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(9) Melting points are uncorrected. NMR spectra were recorded on a Varian T-60 instrument and are reported in parts per million from internal tetramethylsilane. Infrared and mass spectra were recorded on Perkin-Elmer 137 and CEC-110B instruments, respectively. Elemental analyses were conducted under the supervision of Dr. F. Scheidl of our microanalytical laboratory.
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Synthesis and Chemistry of Cyclic Sulfoximines[1]

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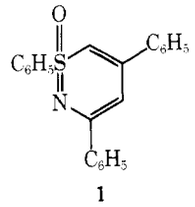
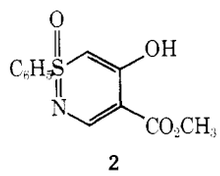
The synthesis of 1,2,4-thiadiazine 1-oxides, which are cyclic sulfoximines exemplified by **16, 19, 27,** and **30,** is reported. Alkylation of **16** with methyl iodide–NaH gives **20,** which in turn can be converted to **21; 16** on treatment with triethyloxonium tetrafluoroborate gives **27.** The unsaturated but nonaromatic 1,2,4-thiadiazine 1-oxide **30** can be prepared by the action of ethyl iodide on the silver salt of **27.** That **27** and **30** are ylidic in nature is shown by their ^1H and ^{13}C NMR spectra, which are discussed, and their ability to undergo electrophilic substitution in the same manner as thiabenzene 1-oxides. The mass spectra of the various thiadiazine 1-oxides show important fragmentation pathways involving phenyl migration from sulfur to the adjacent carbon. These migrations are not important in the spectra of the open-chain intermediates.

The chemistry of sulfoximines has been the focus of much attention in the past several years, and two reviews of this developing area of organosulfur chemistry have recently appeared.[3] Part of the interest in the chemistry of sulfoximines, which are capable of wide structural variations, has been concerned with the synthesis of heterocycles containing this functionality. Two arrangements are possible: (a) with the S=N moiety exocyclic to the ring, and (b) with the S=N moiety an integral part of the ring.[4] We report here the synthesis and chemistry of 1,2,4-thiadiazine 1-oxides, which are sulfoximine heterocycles that exemplify the second category.

Reported syntheses of sulfoximine heterocycles such as **1**[5] and **2**[6] have utilized an existing sulfoximine unit around which to construct a ring. Our initial synthetic goal which would provide access to the thiadiazine 1-oxide system was a diketo structure represented by **3.** The successful preparation of such



1



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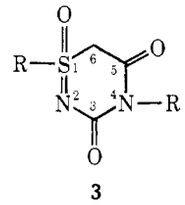


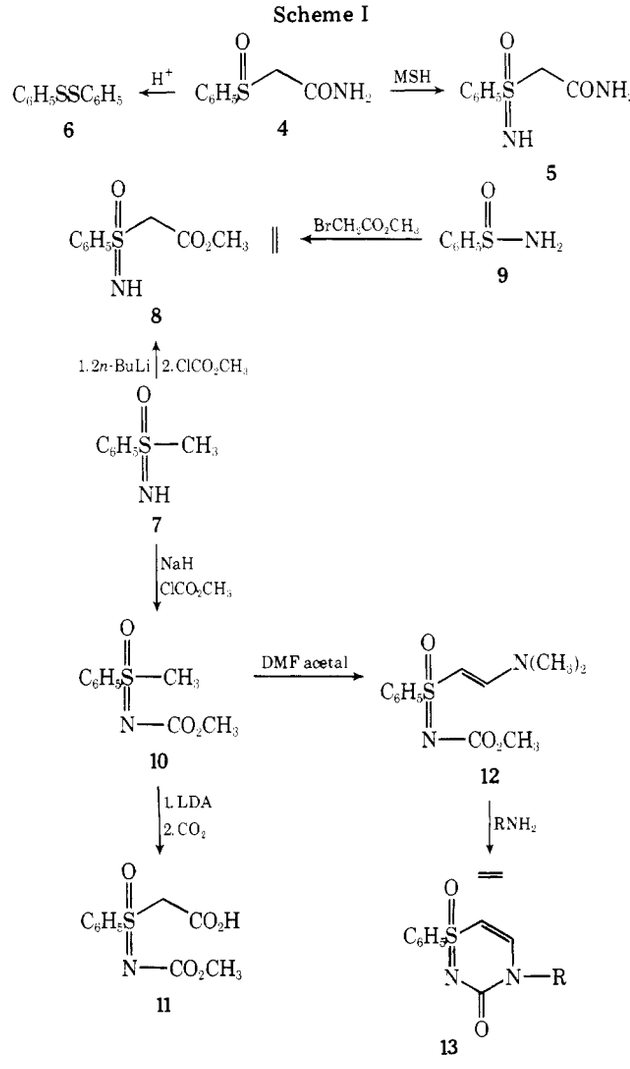
3

a dione was accomplished similarly by starting from an intact sulfoximine.

Scheme I depicts initial unsuccessful approaches. The carboxamidosulfoximine **5** was envisioned as a useful intermediate not only for the synthesis of the dione **3,** but also, by reaction with formic acid, nitrous acid, or reduction–carbonylation, for the generation of other heterocycles as well.

Attempted conversion of the corresponding sulfoxide **4**[7] to **5** by the standard reaction with hydrazoic acid[8] gave exclusively the Pummerer rearrangement product, diphenyl disulfide (**6**). Use of the versatile but unstable amino transfer reagent *O*-mesitylsulfonylhydroxylamine (MSH)[9] did provide the desired intermediate **5** but in less than acceptable yields.

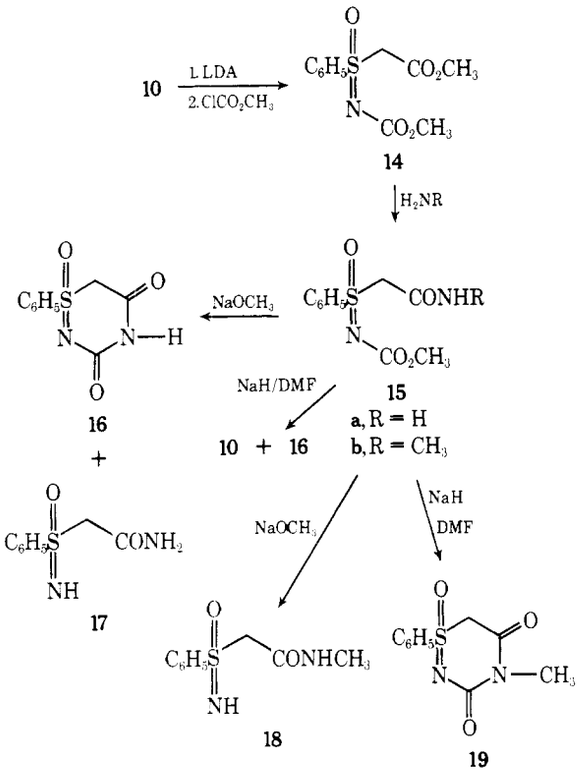
Scheme I



Some effort was made to prepare the ester **8** which would then be converted to **5**. The known and readily accessible methylphenylsulfoximine[10] **7**, on conversion to the dianion and treatment with 1 equiv of methyl chloroformate, gave little of the desired **8**, however. An attempted modification of the well-known preparation of sulfones,[11] where the sulfinamide **9** rather than sodium benzenesulfinate was reacted with methyl bromoacetate, did not yield **8**. Sulfoximine **7** was easily converted to the methoxycarbonyl derivative **10** in good yield. The anion of **10**, generated with LDA, could be carboxylated giving the free acid **11** (39%), stable toward decarboxylation, but offering no advantage over the corresponding ester prepared directly (Scheme II). Finally, later it was found that **10** could undergo condensation with DMF acetal in a manner similar to that of ketones[12] and the enaminosulfoximine **12**, a quite stable yellow solid, was formed in 50% yield. All attempts to convert **12** to **13** (R = H or alkyl) by amination with ammonia, ammonium acetate, amines, or triethyloxonium tetrafluoroborate (Meerwein reagent) followed by ammonia failed.

