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REACTION OF THIOLSULFINATES WITH TRIHALOACETIC ANHYDRIDES—I

EVIDENCE FOR THE FORMATION OF SULFENYL AND SULFINYL CARBOXYLATES

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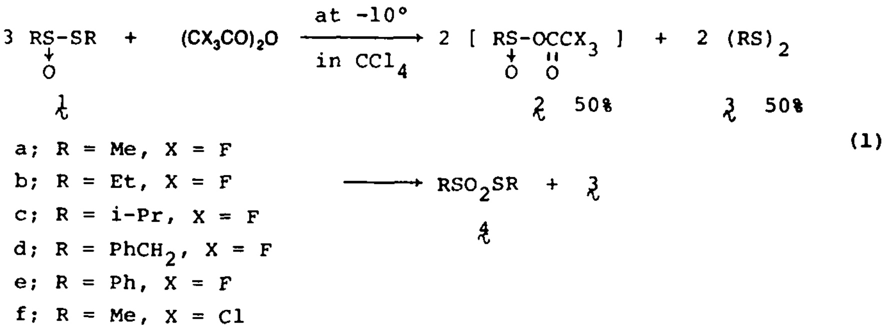
Abstract—Thiolsulfinates react with trifluoro- or trichloroacetic anhydride to give equimolar mixtures of the corresponding disulfides and sulfinyl trifluoro- or trichloroacetates which are in equilibria with sulfenyl carboxylates. Although the equilibrium lies far toward sulfinyl carboxylates at room temperature, addition of olefins to the mixed solution of sulfinyl carboxylate and a corresponding disulfide affords the adducts which are formed in the reaction between the corresponding sulfenyl carboxylates and the olefins. Meanwhile, treatment of carboxylic acid silver salts with sulfinyl chlorides also gives sulfinyl carboxylates, however, sulfinyl carboxylates have not been successfully isolated yet.

Although the Pummerer rearrangement[1] of sulfoxides has been studied extensively, the analogous reaction of thiolsulfinates **1** with acid anhydrides has been reported only in one case: Fukui *et al.*[2] reported that β-lipoic acid reacted with acetic anhydride to give a Pummerer product, 8-C-acetoxylipoic acid but only in 6% yield. Recently, we found that the reaction of thiolsulfinates (**1**) with acetic anhydride containing acetic acid afforded not the Pummerer products but new rearranged products, α-acetylthiosulfoxides in moderate yields.[3] Generally, thiolsulfinates (**1**), having more reaction sites[4] than sulfoxides are highly reactive as compared to sulfoxides. For example, thermolysis of **1** affords rather complicated mixtures of products due to their thermal instability. However, we found recently that a simple and clean reaction takes place between thiolsulfinates (**1**) and trihaloacetic anhydrides at relatively low temperatures.[5] In this paper we wish to describe the formation of sulfinyl carboxylates and sulfenyl carboxylates in the treatment of thiolsulfinates with trihaloacetic anhydrides and a few reactions involving these unstable intermediates.

Formation of sulfinyl carboxylates (**2**). When a trihaloacetic anhydride such as trifluoro- or trichloroacetic anhydride was used instead of acetic anhydride in the Pummerer like reaction of thiolsulfinates (**1**), sulfinyl carboxylates (**2**) were initially formed together with roughly equimolar amounts of the corresponding disulfides as shown in the following eqn (1). However, t-butyl 2-methyl-2-propanethiolsulfinate did not yield the corresponding product (**2**) but afforded di-t-butyl tetrasulfide as the major product. These sulfinyl carboxylates (**2**) formed in this reaction are stable only in solution. Attempts to isolate **2** were unsuccessful since upon evaporation of the solvent containing sulfinyl carboxylates (**2**) and disulfides (**3**) only a mixture of thiolsulfonates (**4**) and **3** was resulted.

Sulfinyl carboxylates (**2**) were also found to be formed by the reaction of silver salts of carboxylic acids with sulfinyl chlorides in carbon tetrachloride solution. Accordingly, the formation of methanesulfinyl trifluoroacetate (**2a**) from methyl methanethiolsulfinate (**1a**) and trifluoroacetic anhydride was able to be proved only spectroscopically by comparing the spectra with those of the authentic sample which was prepared by treatment of silver trifluoroacetate with methanesulfinyl chloride. The IR and NMR spectral data which were obtained from the mixture of sulfinyl carboxylates (**2**) and disulfides (**3**) or from the solution, after silver chloride was removed by filtration, are summarized in Table 1.

