Synthesis of Aziridinylsulfonic Acid Derivatives

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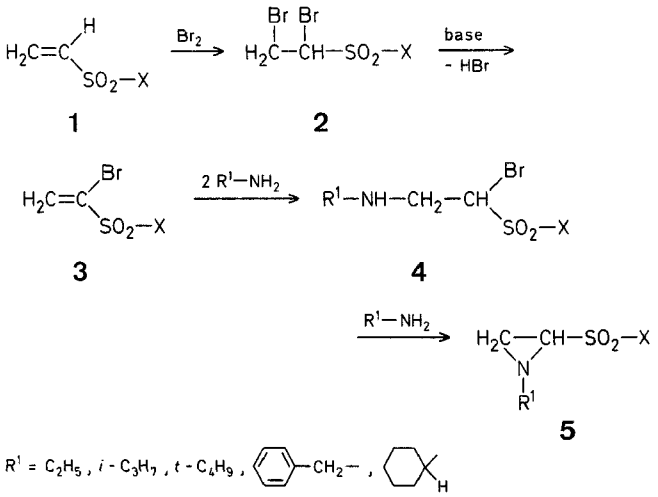
As part of our studies on the reactivity of *C*-functionalized aziridines[1,2], we now report on the synthesis of some previously unknown aziridines bearing sulfonate or sulfonamide groups on a ring carbon atom, **5** (Scheme **A**).

Bromination-dehydrobromination of the ethenesulfonic acid derivatives[3] **1** gives the 1-bromoethenesulfonic acid deriva-



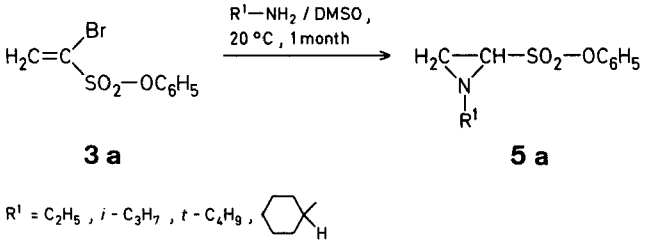
1-5	a	b	c	d	e
X	–O–	–N O	–N	–N C_2H_5 C_2H_5	–N H C_2H_5

Scheme **A**

tives **3**. While the addition of bromine to phenyl ethanesulfonate is almost quantitative in the presence of a radical promoter such as azobisisobutyronitrile or benzoyl peroxide, such promoters are not necessary for bromination of **1**. Products **3** were isolated by column chromatography on silica gel and characterized by ^{1}H-N.M.R. spectral data (Table 1). Treatment of phenyl 1-bromoethenesulfonate **(3a)** or the 1-bromoethenesulfonamides **(3b-e)** in benzene with 2 equivalents of a primary amine yields the 2-alkylamino-1-bromoethenesulfonic acid derivatives **(4a-e)**. Products **4** are isolated by evaporation of the solvent and excess amine, purified by column chromatography, and identified by microanalytical and spectral data (Table 2).

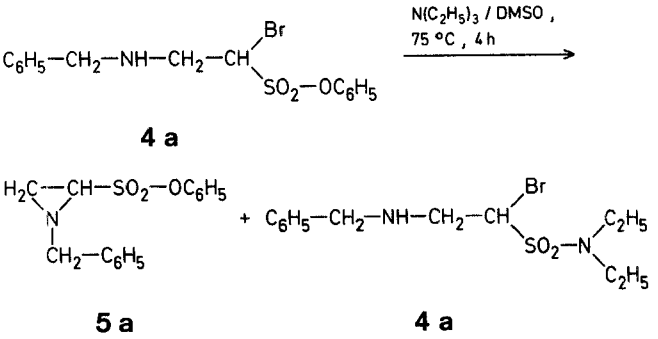
The title compounds are obtained by intramolecular cyclization of compounds **4** (the Cromwell reaction[4]). When benzene solutions of **4** are refluxed in the presence of triethylamine, intramolecular cyclization with aziridine formation is not observed, in agreement with results obtained with 2-alkylamino-1-bromoalkyl sulfones[1].

When a solution of the sulfonate **3a** in dimethyl sulfoxide is stirred for 1 month at room temperature, the aziridinylsulfonate **5a** is formed (Scheme **B**).



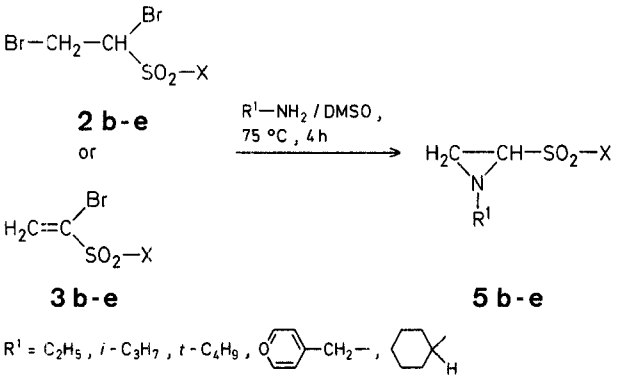
Scheme **B**

When the above reaction is performed at a higher temperature (75°C, 4 h), partial decomposition of the product **5a** is observed. The yield of **5a** ($R^1 = C_6H_5CH_2$) is low when the reaction is performed at room temperature. The best yield of **5a** ($R^1 = C_6H_5CH_2$) is obtained by heating of 1-bromo-1-phenoxysulfonyl-2-benzylaminoethane **(4a)** for 4 h at 75°C with 1 equivalent of triethylamine; however, even under these conditions the yield is not higher than 20%, the cyclization being competitive with sulfonate group ammonolysis (Scheme **C**).



