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 ($CDCl_3$) δ 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) δ 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) δ 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 δ 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 δ 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 ($CDCl_3$) δ 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) δ 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) δ 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) δ 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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(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.

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

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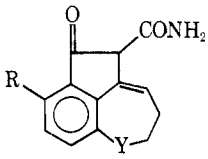
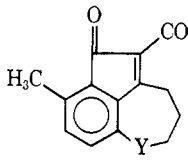
Acidic cyclization of ylidenemalononitriles has proven to be a fruitful route to a variety of fused keto amides.[1,2]

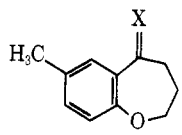
Application of this procedure to the ylidenemalononitrile derivatives of benzosuberone and 2,3,4,5-tetrahydrobenzo[*b*]thiepin[1] has yielded compounds **1** and **2**. This reaction has now been successfully applied to the 3,4-dihydro-1-benzoxepin-5(2*H*)-ylidenemalononitrile (**3**).



1, Y = CH_2; R = H
5, Y = O; R = CH_3

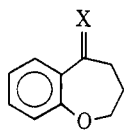


2, Y = S
6, Y = O

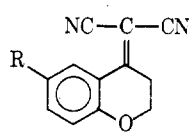


3, X = $C(CN)_2$
4, X = O

Compound **3**, which was readily available[1] from **4**,[3] immediately produced a wine-red solution, similar to the formation of **1**, when placed in polyphosphoric acid at 85°. Quenching the reaction yielded **5** as the only product with no indication of isomer **6**. In contrast to the sulfur series,[1] use of sulfuric acid as the cyclizing media produced only small amounts of **5**. On the other hand, no isolable material resulted when the 7-demethylated ylidenemalononitrile (**7**) was subjected to either polyphosphoric acid or sulfuric acid. This result parallels that in the sulfur series[1,4] in which the position para to the heteroatom is susceptible to electrophilic substitution.



7, X = $C(CN)_2$
8, X = O



9, R = H, CH_3

The structure of **5** was based on several lines of evidence: (a) white color analogous to that of **1**[5] and in contrast to the indenone **2**[1] which is red; (b) infrared bands at 5.82 (ketone carbonyl) and 6.08 μ (amide carbonyl) which are in exact agreement with those recorded in our laboratory for **1**; (c) ultraviolet absorptions at 245 and 268–278 nm similar to those of **1**;[5] and (d) an nmr spectrum analogous to that of **1**[6] possessing a vinylic proton absorption at τ 3.91.

The formation of **5** was unexpected in view of the formation of noncyclized ring-sulfonated products when **9**[7] was subjected to similar conditions. The fact that the reaction of **3** gives **5**, analogous to the carbocyclic system, rather than **6**, which would parallel the sulfur series, may be due simply to the similarity in size of O and CH_2. The larger sulfur atom in the sulfur analog may cause greater puckering in the thiepin ring, favoring the exo double bond.

Experimental Section[8]

3,4-Dihydro-1-benzoxepin-5(2*H*)-ylidenemalononitriles. A 400-ml xylene solution containing 190 mmol of either **4**[4] or **8**,[9] 33 g (500 mmol) of malononitrile, 12 g of ammonium acetate, and 36 ml of glacial acetic acid was refluxed with the aid of a Dean-Stark trap until the collection of water ceased. The xylene solution was cooled and decanted from a polymeric mass of malononitrile in the reaction vessel. After this mass was washed with xylene, the xylene fractions were combined and washed with water (3 × 100 ml). After drying over anhydrous $MgSO_4$, the xylene solution was concentrated *in vacuo* and the residue crystallized upon ice cooling.

3,4-Dihydro-1-benzoxepin-5(2*H*)-ylidenemalononitrile (7) was obtained in 65% yield as white needles from aqueous ethanol: mp 98–100°; ir (KBr) 4.50 μ (CN); nmr ($CDCl_3$) τ 2.36–3.10 (m, 4 H, aromatic), 5.89 (t, J = 6 Hz, 2 H, α to oxygen), 7.0 (t, J = 6 Hz, 2 H, γ to oxygen), 7.74 (pentet, J = 6 Hz, 2 H, β to oxygen).

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.28; H, 4.77. Found: C, 74.30; H, 4.90.

3,4-Dihydro-7-methyl-1-benzoxepin-5(2*H*)-ylidenemalononitrile (3) was obtained in 75% yield as yellow needles from cold aqueous ethanol: mp 60–62°; ir (KBr) 4.50 μ (CN); nmr ($CDCl_3$) τ 2.7 (m, 1 H, aromatic), 2.88–3.15 (m, 2 H, aromatic), 5.91 (t, J = 6 Hz, 2 H, α to oxygen), 7.0 (t, J = 6 Hz, 2 H, γ to oxygen), 7.72 (s, 3 H, methyl), 7.75 (br, 2 H, β to oxygen).

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 75.00; H, 5.35. Found: C, 74.73; H, 5.50.

2,3,5,6-Tetrahydro-7-methyl-6-oxoindeno[7,1-*bc*]oxepin-5-carboxamide (5). Three grams (13.4 mmol) of **3** was slowly added to 40 g of mechanically stirred polyphosphoric acid at 85°. The resulting solution became wine red almost immediately and stirring was continued at 85° for 1 hr. The resultant solution was poured in 1.8 l. of ice water and the insoluble material which resulted was filtered, washed with water, and air dried. Several recrystallizations from 95% ethanol yielded 47% of **5** as white prisms: mp 186–188°; nmr (DMSO-d_6) τ 2.9–3.15 (br, 2 H, aromatic), 3.91 (br, 1 H, vinyl), 5.75 (t, J = 4 Hz, 2 H, α to oxygen), 5.95 (broad s, 1 H, methine), 7.57–7.88 (5 H, methyl singlet superimposed on multiplet of $-CH_2-$ β to oxygen); mass spectrum *m/e* (rel intensity) 243 (72), 226 (62), 200 (79), 198 (47), 185 (50), 141 (47), 128 (48), 115 (94), 44 (100), and 18 (68).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.35. Found: C, 68.97; H, 5.28.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to Dr. T. R. Bosin of the Department of Pharmacology at Indiana University for his assistance in obtaining the mass spectrum for compound **5**.

Registry No.—**3**, 50790-48-2; **4**, 41177-66-6; **5**, 50790-49-3; **7**, 50790-50-6; **8**, 6786-30-7.

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(6) The nmr spectrum of **1**, which has previously not been reported in the literature, was found to be (DMSO-d_6) τ 2.32–2.96 (m, 3 H, aromatic), 3.92 (t, J = 5 Hz, 1 H, vinyl), 5.90 (broad s, 1 H, methine), 6.91 (t, J = 5 Hz, 2 H, CH_2), 7.36 (br, 2 H, CH_2), and 8.02 (br, 2 H, CH_2).
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(8) Melting points were taken on a Mel-Temp capillary melting point apparatus and are uncorrected. The nmr spectra were obtained on a Varian A-60 spectrometer using TMS as an internal standard. The ultraviolet absorption spectrum was determined with a Cary Model 14 recording spectrophotometer using 1-cm sample cells. Ir spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer. The mass spectrum was determined on a Varian MAT CH-7 at Indiana University, Bloomington, Ind. The microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.
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Cyclization of δ- and γ-Alkenenitriles by Triethyloxonium Fluoroborate

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The acid-catalyzed cyclization of δ- and γ-unsaturated nitriles has received little study in the past. In the course of investigating the abnormal Beckmann rearrangement,

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