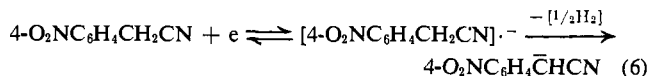


near -0.04 V must arise from the product of anion radical decomposition. Exhaustive, controlled-potential electrolysis of 4-nitrobenzyl cyanide at a potential of -1.5 V *vs.* sce gives an n value of 1 ($n_{\text{expt}} = 1.01$) and a dark, reddish purple solution that contains neither 4,4'-dinitrobenzyl nor 4-nitrotoluene. Since a solution with electrochemical and spectroscopic properties identical with those of the exhaustively electrolyzed solution is obtained by the addition of an equivalent amount of tetraethylammonium hydroxide to a solution of 4-nitrobenzyl cyanide, we conclude that 4-nitrobenzyl cyanide anion radical decomposes with loss of hydrogen to form the stable α -cyano-4-nitrobenzyl anion (eq 6).²¹ Although current reversal



chronopotentiometric and double potential step chronoamperometric studies of the anion radical reveal that decomposition of the anion radical is not a first-order process, neither the decomposition process nor the oxidation of the anion was investigated in greater detail.

Acknowledgment. Support of this work by the National Science Foundation (GP-21316) is gratefully acknowledged.

(21) A. R. Metcalfe and W. A. Waters, *J. Chem. Soc. B*, 918 (1969), also report that 4-nitrobenzyl cyanide behaves as an acid and gives its magenta-colored anion upon electroreduction.

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Received August 16, 1971

The Chemistry of Alkyl Thiolsulfinate Esters. II. Sulfenic Acids from Dialkyl Thiolsulfinate Esters¹

Sir:

Alkanesulfenic acids represent a fundamental yet elusive class of organic sulfur compounds. Postulated as key intermediates in a variety of organic transformations,² the simplest alkanesulfenic acids have not been studied primarily because of difficulty of preparation.³ We wish to report a method of generating and trapping these compounds under relatively mild conditions and present evidence that alkanesulfenic acids play a key role in the chemistry of alkyl thiolsulfinate esters.

In view of the unusual weakness of the thiolsulfinate S-S bond⁴ together with the enhanced acidity of hydro-

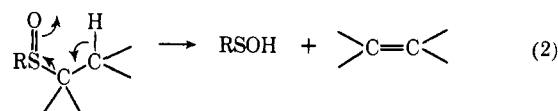
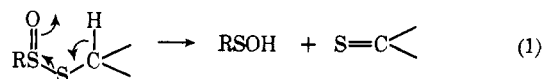
(1) Paper I in this series: R. W. Murray, R. D. Smetana, and E. Block, *Tetrahedron Lett.*, 299 (1971).

(2) See, for example, (a) J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967), *tert*-butylsulfenic acid; (b) J. E. Baldwin, G. Höfe, and S. C. Choi, *ibid.*, **93**, 2810 (1971), allylsulfenic acid; (c) B. C. Pal, M. Uziel, D. G. Doherty, and W. E. Cohn, *ibid.*, **91**, 3634 (1969), pyrimidinesulfenic acids; (d) R. D. G. Cooper, *ibid.*, **92**, 5010 (1970), and D. H. R. Barton, *et al.*, *Chem. Commun.*, 1683 (1970), penicillinsulfenic acids; (e) D. N. Jones, E. Helmy, and A. C. F. Edmonds, *J. Chem. Soc. C*, 833 (1970), D. W. Emerson and T. J. Korniski, *J. Org. Chem.*, **34**, 4115 (1969), and references therein, pyrolysis of sulfoxides.

