TABLE III

REACTIONS OF VARIOUS SULFONATES

Sulfonate	Solvent	Temp., °C	Time, hr.	Product	Yield, %
Cyclohexyl benzene-	Dimethyl sulfoxide	90–95	2	Cyclohexene	65
Cyclohexyl *p*-toluene-	Dimethyl sulfoxide	90–95	5	Cyclohexene	61
Cyclohexyl *p*-toluene-	Hexamethylphosphoramide	100	6	Cyclohexene	62
Cyclohexyl *p*-toluene-	Dimethylformamide	100	5.5	Cyclohexene	55
2-Octyl benzene-	Dimethyl sulfoxide	100–107	0.75	Octene	52
2-Octyl benzene-	Dimethyl sulfoxide	100	1	Octene	58
2-Octyl 2-naphthalene-	Dimethyl sulfoxide	100	1	Octene	30
2-Octyl benzene-	Hexamethylphosphoramide	100	3	Octene	61.5

sulfonate was heated in pyridine solution. The reaction was considerably slower, and a much lower yield of menthenes was obtained (Table I). The olefin composition and degree of racemization of the Δ^3-menthene were similar to those obtained with the other solvents. Hence, it seems likely that pyridine and related bases also promote the decomposition of sulfonate esters by a solvolytic ionization route, although much less effectively.

In summary, the available evidence suggests that in the formation of olefins from sulfonate esters of secondary alcohols, dimethyl sulfoxide and hexamethyl phosphoramide function as highly polar non-reacting solvents, and promote the decomposition by an ionic path.

Experimental

Solvolysis of (−)-Menthyl Benzenesulfonate in Dimethyl Sulfoxide.—A solution of 29.6 g. (0.10 mole) of (−)-menthyl benzenesulfonate in 150 ml. of dimethyl sulfoxide (Stepan Chemical Co.) was heated (solution temperature 89–91°) under reflux for 6 hours. On allowing the solution to cool to room temperature, two layers formed. The mixture was extracted with 50 ml. of ligroin (b.p. 66–75°), which dissolved the upper layer. The lower layer was poured into an equal volume of a mixture of ice and water, and the resulting mixture was extracted with two 50-ml. portions of ligroin. All of the ligroin extracts were combined, washed with two 50-ml. portions of water, 50 ml. of saturated brine and then filtered through anhydrous sodium sulfate. The ligroin was removed by distillation through a 7'' Vigreux column and the residue was fractionated with an efficient semi-micro column.[14] Five fractions were collected and combined to give 10.5 g. (76%) of mixed menthenes, b.p. 60–61.5° (17–19 mm.), n^{25}_D 1.4495 − 1.4500, $[\alpha]_D$ +85° (1% in $CHCl_3$); reported[15] for a mixture containing 24% Δ^2-menthene, b.p. 64.5–65° (22 mm.), n^{25}_D 1.4500, $[\alpha]_D$ +117° (1% in $CHCl_3$). The residue (1.53 g.) solidified and a mixture m.p. with (−)-menthyl benzenesulfonate (m.p. 79–79.5° (cor.)) was 77–79°. The yield of menthenes was 80% based on recovered starting material.

A 500-mg. sample of the menthenes was racemized with hydrogen chloride in chloroform[12] and had $[\alpha]_D$ +27° (1% in $CHCl_3$) after racemization, corresponding to 20.5% of Δ^2-menthene in the original mixture.

Solvolysis of β-Cholestanyl Benzenesulfonate in Dimethyl Sulfoxide.—A mixture of 250 mg. (0.46 millimole) of β-cholestanyl benzenesulfonate and 2.5 ml. of dimethyl sulfoxide was heated at 100° (a clear solution resulted soon after heating) for 150 minutes. When the solution was allowed to cool to room temperature a colorless oil separated which partially solidified on standing. The mixture was added to a mixture of ice and water, this mixture was neutralized with sodium bicarbonate, and the white solid which formed was collected by filtration, washed well with water, and recrystallized from aqueous ethanol. A yield of 139 mg. (82%) of a mixture of Δ^2- and Δ^3-cholestene was obtained, m.p. 69.5–70.5° (cor.).[8]

Solvolysis of Cyclohexyl Benzenesulfonate in Dimethyl Sulfoxide.—A solution of 24 g. (0.10 mole) of cyclohexyl benzenesulfonate in 100 ml. of dimethyl sulfoxide was heated in a distillation flask under a nitrogen atmosphere at 90–95° (130–160 mm.) for 2 hours. The receiver was cooled in a Dry Ice–acetone-bath, and when the reaction was complete, the receiver contents were fractionated through a semi-micro distillation column.[14] A yield of 5.34 g. (65%) of cyclohexene was obtained, b.p. 81–82.5°, n^{25}_D 1.4440–1.4444.

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[14] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[15] H. R. Nace, D. G. Manly and S. Fusco, *J. Org. Chem.*, **23**, 687 (1958).

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Aliphatic Disulfinic Acids; The Unique Stability of 1,4-Butanedisulfinic Acid[1]

BY MICHAEL T. BEACHEM, JOHN T. SHAW, G. DANN SARGENT, ROBERT B. FORTENBAUGH AND
JASON M. SALSBURY

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The preparation of the first stable, crystalline, aliphatic disulfinic acid, 1,4-butanedisulfinic acid, is described. Other disulfinic acids are also described and their reactions with various α,β-unsaturated systems are reported. The preparation of 1,4-bis-(hydroxymethylsulfonyl)-butane and its reactions with various amides and aromatic amines are also reported.

