Tetrahedron Vol. 37, No. 15, pp. 2539 to 2546, 1981
Printed in Great Britain

0040-4020/81/152539-08$02.00/0

REACTION OF THIOLSULFINATES WITH TRIHALOACETIC ANHYDRIDES. II. ADDITION OF SULFENYL TRIHALOACETATES TO OLEFINS

TSUYOSHI MORISHITA, NAOMICHI FURUKAWA and SHIGERU OAE

Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

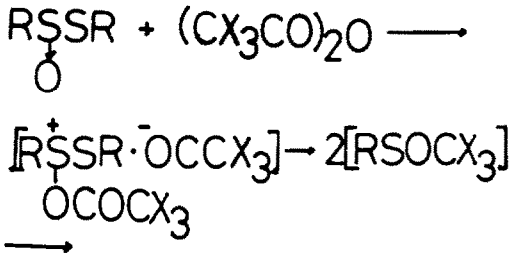
(*Received in Japan* 11 *May* 1981)

Abstract - Treatment of thiolsulfinates with trifluoro- or trichloroacetic anhydride at -20°C in the presence of various olefins in carbon tetrachloride afforded the corresponding β-trifluoro- or trichloroacetoxy sulfides in good yields. The β-trihaloacetoxy sulfides are considered to be resulted by the electrophilic addition of the sulfenyl trihaloacetates, formed as transient intermediates, to olefins. The addition takes place stereospecifically in trans manner and the regioselectivity for the addition with unsymmetrical olefins obeyed the Markownikoff orientation rule, except 3,3-dimethyl-1-butene which gave initially the anti-Markownikoff product 3 due to the steric hindrance, however the adduct 3 is readily converted to the Markownikoff product 22 upon heating. Since the addition is highly regioselective and stereospecific, this is a very convenient procedure for the syntheses of β-trihaloacetoxy sulfides.

Thiolsulfinates[1] are thermally unstable organic sulfur compounds and are known to have complex modes of reactivities by the change of reagent and reaction condition. Therefore, although thiolsulfinates can be readily prepared by oxidation of the disulfides and are considered to be excellent synthons for organic syntheses, fundamental chemical and physical properties of thiolsulfinates have not been explored in detail, due to the lability. However, if thiolsulfinates can be treated under mild reaction conditions with appropriate reagents without thermal decomposition and disproportionation, the compounds may be useful reagents for various synthetic applications.

We have found recently that the Pummerer-like reaction of thiolsulfinates with acetic anhydride in the presence of acetic acid afforded unexpectedly the new rearranged products, α-acetylthio-sulfoxides in moderate yields.[2] However, in some cases treatment of thiolsulfinates with acetic anhydride gives the corresponding thiolsulfinates and disulfides as major products. This result, namely, whether the reaction gives the rearranged products or disproportionation products, seems to depend on the nature of the substituents in the thiolsulfinates and the temperature of the reaction. In order to carry out the rearrangement smoothly and to avoid formation of disproportionation products by thermolysis, trihaloacetic anhydrides which usually acylate the thiolsulfinate oxygen even at relatively low temperatures were used instead of acetic anhydride. However, the final products obtained in this reaction were composed of 1:1 mixture of sulfinyl trihaloacetates and

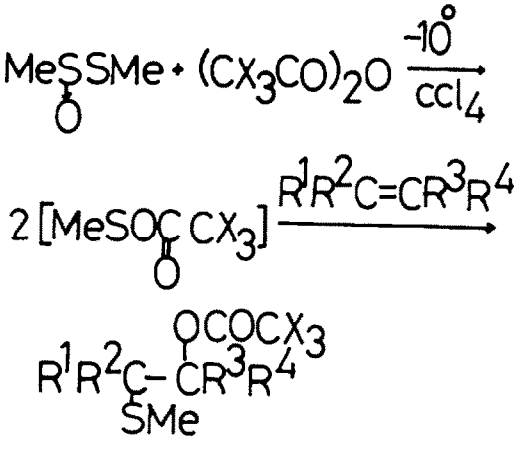
disulfides which are undoubtedly formed via sulfenyl trihaloacetates as transient intermediates after the initial acylation of sulfinyl oxygen, in carbon tetrachloride as shown in the following scheme.