Sulfinyl carboxylates (**2**) have been postulated as unstable intermediates generated in various reactions,[6] however, the formation of **2** has only been confirmed by IR spectra in a matrix of argon or nitrogen at 10–20 K.[7] Recently, Kohn *et al.* and Walter *et al.* successfully obtained different stable five-membered sulfinyl



$$3\ \underset{\mathbf{1}}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{RS}}\mathrm{-SR}} + (CX_3CO)_2O \xrightarrow[\text{in } CCl_4]{\text{at } -10^\circ} 2\ [\,\underset{\mathbf{2}\ \ 50\%}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{RS}}\mathrm{-O}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{CX_3}}\,] + 2\ \underset{\mathbf{3}\ \ 50\%}{(RS)_2} \qquad (1)$$

$$\longrightarrow \underset{\mathbf{4}}{RSO_2SR} + \mathbf{3}$$

a; R = Me, X = F
b; R = Et, X = F
c; R = i-Pr, X = F
d; R = $PhCH_2$, X = F
e; R = Ph, X = F
f; R = Me, X = Cl

Table 1. IR and ^{1}H NMR spectral data of sulfinyl carboxylates, $R^1S(O)–O–C(O)R^2$

No	R^1	R^2	IR(cm^{-1})^a	^{1}H NMR(δ)^b
2a	Me	CF_3^{c,d}	1790, 1225, 1180, 1110	3.00(s)
2b	Et	CF_3^{c}	1785, 1225, 1180, 1105	1.44(t, 3H), 3.16(q, 2H)
2c	i-Pr	CF_3^{c}	1790, 1225, 1175, 1110	1.37(d, 6H), 3.60(m, 1H)
2d	$PhCH_2$	CF_3^{c}	1790, 1225, 1175, 1100	4.31(s, 2H), 7.38(s, 5H)
2e	Ph	CF_3^{c}	1785, 1165, 1105	7.07-7.73(m)
2f	Me	CCl_3^{c}	1770, 1170	3.00(s)
2g	Me	CH_3^{d}	1760, 1155	2.16(s, 3H), 2.72(s, 3H)
2h	Me	Ph^d	1725, 1240, 1160	2.86(s, 3H), 7.28-7.55(m, 3H), 7.83-8.11(m, 2H)

[a] The IR spectra were measured in carbon tetrachloride at room temperature. [b] ^{1}H NMR chemical shifts(ppm) were recorded in carbon tetrachloride-TMS at 35°. Proton-proton coupling in Hz: $(CH_3)_2CH$, 7.0; CH_3CH_2, 7.8. [c] These spectra were measured from the mixture of sulfinyl carboxylates and disulfides. [d] These spectra were obtained from the solution that carboxylic acid silver salts were treated with methanesulfinyl chloride.

carboxylates (**2**) independently.[8] However, their procedure cannot be applied to prepare a wide variety of sulfinyl carboxylates (**2**), because only 5-membered derivatives can be obtained by their procedure. Our method, which uses thiolsulfinates (**1**) and trihaloacetic anhydrides is an excellent *in situ* preparative method of **2** which is stable in solution at room temperature. Another advantage of our method is that one can make a variety of sulfinyl carboxylates (**2**) by changing either thiolsulfinate (**1**) or trihaloacetic anhydride. Meanwhile, sulfinyl carboxylates (**2**) can also be generated readily by employing the procedure which uses silver salts of carboxylic acids and sulfinyl chlorides as starting materials. Although sulfinyl carboxylates (**2**) could not be isolated by our method, the method can give essential information concerning physical properties and chemical behaviors of **2**.

^{18}O *tracer study on the reaction.* In the Pummerer reaction of sulfoxides or sulfinates, the sulfinyl oxygen of the sulfoxide[9] or sulfinate[10] is known to undergo concurrent ^{18}O exchange with that of the acyl anhydride *via* formation of a sulfurane intermediate. If the above reaction of thiolsulfinates (**1**) with trihaloacetic anhydrides involves the initial acylation of sulfinyl oxygen, the O atom in the recovered thiolsulfinate (**1**) is considered to be exchanged at least partially with those of trihaloacetic anhydrides. Thus, benzyl phenylmethanethiolsulfinate (**1g**) labeled with ^{18}O was prepared by treating toluene-α-thiol with [^{18}O]-phenylmethanesulfinyl chloride[3] and tested for possible ^{18}O exchange experiment. After the reaction, general work-up afforded both the thiolsulfonate and recovered the starting thiolsulfinate (**1g**). The ^{18}O contents of both compounds were found to have decreased down to about a half of that of the starting thiolsulfinate (**1g**). The results are shown in Table 2. Inspection of the data indicates clearly that the initial acylation of sulfinyl oxygen of the thiolsulfinate (**1g**) with the trihaloacetic anhydrides did take place to form an incipient intermediate (**6**). The acylated **6** may give rise to the sulfurane (**6'**) upon attack of a carboxylate anion onto the sulfonium S atom of **6**. The rapid equilibrium between **1**, **6** and **6'** may result in the partial oxygen exchange between **1** and the anhydride.

