Anal. Calcd for $C_8H_7NO_3$: C, 58.19; H, 4.27; N, 8.48. Found: C, 58.14; H, 4.36; N, 8.58.

Further elution of the column gave a viscous syrupy material.

***N,N*-Dimethyl-2-chloroacetoacetamide (21).** Diketene (42 g, 0.5 mol) was mixed with ice and water (200 mL) and treated with 25% aqueous dimethylamine (90 mL). On completion of the addition, the solution was allowed to warm to room temperature and stirred for 30 min. It was then cooled with an ice bath, acidified with concentrated HCl (250 mL), and treated with aqueous sodium hypochlorite ("Chlorox"; 800 mL) by rapid dropwise addition. After warming to room temperature, the resulting mixture was extracted three times with 400-mL portions of methylene chloride. After drying and evaporation of solvent, the product was vacuum distilled to give 67.65 g (83%) of pale yellow liquid with bp 97–98 °C (0.05 mm): IR (film) 1730 and 1645 cm^{-1}; NMR ($CDCl_3$) 2.40 (s, 3 H), 3.03 (s, 3 H), 3.20 (s, 3 H), and 5.30 (s, 1 H) ppm; mass spectrum, *m/e* 43 and 163 (M^+).

Anal. Calcd for $C_6H_{10}ClNO_2$: C, 44.05; H, 6.16, Cl, 21.67; N, 8.56. Found: C, 44.31; H, 6.29, Cl, 21.73; N, 8.66.

2-Hydroxy-3-acetyl-4-cyano-5-methylfuran (20). A solution of compound **21** (3.28 g, 0.02 mol) in methanol (10 mL) was treated with the sodium enolate of cyanoacetone (2.1 g, 0.02 mol) and heated on a steam bath for 10 min. It was then cooled and acidified with 3 N HCl. After standing at room temperature for 20 h, the crystals of **20** were collected, washed with cold water, and air-dried. This crop of 2 g, together with a second crop, gave 2.2 g (66.7%) of the higher melting diamorph with mp 148–150 °C. Identity with the sample obtained previously was established by IR and mass spectra and TLC.

Crystallography. Crystals of compound **4** for structure analysis were grown from aqueous ethanol. The crystal data were as follows: space group Ia; a = 7.488 Å; b = 15.297 Å; c = 7.071 Å; β = 97.05°; Z = 4; d_{calcd} = 1.356 g/cm^3; and μ (Cu Kα) = 8.5 cm^{-1}.

The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation; θ–2θ scans; pulse height discrimination). The size of the crystal used for data collection was approximately 0.05 × 0.08 × 0.45 mm; the data were not corrected for absorption. Of the 822 accessible reflections for $\theta < 76°$, 638 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[8] and refined by full matrix least squares. In the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices were R = 0.040 and R_w = 0.038 for the 638 observed reflections. The final difference map had no peaks greater than ±0.2 eA^{-3}.

The C–N and C=O bond lengths of the amino and ketone functions, assumed on the basis of the very weak basicity of **4** to be involved in a resonance interaction, are 1.32 and 1.23 Å, respectively.

Acknowledgment. The interest and suggestions provided by Dr. Willy Leimgruber are greatly appreciated.

Registry No.—**1,** 5765-44-6; **2,** 7064-36-0; **3** ketone form, 60930-76-9; **3** enol form, 67271-59-4; **4,** 67271-60-7; **6,** 67271-61-8; **7,** 609-15-4; **8,** 1694-29-7; **9,** 67271-62-9; **10,** 67271-63-0; **11,**67271-64-1; **12,** 67271-65-2; **13,** 4439-88-7; **14,** 67271-66-3; **15,** 67271-67-4; **16,** 67271-81-2; **17,** 67271-68-5; **18,** 67271-69-6; **19,** 67271-70-9; **20,** 67271-71-0; **21,** 5810-11-7; cyanoacetone sodium enolate, 67271-72-1; ammonia, 7664-41-7; diketene, 674-82-8; *tert*-butylamine, 75-64-9; dimethylamine,124-40-3.