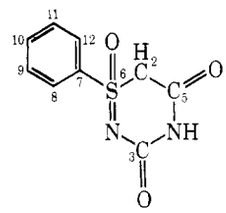
A successful approach to the thiadiazine system was devised (Scheme II) which took advantage of the ability of **10** to undergo acylation on carbon. Inverse addition of the lithio derivative of **10** to 1 equiv of methyl chloroformate gave in good yield, the ester **14**, which could be aminated with ammonia or methylamine in good yields providing the amides **15**. Cyclization of **15a** with sodium methoxide gave the 1,2,4-thiadiazinedione 1-oxide **16** in 47% yield along with 2–5% of the methanolysis product **17**.[13] Attempted cyclization of **15b** with sodium methoxide gave only the methanolysis product **18** (55%). Apparently methanolysis in this case competes effectively with cyclization with the more bulky *sec*-amide anion. When sodium hydride in DMF was employed, however, cyclization readily occurred yielding the *N*-methyl dione **19** (75%). Interestingly, when **15a** was subjected to these same conditions only a 31% yield of **16** was obtained along with a surprising 43% of **10**.[14]

Scheme II



The dione **16** (as well as **19**) is essentially nonenolic; the infrared spectrum indicates carbonyl absorption at 1705 and 1675 cm^{-1}. The NMR spectrum shows an exchangeable proton at δ 10.8 and geminal protons at δ 4.91 (J = 17 Hz), which are exchanged rapidly by D_2O in Me_2SO-d_6 or immediately if acid or base are added. The AB quartet at δ 4.91 collapses to a broad singlet at 100 °C which becomes a sharper singlet at 150 °C while the phenyl protons remain sharp and clear. On cooling to room temperature the original quartet is restored. Although no enol is detected, the collapse of the quartet on heating is consistent with chemical averaging through the enol form which becomes rapid at elevated temperature. ^{13}C NMR spectra which define **16** are seen in Chart I. In the mass spectrum of **16** a base peak of m/e 91 corresponding to C_7H_7 suggests a migration of the phenyl moiety from sulfur to carbon. Oae et al.[15] have reported the migration of aryl groups from sulfur to nitrogen in the mass spectra of aryl alkyl sulfoximines. This migration of phenyl to carbon appears to be electron impact induced and is characteristic of all 1,2,4-thiadiazine 1-oxides discussed in this paper. The migration was of little or no significance in the spectra of the open-chain intermediates.

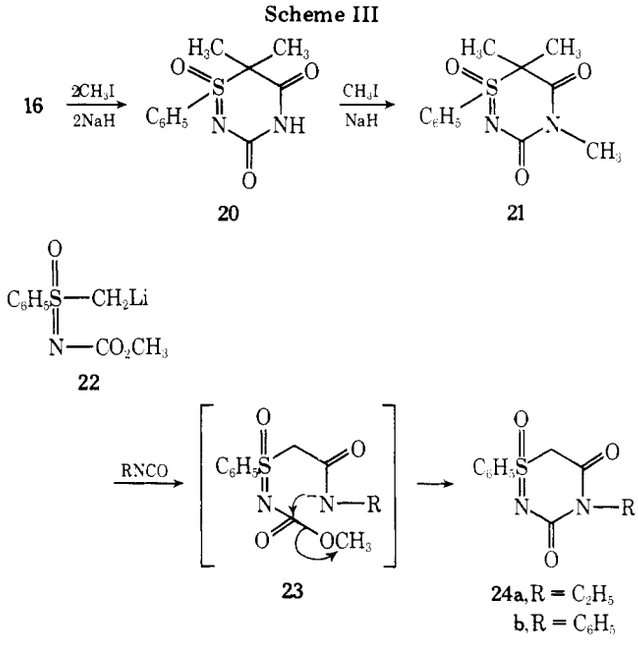
Chart I. ^{13}C Chemical Shifts (ppm from Me_4Si) of **16** in Me_2SO-d_6



Chemical shift, ppm	Assignment
52.8	C-6
128.2	C-9, C-11
129.8	C-8, C-12
135.3	C-7, C-10
152.3	C-3, C-5
161.5	

Alkylation of **16** is shown in Scheme III. Treatment of **16** with 1 equiv of NaH and CH_3I yielded a mixture of several major components probably due to indiscriminate alkylation at several sites. With 2 equiv of base and CH_3I a 37% yield of **20** could be isolated from a mixture. This geminally dialkylated product could be converted smoothly to the trimethyl dione **21** in 70% yield. In spite of geminal methyl groups, fragmentations of m/e 119, ascribable to $[C_6H_5C(CH_3)_2]^+$ resulting from phenyl migration, are seen in the spectra of **20** [25% of base peak at 125 ($C_6H_5S{\equiv}O^+$)] and **21** [100% of base peak relative to m/e 125 (75%)].

Scheme III



A shorter approach to N-substituted diones like **24** was attempted by acylation of the lithio derivative of **10** with

isocyanates. Cyclization was envisioned as occurring directly via **23**, a similar intermediate to the anion involved in the cyclization of **15b** to **19**, to give **24**. Indeed, **24a** and **24b** were obtained but only in very low yields and all attempts to improve this process failed.

Attention was then focused on the conversion of the dione **16** (Scheme IV) to the dichloro derivative **25**. The displacement of the halogens in **25** could then be studied, and their reductive removal to yield the basic 1,2,4-thiadiazine 1-oxide **26** attempted. All efforts to convert **16** to **25** with $SOCl_2$, $POCl_3$, etc., gave unstable yellow mixtures which eluded characterization. Reaction of **16** with 2 equiv of Meerwein reagent, in an attempt to prepare a dialkoxy version of **25** (i.e., **30**) gave a new substance in 80% yield which could be assigned the structure **27**. This new substance showed a one-proton singlet at δ 4.33 that was exchanged with NaOD and DCl. The mass spectrum indicated an M^+ peak at *m/e* 252 and a base peak at *m/e* 118 which was shown by high resolution to be C_8H_6O, most probably attributable to $C_6H_5CH{=}C{=}O$, and a second peak at *m/e* 90 corresponding to C_7H_6. The ^{13}C NMR spectrum (Chart II) showed an important peak at 59.4 ppm.