Scheme 1. Mechanism for Formation of Sulfenyl Carboxylate

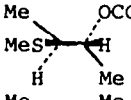
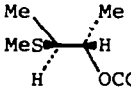
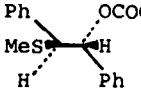
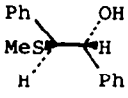
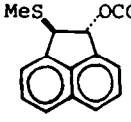
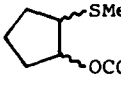
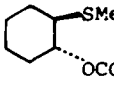
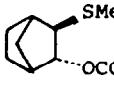
Meanwhile, when the same reaction was carried out in the presence of olefins, the only products obtained was found to be the corresponding β-trihaloacetoxy sulfides which are formed undoubtedly by electrophilic 1,2-addition of sulfenyl trihaloacetates to olefins.[3] This result is consistent with those obtained by Halvlik and Kharasch,[4] in which they found that the addition of 2,4-dinitrobenzenesulfenyl acetate to cyclohexene afforded 2-acetoxycyclohexyl 2,4-dinitrophenyl sulfide. Similar additions of sulfenyl carboxylates to the olefins have also been carried out[3,5] attaining the analogous results to that of the addition of sulfenyl halides to olefins.[6] Recently, Trost et al.[5b] reported that upon treatment of lead tetraacetate with a mixture of a disulfide and trifluoroacetic acid in methylene chloride at 0° or -40°C olefins are converted to the corresponding β-trifluoroacetoxy sulfide. Although Kharasch's and Trost's methods are convenient to prepare β-hydroxysulfides, our procedure using thiolsulfinates would have a certain advantage over those of Kharasch or Trost since this reaction proceeds rapidly even at low temperature(-10°C) and normally gives only one product in an excellent yield, while the treatment and work-up are so simple. The product can be isolated by one distillation under reduced pressure after removal of the solvent. The resulting β-trihaloacetoxy sulfides readily afforded the corresponding β-hydroxysulfides upon treatment with such a base as aqueous sodium hydroxide.

The reaction of methyl methanethiolsulfinate with trifluoro- or trichloroacetic anhydride in the presence of various olefins was carried out in carbon tetrachloride at -10°C and after the usual work-up various adducts were obtained, as summarized in Table 1. All the compounds were identified with NMR, IR and mass spectra, and by elemental analyses.



Inspection of the results reveals that all the olefins employed in this reaction afforded the corresponding β-acetoxy sulfides in good yields. Meanwhile, 1,1-diphenylethene gave directly methyl 2,2-diphenylvinyl sulfide[7] which might be obtained by facile elimination of trifluoroacetic acid from the corresponding β-trifluoroacetoxy sulfide. trans-Stilbene also gave methyl 1,2-diphenyl-2-hydroxyethyl sulfide 9 as the major product together with a small amount of normal addition product 8, methyl 1,2-diphenyl-2-trifluoroacetoxyethyl sulfide 8. Cyclohexene and acenaphthylene yielded also the corresponding trans adducts 12, 10 which were identified from the ^{1}H NMR coupling constants (9.1[8] and 1,4 Hz[8a,9] respectively) of the vicinal methine protons.

Table 1. Reaction of Methyl Methanethiolsulfinate with Trihaloacetic Anhydrides in the Presence of Olefins.

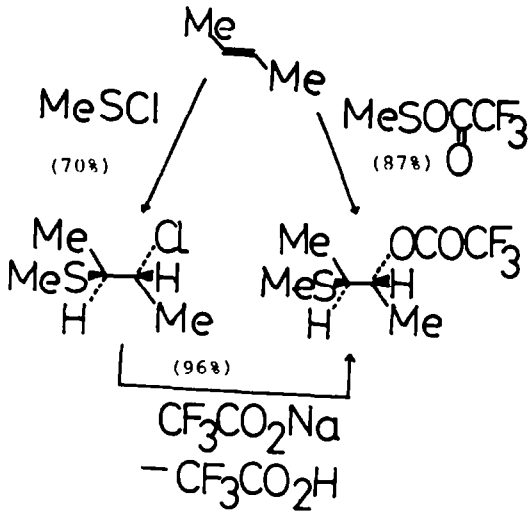
Olefins	Adducts		Yields(%)	b.p.(m.p.)°C/mmHg
1-Octene	$C_6H_{13}CH(OCOCF_3)CH_2SMe$	1	89[a] (60)[b]	130-133/20.5
1-Octene	$C_6H_{13}CH(OCOCCl_3)CH_2SMe$	2	49 (63)	144-147/4
3,3-Dimethyl-1-butene	$t\text{-Bu}CH(SMe)CH_2OCCF_3$ (O)	3	95 (87)	104-107/24
Styrene	$PhCH(SMe)CH_2SMe$	4	84 (87)	63-66/16
1,1-Diphenylethene	$Ph_2C{=}CHSMe$	5	73 (90)	116-120/8
trans-2-Butene		6	87 (80)	70-75/19
cis-2-Butene		7	87 (68)	67-70/30
trans-Stilbene		8	- (18)	130-134[d]/20
		9	- (70)	(75.5-76.0)
Acenaphthylene		10	- (47)[c]	Oil(Decomp.)
Cyclopentene		11	92 (74)	90.5-91.0/28
Cyclohexene		12	72 (87)	70-75/8
Norbornene		13	87 (70)	113-117/18

