ceeded as described for the preparation of 6 to yield 7 as an oily solid which was purified by crystallization from hexane: mp 53–53.5°; ir ($CCl_4$) 6.00, 10.9 $\mu$; nmr ($CDCl_3$) $\delta$ 2.10 (q, 2 H, $J$ = 7.0 Hz), 3.15 (t, 4 H, $J$ = 7.0 Hz). *Anal.* Calcd: C, 64.53; H, 5.10. Found: C, 64.64; H, 5.09.

**Preparation of Salt 5.** Monothio ester 6 (320 mg, 1.5 mmol) was dissolved in acetone–water (99:1, 35.5 ml). Addition of a solution of $HgCl_2$ (815 mg, 3 mmol) in acetone (5 ml) to the above solution immediately gave a white precipitate. After stirring for 15 min the reaction mixture was filtered and washed with cold acetone to yield a white power (510 mg). Evaporation of the filtrate followed by trituration with acetone–water gave additional, less pure powder (87 mg). The salt was insoluble in $CHCl_3$, acetone, and benzene but dissolved in warm THF, dioxane, or DMSO: ir (KBr) 6.01, 10.98 $\mu$; nmr (DMSO-$d_6$) $\delta$ 1.92 (m, 2 H, $J$ = 0 Hz), 3.21 (t, 2 H, $J$ = 7 Hz).

**Benzoic Acid from Salt 5.** Salt 5 (223 mg) was refluxed under nitrogen with a solution of $HgCl_2$ (560 mg) and HgO (176 mg) in 35% aqueous acetone (27 mg) for 24 hr. The reaction mixture was filtered and the filtrate was diluted with $H_2O$ and extracted with $CH_2Cl_2$. The organic layer was separated into acid and neutral fractions. From the acid fraction, after evaporation of the $CH_2Cl_2$, benzoic acid was isolated (32 mg, 52%), mg 122°.

**Reaction of Salt 5 at 22°.** Salt 5 (223 mg) was dissolved in acetone–$H_2O$ (92:8, 12.5 ml) with $HgCl_2$ (560 ml) and stirred for 72 hr at 22°. The reaction mixture was filtered and the filtrate was worked up as above to give an oily solid (19 mg) which was shown to be mostly 7 by tlc and nmr.

**Acknowledgment.** We are grateful to the Graduate School of The University of Wisconsin, which supported this work.

**Registry No.**—1, 34858-82-7; 5, 51025-51-5; 6, 51021-88-6; 7, 51021-89-7; benzoic acid, 65-85-0; benzoyl chloride, 98-88-4; propanedithiol, 109-80-8; $HgCl_2$, 7487-94-7.

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## 2,2-Bis(methylsulfonyl)vinylamines. A New Class of Vinylamines

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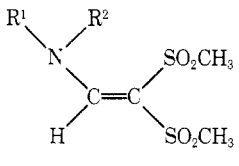
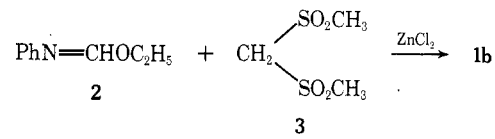
We were interested in preparing compounds of the general formula **1**. Surprisingly, compounds of this type appear not to be known, although many of the corresponding aminomethylene malononitrile and aminomethylene malonic ester derivatives have been reported.[1,2]

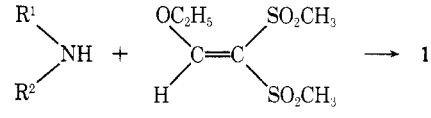


| | $R^1$ | $R^2$ |
|---|---|---|
| **1a** | H | H |
| **b** | Ph | H |
| **c** | $n$-$C_3H_7$ | H |
| **d** | $C_2H_5$ | $C_2H_5$ |
| **e** | PhNH | H |
| **f** | Ph | $CH_3$ |
| **g** | H | O=CPh |
| **h** | H | O=CNHCH$_3$ |
| **i** | H | Ts |

$N$-[2,2-Bis(methylsulfonyl)vinyl]aniline (**1b**) was prepared in 20% yield by the zinc chloride catalyzed reaction of bis(methylsulfonyl)methane[3] (**3**) and ethyl $N$-phenylformimidate (**2**). A more efficient scheme for the preparation of bis(methylsulfonyl)vinylamines was the reaction of an amine with 2,2-bis(methylsulfonyl)vinyl ethyl ether (**4**), obtained by the reaction of **3** and triethyl orthoformate in the presence of acetic anhydride and zinc chloride. The reaction of **4** with amines proceeded under mild conditions to give the 2,2-bis(methylsulfonyl)vinylamines in 70–80% yield. The reaction of **4** with ammonia, propylamine, diethylamine, phenylhydrazine, or hydroxylamine proceeded without the addition of a catalyst. However, addition of acetic acid to the phenylhydrazine reaction gave a higher yield of **1e**. The reaction of **4** with aniline did not proceed smoothly without the addition of an acid catalyst.[5] $N$-Methylaniline would not condense with **4** directly; however, $N$-[2,2-bis(methylsulfonyl)vinyl]methylaniline (**1f**) could be prepared by the reaction of **1b** with dimethyl sulfate.

