carbonate, during which time it lost its active oxygen content. The alkaline solution was continuously extracted with ether for 36 hr. (extract A). The alkaline layer was acidified with hydrochloric acid and extracted with three 50-ml. portions of ether (extract B). From dried extract B was obtained a 26% yield (based on an expected 2 mole equiv.) of benzoic acid (VIIIa) melting at 120–121°. Ether extract A was dried and evaporated, giving 1.53 g. of an oil (from 10 mmoles of Id), which was dissolved in 20 ml. of benzene and chromatographed over an alumina column (25 × 75 mm.). Elution with petroleum ether gave nothing. Elution with nine 100-ml. portions of a 1:1 petroleum ether–benzene solution, two 100-ml. portions of benzene, and two 100-ml. portions of a 1:1 benzene–chloroform solution gave 0.42 g. of benzil melting at 88–91°. Elution with two 100-ml. portions of 1:1 benzene–chloroform gave a mixture of benzil and phenylglyoxal from which was extracted the phenylglyoxal with strong base, in the form of mandelic acid[2] (0.07 g.), leaving 0.11 g. of benzil melting at 88–91°. Elution with 400 ml. of chloroform gave 0.23 g. of phenylglyoxal, identified as its dinitrophenylhydrazone, m.p. 295–298°. All identifications were by mixture melting points with authentic samples. The yield of benzil (IXe) was 25% and the yield of phenylglyoxal (IXa) was 11%.

B. In 90% Acetic Acid. Sodium Iodide Reduction.—The ozonation was carried out as in the preceding experiment, after which the reaction mixture was poured into the sodium iodide solution. The released iodine was reduced with thiosulfate. Filtration of the resulting mixture gave a 32% yield of benzil (IXe) melting at 95–96°. Treatment of the filtrate with 2,4-dinitrophenylhydrazine gave the crude dinitrophenylhydrazone of phenylglyoxal (IXa) which, after recrystallization from ethyl acetate, melted at 293–297° (40% yield, based on an expected 2 mole equiv.) Identifications were by the mixture melting point method. In a similar experiment a 44% yield of phenylglyoxal (IXa) was obtained by pouring the entire ozonation mixture into 2,4-dinitrophenylhydrazine reagent.

C. In Methylene Chloride Solution.—The ozonation was carried out at 0° in methylene chloride with 2 mole equiv. of ozone from ozone–oxygen in the usual manner. Work-up started out as in procedure D for 2,5-diphenylfuran.[1] After the sodium carbonate extraction a sodium hydroxide extraction was made. From the ether solution after the carbonate and hydroxide extractions was obtained benzil (IXe) in 56% crude yield, m.p. 75–86°; recrystallized from ethanol, m.p. 95–96°, 70% recovery. From the carbonate extract, after acidification, extraction with ether, and evaporation of the ether extract, was obtained a 21% yield of benzoic acid (VIIIa), m.p. 119–121°. Similarly, the hydroxide extract gave a 14% yield of *dl*-mandelic acid (from phenylglyoxal, IXa[2]) melting at 116–118°. Another 4% yield of phenylglyoxal (IXa) was obtained in the form of the dinitrophenylhydrazone after treating the extracted reaction mixture with 2,4-dinitrophenylhydrazine; it had m.p. 297–298°. All identifications were by mixture melting points with authentic samples.

Ozonation of 1,2-Diaroylethylenes. A. To Give the Respective Mandelic Acids.—The diaroylethylenes ozonized were *trans*-1,2-di(*p*-bromobenzoyl)ethylene,[16] *trans*-1,2-dianisoylethylene,[12] and *trans*-1,2-dimesitoylethylene.[15] A solution of 10 mmole of the diaroylethylene in 100 ml. of either 1:1 methylene chloride–methanol or 5:1 methylene chloride–90% acetic acid was treated with 10 mmoles of ozone at 0°. Ozone absorption was quantitative, except with the bromobenzoylethylene. The reaction mixture was worked up according to procedure D for 2,5-diphenylfuran.[1] Both a sodium carbonate and a sodium hydroxide extraction were made. From the carbonate layer by the usual procedure was obtained the corresponding substituted benzoic acid, and, from the sodium hydroxide layer, the corresponding substituted mandelic acid.[2] From the *trans*-di(bromobenzoyl)ethylene was obtained a 53% recovery of starting material and 8.2 mmoles of *p*-bromomandelic acid (m.p. 118–120)[17]; *p*-bromobenzoic acid was not determined. From the *trans*-dianisoylethylene was obtained 3.5 mmoles of anisic acid (m.p. 177–182°) and 1.39 mmoles of *p*-methoxymandelic acid (m.p. 107–108°).[18] From the *trans*-dimesitoylethylene was obtained 6.3 mmoles of mesitoic acid (m.p. 148–154°) and 1.35 mmoles of 2,4,6-trimethylmandelic acid (m.p. 155–157°[19]; m.m.p., with mesitoic acid, 122–127°).

