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

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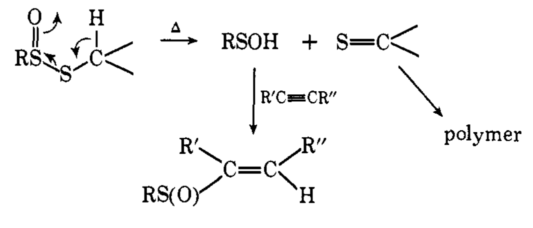
The Chemistry of Alkyl Thiolsulfinate Esters. III. *tert*-Butanethiosulfoxylic Acid

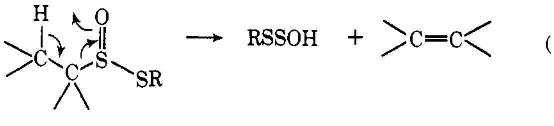
Sir:

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 paper[2] we have described a novel method of generating and trapping *alkanesulfenic acids* under relatively mild conditions through pyrolysis of alkyl thiolsulfinates (eq 1). The possibility of an alternative mode of elimination, shown in general terms in eq 2, finds support in an analogous fragmentation process in the mass spectra of a series of alkyl thiolsulfinates.[3-5]



(1)

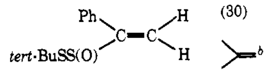
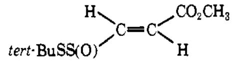
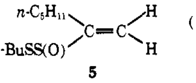
The unambiguous demonstration of reaction 2 required an alkyl thiolsulfinate devoid of α-sulfenyl protons in order to prevent the occurrence of reaction 1. *tert*-Butyl *tert*-butanethiolsulfinate, *t*-BuS(O)SBu-*t* (**2**), which has recently become readily available,[6] seemed particularly suitable since we have shown[2] that *tert*-butyl methanethiolsulfinate, $CH_3S(O)SC_4H_9$-*t*, is unreactive under the pyrolysis–trapping conditions of reaction 1.



(2)

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 alkenylthiolsulfinates **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 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-

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, $(CH_3)_3CSS(O)$–), 6.00 and 6.16 (AB quartet, J = 0.6 cps, 2 H, $=CH_2$), 7.30 (S, 6 H, C_6H_5–); 9.10 (SS=O) and 10.75 ($C=CH_2$)
$HC≡CCO_2CH_3$ (6)	 **4** (56)[c]	1.58 (S, 9 H, $(CH_3)_3SS(O)$–), 3.75 (S, 3 H, $CH_3OC(O)$–), 6.58 and 7.67 (AB quartet, J = 15 cps, 2 H, *trans*-RCH=CHR'); 5.79, 6.20, 9.06 (SS=O), and 10.45 (*trans*-RCH=CHR')
$HC≡CC_5H_{11}$-*n* (8)	 **5** (21)[c]	0.70–1.90 (mult, 18 H; strong S at 1.60 for $(CH_3)_3CSS(O)$–), 2.1–2.4 (mult, 2 H, $-CH_2C=C$), 5.64 (T of D, J_1 for T = 1.2–1.4 cps, J_2 for D ≅ 0.5 cps) and 5.95 (D, J = 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 CCl_4; 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.

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(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. Lacefield, *J. Org. Chem.*, **31**, 3555 (1966).

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

(3) In particular, in the mass spectrum of *i*-$C_3H_7S(O)SCH_3$[4] the base peak corresponds to CH_3SSOH (P − C_3H_6). There is a significant metastable peak at *m/e* 66.7 supporting a direct *m/e* 138 → 96 fragmentation. The mass spectra of $C_2H_5S(O)SCH_3$,[4] $C_2H_5S(O)SC_2H_5$, *t*-$C_4H_9S(O)SCH_3$,[4] and *t*-$C_4H_9S(O)SC_4H_9$-*t* also indicate the occurrence of a similar fragmentation process. A detailed discussion of the mass spectra of alkyl thiolsulfinates will be presented elsewhere.