Scheme IV

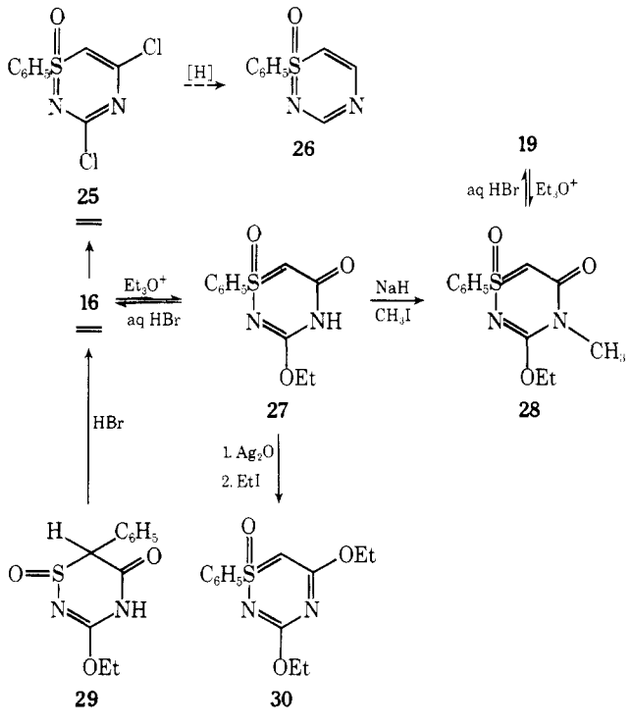
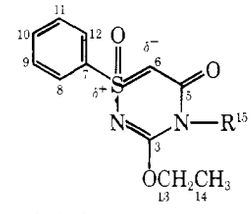


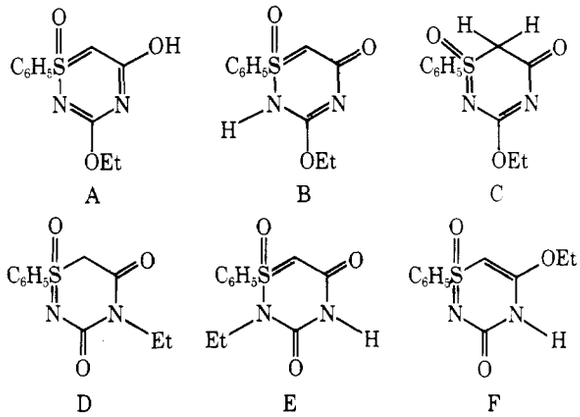
Chart II. ^{13}C Chemical Shifts (ppm from Me_4Si) of **27** and **28** in Me_2SO-d_6



Chemical shift, ppm R = H (27)	Chemical shift, ppm R = CH_3 (28)	Assignment carbon no.
13.9	13.8	14
	27.0	15
59.4	59.3	6
64.9	66.3	13
126.5	126.7	9, 11
129.3	129.2	8, 12
132.9	133.0	10
143.9	143.8	7
157.3	156.2	3, 5
159.4	157.8	

All data indicated that only one ethyl group had entered the new molecule. The indicated ylidic polarization (structure, Chart II) imparts anionic character to carbon 6, shielding it, and explains the unusually high field value for an otherwise vinylic carbon which might be expected to resonate in the 100–140-ppm range. A less plausible structure was **29** which would have resulted from a phenyl migration and change in oxidation state of sulfur during the reaction. The phenyl-bound carbon of **29** could possibly resonate in the 50–60-ppm range, and the molecule might give rise to the phenylketene fragment, *m/e* 118. The coupling constant $J_{^{13}C-H}$ for carbon 6 has a value of 179.9 Hz which should exclude any structure containing an sp^3-hybridized carbon such as in **29**. The $J_{^{13}C-H}$ for carbon 6 in **16** is 146.0 Hz. However, in order to rule out unequivocally **29** and N-alkylated possibilities shown in Chart III, a simple hydrolysis with 16% hydrobromic acid at room temperature was attempted and, indeed, **16** was isolated in 33% yield. The result of this experiment supports structure **27** and definitely rules out structure **29**, as well as D and E (Chart III). The phenyl migration seen in the mass spectrum of **27** then must occur in the spectrometer as it does with **16**, **19**, **20**, **21**, and **28**. Methylation of **27** with NaH–methyl iodide gave the same product **28**, in good yield, as that obtained from **19** and triethyloxonium tetrafluoroborate. Compound **28**, similarly, could be hydrolyzed to **19**. The methyl group of **28** is unequivocally placed on nitrogen at position 4 since **19** was derived from **15** which had been prepared from **14** and methylamine. This is important if one considers the near identity of the ^{13}C NMR spectra of **27** and **28** (Chart II) which suggests structure **27** for the Meerwein product rather than the tautomers A and B (Chart III). A chemical shift difference of 7.7 ppm between carbon 6 in **27** and in **30** (Chart IV and Scheme IV) argues against the enol tautomer A (Chart III). Carbon 6 in A should not be so dissimilar from that of **30**. Other possibilities in Chart III which may be ruled out are C (no methylene protons in the NMR spectrum) and F (it would be difficult to account for the C_8H_6O fragment and the unusually high ylidic shielding (Chart II) of carbon 6[16]).

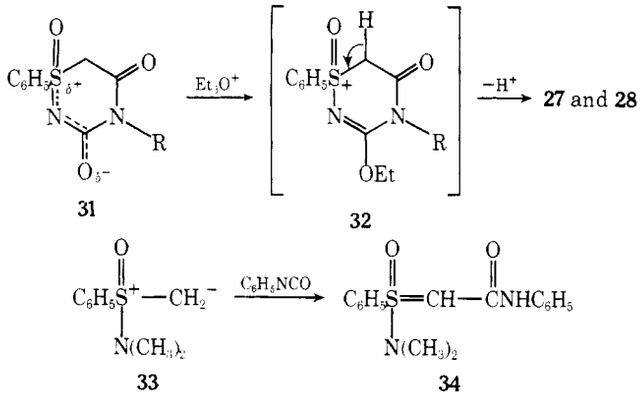
Chart III



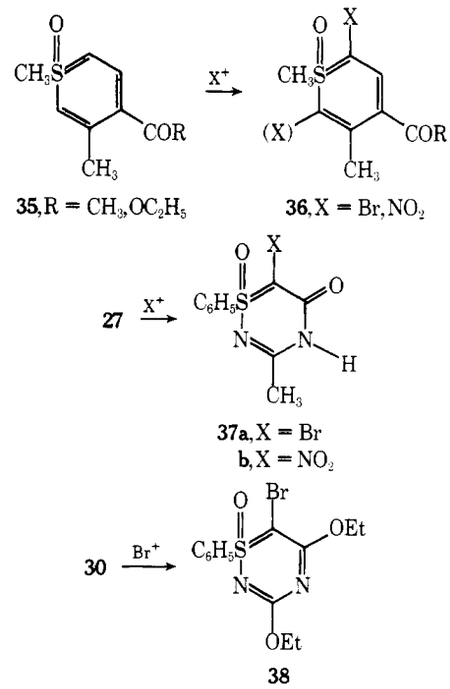
The pathway for formation of **27** and **28** can be seen in Scheme V. Polarization of the acylsulfoximide grouping is strong (**31**) and provides as the most choice site for attack by the oxonium species the carbonyl oxygen of position 3 leading via **32** to **27** and **28**. Some precedent exists for this as shown by the acylation of the ylide **33** with phenyl isocyanate to give **34**.[10]

The action of the Meerwein reagent on the dimethyl dione **20** gave a mixture of several components, and in reaction with the open-chain intermediates **14** and **15** no ylidic product similar to **34** was isolated. Reaction of **27** or its sodium salt with 1 equiv of the Meerwein reagent gave a mixture of at least four major products which was not pursued. The desired product **30**, a probable component of this mixture, could be

Scheme V

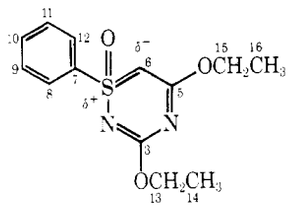


Scheme VI



prepared from **27** by first obtaining the silver salt and treating this in ether at room temperature with ethyl iodide.[17] The ^1H NMR spectrum of **30** shows two nearly identical methylenes and two identical methyls which indicates that the new ethyl group is also on oxygen and not nitrogen. This structure, as might be expected from the electronic nature of **27** and from previous reports,[5,6,18,19] shows chemical and physical properties consistent with ylidic character. The ^{13}C NMR spectrum (Chart IV) shows the ylidic anionic shielding at carbon 6 which

Chart IV. ^{13}C Chemical Shifts (ppm from Me_4Si) of **30** in Me_2SO-d_6



Chemical shift, ppm	Assignment
14.11, 14.29	14, 16
62.20, 63.02	13, 15
67.13	6
126.89, 129.25	9, 11, 8, 12
133.19	10
142.89	7
161.59	5
168.58	3

resonates at 67.13 ppm ($J_{^{13}C-H}$ = 184.4 Hz).[20] This is 7.7 ppm lower field than the same carbon in **27** (Chart II) and is presumably due to the distribution of electron density not only at C-6 but also to the nitrogens at positions 2 and 4. In **27** electron density is more localized at C-6. This is also reflected in the proton chemical shifts of **27** and **30** since the proton at C-6 appears at δ 4.90 with **30** vs. δ 4.33 with **27.** The mass spectrum shows, in addition to M^+ at *m/e* 280, a base peak at *m/e* 118 indicative of the phenyl migration discussed previously. The mass spectrum is best interpreted, however, as a loss of ethylene from the molecular ion to generate the M^+ of **27** followed by the fragmentation of that species.