This article reports the preparation and isolation of a stable, crystalline, aliphatic disulfinic acid, 1,4-butanedisulfinic acid. All of the lower aliphatic monosulfinic acids[2] are unstable and are usually prepared by the reduction of the corresponding sulfonyl chlorides with sodium sulfite under neutral or slightly alkaline conditions.[3] In 1948, Marvel and Johnson[4] prepared for the

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[1] Presented before the Division of Organic Chemistry at the 133rd National Meeting, American Chemical Society, San Francisco, Calif., April 16, 1958.

[2] The chemistry of aliphatic sulfinic acids has been reviewed by (a) P. Allen, *J. Org. Chem.*, **7**, 23 (1942); (b) W. E. Truce and A. N. Murphy, *Chem. Revs.*, **48**, 69 (1951); (c) Houben-Weyl "Methoden der Organischen Chemie," 4th edition, George Thieme, Stuttgart, 1955, pp. 285–299.

[3] H. Bredereck and E. Bäder, *Chem. Ber.*, **87**, 129 (1954).

[4] C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).

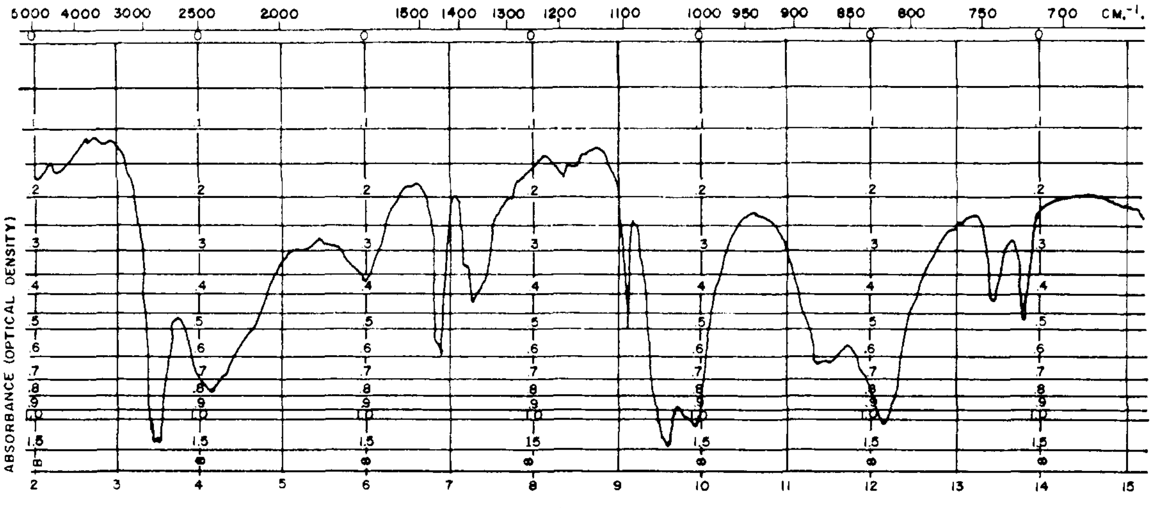

Fig. 1.—Infrared absorption spectrum of 1,4-butanedisulfinic acid in Nujol mull.

first time a crystalline, aliphatic, monosulfinic acid, 1-dodecanesulfinic acid. This material was much more stable than the lower alkane monosulfinic acids, but on standing for two months it disproportionated. The only reference to an aliphatic disulfinic acid appears to be the preparation of the disodium salt of 1,2-ethanedisulfinic acid by Otto and Casanova,[5] who reported that an attempt to prepare the free acid resulted in general decomposition. Later work by Kohler,[6] and Autenrieth and Koburger[7] showed that the starting material, 1,2-ethanedisulfonyl chloride, was converted quite readily to ethylenesulfonic acid in aqueous solution.

We selected the preparation of 1,4-butanedisulfinic acid as a starting point and carried out the reduction of 1,4-butanedisulfonyl chloride, using sodium sulfite and sodium bicarbonate. We were surprised to find that the free 1,4-butanedisulfinic acid could be obtained in good yield as a colorless crystalline solid by acidification of the reaction mixture. This product, which crystallizes as rhombs and six-sided plates, shows a very distinct crystallinity in its X-ray diffraction pattern. Its stability is indicated by the fact that the melting point was unchanged after storage at room temperature for seven months. After twenty months, the sample was only partially decomposed; that is, the crystals were slightly hygroscopic.

The infrared absorption spectrum of 1,4-butanedisulfinic acid, Fig. 1, showed the typical sulfinic acid absorption band[8,9] in the region of 1047 cm.$^{-1}$. The infrared absorption spectrum of the product after twenty months was unchanged and the X-ray diffraction pattern was substantially the same.