(4) The synthesis and characterization of these previously unreported thiolsulfinates 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 thiolsulfinates 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 $(CH_3)_3CSS(O)SR$ appear at δ 1.50,[1b] and in $(CH_3)_3CSS(O)$-CH_3 at δ 1.56; the *tert*-butyl protons in $(CH_3)_3CS(O)$–SCH_3 appear at δ 1.38 while other systems containing the $(CH_3)_3CS(O)$–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 $(CH_3)_3$-CS(O) and $(CH_3)_3CSS(O)$ protons. The assignment of double bond stereochemistry is consistent with known values[8] 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 = $C_{12}H_{16}S_2O$), 152 (P − C_4H_8S), and prominent fragments at *m/e* 103, 102, 77, 54, and 41 (base) while **4**

parently adds to alkynes with the same Markovnikov-type orientational preference exhibited by alkanesulfenic acids.[2]

Pyrolysis of neat **2** at 96° for 7 hr gave isobutylene in 45% isolated yield,[9] water, di-*tert*-butyl polysulfides (disulfide, trisulfide, and tetrasulfide, in molar ratios of *ca.* 1:6:6, representing 44 mol % of isolated products; characterized through comparison with authentic materials), and a colorless, waxy solid identified as *t*-BuSO$_2$SSBu-*t* (**6**; 7 mol % of isolated products).[10] Decomposition of dilute (10^{-2} *M*) solutions of **2** in heptane at 75° and 96° gave good unimolecular kinetics for the disappearance of **2**.

The pyrolysis of di-*tert*-butyl sulfoxide is reported to give *tert*-butanesulfenic acid, *t*-BuSOH, and this latter compound is said to dehydrate to thiolsulfinate **2** (eq 3 and 4).[11] Our results indicate that **2** on pyrolysis may also undergo elimination of isobutylene giving a compound which, on the basis of trapping studies (the results of which closely parallel analogous studies with alkanesulfenic acids[2])[11] and by analogy to the elimination reaction of eq 3, may be formulated as *tert*-butanethiosulfoxylic acid, *t*-BuSSOH (**1**; eq 5). The isolation of water from the pyrolysis of **2** suggests that *t*-BuSSOH may also undergo an intermolecular dehydration (eq 6) analogous to *t*-BuSOH (eq 4) affording sulfinyl compound **7**, which may be a precursor to the observed pyrolysis products of **2**.[12,13]

$$t\text{-BuS(O)Bu-}t \xrightarrow{\Delta} t\text{-BuSOH} + (CH_3)_2C{=}CH_2 \tag{3}$$

$$2t\text{-BuSOH} \longrightarrow \underset{\mathbf{2}}{t\text{-BuS(O)SBu-}t} + H_2O \tag{4}$$

$$\underset{\mathbf{2}}{t\text{-BuS(O)SBu-}t} \xrightarrow{\Delta} \underset{\mathbf{1}}{t\text{-BuSSOH}} + (CH_3)_2C{=}CH_2 \tag{5}$$

$$\underset{\mathbf{1}}{2t\text{-BuSSOH}} \longrightarrow \underset{\mathbf{7}}{t\text{-BuSS(O)SSBu-}t} + H_2O \tag{6}$$

Finally, our results in this and the preceding paper may offer an explanation for the particularly effective inhibitory action of **2** and other dialkyl thiolsulfinates on the reaction of squalene with oxygen and on certain autoxidation processes.[14] From the data of Barnard,[14] it appears that the inhibitory action of **2** at 75° directly parallels the thermal formation of thiosulfoxylic acid **1** from thiolsulfinate **2** (eq 5); a similar parallel would appear to exist between the inhibitory action of alkyl thiolsulfinates possessing α-sulfenyl protons and the production of alkanesulfenic acids according to eq 1. We suggest that sulfenic and thiosulfoxylic acids, thermally produced from alkyl thiolsulfinates according to eq 1 and 2, are the active antioxidants, rather than the thiolsulfinates themselves.[15,16]

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had ions at *m/e* 222 (C$_8$H$_{14}$S$_2$O$_3$, parent), 166 (P − C$_4$H$_8$), 134 (P − C$_4$H$_8$S), 89, 57 (base), and 41. Compound **5** had uv λ_{max} (ethanol) at 261 nm (ε 2960). *Anal.* Calcd for **3**, C$_{12}$H$_{16}$S$_2$O: C, 59.96; H, 6.71; S, 26.68. Found: C, 59.39; H, 6.66; S, 26.90. Calcd for **4**, C$_8$H$_{14}$S$_2$O$_3$: C, 43.22; H, 6.35; S, 28.84. Found: C, 43.99; H, 6.46; S, 29.04. Calcd for **5**, C$_{11}$H$_{22}$S$_2$O: C, 56.36; H, 9.46. Found: C, 56.82; H, 9.84.