Furthermore, upon attack of the carboxylate anion at sulfenyl sulfur of **6**, thiolsulfinates should give two moles of sulfenyl carboxylates (**5**) which may decompose rapidly to afford **2** *via* forming the intermediate (**7**). Therefore, these two processes may be responsible for affording either **2** or the ^{18}O labeled starting material (**1**). Thus the following proposed mechanism would account for the ^{18}O result of Table 2.

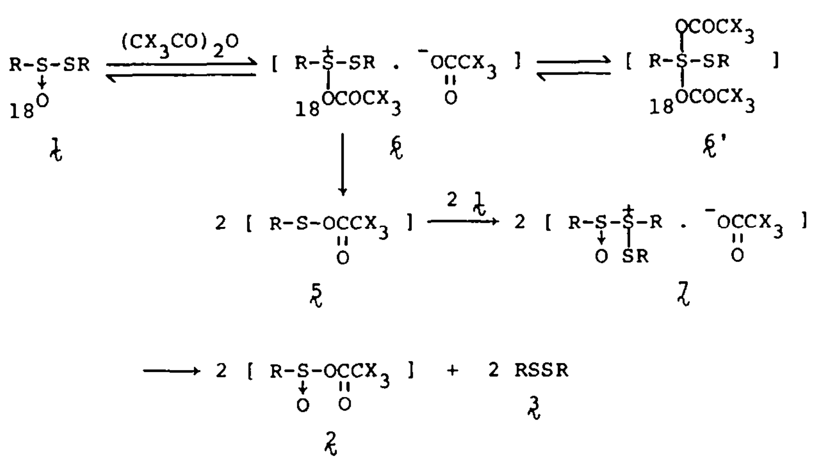
Trapping of sulfenyl carboxylates (**5**) *with olefins or anisole.* The sulfenyl carboxylate (**5**) which was prepared by Kharasch *et al.*[11] in the treatment of silver salts of carboxylic acids with sulfenyl chlorides was found to react with olefins to afford the 1,2-addition products, β-acyloxy sulfides. This observation indicates that sul-

Table 2. Change in ^{18}O content[a] in the reaction of ^{18}O-labeled thiolsulfinate (**1g**) with trifluoroacetic anhydride in methylene chloride at −70°

Run	Starting(**1g**) (%)	Thiolsulfonate (%)	Recovered(**1g**) (%)
1	100.0^b	37.7	-
	100.0	46.6	53.1
2	100.0	47.4	38.7
	100.0	-	37.1
3	100.0	46.0	33.8
	100.0	52.9	-

[a] Measured twice for each sample.

[b] Percentages were measured on the basis of the ^{18}O content of starting material(**1g**); 0.833 ± 0.032 excess atom % for run 1, 0.843 ± 0.015 for runs 2 and 3.



Scheme 1.

fenyl carboxylate (5) is a good sulfenylating agent like sulfenyl chlorides (RSCl). In order to prove that formation of sulfinyl carboxylates (2) proceeds via formation of 5, the trapping experiment of 5 with an olefin was carried out. Indeed, methyl methanethiolsulfinate (**1a**) reacted immediately with trifluoroacetic anhydride at −20° in the presence of 3,3-dimethyl-1-butene to give 3,3-dimethyl-2-methylthiobutyl trifluoroacetate (**8**) in 87% yield. On the other hand, when the reaction was also carried out at room temperature in the presence of anisole it required a day to complete and gave methyl *p*-methoxyphenyl sulfide in 74% yield. Accordingly, these observations demonstrate clearly that sulfenyl carboxylate (5) is formed in the reaction in keeping with the mechanism shown in Scheme 1.†

Evidence for equilibrium formation between sulfenyl (5) *and sulfinyl carboxylates* (2). These experimental observations suggest that both sulfinyl and sulfenyl carboxylates exist as an equilibrium mixture in the solution though the equilibrium is shifted preferentially toward the formation of sulfinyl carboxylate. In order to ascertain the formation of this equilibrium, the following experiment was carried out. After the formation of both methanesulfinyl trifluoroacetate (**2a**) and dimethyl disulfide upon treatment of methyl methanethiolsulfinate (**1a**) with trifluoroacetic anhydride was confirmed by NMR spectrum, the mixture was treated with 3,3-dimethyl-1-butene or anisole. A similar mixture of products was also obtained from the reactions of methanesulfenyl trifluoroacetate (**5a**) with these reagents, together with methyl methanethiol sulfonate (**4a**) and dimethyl disulfide (**3a**).

