In the n.m.r. spectrum, the methyl groups of XI comprised a singlet located at δ 1.84.

2a,3,8,8a-Tetrahydro-2,2-dimethyl-3,8-epoxy-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (XIV).—A solution of 13.3 g. (0.025 mole) of XII[12] and 2.6 g. (0.02 mole) of 2,2-dimethylthiete 1,1-dioxide in 75 ml. of diglyme was heated under reflux with stirring for 16 hr. The cooled solution was evaporated under reduced pressure until a solid began to crystallize. The crude mixture was dissolved in benzene and chromatographed on Woelm neutral alumina. Elution with benzene–hexane (4:1) gave 9.55 g. (100%) of 1,2,3,4-tetraphenylbenzene, m.p. 188–190°. Elution with benzene-methanol (9:1) gave two fractions, m.p. 206–208° and m.p. 193–197°, weighing a total of 4.90 g. (98% yield). Pure adduct was obtained as white prisms from benzene, m.p. 207–208°.

Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.37; H, 5.64; S, 12.81. Found: C, 62.13; H, 5.71; S, 12.83.

1-Dimethylamino-7-thiabicyclo[4.2.0]octane 7,7-Dioxide (XII).—To a stirred solution of 25.0 g. (0.20 mole) of 1-dimethylaminocyclohexene (XXI)[22] and 20.2 g. (0.20 mole) of triethylamine in 150 ml. of dioxane was slowly added dropwise 22.9 g. (0.20 mole) of methanesulfonyl chloride with external cooling to maintain the temperature at 30–40°. The entire procedure was conducted in a nitrogen atmosphere. Triethylamine hydrochloride began to precipitate from solution almost immediately. After standing at room temperature for 48 hr., the mixture was filtered, the salts were washed with a small additional amount of dioxane, and the filtrate was evaporated under reduced pressure. The resulting brown oil was chromatographed on Woelm neutral alumina; elution with ether–hexane (1:1) afforded 29.6 g. (72.8%) of an almost colorless oil.

A sample of this material was converted to its perchlorate salt in the usual manner, fat white blades from ethanol–ether, m.p. 235–236°.

Anal. Calcd. for $C_9H_{18}ClNO_6S$: C, 35.58; H, 5.97; N, 4.61. Found: C, 35.76; H, 6.09; N, 4.52.

A sample of the pure perchlorate was dissolved in water and the solution was made basic with concentrated ammonium hydroxide. Extraction with chloroform and molecular distillation gave a colorless oil, $n^{27.5}\mathrm{D}$ 1.5120.

Trimethyl 7-Thiabicyclo[4.2.0]oct-1-yl Ammonium Iodide 7,7-Dioxide (XXIII).—A solution of 35.4 g. (0.174 mole) of XXII and 71 g. (0.50 mole) of methyl iodide in 300 ml. of ethanol was heated on a steam bath for 1.5 hr. and allowed to stand overnight at room temperature. The precipitated solid was filtered and dried to give 48.2 g. of methiodide, m.p. 204–205°. From the mother liquors, there was obtained an additional 4.4 g. (total yield, 87.4%) of white solid, m.p. 198–200°. Recrystallization from aqueous ethanol–ether gave pure XXIII, m.p. 241° dec.

Anal. Calcd. for $C_{10}H_{20}INO_2S$: C, 34.79; H, 5.84; N, 4.06. Found: C, 34.77; H, 5.92; N, 3.98.

7-Thiabicyclo[4.2.0]oct-8-ene 7,7-Dioxide (XXIV).—A warm solution (warmed for solubility reasons) of 10.4 g. (0.030 mole) of XXIII in 100 ml. of water was eluted through a column of Amberlite IRA-400 in its basic form until the eluates were no longer alkaline. Approximately 800 ml. of solution was collected. This aqueous solution was placed on a rotary evaporator at 35–40° for 30 min. to remove the major portion of the trimethylamine. The aqueous solution was extracted with chloroform and the combined organic layers were dried, filtered, and evaporated to give 4.4 g. (93.6%) of a colorless oil which rapidly crystallized, m.p. 67–72°. Recrystallization from ether and sublimation gave pure white solid, m.p. 89.5–90.5°.[23]

Anal. Calcd. for $C_7H_{10}O_2S$: C, 53.13; H, 6.37; S, 20.27. Found: C, 53.17; H, 6.40; S, 20.54.