(8) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(9) Constituted 49 mol % of isolated products; gas-phase ir spectrum superimposable on that of authentic isobutylene.

(10) Compound **6** had mp 56–60° after recrystallization from pentane; nmr (CCl$_4$) had singlets of equal integrated areas at δ 1.42 and 1.47, precluding a symmetrical (RS)$_2$SO$_2$ structure; ir spectral bands at 7.64 and 9.00 μ (sulfonyl group). Parent ion in mass spectrum at *m/e* 242. *Anal.* Calcd for C$_8$H$_{18}$S$_3$O$_2$: C, 39.63; H, 7.48. Found: C, 39.78; H, 7.55.

(11) J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967).

(12) Various cross dehydration products involving *tert*-butanesulfenic acid and *tert*-butanethiosulfoxylic acid (**1**) may also be formed during the pyrolysis of di-*tert*-butyl sulfoxide.

(13) See J. L. Kice, *Accounts Chem. Res.*, 1, 58 (1968), for a discussion of electrophile–nucleophile catalyzed reactions of thiolsulfinates and related sulfinyl compounds leading to products at the disulfide and thiolsulfonate oxidation states. Also see ref 1b.

(14) D. Barnard, L. Bateman, and J. I. Cunneen, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, Chapter 21; D. Barnard, L. Bateman, M. E. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 5339 (1961); L. Bateman, M. Gain, T. Colclough, and J. I. Cunneen, *ibid.*, 3570 (1962).

(15) It is possible that a fraction of the antioxidant activity of alkyl thiolsulfinates may reflect direct interaction of the thiolsulfinate with peroxy radical or hydroperoxides, as suggested by Barnard.[14] In the case of *t*-BuS(O)SBu-*t*, however, direct interaction is unfavorable on steric grounds.

(16) A similar suggestion has recently been advanced to explain the antioxidant activity of di-*tert*-butyl sulfoxide and sulfinyldipropionate esters: G. Scott, *Mech. React. Sulfur Compounds*, **4**, 99 (1969); C. Armstrong and G. Scott, *J. Chem. Soc. B*, 1747 (1971).

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Synthesis and Structure of Some Novel Transition Metal Arylazo Complexes Involving Metal–σ-Carbon Bonds

Sir:

Despite the formal analogy between the electronic structures of the nitrosonium (N≡O$^+$) and aryldiazonium (ArN≡N)$^+$ ions, the reactions of the latter with transition metal complexes are providing an increasing assortment of novel products,[1–3] several of which are of current interest in connection with the use of the aryldiazonium function as a model for complexed dinitrogen in the nitrogen fixation process. We have already commented[3] on the synthesis of an iridium–tetrazene complex from one such reaction, and now wish to report the structure of a further novel product obtained from the same reaction.

Deeming and Shaw[4] showed that [IrCl(CO)(PPhMe$_2$)$_2$] would oxidatively add C$_6$H$_5$N$_2$$^+BF_4$$^-$ in the presence of LiCl to give [IrCl$_2$(C$_6$H$_5$N$_2$)(CO)(PPhMe$_2$)$_2$]. However, the reaction of [IrCl(CO)(PPh$_3$)$_2$] with (*p*-X-C$_6$H$_4$N$_2$)$^+$BF$_4$$^-$ (X = F, Br) in benzene–ethanol, in the absence of LiCl does not result in the salt [IrCl(*p*-X-C$_6$H$_4$N$_2$)CO(PPh$_3$)$_2$]$^+$BF$_4$$^-$ (**1**) even though the corresponding nitrosyl complex is easily obtained when NO$^+$BF$_4$$^-$ is employed. Instead, red crystals of the iridium–tetrazene complex crystallize from the deep red solution.[3] We repeated the reaction, this time removing solvent by freeze drying before crystallization

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(1) G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967).

(2) L. Toniolo and R. Eisenberg, *Chem. Commun.*, 455 (1971).

(3) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **93**, 1826 (1971).

(4) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969).