B. *cis*-**1,2-Dimesitoylethylene (VIId)**[15] (1 mmole) in 25 ml. of methylene chloride was ozonized at 0° with 1 mmole of ozone from ozone–nitrogen.[9b] Ozone absorption was quantitative, and only a trace of molecular oxygen was evolved.

Acknowledgment.—The authors are grateful for grants from the Robert A. Welch Foundation, the American Chemical Society Petroleum Research Fund, and the National Science Foundation, which made this work possible.

(16) Prepared by the method of J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **47**, 881 (1925)] with m.p. 193–194°.

(17) J. L. Riebsomer, R. Baldwin, J. Buchanan, and H. Burkett, *ibid.*, **60**, 2974 (1938).

(18) K. Kindler, W. Metzendorf, and D-y-Kwok, *Ber.*, **76**, 308 (1943).

(19) R. C. Fuson, W. S. Emerson, and H. W. Gray, *J. Am. Chem. Soc.*, **61**, 480 (1939).

The Reactions of -Aminoalkyl Hydrogen Sulfates. I. The Preparation of Some Substituted Thiazolidine-2-thiones[1]

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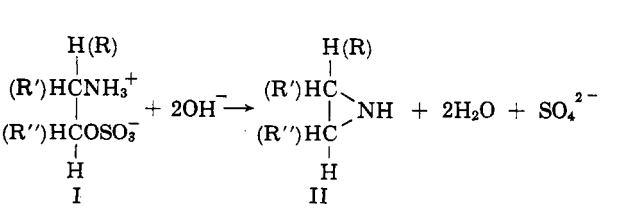
Sodium 2-aminoethyl sulfate reacts with potassium ethyl xanthate to give thiazolidine-2-thione in good yield. This reaction has been used to prepare aryl- and alkyl-substituted thiazolidinethiones from suitably substituted derivatives of 2-aminoethyl hydrogen sulfate. The preparation of the aminoalkyl hydrogen sulfates is described.

The reaction of β-aminoalkyl hydrogen sulfates (I) with strong bases is a convenient method for the preparation of aziridines (II). However, little study has been made of other reactions of these bifunctional compounds. Unlike the β-aminoalkyl halides, the aminoalkylsulfate salts are fairly stable in aqueous alkaline solution at room temperature. They are slowly converted to aziridines only at elevated temperatures.



I II

For example, the half-life of sodium 2-aminoethyl sulfate in alkaline solution at 75° is about 24 hr.,[1] while under the same conditions the half-life of 2-aminoethyl bromide is about 5 sec.[3] In acidic solution,

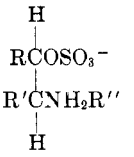
(1) From The Ph.D. Thesis of R. A. Bafford, University of Maryland, June 1960.

(2) To whom inquiries should be addressed at Lucidol Division, Wallace and Tiernan, Inc., 1740 Military Road, Buffalo, N. Y. 14240.

(3) Estimated from the data of H. Freundlich and Kroepelin [*Z. Physik Chem.* (Leipzig), **122**, 139 (1926)].