(3) *tert*-Butylsulfenic acid has been reported.^{2a}

(4) By mass spectrometric appearance potential measurements we have determined the strength of the methyl methanethiolsulfinate S-S bond to be 45 kcal. The similarly determined value for the S-S bond in dimethyl disulfide is 70 kcal: T. F. Palmer and F. P. Lossing, *J. Amer. Chem. Soc.*, **84**, 4661 (1962).

gen on carbon bonded to sulfur, it seemed possible that the elimination reaction depicted in eq 1 might occur under conditions considerably milder than those required for the analogous transformation of alkyl sulfoxides (eq 2).^{5,6} In accord with the reaction



proposed in eq 1, the mass spectra of alkyl thiolsulfinate esters were found to display prominent peaks corresponding to elimination of RSOH, with metastable peaks supporting a direct elimination process.^{8,10}

The intermediacy of alkanesulfenic acids in the pyrolysis of alkyl thiolsulfates was demonstrated by trapping experiments. Thus a mixture of a thiolsulfinate ester and various alkenes or alkynes (in excess), on heating at 96° for 8–16 hr, gave good yields of the sulfenic acid adducts as summarized in Table I. In the case of reactions with methyl alkane-thiolsulfates, RS(O)SCH_3 , a white, highly insoluble solid was also formed, presumably polythioformaldehyde. Depolymerization of this substance in a sublimation apparatus at $200\text{--}210^\circ$ gave a sublimate whose infrared spectrum was indistinguishable from that of authentic 1,3,5-trithiane in the region 3–25 μ . As would be predicted on the basis of the mechanism of eq 1, *tert*-butyl methanethiolsulfinate, $\text{CH}_3\text{S(O)-SC}_4\text{H}_9\text{-}t$,¹¹ failed to react under the above conditions. The stereospecific preparation of α,β -unsaturated sulfoxides utilizing thiolsulfinate esters would appear to be of some synthetic value in view of the relative inaccessibility of the former class of compounds¹² and the ready availability of the latter.¹³ The addition of

(5) For a recent discussion of α elimination in disulfides, see U. Miotti, U. Tonellato, and A. Ceccon, *J. Chem. Soc. B*, 325 (1970).

(6) The thiolsulfinate oxygen is slightly less basic than sulfoxide oxygen as measured by the hydrogen bond strength method.⁷ Thus, the frequency shift of the phenol OH stretching vibration band in the presence of methyl methanethiolsulfinate and ethyl ethanethiolsulfinate is, respectively, 278 and 308 cm^{-1} compared to 360 and 243 cm^{-1} for dimethyl sulfoxide⁷ and methyl methanesulfinate,⁷ respectively.

(7) J. B. F. N. Engberts and G. Zuidema, *Recl. Trav. Chim. Pays-Bas*, **89**, 1202 (1970).

(8) The mass spectra of alkyl sulfoxides reveal a similar fragmentation process. However, recent mass spectral studies with deuterated sulfoxides⁹ indicate a lack of site specificity for hydrogen transfer which contrasts with the well-documented^{2a} thermal β elimination process.

(9) R. Smakman and Th. J. de Boer, *Org. Mass Spectrom.*, **3**, 1561 (1970).

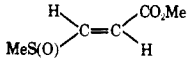
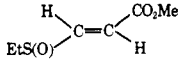
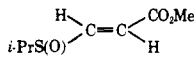
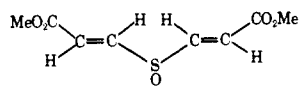
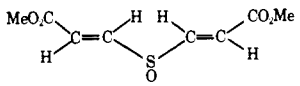
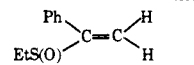
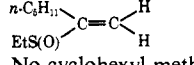
(10) In the mass spectra of $\text{CH}_3\text{S(O)SCH}_3$, $\text{CH}_3\text{S(O)SC}_2\text{H}_5$,¹¹ $\text{C}_2\text{H}_5\text{S(O)SCH}_3$,¹¹ and $\text{C}_2\text{H}_5\text{S(O)SC}_2\text{H}_5$, the intensities (relative to the base peak) of the sulfenic acid fragments (CH_3SOH from the first two and $\text{C}_2\text{H}_5\text{SOH}$ from the last two thiolsulfates) are 91, 91, 70, and 42%, respectively. The mass spectrum of $\text{CH}_3\text{S(O)SCH}_3$ reveals a significant metastable peak at mass number 37.3, as calculated for a direct mass $110 \rightarrow 64$ fragmentation. A detailed discussion of the mass spectra of alkyl thiolsulfates will be presented elsewhere.