The unusual stability of 1,4-butanedisulfinic acid prompted the investigation of the next higher and lower homologs. When an attempt was made to isolate 1,3-propanedisulfinic acid and 1,5-pentanedisulfinic acid similarly, as in the case of the 1,4-butanedisulfinic acid, no sulfinic acids were obtained, but it was possible to precipitate the zinc salt of each acid by the addition of zinc chloride. The free 1,5-pentanedisulfinic acid could then be liberated from the zinc salt, whereas the free 1,3-propanedisulfinic acid could not be isolated. When a portion of the acidified solution of 1,3-propanedisulfinic acid was freeze-dried the resulting residue showed an absorption band at 1176 cm.$^{-1}$, indicating the presence of sulfonic acid groups, and did not form an adduct with acrylamide. To show that 1,3-propanedisulfinic acid was actually formed, acrylamide was added to another portion of the acidified solution and an adduct[10] was obtained.

Similarly, 1,5-pentanedisulfinic acid appeared less stable than 1,4-butanedisulfinic acid, although the difference noted was not as great as in 1,3-propanedisulfinic acid. The 1,5-pentanedisulfinic acid was quite hygroscopic and was best dried and stored over phosphorus pentoxide. The infrared absorption spectrum of this material showed the sulfinic acid band at 1047 cm.$^{-1}$. This material disproportionated on heating.

The next higher homolog, 1,6-hexanedisulfinic acid, was isolated directly by the acidification of the sulfonyl chloride–sulfate reaction mixture. It was found to be more stable than 1,5-pentanedisulfinic acid but it did disproportionate on heating.

In the preparation of 1,10-decanedisulfinic acid, a waxy, crystalline material, which also showed the characteristic sulfinic acid absorption at 1047 cm.$^{-1}$, was obtained. This disulfinic acid apparently disproportionated on heating, since the infrared spectrum after heating showed the additional absorption of the sulfonic acid group at 1176 cm.$^{-1}$ and the product no longer yielded an adduct with acrylamide.

The addition of sulfinic acids to α,β-unsaturated systems was first described by Kohler and Reimer.[10] In our work, this reaction proved to be a convenient, qualitative assay for the presence of a sulfinic acid. It was found that acrylamide formed the most suitable derivatives, while the adducts ob-

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(5) R. Otto and R. C. Casanova, *J. prakt. Chem.*, [2] **36**, 436 (1887); *Ber.*, **15**, 126 (1882).

(6) E. P. Kohler, *Am. Chem. J.*, **19**, 745 (1897).

(7) W. Autenrieth and J. Koburger, *Ber.*, **36**, 3626 (1903).

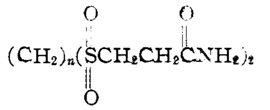
(8) E. N. Guryanova and Ya. K. Syrkin, *Zhur. fiz. Khim.*, **23**, 105 (1949).

(9) S. Dètoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

(10) E. P. Kohler and M. Reimer, *Am. Chem. J.*, **31**, 176 (1904).

TABLE I

REACTION PRODUCTS OF DISULFINIC ACIDS WITH ACRYLAMIDE

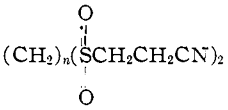


$$(CH_2)_n(\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}CH_2CH_2\overset{O}{\overset{\|}{C}}NH_2)_2$$

n	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
2	16	241–243	$C_8H_{16}N_2O_6S_2$	31.98	31.83	5.33	5.39	9.33	9.10	. . .	. . .
3	41	228–230	$C_9H_{18}N_2O_6S_2$	34.40	34.19	5.76	5.76	8.91	8.75	. . .	. . .
4	91	210–212	$C_{10}H_{20}N_2O_6S_2$	36.55	36.83	6.12	6.18	8.54	8.32	19.54	19.90
5	33	198–200	$C_{11}H_{22}N_2O_6S_2$	38.61	38.33	6.43	6.37	8.19	7.97	18.72	18.86
10	36	205–207	$C_{16}H_{32}N_2O_6S_2$	46.60	46.40	7.82	7.89	6.58	6.63	15.54	15.60

TABLE II

REACTION PRODUCTS OF DISULFINIC ACIDS WITH ACRYLONITRILE

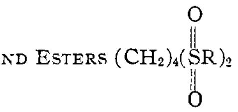


$$(CH_2)_n(\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}CH_2CH_2CN)_2$$

n	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
2	6	190–192	$C_8H_{12}N_2O_4S_2$	36.37	36.46	4.57	4.58	10.58	10.89	. . .	. . .
3	42	150–156	$C_9H_{14}N_2O_4S_2$	38.85	38.34	5.06	5.09	10.07	10.10	23.04	23.06
4	49	152–153	$C_{10}H_{16}N_2O_4S_2$	41.10	40.98	5.52	5.77	9.57	9.93	21.95	22.17
5	7	113–115	$C_{11}H_{18}N_2O_4S_2$	43.12	42.80	5.88	6.08	9.15	9.28	20.93	19.85

TABLE III

REACTION PRODUCTS OF 1,4-BUTANEDISULFINIC ACID WITH α,β-UNSATURATED ACIDS AND ESTERS



$$(CH_2)_4(\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}R)_2$$

Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
67[a]	207–209	$C_{10}H_{18}O_8S_2$	36.35	36.59	5.50	5.53	19.40	19.49
13[b]	139–141	$C_{12}H_{22}O_8S_2$	40.20	40.36	6.18	5.90	17.88	17.80
25[c]	191.5–192.5	$C_{12}H_{22}O_8S_2$	40.16	40.10	6.14	6.11	17.88	18.10
44[d]	217–219	$C_{12}H_{18}O_{12}S_2$	34.45	33.99	4.30	4.29	15.33	15.35