Supplementary Material Available: Final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles of **4** (Tables I–IV, respectively) (2 pages). Ordering information is given on any current masthead page.

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Cyclic Sulfamides: Synthesis of Some Fused Tetrahydrobenzo- and Tetra- and Dihydroheterothiadiazinone 2,2-Dioxides[1]

James A. Kloek* and Kindrick L. Leschinsky

Monsanto Agricultural Products Company, Research Department, St. Louis, Missouri 63166

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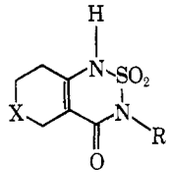
General methods for the synthesis of the title compounds (**1–3**) are described. The two key steps in these syntheses are the regiospecific sulfamoylation of primary enamino esters **9** and an acid-catalyzed ring closure procedure which offers distinct advantages over existing methods. Thus, the title compounds bearing bulky alkyl groups on N-3 are available in high yield from available β-keto esters.

In 1962 Cohen and Klarberg reported a new class of fused ring sulfamides, the 2,1,3-benzothiadiazin-4-one 2,2-dioxides.[2] The subsequent discovery that certain alkylated derivatives of this class of compounds possess uniquely selective phytotoxic properties[3] has made further synthesis in this area a relevent problem. This paper details general methods for the synthesis of some reduced and heterosubstituted reduced forms of these fused ring cyclic sulfamides, including the 5,6,7,8-tetrahydro-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxides **1**, the dihydro-2,1,3-thiopyranothiadiazin-4-one 2,2-dioxides **2**, and the tetrahydro-2,1,3-pyridothiadiazin-4-one 2,2-dioxides **3**.

Our initial synthetic efforts in this area involved attempted direct formation of the desired ring system by condensation



1, X = CH_2
2, X = S
3, X = N–R′

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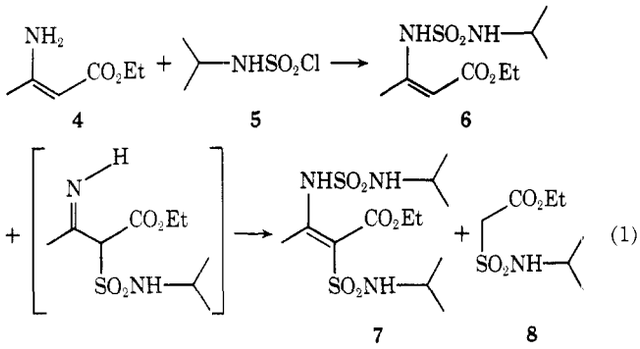
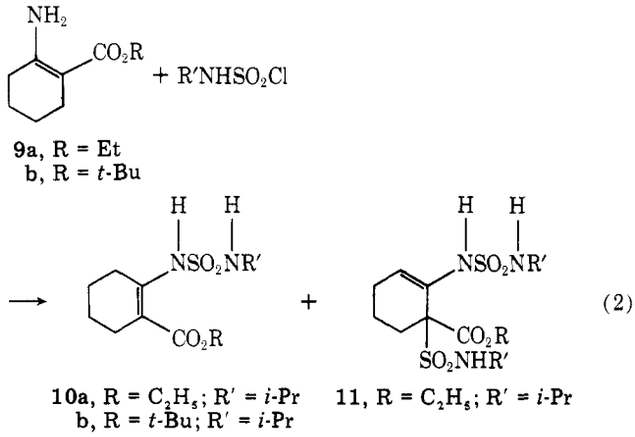
of sulfamide with a β-keto ester. Although such a condensation succeeds with β-diketones,[4] it failed in this case. We therefore adopted a two-step approach conceptually similar to that employed by Cohen and Klarberg,[2] namely, sulfamoylation of a primary β-enamino ester followed by ring closure. To test the potential of this proposed route, a model study was undertaken using ethyl 3-aminocrotonate (**4**) and *N*-isopropylsulfamoyl chloride (**5**).[5] These results are shown in eq 1. Reaction of **4** with **5** in the presence of triethylamine gave rise to the three products shown (**6**, **7**, and **8**) in a ratio of 1:2:3.5. Compounds **7** and **8** could reasonably arise from the common intermediate shown. In this model case, amino crotonate **4**, an ambident nucleophile, was showing a decided preference to react at the α carbon rather than at the nitrogen.