(11) All new compounds have been fully characterized by spectroscopic methods and, except in the case of the thermally labile alkyl thiolsulfinate esters, by elemental analysis. Details will be given in the full report.

(12) For recent syntheses of α,β -unsaturated sulfoxides, see G. A. Russell, E. Sobourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966), and G. A. Russell and L. A. Ochrymowicz, *ibid.*, **34**, 3624 (1969).

(13) See ref 1 and also R. W. Murray and S. L. Jindal, *Prepr., Div. Petrol. Chem., Amer. Chem. Soc.*, **16** (4), A72 (1971); T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, **31**, 3587 (1966); G. Zinner and W. Ritter, *Arch. Pharm.*, **296**, 681 (1963); P. Allen, Jr., and J. W. Brook, *J. Org. Chem.*, **27**, 1019 (1962), and references therein.

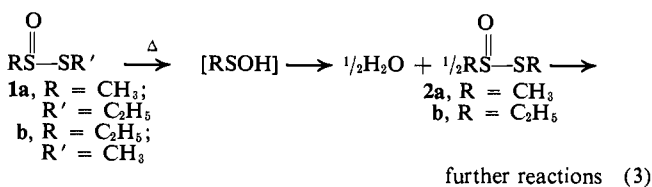
Table I. Reaction of Alkyl Thiolsulfinate Esters with Alkenes and Alkynes

Thiolsulfinate	Coreactant ^a	Product	(Isolated yield, %) ^{f,g}	Nmr (olefinic region) ^b
1. MeS(O)SMe	H ₂ C=CHCO ₂ Et	MeS(O)CH ₂ CH ₂ CO ₂ Et ^e	(90)	
2. MeS(O)SMe	HC≡CCO ₂ Me		(59)	6.60 and 7.72 (each: D, J = 15, 1 H) (1)
3. EtS(O)SEt	HC≡CCO ₂ Me		(67)	6.46 and 7.62 (each: D, J = 15, 1 H) (2)
4. <i>i</i> -PrS(O)SMe ^g	HC≡CCO ₂ Me		(49)	6.47 and 7.55 (each: D, J = 15, 1 H) (2)
			(7) ^e	6.59 and 7.09 (each: D, J = 15, 2 H) (4)
5. <i>t</i> -BuS(O)SMe ^g	HC≡CCO ₂ Me		(46) ^e	6.59 and 7.09 (each: D, J = 15, 2 H) (4)
6. MeS(O) <i>S</i> - <i>t</i> -Bu ^g	HC≡CCO ₂ Me	No reaction		
7. EtS(O)SEt	HC≡CPh		(67)	5.90 and 5.94 (each: S, 1 H) ^d (2) 5.80 and 6.04 (each: S, 1 H) ^d (3)
8. EtS(O)SEt	HC≡CC ₆ H _{11-n}		(33)	5.56 (T, J = 1.3, 1 H) 5.72 (T, J = 0.8, 1 H) (2)
9. MeS(O)SMe	Cyclohexene	No cyclohexyl methyl sulfoxide detectable (complex mixture of >17 products)		