The ylidic nature of thiabenzenes and thiabenzene 1-oxides is now well known, and ylidic electrophilic substitution in the 1-oxides has recently been reported[21] as shown by the conversion of **35** to **36.** In a similar manner, compound **27** was smoothly brominated by bromine in CH_2Cl_2 giving the 6-bromo derivative **37a** in 87% yield. Likewise, nitration was accomplished in 43% yield with acetyl nitrate producing the 6-nitro derivative **37b.** Attempts to reduce the nitro group of **37b** with hydrogen on Zn/HOAc failed. Bromination of **30** yielded as the only isolated product a substance best characterized as the dihydrobromide of **38.**[22] An attempt to hydrolyze **30** to **16,** as had been accomplished with **27,** produced a mixture from which neither **16** nor **27** could be clearly identified.

In summary, physical properties such as ^{13}C NMR spectra and ^1H NMR spectra, and chemical properties such as electrophilic substitution and deuterium exchange at C-7, indicate **27** and **30** to be ylidic 1,2,4-thiadiazine 1-oxides.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were determined on Varian A-60D and CFT-20 spectrometers and are reported in δ units using tetramethylsilane as an internal reference. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Mass spectra were taken on an AEI-MS902 and are reported as *m/e* with relative intensity (percent of base peak) in parentheses. Extractions were usually worked up by washing, finally, with a saturated NaCl solution, drying over $MgSO_4$ followed by vacuum filtration, and evaporation of solvent under water pressure vacuum on a Rotavapor at 25–60 °C.

***S*-Methyl-*S*-phenyl-*N*-methoxycarbonylsulfoximine (10).** To a solution of 79.47 g (0.512 mol) of **7** in 400 ml of anhydrous dimethoxyethane was added under nitrogen at ambient temperature 30.86 g (0.768 mol) of 50% sodium hydride in portions. After complete addition the slurry was stirred for 2.5 h before the dropwise addition of 72.50 g (0.768 mol) of methyl chloroformate over 1 h. This slurry was stirred for 12–15 h. Suspended solid was removed by filtration, and the filtrate concentrated in vacuo to a yellow residue which was dissolved in 500 ml of $CHCl_3$. This solution was washed with 100 ml of water and with saturated NaCl (2 × 100 ml). The organic layer was dried, filtered, and concentrated in vacuo leaving a pale yellow solid which was washed with petroleum ether and recrystallized from ethyl acetate to give off-white crystals, 65.4 g (59.9%): mp 97–98 °C;[23] NMR (Me_2SO-d_6) δ 7.5–8.0 (m, 5 ArH), 3.38 and 3.41 (2 s, $-SCH_3$ and NCO_2CH_3); IR (Nujol) 1675 (s), 1260 (s), 1220 cm^{-1} (s); *m/e* (rel intensity) M^+ not observed, 198 (100), 182 (95).

***S*-Carboxymethyl-*S*-phenyl-*N*-methoxycarbonylsulfoximine (11).** A solution of 77.7 g of isopropylcyclohexylamine in 300 ml of dry THF was cooled to −10 °C and was treated with 324 ml of 2.25 M *n*-butyllithium in hexane. This solution was stirred for 1 h and to this was added at −70 °C 50.4 g of **10** in 400 ml of THF. This mixture was stirred for 2 h at −70 °C and transferred in portions (carefully to control foaming) to a second flask containing 1800 g of dry ice; the resulting slurry was stirred for 15 h and allowed to come to ambient temperature. To this was added 600 ml of water and, after vigorous mixing, the upper organic layer was separated. The aqueous layer was extracted several times with 50-ml portions of ether, then made acidic with acetic acid and extracted several times with $CHCl_3$. The $CHCl_3$

extracts were dried and concentrated in vacuo to give 55 g of amber oil which was taken up in 1–1.5 volumes of ether and allowed to stand overnight. There was obtained 42 g of the isopropylcyclohexylammonium salt of the acid **11**, mp 109 °C dec.

This substance was dissolved in water and passed through a Rexyn 101 (acid phase) column. As the eluent was collected from the column, the free acid crystallized. There was obtained a total of 20.56 g (33.9%) of acid **11**, mp 103–104 °C.

Anal. Calcd for $C_{10}H_{11}NO_5S$: C, 46.68; H, 4.31; N, 5.45. Found: C, 47.10; H, 4.47; N, 5.50. NMR (Me_2SO-d_6) δ 3.47 (s, OCH_3), 4.87 (s, CH_2), 7.4–8.0 (5 ArH), 12.9 (s, $-CO_2H$); IR (Nujol) 1735 (s), 1640 (s), 1260 and 1220 cm^{-1} (s); pK_a = 3.2.

***S*-(2-Dimethylaminovinyl)-*S*-phenyl-*N*-methoxycarbonylsulfoximine (12).** A mixture of 20.0 g (0.094 mol) of **10** and DMF diethyl acetal (23.34 g, 0.1 mol) was heated at reflux temperature for 4 h. The EtOH which formed was removed by a Dean-Stark trap. After standing overnight the crystalline solid which formed was collected and washed with EtOH giving 16.3 g (65%) of product, mp 130–145 °C. This material was essentially one spot on silica gel thin layer (1:9 MeOH/$CHCl_3$). One recrystallization from EtOH gave 12.7 g (50%) of **12**: mp 147–153 °C; NMR (Me_2SO-d_6) δ 7.4–7.9 (m, 5 ArH), 7.3 (1, d, J = 12 Hz), 3.4 (s, OCH_3), 2.85 [broad s, $-N(CH_3)_2$]; IR (Nujol) 1650 (sh, s), 1625 (s), 1220 (s), 965 cm^{-1} (s).

Anal. Calcd for $C_{12}H_{16}N_2O_5S$: C, 53.71; H, 6.01; N, 10.44. Found: C, 53.71; H, 6.18; N, 10.20.

***S*-Methoxycarbonylmethyl-*S*-phenyl-*N*-methoxycarbonylsulfoximine (14).** To a solution of *N*-isopropylcyclohexylamine (54.1 ml, 41.9 g, 0.30 mol) in 225 ml of THF was added via syringe at −70 °C under nitrogen 147 ml (0.30 mol) of a 2.04 M solution of *n*-butyllithium in ether. To the stirred white suspension after 1 h was added a solution of 26.53 g (0.12 mol) of **10** in 280 ml of THF over 0.5 h. The temperature was maintained below −55 ° throughout the addition. The clear orange solution which resulted was stirred at −70 °C for 2 h and then added in portions to a solution of methyl chloroformate (30.8 g, 25.2 ml) in 95 ml of THF at −70 °C at such a rate that the temperature did not rise above −50 °C. After complete addition the clear, orange solution was stirred at −70 °C for 2 h and stored for ca. 18 h at −50 °C.