The n.m.r. spectrum of XXIV showed a complex set of signals centered at δ 4.52 for the 6-proton and a doublet for the vinyl hydrogen at 6.32. The olefinic proton is coupled by slightly less than 1 cycle with the 6-proton across the ring.[24]

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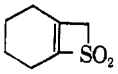
(22) E. P. Blanchard, Jr., *J. Org. Chem.*, **28**, 1397 (1963).

(23) N.m.r. examination of the mother liquors indicated that a small amount of a second component, probably ii, was present in the crude product. We have failed in our attempts to isolate this substance in a pure state, *i.e.*, free of XXIV.



ii

(24) Compare the spectrum of thiete sulfone (Ia).[3]

Sulfinate Esters. I. Their Preparation and Some Properties[1,2]

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Alkane- and arenesulfinate esters are made available for further study by a convenient new procedure. The synthesis involves converting a mercaptan, thiophenol, or disulfide to a sulfinyl chloride, which, without isolation, is caused to react with the appropriate alcohol. The crude esters thus prepared may be freed from sulfonyl chloride contaminants by treatment with an aromatic amine. Methyl methanesulfinate is slowly hydrolyzed by hot water, more rapidly in acid solution, and with great speed in the presence of alkali. It reacts readily with chlorine or bromine to form the corresponding methanesulfonyl and methyl halides. It also reacts with methylsulfur trichloride to form methyl chloride, methanesulfonyl chloride, and other products resulting from the secondary reaction of methanesulfenyl chloride with the ester.

The availability of a convenient method for preparing sulfinyl chlorides[3] has led us to investigate the preparation of sulfinate esters. These compounds have been prepared previously by a variety of methods, but that most commonly used is the reaction of an alcohol with a sulfinyl chloride. This is the method of choice, especially in view of the ease with which sulfinyl chlorides can be prepared.

Our early attempts to prepare esters by this method gave products which were contaminated with chlorine-containing impurities. These impurities could not be removed by fractional distillation and they seemed to be more resistant to hydrolysis than the esters themselves. The contaminants were finally identified as sulfonyl chlorides present in the sulfinyl chlorides used. In a recent Note[4] we pointed out that sulfinyl chlorides tend to disproportionate into sulfonyl and sulfenyl

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(1) Some of the esters here reported were prepared by Donald A. Koop, using conventional methods, for a thesis submitted in partial fulfillment of the requirements for the Ph.D., University of Maine, 1962.

(2) The following undergraduate students have assisted with experimental details of the work described: Stephen M. Belanger, Miriam L. Douglass, Thomas A. Foley, Alice L. Norton, and Judith A. Stearns.

(3) I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961); *Org. Syn.*, **40**, 62 (1960).

(4) I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **29**, 951 (1964).

chlorides. Sulfonyl chlorides may also be formed as by-products during the chlorination of disulfides in the presence of acetic acid.[3] It is not surprising, therefore, that even the most carefully prepared sample of sulfinyl chloride may contain traces of the sulfonyl chloride.

In the present study we have found that methanesulfinyl chloride reacts with methanol at a rate too fast to measure without more elaborate procedures than we have used. On the other hand, methanesulfonyl chloride reacts with methanol much more slowly. If these first members of the respective families are typical of their homologs, the initial reaction in forming a sulfinate ester rapidly consumes the sulfinyl chloride but leaves any sulfonyl chloride present essentially unchanged.

The sulfonyl chloride impurity may readily be removed from the crude ester by treatment with an aromatic amine, such as p-toluidine. The low molecular weight alkyl alkanesulfinates are then best separated from excess amine by distillation. Those of higher molecular weight and lower water solubility can be extracted with dilute acid to remove the excess amine. Subsequent distillation in both procedures gives a chlorine-free product.

