Tetrahedron Letters No. 41, pp 3973 - 3976.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/1008-3973$02.00/0

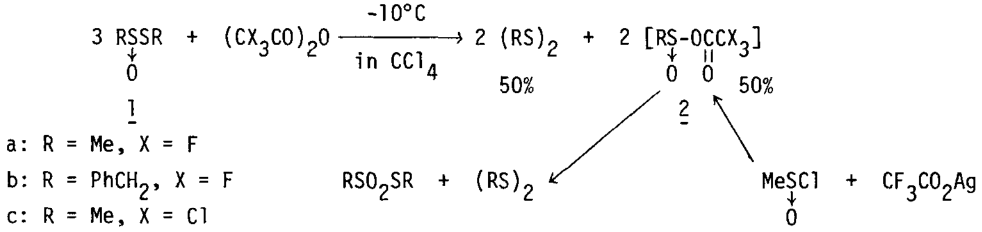
THE REACTION OF THIOLSULFINATES WITH TRIFLUOROACETIC ANHYDRIDE: A CONVENIENT PREPARATION OF β-TRIFLUORO- AND β-TRICHLOROACETOXYSULFIDES.

Naomichi Furukawa, Tsuyoshi Morishita, Takeshi Akasaka and Shigeru Oae

Department of Chemistry, University of Tsukuba, Niihari-gun, Ibaraki 300-31, Japan

Summary: The reaction of thiolsulfinates (1) with trifluoro- or trichloroacetic anhydride gives sulfinyl carboxylates (2) via formation of sulfenyl trihaloacetate (3), which in the presence of olefins, can be trapped to afford β-trifluoro- or β-trichloroacetoxysulfides (5) in good yields.

The Pummerer reaction of sulfoxides with acetic or trifluoroacetic anhydride has been studied extensively.[1)] As to the similar reactions of thiolsulfinates,[2)] the reaction of α-lipoic acid with acetic anhydride is the only reported example of the Pummerer rearrangement.[3)] Recently we found a new rearrangement reaction of thiolsulfinates to yield α-acetylthiosulfoxides by treatment with acetic anhydride.[2b)] As an extention of our studies on the Pummerer and related reactions we now have treated thiolsulfinates with trifluoroacetic anhydride and found a new rearrangement to yield sulfinyl carboxylates (2).[4)] 2 was postulated to be obtained via formation of unstable sulfenyl carboxylates (3) which were successfully trapped with nucleophilic olefins affording the corresponding β-trifluoroacetoxysulfides (5) in high yields. This paper describes this new reaction of thiolsulfinates with trifluoroacetic anhydride and an useful application of these intermediates (3) to organic synthesis.



$$3\ \underset{\underset{O}{\downarrow}}{RSSR} + (CX_3CO)_2O \xrightarrow[\text{in } CCl_4]{-10^\circ C} \underset{50\%}{2\ (RS)_2} + \underset{50\%}{2\ [\underset{\underset{O}{\downarrow}}{RS}\text{-}O\overset{\|}{\underset{O}{C}}CX_3]}$$

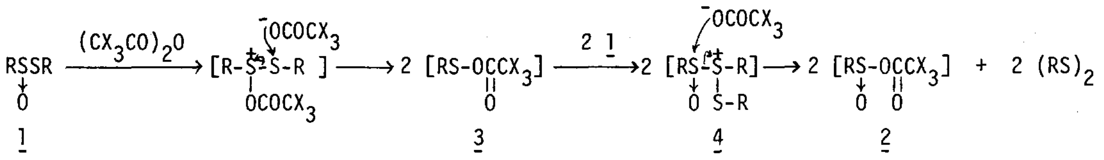
$$2 \rightarrow RSO_2SR + (RS)_2 \qquad \underset{\underset{O}{\downarrow}}{MeSCl} + CF_3CO_2Ag \rightarrow 2$$

1

a: R = Me, X = F
b: R = PhCH$_2$, X = F
c: R = Me, X = Cl

Treatment of methyl methanethiolsulfinate (1a) or benzyl phenylmethanethiolsulfinate (1b) with trifluoro- or trichloroacetic anhydride in carbon tetrachloride at -10°C under an inert atmosphere gave a solution of the mixture (50:50) of the corresponding disulfide and sulfinyl carboxylate (2) which was difficult to be isolated, since evaporation of the solvent converted 2 to the corresponding disulfide and the thiolsulfonate. The pmr spectra of 2 in carbon tetrachloride show a singlet [δ(TMS) 2.98 or 3.09 ppm] for 2a or 2c and two singlets [4.31 and 7.38 ppm] for 2b. The ir spectra (CCl_4) show a C=O absorption at 1790 (2a or 2b) and S→O absorption band at 1110 (2a) or 1100 cm^{-1} (2b). 2a formed in this reaction was also found to be spectroscopically identical to the authentic sample prepared separately by addition of methanesulfinyl chloride to silver trifluoroacetate in carbon tetrachloride.