TABLE I

CONSTANTS OF SOME AMINOALKYL HYDROGEN SULFATES

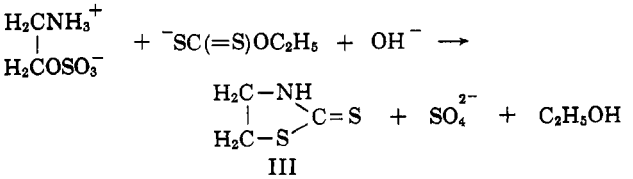


R	R′	R″	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	H	H	96	277–279[a]	17.02	17.28	4.96	5.12		
CH_3	H	H	56	254–256	23.22	23.25	5.80	5.56		
H	CH_3	H	60	242–243	23.22	23.27	5.80	6.00		
H	H	CH_3	61	147–149	23.22	23.25	5.80	5.92		
C_2H_5	H	H	83	228–230[b]	28.44	28.76	6.50	6.44		
H	C_2H_5	H	48[c]	255–256	28.44	28.61	6.50	6.69		
H	H	C_2H_5	60	207–209	28.44	28.66	6.50	6.98		
CH_3	CH_3 (*threo*)	H	63	263–265	28.44	28.66	6.50	6.77		
CH_3	CH_3 (*erythro*)	H	79	278–279	28.44	28.59	6.50	6.82		
$(CH_3)_2CH$	H	H	82	278–279	32.75	32.83	7.10	7.39	7.65	7.48
$(CH_3)_3C$	H	H	62	299–300	36.52	36.74	7.61	7.53	7.10	7.25
C_6H_5	H	H	35	255–255.5	44.20	44.03	5.06	5.82	6.45	6.35
H	C_6H_5	H	40	247–247.5	44.20	44.43	5.06	5.23		
H	H	C_6H_5	40	206–207	44.20	44.15	5.06	5.15	6.45	6.22
	$-(CH_2)_3-$	H	53	285–286[d]						
	$-(CH_2)_4-$	H	84	300[e]						
	$-(CH_2)_5-$	H	73	280–281[f]						
	$-(CH_2)_6-$	H	77	271–272.5[g]						
$C_6H_5CH_2$	H	H	80	294–295	46.75	46.72	5.66	5.86		
$^+H_3NC(CH_3)_2CH_2OSO_3^-$			60	265–267	28.44	28.62	6.50	6.48	8.29	8.55
$^+H_3NCH_2CH_2CH_2OSO_3^-$			62	226–227.5	23.22	23.25	5.80	6.02		
$^+H_3NCH_2CH_2CH_2CH_2OSO_3^-$			63	226–227	28.44	28.20	6.50	6.63		
$^+H_3NCH_2CH_2CH(CH_3)CH_2OSO_3^-$			37	201–202	28.44	28.84	6.50	6.34		

[a] M.p. 230°, S. Gabriel, *Ber.*, **21**, 1056 (1888). [b] M.p. 224–226°, ref. 26. [c] Prepared from the amino alcohol hydrochloride and chlorosulfonic acid, ref. 7. [d] M.p. 280°, P. E. Fanta, *J. Chem. Soc.*, 1441 (1957). [e] M.p. 304–305°, ref. 15. [f] M.p. 282–284°, ref. 24. [g] M.p. 270–275°, D. Kashelikan and P. Fanta, *J. Am. Chem. Soc.*, **82**, 4927 (1960).

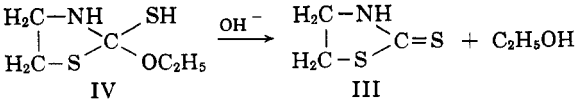
the sulfates are slowly hydrolyzed to the parent amino alcohols.

It has been reported that 2-aminoethyl hydrogen sulfate and potassium ethyl xanthate react in an alkaline medium to give thiazolidine-2-thione (III).[4] Maier



III

reported that the initial product was 2-ethoxy-2-mercaptothiazolidine IV, convertible upon further treatment with caustic to III and ethanol.[5]



IV III

A study was undertaken to determine if IV is an intermediate in the reaction and to elucidate the reaction mechanism. The accompanying paper will cover the kinetics and postulated mechanism for the reaction. The purpose of this communication is to report on the preparation of some alkyl- and aryl-substituted thiazolidine-2-thiones and of their β-aminoalkyl hydrogen sulfate precursors.

(4) S. D. Shinkle, U. S. Patent 2,328,929 (1943).

(5) W. Maier, U. S. Patent 2,148,909 (1939).

Aminoalkyl hydrogen sulfates can be prepared from amino alcohols and sulfuric acid[6] or from amino alcohol hydrochlorides and chlorosulfonic acid.[7]

The first method, in which a modified Wenker technique was used, generally gave better results in this study. The hydrogen sulfates of phenyl-substituted amino alcohols were successfully prepared despite published reports to the contrary.[8]

The properties of the sulfates are listed in Table I.