[a] R = 2-carboxyethyl. [b] R = 2-methoxycarbonylethyl. [c] R = 1-methyl-2-carboxyethyl. [d] R = 1,2-dicarboxyethyl.

tained with acrylonitrile, acrylic acid, crotonic acid and maleic acid were not quite as easily isolated or purified. When aqueous solutions of 1,2-ethanedisulfinic acid and 1,3-propanedisulfinic acid were treated with acrylamide, the formation of high-melting crystalline products in both cases indicated the amount of disulfinic acid present. Similarly, the acrylamide adducts of 1,4-butane-, 1,5-pentane-, 1,6-hexane- and 1,10-decanedisulfinic acids were also prepared and characterized (Table I). The bis-(*N*-methylol) derivative of the acrylamide adduct of 1,3-propanedisulfinic acid was also prepared.

The adducts of aliphatic disulfinic acids with acrylonitrile (Table II) were obtained readily, but the yields were not as high as in the acrylamide reaction. The excellently crystalline adducts of Table III were also obtained by reactions with acrylic, crotonic and maleic acids.

When Kohler and Reimer[10] added *p*-toluenesulfinic acid to fumaric and maleic acids at high temperature, the adducts decarboxylated to form β-tosylpropionic acid, but we obtained the undecarboxylated acid by treating 1,4-butanedisulfinic acid and maleic acid at room temperature.

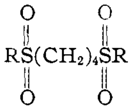
The presence of a methyl group on the α-carbon of the α,β-unsaturated system interferes with the formation of an adduct with the disulfinic acids. Thus, in the reaction of 1,4-butanedisulfinic acid with methacrylic acid, polymethacrylic acid was the only product isolated. This behavior of methacrylic acid with monoarylsulfinic acids has been reported.[3] Similarly, the use of methyl methacrylate led only to polymethyl methacrylate, whereas methyl acrylate gave a crystalline adduct with 1,4-butanedisulfinic acid.

Several disulfones (Table IV) were prepared by refluxing the sodium or the potassium salts of 1,4-butanedisulfinic acid with the following active halides: allyl bromide, 2-hydroxy-3,5-dichlorobenzyl chloride, 2,4-diamino-6-chloromethyl-*s*-triazine and 1-chloro-2,4-dinitrobenzene.

Aliphatic monosulfinic acids are known to react with aldehydes to give α-hydroxy substituted sulfones.[3] Since the disulfinic acids had not been previously described, it was of interest to prepare their formaldehyde adducts. Only the butane derivative, 1,4-bis-(hydroxymethylsulfonyl)-butane, was obtained by treating the disulfinic acids with formalin. The surprising stability of 1,4-butanedisulfinic acid is mirrored by its formaldehyde adduct which showed no appreciable change in melting point after storage for one year in a stoppered bottle. Reaction of 1,4-bis-(hydroxymethylsulfonyl)-butane with acetic anhydride gave the corresponding diacetoxy derivative in 95% crude yield. Neither 1,3-propanedisulfinic acid nor 1,5-pentanedisulfinic acid gave a stable adduct with formaldehyde. Propionaldehyde was also treated with 1,4-butanedisulfinic acid to give 1,4-bis-(α-hydroxypropylsulfonyl)-butane.

TABLE IV

SULFONES PREPARED FROM 1,4-BUTANEDISULFINIC ACID



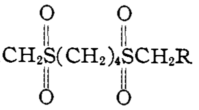
$$R\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}(CH_2)_4\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}R$$

R	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Other element, % Calcd.	Other element, % Found
$CH_2{=}CHCH_2$[a]	37.5	90–95	$C_{10}H_{18}O_4S_2$	44.9	44.9	6.79	6.62	24.1	24.5	.....	.....
$C_7H_5Cl_2O$[b]	70.0	210–213	$C_{18}H_{18}Cl_4O_6S_2$	40.3	40.2	3.39	3.27	11.9	12.3	Cl, 26.4	Cl, 26.3
$C_4H_6N_5$[c]	64.0	250 d.	$C_{12}H_{20}N_{10}O_4S_2\cdot 2H_2O$	30.7	29.8	5.10	4.88	13.6	13.3	N, 29.9	N, 29.5
$C_6H_3N_2O_4$[d]	88.0	275–280 d.	$C_{16}H_{14}N_4O_{12}S_2$	37.0	36.2	2.72	2.76	12.3	12.6	N, 10.8	N, 10.7

[a] Refluxed three hours; recrystallized from isopropyl alcohol. [b] 3,5-Dichloro-2-hydroxyphenylmethyl; product precipitates immediately at room temperature; recrystallized from aqueous acetone. [c] 4,6-Diamino-2-pyrimidylmethyl; refluxed for 24 hours; recrystallized from hot water; product does not melt but undergoes continuous decomposition. Analysis indicates the presence of two moles of water of hydration. Calcd. H_2O, 7.7%. Found: H_2O, 7.5%. [d] 2,4-Dinitrophenyl; refluxed for 17 hours.