Scheme **C**

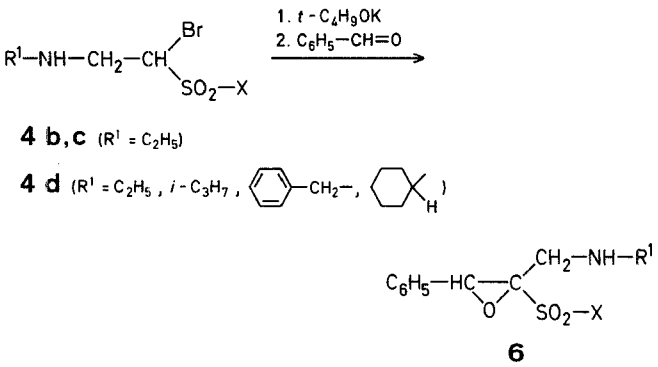
The aziridinylsulfonamides **5b-e** are thermally more stable than the sulfonate **5a**, also their preparation can be carried out at a higher temperature (75°C, 4 h); they are obtained starting from either 1,2-dibromoethanesulfonamides **2b-e** or from 1-bromoethenesulfonamides **3b-e** (Scheme **D**). The aziridines **5** are characterized by microanalytical and ^{1}H-N.M.R. and ^{13}C-N.M.R. spectroscopic data (Table 3).



Scheme **D**

The cyclization reactions have been performed in several solvents, the rate of the reaction was found to decrease in the order dimethyl sulfoxide > hexamethylphosphoric triamide > dimethylformamide > acetonitrile > benzene or diethyl ether. The reaction is easier with dipolar aprotic solvents.

The great stability of the 1-bromo-2-aminoethanesulfonamides **4b-d** allows their utilization for the introduction of the sulfonamido group to small-ring heterocycles, for instance for the preparation of *gem*-aminosulfonylmethylaminooxiranes **6** (Scheme **E**). Products **6** were identified by microanalytical and ^{1}H-N.M.R. spectroscopic data (Table 4).



Scheme **E**

Ethenesulfonic Acid Derivatives 1a-e:
Phenyl ethenesulfonate (**1a**) is prepared according to Ref.[5]. Ethenesulfonamides **1b** and **1d** are prepared by a modification of Ref.[6] as are ethenesulfonamides **1c** and **1e** (see below).

Ethenesulfonamides 1c or 1e:
A solution of 2-chloroethanesulfonyl chloride (16.3 g, 0.1 mol) in dry ether (100 ml) is treated dropwise during 15 min at −70°C with a mixture of the primary or secondary amine (0.1 mol) and triethylamine (0.1 mol) in dry ether (50 ml). The temperature is maintained below −50°C during the addition. Triethylamine (0.1 mol) is then added to the ether solution and the addition continued. After the end of addition, the mixture is stirred and the temperature increased to ambient temperature. The crude product is dissolved in ice-cold water (200 ml) and neutralized by addition of 10% hydrochloric acid. The ether layer is separated, extracted with chloroform (2 × 50 ml), the extract washed with water until the pH is about 6, and dried with magnesium sulfate. The solvent is removed and the residual crude product is distilled, recrystallized, or purified by column chromatography on silica gel with hexane/ethyl acetate as eluent.

1c; yellow oil; yield: 5.6 g (35%).

^{1}H-N.M.R. ($CDCl_3$): δ = 1.8–2.2 (m, 4H); 3.2–3.6 (m, 4H); 6.00 (dd, J = 9.6 Hz, 2 Hz, 1H); 6.20 (dd, J = 16 Hz, 2 Hz, 1H); 6.60 ppm (dd, J = 9.6 Hz, 16 Hz, 1H).

1e; yellow oil; yield: 6.2 g (46%).

^{1}H-N.M.R. ($CDCl_3$): δ = 1.30 (t, J = 7 Hz, 3H); 3.10 (q, J = 7 Hz, 2H); 5.95 (dd, J = 9.2 Hz, 1.2 Hz, 1H); 6.15 (dd, J = 16 Hz, 1.2 Hz, 1H); 6.60 ppm (dd, J = 9.2 Hz, 16 Hz, 1H).

Phenyl 1,2-Dibromoethanesulfonate (2a):
Bromine (4 ml) dissolved in carbon tetrachloride (20 ml) is added under nitrogen to a stirred solution of **1a** (3.68 g, 0.02 mol) in carbon tetrachloride (100 ml) containing azodiisobutyronitrile (0.2 g). The mixture is warmed at 70°C during the addition and the promoter (0.2 g) is again added; the solution is refluxed during 4 h and stirred for 48 h at room temperature. The solvent is removed and the crude product is recrystallized; yield: 6.5 g (95%); m.p. 75–76°C (ethanol).

^{1}H-N.M.R. ($CDCl_3$): δ = 3.70 (dd, J = 10 Hz, 12 Hz, 1H); 4.27 (dd, J = 4 Hz, 12 Hz, 1H); 5.00 (dd, J = 4 Hz, 10 Hz, 1H); 7.35 ppm (s, 5H).

1,2-Dibromoethanesulfonamides 2b-e:
Bromine (5 ml) dissolved in carbon tetrachloride (20 ml) is added to a stirred solution of **1b-e** (0.02 mol) in carbon tetrachloride (100 ml). The mixture is stirred for 48 h at room temperature. The solvent is removed and the crude product is purified by column chromatography on silica gel with hexane/ethyl acetate as eluent.

2b; yield: 5.8 g (86%); m.p. 66–67°C (ethanol).

^{1}H-N.M.R. ($CDCl_3$): δ = 3.3–3.6 (m, 4H); 3.6–4.0 (m, 5H); 4.20 (dd, J = 3.2 Hz, 11.6 Hz, 1H); 4.95 ppm (dd, J = 3.2 Hz, 10 Hz, 1H).

2c; yield: 5.3 g (83%); oil.