Surprisingly, however, methanesulfinyl trifluoroacetate (**2a**), which was prepared by treatment of silver trifluoroacetate with methanesulfinyl chloride did not react with 3,3-dimethyl-1-butene, while it reacted with anisole affording di(*p*-methoxyphenyl) sulfide as a major product. Therefore, dimethyl disulfide is considered to be playing an important role in this reaction, seemingly suggesting that without the disulfide sulfinyl carboxylate (2) does not return to the sulfenyl carboxylate (5). Apparently there is an equilibrium between sulfenyl (5) and sulfinyl carboxylate (2) as shown in Scheme 2 and without olefins, the equilibrium is shifted toward **2a** rather than toward **5a**.

Therefore, in the absence of such trapping reagents of sulfenyl carboxylate (5) as olefins and anisole, only thermodynamically stable thiolsulfonates (4) and disulfides (3) were formed according to the path shown in Scheme 2. In the presence of 3,3-dimethyl-1-butene, however, 3,3-dimethyl-2-methylthiobutyl trifluoroacetate (**8**) was obtained as the sole product in an excellent yield. When anisole was used instead of the olefin, methyl *p*-methoxyphenyl sulfide was obtained in a rather small yield, because the reaction of **5** with anisole proceeded more slowly than the formation of the thiolsulfonate (**4a**) and disulfide (**3a**). Furthermore, the trapping efficiency of anisole for the sulfenyl carboxylate (5) is far lower than the olefin and this may also account for the large difference in yields of the adduct (**8**) and methyl *p*-methoxyphenyl sulfide since the rate of the addition of sulfenyl carboxylate (5) to the olefin should be much higher than that of the transformation of 7–4.

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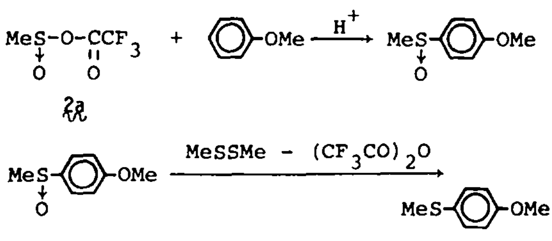
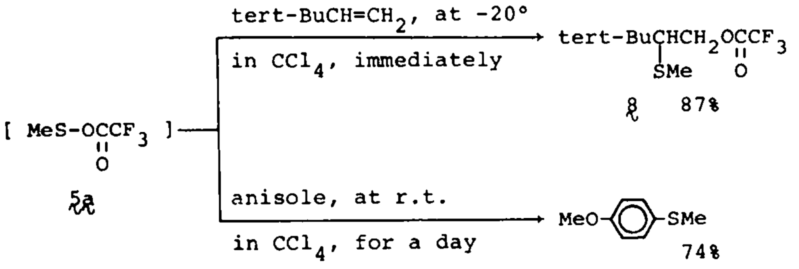
†A Referee suggested the following mechanism for formation of methyl *p*-methoxyphenyl sulfide: anisole does not react initially with methanesulfenyl trifluoroacetate (**5a**) but does with methanesulfinyl trifluoroacetate (**2a**), to afford methyl *p*-methoxyphenyl sulfoxide which then is reduced by MeSSMe–$(CF_3CO)_2O$ system. However, when anisole was added to the



mixture of both methanesulfinyl trifluoroacetate (**2a**) and dimethyl disulfide, methyl *p*-methoxyphenyl sulfide was obtained only in 12% yield [eqn (3)], whereas under the similar reaction condition when the mixture of methyl methanethiolsulfinate (**1a**) and anisole was treated with trifluoroacetic anhydride, the sulfide was obtained in an excellent yield [eqn (2)]. In the latter reaction, the formation of $MeS–OCOCF_3–PheOMe$ complex is expected since the colorless solution turned suddenly to green. Accordingly, the sulfenyl carboxylate (**2a**) is considered to be the reactive species to react with anisole. Trifluoroacetic anhydride employed through the reactions described in this paper, was purified by distillation. However, even when these reactions were carried out in the presence of a small amount of trifluoroacetic acid, both addition to olefins and substitution with anisole were found to proceed similarly as in the reaction without trifluoroacetic acid.