To the reaction mixture was added 250 ml of ice water and 300 ml of THF, and this mixture was stirred until room temperature was attained. The organic layer was separated, dried, and concentrated in vacuo to give a partially crystalline yellow-orange residue which was slurried, collected, and washed with a 2:1 ether–petroleum ether mixture. There was obtained after drying in vacuo for 3 h 21.9 g of **14**, mp 89–92 °C (67%). A second crop was obtained by washing the aqueous layer with ether and working up the residue as above to give 3.56 g, mp 88–91 °C; total yield 25.5 g (78%).

Anal. Calcd for $C_{11}H_{13}NO_5S$: C, 48.70; H, 4.83; N, 5.16; S, 11.82. Found: C, 48.89; N, 5.23; S, 11.68. NMR (Me_2SO-d_6) δ 7.50–8.00 (m, 5 ArH), 4.87 (s, $-CH_2-$), 3.48 (s, accidentally equivalent methoxyls); IR (Nujol) 1760 (ester C=O), 1660 cm^{-1} (=NC=O); *m/e* (rel intensity) M^+ not observed, 240 (30), 198 (100), 125 (15).

***S*-Aminocarbonylmethyl-*S*-phenyl-*N*-methoxycarbonylsulfoximide (15a).** To 360 ml of ammonia-saturated MeOH at 40 °C was added 32.2 g (0.12 mol) of **14** as the introduction of ammonia continued. Upon complete addition the yellow solution was maintained at 40 °C for 0.75 h. A thick white suspension formed; the reaction mixture was heated at reflux for 0.75 h while the passage of ammonia was continued. The suspension was cooled in an ice bath and the white product collected, washed with MeOH, and dried in vacuo to give 28.0 g (91%) of amide **15a**, mp 171–172 °C.

Anal. Calcd for $C_{10}H_{12}N_2O_4S$: C, 46.87; H, 4.72; N, 10.93; S, 12.52. Found: C, 46.92; H, 4.88; N, 10.85; S, 12.51. NMR (Me_2SO-d_6) δ 7.5–8.1 (5 ArH), 7.37 (s, NH_2), 4.64 (s, $-CH_2-$), 3.56 (s, OCH_3); IR (Nujol) 3300 (s), 3100 (s), 1640 (s), 1250 and 1210 cm^{-1} (s); *m/e* (rel intensity) 256 (M^+, 5), 225 (15), 198 (100), 125 (20), 58 (45).

***S*-Methylaminocarbonylmethyl-*S*-phenyl-*N*-methoxycarbonylsulfoximine (15b).** Methylamine was introduced into absolute MeOH (540 ml) for 1 h. While gassing was continued, 27.47 g (0.10 mol) of the diester **14** was added in one position. The resulting yellow solution was stirred at 30 °C (without external heating) for 3 h. The solution was concentrated in vacuo to give a white solid, 29 g, which on recrystallization from EtOH gave **15b**, 22.6 g (82.8%), as white crystals, mp 131.5–133.5 °C.

Anal. Calcd for $C_{11}H_{14}N_2O_4S$: C, 48.87; H, 5.22; N, 10.37. Found: C, 49.01; H, 5.32; N, 10.64. NMR (Me_2SO-d_6) δ 7.50–8.20 (m, 5 ArH and NH), 4.56 (s, $-CH_2-$), 3.50 ($-CO_2CH_3$), 2.50 (d, $-NCH_3$); IR 3450 (s), 1750 (s), 1600 (s), 1530–1500 (s), 1310 (s), 1260 cm^{-1} (s); UV max (EtOH, pH 2.0) 221 (ϵ 11 034), 961 (922), 267 (1209), 274 nm (984); (EtOH, pH 6.86) 221 (11 347), 260 (877), 266 (1174), 274 nm (954); (EtOH, pH 10.0) 221 (11 454), 260 (943), 266 (1209), 274 (989).

1-Phenyl-1,2,4-thiadiazine-3,5(4*H*,6*H*)-dione 1-Oxide (16). To a freshly prepared solution of sodium methoxide [from 3.61 g (0.157 mol) of sodium] in 750 ml of absolute MeOH was added under nitrogen at ambient temperature 19.57 g (0.076 mol) of amide **15a** in portions over 10 min. After complete addition the reaction mixture was heated at reflux temperature for 1.5 h. The near-solution was cooled and concentrated to a solid residue which was treated with 50 ml of 25% hydrochloric acid solution. This mixture was concentrated in vacuo, and the solid residue collected, washed with water, and dried at 60 °C (0.2 mmHg) for 4–5 h to give a white solid, 7.96 g (46.7%), mp 207–212 °C. The analytical sample was prepared by recrystallization from water, mp 223 °C.

Anal. Calcd for $C_9H_8N_2O_3S$: C, 48.20; H, 3.60; N, 12.49; S, 14.30. Found: C, 48.27; H, 3.72; N, 12.41; S, 14.41. NMR (Me_2SO-d_6) δ 11.30 (s, NH), 7.60–8.20 (m, 5 ArH), 4.90 (q, J = 17.0 Hz, $-CH_2-$); IR (Nujol) 3150 (m), 1705 (sh, s), 1675 (s), 1365 and 1350 (s), 1240 and 1225 cm^{-1} (s); *m/e* (rel intensity) 224 (M^+, 5), 181 (25), 125 (10), 91 (100), 77 (50); UV max (H_2O, pH 2.0) 219 (ϵ 15 614), 261 (1226), 267 (1510), 274 nm (1211); (H_2O, pH 6.86) 210 (15 205), 256 nm (5212); (H_2O, pH 10.0) 220 (14 991), 265 nm (5234).

The above filtrate from the isolation of **16** was concentrated in vacuo leaving a white residue which was suspended in 30 ml of hot water. This was slurried for 0.5 h and the suspended solid was collected to give 1.83 g, mp 164–166 °C, of a solid identified by spectral data as **17**: NMR (Me_2SO-d_6) δ 9.05 (s, NH_2), 7.50–8.30 (m, 5 ArH), 5.15 (s, $-CH_2$); IR (Nujol) 3200 (s), 3075 (s), 1680 (s), 1260 cm^{-1} (s); *m/e* (rel intensity) M^+ not observed, 155 (10), 92 (40), 77 (60), base peak at 36.

***S*-Methylaminocarbonylmethyl-*S*-phenylsulfoximine (18).** To a mixture of 3.40 g (0.013 mol) of **15b** in 100 ml of EtOH under nitrogen at ambient temperature was added 0.70 g (0.013 mol) of sodium methoxide in one portion. As the mixture was heated to reflux a clear solution was obtained; the solution was held at reflux for 1.5 h and allowed to stand overnight. The solution was then concentrated in vacuo to a white foam which was dissolved in 5 ml of water (pH of solution 10) and extracted with 2 × 25 ml of $CHCl_3$. The organic layers were dried and concentrated to give a white solid, 1.70 g (54.8%), mp 106–109 °C, which was suspended in ether and collected to give 1.23 g of **18**, mp 107–109 °C.

Anal. Calcd for $C_9H_{12}N_2O_2S$: C, 50.91; H, 5.70; N, 13.20. Found: C, 50.81; H, 5.75; N, 13.29. NMR ($CDCl_3$) δ 7.40–8.05 (5 ArH), 7.60 (1 H, –CONH), 5.02 (s, SCH_2CO), 3.72 (s, S=NH, exchanges with D_2O), 2.82 (s, NCH_3); mass spectrum *m/e* (rel intensity) M^+ not observed, 155 (45), 140 (20), 175 (30), 92 (80), 91 (70), 77 (100); IR (Nujol) 3700 (vs), 1620 (s), 1260 cm^{-1} (s).