(1)

This result was not overly discouraging for it was expected that in the synthesis of the desired bicyclo compounds (**1–3**) the intermediates required (e.g., enamino esters **9**) would already bear substitution at the α carbon and that this substitution would promote reaction at nitrogen. Accordingly, the model system was abandoned and attention was focused on the cyclic β-enamino esters needed for the bicyclic compounds desired.

These enamino esters are available from the corresponding β-keto esters by a number of routes.[6] When **9a** was allowed to react with isopropylsulfamoyl chloride in the presence of triethylamine, the result was a 4:1 mixture of monosubstituted product **10a** to disubstituted **11** (eq 2). This dramatic shift in the ratio of N-substitution to C-substitution corroborated the expectation that partially blocking the β carbon would alter the course of the reaction.



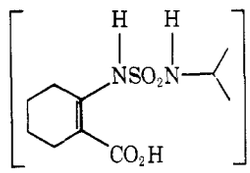
(2)

Nevertheless, better ratios were needed for this to be a synthetically useful transformation. In the presence of a base, sulfamoyl chlorides are dehydrohalogenated to *N*-sulfonylamines,[7] which are then attacked by nucleophiles to give products. It was reasoned that the use of a base much weaker than triethylamine would increase the regioselectivity of the reaction by either lowering the concentration of *N*-sulfonylamine in solution or by allowing the reaction to proceed through a different mechanism. This reasoning proved sound, for when a second equivalent of enamino ester **9a** was employed in lieu of triethylamine, the only product isolated was sulfamoyl ester **10a.**

Having thus achieved regiospecificity in the sulfamoylation step, there remained only the task of cyclizing the intermediate sulfamoyl esters (**10**) to the desired compounds **1.** Cohen and Klarberg had employed aqueous base to cyclize their compound which was lacking alkyl substitution on nitrogen.[2] Compounds such as **10a,** wherein R′ is a primary alkyl group, cyclize equally well under these conditions. Dissolution in 5% aqueous sodium hydroxide followed shortly by precipitation with hydrochloric acid provided tetrahydrobenzothiadiazinones **1** (R = primary alkyl) in good yields. However, when R′ became a branched alkyl group such as isopropyl, yields for this procedure dropped precipitously. The starting material was consumed, and NMR spectra of the reaction residues suggested that a competing process was resulting in loss of the isopropyl group.

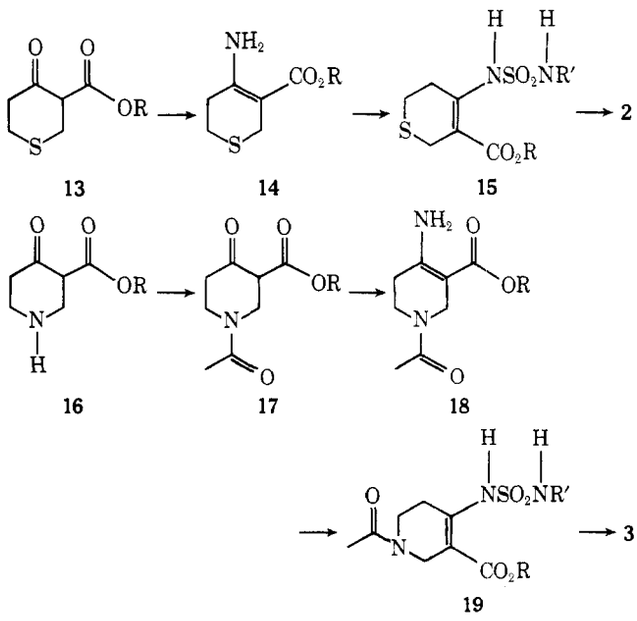
This result and those of other experiments aimed at ameliorating this problem suggested that a successful ring closure procedure would rely upon activation of the ester portion of the molecule rather than the sulfamide.