^{1}H-N.M.R. ($CDCl_3$): δ = 1.8–2.2 (m, 4H); 3.4–3.7 (m, 5H); 4.20 (dd, J = 3.4 Hz, 11.6 Hz, 1H); 5.00 ppm (dd, J = 3.4 Hz, 9.6 Hz, 1H).

2d; yield: 6.13 g (95%); oil.

^{1}H-N.M.R. ($CDCl_3$): δ = 1.25 (t, J = 7 Hz, 6H); 3.8–4.0 (m, 5H); 4.20 (dd, J = 2.8 Hz, 12 Hz, 1H); 4.80 ppm (dd, J = 2.8 Hz, 10.6 Hz, 1H).

2e; yield: 3.9 g (66%); oil.

^{1}H-N.M.R. ($CDCl_3$): δ = 3.70 (dd, J = 9.2 Hz, 11.6 Hz, 1H); 4.20 (dd, J = 3.6 Hz, 11.6 Hz, 1H); 5.00 (dd, J = 3.6 Hz, 9.2 Hz); 4.8–5.4 ppm (m, 1H).

1-Bromoethenesulfonic Acid Derivatives 3a-e:
To a stirred solution of **2a-e** (0.04 mol) in benzene (200 ml) is added triethylamine (0.042 mol) in benzene (10 ml). The mixture is stirred for 24 h at room temperature and filtered. The solid is washed several times with benzene, and the filtrate is combined with the organic layer. The organic phase is washed with water (2 × 100 ml) until the pH is about 6, dried with magnesium sulfate, and the solvent is removed under reduced pressure. The crude product is purified by column chromatography on silica gel with hexane/ethyl acetate as eluent (Table 1). Product **3b** is recrystallized from ethanol.

Table 1. Phenyl 1-Bromoethenesulfonate (**3a**) and 1-Bromoethenesulfonamides (**3b-e**)

Product	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
3a	80	oil	$C_8H_7BrO_3S$ (263.1)	7.40 (s, 5H); 6.80 (d, 1H, J = 3.2 Hz); 6.35 (d, 1H, J = 3.2 Hz)
3b	60	78–79°	$C_6H_{10}BrNO_3S$ (256.1)	6.75 (d, 1H, J = 3 Hz); 6.25 (d, 1H, J = 3 Hz); 4.0–3.2 (m, 8H)
3c	80	oil	$C_6H_{10}BrNO_2S$ (240.1)	6.70 (d, 1H, J = 2.8 Hz); 6.15 (d, 1H, J = 2.8 Hz); 3.6–3.2 (m, 4H); 2.2–1.8 (m, 4H)
3d	75	oil	$C_6H_{12}BrNO_2S$ (242.2)	6.70 (d, 1H, J = 2 Hz); 6.05 (d, 1H, J = 2 Hz); 3.30 (q, 4H, J = 7 Hz); 1.30 (t, 6H, J = 7 Hz)
3e	75	oil[b]	$C_4H_8BrNO_2S$ (214.1)	6.80 (d, 1H, J = 2.8 Hz); 6.20 (d, 1H, J = 2.8 Hz); 3.30 (q, 2H, J = 7 Hz); 3.4–3.0 (m, 1H); 1.25 (t, 3H, J = 7 Hz)

[a] Satisfactory microanalyses obtained: C ±0.43; H ±0.05; Br ±0.28; N ±0.44; S ±0.35; exception: **3a**, C −0.51. [b] Not analyzed.

Table 2. Phenyl 1-Bromoethanesulfonate (**4a**) and 2-Alkylamino-1-bromoethanesulfonamides (**4b-e**)

Product	R^1	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
4a	C_2H_5	64	oil	$C_{10}H_{14}BrNO_3S$ (308.2)	7.35 (s, 5H); 5.50 (dd, 1H, J = 8 Hz, 5 Hz); 3.60 (dd, 1H, J = 5 Hz, 14 Hz); 3.30 (dd, 1H, J = 8 Hz, 14 Hz); 2.70 (q, 2H, J = 7 Hz); 1.55 (s, 1H); 1.10 (t, 3H, J = 7 Hz)
	i-C_3H_7	60	47° (hexane)	$C_{11}H_{16}BrNO_3S$ (322.2)	7.40 (s, 5H); 5.05 (dd, 1H, J = 8 Hz, 5 Hz); 3.60 (dd, 1H, J = 5 Hz, 14 Hz); 3.25 (dd, 1H, J = 8 Hz, 14 Hz); 3.2–2.6 (m, 1H); 2.05 (s, 1H); 1.05 (d, 6H, J = 6 Hz)
	t-C_4H_9	55	52.5–53° (hexane)	$C_{12}H_{18}BrNO_3S$ (336.3)	7.40 (s, 5H); 4.98 (dd, 1H, J = 8 Hz, 5 Hz); 3.50 (dd, 1H, J = 5 Hz, 14 Hz); 3.20 (dd, 1H, J = 8 Hz, 14 Hz); 1.45 (s, 1H); 1.10 (s, 9H)
	c-C_6H_{11}	60	oil	$C_{14}H_{20}BrNO_3S$ (362.3)	7.40 (s, 5H); 5.05 (dd, 1H, J = 8 Hz, 5 Hz); 3.65 (dd, 1H, J = 5 Hz, 14 Hz); 3.30 (dd, 1H, J = 8 Hz, 14 Hz); 3.0–2.0 (m, 1H); 2.0–1.0 (m, 11H)
	CH_2—C_6H_5	41	oil	$C_{15}H_{16}BrNO_3S$ (370.3)	7.35 (s, 5H); 7.30 (s, 5H); 5.05 (dd, 1H, J = 8 Hz, 5 Hz); 3.85 (s, 2H); 3.60 (dd, 1H, J = 5 Hz, 14 Hz); 3.30 (dd, 1H, J = 8 Hz, 14 Hz); 2.10 (s, 1H)