Commercially unavailable amino alcohols were prepared by the following sequence of reactions. The appropriate olefin was treated with aqueous N-bromosuccinimide to give the bromohydrin,[9] which, with caustic, formed the epoxide. (*cis*-Cyclooctene oxide could not be prepared by this method, since treatment of the bromohydrin with hot aqueous sodium hydroxide gave a mixture of products that contained neither *cis*- nor *trans*-cyclooctene oxide. The epoxide was prepared in good yield from *cis*-cyclooctene and perbenzoic acid.) Ammonolysis of the epoxides gave improved yields of the amino alcohols when the reaction was carried out in a homogeneous system containing a large excess of ammonia.[10] Ring opening occurs with inversion of configuration and formation of predomi-

(6) H. Wenker, *J. Am. Chem. Soc.*, **57**, 2328 (1935).

(7) R. Elderfield and H. A. Hageman, *J. Org. Chem.*, **14**, 605 (1949).

(8) (a) J. S. Fruton in "Heterocyclic Compounds," Vol. I, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 63; (b) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 729.

(9) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77**, 2549 (1955).

(10) L. R. Hawkins and R. A. Bannard, *Can. J. Chem.*, **36**, 220 (1958).

TABLE II

CONSTANTS OF SOME THIAZOLIDINE-2-THIONES

Substituents	Yield, %	M.p., °C. Obsd.	M.p., °C. Lit.	ν(-N-C=S),[a] cm.⁻¹	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	73	105–106	104.8–105.1[b]	1502						
4-Methyl	63	100.5–101	99.0–99.5[b]	1505						
5-Methyl	52	92.5–93.0	91.0–91.5[b]	1498						
N-Methyl	69	69.5–69.5		1490						
4-Ethyl	52	51.0–51.5	48.8–49.4[b]	1495						
5-Ethyl	56	76.6–76.9	...	1500	40.78	40.73	6.16	6.10	9.51	9.39
5-Isopropyl	70	110.1–111.2	...	1502	44.68	44.80	6.87	6.83		
5-*t*-Butyl	25	151.8–152.4	...	1505	48.02	48.17	7.48	7.39	8.00	7.98
cis-4,5-Dimethyl	70	119.2–120.1	...	1488	40.78	40.88	6.16	6.13	9.51	9.92
trans-4,5-Dimethyl	60	100.5–101.5	...	1498	40.78	41.05	6.16	6.33	9.51	9.25
4,4-Dimethyl	60	118–118.3	117.8–118.3[b]	1492						
cis-4,5-Trimethylene	11	106.5–107.2	...	1502	45.25	45.55	5.70	5.80		
cis-4,5-Tetramethylene	64	103.5–104.5	102–103[c]	1486						
4-Phenyl	65	188.5–189.0	191[d]	1490						
5-Phenyl	29	167.8–168.0	169–170[e]	1500						
N-Phenyl	68	129–130	133–134[f]	1480						
5-Benzyl	69	95.5–96.0	...	1505	57.39	57.22	5.66	5.69	6.05	6.30

[a] L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 294. [b] L. Clapp and J. Watjen, *J. Am. Chem. Soc.*, **75**, 1490 (1953). [c] Ref. 16. [d] S. Gabriel and J. Colman, *Ber.*, **47**, 1871 (1914). [e] F. Wolfheim, *ibid.*, **47**, 1449 (1914). [f] Yu. K. Yur'ev and S. K. Dyatdovitskaya, *Zh. Obsch. Khim.*, **27**, 3152 (1957); *Chem. Abstr.*, **52**, 9077 (1958).

TABLE III

CONSTANTS OF SOME 3-*p*-NITROBENZOYLTHIAZOLIDINE-2-THIONES

Substituents	M.p., °C. Obsd.	M.p., °C. Lit.[a]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	163.0–164.0	162.6–163.2				
4-Methyl	159.2–160.3	159.0–160.0				
5-Methyl	139.0-140.0	139.0–139.2				
4-Ethyl	121.5–122.5	121.6–122.4				
5-Ethyl	130.5–130.7	...	48.63	48.82	4.08	4.30
5-Isopropyl	129.0–129.2	...	50.30	50.47	4.55	4.70
5-*t*-Butyl	200.2–200.8	...	51.83	51.95	4.97	4.65
cis-4,5-Dimethyl	121.0–121.3	...	48.63	48.65	4.08	4.02
trans-4,5-Dimethyl	171.0–172.0	...	48.63	49.31	4.08	4.09
4,4-Dimethyl	186.8–187.9	168.0–168.5	48.63	48.30	4.08	3.76
cis-4,5-Trimethylene	162.9–163.1	...	50.63	50.83	3.92	4.08
cis-4,5-Tetramethylene	188.8–189.0	...	52.15	52.30	4.38	4.60
4-Phenyl	148.9–149.1	...	55.79	56.02	3.49	3.30
5-Phenyl	193.8–194.1	...	55.79	55.52	3.49	3.26
5-Benzyl	133.8–134.2	...	56.96	57.18	3.94	3.97

