 160° for at least 0.5 hour. Upon distillation of the combined receiver and trap contents through a small spinning-band still, there was obtained 5.8 g (65%) of (trifluoromethylthio)acetonitrile as a colorless liquid distilling at 59° (34 mm), $n^{25}D$ 1.3831.

Anal. Calcd for $C_3H_2F_3NS$: C, 25.7; H, 1.4; N, 9.9; S, 22.7. Found: C, 26.2; H, 1.6; N, 10.2; S, 23.6.

Reaction of Carbonyl Compounds with (Trifluoromethylthio)-acetonitrile.—All of these reactions were carried out in about the same manner. The reaction with benzaldehyde is described below in detail. The results of the other experiments are given in Tables III, IV, and V.

A mixture of 16 g (0.151 mol) of benzaldehyde, 20 g (0.142 mol) of (trifluoromethylthio)acetonitrile, 3 ml of piperidine, and 145 ml of benzene was refluxed in an apparatus fitted with a water separator. After 0.5 hr of refluxing, the separation of water had stopped. The reaction mixture was extracted twice with 50 ml of water, twice with 50 ml of 3% aqueous hydrochloric acid, and once with 50 ml of saturated aqueous sodium bicarbonate solution. After being dried over anhydrous magnesium sulfate, the mixture was distilled. There was thus obtained 23.06 g (83%) of β-phenyl-α-(trifluoromethylthio)acrylonitrile as a colorless liquid distilling at 69° (0.15 mm), $n^{25}D$ 1.5509.

Anal. Calcd for $C_{10}H_6F_3NS$: F, 24.9; S, 14.0. Found: F, 25.1; S, 13.6.

A ^{19}F nmr spectrum on a similar mixture after the distillation of the benzene, but before the distillation of the product, showed two major fluorine-containing components which are presumably the cis and trans isomers in a ratio of 90.1:8.6. Distillation through a spinning-band still gave a fraction which was 98% one isomer.

Addition of Trifluoromethanethiol to Methyl Propiolate.—A mixture of 42 g (0.50 mol) of methyl propiolate and 62 g (0.607 mol) of trifluoromethanethiol contained in a quartz tube (12 × 1.5 in.) fitted with a Dry Ice condenser was irradiated with a spiral-shaped, low-pressure mercury resonance lamp for 46.25 hr. After the excess volatiles had been allowed to evaporate, the reaction mixture was distilled through a small spinning-band still. There was obtained 14.09 g of recovered methyl propiolate and 35.25 g (57%) of a 1:1 adduct fraction distilling at 62° (95 mm) and 46° (13 mm). There remained 20.12 g of viscous residue.

Anal. Calcd for $C_5H_5F_3O_2S$: C, 32.3; H, 2.7; F, 30.6. Found: C, 32.8; H, 3.0; F, 31.6.

A gas chromatogram indicated the presence of both the cis and trans isomers in a ratio of 77.5 (cis):22.5 (trans). Pure samples of each were obtained by preparative-scale gas chromatography with a 12 ft × 0.75 in. column packed with 20% "Diglyceride" on Chromasorb at 125°.

Methyl *cis*-β-(trifluoromethylthio)acrylate had bp 56° (20 mm), $n^{24}D$ 1.4246.

Anal. Calcd for $C_5H_5F_3O_2S$: C, 32.3; H, 2.7; F, 30.6; S, 17.2. Found: C, 32.7; H, 2.5; F, 30.6; S, 17.3.

Methyl *trans* β-(trifluoromethylthio)acrylate (not distilled) had $n^{24}D$ 1.4211.

The ^1H and ^{19}F nmr spectra of these isomers are tabulated in Table II.

Hydrolysis of Methyl β-(Trifluoromethylthio)acrylate (Cis and Trans Isomers).—A mixture of 62 g (0.335 mol) of methyl β-(trifluoromethylthio)acrylate, 1 l. of distilled water, and 250 ml of concentrated HCl was refluxed for 18.5 hr. After being cooled to room temperature, the mixture was extracted three times with 200 ml of ether. The extracts were dried over anhydrous magnesium sulfate and distilled through a small Vigreux still. There was obtained 5.80 g of recovered methyl β-(trifluoromethylthio)acrylate and 45.15 g (87%) of β-(trifluoromethylthio)acrylic acid as a colorless liquid distilling at 93–96° (13 mm).

Anal. Calcd for $C_4H_3F_3O_2S$: C, 27.9; H, 1.8; F, 33.1. Found: C, 28.1; H, 1.7; F, 32.3.