Table 2. (Continued)

Product	R^1	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
4b	C_2H_5	62	41°	$C_8H_{17}BrN_2O_3S$ (301.2)	5.10 (dd, 1 H, J = 7.6 Hz, 5.0 Hz); 3.8–3.4 (2 m, 8 H); 3.60–3.20 (dd, 1 H, J = 7.6 Hz, 14 Hz); 3.20 (dd, 1 H, J = 7.60 Hz, 14 Hz); 2.90 (s, 1 H); 2.70 (q, 2 H, J = 7 Hz); 1.10 (t, 3 H, J = 7 Hz)
	i-C_3H_7	61	44°	$C_9H_{19}BrN_2O_3S$ (315.2)	4.95 (dd, 1 H, J = 7.80 Hz, 5.0 Hz); 4.0–3.2 (2 m, 8 H); 3.8–3.2 (m, 2 H); 3.2–2.5 (m, 1 H); 1.80 (s, 1 H); 1.10 (d, 6 H, J = 6.0 Hz)
	t-C_4H_9	80	55°	$C_{10}H_{21}BrN_2O_3S$ (329.3)	4.90 (dd, 1 H, J = 7.60 Hz, 4.80 Hz); 3.9–3.3 (m, 9 H); 3.10 (dd, 1 H, J = 7.6 Hz, 13.6 Hz); 1.50 (s, 1 H); 1.05 (s, 9 H)
	c-C_6H_{11}	80	43°	$C_{12}H_{23}BrN_2O_3S$ (355.3)	5.00 (dd, 1 H, J = 7.60 Hz, 4.80 Hz); 4.0–3.4 (m, 9 H); 3.25 (dd, 1 H, J = 7.60 Hz, 14 Hz); 2.7–2.3 (m, 1 H); 2.0–1.0 (m, 11 H)
	CH_2—C_6H_5	85	oil	$C_{13}H_{19}BrN_2O_3S$ (363.3)	7.35 (s, 5 H); 4.95 (dd, 1 H, J = 7.40 Hz, 5.20 Hz); 3.85 (s, 2 H); 3.8–3.2 (m, 9 H); 3.20 (dd, 1 H, J = 7.40 Hz, 14 Hz); 2.00 (s, 1 H)
4c	C_2H_5	44	oil	$C_8H_{17}BrN_2O_2S$ (285.2)	5.10 (dd, 1 H, J = 5 Hz, 8 Hz); 3.8–3.4 (m, 5 H); 3.20 (dd, 1 H, J = 8 Hz, 14 Hz); 2.70 (q, 2 H, J = 7 Hz); 2.40 (s, 1 H); 2.1–1.8 (m, 4 H); 1.10 (t, 3 H, J = 7 Hz)
	i-C_3H_7	35	oil	$C_9H_{19}BrN_2O_2S$ (299.2)	5.10 (dd, 1 H, J = 5 Hz, 8 Hz); 3.7–3.4 (m, 5 H); 3.30 (dd, 1 H, J = 8 Hz, 14 Hz); 3.80–2.8 (m, 1 H); 3.1–2.6 (m, 1 H); 2.1–1.2 (m, 4 H); 1.10 (d, 6 H, J = 6 Hz)
	t-C_4H_9	44	oil	$C_{10}H_{21}BrN_2O_2S$ (313.3)	5.10 (dd, 1 H, J = 5 Hz, 8 Hz); 3.8–3.3 (m, 5 H); 3.20 (dd, 1 H, J = 8 Hz, 14 Hz); 2.70 (s, 1 H); 2.0–1.6 (m, 4 H); 1.10 (s, 9 H)
	c-C_6H_{11}	19	oil	$C_{12}H_{23}BrN_2O_2S$ (339.3)	5.20 (dd, 1 H, J = 5.2 Hz, 8 Hz); 3.8–3.3 (m, 5 H); 3.25 (dd, 1 H, J = 8 Hz, 14 Hz); 3.05 (s, 1 H); 2.2–1.8 (m, 4 H); 1.8–1.0 (m, 11 H)
	CH_2—C_6H_5	28	oil	$C_{13}H_{19}BrN_2O_2S$ (347.3)	7.30 (s, 5 H); 5.10 (dd, 1 H, J = 5.2 Hz, 7.6 Hz); 3.80 (s, 2 H); 3.7–3.3 (m, 6 H); 3.15 (dd, 1 H, J = 7.6 Hz, 14 Hz); 2.0–1.7 (m, 4 H)
4d	C_2H_5	42	oil	$C_8H_{19}BrN_2O_2S$ (287.2)	4.98 (dd, 1 H, J = 8 Hz, 5 Hz); 3.8–3.0 (m, 6 H); 2.80 (q, 2 H, J = 7 Hz); 2.30 (s, 1 H); 1.26 (t, 6 H, J = 7 Hz); 1.10 (t, 3 H)
	i-C_3H_7	41	oil	$C_9H_{21}BrN_2O_2S$ (301.3)	4.90 (dd, 1 H, J = 8 Hz, 5 Hz); 3.8–3.0 (m, 6 H); 3.4–2.6 (m, 1 H); 1.98 (s, 1 H); 1.22 (t, 6 H, J = 7 Hz); 1.08 (d, 6 H, J = 6 Hz)
	t-C_4H_9	57	oil	$C_{10}H_{23}BrN_2O_2S$ (315.3)	4.88 (dd, 1 H, J = 8 Hz, 5 Hz); 3.8–3.0 (m, 6 H); 2.30 (s, 1 H); 1.20 (t, 6 H, J = 7 Hz); 1.18 (s, 9 H)
	c-C_6H_{11}	51	oil	$C_{12}H_{25}BrN_2O_2S$ (341.3)	4.90 (dd, 1 H, J = 8 Hz, 5 Hz); 3.8–3.0 (m, 6 H); 2.15 (s, 1 H); 2.0–1.0 (m, 11 H); 1.25 (t, 6 H, J = 7 Hz)
	CH_2—C_6H_5	58	oil	$C_{13}H_{21}BrN_2O_2S$ (349.3)	7.30 (s, 5 H); 4.90 (dd, 1 H, J = 8 Hz, 5 Hz); 3.80 (s, 2 H); 3.6–2.8 (m, 6 H); 2.40 (s, 1 H); 1.20 (t, 6 H, J = 7 Hz)
4e	C_2H_5	50	oil	$C_7H_{15}BrN_2O_2S$ (259.2)	5.0 (dd, 1 H, J = 5.6 Hz, 7 Hz); 3.6–3.0 (m, 6 H); 2.80 (q, 2 H, J = 7 Hz); 1.20 (t, 3 H, J = 7 Hz); 1.10 (t, 3 H, J = 7 Hz)
	i-C_3H_7	74	oil	$C_7H_{17}BrN_2O_2S$ (279.2)	4.95 (dd, 1 H, J = 5.6 Hz, 7.2 Hz); 4.0–2.6 (m, 7 H); 1.20 (t, 3 H, J = 7 Hz); 1.10 (d, 6 H, J = 6 Hz)
	t-C_4H_9	50	94–94.5°	$C_8H_{19}BrN_2O_2S$ (287.2)	4.95 (dd, 1 H, J = 5.4 Hz, 6.8 Hz); 3.6–3.0 (m, 6 H); 1.20 (t, 3 H, J = 7 Hz); 1.15 (s, 9 H)
	c-C_6H_{11}	44	oil	$C_{10}H_{21}BrN_2O_2S$ (313.3)	4.95 (dd, 1 H, J = 5.6 Hz, 7.2 Hz); 3.8–3.0 (m, 6 H); 2.0–1.0 (m, 11 H); 1.25 (t, 3 H, J = 7 Hz)
	CH_2—C_6H_5	55	75–75.5°	$C_{11}H_{17}BrN_2O_2S$ (321.3)	7.30 (s, 5 H); 4.90 (dd, 1 H, J = 5.4 Hz, 7.2 Hz); 3.80 (s, 2 H); 3.6–3.0 (m, 6 H); 1.20 (t, 3 H, J = 7 Hz)