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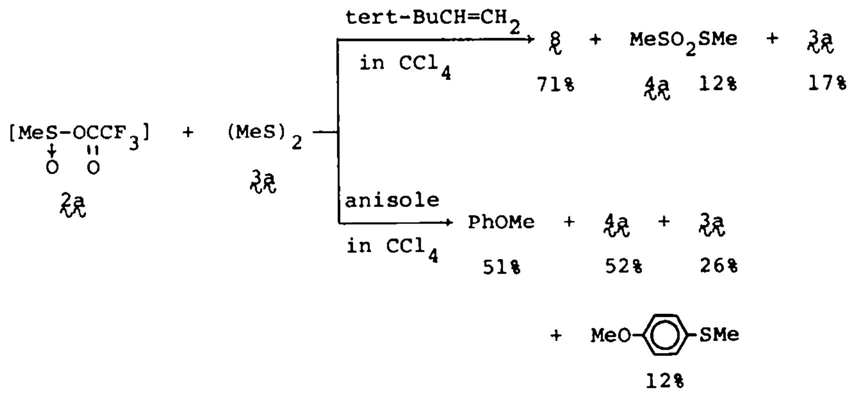

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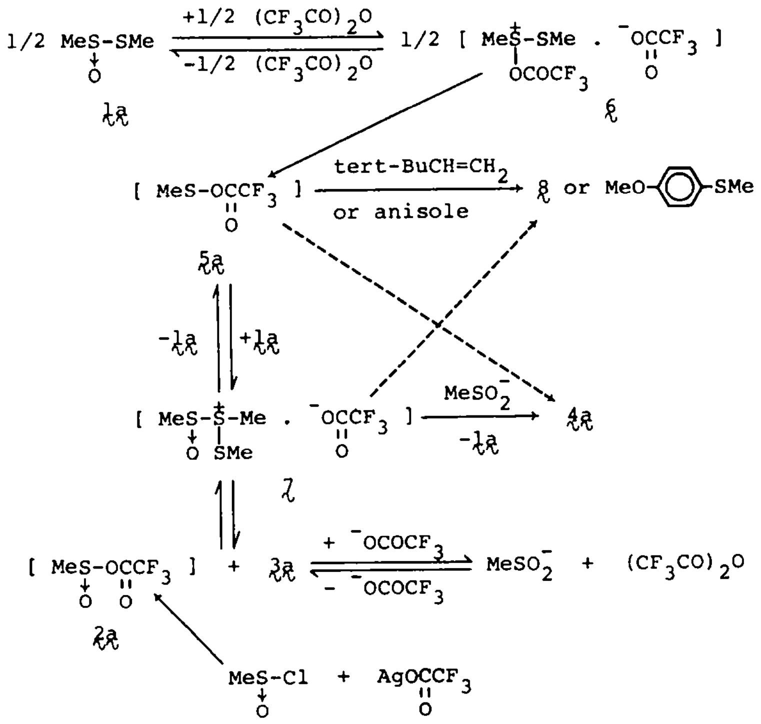


Scheme 2.

Methanesulfinyl trifluoroacetate (**2a**) also reacted with dibenzyl disulfide to give benzyl methanethiolsulfonate as a major product together with some other products, suggesting the formation of methanesulfinate anion.

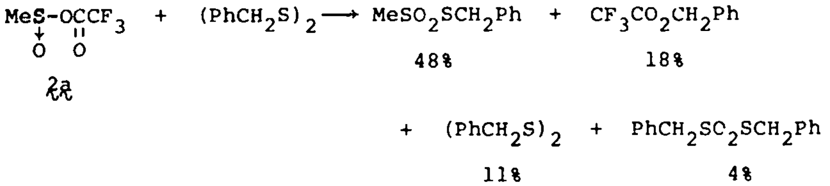
^{13}C *Tracer study on the reaction mechanism.* A ^{13}C tracer experiment was carried out by employing [α-^{13}C]-benzyl phenylmethanethiolsulfinate (**1h**)[3] and the result also supports the mechanism shown in Scheme 2. After the thiolsulfinate (**1h**) was treated similarly with trifluoroacetic anhydride, the products were isolated and their position and contents of ^{13}C were determined by ^{13}C NMR. The results of ^{13}C tracer experiment of the reaction are summarized in Table 3.