^a Present in about tenfold excess; in run 8, 1-heptyne present in 75-fold excess. ^b Ppm from internal TMS; solvents: (1) CDCl₃, (2) CCl₄, (3) 1:1 CCl₄:C₆D₆, (4) C₆D₆. ^c Reported from pyrolysis of (*tert*-Bu)₂S=O in methyl propiolate;^{2a} no yield given. ^d Singlets are broadened; studies on structurally related α -sulfinylstyrenes indicate a further coupling of 0.6 cps, as expected for the =CH₂ group; *trans*- β -(methylsulfinyl)styrene shows doublets at δ 6.91 and 7.20 with *J* = 15.5 cps.¹² ^e Identical with authentic material. ^f The products were isolated from the reaction mixtures by concentration (*in vacuo*) followed by preparative tlc (silica gel-ethyl acetate) and molecular distillation or, in the case of C₂H₅S(O)CH=CHCO₂CH₃, C₂H₅S(O)C(Ph)=CH₂, and OS(CH=CHCO₂CH₃)₂, by recrystallization from hexane, carbon disulfide, and carbon tetrachloride, respectively. ^g See ref 11.

sulfenic acids to olefins has been considered a reversible thermal six-electron sigmatropic rearrangement.^{2d} Our results indicate an orientational preference akin to that realized for Markovnikov addition to alkynes, making available α,β -unsaturated sulfoxides not readily prepared by known methods.¹²

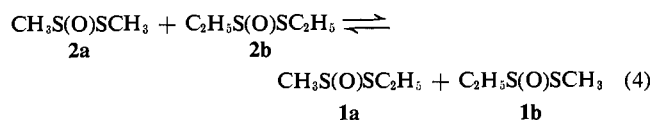
In the absence of unsaturated trapping agents, sulfenic acids are known to dehydrate to thiolsulfonates.^{2a,b} We have observed the transient formation of *symmetrical* thiolsulfonates, in addition to water, during the thermal decomposition of *unsymmetrical* alkyl thiolsulfonates and suggest the involvement of sulfenic acids as represented in eq 3.¹⁴ In addition we



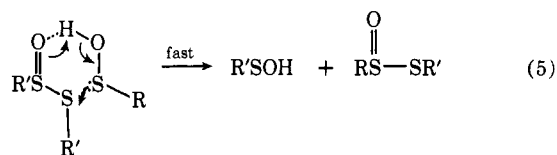
have found that a rapid equilibrium is established on mixing two *different* thiolsulfonate esters resulting in the complete scrambling of the sulfinyl and sulfenyl fragments (eq 4).¹⁵ It is suggested that a slow step

(14) During the decomposition of neat 1a or 1b at room temperature or at 96°, the maximum yield of 2a or 2b detected is about 4%; in the decomposition of *t*-BuS(O)SMe¹¹ yields of *t*-BuS(O)S*t*-Bu as high as 40% may be isolated.

(15) The scrambling reaction 4 occurs in the dark in an inert atmosphere at room temperature or at 96° with neat mixtures or in benzene solution at a rate several orders of magnitude faster than the rate



(eq 1) is followed by a rapid sulfenic acid-thiolsulfonate exchange process as indicated in eq 5.¹⁶ The



fact that the rate of the scrambling reaction is essentially invariant over a thiolsulfonate concentration range of 100 favors the proposed mechanism over a bimolecular process involving two thiolsulfonate molecules.¹⁷ Also supportive of the proposed mechanism is the dramatic catalysis of reaction 4 by added acid, the modest (20%) retardation by added base (2,6-

of disproportionation of thiolsulfonate to give disulfide and thiolsulfonate. A more detailed discussion of reactions 3 and 4 as well as a mechanistic study of the disproportionation of dialkyl thiolsulfonates will be presented elsewhere.

(16) The hydrogen-bonded transition state represented in eq 5 is consistent with our hydrogen bonding studies⁶ and suggestions by others^{2a} on the hydrogen bonding ability of sulfenic acids.

(17) A third mechanistic possibility would involve a radical chain process of the type: RSO· + R'S(O)SR' ⇌ R'SO· + RS(O)SR'. There is, however, no evidence from esr or spin-trapping studies for the involvement of free radicals in this process. We thank Professor M. T. Jones for the esr measurements.

lutidine), and the complete inhibition by added methyl acrylate.