[a] Satisfactory microanalyses obtained: C ±0.50, H ±0.28, Br ±0.42, N ±0.49, S ±0.42.

Table 3. 1-Alkyl-2-phenoxysulfonylaziridines **5a** and 1-Alkyl-2-alkylaminosulfonylaziridines **5b–e**

Product	R^1	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) δ [ppm]
5a	C_2H_5	41	oil	$C_{10}H_{13}NO_3S$ (227.3)	7.35 (s, 5 H); 3.05 (dd, 1 H, J = 3 Hz, 6 Hz); 2.40 (qd, 2 H, J = 1 Hz, 7 Hz); 2.38 (d, 1 H, J = 3 Hz); 1.78 (d, 1 H, J = 6 Hz); 1.18 (t, 3 H, J = 7 Hz)	–
	i-C_3H_7	57	oil	$C_{11}H_{15}NO_3S$ (241.3)	7.35 (s, 5 H); 3.10 (dd, 1 H, J = 3 Hz, 6 Hz); 2.28 (d, 1 H, J = 3 Hz); 1.82 (d, 1 H, J = 6 Hz); 2.0–1.4 (m, 1 H); 1.25 (d, 3 H, J = 6 Hz); 1.20 (d, 3 H, J = 6 Hz)	–
	t-C_4H_9	53	oil	$C_{12}H_{17}NO_3S$ (255.3)	7.35 (s, 5 H); 3.40 (dd, 1 H, J = 3 Hz, 6 Hz); 2.25 (dd, 1 H, J = 3 Hz); 2.02 (dd, 1 H, J = 6 Hz); 1.10 (s, 9 H)	26.2 (t-C_4H_9); 27.1 (>C); 46.7 (C-3); 54.3 (C-2); 122.1, 127.0, 129.8, 149.6 (C_6H_5)
	c-C_6H_{11}	59	91–92° (ethanol)	$C_{14}H_{19}NO_3S$ (281.4)	7.35 (s, 5 H); 3.15 (dd, 1 H, J = 3 Hz, 6 Hz); 2.40 (d, 1 H, J = 3 Hz); 1.85 (d, 1 H, J = 6 Hz); 2.0–1.0 (m, 11 H)	24.2, 25.7, 32.1 (cyclohexyl); 50.5 (C-3); 67.8 (C-2); 122.0, 127.1, 129.8, 149.6 (C_6H_5)

Table 3. (Continued)