4-Methyl-1-phenyl-1,2,4-thiadiazine-3,5(4*H*,6*H*)-dione 1-Oxide (19). To a suspension of 0.48 g (0.01 mol) of NaH (50% in mineral oil) in 40 ml of DMF under nitrogen at ambient temperature was added 2.80 g (0.01 mol) of **15b** in portions over 10 min. A clear solution resulted in about 0.5 h after addition. After stirring for 20 h TLC (silica gel, $CHCl_3$/MeOH, 8:2) showed incomplete reaction. The temperature was raised to 100 °C for 3 h at which time TLC indicated that the reaction was complete. The solution was cooled, treated with 50 ml of water, and concentrated to a clear, caramel-colored oil which was then triturated with petroleum ether twice to remove mineral oil. After decantation the residue was treated with 25 ml of 3 N HCl, and the solid, which formed immediately, was collected, washed with water, and air dried to give 1.78 g (74.8%) of **19**, mp 137–138 °C. TLC (8:2 $CHCl_3$–MeOH) was one spot.

Anal. Calcd for $C_{10}H_{10}N_2O_3S$: C, 50.41; H, 4.23; N, 11.76. Found: C, 50.18; H, 4.20; N, 11.52. NMR (Me_2SO-d_6) δ 7.6–8.2 (5 ArH), 5.13 (d, $-CH_2-$, J = 16 Hz), 3.25 (s, NCH_3); IR (Nujol) 1715 (s), 1675 (s), 1260 cm^{-1} (s); UV max (EtOH, pH 2.2) 222 (ϵ 16 854), 274 (1230), 2665 (1549), and 260 nm (1280); (EtOH, pH 6.86) 222 (14 188), 267 nm (4694); (EtOH, pH 10.0) 222 (13 481), 266 (4698) and 272 nm (4660); mass spectrum *m/e* (rel intensity) 238 (M^+, 40), 181 (50), 148 (20), 91 (100), 77 (40).

6,6-Dimethyl-1-phenyl-1,2,4-thiadiazine-3,5(4*H*,6*H*)-dione 1-Oxide (20). To a suspension of 2.59 g (0.054 mol) of 50% NaH in 150 ml of DMF under nitrogen was added at ambient temperature 6.00 g (0.027 mol) of **16**. The resulting mixture was stirred for 0.5 h, cooled to ca. 15 °C, and treated dropwise with a solution of 14.76 g (0.104 mol) of methyl iodide in 10 ml of DMF. This mixture was stirred for ca. 15 h. Addition of two volumes of ether to the reaction mixture caused a voluminous inorganic precipitate to form which was removed by filtration. The filtrate was concentrated in vacuo to a thick, dark amber oil which was heated at 50 °C (0.2 mmHg) to remove traces of DMF. Treatment of this oil with ethanol produced a solid which was collected, washed with EtOH, and pulled dry, yielding a white solid,

2.55 g (37.4%), mp 178–180 °C.

Anal. Calcd for $C_{11}H_{12}N_2O_3S$: C, 52.36; H, 4.80; N, 11.11. Found: C, 52.19; H, 5.07; N, 11.09. NMR (Me_2SO-d_6) δ 11.28 (s, NH), 7.65–8.20 (5 ArH), 1.30 and 1.54 (2 s, gem CH_3's); IR (Nujol) 3150 (m), 1700 (s), 1650 (broad, s), 1230 cm^{-1} (s); *m/e* (rel intensity) M^+ 252 (30), 209 (15), 125 (100), 77 (40), 69 (50); UV max (EtOH, pH 2.0) 223 (ε 16 480), 261 (1460), 268 (1648), 275 (1272); (EtOH, pH 6.86) 223 (16 318), 261 (1690), 268 (1889), 275 (1487); (EtOH, pH 10.0) 221 (12 418), 253 (1141), 260 (1259), 266 (1444), 274 (1109).

4,6,6-Trimethyl-1-phenyl-1,2,4-thiadiazine-3,5(4*H*,6*H*)-dione 1-Oxide (21). To a suspension of 0.08 g (0.0016 mol) of sodium hydride in 25 ml of DMF at ambient temperature was added dropwise a solution of 0.36 g (0.0016 mol) of **20** in 5 ml of DMF, and the resulting slurry stirred for 1 h. To this suspension was added dropwise 0.45 g (0.0032 mol) of methyl iodide in the same solvent, and this was stirred for 21 h. On dilution with ether an inorganic precipitate formed which was removed by filtration. The filtrate was concentrated in vacuo, and the residue treated with water and again concentrated in vacuo. The residue was successively slurried with EtOH and benzene and again evaporated to dryness in vacuo each time. Finally, the residue was triturated with petroleum ether–EtOH (1:1) and collected to yield 0.299 g (69.8%) of **21,** mp 135–137 °C.

NMR ($CDCl_3$) δ 7.6–8.2 (m, 5 ArH), 3.38 (s, NCH_3), 1.38 and 1.68 (singlets, CCH_3's); mass spectrum *m/e* (rel intensity) 266 (M^+, 25), 209 (50), 119 (100), 125 (70), 69 (25).

1,5-Diphenyl-1,2,4-thiadiazine-3,5(4*H*,6*H*)-dione 1-Oxide (24b). To a solution of *N*-isopropylcyclohexylamine (6.5 g, 0.046 mol) in 30 ml of THF at −20 °C under nitrogen was added 21 ml (0.046 mol) of a 2.2 M solution of *n*-BuLi in hexane via hypodermic syringe. After complete addition the clear solution was stirred at −60 to −70 °C for 1 h during which time a suspension formed. To this was added a solution of 5.0 g (0.023 mol) of **10** in 45 ml of THF dropwise. The clear yellow solution was stirred at −70 °C for 1.5 h prior to the addition of 2.74 g (0.023 mol) of phenyl isocyanate. During the dropwise addition an exotherm to −60 °C was noted. The mixture was stirred at −60 °C for 1.5 h and was then allowed to warm to room temperature during which time it changed to an orange suspension. The reaction mixture was diluted with water, the organic layer separated, and the aqueous layer washed with 50 ml of ether. The combined organic layers were dried and concentrated, leaving a partially crystalline residue. This was passed through a column of neutral alumina with $CHCl_3$. The crude crystalline product obtained was recrystallized from EtOH giving 520 mg (8%) of **24b,**[24] mp 184–186 °C.

Anal. Calcd for $C_{15}H_{12}N_2O_3S$: C, 59.98; H, 4.03; N, 9.33. Found: C, 59.79; H, 4.12; N, 9.32. NMR (Me_2SO-d_6) δ 7.1–8.2 (10 ArH in three multiplets), 4.82 (2 H, d, *J* = 16 Hz, exchanged by D_2O).

3-Ethyl-1-phenyl-1,2,4-thiadiazin-5(4*H*)-one 1-Oxide (27). To a suspension of 7.70 g (0.034 mol) of **16** in 150 ml of methylene chloride under nitrogen was added 68 ml (0.068 mol) of a 1.0 M solution of triethyloxonium tetrafluoroborate.[25] The suspension obtained was stirred at room temperature for 3.5 h at which time a clear solution had resulted. After an additional 2 h at room temperature the solution was washed with 2 × 25 ml of ice-cold 5% Na_2CO_3 solution and 1 × 25 ml of brine solution. The organic layer was dried, filtered, and concentrated in vacuo to give 10.4 g of a clear, colorless oil which on trituration with hot EtOH crystallized. The solid was collected and washed with EtOH to give 6.90 g (80.4%) of **27,** mp 174–176.5 °C. One recrystallization from EtOH gave mp 180–182 °C.