[a] L. Clapp and J. Watjen, *J. Am. Chem. Soc.*, **75**, 1490 (1953).

nantly the secondary alcohol.[11] Unlike most epoxides, *cis*-cycloheptene oxide and *cis*-cyclooctene oxide were quite resistant to ammonolysis. Prolonged heating at higher temperatures was required in order to obtain satisfactory yields of the amino alcohols from these two epoxides.

2-Nitro-1-propanol, obtained by the base-catalyzed addition of formaldehyde to nitroethane, was reduced catalytically with Raney nickel at 3000 p.s.i.g. of hydrogen to 2-amino-1-propanol.[12] 2-Phenyl-2-aminoethanol was prepared by the catalytic hydrogenation of the compound resulting from the reaction of styrene oxide with aqueous sodium azide.[13]

The substituted thiazolidine-2-thiones were prepared by heating an aqueous solution of equimolar amounts of the β-aminoalkyl hydrogen sulfate, potassium ethyl xanthate, and sodium hydroxide. In general, pure thiazolidines crystallized from the reaction mixtures. These colorless, crystalline compounds possessed a very bitter taste and a mildly unpleasant odor typical of sulfur compounds. They are soluble in aromatic and oxygenated solvents and in solutions of strong bases. Their chemistry has been reviewed.[14] The properties of the thiazolidines are recorded in Table II; the properties of their 3-*p*-nitrobenzoyl derivatives are listed in Table III.

In all preparations except two, the thiazolidines were free of isomers. When *threo*-2-amino-3-butyl hydrogen sulfate (V) was converted to 4,5-dimethylthiazolidine by the procedure described, the product was a mixture of 57% of the *cis*-4,5-dimethylthiazolidine-2-thione and 43% of the *trans* isomer. Contrariwise, the *erythro* compound VI gave a mixture of 65% of *trans* isomer and 35% *cis* isomer. However, when the reaction was carried out with a 200% excess of potassium ethyl xanthate, V gave 86% *cis* and VI gave 95% *trans*. The assignment of configuration was made by corre-

(11) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 742 (1959).

(12) F. F. Blicke, J. A. Faust, R. J. Warzynski, and J. E. Gearien, *J. Am. Chem. Soc.*, **67**, 206 (1945).

(13) E. E. McEwen, W. E. Conrad, and C. A. VanderWerf, *ibid.*, **74**, 1168 (1952).

(14) J. M. Sprague and O. H. Land, "Heterocyclic Compounds," Vol. V, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 692.

lating the products with authentic samples prepared from *cis*-2,3-butylenimine and *trans*-2,3-butylenimine by their reaction with carbon disulfide (it is generally recognized that the ring opening of imines occurs in a *trans* manner[15,16]).

Experimental[17]

t-Butylethylene.—Pinacolyl alcohol was prepared in 47–65% yield from *t*-butylmagnesium chloride and acetaldehyde. The alcohol was acetylated in quantitative yield with acetic anhydride containing 2–3% by weight of fused sodium acetate.

Pinacolyl acetate was pyrolyzed to give *t*-butylethylene in 76–79% conversion.[18] Pyrolysis at 500° rather than at 400° gave better conversions to the olefin. Recycling of the uncracked ester raised the yield to 85%. Physical properties of *t*-butylethylene are b.p. 40.5–41.1° (754 mm.), $n^{25}D$ 1.3731, lit.[18] b.p. 41.18° (760 mm.), $n^{20}D$ 1.3765.