An attractive alternate intermediate therefore became *tert*-butylenamino ester **9b.**[6] This compound was sulfamoylated as described above to provide the sulfamoyl ester **10b.** Dissolution of this compound in 1:1 trifluoroacetic acid/trifluoroacetic anhydride for 10 min followed by evaporation of the solvents afforded the *N*-isopropyltetrahydrobenzothiadiazinone (**1**; R = *i*-Pr) in 89% yield. Presumably the strong acid effects cleavage of the ester to provide the sulfamoyl acid intermediate **12,** which then cyclizes, possibly via a mixed anhydride.



12

Methodology is therefore in hand for construction of a wide variety of tetrahydrobenzothiadiazinone 2,2-dioxides, with the only synthetic precursor being an available β-keto ester. To demonstrate the generality of this methodology, several examples of two new heterocyclic ring systems were synthesized using various combinations of the procedures described above. Keto esters of general structure **13**[8] were converted to



the corresponding dihydro-2,1,3-thiopyranothiadiazin-4-one 2,2-dioxides **2**, while keto esters of gross structure **16**[9] gave rise to the tetrahydro-2,1,3-pyridothiadiazin-4-one 2,2-dioxides **3**. A detailed description of the preparation of a specific example of each of these ring systems [**2** (R = CH_3) from **13** (R = CH_3) and **3** (R = CH_3) from **16** (R = C_2H_5)] is included in the Experimental Section.

Experimental Section

General. Melting points were determined on a Laboratory Devices Melt-Temp apparatus and are uncorrected. Nuclear magnetic resonance spectra (NMR) were recorded on Varian T-60 and EM-360 spectrometers. Spectra were run using tetramethylsilane as an internal standard, and chemical shifts are reported in parts per million (ppm) downfield (δ) relative to Me_4Si = 0. Combustion analyses were performed by Atlantic Microlabs, Galbraith Laboratories, or the Monsanto Physical Sciences Center. Analytical thin-layer chromatography was performed using Baker-flex precoated silica gel slides.

Condensation of Ethyl 3-Aminocrotonate with *N*-Isopropylsulfamoyl Chloride. To a solution of 6.46 g (0.05 mol) of ethyl 3-aminocrotonate (**4**) and 7.8 g (0.05 mol) of *N*-isopropylsulfamoyl chloride in benzene was added 5.06 g (0.05 mol) of triethylamine. The resulting suspension was stirred at 50 °C for 24 h and cooled. The solution was washed with 2.5% hydrochloric acid and water, dried over magnesium sulfate, and concentrated to an oil. This oil was chromatographed on a silica gel column (10–50% ethyl acetate/cyclohexane) to afford three products. The first, ethyl 3-(*N*-isopropylsulfamoylamino)crotonate (**6**; 0.8 g, 7%), was isolated as an oil: NMR ($CDCl_3$) δ 1.20 (d, J = 6 Hz, 6 H), 1.22 (t, J = 8 Hz, 3 H), 2.15 (s, 3 H), 3.30–3.80 (m, 1 H), 4.20 (q, J = 8 Hz, 2 H), 4.95 (m, 1 H), 5.10 (broad d, J = 8 Hz, 1 H).

The second product, ethyl α-(*N*-isopropylsulfamoyl)acetate (**8**; 3.6 g, 34%), was isolated as an oil: bp 150 °C (0.05 mm); NMR ($CDCl_3$) δ 1.25 (d, J = 6 Hz, 6 H), 1.30 (t, J = 8 Hz, 3 H), 3.40–4.00 (m, 1 H), 4.05 (s, 2 H), 4.30 (q, J = 8 Hz, 2 H), 5.10 (broad d, 1 H).

Anal. Calcd for $C_7H_{15}NO_4S$: C, 40.18; H, 7.23; N, 6.69. Found: C, 39.99; H, 7.31; N, 7.13.

The third product, ethyl *N*,2-bis(*N'*-isopropylsulfamoyl)-3-aminocrotonate (**7**; 3.6 g, 20%), was also an oil: NMR ($CDCl_3$) δ 1.20 (d, J = 6 Hz, 12 H), 1.22 (t, J = 6 Hz, 3 H), 2.45 (2 singlets, 3 H), 3.10–3.20 (m, 2 H), 4.00–4.50 (m, 2 H), 4.90–5.15 (broad, m, 2 H).