A simplified procedure for the preparation of sulfinate esters was developed starting with a mercaptan, thiophenol, or disulfide. The sulfinyl chloride was first prepared by the method already referred to[3] and illustrated in eq. 1. When chlorination was complete,

$$\mathrm{RSSR} + 2\mathrm{CH_3COOH} + 3\mathrm{Cl_2} \longrightarrow 2\mathrm{RS(O)Cl} + 2\mathrm{CH_3COCl} + 2\mathrm{HCl} \quad (1)$$

the hydrogen chloride and acetyl chloride were removed but no attempt was made to purify the sulfinyl chloride. The crude product thus obtained was then used to prepare the sulfinate esters in the manner described in the Experimental section.

An attempt was made to prepare methyl methanesulfinate directly from methylsulfur trichloride. This seemed possible since the sulfur trichloride has previously been shown to yield the sulfinyl chloride on treatment with methanol[5] and excess alcohol should carry the reaction on to the sulfinate ester. The ester was formed in good yield but it was heavily contaminated with methanesulfonyl chloride, apparently due to a tendency for unchanged methylsulfur trichloride to chlorinate some of the ester as soon as it was formed (eq. 2). Methylsulfur trichloride has previously been shown to act as a chlorinating agent.[6] Subsequent experiments demonstrated that methyl methanesulfinate is readily converted by chlorine and bromine to methanesulfenyl chloride and bromide.

$$\mathrm{CH_3S(O)OCH_3} + \mathrm{CH_3SCl_3} \longrightarrow \mathrm{CH_3SO_2Cl} + \mathrm{CH_3Cl} + \mathrm{CH_3SCl} \quad (2)$$

Methyl methanesulfinate is hydrolyzed to only a negligible extent in water at 25°, slowly in dilute hydrochloric acid at 25°, more rapidly in water at 100°, and still more rapidly in acid at 100°. It is hydrolyzed at a rapid rate, even at 0°, in dilute sodium hydroxide. Methyl methanesulfinate is miscible in water but the other alkyl alkanesulfinates show a greater tendency to dissolve water than to dissolve in water themselves.

TABLE I

PHYSICAL CONSTANTS OF SULFINATE ESTERS

RS(O)OR′		B.p., °C.			
R	R′	(mm.)	$n^{25}{}_D$	$d^0{}_4$	$d^{25}{}_4$
CH_3	CH_3[a]	45.5 (18)	1.4360	1.1802	1.1512
CH_3	C_2H_5[b]	57–58 (25)	1.4333	1.1049	1.0780
CH_3	1-C_3H_7[c]	67–68 (17)	1.4368	1.0630	1.0379
CH_3	1-C_4H_9[d]	81–82 (18)	1.4395	1.0350	1.0103
C_2H_5	CH_3[e]	64–65 (30)	1.4385	1.1153	1.0893
C_2H_5	C_2H_5[f]	60–61 (14)	1.4375	1.0619	1.0364
C_2H_5	1-C_4H_9[f]	90–91 (16)	1.4411	1.0105	0.9873
1-C_3H_7	C_2H_5[f]	80–81 (18)	1.4399	1.0296	1.0057
2-C_3H_7	C_2H_5[g]	59–60 (11)	1.4345	1.0324	1.0090
1-C_4H_9	CH_3[h]	72–73 (10)	1.4438	1.0388	1.0153
1-C_4H_9	C_2H_5[i]	87–88 (13)	1.4415	1.0102	0.9871
C_6H_5	CH_3[j]	88–89 (0.3)	1.5437	1.2180	1.1948
4-$CH_3C_6H_4$	CH_3[k]	86–88 (0.4)	1.5416	1.1772	1.1498

