Table I
Disulfides Prepared from the Thiols and Dimethyl Dithiobis(thioformate)

Thiol	Registry no.	Disulfide Registry no.	Obsd mp, °C	Lit. mp, °C	Yield, %
C_6H_5SH	108-98-5	882-33-7	57–58	61–62[5]	100
p-ClC_6H_4SH	106-54-7	1142-19-4	67–69	71–73[5]	100
$HSCH_2CH(NH_2)COOH$	52-89-1	56-89-3	260 dec	260 dec[6]	89
$HSCH_2CH_2SH$	540-63-6	287-39-8	130–150	132–145[4]	71
p-HOC_6H_4SH	637-89-8	15015-57-3	146–148	150[7]	92
$HSCH_2CH_2CO_2H$	107-96-0	1119-62-6	154–156	156–157[5]	100

after treatment of five thiols and one dithiol with dimethyl dithiobis(thioformate).

The product from the oxidation of 1,2-ethanedithiol is apparently poly(ethylene disulfide), which as described by Kobayashi, *et al.*,[4] is insoluble in all common organic solvents. Where applicable, the structures of the disulfides were established by comparison with authentic samples.

The conversions, complete in a few minutes, are conveniently carried out at room temperature. The by-products, methanol and carbon disulfide, and the pyridine (catalyst) were removed by evaporation under a stream of air to leave the solid (usually crystalline) disulfide in essentially pure form. Another advantage of this procedure is its specificity. Oxidants such as iodine, hydrogen peroxide, potassium ferricyanide, and nitric acid are commonly used for converting thiols to disulfides. However, these reagents are also capable of reacting with oxidizable sites in the molecule. Thiols may also be oxidized by air, but considerable time is required and conditions vary for each thiol.

Experimental Section

Preparation of Dimethyl Dithiobis(thioformate). A solution of KOH (10 g) in 10 ml of H_2O was cooled in an ice bath and methanol (20 ml) was added. Then carbon disulfide (20 ml) was added and the mixture was stirred for 1 hr. To the resulting yellow solution was added $NaNO_2$ (3.0 g) and the solution was acidified to pH 4.0 with acetic acid. The mixture was extracted with ether (twice, 75-ml portions). The ether extracts were washed with water, dried with Na_2SO_4, treated with charcoal, and filtered. Solvent was removed at 40° under reduced pressure to give the dimethyl dithiobis(thioformate) (15.7 g) as a yellow oil.

Oxidation of Benzenethiol. To benzenethiol (1.0 g) were added dimethyl dithiobis(thioformate) (1.0 g) and pyridine (0.3 g). The resulting solution was stirred for 1 min, allowed to stand for 5 min, and evaporated to leave a crystalline solid (1.0 g). The product was recrystallized from ethanol, mp 57–58°. Further purification gave mp 60–61° which was unchanged when the product was mixed with an authentic sample.

Anal. Calcd for $C_{12}H_{10}S_2$: S, 29.4. Found: S, 29.4.

In a similar manner p-chlorobenzenethiol and p-mercaptophenol were oxidized to the corresponding disulfides in 100 and 92% yields, respectively.

Oxidation of 1,2-Ethanedithiol. To 1,2-ethanedithiol (1.5 g) were added dimethyl dithiobis(thioformate) (3.52 g) and pyridine (3.0 ml). Within 1 min the product precipitated as a white solid, which was washed with acetone, yield 1.1 g, mp 130–150°. The product was insoluble in all common organic solvents.

Anal. Calcd for $C_2H_4S_2$: S, 69.6. Found: S, 71.0.

Oxidation of Cysteine Hydrochloride. To a solution of cysteine hydrochloride (1.75 g) in ethanol (5.0 ml) were added dimethyl dithiobis(thioformate) (1.07 g) and pyridine (0.5 ml). Immediately, a white percipitate formed. The mixture was stirred for 1 min, kept for 5 min, and filtered. The solid was washed with ethanol (10 ml) and acetone (10 ml) and dried, yield 1.09 g (89%), mp 260° dec.