Product	R^1	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) δ [ppm]
	CH_2—C_6H_5	17	60–61° (ethanol)	$C_{15}H_{15}NO_3S$ (289.4)	7.3–7.0 (m, 10H); 3.60 (s, 2H); 3.21 (dd, 1H, J=3 Hz, 6 Hz); 2.45 (d, 1H, J=3 Hz); 1.90 (d, 1H, J=6 Hz)	32.8 (CH_2); 50.6 (C-3); 62.3 (C-2); 121.8, 121.9, 127.0, 149.7 (C_6H_5); 127.9, 128.6, 136.2 (C_6H_5)
5b	C_2H_5	61	oil	$C_8H_{16}N_2O_3S$ (220.3)	3.8–3.2 (2m, 8H); 2.80 (dd, 1H, J=2.8 Hz, 6.0 Hz); 2.45 (q, 2H, J=7 Hz); 2.30 (d, 1H, J=2.80 Hz); 1.70 (d, 1H, J=6 Hz); 1.20 (t, 3H, J=7 Hz)	13.8 (CH_3); 31.7 (CH_2); 45.9 (morph.); 49.8 (C-3); 53.7 (C-2); 66.2 (morph.)
	i-C_3H_7	52	81–82° (ethanol)	$C_9H_{18}N_2O_3S$ (234.3)	4.0–3.2 (2m, 8H); 2.85 (dd, 1H, J=2.80 Hz, 6.0 Hz); 2.25 (d, 1H, J=2.80 Hz); 2.0–1.0 (m, 1H); 1.70 (d, 1H, J=6 Hz); 1.25 (d, 3H, J=6 Hz); 1.15 (d, 3H, J=6 Hz)	21.5, 22.0 [$(CH_3)_2$]; 31.5 (>CH); 46.0 (morph.); 50.5 (C-3); 60.4 (C-2); 66.5 (morph.)
	t-C_4H_9	47	37–38° (ethanol)	$C_{10}H_{20}N_2O_3S$ (248.4)	3.9–3.2 (2m, 8H); 3.05 (dd, 1H, J=2.4 Hz, 6 Hz); 2.05 (d, 1H, J=2.4 Hz); 1.90 (d, 1H, J=6 Hz); 1.05 (s, 9H)	26.0 (>C); 26.4 [$(CH_3)_3$]; 46.3 (morph.); 46.5 (C-3); 53.9 (C-2); 66.8 (morph.)
	c-C_6H_{11}	66	132–133° (ethanol)	$C_{12}H_{22}N_2O_3S$ (274.4)	3.9–3.2 (2m, 8H); 2.80 (dd, 1H, J=2.80 Hz, 6 Hz); 2.30 (d, 1H, J=2.8 Hz); 2.0–1.0 (m, 11H), 1.70 (d, 1H, J=6 Hz)	24.5, 25.8, 31.1, 32.2, 32.7 (cyclohexyl); 46.3 (morph.); 50.3 (C-3); 66.8 (morph.); 68.2 (C-2)
	CH_2—C_6H_5	32	88–89° (ethanol)	$C_{13}H_{18}N_2O_3S$ (250.3)	7.40 (s, 5H); 4.0–3.3 (m, 6H); 3.2–2.8 (m, 5H); 2.40 (d, 1H, J=2.8 Hz); 1.80 (d, 1H, J=6 Hz)	32.7 (CH_2); 45.9 (morph.); 50.1 (C-3); 63.4 (C-2); 66.5 (morph.); 128.1, 128.8, 129.0, 136.7 (C_6H_5)
5c	C_2H_5	40	oil	$C_8H_{16}N_2O_2S$ (204.3)	3.7–3.3 (m, 4H); 2.85 (dd, 1H, J=2.8 Hz, 6 Hz); 2.6–2.2 (m, 3H); 2.2–1.8 (m, 4H); 1.65 (d, 1H, J=6 Hz); 1.20 (t, 3H, J=7 Hz)	14.2 (CH_3); 26.0 (pyrrolidine); 32.4 (CH_2); 48.2 (pyrrolidine); 50.9 (C-3); 54.6 (C-2)
	i-C_3H_7	37	oil	$C_9H_{18}N_2O_2S$ (218.3)	3.7–3.3 (m, 4H); 2.85 (dd, 1H, J=2.8 Hz, 6 Hz); 2.30 (d, 1H, J=2.8 Hz); 2.1–1.8 (m, 4H); 2.0–1.4 (m, 2H); 1.25 (d, 3H, J=3 Hz); 1.20 (d, 3H, J=3 Hz)	21.9, 22.0 [$(CH_3)_2$]; 25.9 (pyrrolidine); 31.0 (>CH); 48.1 (pyrrolidine); 51.0 (C-3); 60.8 (C-2)
	t-C_4H_9	28	59–60°	$C_{10}H_{20}N_2O_2S$ (232.4)	3.6–3.3 (m, 4H); 3.10 (dd, 1H, J=3 Hz, 6 Hz); 2.1–2.0 (m, 2H); 2.2–1.7 (m, 4H); 1.00 (s, 9H)	25.9 (pyrrolidine); 26.2 (>C); 26.4 [$(CH_3)_3$]; 46.4 (C-3); 48.1 (pyrrolidine); 53.9 (C-2)
	c-C_6H_{11}	23	oil	$C_{12}H_{22}N_2O_2S$ (258.4)	3.7–3.3 (m, 4H); 2.90 (dd, 1H, J=2.8 Hz, 6 Hz); 2.30 (d, 1H, J=2.8 Hz); 2.0–1.0 (m, 15H); 1.65 (d, 1H, J=6 Hz)	24.56 (cyclohexyl); 25.9 (pyrrolidine); 31.3, 32.2, 32.6 (cyclohexyl); 48.0 (pyrrolidine); 50.4 (C-3); 68.4 (C-2)
	CH_2—C_6H_5	16[b]	oil	$C_{13}H_{18}N_2O_2S$ (266.4)	7.30 (s, 5H); 3.80 (s, 2H); 3.20–2.90 (m, 5H); 2.40 (d, 1H, J=2.8 Hz); 1.85 (d, 1H, J=6 Hz); 1.70–1.40 (m, 4H)	
5d	C_2H_5	57	oil	$C_8H_{18}N_2O_2S$ (206.3)	3.45 (q, 2H, J=7 Hz); 3.40 (q, 2H, J=2 Hz); 2.70 (dd, 1H, J=2.8 Hz, 6 Hz); 2.35 (q, 2H, J=7 Hz); 2.25 (d, 1H, J=2.8 Hz); 1.65 (d, 1H, J=6 Hz); 1.20 (t, 6H, J=7 Hz); 1.15 (t, 3H, J=7 Hz)	14.2 (CH_3); 14.9 (CH_3); 32.7 (CH_2); 52.6 (C-3); 54.5 (C-2)
	i-C_3H_7	75	oil	$C_9H_{20}N_2O_2S$ (220.3)	3.40 (q, 2H, J=7 Hz); 3.30 (q, 2H, J=7 Hz); 2.75 (dd, 1H, J=2.8 Hz, 6 Hz); 2.25 (d, 1H, J=2.8 Hz); 1.65 (d, 1H, J=6 Hz); 1.8–1.0 (m, 1H); 1.4–1.0 (m, 12H)	15.1 (CH_3); 21.7, 22.0 [$(CH_3)_2$]; 32.0 (>CH); 42.6 (CH_2); 52.4 (C-3); 60.6 (C-2)
	t-C_4H_9	59	oil	$C_{10}H_{22}N_2O_2S$ (234.4)	3.8–3.2 (m, 4H); 3.00 (dd, 1H, J=2.4 Hz, 6 Hz); 2.05 (d, 1H, J=2.40 Hz); 1.85 (d, 1H, J=6 Hz); 1.20 (t, 3H, J=7 Hz); 1.05 (s, 9H)	15.1 (CH_3); 26.2 (>C); 26.4 [$(CH_3)_3$]; 42.6 (CH_2); 47.7 (C-3); 53.7 (C-2)
	c-C_6H_{11}	70	56–57° (ethanol)	$C_{12}H_{24}N_2O_2S$ (260.4)	3.40 (q, 2H, J=7 Hz); 3.30 (q, 2H, J=7 Hz); 2.75 (dd, 1H, J=2.8 Hz, 6 Hz); 2.20 (d, 1H, J=2.80 Hz); 1.65 (d, 1H, J=6 Hz); 2.0–1.0 (m, 11H); 1.20 (t, 3H, J=7 Hz)	15.1 (CH_3); 24.5, 25.9, 31.4, 32.1, 32.5 (cyclohexyl); 42.7 (CH_2); 51.8 (C-3); 68.1 (C-2)
	CH_2—C_6H_5	46	oil	$C_{13}H_{20}N_2O_2S$ (268.4)	7.30 (s, 5H); 3.70 (d, 1H, J=13 Hz); 3.25 (d, 1H, J=13 Hz); 3.2–2.6 (m, 5H); 2.35 (d, 1H, J=2.8 Hz); 1.75 (d, 1H, J=6 Hz); 1.05 (t, 3H, J=7 Hz)	14.4 (CH_3); 14.9 (CH_3); 32.9 (CH_2, benzyl); 42.4 (CH_2); 42.8 (CH_2); 52.0 (C-3); 63.5 (C-2); 127.8, 128.2, 128.5, 129.0, 137.1 (C_6H_5)
5e	i-C_3H_7	29	oil	$C_7H_{16}N_2O_2S$ (192.3)	5.00 (s, 1H); 3.30 (q, 2H, J=7 Hz); 3.1–2.8 (m, 1H); 2.9 (dd, 1H, J=2.8 Hz, 6 Hz); 2.30 (d, 1H, J=2.8 Hz); 1.70 (d, 1H, J=6 Hz); 1.4–1.0 (m, 9H)	16.0 (CH_3); 21.6, 21.8 [$(CH_3)_2$]; 32.5 (>CH); 38.6 (CH_2); 52.2 (C-3); 60.6 (C-2)