Inspection of the ^{13}C experimental results indicate that

Table 3. Change in ^{13}C content in the reaction of [α-^{13}C]-benzyl phenylmethanethiolsulfinate (**1h**) with trifluoroacetic anhydride in methylene chloride at −70°

No	Starting(1h)		Thiolsulfonate		Recovered(1h)		Disulfide
	Sulfinyl(%)	Sulfenyl(%)	Sulfonyl(%)	Sulfenyl(%)	Sulfinyl(%)	Sulfenyl(%)	(%)
1[a]	0.0	32.0(100)	0.2	15.9(50)	0.0	15.9(50)	19.4(61)
2[b]	0.0	26.0(100)	0.0	20.0(77)	0.0	21.0(81)	19.0(73)

[a] ^{13}C content was determined by ^{13}C NMR. [b] Determined by ^{1}H NMR by ^{13}C satellite method.



$$\underset{\textbf{2a}}{\mathrm{MeS(\rightarrow O)\text{-}OC(=O)CF_3}} + \mathrm{(PhCH_2S)_2} \longrightarrow \underset{48\%}{\mathrm{MeSO_2SCH_2Ph}} + \underset{18\%}{\mathrm{CF_3CO_2CH_2Ph}} + \underset{11\%}{\mathrm{(PhCH_2S)_2}} + \underset{4\%}{\mathrm{PhCH_2SO_2SCH_2Ph}} \qquad (4)$$

^{13}C contents of the sulfenyl groups in the thiolsulfonate, the disulfide, and the recovered thiolsulfinate are nearly identical. This result can be rationalized only by considering that the sulfenyl groups are pretty well scrambled each other according to the equilibrium between the sulfinyl carboxylate (**2h**) and sulfenyl carboxylate (**5h**) as shown in Scheme 2.

Furthermore, both the sulfinyl group of the recovered thiolsulfinate (**1h**) and the sulfonyl group of the thiolsulfonate (**4h**) did not possess any excess ^{13}C isotope at all, revealing that no reverse reaction from the O-trifluoroacetylated thiolsulfinate (**6**) to the sulfenyl carboxylate (**5h**) did take place.

CONCLUSION

Although the NMR and IR spectral data at room temperature suggest that the equilibrium lies so far toward sulfinyl carboxylates (**2**) and disulfides, the equilibrium mixture of **2** and **5** reacted with such reagents as an olefin or anisole to give the same products as those obtained in the reaction with **5**. Accordingly, **2** is thermodynamically more stable than **5** while the reactivity of **5** is higher than that of **2**. Although characterization of **5** is rather difficult, it can be trapped with such a reagent as an olefin. The formation of sulfinyl carboxylates (**2**) can be confirmed spectroscopically, however, the isolation of **2** from the equilibrium mixture has been unsuccessful because they react so easily with the disulfides which coexist in equilibria, and are very moisture-sensitive substances.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra, unless otherwise noted, were determined as a soln in CCl_4 on a Hitachi 265-50 IR Spectrophotometer. ^{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. Mass spectra were determined on a Hitachi RMU-6MG mass spectrometer. Vpc was carried out on a Hitachi 163 gas chromatograph. A 1 m × 5 mm column of 10% SE-30 on 60 ~ 80 mesh Chromosorb W(AW) was used for analytical purposes.

Thiolsulfinates and the related isotope-labeled compounds were prepared by methods similar to that previously reported.[3]

Reaction of thiolsulfinates (**1**) *with trihaloacetic anhydrides.* A typical procedure is as follows. To a soln of **1d** (155 mg, 0.59 mmol) in CCl_4 (2 ml) at −10° under N_2 or Ar was added trifluoroacetic anhydride (166 mg, 0.31 mmol). After the soln was allowed to stand until the temp of the mixture rose to room temp, the formation of **2d** (50%) and dibenzyl disulfide (50%) was confirmed by NMR and IR spectral data (Table 1). The solvent was removed *in vacuo*. The residue was chromatographed on a silica gel column (Wakogel C-300) using benzene as eluent. Benzyl phenylmethanethiolsulfinate (79 mg, 48%) and dibenzyl disulfide (62 mg, 43%) were collected. Compound **4d**; m.p. 108–110°; ^{1}H NMR(CCl_4): 3.91 (s, 2H), 4.05 (s, 2H) and 7.21 (broad s, 10H); IR(KBr): 1330, 1140 and 1120 cm^{-1} (SO_2). Dibenzyl disulfide (**3d**); m.p. 72°; ^{1}H NMR(CCl_4): 3.50 (s, 2H) and 7.71 (s, 5H). The other compound (**2**) were prepared similarly, and the results are summarized in Table 1. In a similar manner, ^{18}O-(**1g**) or ^{13}C-labeled **1h** was treated with trifluoroacetic anhydride to afford the corresponding dibenzyl disulfide (41–52%), and benzyl phenylmethanethiolsulfonate (18–37%), recovering thiolsulfinate (15–23%). The ^{18}O- and ^{13}C-contents of the products were summarized in Tables 2 and 3, respectively.