[a] *Anal.* Calcd. for $C_2H_6O_2S$: C, 25.52; H, 6.43; S, 34.06. Found: C, 25.67; H, 6.68; S, 34.30. [b] *Anal.* Calcd. for $C_3H_8O_2S$: C, 33.30; H, 7.45; S, 29.65. Found: C, 33.41; H, 7.30; S, 29.57. [c] *Anal.* Calcd. for $C_4H_{10}O_2S$: C, 39.32; H, 8.25; S, 26.24. Found: C, 39.29; H, 7.95; S, 26.10. [d] *Anal.* Calcd. for $C_5H_{12}O_2S$: C, 44.09; H, 8.88; S, 23.54. Found: C, 44.17; H, 9.05; S, 23.85. [e] L. Field, C. Hoelzel, and J. E. Lawson, *J. Org. Chem.*, **27**, 3313 (1962). [f] P. Carré and D. Libermann, *Compt. rend.*, **200**, 2086 (1935). [g] *Anal.* Calcd. for $C_5H_{12}O_2S$: C, 44.09; H, 8.88; S, 23.54. Found: C, 44.11; H, 8.81; S, 23.39. [h] *Anal.* Calcd. for $C_5H_{12}O_2S$: C, 44.09; H, 8.88; S, 23.54. Found: C, 44.41; H, 9.01; S, 23.20. [i] J. Michalski, J. Wieczorkowski, and T. Modro, *Roczniki Chem.*, **32**, 1409 (1958); *Chem. Abstr.*, **53**, 15951 (1959). [j] S. Detoni and D. Hadzi; *J. Chem. Soc.*, 3163 (1955). [k] A. J. H. Houssa, J. Kenyon, and H. Phillips, *ibid.*, 1707 (1929).

The physical properties of some sulfinate esters prepared in the course of this study are shown in Table I.

Experimental

Methyl Methanesulfinate.—Exactly 0.50 mole of methyl disulfide and 1.00 mole of glacial acetic acid were mixed in a three-neck reaction flask fitted with stirrer, gas inlet tube terminating above the liquid surface, thermometer, and gas outlet tube. The reaction mixture was cooled to 0° by means of a Dry Ice bath and chlorine was passed in at such a rate that the temperature did not rise above 10°. As the reaction proceeded the temperature was lowered to −20°. At first the color of the reaction mixture turned red as methanesulfenyl chloride formed but as more chlorine was added the color decreased until the mixture was nearly colorless and did not change on adding additional chlorine. This point was reached when 1.5 moles of chlorine had been added although we found it unnecessary actually to measure the chlorine. A slight excess of chlorine seemed to have no adverse effect. Equally good results were obtained when sulfuryl chloride was used as the chlorinating agent.

When addition of chlorine was complete, the cold bath was removed and the mixture was allowed to warm slowly to room temperature with continuous stirring to facilitate the escape of hydrogen chloride. The mixture was then transferred to a distilling flask and heated gently, first at atmospheric pressure to 70° and then, after cooling, under the reduced pressure of an aspirator until the pot contents had reached approximately 35° (20 mm.). A Dry Ice trap to collect acetyl chloride and a water trap to absorb hydrogen chloride were inserted between the distillation system and the aspirator.

The crude methanesulfinyl chloride remaining in the distilling flask was transferred to a large tube, cooled to −30°, and mixed with 1.1 moles of previously chilled anhydrous methanol. The mixture was then returned to the distilling flask, evacuated as before to remove hydrogen chloride, and finally heated to 35° (20 mm.) until evolution of gas had practically ceased. The crude sulfinate ester was then removed, cooled, and immediately mixed with a solution of 10 g. of p-toluidine dissolved in anhydrous ether. After a few minutes the precipitated p-toluidine hydrochloride was filtered out and washed with anhydrous ether, the washings being added to the filtrate. An additional 1–2 g. of p-

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(5) I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).

(6) K. R. Brown and I. B. Douglass, *J. Am. Chem. Soc.*, **73**, 5787 (1951).

toluidine was added to ensure that no sulfonyl chloride had survived the first treatment.

Distillation of the resulting mixture of ether, ester, excess amine, and methanesulfon-*p*-toluidide through an 18-in. Vigreux column yielded 67 g. (71% yield based on disulfide) of chloride-free methyl methanesulfinate boiling at 39–42° (14 mm.) or 42–43° (18 mm.) and having $n^{25}\text{D}$ 1.4350–1.4370. Redistillation gave a product with the properties shown in Table I.