Acknowledgment. We thank Mr. Daniel Kleypas for technical assistance and gratefully acknowledge support from the donors of the Petroleum Research Fund administered by the American Chemical Society (Grants 1153-G and 4109-B), the Air Pollution Control Office, Environmental Protection Agency (AP-1496-01), and the University of Missouri, St. Louis.

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Received September 23, 1971

The Chemistry of Alkyl Thiolsulfinate Esters. III. *tert*-Butanethiosulfoxylic Acid

Sir:

We report here evidence for the formation and trapping of *tert*-butanethiosulfoxylic acid (1), *t*-BuSSOH, the first example of a hitherto unknown class of sulfur oxyacids.¹ In the accompanying paper² we

The unambiguous demonstration of reaction 2 required an alkyl thiolsulfinate devoid of α -sulfonyl protons in order to prevent the occurrence of reaction 1. *tert*-Butyl *tert*-butanethiosulfinate, *t*-BuS(O)SBu-*t* (2), which has recently become readily available,⁶ seemed particularly suitable since we have shown² that *tert*-butyl methanethiosulfinate, CH₃S(O)SC₄H₉-*t*, is un-



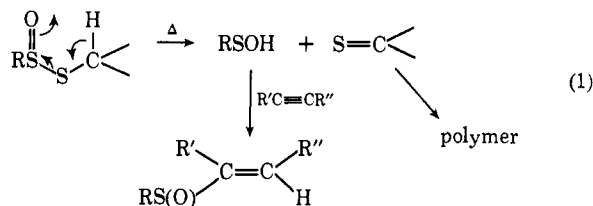
reactive under the pyrolysis-trapping conditions of reaction 1. The intermediacy of *t*-BuSSOH (1) in the pyrolysis of 2 was demonstrated by trapping experiments. Thus, heating solutions of 2 in phenylacetylene (tenfold excess), methyl propiolate (tenfold excess), or 1-heptyne (100-fold excess) at 96–100° for 6–8 hr afforded, respectively, *tert*-butyl alkenylthiosulfonates 3, 4, and 5 as indicated in Table I, in addition to isobutylene. The adducts, all colorless liquids, were isolated by preparative tlc or dry column

Table I. Pyrolysis of *t*-BuS(O)S-*t*-Bu (2) in the Presence of Alkynes

Alkyne (Pyrolysis time, hr)	Products (Isolated yield, %)	Adduct nmr, ppm from TMS; ^a adduct ir, μ
HC≡CPh (7)	 3 (30) ^b	1.50 (S, 9 H, (CH ₃) ₃ CSS(O)-), 6.00 and 6.16 (AB quartet, <i>J</i> = 0.6 cps, 2 H, =CH ₂), 7.30 (S, 6 H, C ₆ H ₅ -); 9.10 (SS=O) and 10.75 (C=CH ₂)
HC≡CCO ₂ CH ₃ (6)	 4 (56) ^c	1.58 (S, 9 H, (CH ₃) ₃ CSS(O)-), 3.75 (S, 3 H, CH ₃ OC(O)-), 6.58 and 7.67 (AB quartet, <i>J</i> = 15 cps, 2 H, <i>trans</i> -RCH=CHR'); 5.79, 6.20, 9.06 (SS=O), and 10.45 (<i>trans</i> -RCH=CHR')
HC≡CC _n H _{11-n} (8)	 5 (21) ^c	0.70–1.90 (mult, 18 H; strong S at 1.60 for (CH ₃) ₃ CSS(O)-), 2.1–2.4 (mult, 2 H, -CH ₂ C=C), 5.64 (T of D, <i>J</i> ₁ for T = 1.2–1.4 cps, <i>J</i> ₂ for D \cong 0.5 cps) and 5.95 (D, <i>J</i> = 0.6 cps, 1 H) (=CH ₂ protons); 6.10 (C=C), 9.14 (SS=O), and 10.8 (C=CH ₂)