Authentic methanesulfinyl trifluoroacetate (**2a**). This compound was prepared by addition of methanesulfinyl chloride (107 mg, 1.1 mol) to silver trifluoroacetate (250 mg, 1.1 mmol) in CCl_4 (5 ml) at 0°.

Reaction of methanesulfinyl trifluoroacetate (**2a**) *with 3,3-dimethyl-1-butene or anisole.* To a soln of **2a** in CCl_4 was added a proper quantity of 3,3-dimethyl-1-butene or anisole at room temp. The reaction was monitored by NMR spectrum. Compound **2a** did not react with 3,3-dimethyl-1-butene, whereas **2a** reacted with anisole to afford di(*p*-methoxyphenyl) sulfide, together with several other unidentified products. The formation of di(*p*-methoxyphenyl) sulfide was confirmed by GC-MS spectrum.

Trapping of methanesulfenyl trifluoroacetate (**5a**) *with 3,3-dimethyl-1-butene.* To a soln of **1a** (367 mg, 3.3 mmol) and 3,3-dimethyl-1-butene (1 ml) in CCl_4 (4 ml) was added trifluoroacetic anhydride (1.23 g, 5.9 mmol) at −20°. The mixture was stirred until the temp rose to room temp. After excess of the anhydride and 3,3-dimethyl-1-butene were removed under reduced pressure, vacuum distillation afforded **8** (1.41 g, 87%), b.p. 104–107°/24 mmHg; ^{1}H NMR(CCl_4) δ: 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); IR (Neat): 1783 (C=O), 1230 and 1165 cm^{-1} (C–O–C and C–F); (Found: C, 44.15; H, 6.15. $C_9H_{15}F_3O_2S$ requires: C, 44.25; H, 6.19%).

Trapping of methanesulfenyl trifluoroacetate (**5a**) *with anisole.* To a soln of **1a** (361 mg, 3.3 mmol) and anisole (1 ml) in CCl_4 (4 ml) was added trifluoroacetic anhydride (1.17 g, 5.6 mmol) at −20°. The colorless soln turned suddenly to green. When the soln was allowed to stand for a day at room temp, the color disappeared. The organic phase was washed with aqueous base, dried ($MgSO_4$), and concentrated *in vacuo*. Vacuum distillation at 68–70° and 3 mmHg afforded methyl *p*-methoxyphenyl sulfide (752 mg, 74%); ^1H NMR(CCl_4) δ: 2.39 (s, 3H), 3.75 (s, 3H), 6.76 and 7.20 (A_2B_2, each 2H, *J* 18.0 Hz); IR (Neat): 2850 (νCH_3), 1250 and 1040 (C–O–C), and 825 cm^{-1} (δCH); MS *m/e*: 154 (11.4, M^+), 153 (Base) and 138 (67.4).

Reaction of 3,3-*dimethyl*-1-*butene with the mixed soln of methanesulfinyl trifluoroacetate* (**2a**) *and dimethyl disulfide.* Compound **1a** (56 mg, 0.51 mmol) was treated with one-thirds equivalent of trifluoroacetic anhydride (40 mg, 0.19 mmol) in CCl_4 (0.5 ml) at −10°. After the formation of **2a** and the disulfide were confirmed by NMR spectrum, 3,3-dimethyl-1-butene was added to the mixed soln at room temp. The reaction was carried out until the **2a** was completely consumed. The yields of the products **8** 71%, methyl methanethiolsulfonate 12%, and dimethyl disulfide 17%) were determined from the NMR spectral data.

Reaction of anisole with a soln containing methanesulfinyl trifluoroacetate (**2a**) *and dimethyl disulfide.* In a similar manner as in the previous experiment an excess of anisole was added to a soln of **2a** and dimethyl disulfide at −10°. After the soln was allowed to stand for a day at room temp, the products were analyzed by gas chromatography and the yields of methyl methanethiolsulfonate, dimethyl disulfide, and methyl *p*-methoxyphenyl sulfide were found to be 52, 26 and 12%, respectively.