Bromohydrins.—The bromohydrins were prepared by adding the appropriate olefin to a well-stirred mixture of water and N-bromosuccinimide. The reaction was exothermic and cooling was necessary to avoid undue losses of the olefin. When the reaction was completed, the denser bromohydrin layer was separated from the aqueous layer. The aqueous layer was extracted several times with ether and the ether washings were combined with the bromohydrin. The magnesium sulfate dried solution was stripped of ether *in vacuo*. The residue was diluted with 100 ml. of hexane/mole of bromohydrin and was kept overnight at 0°. Any succinimide that precipitated was removed by filtration. The hexane was removed by vacuum stripping and the residue was distilled or used directly in the preparation of the epoxide. The remainder of the succinimide could be quantitatively recovered by allowing the aqueous layer to evaporate to dryness. The bromohydrins are listed below, followed by the yield, boiling point, and refractive index at 25°: 1-bromo-2-butanol, 81–82%, 63° (13 mm.), 1.4758; *threo*-3-bromo-2-butanol, 77–81%, 51° (12.5 mm.), 1.4742, lit.[19] 49.5–51° (13 mm.), 1.4748; *erythro*-3-bromo-2-butanol, 74–86%, 57° (14.5 mm.), 1.4758, lit.[20] 49° (10 mm.), 1.4757; 3-methyl-1-bromo-2-butanol, 79–89%, 77–79° (21 mm.), 1.4760; 3,3-dimethyl-1-bromo-2-butanol, 63%, 67–68° (8 mm.); *trans*-2-bromocyclopentanol and *trans*-2-bromocycloheptanol were not distilled.

Epoxides.—The epoxides were prepared by methods previously reported in the literature.[21] The usual procedure was to add the bromohydrin to concentrated aqueous alkali kept at a temperature high enough to allow the epoxide to distil out as it was formed. The epoxides are listed below, followed by yield from the bromohydrin, boiling point, and refractive index at 25°: 1,2-butylene oxide, 80–82%, 63°, 1.3814, lit.[22] 62°, $n^{17}D$ 1.3855; *cis*-2,3-butylene oxide, 81–92%, 59.5–60.5°, 1.3794, lit.[21] 59.7° (742 mm.), 1.3802; *trans*-2,3-butylene oxide, 89–92%, 53–54°, 1.3706, lit.[21] 53.5° (742 mm.), 1.3705; isopropylethylene oxide, 78–89%, 81–81.5°, 1.3888; *t*-butylethylene oxide, 46–57%, 95.9–96.8°, 1.3976, lit.[23] 86°, 1.3976; cyclopentene oxide, 52–68% (based on olefin), 99–100°, 1.4330, lit. 102°, 1.4330; cycloheptene oxide, 63% (based on olefin), 157–160°, 1.4618, lit.[24] 82–84° (50 mm.), 1.4621. *cis*-Cyclooctene oxide was prepared in 95% yield from *cis*-cyclooctene and excess perbenzoic acid: b.p. 63–64° (9 mm.), m.p. 52–55°, lit.[25] 90–93° (37 mm.), m.p. 52.5–56.6°.

Amino Alcohols.—A solution of the appropriate epoxide, a 20-fold excess of concentrated aqueous ammonia, and sufficient ethanol to achieve homogeneity was heated for 2 hr. at 100° in an autoclave. Cyclooctene oxide was heated at 150° for 20 hr. in order to obtain a satisfactory yield of the amino alcohol. The amino alcohols are listed below, followed by the yield, boiling point, and refractive index at 25°: 1-amino-2-butanol, 75%, 170°, 1.4472, lit.[26] 82–83° (20 mm.), 1.4482; *threo*-2-amino-3-butanol, 74%, 157°, 1.4436, lit.[21] 69–70° (20 mm.), 1.4445; *erythro*-2-amino-3-butanol, 55%, 160.5–161°, 1.4478, m.p. 43–44°, lit.[21] 75–75.5° (20 mm.), 1.4480, m.p. 43.0–44.8°; 1-amino-3-methyl-2-butanol, 68%, 70.5–71.0° (6 mm.), m.p. 29°, lit.[27] 174° (754 mm.), m.p. 26–27°; *trans*-2-aminocyclopentanol, 76%, 126–128° (26 mm.), 1.4921, lit.[28] 114–115° (13 mm.), $n^{15}D$ 1.4965; *trans*-2-aminocyclohexanol, 88%, 98–100° (1 mm.), m.p. 68°, lit.[29] m.p. 68°; *trans*-2-aminocycloheptanol, 29%, m.p. 74–76°, lit.[24] m.p. 75–75.5°; *trans*-2-aminocyclooctanol, 66%, 122–123° (11 mm.), m.p. 73–74°, lit.[30] 132–133° (16 mm.), m.p. 77–78°; 1-benzyl-2-aminoethanol, 52%, hydrochloride, m.p. 169–171°, lit.[31] m.p. 174–176°; 1-amino-3,3-dimethyl-2-butanol, 56%, hydrochloride, m.p. 280°.