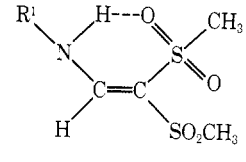


**2** **3**

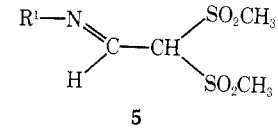


**4**

Infrared and pmr evidence indicate that the compounds **1a, 1b, 1c,** and **1e** exist mainly as the vinylamines and not as the tautomeric aldimines (**5**). This evidence includes a strong ir band at ~1600 $cm^{-1}$ for the enamine sulfone system[4] of **1a, 1b, 1c,** and **1e,** as well as for **1d,** which cannot tautomerize, and an NH absorption for compounds **1b** and **1c.** The pmr evidence includes the large ($J$ = 12–15 Hz) NHCH= coupling for compounds **1a, 1b, 1c,** and **1e.**

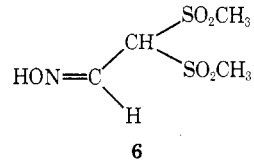


**1a, b, c, e,**



**5**

The reaction of hydroxylamine and **4** does not give $N$-[2,2-bis(methylsulfonyl)vinyl]hydroxylamine but rather, from ir (no 1600-$cm^{-1}$ band) and pmr evidence, 2,2-bis(methylsulfonyl)acetaldehyde oxime (**6**). Although the melting point of **6** is sharp, its pmr in dimethyl sulfoxide-$d_6$ suggests a 2:1 mixture of the $E$ and $Z$ oximes.[7] 2,2-Bis(methylsulfonyl)vinylamine (**1a**) reacts as an amine with acylation-type reagents, benzoyl chloride, or methyl isocyanate, to yield the benzamide **1g** or methylurea **1h.** However, **1a** did not react with $p$-toluenesulfonyl chloride in the presence of triethylamine. Conversion to the anion ($n$-butyllithium) permitted preparation of the sulfonamide **1i.**



**6**

## Experimental Section

**2,2-Bis(methylsulfonyl)vinyl Ethyl Ether (4).** Into a magnetically stirred 250-ml round-bottom flask equipped with a 10-in. Vigreux column were placed triethyl orthoformate (22.2 g, 0.15 mol), acetic anhydride (15.3 g, 0.15 mol), bis(methylsulfonyl)methane[3] (8.6 g, 0.05 mol), and anhydrous zinc chloride (1.5 g). The reaction mixture was heated to 140° in an oil bath, and, after 6 hr, more triethyl orthoformate (22.2 g) and acetic anhydride (15.3 g) were added. The oil bath temperature was raised to 160° and the remaining volatiles were distilled. The mixture was cooled to 25° and washed with hexane. The residue (12.6 g) was extracted with cold chloroform, the chloroform was evaporated under reduced pressure, and the residue (9.6 g) was recystallized from benzene (8.2 g, 72%): mp 124°; pmr ($CDCl_3$) $\delta$ 7.98 (s, 1), 4.47 (q, 2), 3.28 (s, 3), 3.17 (s, 3), 1.48 (t, 3).

*Anal.* Calcd for $C_6H_{12}O_5S_2$: C, 31.57; H, 5.30; S, 28.09. Found: C, 31.17; H, 5.62; S, 27.95.

**2,2-Bis(methylsulfonyl)vinylamine (1a).** 2,2-Bis(methylsulfonyl)vinyl ethyl ether (4, 41.7 g of 90% pure material, 0.167 mol) was dissolved in dry tetrahydrofuran (500 ml). The solution was cooled to −10° and anhydrous ammonia (3.9 g, 0.23 mol) was added. After 20 min the reaction was warmed to room temperature. After 20 hr the reaction mixture was filtered to obtain the first crop (17.6 g) of the amine. Additional crops of **1a** were obtained from the filtrate for a total yield of 29.1 g (88%). An analytical sample recrystallized from ethyl acetate–benzene melted at 179–181°, pmr (DMSO-$d_6$) $\delta$ 8.62–7.33 (broad, 2), 7.83–7.50 (broad, 1), 3.08 (s, 3), 3.05 (s, 3).

*Anal.* Calcd for $C_4H_9NO_4S_2$: C, 24.14; H, 4.52; N, 7.04; S, 32.15. Found: C, 24.27; H, 4.41; N, 7.03; S, 32.28.