a) Determined by vpc analysis. Some compounds were decomposed during the analysis. b) Isolated yields. c) Determined by ^{1}H-NMR. Dimethyl disulfide(30%) was obtained together with the adduct and the starting olefin was also recovered. d) Sublimation temperature.

The structure of exo-2-ethylthio-endo-3-trifluoroacetoxynorbornane 13 was determined by comparing the ^{1}H NMR spectra with those of the corresponding chloride.[8a] Electrophilic olefins, such as methyl acrylate, acrylonitrile ethyl vinyl ether, etc. did not give the adducts under the reaction condition employed. When the reactions were carried out in the presence of such conjugated dienes as 1,3-butadiene, cyclopentadiene, furane and thiophene, neither 1,2- nor 1,4-addition products were obtained, only resulting in the formation of a tarry polymeric materials. No addition of methanesulfenyl trifluoroacetate to the C=N double bond of N-p-tolyl benzalimine was observed since trifluoroacetic anhydride reacts

faster with the imino nitrogen to give N-α-trifluoroacetoxybenzyl-N-p-tolyl trifluoroacetoamide than with methyl methanethiolsulfinate. Azobenzene did not react in this reaction system and was recovered quantitatively. Meanwhile, for further evidence to support the formation of methanesulfenyl trifluoroacetate in the reaction, anisole was added to the reaction mixture instead of the olefin. Indeed, anisole afforded methyl p-methoxyphenyl sulfide in this system in 80% yield, but toluene or biphenyl was unreactive under the present reaction condition.

These additions to olefins are shown to be highly regioselective and stereospecific. Styrene, 1-octene and 1,1-diphenylethene gave only the Markownikoff addition products, while only 3,3-dimethyl-1-butene gave the anti-Markownikoff-addition product 3. cis- or trans-2-Butene provided either threo 6 or erythro 7 adduct as a sole product, respectively. The stereochemistry for the addition of methanesulfenyl trifluoroacetate to olefins was established by comparing the spectral data with that of the authentic product obtained by the addition of sulfenyl chlorides to olefins.* Namely, threo-methyl 1-methyl-2-chloropropyl sulfide,[4] prepared by addition of methanesulfenyl chloride to cis-2-butene, was treated with sodium trifluoroacetate in trifluoroacetic acid at room temperature to afford the corresponding β-trifluoroacetoxy sulfide 7. Since this replacement of chloride by trifluoroacetate ion proceeds with complete retention of the configuration due to the neighboring group participation of sulfenyl group, the threo isomer 7 of the β-trifluoroacetoxy sulfide was obtained in 84% chemical yield. The spectral analyses of the adduct of methanesulfenyl trifluoroacetate to cis-2-butene agreed well with those of threo-methyl 1-methyl-2-trifluoroacetoxypropyl sulfide 7, while the erythro-isomer 6 was also characterized similarly by comparing the spectra of authentic erythro-methyl 1-methyl-2-trifluoroacetoxypropyl sulfide 6. Accordingly, the addition of sulfenyl trihaloacetates to olefins proceeds stereospecifically in trans manner analogously to that of sulfenyl chlorides to olefins as shown below.



Similarly, most of other thiolsulfinates having either alkyl or aryl substituents such as methyl, ethyl, isopropyl, phenyl benzyl derivatives, reacted with trifluoroacetic anhydride in the presence of 1-octene to give the corresponding alkyl or aryl 2-trifluoroacetoxyacetyl sulfides in excellent yields except tert-butyl 2-methyl-2-propanethiolsulfinate which did not give the expected adduct but a number of unidentified products. The results are shown in Tables 2 and 4.

All the additions of sulfenyl trihaloacetates to olefins in carbon tetrachloride solution at -20°C yielded only the Markownikoff oriented products except in case of 3,3-dimethyl-1-butene as shown in Table 2.

*Methanesulfenyl chloride adds to cis or trans-2-butene to give either threo- or erythro-methyl 1-methyl-2-chloropropyl sulfide, respectively.[4]

Table 2. Reaction of Thiolsulfinates, $R^1S(O)-SR^1$, with Trifluoroacetic Anhydride in the Presence of Terminal Olefins $R^2CH=CH_2$.