TABLE V

REACTIONS OF 1,4-BIS-(HYDROXYMETHYLSULFONYL)-BUTANE WITH AMINES AND AMIDES

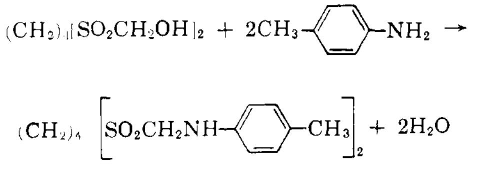


$$RCH_2\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}(CH_2)_4\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}CH_2R$$

R	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Cl-*p*-C_6H_4NH–	92.5	183–184	$C_{18}H_{22}Cl_2N_2O_4S_2$	46.4	46.2	4.73	4.39	6.02	6.33
CH_3-*p*-C_6H_4NH–	85.0	165–166	$C_{20}H_{28}N_2O_4S_2$	56.6	56.5	6.69	6.90	6.59	6.97
$C_6H_5N(C_2H_5)$–[a]	84.0	108–110	$C_{22}H_{32}N_2O_4S_2$	58.3	58.1	7.11	7.09	6.19	6.20
$(C_6H_5)_2N$–[a]	45.5	118–120	$C_{30}H_{32}N_2O_4S_2$	..	..	..	..	5.11	5.11
$(CH_3)_2N$-*p*-C_6H_4–[b]	10.5	214–215	$C_{22}H_{32}N_2O_4S_2$	58.3	58.6	7.11	6.89	...	
$CH_3\overset{O}{\overset{\|}{C}}\overset{H}{\overset{\mid}{N}}$–[c]	91.5	Colorless oil	$C_{10}H_{22}N_2O_7S_2$	..	..	..	..	8.10	8.18
$H_2N\underset{O}{\underset{\|}{C}}\underset{H}{\underset{\mid}{N}}$–[d]	84.0	145–150	$C_8H_{18}N_4O_6S_2$	29.1	29.2	5.45	5.63	17.0	17.1
$CH_2{=}CHCH_2\underset{H}{\underset{\mid}{N}}{-}\underset{O}{\underset{\|}{C}}{-}\underset{H}{\underset{\mid}{N}}{-}$	95.0	Yellow oil	$C_{14}H_{26}N_4O_4S_4$	38.0	37.8	5.92	6.50	12.7	12.4

[a] Reaction carried out at 6–9°. [b] Refluxed for one hour; product recrystallized from dimethylformamide. [c] Refluxed for four hours. [d] Refluxed for one hour. [e] Refluxed for 15 hours.

The reaction of aromatic and aliphatic monohydroxylmethyl sulfones with various amines to give N-substituted aminomethyl sulfones has been disclosed by Bredereck and Bäder.[3] A similar reaction, illustrated below, was carried out with aromatic amines and 1,4-bis-(hydroxymethylsulfonyl)-butane.



The syntheses involved adding a methanolic solution of the aromatic amine to a methanolic solution of 1,4-bis-(hydroxymethylsulfonyl)-butane. Most of the products (Table V) precipitated, within a few minutes, in good yields. The results with N-ethylaniline and diphenylamine depended on the reaction temperature. At 0°, cream-colored solids were obtained in good yields, whereas reaction at room temperature gave oils in both cases. The oils were probably mixtures of several products, since it has been reported[11] that *p*-unsubstituted aromatic amines can undergo both N- and ring-substitution. That the solid product from the N-ethylaniline reaction, in the cold, was the N-substituted derivative was shown by the fact that phosphoric acid cleavage gave the theoretical amount of formaldehyde. The ring-substituted compound would not be expected to cleave under these conditions. The reaction with N,N-dimethylaniline gave a product in 10.5% yield whose analysis fitted the ring-substituted derivative.

The reaction of 1,4-bis-(hydroxymethylsulfonyl)-butane with aliphatic amines, such as propylamine, diethylamine or pyrrolidine, gave low-melting, hygroscopic solids or oils, whose analyses did not fit the expected compounds, while reaction with ammonia resulted in the formation of the diammonium salt of 1,4-butanedisulfinic acid.[1]

1,4-Bis-(hydroxymethylsulfonyl)-butane was also treated with urea, acetamide and allylthiourea (Table V). These reactions involve refluxing two moles of the amide with one of the bis-hydroxymethyl sulfone for several hours. The expected products resulted in each case.

Acknowledgment.—The authors thank Mrs. Cecilia Jorgensen, Mr. A. Pollara and Mr. G. Weiss for the infrared absorption data, Mr. O. E. Sundberg and his associates for the microanalyses, and Mr. R. L. Cox and Mr. S. P. Kodama for determining the optical properties reported.

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(11) E. Bäder and H. D. Hermann, *Chem. Ber.*, **88**, 41 (1955).