Anal. Calcd for $C_6H_{12}N_2O_4S_2$: S, 26.7. Found: S, 26.5.

Registry No. Dimethyl dithiobis(thioformate), 1468-37-7.

References and Notes

(1) Agricultural Research Service, U. S. Department of Agriculture.
(2) D. Trimnell, B. S. Shasha, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **17**, 1607 (1973).
(3) B. S. Shasha, E. I. Stout, W. M. Doane, and C. R. Russell, *Carbohyd. Res.*, **24**, 115 (1972).
(4) N. Kobayashi, A. Osawa, and T. Fujisawa, *Polym. Lett.*, **11**, 225 (1973).
(5) C. N. Yiannios and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963).
(6) "The Merck Index of Chemicals and Drugs," 7th ed, P. G. Stecher, Ed., Merck & Co., Inc., 1960, p 316.
(7) H. Bohme and H. W. Goubeaud, *Chem. Ber.*, **92**, 366 (1959); *Chem. Abstr.*, **53**, 1014*a* (1959).

Sulfinic Esters. III. A New Sulfinic Ester Synthesis[1]

Irwin B. Douglass

Department of Chemistry, University of Maine at Orono, Orono, Maine 04473

Received October 19, 1973

In previous publications[2,3] from this laboratory we described the preparation of sulfinic esters by the reaction of alcohols with sulfinyl chlorides. This remains a good general method of wide application especially in view of the ease with which sulfinyl chlorides may be prepared by the chlorination of disulfides or thiol esters in acetic anhydride.[4,5]

We have recently observed that sulfinic esters may also be synthesized directly by the low-temperature chlorination of disulfides in alcohols (eq 1). When the disulfide and chlorine are used in stoichiometric amounts with a small excess over the theoretical amount of alcohol, the crude ester is produced in 60–85% yield. The crude product is contaminated with chlorine-containing by-products, chiefly the sulfinyl and sulfonyl chlorides, and the yield is somewhat further reduced by the formation of the corresponding thiolsulfonic ester, RSO_2SR. The symmetrical thiolsulfonic esters boil higher than the sulfinic esters and can be removed by distillation. The sulfinyl and sulfonyl chloride impurities may be removed by treatment with additional alcohol[6] and with a high-boiling primary amine, such as p-toluidine, and subsequent distillation.

$$RSSR + 4R'OH + 3Cl_2 \xrightarrow{-20^\circ} 2RS(O)OR' + 2R'Cl + 4HCl \quad (1)$$

The reaction by which sulfinic esters are formed by direct chlorination of disulfides in alcohols undoubtedly involves a series of sequential steps, the first of which is the formation of the sulfenyl chloride, which then reacts as outlined in previous papers from this laboratory.[5,7] When methyl disulfide is chlorinated in methanol, for example, the succession of compounds formed is believed to be CH_3SCl, CH_3SOCH_3, $CH_3S(O)SCH_3$, $CH_3S(O)Cl$, and $CH_3S(O)OCH_3$.

The sulfinyl chloride found in the final product remains from the equilibrium reaction by which the sulfinic ester is formed (eq 2). The sulfonyl chloride results, at least in

$$CH_3S(O)Cl + CH_3OH \rightleftharpoons CH_3S(O)OCH_3 + HCl \quad (2)$$

part, from the action of chlorine on the sulfinic ester (eq 3). At temperatures above 10° this is a quantitative reac-

$$CH_3S(O)OCH_3 + Cl_2 \longrightarrow CH_3SO_2Cl + CH_3Cl \qquad (3)$$

tion but takes place at a very slow rate or is inhibited at −20°. Some of the sulfonyl chloride may also result from the attack of methanesulfenyl chloride on the alkoxide oxygen of the sulfinic ester[8] (eq 4).

$$\begin{aligned} CH_3S(O)OCH_3 \xrightarrow{CH_3SCl} [CH_3S(O)OSCH_3] + CH_3Cl \qquad (4) \\ \xrightarrow{CH_3SCl} CH_3SO_2Cl + CH_3SSCH_3 \end{aligned}$$