Adducts R^1	Adducts R^2		Yields (%)		Orientation[a]	B.P. (°C/mmHg)
Me	C_6H_{13}	1	89[b]	(60)[c]	M	130-133/20.5
Et	C_6H_{13}	14	86	(91)	M	146-150/35
i-Pr	C_6H_{13}	15	88	(58)	M	112-114/5
Ph	C_6H_{13}	16	67[d]	(71)	M	138-141/2.5
$PhCH_2$	C_6H_{13}	17	48[d]	(46)	M	68-75[e]/3.5
Me	Et	18	86	(75)	M	89-94/25
Me	i-Pr	19	73	(54)	M	80-85/19
Et	i-Pr	20	68	(81)	M	100-120/32
i-Pr	i-Pr	21	97	(75)	M	95-97/19
Me	t-Bu	3	95	(87)	aM	104-107/24

a) M=Markownikoff orientation; aM=anti-Markownikoff orientation.
b) Determined by vpc analysis. c) Isolated yields.
d) Diphenyl disulfide(12%) or dibenzyl disulfide(18%) was obtained together with 16 or 17, respectively. e) Sublimation temperature.

The orientation is independent of the steric effect of alkyl residues of thiolsulfinates, whereas the bulky substituents in olefins have a dramatic effect on the orientation of addition. Namely, when 3-methyl-1-butene was treated with methanesulfenyl trifluoroacetate only the Markownikoff adduct was resulted, while 3,3-dimethyl-1-butene gave only the anti-Markownikoff adduct 3.

Schmid et al.[10] and Hogg et al.[11] reported that the addition of p-chlorobenzenesulfenyl chloride to such olefins as 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene gave predominantly the adducts of anti-Markownikoff orientation in all cases. However, these adducts were found to isomerize slowly at 25°C to the Markownikoff orientation products. Meanwhile, although methyl 3,3-dimethyl-1-trifluoroacetoxy-2-butyl sulfide 3 is stable at room temperature, it isomerized completely to the Markownikoff adduct 22 upon heating at 100°C for overnight. Furthermore, a series of adducts obtained from sulfenyl trifluoroacetates and monoalkyl-substituted ethylenes were found as a mixture of both the Markownikoff and the anti-Markownikoff β-trifluoroacetoxy sulfides as shown in Table 3, when the adducts were analyzed by NMR spectrum before distillation. Upon heating the mixtures for 0.5 to 8 hrs at 70°C, the mixtures completely changed to the sole isomeric Markownikoff product. The structures of anti-Markownikoff products were confirmed on the basis of the ^1H-NMR spectra. The ratio of Markownikoff products of which NMR spectra show the methine proton signals at 5.00 to 5.14 ppm and anti-Markownikoff products of which NMR spectra show the methylene proton signals at 4.31 to 4.65 ppm was easily determined since both the signals which are attributable to the protons at the carbon adjacent to the trifluoroacetoxy group were clearly distinguishable from the others. Accordingly, it was concluded that the initial product obtained at low temperatures in a short reaction time is a kinetically controlled, anti-Markownikoff adduct which isomerized to the thermodynamically controlled, Markownikoff adduct at higher temperature or/and in a prolonged reaction time.

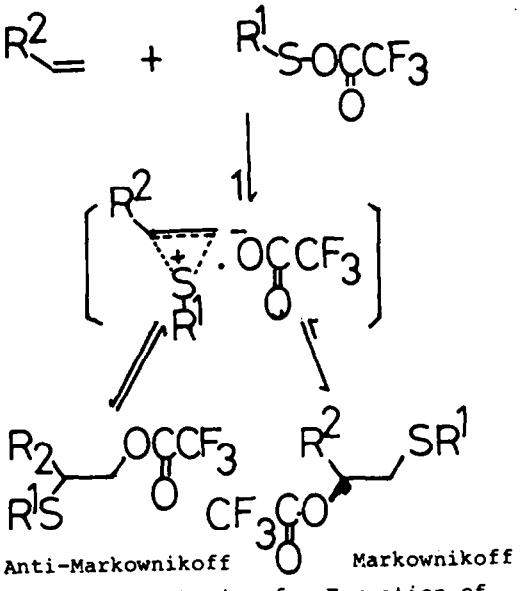
These observations suggest that the mechanism of addition of trihaloacetates to olefin resembles that of sulfenyl chlorides to olefins proposed

Table 3. Kinetically Controlled Products for Addition of Sulfenyl Trifluoroacetates $R^1S\text{-}OCOCF_3$, to Terminal Olefins, $R^2CH=CH_2$, in CCl_4 at -20°C.