**2,2-Bis(methylsulfonyl)vinylaniline (1b).** A solution of 4 (8.15 g of 90% pure material, 0.032 mol), aniline (3.0 g, 0.032 mol), and toluenesulfonic acid (100 mg) was combined in chloroform (100 ml). After standing for 4.5 hr, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with ethyl acetate–chloroform (1:6) gave the crude product (7.4 g, 83%). The analytical sample was recrystallized from benzene: mp 190–192°; pmr (DMSO-$d_6$) $\delta$ 9.82 (d, 1, $J$ = 15 Hz, NH). 8.20 (d, 1, $J$ = 15 Hz, HC=), 7.55–7.22 (m, 5), 3.28 (s, 1), 3.22 (s, 1).

*Anal.* Calcd for $C_{10}H_{13}NO_4S_2$: C, 43.67; H, 4.73; N, 5.09. Found: C, 43.90; H, 4.69; N, 5.10.

**Compounds 1c, 1d, and 1e.** Compounds **1c, 1d,** and **1e** were prepared similarly; yields, melting points, and analyses are as follows.

**1c,** 65%, 161–163°. *Anal.* Calcd for $C_7H_{15}NO_4S_2$: C, 34.85; H, 6.23; N, 5.82; S, 26.58. Found: C, 35.13; H, 6.41; N, 5.84; S, 26.34.

**1d,** 79%, 106–108°. *Anal.* Calcd for $C_8H_{17}NO_4S_2$: C, 37.63; H, 6.71; N, 5.48. Found: C, 37.39; H, 6.73; N, 5.54.

**1e,** 82%, 132–136°. *Anal.* Calcd for $C_{10}H_{14}N_2O_4S_2$: C, 41.41; H, 4.83; N, 9.66. Found: C, 41.38; H, 4.90; N, 9.53.

**2,2-Bis(methylsulfonyl)acetaldehyde Oxime (6).** A solution of 4 (22.8 g, 0.10 mol) in tetrahydrofuran (200 ml) was treated with hydroxylamine in methanol[6] (0.105 mol). After standing for 16 hr at 25° the solvent was removed under reduced pressure. The residue was taken up in hot ethyl acetate, filtered, and crystallized to yield 6 (12.4 g, 58%): mp 171–173°; pmr (DMSO-$d_6$) *E* (major) isomer $\delta$ 12.3 (s, 1, OH), 7.63 (d, 1, $J$ = 8.5 Hz, HC=N), 6.33 (d, 1, $J$ = 8.5 Hz, $SO_2CHSO_2$), 3.30 (s, 6, Me); *Z* (minor) isomer $\delta$ 12.6 (s, 1, OH), 7.18 (d, 1, $J$ = 8.5 Hz, HC=N), 6.82 (d, 1, $J$ = 8.5 Hz, $SO_2CHSO_2$), 3.30 (s, 6, Me).

*Anal.* Calcd for $C_4H_9NO_5S_2$: C, 22.35; H, 4.18; N, 6.52. Found: C, 22.55; H, 4.29; N, 6.70.

***N*-[2,2-Bis(methylsulfonyl)vinyl]-*N*-methylaniline (1f).** 2,2-Bis(methylsulfonyl)vinylaniline (**1b,** 2.75 g, 0.01 mol), dimethyl sulfate (1.26 g, 0.01 mol), and potassium carbonate (2.76 g, 0.02 mol) in acetone (70 ml) were heated at reflux for 20 hr. The reaction mixture was cooled, filtered, and concentrated. The residue, 3.0 g, was recrystallized from benzene–hexane, yield 2.15 g (75%). The analytical sample was recrystallized from benzene: mp 157–158°; pmr ($CDCl_3$) $\delta$ 7.93 (s, 1), 7.63–7.12 (m, 5), 3.70 (s, 3), 3.32 (s, 3), 3.27 (s, 3).

*Anal.* Calcd for $C_{11}H_{15}NO_4S_2$: C, 45.66; H, 5.23; N, 4.84. Found: C, 45.86; H, 5.32; N, 4.92.

***N*-[2,2-Bis(methylsulfonyl)vinyl]benzamide (1g).** 2,2-Bis(methylsulfonyl)vinylamine (3.98 g, 0.02 mol), benzoyl chloride (2.81 g, 0.02 mol), and triethylamine (2.02 g, 0.02 mol) were combined in tetrahydrofuran (100 ml) and heated at reflux for 20 hr. The mixture was cooled to room temperature, filtered to remove triethylamine hydrochloride, and concentrated under reduced pressure. The residue was washed with hexane (125 ml) and chromatographed over silica gel. The product was eluted with ethyl acetate–hexane (2:1) and recrystallized from isopropyl alcohol: yield 3.92 g (65%); mp 179–181°; pmr (DMSO-$d_6$) $\delta$ 10.95 (d, 1, $J$ = 12.5 Hz), 8.61 (d, 1, $J$ = 12.5 Hz), 8.17–7.50 (m, 5), 3.50 (s, 3), 3.37 (s, 3).