^a Solvent is CCl₄; abbreviations used: S = singlet, D = doublet, T = triplet. ^b Gas-phase ir spectrum superimposable on that of authentic isobutylene; yield not determined. ^c No attempt was made to isolate isobutylene.

have described a novel method of generating and trapping *alkanesulfenic acids* under relatively mild conditions through pyrolysis of alkyl thiolsulfonates (eq 1). The possibility of an alternative mode of elim-



ination, shown in general terms in eq 2, finds support in an analogous fragmentation process in the mass spectra of a series of alkyl thiolsulfonates.^{3–5}

(1) (a) The first example of a thiosulfoxylate ester has recently been reported: J. E. Baldwin, G. Höfle, and S. C. Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971). (b) Compounds related to 1 have been invoked as reaction intermediates: N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 236 (1962); L. Field and W. B. Laceyfield, *J. Org. Chem.*, **31**, 3555 (1966).

(2) E. Block, *J. Amer. Chem. Soc.*, **94**, 642 (1972).

(3) In particular, in the mass spectrum of *t*-C₄H₉S(O)SCH₃⁴ the base peak corresponds to CH₃SSOH (P - C₃H₆). There is a significant

chromatography and further purified by molecular distillation. The structural assignments for 3–5 indicated in Table I are fully consistent with the spectral and analytical data.⁷ Thiosulfoxylic acid (1) ap-

metastable peak at *m/e* 66.7 supporting a direct *m/e* 138 → 96 fragmentation. The mass spectra of C₂H₅S(O)SCH₃,⁴ C₂H₅S(O)SC₂H₅, *t*-C₄H₉S(O)SCH₃,⁴ and *t*-C₄H₉S(O)SC₄H₉-*t* also indicate the occurrence of a similar fragmentation process. A detailed discussion of the mass spectra of alkyl thiolsulfonates will be presented elsewhere.

(4) The synthesis and characterization of these previously unreported thiolsulfonates will be reported elsewhere.

(5) For evidence for a lack of site specificity for hydrogen transfer in the analogous mass spectral fragmentation of alkyl sulfoxides, see R. Smakman and Th. J. de Boer, *Org. Mass Spectrom.*, **3**, 1561 (1970).

(6) R. W. Murray, R. D. Smetana, and E. Block, *Tetrahedron Lett.*, 299 (1971); R. W. Murray and S. L. Jindal, *Prepr., Div. Petrol. Chem. Amer. Chem. Soc.*, **16** (4), A72 (1971).

(7) The S=O band in dialkyl thiolsulfonates appears in the infrared at 9.2–9.3 μ while the corresponding band in α,β -unsaturated sulfoxides of the type RS(O)CR'=CHR'' comes at 9.4–9.7 μ .² The *tert*-butyl protons in (CH₃)₃CSS(O)SR appear at δ 1.50,^{1b} and in (CH₃)₃CSS(O)-CH₃ at δ 1.56; the *tert*-butyl protons in (CH₃)₃CS(O)-SCH₃ appear at δ 1.38 while other systems containing the (CH₃)₃CS(O)-C grouping have singlets at δ 1.20–1.30; the bands at δ 1.32 and 1.53 in the nmr spectrum of *tert*-BuS(O)SBu-*tert* (2) may be assigned respectively to the (CH₃)₃-CS(O) and (CH₃)₃CSS(O) protons. The assignment of double bond stereochemistry is consistent with known values⁸ for olefinic coupling constants (*gem*-vinyl 0.5–3.5, *cis* 6–14, *trans* 11–18 cps). The mass spectrum of 3 had ions at *m/e* 240 (parent = C₁₂H₁₆S₂O), 152 (P - C₄H₈S), and prominent fragments at *m/e* 103, 102, 77, 54, and 41 (base) while 4