R^1	R^2	Adducts[a] M(%)	aM(%)		^1H δ Chemical Shifts(ppm)[b]
Me	Et	18 47	23 53	23	1.26(t, 3H, J 6.9 Hz), 1.50-2.08(m, 2H), 2.18 (s, 3H), 2.28-2.51(m, 1H), 4.31 and 4.61(AB part of ABX pattern, each 1H, J_{ab} 11.1, J_{ax} 7.0 and J_{bx} 6.3 Hz).
Me	i-Pr	19 23	24 77	24	1.15(d, 6H, J 6.5Hz), 1.81-2.33(m, 1H), 2.21 (s, 3H), 2.33-2.96(m, 1H), 4.51(d, 2H, J 7.3 Hz).
Et	i-Pr	20 15	25 85	25	1.02(d, 6H, J 6.7 Hz), 1.22(t, 3H, J 7.5 Hz), 1.81-2.40(m, 1H), 2.40-3.13(m, 1H), 2.65(q, 2H J 7.5 Hz), 4.31 and 4.65(AB part of ABX , pattern, each 1H, J_{ab} 11.0, J_{ax} 7.8 and J_{bx} 7.0 Hz).
i-Pr	i-Pr	21 14	26 86	26	0.99(d, 6H, J 7.2 Hz), 1.26(d, 6H, J 7.0 Hz), 1.70-2.48(m, 1H), 2.64-3.85(m, 2H), 4.34 and 4.61(AB part of ABX pattern, each 1H, J_{ab} 10.5, J_{ax} 8.6 and J_{bx} 6.3 Hz).
Me	t-Bu	22 0	3 100	22	1.05(s, 9H), 2.13(s, 3H), 2.61, 2.82 and 5.00 (ABX, each 1H, J_{ab} 14.1, J_{ax} 11.1 and J_{bx} 2.5 Hz).

a) M=Markownikoff orientation; aM= anti-Markownikoff orientation. b) In CCl_4

by Hogg et al.[11] as shown in the following scheme.



Scheme 2. Mechanism for Formation of Markownikoff Adduct.

Although the attack of trifluoroacetate anion on the episulfonium ion is sterically favored at the secondary carbon, thus resulting in the predominant formation of anti-Markownikoff products, tri-fluoroacetate anion eventually migrates to the adjacent position, resulting in the formation of the thermodynamically more stable Markownikoff products.

Meanwhile, monothiocarbonate S-oxides have been found as another good source of sulfenyl trihaloacetates. Treatment of dibenzyl monothiocarbonate S-oxide with trifluoroacetic anhydride in chloroform at -20°C in the presence of 1-octene afforded benzyl 2-trifluoroacetoxy-1-octyl sulfide 1 quantitatively together with benzyl tri-fluoroacetate(96%) which was formed by decarboxylation of monobenzylcarbonic and trifluoroacetic anhydride.(Scheme 3)**

** $PhCH_2OC(O)\text{-}S(O)Ph + (CF_3CO)_2O$ → (-20°C, in CCl_4) → $[PhCH_2S\text{-}OC(O)CF_3]$ + $[PhCH_2OC(O)\text{-}OCCF_3]$

$[PhCH_2S\text{-}OC(O)CF_3]$ + $C_6H_{13}CH=CH_2$ → $C_6H_{13}CH(OCOCF_3)CH_2SCH_2Ph$

$[PhCH_2OC(O)\text{-}OCCF_3]$ → (-CO_2) → $PhCH_2OCCF_3$

Scheme 3. Formation of Phenylmethanesulfenyl Trifluoroacetate from Dibenzyl Monothiocarbonate S-Oxide.

This procedure is convenient for the synthesis of the adducts of phenylmethanesulfenyl trifluoroacetate to olefins, because no dibenzyl disulfide is formed together with the desired compounds.***

***Since both column chromatography

and distillation are not adequate for the separation of the adducts from the mixture containing dibenzyl disulfide because of the similarity in the physical properties of the two compounds, the purification of the adducts is difficult in the presence of the disulfide.

Experimental

All m.ps and b.ps are uncorrected. ^{1}H NMR spectra were obtained with either a Hitachi R-24A or a Hitachi Perkin Elmer R-20 high resolution spectrometer using TMS as an internal standard. IR spectra, unless otherwise noted, were determined as a soln in CCl_4 on a Hitachi 265-50 Infrared Spectrophotometer.