*Anal.* Calcd for $C_{11}H_{13}NO_5S_2$: C, 43.60; H, 4.28; N, 4.62; S, 21.12. Found: C, 43.66; H, 4.38; N, 4.59; S, 21.28.

**1-[2,2-Bis(methylsulfonyl)vinyl]-3-methylurea (1h).** 2,2-Bis(methylsulfonyl)vinylamine (3.98 g, 0.02 mol), methyl isocyanate (1.5 ml, 0.025 mol), and triethylamine (0.25 ml) were allowed to react at 25° in acetone (100 ml). After 1 hr the reaction mixture was heated at reflux for 30 min and cooled and the acetone was removed under reduced pressure. The residue was recrystallized from acetone–hexane to give the product (4.63 g, 90%): mp 229–231°; pmr (DMSO-$d_6$) $\delta$ 9.67 (broad d, 1, $J$ = 13 Hz), 8.34, (d, 1, $J$ = 13 Hz), 8.00 (broad, 1), 3.17 (s, 6), 2.66 (d, 3, $J$ = 4 Hz).

*Anal.* Calcd for $C_6H_{12}N_2O_5S_2$: C, 28.15; H, 4.68; N, 10.93. Found: C, 28.55; H, 4.63; N, 11.03.

***N*-[2,2-Bis(methylsulfonyl)vinyl]-*p*-toluenesulfonamide (1i).** 2,2-Bis(methylsulfonyl)vinylamine (3.98 g, 0.02 mol) was dissolved in dry tetrahydrofuran (150 ml). A solution of *n*-butyllithium in hexane (13 ml, 0.02 mol) was slowly added, keeping the reaction temperature at 25°. *p*-Toluenesulfonyl chloride (3.81 g, 0.02 mol) in tetrahydrofuran (25 ml) was added dropwise. After 3 hr a second equivalent of *n*-butyllithium (0.02 mol) was added. After an additional 45 min the reaction mixture was poured into ice water (500 ml), acidified with hydrochloric acid, extracted with methylene chloride, dried ($MgSO_4$), and concentrated to give the crude product (6.95 g). Recrystallization from 95% ethanol gave the pure product (4.0 g, 57%): mp 219–222°; pmr (DMSO-$d_6$) $\delta$ 10.9 (s, 1), 8.25 (s, 1), 7.91 (d, 2), 7.50 (d, 2), 3.25 (s, 6), 2.43 (s, 3).

*Anal.* Calcd for $C_{11}H_{15}NO_6S_3$: C, 37.42; H, 4.25; N, 3.97. Found: C, 37.78; H, 4.41; N, 4.26.

**Acknowledgment.** The authors would like to thank the Physical Analytical Chemistry staff of The Upjohn Co. for the elemental analyses.

**Registry No.—1a,** 51022-16-3; **1b,** 51022-17-4; **1c,** 51022-18-5; **1d,** 51022-19-6; **1e,** 51022-20-9; **1f,** 51022-21-0; **1g,** 51022-22-1; **1h,** 51022-23-2; **1i,** 51022-24-3; **4,** 51022-25-4; (*E*)-**6,** 51021-67-1; (*Z*)-**6,** 51021-68-2; bis(methylsulfonyl)methane, 1750-62-5; ammonia, 7664-41-7; aniline, 62-53-3; hydroxylamine, 7803-49-8; dimethyl sulfate, 77-78-1; benzoyl chloride, 98-88-4; methyl isocyanate, 624-83-9; propylamine, 107-10-8; diethylamine, 109-89-7; phenylhydrazine, 100-63-0.

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(2) (a) T. Passalacqua, *Gazz. Chim. Ital.*, **43**, 566 (1913); (b) C. C. Price and V. Boekelheide, *J. Amer. Chem. Soc.*, **68**, 1246 (1946).
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(4) (a) A. R. Friedman and D. R. Graber, *J. Org. Chem.*, **37**, 1902 (1972); (b) W. E. Truce and D. G. Brady, *ibid.*, **31**, 3543 (1966).
(5) Boron trifluoride or *p*-toluenesulfonic acid worked equally well.
(6) Prepared from hydroxylamine hydrochloride and sodium methoxide in methanol. After stirring for 30 min the precipitated sodium chloride was filtered and the solution was used for the preparation of **5.**
(7) (a) The major isomer is assigned the *E* configuration from the chemical shift of the formyl proton, 0.45 ppm downfield from the formyl proton of the minor isomer. (b) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 226.

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## Cyclization of a 3,4-Dihydro-1-benzoxepin-5(2*H*)-ylidenemalononitrile

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Acidic cyclization of ylidenemalononitriles has proven to be a fruitful route to a variety of fused keto amides.[1,2]