Experimental[12]

Materials.—The α,ω-disulfonyl chlorides were prepared by oxidative chlorination of the corresponding diisothiuronium salts[13] by the method of Sprague and Johnson,[14] and then converted to the disodium sulfinate, with sodium sulfite in the presence of sodium bicarbonate.[3]

1,4-Butanedisulfinic Acid; Preparation from the Zinc Salt.—To a solution of 332 g. (2.63 moles) of sodium sulfite and 453 g. (5.38 moles) of sodium bicarbonate, in 120 ml. of water, 321 g. (1.25 moles) of 1,4-butanedisulfonyl chloride was added, with stirring, at 45–55° during one hour. The reaction mixture was heated at 75–85° for 1.5 hr., cooled to room temperature and filtered to separate some insoluble salts. The filtrate was mixed with a solution of 510 g. (3.74 moles) of zinc chloride in 400 ml. of water and the resulting mixture, containing precipitated zinc salt, was stirred for one hour at room temperature, filtered, and the salt washed with a little water. The product was dissolved in 530 ml. of 20% hydrochloric acid by warming gently on a steam-bath and the mixture filtered, while hot, to remove additional salts. The filtrate was cooled and let stand at 5° for several hours. The colorless crystalline precipitate which separated was collected, washed with two 50-ml. portions of ice-cold water and dried. The product weighed 153 g. (66%) and melted at 119–122°. On recrystallization from water the m.p. was 124–125°. The infrared absorption spectrum showed the sulfinic acid absorption band at 1047 cm.$^{-1}$ and none at 1176 cm.$^{-1}$, indicative of a sulfonic acid group.

Anal. Calcd for $C_4H_{10}O_4S_2$: C, 25.8; H, 5.38; S, 34.4. Found: C, 25.9; H, 5.28; S, 34.4.

The following optical properties of 1,4-butanedisulfinic acid were determined: interference figure, biaxial; optical character, negative; optical axial angle (2V), 13 ± 1°; extinction, parallel and symmetrical; refractive indices, negative; 13 ± 1°; parallel and symmetrical; $\alpha = 1.494 \pm 0.002$, $\beta = 1.610 \pm 0.002$, $\gamma = 1.612 \pm 0.002$.

The following crystal morphology was observed: crystal system, orthorhombic; crystal habit (recrystallized from water) six-sided plates, also rhombs; optical axial plane, 001; optical orientation, $a = \gamma$, $b = \alpha$, $c = \beta$.

1,4-Butanedisulfinic Acid, Direct Isolation from the Reaction Solution.—To a solution of 26.5 g. (0.21 mole) of sodium sulfite and 36.1 g. (0.43 mole) of sodium bicarbonate in 100 ml. of water, 25.5 g. (0.1 mole) of 1,4-butanedisulfonyl chloride was added with stirring at 45–50° over a period of one hour. The solution was stirred at 70–80° for two hours, cooled to 50° and filtered. The filtrate was cooled to 5°, filtered again to remove additional inorganic solids and acidified by adding 19 ml. of concd. hydrochloric acid. The resulting colorless precipitate was collected and stirred with 30 ml. of water at room temperture. The colorless crystalline product weighed 11.25 g. (60.3% yield), m.p. 124–125°. The mixture melting point and infrared spectrum showed this product to be identical with the one obtained *via* the zinc salt.

Attempted Isolation of 1,3-Propanedisulfinic Acid.—A mixture of the zinc salt of 1,3-propanedisulfinic acid and other salts was prepared by the reduction of 1,3-propanedisulfonyl chloride according to the procedure used in preparing the zinc salt of 1,4-butane-disulfinic acid. A portion of this material, 18.0 g., which contained about 7.2 g. of the zinc salt of 1,3-propanedisulfinic acid, as determined by the yield of the acrylamide adduct, was dissolved in a solution of 13 ml. of concentrated hydrochloric acid in 20 ml. of water. The solution was filtered and freeze-dried overnight. The residue, 21.2 g. of solid plus some liquid, showed absorption in the infrared at 1047 and 1176 cm.$^{-1}$. This material did not form an adduct with acrylamide.

1,5-Pentanedisulfinic Acid.—To a solution of 422 g. (3.35 moles) of sodium sulfite and 563 g. (6.70 moles) of sodium bicarbonate in 1675 ml. of water, 450 g. (1.67 moles) of 1,5-pentanedisulfonyl chloride was added with stirring at 40–50° over a period of one hour. The reaction mixture was heated at 75–85° for 1.5 hours, cooled to room temperature and filtered. A solution of 479 g. (3.52 moles) of zinc chloride in 500 ml. of water was added to 1525 ml. (70%) of the filtrate. The copious precipitate was diluted with 400 ml. of water and stirred for one hour. After the product was filtered and dried at 65°, a portion of this material, 270 g., was dissolved in 180 ml. of 13% hydrochloric acid by warming on a steam-bath. The resulting solution was filtered, cooled to −10° and the colorless crystalline precipitate which separated was collected. After two recrystallizations from the minimum amount of 13% hydrochloric acid the product melted at 86–95°. A third recrystallization yielded a fine white crystalline solid melting at 92–95°. After drying over phosphorus pentoxide *in vacuo*, this material became very waxy and the melting point changed to 72–86°. The infrared absorption spectrum of this waxy material showed strong absorption band at 1047 cm.$^{-1}$ and no absorption band at 1175 cm.$^{-1}$ to indicate the presence of the sulfonic acid group. *Anal.* Calcd. for $C_5H_{12}O_4S_2$: C, 30.0; H, 6.00; S, 31.9. Found: C, 29.6; H, 6.00; S, 31.9.