Synthesis of β-Trihaloacetoxy Sulfides A typical procedure is as follows. To a soln of a mixture of ethyl ethanethiolsulfinate(366 mg, 2.65 mmol) and 1-octene(2ml) in CCl_4(1ml) at -20°C was added trifluoroacetic anhydride (840 mg, 4.0 mmol). After the mixture was allowed to stand until the temp rose to room temp, the solvent and excess of 1-octene were removed in vacuo. Vacuum distillation afforded ethyl 2-trifluoroacetoxyoctyl sulfide 1 1.37 g, 91%; b.p. 146-150°C at 35 mmHg. The results of elemental analysis and the chemical shift in NMR spectra of other β-trihaloacetoxy sulfides prepared by the same method were described in the following Table 4.(cf. see also Table 1 and 2).

Addition of Methanesulfenyl Chloride to trans- or cis-2-Butene trans-2-Butene was cooled with a dry ice-acetone bath and then compressed in the vessel sealed with a rubber cap. Into a soln of excess lipuified olefin in CCl_4(4 ml) at -20°C was poured methanesulfenyl chloride(3.31 g, 40.1 mmol). After the mixture was stirred for 2 hr at room temp, the solvent and excess of the olefin were evaporated in vacuo. Vacuum distillation at 70°C and 31 mmHg afforded erythro-methyl-2-chloropropyl sulfide(3.88 g, 70%): ^{1}H-NMR(CCl_4) δ 1.04(d, 3H, J 7.2Hz), 1.63(d, 3H,J 6.9Hz), 2.11(s, 3H), 2.71 (dq, 1H, J 7.2 and 6.2Hz), 3.99(dq, 1H, J 6.9 and 6.2Hz); IR(neat) 1442, 1378, 640 cm^{-1}.

Similarly, the addition of methanesulfenyl chloride to cis-2-butene afforded the threo-isomer; 75%, b.p. 71.5-72.0°C at 34 mmHg; ^{1}H-NMR(CCl_4) δ 1.28(d, 3H, J 6.9Hz), 1.49(d, 3H, J 6.7Hz), 2.17(s, 3H), 2.96(dq, 1H, J 6.9 and 3.6 Hz), 4.22(dq, 1H, J 6.7 and 3.6Hz) ; IR(neat) 1445, 1380, 645 cm^{-1}.

Reaction of erythro- or threo-Methyl 1-Methyl 1-Methyl-2-chloropropyl Sulfide A soln of the erythro-chlorosulfide(36 mg, 0.26 mmol) and sodium trifluoroacetate(47 mg, 0.34 mmol) in trifluoroacetic acid(0.5 ml) was stirred for a day at room temp. After NaCl precipitated was filtrated off, the solvent was removed in vacuo. The yield(96%) of erythro-methyl 1-methyl-2-trifluoroacetoxypropyl sulfide 6 was determined by vpc analysis; ^{1}H-NMR(CCl_4) δ 1.30(d, 3H, J 7.7 Hz), 1.46(d, 3H, J 6.8Hz), 2.12(s, 3H), 2.28(dq, 1H, J 7.7 and 5.8Hz), 5.16(dq, 1H, J 6.8 and 5.8Hz); IR(neat) 1780, 1220, 1165 cm^{-1}.

The threo-chlorosulfide was also treated with sodium trifluoroacetate in similar manner and the corresponding threo-trifluoroacetoxy sulfide 7 was obtained in 84% yield; ^{1}H-NMR(CCl_4) δ 1.28(d, 3H, J 7.1Hz), 1.41(d, 3H, J 6.6Hz), 2.15(s, 3H), 2.86(dq, 1H, J 7.1 and 5.1Hz), 5.22(dq, 1H, J 6.6 and 5.1Hz); IR(neat) 1780, 1222, 1165 cm^{-1}.

Reaction of O-Benzyl S-Benzyl Monothiocarbonate S-Oxide with Trifluoroacetic Anhydride in the Presence of 1-Octene To a soln of the S-oxide(236 mg, 0.86 mmol) and 1-octene(1 ml) in CCl_4(1 ml) and $CHCl_3$(1 ml) at -20°C was added trifluoroacetic anhydride(273 mg, 1.3 mmol). After stirring was continued until the temp of the mixture rose to room temp, the solvents and excess of 1-octene were evaporated in vacuo. Vacuum distillation afforded benzyl trifluoroacetate(93 mg, 53%), b.p. 115-125°C at 40 mmHg and benzyl 2-trifluoroacetoxyoctyl sulfide 17(262 mg, 88% , b.p. 160-165°C at 3 mmHg. The yields determined by vpc analysis were 96 and 100%, respectively. Benzyl trifluoroacetate; ^{1}H-NMR(CCl_4) δ 5.33(s, 2H), 7.14(s, 5H); IR(neat) 1775, 1210, 1135 cm^{-1}. Benzyl trifluoroacetoxy sulfide 17: ^{1}H-NMR(CCl_4) δ 0.66-1.96(m, 13H), 2.59(d, 2H, J 6.7 Hz), 3.69(s, 2H), 4.99(m,1H), 7.27(s, 5H); IR(neat) 1780, 1225, 1160 cm^{-1}.