Anal. Calcd. for $C_6H_{16}ClNO$: C, 46.92; H, 10.5; Cl, 23.14. Found: C, 47.13; H, 10.0; Cl, 23.07.

The ammonolysis of styrene oxide was carried out in methanol saturated with anhydrous ammonia to give 74% of 1-phenyl-2-aminoethanol: b.p. 133–137° (6–8 mm.), lit.[32] 149–155° (16 mm.).

4-Amino-1-butanol was prepared in 24% yield by the ammonolysis of 4-chlorobutanol: b.p. 200–202°, 101–102° (12 mm.), $n^{25}D$ 1.4613, lit.[33] 206° (776 mm.).

β-Aminoalkyl Hydrogen Sulfates.—The following procedure was used to prepare the compounds reported in Table I. One mole of concentrated sulfuric acid was added to 1 mole of vigorously stirred amino alcohol, while the temperature was maintained below 40°. Addition of water was sometimes necessary if the reaction mixture became too viscous.

The mixture was heated on a steam bath and water was taken off at water-pump vacuum. When the evolution of water diminished, the flask was transferred to an oil bath and heated at 140–160° (1 mm.) until the viscous syrup crystallized or until no further water was evolved. Prolonged heating led to charring and reduced yields.

The crude product was recrystallized several times from water or aqueous methanol until an aqueous solution failed to give a precipitate with aqueous barium chloride solution. Yields were improved by the recycling of mother liquors. The yields reported in Table I are the average of two or three preparations.

Potassium Ethyl Xanthate.—Fisher Scientific Co.'s pure grade was recrystallized twice from absolute alcohol and dried over silica gel in a vacuum desiccator. The dry xanthate was dissolved in acetone, filtered, and reprecipitated by the addition of anhydrous ether. The material was finally recrystallized from acetone at −20°.

Thiazolidine-2-thiones.—The following procedure was used to prepare the compounds reported in Table II. A glass pressure bottle was charged with 0.05 mole of the aminoalkyl hydrogen sulfate, 8 g. (0.05-g. formula wt.) of potassium ethyl xanthate, and 100 ml. of 0.500 *N* sodium hydroxide. The bottle was sealed and heated at 75° for 20 hr. The bottle was cooled in ice and the crude product was filtered. The crude thiazolidine was recrystallized from benzene or benzene–cyclohexane. Where the crude product separated as an oil, it was taken up in aqueous sodium hydroxide, clarified with charcoal, and reprecipitated by the addition of hydrochloric acid to the alkaline filtrates.

Separation of *cis*- and *trans*-4,5-dimethylthiazolidine-2-thiones from mixtures of the two was accomplished by fractional crystallization from two solvent pairs: benzene–cyclohexane and ethanol–water.

The acyl derivatives were prepared according to published procedures.

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cis-4,5-Dimethylthiazolidine-2-thione.—A mixture of 1 g. of *trans*-2,3-butylenimine[21] and 2 g. of carbon disulfide was sealed in a glass ampoule and heated at 100° for 5 hr. The contents of the ampoule were dissolved in hot 10% aqueous sodium hydroxide solution. The solution was decolorized with charcoal, filtered, and cooled. Acidification with hydrochloric acid precipitated the colorless thiazolidinethione: The crude product was recrystallized from benzene–cyclohexane: yield, 0.70 g. (34%). In like manner, *trans*-4,5-dimethylthiazolidine-2-thione was prepared in 49% yield from *cis*-2,3-butyleneimine.[21]

The Reactions of β-Aminoalkyl Hydrogen Sulfates. II. The Reaction of Sodium β-Aminoalkyl Sulfate with Potassium Ethyl Xanthate[1]