1,6-Hexanedisulfinic Acid.—To a solution of 26.5 g. (0.21 mole) of sodium sulfite and 36.2 g. (0.43 mole) of sodium bicarbonate in 100 ml. of water, 37.4 g. (0.10 mole) of 1,6-hexanedisulfonyl bromide was added with stirring at 40–50° over a period of one hour. The reaction was heated at 75–85° for 1.5 hours and then filtered. The filtrate was cooled to 10° and acidified by the dropwise addition of 33 ml. of 6 *N* hydrochloric acid. The colorless crystalline precipitate was collected and washed with 30 ml. of ice-water. After drying *in vacuo* overnight, the product weighed 25.0 g. An amount of 10.0 g. of this material was recrystallized from 10 ml. of water and dried *in vacuo* overnight. The infrared absorption spectrum of the recrystallized product showed the sulfinic acid absorption band at 1047 cm.$^{-1}$. This material was used directly for the preparation of the acrylamide adduct.

1,10-Decanedisulfinic Acid.—To a solution of 108.3 g. (1.29 moles) of sodium bicarbonate and 79.5 g. (0.63 mole) of sodium sulfite in 300 ml. of water, 105 g. (0.31 mole) of 1,10-decanedisulfonyl chloride was added at 45–55° with stirring over a period of one hour. The reaction mixture was heated at 75–85° for 1.5 hours, cooled to room temperature and filtered. The clear filtrate was added to a solution of 200 ml. of concentrated hydrochloric acid in 200 ml. of water and resulting colorless precipitate was collected and dried; 65 g. (77% crude yield), m.p. 91–101°. The infrared absorption spectrum of the crude product showed the characteristic sulfinic acid band at 1047 cm.$^{-1}$. No absorption band at 1175 cm.$^{-1}$, due to the presence of sulfonic acid groups, was found. This material was used without further purification for the preparation of the acrylamide adduct.

Preparation of Adducts of α,β-Unsaturated Compounds.—Unless otherwise noted, the general procedure was to reduce the disulfonyl chloride and acidify the reduction filtrate with concentrated hydrochloric acid. The acidified solution was treated with a 20% molar excess of the appropriate α,β-unsaturated compound based on the initial charge of disulfonyl chloride. The solution was stirred overnight at room temperature and the precipitated adduct was collected, washed with water and recrystallized from water.

In the case of 1,4-butanedisulfinic acid, the free acid was isolated, recrystallized from water and then used to prepare the desired adducts.

3,3′-(Trimethylenedisulfonyl)-bis-(N-hydroxymethylpropionamide).—An amount of 7.8 g. (0.025 mole) of 3,3′-(trimethylenedisulfonyl)-bis-propionamide was added to a solution of 24.2 g. (0.3 mole) of formalin (37%) which had been previously adjusted to *p*H 11.6 with 10% sodium hydroxide. The solution was heated at 80° for three hours and, at the end of this time, the *p*H was adjusted to 8 by the addition of 10% sodium hydroxide, the reaction mixture was cooled to 60° and filtered. The filtrate on cooling deposited a solid which weighed 3.5 g. (37% yield), m.p. 167–168°; recrystallized from aqueous dimethylformamide, m.p. 172–174°. *Anal.* Calcd. for $C_{11}H_{24}N_2O_8S_2$: CH_2O, 16.1. Found: CH_2O, 16.7.

Preparation of Disulfones.—The disulfone derivatives were prepared by treating either sodium or potassium 1,4-butanedisulfinate with an equivalent amount of the appropriate alkyl or aryl halide in methanol. The reaction conditions are indicated in Table IV.

1,4-Bis-(hydroxymethysulfonyl)-butane.—To a stirred solution of 6.88 g. (0.086 mole) of 37% formaldehyde was added 5.7 g. (0.031 mole) of 1,4-butanedisulfinic acid. The temperature rose spontaneously to about 50° and was held within the range of 40–50° by external cooling. When the

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(12) All melting points are uncorrected.

(13) C. H. Grogan, L. M. Rice and M. X. Sullivan, *J. Org. Chem.*, **18**, 728 (1953).

(14) J. M. Sprague and T. B. Johnson, THIS JOURNAL, **59**, 2440 (1937).

exothermic reaction subsided, the white slurry was stirred and heated for an additional five minutes at 40–50°. In an attempt to obtain complete solution at this temperature, 6.8 g. of 37% formaldehyde was added to the mixture; no solution resulted. After stirring at the same temperature, for five minutes, the mixture was cooled, filtered and the product was air-dried overnight; 5.8 g. (77% yield), m.p. 143–144°. *Anal.* Calcd. for $C_6H_{14}O_6S_2$: C, 29.2; H, 5.72; S. 26.1. Found: C, 29.1; H, 5.59; S, 26.1.

This product was also obtained in an over-all yield of 70% by treating the reduction filtrate from 14-butanedisulfonyl chloride with formalin at a *p*H of 2-3, but our attempts to prepare the bis-(hydroxymethyl) sulfones from the corresponding 1,2-ethane-disulfonyl chloride,[15] 1,3-propanedisulfonyl chloride[16] and 1,5-pentanedisulfonyl chloride[17] in the same way were not successful.

