It is seen that this relation is much simpler than that obtained in ref 5.

Using the polar substituent constants, σ^*, one obtains a correlation from which it is found

$$E_{RSH} = E_{MeSH} + a^*\sigma^* = 9.44 + 2.08\sigma^* \qquad (2)$$

These correlations indicate that the effect of alkyl substituents on the S atom is primarily an inductive one.

In the last two columns of Table I we show a comparison between the experimental ionization energies and those calculated using eq 1a and 2. The agreement is excellent. A calculated value is also given for Me_2CHSH for which an experimental value has not yet been obtained.

The a_I and the a^* constants are, of course, analogous to the reaction constants ρ_I and ρ^*, and are a measure of the susceptibility of the reaction site (the S atom) to substituent effects. The a_I value of 22.2 obtained here may be compared to those observed in the correlation of E_I's of alcohols[2] (a_I = 37.5) and for ethers[3] (a_I = 28.0). These comparisons show that the S atom is considerably less sensitive to inductive effects than is the O atom, probably due to the larger radius of the S atom.

Registry No.—Hydrogen sulfide, 7783-06-4; methanethiol, 74-93-1; ethanethiol, 75-08-1; 1-propanethiol, 107-03-9; 1-butanethiol, 109-79-5; 2-propanethiol, 75-33-2; 2-methyl-2-propanethiol, 75-66-1.

Silver-Assisted Displacements on Sulfur. A New Thiolsulfonate Ester Synthesis

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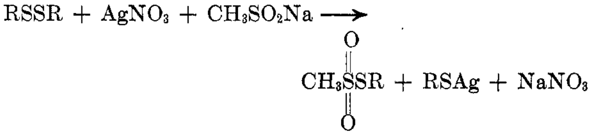
Kice[2,3] has recently described the dramatic effects of cooperative electrophilic–nucleophilic assistance in scission of sulfur–sulfur bonds. In the present paper, we report a probable member of this mechanistic class, the facile cleavage of alkyl disulfides by silver nitrate and sodium methanesulfinate to produce thiolsulfonate esters in high yield.

We have found that addition of a solution of silver nitrate in aqueous acetone to a solution of equivalent quantities of sodium methanesulfinate and alkyl disulfide in the same solvent leads to rapid formation of thiol ester and insoluble silver alkylmercaptide according to eq 1.

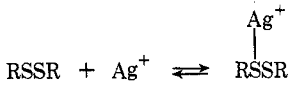


$$RSSR + AgNO_3 + CH_3SO_2Na \longrightarrow CH_3\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}SR + RSAg + NaNO_3 \qquad (1)$$

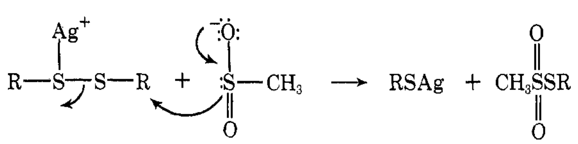
$R = CH_3, C_2H_5$, or $(CH_3)_2CH$

In the case of di-*tert*-butyl disulfide, the corresponding thiol ester was not obtained after heating the reaction mixture under reflux either 2 hr in aqueous acetone or 4 hr in aqueous dioxane. A black silver sulfide precipitate slowly formed and isobutylene was detected in the gas phase above the reaction mixture. The large steric factor associated with the *tert*-butyl groups apparently prevents nucleophilic displacement by the methanesulfinate anion and elimination slowly occurs instead.

Although we have not yet applied kinetic techniques to elucidate the mechanism of this reaction, it seems reasonable to postulate that the transformation is initiated by silver ion–disulfide complex formation followed by nucleophilic displacement on sulfur (eq 2, 3).



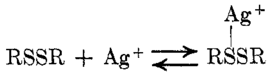
$$RSSR + Ag^+ \rightleftharpoons R\overset{Ag^+}{\overset{|}{S}}SR \qquad (2)$$



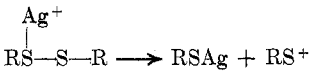
(3)

The disulfide sulfur on which the attack occurs would be rendered more electrophilic by metal ion coordination by the adjacent sulfur, while the very insoluble silver mercaptide would become an effective leaving group.