Condensation of Ethyl 2-Amino-1-cyclohexene-1-carboxylate (9a) and *N*-Isopropylsulfamoyl Chloride in the Presence of Triethylamine. To a solution of 8.45 g (0.05 mol) of β-enamino ester **9a** and 10.1 g (0.1 mol) of triethylamine in benzene at 10 °C was added dropwise 8.7 g (0.055 mol) of *N*-isopropylsulfamoyl chloride. When the addition was complete, the solution was stirred for 1 h, washed with water, dried over magnesium sulfate, and concentrated to a viscous oil. This oil was chromatographed on a silica gel "dry column" (20% ethyl acetate/cyclohexane) to afford two products. The first of these, ethyl *N*-(*N'*-isopropylsulfamoyl)-2-amino-1-cyclohexene-1-carboxylate (**10a**; 5.9 g, 41%), was isolated as an oil: NMR ($CDCl_3$) δ 1.2 (d, J = 6 Hz, 6 H), 1.22 (t, J = 8 Hz, 3 H), 1.50–2.90 (m, 8 H), 3.40–3.80 (m, 1 H), 4.25 (q, J = 8 Hz, 2 H), 4.65 (broad d, 1 H); IR (film) 1680 cm^{-1}.

Anal. Calcd for $C_{12}H_{22}N_2O_4S$: C, 49.63; H, 7.64; N, 9.65. Found: C, 49.36; H, 7.76; N, 9.50.

The second product, ethyl 1,*N*-bis(*N'*-isopropylsulfamoyl)-2-amino-2-cyclohexene-1-carboxylate (**11**; 2.0 g, 10%), was isolated as a solid: mp 88–92 °C; NMR ($CDCl_3$) δ 1.2 (d, J = 6 Hz, 12 H), 1.22 (t, J = 8 Hz, 3 H), 1.50–2.80 (m, 6 H), 3.40–3.95 (m, 2 H), 4.35 (q, J = 8 Hz, 2 H), 4.80 (broad d, 1 H), 5.20 (broad d, 1 H), 6.10 (t, J = 4 Hz, 1 H), 6.95 (broad s, 1 H); IR (film) 1715 cm^{-1}.

Anal. Calcd for $C_{15}H_{29}N_3O_6S_2$: C, 43.78; H, 7.10; N, 10.21. Found: C, 44.06; H, 7.21; N, 10.08.

Also isolated was 3.6 g (42%) of 2-carbethoxycyclohexanone.

Condensation of 2-Amino-1-cyclohexene-1-carboxylates (9a and 9b) with Isopropylsulfamoyl Chloride in the Absence of Triethylamine. A solution of 2 equiv of β-enamino ester **9a** or **9b** in benzene was cooled to 5 °C and treated with 1 equiv of *N*-isopropylsulfamoyl chloride. The resulting solution was stirred for 48 h at room temperature, washed with water, dried over magnesium sulfate, and concentrated to afford the crude product.

Ethyl ester **10a** (see above) was isolated in 78% yield.

tert-Butyl ester **10b** was isolated in 73% yield: mp 97–99 °C (from pentane); NMR ($CDCl_3$) δ 1.20 (d, J = 6 Hz, 6 H), 1.55 (s, 9 H), 1.40–2.90 (m, 8 H), 3.40–3.90 (m, 1 H), 4.45 (broad d, 1 H).

Anal. Calcd for $C_{14}H_{26}N_2O_4S$: C, 52.80; H, 8.23; N, 8.80. Found: C, 52.68; H, 8.28; N, 8.71.

3-Isopropyl-5,6,7,8-tetrahydro-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-Dioxide (1; R = *i*-Pr). A solution of 0.75 g of sulfamoyl ester **10b** in 5 mL of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride was stirred at room temperature for 5 min. The solvents were evaporated, and the resulting solid was triturated with hexane to provide 0.5 g (87%) of cyclic sulfamide **1** (R = *i*-Pr) as a solid: mp 188–192 °C; NMR ($CDCl_3$) δ 1.50 (d, J = 6 Hz, 6 H), 1.40–2.5 (m, 8 H), 4.60–5.20 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}N_2O_3S$: C, 49.16; H, 6.60; N, 11.47. Found: C, 49.19; H, 6.60; N, 11.42.