1,4-Bis-(α-hydroxypropylsulfonyl)-butane.—To a stirred solution of 1.86 g. (0.01 mole) of 1,4-butanedisulfinic acid in 20 ml. of water was added 1.16 g. (0.02 mole) of propionaldehyde and the colorless precipitate which formed was diluted with 10 ml. of water. The precipitate was stirred for 15 minutes, collected, and washed successively with water, ethanol and ether. The product weighed 1.4 g., 46% yield, m.p. 117–120°; recrystallized from a mixture of 20 ml. of water and 10 ml. of propionaldehyde, m.p. 114–116°. *Anal.* Calcd. for $C_{10}H_{22}O_6S_2$: C, 39.8; H, 7.35. Found: C, 39.2; H, 7.20.

1,4-Bis-(acetoxymethylsulfonyl)-butane.—A mixture of 50 ml. of acetic anhydride and 9.84 g. (0.04 mole) of 1,4-bis-(hydroxymethylsulfonyl)-butane was heated on the steam-bath for 15 minutes with 10 drops of concentrated sulfuric. The solution was cooled to room temperature, chilled, filtered and the precipitate was washed with ether; 12.5 g., m.p. 104–113°. Recrystallization from ethyl acetate gave 9.4 g., 71.5% yield, m.p. 122–125°. *Anal.* Calcd. for $C_{10}H_{18}O_8S_2$: C, 36.35; H. 5.46; S, 19.4. Found: C, 36.35; H, 5.51, S, 19.4.

Preparation of 1,4-Bis-(N-substituted)-aminomethylsulfonyl-butanes.—The general procedure involved the addition of a methanolic solution of the amine or amide to a methanolic solution of 1,4-bis-(hydroxymethyl)-sulfonyl-butane. The reaction conditions are indicated in Table V.

BOUND BROOK, N. J.

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[15] T. B. Johnson and J. M. Sprague, THIS JOURNAL, **58**, 1348 (1936).

[16] F. Asinger, F. Ebeneder and E. Böck, *Ber.*, **75B**, 42 (1942).

[17] P. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, 120 (1922).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Stereochemistry of Conjugate Additions. Convergent Configuration Control in Additions of Morpholine and N-Bromomorpholine to cis- and trans-α,β-Unsaturated Ketones

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Addition of N-bromomorpholine yields the same α-bromo-β-morpholino-*p*-nitrobenzylacetophenone (form B) from either *cis*- or *trans*-4-nitrochalcone. This product is the diastereoisomer of the compound (form A) produced by adding morpholine to either *cis*- or *trans*-α-bromo-4-nitrochalcone. Likewise, 3-bromo-2-keto-4-morpholino-4-phenylbutyl benzoate was obtained in only one of the two possible configurations by addition of morpholine to the *cis*- or *trans*-3-bromo-2-keto-4-phenyl-3-butenyl benzoates. In the cases of the α-bromo-β-morpholinobenzylacetophenones and the α-bromo-β-morpholino-*p*-nitrobenzylacetophenones the diastereoisomer produced by the morpholine addition (form A) was converted by heating or by standing in solution into the apparently more stable diastereoisomer (form B), produced by N-bromomorpholine addition. The two diastereoisomeric α-bromo-β-morpholinobenzylacetophenones differ in their behavior when heated in methanol; form B undergoes solvolysis with rearrangement, but form A undergoes only rearrangement to give one of the β-bromo-α-morpholinobenzylacetophenones. These observations may indicate that form A has the *threo* configuration, form B the *erythro*. A mechanism involving protonation or bromination of a chelated enolic intermediate from the less hindered direction is advanced as a possible explanation of the observed convergent configuration control in these conjugate additions of morpholine and N-bromomorpholine.

In a previous investigation[2a] it was shown (see Chart I) that N-bromomorpholine adds to the olefinic bond of *trans*-chalcone (Ia) to yield chiefly the α-bromo-β-morpholinobenzylacetophenone (Va) (form B) which is the diastereoisomer of the compound (VIa) (form A) obtained by the addition of morpholine to the *cis* or *trans* forms (IVa or IIIa) of α-bromochalcone.[3,4] The present investigation represents an effort to discover the basis for the configuration control which has permitted these two conjugate addition reactions each to yield a different diastereoisomer. To this end, new experiments have been performed for the purpose of answering the following questions: (1) whether the configuration (*erythro* or *threo*) of an N-bromomorpholine adduct might be determined by the *cis* or *trans* configuration of the α,β-unsaturated ketone to which the addition occurred; (2) which of the diastereoisomeric adducts represents the thermally stable configuration; and (3) whether a comparison of reactivities might make it possible to establish *erythro* and *threo* configurations for the form A and form B adducts. The results of these experiments, which are described in the sections to follow, have delineated the major requirements for any theory which could account for the kind of configuration control peculiar to these conjugate additions.

Comparison of Additions to *cis* and *trans* Isomers.—It had been suggested that in the N-bromomorpholine addition to *trans*-chalcone the steric outcome might reflect some kind of concerted *trans* addition process.[2] This view of of the reaction implied that it might be possible to demonstrate that addition of N-bromomorpholine to a *cis*-α,β-unsaturated ketone would yield an addition product diastereoisomeric with that obtained from addition of N-bromomorpholine to the corresponding *trans* compound. This question has now

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[2] (a) P. L. Southwick and W. L. Walsh, THIS JOURNAL, **77**, 405 (1955); (b) P. L. Southwick and D. R. Christman, *ibid.*, **75**, 629 (1953).

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