Hydrolysis of Methyl 2-Trifluoroacetoxy Sulfide 1 The mixture of the sulfide 1 (205 mg, 0.75 mmol) and 10% aqueous NaOH soln(5 ml) was heated at 100°C for a day. The soln was extracted with ether and the organic layer was dried over anhydrous Na_2SO_4. After the solvent was removed in vacuo, vacuum distillation at 124-127°C and 22 mmHg gave methyl 2-hydroxyoctyl sulfide(114 mg, 86%); ^{1}H-NMR(CCl_4) δ 0.75-1.79(m, 13H), 2.15(s, 3H), 2.36, 2.73 and 3.60 (ABX, each 1H, J_{ab} 13.3, J_{ax} 7.5 and J_{bx} 4.4Hz), 2.67-2.51(br, 1H); IR(neat) 3420, 2925, 2855, 1040 cm^{-1}.

References

1. S.Oae and G. Tsukamoto, Kagaku 26, 172 (1971).
2. a) N.Furukawa, T.Morishita, T. Akasaka and S.Oae, Tetrahedron Letters 1653 (1977). b) Idem. Ibid. 1567 (1978); c) Idem. J. Chem. Soc. Perkin II 432 (1980).
3. Idem. Tetrahedron Letters 3973 (1979)
4. A. J.Halvlik and N. Kharasch, J. Am. Chem. Soc. 78, 1207 (1956).
5. a) R. E. Putnam and W. H. Sharkey, Ibid. 79, 6526 (1957). ; b) B. M. Trost, M. Ochiai and P. M. McDougal Ibid. 100, 7103 (1978).
6. W. A. Smit, N. S. Zefirov, I. V. Bordrikov and M. Z. Krimer, Accounts Chem. Res. 12, 282 (1979).
7) a) M. Oki and K. Kobayashi, Bull. Chem. Soc. Japan 46, 687 (1973); b) M.Oki, A. Nakamura and K. Kobayashi

Ibid. 46, 3610 (1973).
8) a) W. H. Mueller and P. E. Butler, J. Am. Chem. Soc. 88, 2866 (1966); b) P. M. Subramanian, M. T. Emerson and N. A. LeBel, J. Org. Chem. 30, 2624 (1965); c) F. A. L. Anet, Tetrahedron Letters 3399 (1964); d) J. I. Musher, Mol. Phys. 6, 93 (1963).
9) M. J. S. Dewar and R. C. Fahey, J. Am. Chem. Soc. 85, 2245, 2704 (1963).
10.a) G. H. Schmid, C. L. Dean and D. G. Garratt, Can. J. Chem. 54, 1253 (1976); b) C. L. Dean, D. G. Garratt, T. T. Tidwell and G. H. Schmid, J. Am.Chem. Soc. 96, 4958 (1974).
11.G. M. Beverly and D. R. Hogg, J. Chem. Soc. Chem. Commun. 138 (1966).

Table 4. ^{1}H-NMR Spectra and Analytical Data for Sulfenyl Trihaloacetate Adducts.