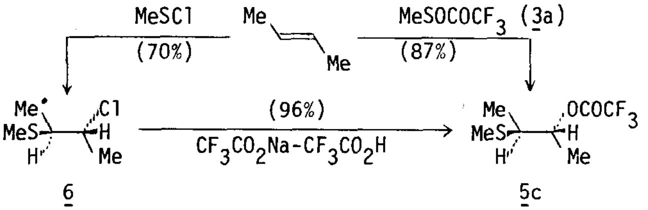
Sulfinyl carboxylates (2) are considered to arise via initial formation of sulfenyl carboxylates (3)⁵⁾ which are very reactive intermediates and react immediately with the starting thiolsulfinates (1) as shown in Scheme 1. Actually, the sulfenyl carboxylates (3) were nicely trapped with olefins$^{5a,b)}$ to give the corresponding β-trifluoroacetoxysulfides (5) in good yields (Table I). 5 can be hydrolyzed readily to afford the corresponding β-hydroxysulfide. Therefore, this is a convenient and versatile method for syntheses of various β-hydroxysulfides. Recently, Trost and his co-workers$^{6)}$ also reported hydroxysulfenylation of olefins with combination of a lead (+4) salt and a disulfide.



Scheme 1

For a typical run, trifluoroacetic anhydride$^{7)}$ (1.17 g, 5.86 mmol) was added at -20°C to a solution of styrene (907 mg, 8.72 mmol) and methyl methanethiolsulfinate (378 mg, 3.43 mmol) in 4 ml of carbon tetrachloride. After the usual work-up, vaccum distillation at 90-95°C / 3 mmHg gave methyl 2-phenyl-2-trifluoroacetoxyethyl sulfide (5a): pmr (δ_{CCl_4}, TMS) 2.08 (s, 3H), 2.84, 3.04 and 6.00 (each 1H) ABX pattern, J_{AB}= 14.7, J_{AX}= 8.0 and J_{BX}= 6.4 Hz, 7.42 (s, 5H) ppm; ir carbonyl frequency at 1780 cm^{-1}. Other examples are summarized in Table I.

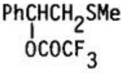
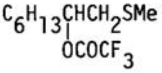
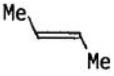
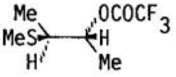
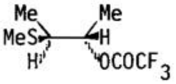
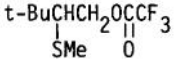
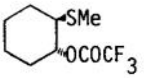
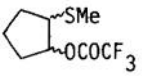
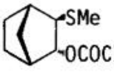
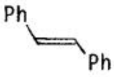
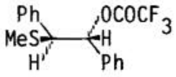
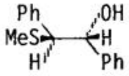
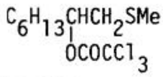
The addition proceeds highly regioselectively and also stereospecifically. Styrene, 1,1-diphenylethylene or 1-octene gave only the Markownikoff addition product but 3,3-dimethyl-1-butene gave an anti-Markownikoff addition product.$^{8)}$ Cis- or trans-2-butene gave either 5c or 5d as a sole product, respectively. The following reactions may establish the stereochemistry of addition of the sulfenyl carboxylate (3), i.e. cis or trans.$^{5a)}$ Thus the erythro-adduct (6)$^{9)}$ of methanesulfenyl chloride to trans-2-butene was treated with sodium trifluoroacetate in trifluoroacetic acid to afford the corresponding erythro-trifluoroacetate (5c) in 96% yield. Similarly, the same trifluoroacetate (5c) was obtained (87% yield) upon addition of methanesulfenyl trifluoroacetate (3a) (which was prepared upon treatment of methyl methanethiolsulfinate with trifluoroacetic anhydride) to the olefin.



The structures of the products prepared by these two different routes were confirmed by pmr and ir spectra. These results demonstrate clearly that the addition of either methanesulfenyl chloride or 3a to trans- or cis-2-butene occurs stereospecifically in a trans manner and that the replacement of the β-chlorosulfide (6) with trifluoroacetate proceeds with retention of configuration around the carbon atom involving neighboring group participation by sulfur.$^{5a)}$ Cyclohexene afforded trans-methyl 2-trifluoroacetoxycyclohexyl

$$\underset{\underline{3}}{[RS\text{-}OCOCX_3]} + R_1R_2C{=}CR_3R_4 \longrightarrow \underset{\underline{5}}{R_1R_2C(SR)\text{-}C(OCOCX_3)R_3R_4}$$

Table I. Reaction of methyl methanethiolsulfinate with anhydrides in the presence of olefins.