Table 3. (Continued)

Product	R^1	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) δ [ppm]
	t-C_4H_9	34	106°	$C_8H_{18}N_2O_2S$ (206.3)	4.7 (s, 1H); 3.15 (q, 2H, J=7 Hz); 3.10 (dd, 1H); 2.10 (d, 1H, J=2.4 Hz); 1.95 (d, 1H, J=6 Hz); 1.20 (t, 3H, J=7 Hz); 1.10 (s, 9H)	16.0 (CH_3); 26.3 [$(CH_3)_3$]; 26.8 (>C); 38.8 (CH_2); 47.6 (C-3); 53.9 (C-2)
	c-C_6H_{11}	37	71–71.5°	$C_{10}H_{20}N_2O_2S$ (244.4)	4.9 (s, 1H); 3.25 (q, 2H, J=7 Hz); 2.95 (dd, 1H, J=2.8 Hz, 6 Hz); 2.30 (d, 1H, J=2.8 Hz); 1.70 (d, 1H, J=6 Hz); 1.25 (t, 3H, J=7 Hz); 2.0–1.0 (m, 11H)	16.1 (CH_3); 24.5, 25.7, 32.1, 32.3 (cyclohexyl); 38.7 (CH_2); 51.8 (C-3); 68.2 (C-2)
	CH_2—C_6H_5	34	103–103.5°	$C_{11}H_{16}N_2O_2S$ (240.3)	7.40 (s, 5H); 4.45 (s, 1H); 3.72 (d, 1H, J=13 Hz); 3.25 (d, 1H, J=13 Hz); 3.00 (dd, 1H, J=2.8 Hz, 6 Hz); 2.9–2.5 (m, 2H); 2.40 (d, 1H, J=2.8 Hz); 1.90 (d, 1H, J=6 Hz); 0.90 (t, 3H, J=7 Hz)	15.7 (CH_3); 33.8 (CH_2, benzyl); 38.2 (CH_2); 51.7 (C-3); 63.2 (C-2); 127.9, 128.2, 128.7, 128.8, 137.0 (C_6H_5)

[a] Satisfactory microanalyses obtained: C ±0.46, H ±0.24, N ±0.49, S ±0.40.
[b] Not obtained in a pure state.