4-Amino-3-carbomethoxy-5,6-dihydro-2*H*-thiopyran (14). A solution of 52.75 g of 4-oxo-3-carbomethoxy-5,6-dihydro-2*H*-thiopyran (0.3 mol), 27 g of urethane (0.3 mol), and a catalytic amount of *p*-toluenesulfonic acid in 300 mL of benzene was refluxed for 20 h, using a Dean-Stark trap to separate water. The solution was cooled and the solvent evaporated to provide an oil. This oil was added to a solution of 35 g of sodium methoxide in 600 mL of methanol and refluxed under nitrogen for 18 h. The solution was then cooled and poured into 1200 mL of ice/water. This mixture was extracted five times with a total of 2 L of ether. These extracts were combined, washed with brine, dried over magnesium sulfate, and concentrated to an oil. Distillation provided 28 g (54%) of enamino ester **14**: bp 124 °C (0.45 mm); NMR ($CDCl_3$) δ 2.40–3.00 (m, 4 H), 3.50 (s, 2 H), 3.80 (s, 3 H), 6.5 (broad, 2 H).

Anal. Calcd for $C_7H_{11}NO_2S$: C, 48.53; H, 6.40; N, 8.09. Found: C, 48.60; H, 6.42; N, 8.18.

3-Methyl-7,8-dihydro-1*H*,5*H*-thiopyrano[3,4-*e*]-2,1,3-thiadiazin-4(3*H*)-one 2,2-Dioxide (2; R = CH_3). A solution of 4 g (23.1 mmol) of enamino ester **14** and 1.5 g (11.6 mmol) of *N*-methylsulfamoyl chloride in 60 mL of benzene was stirred for 18 h at room temperature under nitrogen. The solution was diluted with an equal volume of ether and washed two times with water. The organic fraction was then poured into 60 mL of 5% aqueous sodium hydroxide, and the resulting suspension was stirred vigorously for 1 h. The layers were separated, and the aqueous layer was cooled in an ice bath. Acidification with concentrated hydrochloric acid precipitated 2 g (77%) of cyclic sulfamide **2** (R = CH_3) as a solid. Recrystallization from acetonitrile provided an anayltical sample: mp 205–207 °C dec; NMR (Me_2SO-d_6) δ 2.3–2.9 (m, 4 H), 3.1 (s, 3 H), 3.35 (s, 2 H).

Anal. Calcd for $C_7H_{10}N_2O_3S_2$: C, 35.88; H, 4.30; N, 11.96. Found: C, 35.89; H, 4.32; N, 12.03.

Ethyl *N*-Acetyl-4-oxopiperidine-3-carboxylate (17; R = C_2H_5). To a vigorously stirred suspension of 95 g (0.46 mol) of ethyl 4-oxopiperidine-3-carboxylate hydrochloride in 600 mL of benzene, cooled in an ice bath and under nitrogen, was added 101 g (1 mol) of triethylamine. Immediately following, 39.5 g (0.5 mol) of acetyl chloride was added dropwise. The resulting pasty suspension was stirred overnight, and the solids were filtered off. The filtrate was washed two times with water, dried over magnesium sulfate, and concentrated to a semisolid. This was taken up in a minimum amount of warm ether, pentane was added to the cloud point, and the solution was allowed to stand. Filtration provided 69 g (71%) of *N*-acetylpiperidine **17**: NMR ($CDCl_3$) δ 1.35 (t, J = 7 Hz, 3 H), 2.10 (s, 3 H), 2.20–2.55 (m, 2 H), 3.40–4.50 (m, 6 H), 11.40 (s, 1 H). This crude product was satisfactory for use in the next step.

