talline hydrochloride, mp 298-300° dec (lit.[7] mp 300° dec), $[\alpha]^{25}\mathrm{D}$ (EtOH) +207°.

(+)-Nandigerine (10) from (+)-*N*-Methylnandigerine (8).—The usual conditions afforded **10** (22% from **8**), isolated as the crystalline hydrochloride, mp 242-245° dec (lit.[7] mp 245-247° dec), $[\alpha]^{25}\mathrm{D}$ (EtOH) +240°.

(+)-Hernovine (11) from (+)-*N*-Methylhernovine (9).—The usual conditions afforded **11** (18% from **9**) as crystals, mp 235-237° dec (lit.[7] mp 236-240° dec), $[\alpha]^{25}\mathrm{D}$ (EtOH) +253°.

Reaction of *N*-Oxide 2 with Sulfur Dioxide in Methanol-Benzene.—Dried *N*-oxide **2** (50 mg) was dissolved in 1:1 methanol-benzene (20 ml) and SO_2 was passed into the mixture for 0.5 hr. Aqueous hydrochloric acid (2 *N*, 10 ml) was added and the solution was refluxed for 3 hr. Basification with ammonia, followed by chloroform extraction, gave a crude product (40 mg), shown by tlc to contain only nuciferine (**1**) and nornuciferine (**3**). Chromatography on neutral alumina gave **1** (25 mg) and **3** (10 mg).

The above experiment was repeated, with the modification that the *N*-oxide SO_2 complex was refluxed not with acid, but with 5% aqueous sodium hydroxide. Preparative tlc (2% MeOH in $CHCl_3$, Al_2O_3) gave **1** (38 mg), **3** (18 mg), and dehydronuciferine (12, 25 mg).

Registry No.—**3**, 32557-14-5; **4**, 25394-59-6; **7**, 6410-87-3; **10**, 5544-70-7; **11**, 5544-69-4.

Acknowledgment.—We thank the National Institutes of Health for a grant (CA 11445) in support of this work.

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[7] M. P. Cava, K. Bessho, B. Douglas, S. Markey, R. F. Raffauf, and J. A. Weisbach, *Tetrahedron Lett.*, 1577 (1966).

Inductive Effects on Molecular Ionization Potentials. IV. Hydrogen Sulfide and Mercaptans

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Received June 17, 1971

The ionization potentials of alkyl free radicals, R·, have been correlated[1] with the polar substituent constants, σ^*, and we have shown recently that the ionization energies of alcohols,[2] ethers,[3] and amines[4] are linear functions of both σ^* and the inductive substituent constants, σ_{I}.

We now demonstrate that the ionization energies of thiols, RSH, are also linear functions[5] of both σ^* and σ_{I}. The gas-phase expulsion of an electron from the nonbonding lone pair on the sulfur atom of a mercaptan molecule is in accord with the equation

$$\mathrm{R{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}{-}H} \xrightarrow{E_{\mathrm{I}}} \mathrm{R{-}\underset{\cdot\cdot}{\overset{\cdot +}{S}}{-}H} + e^-$$

and the ionization potential, E_{I}, of course, corresponds approximately to the energy of the highest occupied molecular orbital.[6-8] The entire chemistry of thiols, in fact, is dependent upon the behavior of the 3p sulfur lone pair electrons. Electron-releasing alkyl groups bonded to the S atom of a thiol molecule should obviously facilitate the electron removal, and thereby lower the E_{I}; and the presence of electron-withdrawing groups should likewise cause an increase in the requisite ionization energy.[9] It is interesting that we are able to include hydrogen sulfide as the simplest thiol in the series.

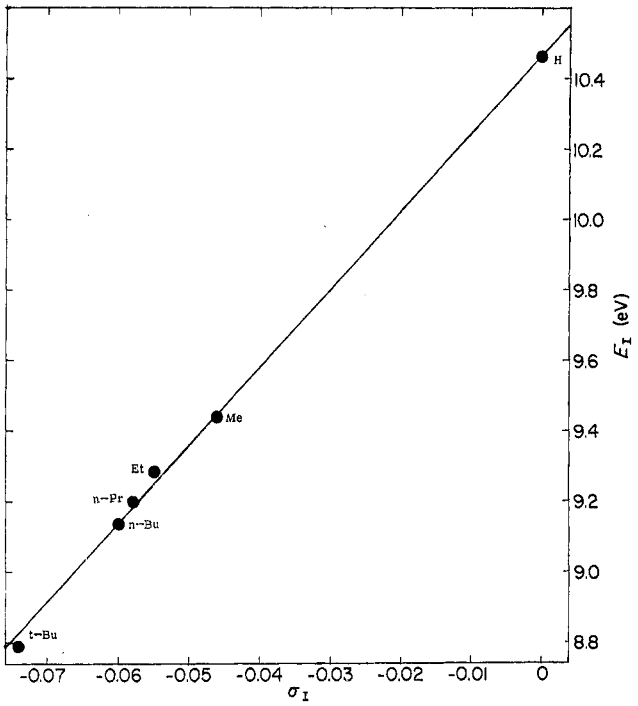

Figure 1.—A plot of ionization potentials, E_{I}, of the thiols *vs.* the inductive substituent constants, σ_{I}, of the corresponding R groups.