Anal. Calcd for $C_{11}H_{12}N_2O_3S$: C, 52.36; H, 4.80; N, 11.11. Found: C, 52.53; H, 4.95; N, 11.17. NMR (Me_2SO-d_6) δ 11.3 (NH, broad), 7.5–8.0 (5 ArH), 4.35 (s, S=CHCO, exchanges with NaOD or DCl), 4.28 (q, *J* = 7 Hz, $-OCH_2CH_3$), 1.24 (t, *J* = 7 Hz, $-CH_2CH_3$); IR (Nujol) 2700 (m), 1630–1580 (s), 1550 (s), 1520 (s), 1285 (s), 1245 (s), 1210 cm^{-1} (s); *m/e* (rel intensity) 252 (M^+, 80), 237 (10), 224 (10), 208 (10), 118 (100, C_8H_6O), 90 (25, C_7H_6); UV max (H_2O, pH 2.0) 217 (ε 13 807), 260 (2052), 266 (2166), 274 (1818); (H_2O, pH 6.86) 220 (16 650), 260 (3978), 266 (4010), 273 (3544); (H_2O, pH 10) 229 (12 997), 265 (3736), 273 (3672).

3-Ethoxy-4-methyl-1-phenyl-1,2,4-thiadiazin-5(4*H*)-one 1-Oxide (28). A. By Action of Meerwein Reagent on 19. To a mixture of 1.51 g (0.006 mol) of **19** in 15 ml of CH_2Cl_2 at room temperature was added 6.0 ml (0.006 mol) of a 1 M solution of triethyloxonium tetrafluoroborate in CH_2Cl_2. The cloudy suspension was stirred for 2 h [TLC (silica gel, 9:1 $CHCl_3$–MeOH) showed no change after 1 h] and washed with 5% Na_2CO_3 solution (2 × 5 ml) followed by a brine wash (1 × 5 ml). The organic layer was dried, filtered, and concentrated in vacuo to give 1.61 g of a clear, amber oil which on standing partially crystallized. The solid which formed was collected and washed with EtOH to give a white solid, 0.63 g (39.4%) of **28,** mp 117–119 °C. One recrystallization (EtOH) raised the melting point to 118–120 °C.

B. By Methylation of 27. To a suspension of 100 mg (0.002 mol) of NaH in 20 ml of DMF at room temperature under nitrogen was added 500 mg (0.002 mol) of **27** in one portion. A slight exotherm was seen and the mixture was allowed to stir for 20 min while cooling to room temperature. A solution of 0.85 g (0.006 mol) of methyl iodide in 5 ml of DMF was added dropwise and the resulting solution was stirred overnight at ambient temperature. It was then diluted with ether and a solid formed which was removed by filtration. The filtrate was then concentrated, first on a rotary evaporator, then at 50 °C (20 mmHg) to remove DMF. The resulting brown oil partially crystallized on standing. TLC (silica gel, 9:1 $CHCl_3$–MeOH) suggested the same product as in A which was confirmed by NMR and mass spectra.

Anal. Calcd for $C_{12}H_{14}N_2O_3S$: C, 54.12; H, 5.30; N, 10.52. Found: C, 54.19; H, 5.24; N, 10.26. NMR (Me_2SO-d_6) δ 7.5–8.2 (5 ArH), 4.40 (q, *J* = 7 Hz, $-CH_2CH_3$), 4.38 (s, S=CCO, exchange with D_2O), 3.35 (s, NCH_3), 1.35 (t, *J* = 7 Hz, $-CCH_3$); IR (Nujol) 1635 (s), 1550 (s), 1220 cm^{-1} (s); *m/e* (rel intensity) 266 (M^+, 60) 208 (10), 118 (100), 77 (50).

3,5-Diethoxy-1-phenyl-1,2,4-thiadiazine 1-Oxide (30). To a suspension of 1.0 g (0.004 mol) of **27** in 25 ml of water at room temperature was added 1.6 ml of a solution of 10 g of NaOH in 100 ml of water. To the resulting clear solution was added dropwise a solution of 0.68 g (0.004 mol) of silver nitrate in 7 ml of water. A white precipitate formed immediately. After complete addition the suspension was stirred for ca. 1 h and the solid was collected by filtration, washed with water and EtOH, and dried in vacuo, giving 1.29 g, mp 196–199 °C dec, of the crude silver salt of **27:** infrared (Nujol) 1560 (sh, s), 1525 (vs), 1350 (s), and 1210 cm^{-1} (s).

To a suspension of this material (1.29 g, 3.6 mmol) in 50 ml of ether was added 0.56 g (3.6 mmol) of ethyl iodide all at once. The resulting suspension was stirred in the dark for 23 h and in the light for 1 h. The slurry was filtered and the filtrate concentrated to a clear, colorless oil, 260 mg (26%) of **30.** TLC (silica gel, $CHCl_3$–MeOH, 9:1) indicated one clean component: NMR (Me_2SO-d_6) δ 7.4–7.9 (m, 5 ArH), 4.33 (center of two overlapping $-CH_2-$ groups, *J* = 6.5 Hz for each), 1.35 (two CH_3's, *J* = 6.5 Hz); *m/e* (rel intensity) 280 (M^+, 35), 265 (50), 252 (25), 237 (25), 125 (90), 118 (100), 77 (80); IR (Nujol) 1610 (m), 1575 (sh, m), 1545 (s), 1320 (s), and 1240 cm^{-1} (s).

Electrophilic Substitution of 27. A. Bromination. To a clear, colorless solution of 100 mg of **27** in 5 ml of $CHCl_3$ at room temperature was added dropwise a dilute solution of bromine in $CHCl_3$ until the color of bromine just failed to be discharged. The yellow solution became cloudy in ca. 15 min as a solid formed. After 0.5 h this solid was collected and washed with $CHCl_3$ leaving 116 mg (87%) of **37a:** mp 97 °C dec; NMR (Me_2SO-d_6) δ 7.6–8.0 (5 ArH), 4.33 (q, *J* = 7 Hz, $-OCH_2CH_3$), 1.23 (t, *J* = 7 Hz, $-CH_2CH_3$); IR (Nujol) 3400 (w), 2700 (m), 1740 (m), 1650 (m), 1550 (s), 1250 (s), 1260 cm^{-1} (s); high resolution *m/e* (rel intensity) 330 (M^+, 10), 302 (5), 259 (5), 184 (80, $C_7H_6NO_3S$), 141 (30), 125 (100), 77 (80).

B. Nitration. A solution of 630 mg of **27** in 10 ml of Ac_2O and 4 ml of HOAc was added dropwise to a cold solution (−5 °C) of acetyl nitrate which had been prepared by addition of 1.8 ml of 70% HNO_3 to 12 ml of Ac_2O at −5 °C. After addition was complete the resulting orange solution was stirred for 10 min at −5 °C, allowed to warm to room temperature (ca. 1 h), poured into ice and water, and stirred for 1 h. The orange solid which separated was collected by filtration and washed with water, leaving 0.32 g (43%) of **37b,** mp 204 °C dec.

Anal. Calcd for $C_{11}H_{11}N_3O_5S$: C, 44.44; H, 3.73; N, 14.13; Found: C, 44.54; H, 4.00; N, 13.90. NMR (Me_2SO-d_6) δ 12.45 (s, broad, NH), 7.48–8.25 (5 ArH), 4.36 (q, *J* = 7 Hz, $-CH_2CH_3$), 1.25 (t, *J* = 7 Hz, $-CH_2CH_3$); IR (Nujol) 3350 (w), 1675 (s), 1580 (s), 1540 (s), 1300 (s), 1250 (s), 915 cm^{-1} (s); *m/e* (rel intensity) 297 (M^+, 15), 125 (100), 77 (95).