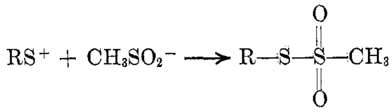
An alternate pathway (eq 4–6) is not ruled out, but



$$RSSR + Ag^+ \rightleftharpoons R\overset{Ag^+}{\overset{|}{S}}SR \qquad (4)$$



$$R\overset{Ag^+}{\overset{|}{S}}—S—R \longrightarrow RSAg + RS^+ \qquad (5)$$

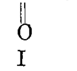


$$RS^+ + CH_3SO_2^- \longrightarrow R—S—\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}—CH_3 \qquad (6)$$

seems less likely since there was no evidence of alkanesulfenic acid formation (*i.e.*, disproportionation products) which should occur by competitive nucleophilic attack on the sulfenium ion by water.

The isolation of solid silver nitrate–alkyl disulfide complexes has been reported.[4] In several instances, we have observed formation of a white precipitate, probably the disulfide complex, which rapidly disappeared with formation of the yellow alkyl mercaptide. The silver mercaptides, identified by gas chromatography of the mercaptans formed by acidification of the salts with concentrated HCl, were formed quantitatively and there was no evidence for the presence of silver ion–disulfide complex in the final product mixtures.

It is significant that no alkyl sulfenylmethanesulfinates (I) could be detected as products of our reac-



$$RSO\underset{O}{\underset{\|}{S}}CH_3$$

I

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[1] Author to whom correspondence should be addressed.

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tions. These would have occurred *via* nucleophilic displacement by sulfinate oxygen, rather than sulfinate sulfur, on the silver ion–disulfide complex. This observation is consistent with the recent study of Meek and Fowler[5] on alkylation of the ambident *p*-toluenesulfinate anion, where it was shown that alkylation with hard alkylating agents yielded esters while similar reaction with soft alkylating agents resulted in sulfone formation.

Experimental Section

Methyl Methanethiolsulfonate.—To a solution of dimethyl disulfide [0.5 g, 0.0053 mol, bp 108° (1 atm)] in 20 ml of 75% acetone–water was added a solution of silver nitrate (Fisher-ACS, 0.99 g, 0.00585 mol) and sodium methanesulfinate[6,7] (0.542 g, 0.0053 mol) in 20 ml of water. A bright yellow precipitate formed immediately. The mixture was stirred at room temperature for 30 min and the silver methylmercaptide was separated by suction filtration. The filtrate was diluted with water and extracted with several portions of ether. The combined ethereal extracts were dried over sodium sulfate and the ether was evaporated under reduced pressure to yield a colorless oil (0.63 g, 94%) whose ir and nmr spectra were identical with those of authentic methyl methanethiolsulfonate. In addition, the compound exhibited a parent peak in the mass spectrum at *m/e* 126 and was also shown to be pure by gas chromatography on a 6 ft Triton-X305 column at 160°.

Ethyl Methanethiolsulfonate.—To a solution of 2.44 g (0.02 mol) of diethyl disulfide in 75 ml of a 50% aqueous acetone solution was added 75 ml of a 50% aqueous acetone solution containing 4.25 g (0.025 mol) of silver nitrate and 2.53 g (0.025 mol) of sodium methanesulfinate. A white precipitate formed immediately. The mixture was brought to reflux temperature and the precipitate rapidly became bright yellow. Heating at reflux was continued for 4 hr and the product mixture was filtered. The cooled filtrate was extracted several times with ether and the combined ethereal extracts were dried (Na_2SO_4) and evaporated to yield 2.6 g (93%) of a colorless oil whose nmr spectrum in $CDCl_3$ (δ 3.37, s, 3 H; 3.21, q, J = 7.5 Hz, 2 H; 1.45 t, J = 7.5 Hz, 3 H) was consistent with that expected for pure ethyl methanethiolsulfonate. The distilled ester, bp 101° (4 mm), had a refractive index, $n^{25}{}_D$ 1.5005. The mass spectrum showed a parent peak at *m/e* 140 and the ir spectrum exhibited strong absorptions at 1310, 1130, 955, and 750 cm^{-1}. *Anal.* Calcd for $C_3H_8O_2S_2$: C, 25.76; H, 5.75; S, 45.74. Found: C, 25.88; H, 5.72; S, 45.88.