Methyl Benzenesulfinate.—Thiophenol (110.2 g., 1.0 mole), glacial acetic acid (60.0 g., 1.0 mole), and 125 ml. of methylene chloride were mixed in the reaction flask described above, cooled to −10°, and chlorinated to a straw color which did not change on adding additional chlorine. Acetyl chloride, hydrogen chloride, and solvent methylene chloride were removed from the reaction mixture by warming to room temperature and heating to 70° at atmospheric pressure and, after cooling, to 70° (20 mm.) until evolution of volatile matter had virtually ceased. The residue weighed 161.5 g. in contrast to a theoretical yield for benzenesulfinyl chloride of 160.5 g.

After mixing the crude benzenesulfinyl chloride with 1.1 mole of methanol at −30° the reaction mixture was transferred to a distilling flask and gently heated under reduced pressure until it reached 70° (20 mm.) and evolution of hydrogen chloride had practically ceased. The crude ester was then cooled, diluted with ether, and treated with 10 ml. of aniline. After allowing a few minutes for any benzenesulfonyl chloride to react, the mixture was shaken with water to dissolve the aniline hydrochloride and then twice with 50-ml. portions of hydrochloric acid prepared by diluting 10 ml. of concentrated acid to 100 ml. A portion of the first acid wash, on being made alkaline with sodium hydroxide solution, liberated aniline, thus indicating that all sulfonyl chloride in the ester had been destroyed.

The nonaqueous layer was dried over anhydrous magnesium sulfate and, after removal of ether, was distilled under the reduced pressure of a mechanical pump. The yield was 117 g. (65% based on thiophenol) of chloride-free product boiling at 76–81° (0.45 mm.) and having $n^{25}\text{D}$ 1.5434–1.5443. A middle fraction had the properties shown in Table I.

Methyl *p*-toluenesulfinate was prepared in 52% yield by the above method from 26 g. of *p*-thiocresol. Its properties are shown in Table I.

The density and refractive index data from Table I were used to calculate $MR\text{D}$ values for the –S(O)O– group, using group refractivities for the R and R′ groups reported by Vogel.[7] A mean value of 10.269 was obtained, with extreme values of 10.072 for –S(O)O– in $CH_3S(O)OCH_3$ and 10.450 in $1\text{-}C_4H_9S(O)OC_2H_5$.

Attempt to Prepare Methyl Methanesulfinate from Methylsulfur Trichloride.—Methyl disulfide (0.25 mole) in 100 ml. of methylene chloride was chlorinated in the reaction equipment described above at −30° with chlorine (0.75 mole, 52.2 g.), previously condensed and weighed in a large tube, producing a white slurry of methylsulfur trichloride. Methanol (33 g., 1.03 moles) was run in slowly and caused the solid to dissolve leaving a straw-colored solution. Distillation gave 34 g. of colorless product, or 72% assuming it to be methyl methanesulfinate. The product, however, gave a strong Beilstein test for halogen.

Repetition of the experiment starting with 0.5 mole of methyl disulfide and treating the crude product with *p*-toluidine resulted in a yield of 60 g. (64%) of chloride-free ester. An attempt to improve the yield by adding the methanol more slowly led to a decreased yield of ester and more sulfonyl chloride contaminant. The result suggested that a secondary reaction was occurring between the ester and unchanged methylsulfur trichloride, and led to the following experiment.

Reaction of Methyl Methanesulfinate with Methylsulfur Trichloride.—Methylsulfur trichloride (0.2 mole) was prepared in the usual manner from 9.4 g. (0.1 mole) of methyl disulfide and treated at −10 to −20° with 28 g. (0.3 mole) of methyl methanesulfinate at a rate of about 1 drop/second. The solid methylsulfur trichloride disappeared as the ester was added and, when addition was complete, the solution had acquired a yellow color, suggesting the presence of methanesulfenyl chloride, CH_3SCl. An additional 1.7 g. of ester was added but the color did not change. The reaction mixture was then warmed to 35° with stirring and evolved a gas which was condensed in a cold trap. The condensed gas, after being separated from entrained methylene chloride by repeated distillation, was shown to be methyl chloride by its infrared spectrum.