Adducts	Analysis(%) C Calcd.	C Found	H Calcd.	H Found	^{1}H Chemical Shifts(δ, TMS)[a]
1	48.52	48.29	7.03	6.99	0.77-2.00(m, 13H), 2.13(s, 3H), 2.69(d, 2H, J 6.5 Hz), 5.16(dt, 1H, J 6.6 and 6.5 Hz).
2	41.07	41.35	5.95	6.02	0.67-2.00(m, 13H), 2.16(s, 3H), 2.68(d, d, 2H, J 6.7 Hz), 5.03(dt, 1H, J 6.7 and 5.5Hz).
3	44.25	44.15	6.19	6.15	1.11(s, 9H), 2.22(s, 3H), 2.51, 4.51, and 4.63(ABX, each 1H, J_{ab} 11.3 and J_{ax}=J_{bx} 6.3 Hz).
4	50.00	50.02	4.20	4.18	2.08(s, 3H), 2.84, 3.04 and 6.00(ABX, each 1H, J_{ab} 14.7, J_{ax} 8.0 and J_{bx} 6.4 Hz), 7.42 (s, 5H).
5	79.60	79.45	6.23	6.06	2.31(s, 3H), 6.45(s, 1H), 7.19 and 7.31(ds, 10H).
6	38.88	38.84	5.13	5.16	1.30(d, 3H, J 7.7 Hz), 1.46(d, 3H, J 6.8 Hz) 2.12(s, 3H), 2.82(dq, 1H, J 7.7 and 5.8 Hz), 5.16(dq, 1H, J 6.8 and 5.8 Hz).
7	38.88	38.53	5.13	5.09	1.28(d, 3H, J 7.1 Hz), 1.41(d, 3H, J 6.6 Hz), 2.15(s, 3H), 2.86(dq, 1H, J 7.1 and 5.1 Hz), 5.22(dq, 1H, J 6.6 and 5.1 Hz).
8					1.75(s, 3H), 4.15(d, 1H, 8.7 Hz), 6.22(d, 1H, J 8.7 Hz), 7.32 and 7.38(ds, 10H).
9	73.73	73.76	6.60	6.45	1.80(s, 3H), 2.34(br. s, 1H), 3.97(d, 1H, J 7.5 Hz), 5.00(br.d, 1H, J 7.5 Hz), 7.35(s, 10H).
10					1.93(s, 3H), 4.67(d, 1H, J 1.4 Hz), 6.73(d, 1H, J 1.4 Hz), 7.00-7.94(m, 6H).
11	42.10	41.64	4.86	4.86	1.26-2.71(m, 6H), 2.19(s, 3H), 3.10(m, 1H), 5.27(m, 1H).
12[b,c]	44.62	44.44	5.41	5.28	1.15-2.38(m, 8H), 2.11(s, 3H), 2.63(dt,1H, Jaα 4.0 and Jaβ=Jab 9.1 Hz), 4.91(dt, 1H, Jbβ 4.2 and Jbα=Jab 9.1 Hz).
13	47.24	47.21	5.15	5.15	1.11-1.96(m, 6H), 2.09(s, 3H), 2.71-2.39(m, 1H), 2.39-2.62(m, 1H), 2.62-2.88(m, 1H), 4.85-5.07(m, 1H).
14	50.03	50.35	7.39	7.42	0.59-2.05(m, 13H), 1.28(t, 3H, J 7.5 Hz), 2.57(q, 2H, J 7.5 Hz), 2.71(d, 2H, J 6.8 Hz) 5.08(dt, 1H).[d]
15	51.98	52.12	7.72	7.65	0.69-1.97(m, 13H), 1.38(d, 6H, J 7.1 Hz), 2.71(d, 2H, J 6.3 Hz), 2.94(m, 1H), 5.07 (dt, 1H).[d]
16	57.47	57.69	6.33	6.37	0.63-2.07(m, 13H), 3.03(d, 2H, J 6.7 Hz), 4.99(m, 1H), 6.98-7.43(m, 5H).
17	58.60	58.37	6.65	6.63	0.66-1.96(m, 13H), 2.59(d, 2H, J 6.7 Hz), 3.96(s, 2H), 4.99(dt, 1H),[d] 7.29(s, 5H).
18	38.88	38.88	5.13	5.17	1.07(br.t, 3H, J 6.6 Hz), 1.84(br.q, 2H, J 6.6 Hz), 2.22(s, 3H), 2.75(d, 2H, J 6.4 Hz), 5.14(m, 1H).
19	41.73	41.96	5.69	5.68	1.07(d, 6H, J 6.5 Hz), 1.78-2.51(m, 1H), 2.19(s, 3H), 2.70(br.s, 1H), 2.80(s, 1H), 5.06(m, 1H).
20	44.25	44.33	6.19	6.13	1.06(d,6H, J 6.6 Hz), 1.32(t, 3H, J 7.2 Hz), 1.95-2.38(m, 1H), 2.61(q, 2H, J 7.2 Hz), 2.56, 2.85 and 5.00(ABX, each 1H, Jab 13.6, Jax 5.7 and J_{bx} 5.1 Hz).
21	46.50	47.00	6.63	6.72	1.06(d, 6H, J 6.5 Hz), 1.33(d, 6H, J 6.7 Hz), 1.91-2.53(m, 1H), 2.78(AB part of ABX pattern, 2H),[d] 2.98(m, 1H), 5.02(m, 1H).

a) In CCl_4(ppm). b) In $CDCl_3$. c)
d) J-Values were not determined