Conversion of β-(Trifluoromethylthio)acrylic Acid to β-(Trifluoromethylthio)acrylonitrile. A. Preparation of β-(Trifluoromethylthio)acrylyl Chloride.—A mixture of 100.7 g (0.583 mol) of β-(trifluoromethylthio)acrylic acid and 60 ml of thionyl chloride was stirred for 16 hr and then gently refluxed for 4 hr. Upon distillation of the reaction mixture through a small spinning-band still there was obtained 73 g (65.5%) of β-(trifluoromethylthio)acrylyl chloride distilling at 48° (29 mm), $n^{25}D$ 1.4553. There was also recovered 16.5% of β-(trifluoromethylthio)acrylic acid.

B. Preparation of β-(Trifluoromethylthio)acrylamide.—Ammonia was passed through an ice-cooled solution of 11.6 g (0.0746 mol) of β-(trifluoromethylthio)acrylyl chloride in 100 ml of anhydrous ether until there was no more precipitation. The reaction mixture was filtered, the solid was rinsed on the filter with ether, and the filtrate and rinsings were evaporated to dryness. There was obtained 9.88 g (94%) of crude β-(trifluoromethylthio)acrylamide melting at 95–98°. After recrystallization from benzene (11 ml/g), the product was obtained as fine white needles melting at 102–102.5°.

Anal. Calcd for $C_4H_4F_3NOS$: F, 33.3; N, 8.2; S, 18.7. Found: F, 34.1; N, 8.0; S, 17.6.

C. Dehydration of β-(Trifluoromethylthio)acrylamide.—A mixture of 8.85 g (0.0577 mol) of finely ground β-(trifluoromethylthio)acrylamide and 25 g (0.176 mol) of anhydrous P_2O_5 was placed in a small, round-bottomed flask fitted with an oil bath and a small still head whose receiver was connected through an acetone–Dry Ice cooled trap to a water aspirator. The system was evacuated, and during 2.5 hr the oil bath was heated to 175°. During this time, 6.76 g of distillate collected in the receiver. Distillation of this material through a small spinning-band still yielded 5.29 g (67%) of β-(trifluoromethylthio)acrylonitrile distilling at 62° (48 mm), $n^{25}D$ 1.4203.

Anal. Calcd for $C_4H_2F_3NS$; F, 37.2; N, 9.1; S, 20.9. Found: F, 36.8; N, 9.4; S, 21.4.

The infrared spectrum is consistent with a mixture of the cis and trans isomers of β-(trifluoromethylthio)acrylonitrile: ir 3067 (=CH), 2217 (-C≡N), 1577 (C=C), 1111 (CF), 756 ($-SCF_3$), 950 (trans CH=CH), 711 cm^{-1} (cis CH=CH). A gas chromatogram showed the presence of two isomers in a ratio of 70.5 (cis):29.5 (trans). Samples of each were separated with a 12 ft × 0.75 in. column packed with 20% "Diglyceride" on Chromosorb at 100°.

***cis*-β-(Trifluoromethylthio)acrylonitrile** had bp 62° (45 mm), $n^{24}D$ 1.4158.

Anal. Calcd for $C_4H_2F_3NS$: F, 37.2; N, 9.1; S, 20.9. Found: F, 37.2; N, 9.3; S, 20.6.

***trans*-β-(Trifluoromethylthio)acrylonitrile** had bp 64° (45 mm), $n^{24}D$ 1.4242.

The ^1H and ^{19}F nmr resonances of these isomers are tabulated in Table II.

Nmr and Infared Spectra.—^{19}F nmr spectra (56.4 MHz) were obtained from 10% solutions of the compounds in carbon tetrachloride with a Varian A-56/60 spectrometer. All ^1H nmr spectra were also obtained from carbon tetrachloride solutions with a Varian A-60 spectrometer, except in one case (Table V) in which a Varian HR-220 spectrometer was used. The ^{13}C spectrum (25.1 MHz) was obtained with a Varian HA-100 spectrometer modified for noise decoupling. Chemical shifts are reported in parts per million from the resonance of tetramethylsilane (^1H) or fluorotrichloromethane (^{19}F) as internal standards and methyl iodide (^{13}C) as an external standard. In accordance with the recommendations published in ASTM E-386-69 T, chemical shifts at higher field than the resonance of the standard are designated as negative.

The infrared spectra were determined with a Perkin-Elmer 21 (prism) spectrometer.

Registry No.—**1**, 34033-72-2; **3**, 34033-73-3; **4**, 34033-74-4; **5**, 13122-60-6; **6**, 13137-45-6; **7**, 34033-77-7; **8**, 34145-34-1; **9**, 7347-10-6; **10**, 34033-79-9; **11**, 13122-56-0; **11a**, 34033-81-3; **11b**, 34033-82-4; **12**, 7347-02-6; **13**, 7347-01-5; **14**, 7347-00-4; **15a**, 34033-86-8; **15b**, 34033-87-9; (trifluoromethylthio)-acetyl chloride, 1645-79-0; (trifluoromethylthio)acetamide, 1737-79-7.