The reaction mixture, after removing methylene chloride at atmospheric pressure, was fractionally distilled through a Vigreux column and yielded nearly 0.2 mole of methanesulfonyl chloride and other small fractions consisting chiefly of methyl disulfide, methyl methanethiosulfonate, $CH_3SO_2SCH_3$, and methanesulfinyl chloride as indicated by their boiling points, refractive indices, and infrared spectra. The last three compounds have been shown to result from the reaction of methanesulfenyl chloride with methyl methanesulfinate.[8]

Reaction of Methanol with Methanesulfinyl and Methanesulfonyl Chlorides.—Methanesulfinyl chloride, 0.137 g., was introduced into each of several dry test tubes and cooled in an ice bath to 0°. To each tube in turn, except those used as blanks, 1 ml. of cold anhydrous methanol was added and, after various time intervals, the reaction was quenched with 25 ml. of cold water. Titration with standard sodium hydroxide revealed 2 equiv. of acid from each mole of unreacted sulfinyl chloride but only 1 mole of acid for each mole of ester formed. The experiments demonstrated that within 2 sec. the reaction between sulfinyl chloride and alcohol was at least 93% complete. Benzenesulfinyl chloride reacted equally fast. In contrast, the reaction between methanesulfonyl chloride and methanol at 25° was less than 15% complete in 1 hr.

Hydrolysis of Methyl Methanesulfinate.—A solution of 0.23 g. of methyl methanesulfinate in 10 ml. of distilled water was allowed to stand at room temperature for 30 min. Titration of the resulting solution with standard alkali indicated no detectable hydrolysis. At 100° a similar solution underwent 2.8% hydrolysis in 30 min., 7.2% in 1.0 hr., and 42% in 2.0 hr.

When 0.115 g. of the ester was dissolved in 10 ml. of 0.06 *N* hydrochloric acid at 25°, less than 5% hydrolysis had taken place in 3 hr. At 100° hydrolysis was 17% complete in 3 min., 37% in 7 min., 65% in 20 min., 73% in 35 min., and 95% in 45 min. In 0.1 *N* sodium hydroxide at 0° hydrolysis was complete in 5 min.

These results are consistent with the observations of Bunton and Hendy who studied the hydrolysis of methyl *p*-toluenesulfinate.[9]

Reaction of Methyl Methanesulfinate with Halogens.—Chlorination of 9.4 g. (0.1 mole) of methyl methanesulfinate at 0° to a persistent yellow color of excess chlorine gave methyl chloride and methanesulfonyl chloride. The latter, after distillation, was recovered in 90% yield. Both products were identified by their infrared spectra.

Bromination, likewise, took place readily at ice temperature. From 0.1 mole of the ester there was obtained 11.6 g. (75% yield) of methanesulfonyl bromide boiling at 75° (15 mm.) and having $n^{25}\text{D}$ 1.5080, a value identical with that reported by Johnson and Sprague.[10] The sample also had d^0_4 1.9888 and d^{25}_4 1.9462.

Solubility of Sulfinate Esters in Water.—Nine small test tubes containing, respectively, 0.1 to 0.9 ml. of sulfinate ester and 0.9 to 0.1 ml. of water were prepared and observed at different temperatures. A clear solution indicated mutual solubility, but a cloudy appearance or two distinct layers indicated incomplete solubility. The following results were obtained. Methyl methanesulfinate is completely miscible in water at 25°. Ethyl ethanesulfinate is partially miscible, forming clear solutions containing up to 60% water at 0° or 70% at 25°; at 57° 0.05 ml. of ester formed a clear solution in 0.95 ml. of water although 0.1 ml. of ester in 0.9 ml. water remained cloudy. Butyl methanesulfinate was partially miscible, forming clear solutions containing 20% water at 70° or 30% at 80°. The isomeric methyl butanesulfinate dissolved only 10% water at 60° or 20% at 88°. Ethyl butanesulfinate, on the other hand, showed two phases at all concentrations up to 83°.

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(10) T. B. Johnson and J. L. Sprague, *J. Am. Chem. Soc.*, **58**, 1348 (1936).