The thiolsulfonic ester by-product has two possible sources. Thiolsulfinic esters, RS(O)SR, among the postulated intermediate compounds referred to above, are known to disproportionate in the presence of acid[7] into the corresponding thiosulfonic esters and disulfides (eq 5).

$$2RS(O)SR \longrightarrow RSO_2SR + RSSR \qquad (5)$$

We have also demonstrated that sulfenyl chlorides react with sulfinic esters by attack at the sulfoxide sulfur to yield thiosulfonates[8] (eq 6).

$$CH_3S(O)OCH_3 + CH_3SCl \longrightarrow CH_3SO_2SCH_3 + CH_3Cl \qquad (6)$$

The experimental procedure outlined below is based on the chlorination of methyl disulfide in methanol. The limits to the applicability of the reaction have not yet been determined. Our experience suggests that sulfinic esters with higher molecular weights may be obtained in better yields. Using procedures similar to or slightly modified from those described, the following sulfinic esters were obtained in the yields indicated: ethyl methanesulfinate, $CH_3S(O)OC_2H_5$, 78%; *n*-butyl methanesulfinate, $CH_3S(O)OC_4H_9$-*n*, 84%; and ethyl ethanesulfinate, $C_2H_5S(O)OC_2H_5$, 75%.

Experimental Section

Chlorination of Methyl Disulfide in Methanol. A mixture of methyl disulfide (47.1 g, 0.5 mol) and methanol (67.3 g, 2.1 mol) was placed in a three-neck flask fitted with mechanical stirrer, an inlet tube terminating above the liquid surface, an internal thermometer, and an outlet protected by a drying tube. After the reaction mixture was cooled by means of a Dry Ice–acetone bath to −20°, chlorine was passed in from a small tank previously weighed and supported on a platform balance. Addition of chlorine was regulated so that the temperature was maintained at −20 to −25°. (Lower temperature did not seem to have an adverse effect other than to cause problems due to the separation of crystals, but higher temperatures favored the formation of methanesulfonyl chloride.) As the reaction proceeded, the reddish-orange color of methanesulfenyl chloride developed but faded when the stoichiometric amount of chlorine (106.4 g, 1.5 mol) was approached. The best yields of sulfinic ester and the least amounts of sulfonyl chloride were obtained when the stoichiometric amount of chlorine was used. At the end of the reaction the reaction mixture should be water clear or only faintly colored.

After the addition of chlorine was completed, the cold reaction mixture was transferred immediately to a distilling flask having a thermometer well, and attached to the 18-in. Vigreux column of a vacuum still connected to an efficient water pump. The hydrogen chloride and methyl chloride were removed at reduced pressure with gentle heat. (Because of the toxic nature of methyl chloride, it is important that the water pump be located in a hood.) The methyl chloride, if desired, may be collected in a Dry Ice trap located between the water pump and the still. During the removal of the gaseous products the temperature in the pot remained well below 0°.

The reaction mixture remaining when the pot temperature reached 25° (18 mm), analyzed by nuclear magnetic resonance (nmr) on a Varian A-60, consisted of approximately 86% methyl methanesulfinate, $CH_3S(O)OCH_3$; 6% methanesulfinyl chloride, $CH_3S(O)Cl$; 4% methanesulfonyl chloride, CH_3SO_2Cl; and 4% methyl methanethiolsulfonate, $CH_3S(O_2)SCH_3$.