Isopropyl Methanethiolsulfonate.—The procedure used was similar to that described for ethyl methanethiolsulfonate with the modification that the mixture was heated under reflux for 6 hr. From 3.0 g (0.02 mol) of diisopropyl disulfide (K and K) was obtained 2.5 g of product whose nmr in $CDCl_3$ (δ 1.47, d, J = 7 Hz, 6 H; 3.32, s, 3 H; 3.70, h, J = 7 Hz, 1 H) was consistent with that expected for isopropyl methanethiolsulfonate. The ester, distilled at 102° (5 mm), exhibited a refractive index ($n^{25}{}_D$) of 1.4910. The ir spectrum (neat) consisted of strong absorptions at 2980, 2940, 1320, 1130 ,1055, and 750 cm^{-1}, and the mass spectrum exhibited a parent peak at *m/e* 154. *Anal.* Calcd for $C_4H_{10}O_2S_2$: C, 31.14; H, 6.53; S, 41.58. Found: C, 31.23; H, 6.54; S, 41.71.

Registry No.—Methyl methanethiolsulfonate, 2949-92-0; ethyl methanethiolsulfonate, 2043-76-7; isopropyl methanethiolsulfonate, 32846-80-3; silver nitrate, 7761-88-8; sodium methanesulfinate, 20277-69-4.

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Synthesis of *N*-Fluoronitramines[1]

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Little work has been reported on the synthesis and reactions of *N*-halo-*N*-nitro amine derivatives. *N,N'*-Dichloro-*N,N'*-dinitro-1,2-ethylenediamine, isolated by Smart and Wright[2] in 1948, remained the sole example of this class of compounds until the recently reported synthesis of simple *N*-chloro-*N*-nitroalkylamines by the chlorination of aqueous salts of alkylnitramines.[3] The synthesis of *N*-chloro-*N*-nitrocarbamates by this method was reported by Thomas[4] in 1955. *N*-Bromo-*N*-nitro amine derivatives have not been reported. *N*-Chloro-*N*-nitro amines and *N*-chloro-*N*-nitrocarbamates are explosive compounds[2] and decompose rapidly on storage.[4]

We have synthesized *N*-fluoro-*N*-nitrobutylamine, the first *N*-fluoronitramine, by two independent, generally applicable procedures. The compound was obtained in 84% yield in the fluorination of aqueous alkali salts of butylnitramine under reaction conditions similar to those employed in the fluorination of aqueous nitronate salts[5] and carboxylic acid salts (eq 1).[6] The

$$C_4H_9NNO_2^-K^+ + F_2 \longrightarrow C_4H_9NFNO_2 + KF \quad (1)$$

compound was characterized by elemental analysis as well as infrared and nmr spectra. Its fluorine nmr spectrum exhibited a triplet at ϕ −1.10. *N*-Fluoro-*N*-nitrobutylamine was stored at room temperature for several months without apparent decomposition. On the other hand, in one instance a sample of the compound exploded on distillation at 60°. This method of preparation of *N*-fluoro-*N*-nitro amines is of general utility. Graff, *et al.*,[7] used our general procedure[8] to synthesize other *N*-fluoronitramines for thermal stability studies.

N-fluoro-*N*-nitrobutylamine was also synthesized by treating methyl *N*-butyl-N-fluorocarbamate with 100% nitric acid (eq 2). Since *N*-alkyl-*N*-fluorocarbamates

$$C_4H_9NFCOOCH_3 + HNO_3 \longrightarrow C_4H_9NFNO_2 + CO_2 + CH_3ONO_2 \quad (2)$$

are readily available by the fluorination of alkylcarbamates,[9] this route to *N*-fluoro-*N*-nitro amines is also of general synthetic utility.

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