Table 4. 2-Alkylamino-2-aminosulfonyloxiranes **6**

Product No.	R^1	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
6b	C_2H_5	45	oil	$C_{15}H_{22}N_2O_4S$ (326.4)	7.35 (s, 5H); 4.70 (s, 1H); 4.0–3.4 (m, 8H); 3.00 (s, 1H); 2.80 (s, 1H); 2.50 (q, 2H, J=7 Hz); 1.60 (s, 1H); 1.10 (t, 3H, J=7 Hz)
6c	C_2H_5	48	oil	$C_{15}H_{22}N_2O_3S$ (310.4)	7.35 (s, 5H); 4.65 (s, 1H); 3.7–3.4 (m, 4H); 3.05 (s, 1H); 2.90 (s, 1H); 2.50 (q, 2H, J=7 Hz); 2.1–1.8 (m, 4H); 1.20 (s, 1H); 0.95 (t, 3H, J=7 Hz)
6d	C_2H_5	29	oil	$C_{15}H_{24}N_2O_3S$ (312.4)	7.40 (s, 5H); 4.60 (s, 1H); 3.45 (q, 4H, J=7 Hz); 3.00 (s, 1H); 2.90 (s, 1H); 2.40 (q, 2H, J=7 Hz); 1.70 (s, 1H); 1.25 (t, 6H, J=7 Hz); 0.85 (t, 3H, J=7 Hz)
6d	i-C_3H_7	34	oil	$C_{16}H_{26}N_2O_3S$ (326.5)	7.35 (s, 5H); 4.60 (s, 1H); 3.45 (q, 4H, J=7 Hz); 2.95 (s, 1H); 2.90 (s, 1H); 2.8–2.2 (m, 1H); 2.2–2.0 (m, 1H); 1.25 (t, 6H, J=7 Hz); 0.85 (d, 3H, J=3 Hz); 0.75 (d, 3H, J=3 Hz)
6d	c-C_6H_{11}	71	oil	$C_{19}H_{30}N_2O_3S$ (366.5)	7.35 (s, 5H); 4.60 (t, 1H); 3.70–3.0 (m, 4H); 2.95 (d, 1H, J=2 Hz); 2.90 (d, 1H, J=2 Hz); 2.0–1.0 (m, 18H)
6d	CH_2—C_6H_5	16	oil	$C_{20}H_{26}N_2O_3S$ (374.5)	7.30 (s, 5H); 7.20 (s, 5H); 4.60 (s, 1H); 3.60 (s, 2H); 3.6–3.0 (m, 1H); 3.40 (q, 4H, J=7 Hz); 2.95 (s, 1H); 2.90 (s, 1H); 1.25 (t, 6H, J=7 Hz)

[a] Satisfactory microanalyses obtained: C ±0.38, H ±0.36, N ±0.33; exception: **6d** (R^1=i-C_3H_7), C −0.69.

2-Alkylamino-1-bromoethenesulfonic Acid Derivatives 4a–e:
A solution of **2a–e** or **3a–e** (0.01 mol) in benzene (100 ml) is cooled at 0°C. The solution is treated dropwise with the primary amine (0.02 mol for **3a–e** or 0.03 mol for **2a–e**). The mixture is stirred for 24 h at room temperature. The solvent is removed in vacuum and chloroform (100 ml) is added to the oily residue. The organic layer is washed with water until the pH is about 7 and dried with magnesium sulfate. The chloroform is removed and the crude product is purified by column chromatography on silica gel with hexane/ethyl acetate or recrystallized (Table 2).

2-Sulfonylaziridines 5:
A solution of **2a–e, 3a–e,** or **4a–e** (0.01 mol) in dimethyl sulfoxide (30 ml) is treated with the primary amine (0.033 mol with **2a–e**, 0.022 mol with **3a–e**) or with triethylamine (0.11 mol with **4a–e**). The mixture is allowed to stand at room temperature or warmed for 4 h at 75°C (**5a:** 30 days at room temperature; **5b, 5d:** 4 h at 75°C; **5e** R^1=C_2H_5, i-C_3H_7, t-C_4H_9, c-C_6H_{11}: 48 h at room temperature; **5e** R^1=$CH_2C_6H_5$: 4 h at 75°C). The mixture is treated with water (50 ml) and extracted with chloroform (2 × 50 ml), washed with water until the pH is about 7. The organic layer is dried with magnesium sulfate and the solvent evaporated. The residue is recrystallized or purified by column chromatography on silica gel with hexane/ethyl acetate as eluent (Table 3).

2-Alkylamino-2-sulfonyloxiranes 6:
To a solution of benzaldehyde (0.01 mol) and **4d** (R^1=C_2H_5, i-C_3H_7, c-C_6H_{11}, C_6H_5—CH_2), or **4b** (R^1=C_2H_5), or **4c** (R^1=C_2H_5) (0.01 mol) in 2:1 (v/v) t-butyl alcohol/diethyl ether (30 ml), is added a solution of potassium t-butoxide (0.01 mol) in t-butyl alcohol (20 ml). The mixture is stirred for 1 h at < 10°C and for 24 h at room temperature. The mixture is poured on ice (150 g) and extracted with ether (3 × 100 ml). The organic extract is dried with magnesium sulfate and evaporated. The crude product is purified by column chromatography with hexane/ethyl acetate as eluent (Table 4).

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[1] P. Carlier, Y. Gelas-Mialhe, R. Vessière, *Can. J. Chem.* **55**, 3190 (1977).
[2] J. M. Gaillot, Y. Gelas-Mialhe, R. Vessière, *Can. J. Chem.* **57**, 1958 (1979).
[3] H. Distler, *Angew. Chem.* **77**, 291 (1965); *Angew. Chem. Int. Ed. Engl.* **4**, 300 (1965).
[4] N. H. Cromwell, G. V. Hudson, R. A. Wankel, P. J. Vanderhorst, *J. Am. Chem. Soc.* **75**, 5384 (1963).
[5] H. Distler, W. Müller, A. Palm, *German Patent (DBP)* 1135898 (1960), BASF AG.
[6] C. S. Rondesvedt, *J. Am. Chem. Soc.* **76**, 1926 (1954).
[7] G. Lonchambon, *Doctorat d'Etat ès Sciences Physiques*, Paris, 1973.