After removal of the gaseous products, the crude reaction mixture was immediately treated with 10 ml of methanol to convert the sulfinyl chloride present to ester and was then distilled, yielding 71 g of product boiling over a 10° range which included the boiling point of methyl methanesulfinate, 46° (20 mm). This crude product, which gave a strong Beilstein test for chlorine, was diluted with an equal volume of ether and treated with 10 g of *p*-toluidine. After standing for 30 min to permit complete reaction between the sulfonyl chloride impurity and the amine, the amine hydrochloride was removed by suction filtration and the ether solution was treated with an additional 2 g of *p*-toluidine and allowed to stand until it was evident that no further amine hydrochloride would form. Ether was then removed at atmospheric pressure and the residue was distilled under reduced pressure, yielding 50.5 g (54% yield) of colorless, chlorine-free liquid, bp 49–51° (30 mm), $n^{27}{}_D$ 1.4352 (lit.[2] $n^{25}{}_D$ 1.4360). This fraction remained colorless on standing at room temperature but, had it darkened due to *p*-toluidine contamination, redistillation after adding 2 ml of concentrated sulfuric acid would have given a stable product.

Acknowledgment. This research has been made possible by a grant from the Faculty Research Fund of the University of Maine.

Registry No. Methyl disulfide, 624-92-0; methanol, 67-56-1; $CH_3S(O)OCH_3$, 666-15-9; $CH_3S(O)OC_2H_5$, 819-75-0; $CH_3S(O)OC_4H_9$-*n*, 675-87-6; $C_2H_5S(O)OC_2H_5$, 673-54-1.

References and Notes

(1) This paper is based in part on work reported at the V Symposium on Organic Sulphur Chemistry, Lund, Sweden, June 5–9, 1972.
(2) I. B. Douglass, *J. Org. Chem.*, **30**, 633 (1965).
(3) I. B. Douglass, F. J. Ward, and R. V. Norton, *J. Org. Chem.*, **32**, 324 (1967).
(4) I. B. Douglass and R. V. Norton, *J. Org. Chem.*, **33**, 2104 (1968).
(5) M. L. Kee and I. B. Douglass, *Org. Prep. Proced.*, **2**(3), 235 (1970).
(6) Although sulfinyl chlorides react rapidly with alcohols, sulfonyl chlorides react slowly; the reaction of methanesulfonyl chloride with methanol, *e.g.*, at 25° only approaches 90% completion after 20 hr.
(7) I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **27**, 1398 (1962).
(8) I. B. Douglass, R. V. Norton, P. M. Cocanour, D. A. Koop, and M. L. Kee, *J. Org. Chem.*, **35**, 2131 (1970).

Diels–Alder Cycloadditions of Sulfonyl Cyanides with Cyclopentadiene. Synthesis of 2-Azabicyclo[2.2.1]hepta-2,5-dienes

J. C. Jagt and A. M. van Leusen*

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

Received September 25, 1973

Diels–Alder cycloadditions of nitriles with dienes have been known for many years.[1] To date, however, the expected primary cycloadducts have not been isolated. Rather, at the temperatures at which these reactions usually are carried out (200–400°), aromatization to pyridine derivatives occurs,[2] either by dehydrogenation of the initially formed 2,5-dihydropyridines,[1] or, in case of bicycloadducts, by various types of ring-opening reactions.[1,3,4] Loss of carbon monoxide from the cycloadducts of cyclopentadienones is a typical example of the latter process.[1]

Recently, we established that sulfonyl cyanides are good dienophiles.[5] For example, tosyl cyanide (**1a**) reacts at room temperature with 2,3-dimethylbutadiene, but even under these mild conditions the primary cycloadduct was not observed.[6] We now wish to report the even faster reaction between cyclopentadiene and a number of sulfonyl cyanides. At room temperature, tosyl cyanide (**1a**), dissolved in cyclopentadiene, is converted in 30 min into 3-tosyl-2-azabicyclo[2.2.1]hepta-2,5-diene (**2a**), isolated in 95% yield. This is the first example of the formation of a primary Diels–Alder cycloadduct of a nitrile not accompanied by aromatization. *p*-Chlorobenzenesulfonyl cyanide (**1b**) and phenylmethanesulfonyl cyanide (**1c**) react similarly to **2b** and **2c** (84 and 73% yield, respectively). Compounds **2** are of particular interest because of their 2-azanorbornadiene structure, which has not been reported previously.