Table I presents the σ^* and the σ_{I}[10] values together with the photoionization potentials[11] (eV) for various aliphatic mercaptans and hydrogen sulfide.

Table I

Thiol	σ^*	σ_{I}	E_{I}, eV (exptl)[a]	E_{I}, eV (eq 1a)	E_{I}, eV (eq 2)
H_2S	+0.49	0	10.46	10.46	10.46
MeSH	0	−0.046	9.44	9.45	9.44
EtSH	−0.10	−0.055	9.29	9.25	9.24
n-PrSH	−0.12	−0.058	9.20	9.18	9.17
n-BuSH	−0.13	−0.060[b]	9.14	9.14	9.13
i-PrSH	−0.19	−0.064	*c*	9.05	9.04
tert-BuSH	−0.30	−0.074	8.79	8.77	8.81

[a] Reference 11. [b] Value suggested in ref 3. [c] Experimental value not available.

An excellent correlation is shown in Figure 1 where the E_{I} values are plotted *vs.* σ_{I}. The equation for the correlation line is given by

$$E_{\mathrm{RSH}} = E_{\mathrm{H_2S}} + a_{\mathrm{I}}\sigma_{\mathrm{I}} \tag{1}$$

The slope, a_{I}, is found to be 22.2 and therefore we have

$$E_{\mathrm{RSH}} = 10.46 + 22.2\sigma_{\mathrm{I}} \tag{1a}$$

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[1] A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **1**, 1 (1963).

[2] L. S. Levitt and B. W. Levitt, *Chem. Ind. (London)*, 990 (1970).

[3] B. W. Levitt and L. S. Levitt, *Experientia*, **26**, 1183 (1970).

[4] B. W. Levitt and L. S. Levitt, *Israel J. Chem.*, **9**, 71 (1971).

[5] The ionization potentials of X-SH have been correlated with the three-parameter extended Hammett equation: $E_{\mathrm{I}} = 3.22\sigma_{\mathrm{I}} + 9.06\sigma_{\mathrm{R}} + 10.37$ [M. Charton and B. I. Charton, *J. Org. Chem.*, **34**, 1882 (1969)].

[6] R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

[7] T. Koopmans, *Physica*, **1**, 104 (1933).

[8] J. C. Lorquet, *Rev. Mod. Phys.*, **32**, 312 (1960).

[9] The same effect manifests itself in a greater basicity, the greater is the electron density at the S atom of the mercaptan molecule, similar to that recently demonstrated for alcohols: L. S. Levitt and B. W. Levitt, *J. Phys. Chem.*, **74**, 1812 (1970); also *Tetrahedron*, **27**, 3777 (1971).

[10] R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **5**, 210 (1959).

[11] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

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

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

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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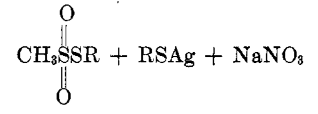
Received July 29, 1971

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.

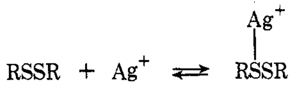


$$\mathrm{RSSR + AgNO_3 + CH_3SO_2Na \longrightarrow CH_3\overset{O}{\underset{O}{S}}SR + RSAg + NaNO_3} \qquad (1)$$

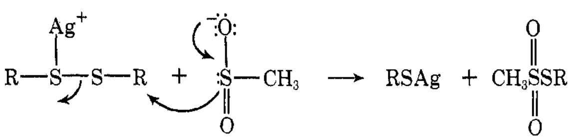
$R = CH_3, C_2H_5,$ or $(CH_3)_2CH$

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).



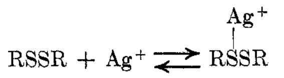
$$\mathrm{RSSR + Ag^+ \rightleftharpoons R\overset{Ag^+}{S}SR} \qquad (2)$$



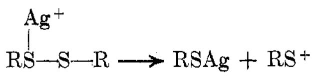
$$\mathrm{R{-}\overset{Ag^+}{S}{-}S{-}R + \overset{-O:}{\underset{O}{:S}}{-}CH_3 \longrightarrow RSAg + CH_3\overset{O}{\underset{O}{S}}SR} \qquad (3)$$

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.

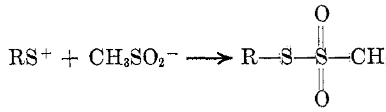
An alternate pathway (eq 4–6) is not ruled out, but



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



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



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

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-

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

I

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[1] Author to whom correspondence should be addressed.

[2] John L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968).

[3] John L. Kice, "Sulfur in Organic and Inorganic Chemistry," A. Senning, Ed., Marcel Dekker, New York, N. Y., 1971, p 197.

[4] P. C. Ray, N. Adhikari, and H. Ray, *J. Indian Chem. Soc.*, **8**, 689 (1931).