***N*-Acetyl-4-amino-3-carbomethoxy-1,2,5,6-tetrahydropyridine (18; R = CH_3).** A solution of 69 g (0.33 mol) of keto ester **17**, 29 g (0.33 mol) of urethane, and a catalytic amount of *p*-toluenesulfonic acid in 800 mL of benzene was refluxed for 18 h, using a Dean-Stark trap to remove water. The solution was cooled and concentrated to provide a solid. The solid was dissolved in a solution of 7.5 g of sodium methoxide in 700 mL of methanol and refluxed under nitrogen for 18 h. A major portion of the methanol was distilled out, and the residue was poured into 700 mL of brine. This was continuously extracted with ethyl acetate. The extracts were combined and concentrated to a solid. Recrystallization from toluene provided 30 g (58%) of enamino ester **18**: mp 138–140 °C; NMR ($CDCl_3$) δ 2.10 (s, 3 H), 2.10–2.55 (m, 2 H), 3.70 (s, 3 H), 3.35–3.80 (m, 2 H), 4.05–4.30 (m, 2 H), 6.00–6.80 (broad, 2 H).

Anal. Calcd for $C_9H_{14}N_2O_3$: C, 54.33; H, 7.12; N, 14.13. Found: C, 53.89; H, 7.18; N, 13.96.

6-Acetyl-3-methyl-5,6,7,8-tetrahydro-1*H*-pyrido[3,4-*e*]-2,1,3-thiadiazin-4(3*H*)-one 2,2-Dioxide (3; R = CH_3). A solution of 5 g (25.2 mmol) of enamino ester **18** and 1.63 g (12.6 mmol) of *N*-methylsulfamoyl chloride in 60 mL of benzene was stirred for 18 h under nitrogen. The solution was washed with water and then extracted with three 20-mL portions of 5% aqueous sodium hydroxide. These extracts were cooled in an ice bath and acidified with concentrated hydrochloric acid. Extraction with ethyl acetate followed by drying over magnesium sulfate and concentration provided 2 g of an

oil which crystallized from acetonitrile to provide 0.9 g (29%) of cyclic sulfamide **3** (R = CH_3): mp 199–201 °C; NMR ($CDCl_3$) δ 2.1 (s, 3 H, 2.20–2.65 (m, 2 H), 3.15 (s, 3 H), 3.65 (t, J = 6 Hz, 2 H), 4.15 (broad s, 2 H).

Anal. Calcd for $C_9H_{13}N_3O_4S$: C, 41.69; H, 5.05; N, 16.21. Found: C, 41.69; H, 5.08; N, 16.23.

Registry No.—1 (R = *i*-Pr), 67210-12-2; **2** (R = CH_3), 67210-13-3; **3** (R = CH_3), 67210-14-4; **4**, 7318-00-5; **5**, 26118-67-2; **6**, 67210-15-5; **7**, 67210-16-6; **8**, 67210-17-7; **9a**, 1128-00-3; **9b**, 65277-17-0; **10a**, 67210-18-8; **10b**, 67210-19-9; **11**, 67210-20-2; **13** (R = CH_3), 4160-61-6; **14** (R = CH_3), 67210-21-3; **16** (R = C_2H_5) HCl, 4644-61-5; **17** (R = C_2H_5), 4451-85-8; **18** (R = CH_3), 67210-22-4; 2-carbethoxycyclohexanone, 1655-07-8; urethane, 51-79-6; *N*-methylsulfamoyl chloride, 10438-96-7.

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Sulfoxides, Sulfilimines, Methoxysulfonium Salts, and Sulfoximines Derived from 3-Methyl-3-phenylthietane[1]