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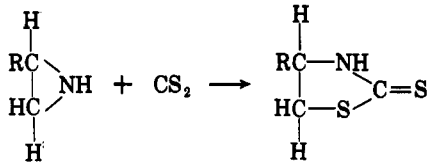
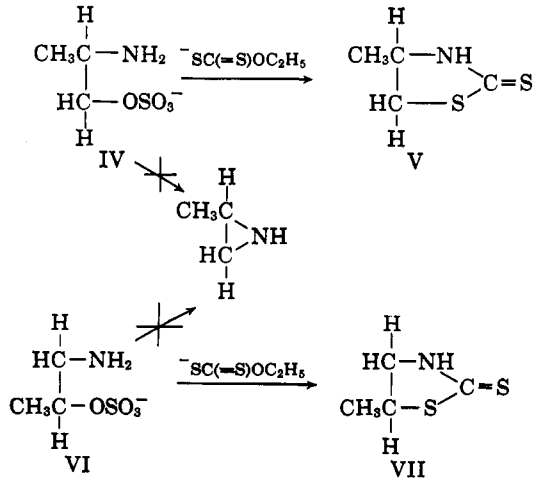
The kinetics of the reaction of sodium β-aminoethyl sulfate (I) and its α- and β-alkyl derivatives with potassium ethyl xanthate to give thiazolidine-2-thiones (II) have been studied. The rate-controlling step is the first-order decomposition of the ethyl xanthate anion to give carbon disulfide which reacts with I to give a dithiocarbamate intermediate III. The latter is converted to II by an intramolecular displacement of the sulfate group by the dithiocarbamate group. A competing reaction, the intramolecular displacement of the sulfate group of I by the neighboring amino group, gives aziridine which reacts with potassium ethyl xanthate and gives II. The two paths to II are not stereochemically equivalent.

Sodium β-aminoethyl sulfate and potassium ethyl xanthate (KEX) react to give thiazolidine-2-thione. The stoichiometry and scope of the reaction have been covered in the accompanying paper.[3] The purpose of this paper is to report on the observed kinetics and to propose a mechanism consistent with the kinetics, stoichiometry, and stereochemistry of the reaction.

Aziridines are opened by carbon disulfide giving thiazolidine-2-thiones.[4] Ring opening of 2-alkylaziridines occurs between the nitrogen and least-substituted carbon atom to give 4-alkyl-thiazolidine-2-thiones.[4b] The reaction of the β-aminoalkyl sulfate anion (I) with potassium ethyl xanthate (KEX) did



not appear to proceed through the aziridine intermediate since the product from sodium 2-aminopropyl sulfate (IV) and KEX was 4-methylthiazolidine-2-thione (V) while that from sodium 1-amino-2-propyl sulfate (VI) was 5-methylthiazolidine-2-thione (VII).[3] Similar results were observed in the preparation of the 4-ethyl, 5-ethyl, 4-phenyl, and 5-phenyl thiazolidines.[3]



Results and Discussion

In an attempt to uncover the mechanism of the reaction, the rate constants of three reactions were determined: (A) the formation of aziridine from sodium 2-aminoethyl sulfate (I) in aqueous alkali; (B) the decomposition of potassium ethyl xanthate (KEX) in alkaline solution; and (C) the formation of thiazolidine-2-thione (II) from I and KEX. A reaction temperature of 75° was chosen solely for convenience so that a kinetic run could be completed in a reasonable period. The data for the three reactions are summarized in Table I.

TABLE I

THE DECOMPOSITION OF SODIUM 2-AMINOETHYL SULFATE AND POTASSIUM ETHYL XANTHATE

Reaction	[I], *M*	[KEX], *M*	[NaOH], *M*	10^3 *k* (min.$^{-1}$)
A	0.5	...	0.5	0.48 ± 0.01
B	...	1×10^{-4}	pH 8	4.3 ± 0.3
B	...	1×10^{-4}	pH 9	4.9
B	...	1×10^{-4}	pH 10	8.7 ± 0.3
C	0.5	0.5	...	3.62 ± 0.07[a] (3.34)[b]
C	0.5	1.0	...	2.86[a]
C	1.0	0.5	...	3.14[a]

[a] Calculated from rate of disappearance of I. [b] Calculated from rate of formation of thiazolidine-2-thione.

The formation of aziridine from I was carried out in an equivalent amount of 0.5 *N* sodium hydroxide. The reaction was followed by determining the decrease in concentration of hydroxide ion as a function of time. The reaction is first order in I and zero order in hydroxide ion. The results of a typical run are shown in Figure 1.

(1) (a) From the Ph.D. Thesis of R. A. Bafford, University of Maryland, June 1960. (b) Presented at the 148th National Meeting of the American Chemical Society, Sept. 1964, Abstracts, p. 42S.

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