Bromination of 30. To a solution of 19 mg of **30** in 4 ml of $CHCl_3$ was added dropwise at room temperature approximately 1 ml of a solution prepared from 1 ml of bromine and 9 ml of $CHCl_3$. Addition was carried out until the bromine color was no longer discharged.[22] The solution was stirred for 1 h at which time a precipitate had formed. The mixture was concentrated in vacuo, yielding a yellow solid which was suspended in $CHCl_3$ and collected by vacuum filtration to give 65 mg of yellow solid, mp 117 °C dec. The analysis best fits a dihydrobromide.

Anal. Calcd for $C_{13}H_{15}BrN_2O_3S \cdot 2HBr$: C, 29.96; H, 3.29; N, 5.38. Found: C, 28.36; H, 2.91; N, 5.05. NMR (Me_2SO-d_6) δ 7.5–7.75 (5 ArH + 2 HBr, exchanges), 4.25 (center of two overlapping CH_2's), 1.23 (two $-CH_2CH_3$, s); IR (Nujol) 1620 (vs), 1260 cm^{-1} (vs); *m/e* (rel intensity) 358 (M^+, 15), 343 (5), 330 (5), 315 (5), 302 (5), 125 (100), 80 (45, HBr).

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Registry No.—**7,** 4381-25-3; **10,** 61177-70-6; **11,** 61177-71-7; 11 isopropylcyclohexylammonia salt, 61218-49-3; **12,** 61177-72-8; **14,** 61177-73-9; **15a,** 61177-74-0; **15b,** 61177-75-1; **16,** 61177-76-2; **17,** 61202-86-6; **18,** 61177-77-3; **19,** 61177-78-4; **20,** 61177-79-5; **21,** 61177-80-8; **24b,** 61177-81-9; **27,** 61177-82-0; **27** Ag salt, 61177-83-1; **28,** 61177-84-2; **30,** 61177-85-3; **37a,** 61177-86-4; **37b,** 61177-87-5; 38 2HBr, 61177-88-6; methyl chloroformate, 79-22-1; *N*-isopropylcyclohexylamine, 1195-42-2; DMF diethyl acetal, 1188-33-6; phenyl isocyanate, 103-71-9; acetyl nitrate, 591-09-3; methyl iodide, 74-88-4; ethyl iodide, 75-03-6; bromine, 7726-95-6.

References and Notes

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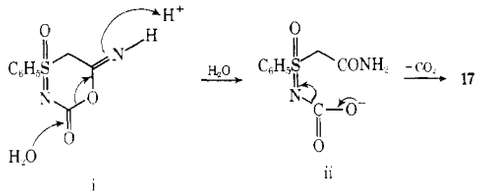
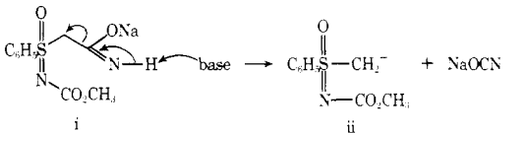
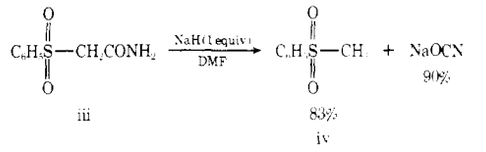
(13) The amide **17** might arise from simple attack of methoxide on the *N*-methoxycarbonyl of **15a** or by internal attack of the amide oxygen of **15a** giving rise to i which on hydrolysis and decarboxylation would give **17.**



(14) One possible explanation of this cleavage reaction which occurs with **15a** but *not* with **15b** would be the generation, even with 1 equiv of NaH, of the dianion of i which cleaves, as shown, to give ii and NaOCN. Proton abstraction by ii, now fulfilling the role of base would form **10.** Such a cleavage



would be unavailable to the *sec*-amide. Deprotonation of i could be accomplished by NaH but not by $NaOCH_3$. Treatment of the model sulfone iii with 1 equiv of NaH under these same conditions gave complete cleavage in 3 h at 100 °C with products isolated and identified as shown. No sulfone iv is formed in refluxing methanol–$NaOCH_3$. We intend to examine this



cleavage process more closely. The formation of LiOCN via a cleavage process has been reported by U. Schöllkopf and F. Gerhart, *Angew. Chem.*, **80,** 842 (1968).
(15) S. Oae, K. Harada, K. Isiyikara, and N. Furukawa, *Int. J. Sulfur Chem., Part A,* 49 (1972).
(16) The β carbon of vinyl ethers is somewhat shielded and appears in the 85–90-ppm (relative to Me_4Si) range, far below the 59.3-ppm value for **27.** See J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, Table 5.47, p 184.
(17) (a) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77,** 6269 (1955); (b) H. vonPechmann and O. Baltzer, *Chem. Ber.*, **24,** 3148 (1891).
(18) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Am. Chem. Soc.*, **96,** 5648, 5650, 5651 (1974).
(19) A. Hortmann and R. L. Harris, *J. Am. Chem. Soc.*, **93,** 2471 (1971); A. Hortmann, R. L. Harris, and J. A. Miles, *ibid.*, **96,** 6119 (1974).
(20) For comparison, the comparable carbon in **2** resonates at 78.9 ppm, in 1,3,5-trimethylthiabenzene 1-oxide at 83.7 ppm, and in **35** (R = CH_3) at 92.1 ppm relative to Me_4Si.
(21) Y. Tamura, H. Taniguchi, T. Miyamoto, M. Isumekawa, and M. Ikeda, *J. Org. Chem.*, **39,** 3519 (1974).
(22) Unfortunately an excess of bromine was mistakenly employed in this final experiment which exhausted our supply of **30.**
(23) The ethoxycarbonyl derivative of **7** is reported as an oil in ref 5.
(24) Compound **24b,** mp 148–151 °C, was obtained in a similar manner in 4% yield.
(25) H. Meerwein, *Org. Synth.*, **46,** 113 (1966).

Reactions of Alkyl or Aryl Chlorosulfites with Thiocarboxylic Acids

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Alkyl or aryl chlorosulfites (**7**) reacted with *p*-nitrothiobenzoic acid to give *S*-acylalkyl or *S*-acylaryl thiosulfites (**6**). However, treatment of alkyl chlorosulfites with aliphatic thiocarboxylic acids afforded acylalkyl sulfites (**5**) and acylalkoxy trisulfides (**8**) as a result of disproportionation of **6.** These trisulfides were also obtained by the reaction of dialkoxy disulfides with thiocarboxylic acids. Thermal decomposition of **6** gave **8** and carboxylic esters.

In contrast to ordinary sulfites and monothiosulfites,[1] RSS(O)OR′ (**1**), dithiosulfites,[2] RSS(O)SR (**2**) (R = Ar or *tert*-alkyl), prepared from thionyl chloride and mercaptans are relatively unstable compound and readily decompose to give di- and trisulfides. Previously, we have reported the preparation of diacyl dithiosulfites,[3] RCOSS(O)SCOR′ (**3**), and acylaryl dithiosulfites,[4] RCOSS(O)SR′ (**4**), by the reaction of acyl thiochlorosulfites with thiocarboxylic acids or thiophenols. These acyl derivatives of dithiosulfites were found to be reasonably stable on standing but decomposed to afford carboxylic anhydrides (from **3**) or disulfides and carboxylic anhydrides (from **4**) on heating. Acyl derivative of ordinary sulfites,[5] RCOOS(O)OR′ (**5**), are stable at room temperature but decompose on heating into carboxylic esters or carboxylic