Reaction of methanesulfinyl trifluoroacetate (**2a**) *with dibenzyl disulfide.* Compound **2a**, which was prepared by treatment of silver trifluoroacetate (121 mg, 0.55 mmol) with methanesulfinyl chloride (48.9 mg, 0.50 mmol) in CCl_4 (1 ml) at room temp, was allowed to react with dibenzyl disulfide (124 mg, 0.50 mmol). After the reaction was continued overnight at room temp, the yields of benzyl trifluoroacetate (18.5 mg, 18%) and dibenzyl disulfide (13.4 mg, 11%) were determined by gas chromatography. The solvent was evaporated *in vacuo* and the residue was chromatographed on a silica gel column (Wakogel C-300) using the mixed solvent of benzene and hexane as eluent. Benzyl methanethiolsulfonate (47.7 mg, 48%) and benzyl phenylmethanethiolsulfonate (6.3 mg, 4.5%) were collected. Benzyl trifluoroacetate; MS *m/e*: 204 (80.9, M^+), 91 (81.9) and 90 (Base). Benzyl methanethiolsulfonate; oil, ^1H NMR($CDCl_3$) δ: 2.93 (s, 3H), 4.39 (s, 2H) and 7.45 (s, 5H); IR (Neat): 1320 and 1130 cm^{-1} (SO_2).

Methanesulfinyl acetate (**2g**). Silver acetate (385 mg, 2.3 mmol) was treated with methanesulfinyl chloride (210 mg, 2.1 mmol) in CCl_4 (5 ml) at −20°. The mixture was stirred until the temp rose to room temp. After silver chloride was filtered off under N_2, the filtrate was used for the analytical purposes (Table 1). When the solvent was removed *in vacuo*, **2g** was almost completely decomposed and AcOH and methyl methanethiolsulfonate were obtained together with unidentified products. Compound **2h** was also prepared by this procedure.

REFERENCES

[1a] S. Oae, *The Pummerer Rearrangements* in *Topics in Organic Sulfur Chemistry* (Edited by M. Tisler), Chap. 11, Ljubljana (1978); [b]S. Oae, *The Chemistry of Organic Sulfur Compounds* Vol. 2, p. 214. Kagaku Dojin, Kyoto, (1969); [c]G. A. Russell and G. J. Mikol, *Mechanisms of Molecular Migrations* (Edited by B. S. Thyagarajan) Vol. 1, p. 157. Interscience, New York (1968); [d]T. Durst, *Adv. Org. Chem.* **6**, 285 (1969); [e]T. Numata and S. Oae, *J. Org. Synth. Chem. Japan* **35**, 726 (1977); [f]S. Oae and T. Numata, *The Pummerer Rearrangements and Related Reactions*, in *Isotopes in Organic Chemistry* (Edited by E. Buncel and C. C. Lee), Vol. 5, Chap. 2, p. 45 (1980).

[2] I. Saito and S. Fukui, *J. Vitaminol Kyoto* **12**, 244 (1966).

[3] N. Furukawa, T. Morishita, T. Akasaka and S. Oae, *J. Chem. Soc.* Perkin II 432 (1980).

[4a] E. Block, *J. Am. Chem. Soc.* **94**, 642, 644 (1972); [b]E. Block and S. W. Weidman, *Ibid.* **95**, 5046 (1973); [c]E. Block and J. O'Conner, *Ibid.* **95**, 5048 (1973); [d]E. Block and J. O'Conner, *Ibid.* **96**, 3921, 3929 (1974); [e]K. Kondo and A. Negishi, *Chem. Lett.* 1525 (1974).

[5] N. Furukawa, T. Morishita, T. Akasaka and S. Oae, *Tetrahedron Letters* 3973 (1979).

[6a] M. Kobayashi, *Bull. Chem. Soc. Japan* **39**, 967 (1966); [b]K. Schank, *Liebigs Ann. Chem.* **702**, 75 (1967); [c]L. Panizzi and R. A. Nicolaus, *Gazz. chim. Ital.* **80**, 431 (1950); [d]H. Boehme and K. H. Meyer-Dulheuer, *Liebigs Ann. Chem.* **688**, 78 (1965); [e]Y. H. Chiang, J. S. Luloff, and E. Schipper, *J. Org. Chem.* **34**, 2397 (1969); [f]J. G. Kasperek and G. J. Kasperek, *Ibid.* **43**, 3393 (1978).

[7a] I. R. Dunkin and J. G. MacDonald, *J. Chem. Soc.* Chem. Commun. 1020 (1978); [b]E. Tempesti, L. Giuffre, M. Fornaroli, and G. Airoldi, *Chem. Ind.* 183 (1973).

[8a] H. Kohn, P. Charumilind, and S. H. Simonsen, *J. Am. Chem. Soc.* **101**, 5431 (1979); [b]W. Walter, B. Krische, G. Adiwidjaja, and J. Voss, *Chem. Ber.* **111**, 1685 (1978).

[9] S. Oae and M. Kise, *Tetrahedron Letters* 1409 (1967).

[10] J. Drabowicz and S. Oae, *Tetrahedron* **34**, 63 (1978).

[11] A. J. Havlik and N. Kharasch, *J. Am. Chem. Soc.* **78**, 1207 (1956).