Maris Buza,[2] Kenneth K. Andersen,* and Michael D. Pazdon

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

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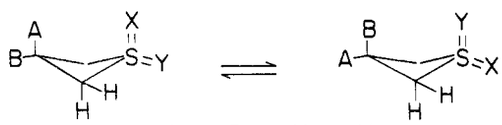
3-Methyl-3-phenylthietane (**1**), 3-isopropyl-3-phenylthietane (**10**), 3-(*p*-bromophenyl)-3-methylthietane (**11**), 2-thiaspiro[3.5]nonane (**12**), 2-thiaspiro[3.5]non-6-ene (**13**), 3-methyl-3-nitrothietane (**14**), 5-methyl-2-thiaspiro[3.5]nonane (**15**), 6-methyl-2-thiaspiro[3.5]nonane (**16**), and 7-methyl-2-thiaspiro[3.5]nonane (**17**) were prepared by treating the corresponding 2,2-disubstituted 1,2-trimethylene bis(benzenesulfonates) with sodium sulfide in dimethyl sulfoxide. Oxidation of **1** by hydrogen peroxide or by sodium hypochlorite gave 3-methyl-*t*-3-phenylthietane *r*-1-oxide (**2**) and 3-methyl-*c*-3-phenylthietane *r*-1-oxide (**3**). Configurations were determined by NMR spectroscopy. Thermal interconversion of **2** and **3** proceeds at rates comparable to acyclic analogues and much slower than the rate reported for 3-*tert*-butylthietane 1-oxide. Relative rates of reaction of water and hydroxide ion at sulfur and methyl carbon in the hydrolysis of the diastereomeric methoxysulfonium salts derived from **2** and **3** were determined. Mass spectra of 2,2,4,4-tetradeuterated derivatives of **1**, **2**, **3**, and 3-methyl-3-phenylthietane 1,1-dioxide (**18**) were obtained. Sulfoxides **2** and **3** showed no differences in their mass spectra. An improved synthesis of *N*-*p*-toluenesulfilimines by the reaction of sulfides with anhydrous Chloramine-T–dimethylformamide solutions was used to synthesize 3-methyl-*c*-3-phenylthietane-*r*-*N*-(*p*-toluenesulfonyl)sulfilimine (**6**) and its diastereomer (**7**). Their rates of interconversion measured at 165 °C were somewhat slower than that for an acyclic arylalkyl analogue, but faster than that for an acyclic dialkyl *N*-acylsulfilimine. Silver ion formed complexes with sulfilimines with bonding at the N atom.

Thietanes and their S-substituted derivatives have been investigated extensively in recent years, but no 3-alkyl-3-arylthietanes or derivatives are included in these studies.[3–8] In fact, we found no mention of such compounds in the literature at all. We have synthesized 3-methyl-3-phenylthietane (**1**), converted it to diastereomeric sulfoxides **2** and **3**, methoxysulfonium salts **4** and **5**, sulfilimines **6** and **7**, and sulfoximines **8** and **9**, assigned configurations to these derivatives, determined the equilibrium between **2** and **3** and between **6** and **7**, and also studied some additional chemistry of these and related compounds. Our results and their relationship to previous investigations of various sulfoxides, sulfilimines, and sulfoximines, especially cyclic analogues, are described below.



	A	B	X	Y
1	Ph	Me	–	–
2	Ph	Me	–	O
3	Me	Ph	–	O
6	Me	Ph	–	NTs
7	Ph	Me	–	NTs
8	Me	Ph	O	NTs
9	Ph	Me	O	NTs
18	Ph	Me	O	O

Results and Discussion

3-Methyl-3-phenylthietane 1-Oxides (2 and 3). Thietane 1-oxides are prepared by oxidation of thietanes which are obtained most often through ring closure of 1,3-dibromides or 1,3-disulfonate esters[3,10,11] by sulfide ion, through fusion of cyclic carbonate esters of 1,3-diols with thiocyanate ion,[4,9] or by reduction of thietane 1,1-dioxides obtained by the cycloaddition of enamines with sulfene (CH_2=SO_2).[12–17] But 3-alkyl-3-arylthietanes and their derivatives had not been synthesized prior to our work; in fact, an attempt to prepare 3-ethyl-3-phenylthietane via the cyclic carbonate had failed.[18] Our preparation of 3-methyl-3-phenylthietane (**1**) was achieved by treatment of 2-methyl-2-phenyltrimethylene bis(benzensulfonate) with sodium sulfide in dimethyl sulfoxide. This modification of a standard thietane synthesis was also successful in preparing 3-isopropyl-3-phenylthietane (**10**) as well as the other 3,3-disubstituted thietanes (**11–17**) listed in Table I. In the two cases where comparisons are possible,

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