olefins	products		yield(%)[a]	SMe[b]	CHS[b]	CHO[b]	$J_{H\text{-}H}$(Hz)	ν_{max}[c]
$PhCH{=}CH_2$	 $Ph\underset{OCOCF_3}{C}HCH_2SMe$	5a	84	2.08	2.84 3.04	6.00	8.0 6.4	1780
$C_6H_{13}CH{=}CH_2$	 $C_6H_{13}\underset{OCOCF_3}{C}HCH_2SMe$	5b	89	2.13	2.69	5.16	6.5	1783
		5c	87	2.12	2.82	5.16	5.8	1780
		5d	87	2.15	2.86	5.22	5.1	1780
$t\text{-}BuCH{=}CH_2$	 $t\text{-}Bu\underset{SMe}{C}HCH_2O\underset{O}{C}CF_3$	5e	95	2.22	2.51	4.51 4.63	6.3 6.3	1783
		5f	72	2.10	2.63	4.91	9.1	1780
		5g	92	2.19	3.10	5.27	d)	1780
	 10)	5h	87	2.09	2.51	4.96	d)	1780
$Ph_2C{=}CH_2$	$Ph_2C{=}CHSMe$	7	73	2.31	6.45	-	-	-
		5j	18[e]	1.75	4.15	5.22	8.7	1780
		8	70[e]	1.80	3.97	5.00	7.5	3340[f]
$C_6H_{13}CH{=}CH_2$	 $C_6H_{13}\underset{OCOCCl_3}{C}HCH_2SMe$	5k	63[e]	2.16	2.68	5.03	6.7	1760

a) Yields were determined by vpc analysis. b) In CCl_4 (ppm). c) Liquid film (cm^{-1}). d) J-Values were not determined. e) Isolated yield. f) OH absorption (KBr).

sulfide (5f) which was identified from the coupling constant (9.1 Hz) of the methine protons at 1- and 2-positions.

1,1-Diphenylethylene gave directly the vinylic sulfide (7)[11] derived by elimination of trifluoroacetic acid from the corresponding β-trifluoroacetoxysulfide (5i). 1,2-Diphenyl-2-

trifluoroacetoxyethyl methyl sulfide (5j) was hydrolyzed readily to afford β-hydroxysulfide (8) during the reaction. Such electron deficient-olefins as methyl acrylate and acrylonitrile did not produce the corresponding adducts under the reaction condition employed.

This reaction has an advantage in that two mole of sulfenyl carboxylate (3) can be generated from one mole of thiolsulfinate stoichiometrically in situ and can be used to react with various reagents before transformation to the stable 2. Further reactions with sulfenyl (3) and sulfinyl carboxylate (2) with various reagents are now undergoing in these laboratories.

References and Notes

1) a) S. Oae, "The Pummerer Rearrangements" in "Topics in Crganic Sulfur Chemistry" edited by M. Tisler, Ljubljana 1978. b) T. Numata and S. Oae, J. Org. Syn. Chem., Japan, 35, 726 (1977).
2) a) E. Block, J. Org. Chem., 39, 734 (1978); b) N. Furukawa, T. Morishita, T. Akasaka and S. Oae, Tetrahedron Lett., 1653 (1977); 1567 (1978).
3) I. Saito and S. Fukui, J. Vitaminol. (Kyoto), 12, 244 (1966).
4) Only one example of the isolation of sulfinyl carboxylates has been reported by Chiang et al.; Y. H. Chiang, J. S. Luloff and E. Schipper, J. Org. Chem., 34, 2397 (1969).
5) a) A. J. Havlik and N. Kharasch, J. Am. Chem. Soc., 78, 1207 (1956); b) R. E. Putnam and W. H. Sharkey, ibid., 79, 6526 (1957); c) D. H. R. Barton, Y. L. Chow, A. Cox and G. W. Kirly, J. Chem. Soc., 3571 (1965); d) L. Field, P. M. Giles, Jr. and D. L. Tuleen, J. Org. Chem., 36, 623 (1971); e) P. A. Bell, D. R. Hogg and A. Robertson, J. Chem. Soc. Perkin I, 1246 (1978).
6) B. M. Trost, M. Ochiai and P. G. McDougal, J. Am. Chem. Soc., 100, 7103 (1978).
7) This reaction was not prevented even in the presence of a small amount of trifluoroacetic acid.
8) Presumably through sterically favorable displacement by trifluoroacetate ion on the episulfonium ion.[10,12]
9) This adduct is erythro-methyl 1-methyl-2-chloropropyl sulfide since the addition of methanesulfenyl chloride to trans-2-butene occurs in a trans manner. N. Kharasch and A. J. Havlik, J. Am. Chem. Soc., 75, 3734 (1953).
10) exo-2-Methylthio-endo-3-trifluoroacetoxynorbornane. See W. H. Mueller and P. E. Butler, J. Am. Chem. Soc., 88, 2866 (1966).
11) a) M. Ohki and K. Kobayashi, Bull. Chem. Soc. Japan, 46, 687 (1973); b) M. Ohki, A. Nakamura and K. Kobayashi, ibid., 46, 3610 (1973).
12) W. H. Mueller, Angew. Chem. Int. Ed. Engl., 8, 482 (1969).

(Received in Japan 8 July 1979)