Stereochemistry of Sulfur Compounds. IV. New Ring Systems of Carbon, Nitrogen, and Chiral Sulfur[1,2]

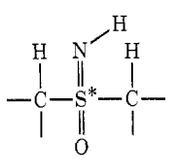
TODD R. WILLIAMS AND DONALD J. CRAM*

Contribution No. 3002 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California 90024

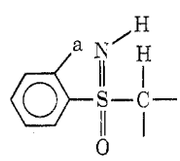
Received August 15, 1972

Six new chiral heterocyclic systems have been prepared in which the sulfur, nitrogen, and carbon of the sulfoximide function are part of the ring system (compounds 1–6). From *S*-methyl-*S*-phenylsulfoximide (9a), butyllithium, and carbon dioxide was obtained 1-phenyl-3-oxo-1,2-thiazet-1-ine oxide (1). From *S*-methyl-*S*-*p*-tolylsulfoximide (9b) was formed 1-*p*-tolyl-4-oxo-2,5-dihydroisothiazole oxide (2b). The similarly prepared phenyl analog (2a) with diazomethane gave 1-phenyl-4-oxo-2,5-dihydroisothiazole oxide methyl ether (11). Treatment of *S*,*S*-dimethylsulfoximide with 1,3-diphenylpropynone and sodium hydride gave 1-methyl-3,5-diphenyl-1,2-thiazene oxide (18). Similarly optically active (−)-(*R*)-1-*p*-tolyl-3,5-diphenyl-1,2-thiazene oxide [(−)-(*R*)-3] was prepared from (−)-(*R*)-*S*-methyl-*S*-*p*-tolylsulfoximide [(−)-(*R*)-9b]. From methyl 2-methylthio-5-methylphenyl ketone (19) was synthesized 4*H*-1,6-dimethyl-3-oxo-1,2-thiazanaphthalene oxide (4) and 1,5-dimethyl-3-oxobenzo[*d*]-1,2-isothiazole oxide (20). From methyl 2-methylsulfinyl-5-methylphenyl ketone (24) was obtained 1,3,6-trimethylbenzo[*e*]-1,2,4-thiadiazene oxide (5), 1,6-dimethyl-3-oxobenzo[*e*]-4*H*-1,2,4-thiadiazine oxide (6), 1,6-dimethyl-3-carbomethoxybenzo[*e*]-1,2,4-thiadiazene oxide (27), 1,6-dimethyl-3-carboxylbenzo[*e*]-1,2,4-thiadiazene oxide (28), and 1,6-dimethylbenzo[*e*]-1,2,4-thiadiazene oxide (26).

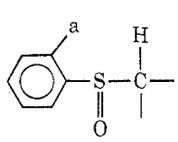
The potential chirality, the stability, and the amphoteric properties of the sulfoximide group[3] make compounds containing this function of particular interest. Three of the four ligands of sulfur in sulfoximides are capable of wide structural variation, and suggest that many new heterocycles might be prepared which contain the sulfur, nitrogen, and carbons of the sulfoximide group as part of a ring system. In principle, rings of all sizes might be constructed that link one carbon to the nitrogen, one carbon to the second carbon, or each carbon to the other and to the nitrogen to give a bicyclic system.



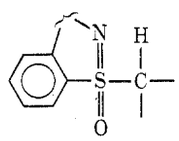
A



B



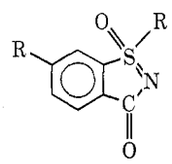
C



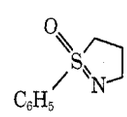
D

Two general strategies for synthesis are envisioned, the first of which involves reactions of a sulfoximide already in being. All three protons of A are slightly acidic, and by proton abstraction with base might be turned into nucleophilic reaction sites. In addition to the two potential nucleophilic sites of B, substituent a of the aromatic ring might be manipulated for synthetic purposes. In the second approach, the sulfoximide unit might be generated from a sulfoxide in a ring-closing nitrenation reaction (C → D).

This paper reports the syntheses of six new heterocyclic ring systems (1–6) that make use of one or the other of these strategies. The first two heterocyclic systems based on the sulfoximide function (7[4] and 8[5])



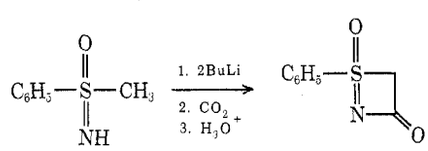
7



8

were announed when all our new systems except 3 and 20 were in hand. The syntheses of compounds 1, 2, and 3 make use of the potential nucleophilic properties of a sulfoximide unit in being, whereas those of the others involve generation of the sulfoximide during ring closure.

Sulfoximides as Potential Nucleophiles in Syntheses.—Preparation of the β-lactam-like compound 1 involved use of anions derived from the SCH_3 and S=NH groups of *S*-methyl-*S*-phenylsulfoximide (9a).



9a 1 (14%)

The carbonyl group of 1 absorbs at 1690 cm^{-1} in chloroform in the infrared at somewhat lower energy than the 1745 cm^{-1} of a normal lactam.[6] Thus, the carbonyl of 1 has more single bond character than a usual β-lactam. Possible explanations are that the N–C–C bond angle is expanded to >90° to accommodate the length of the S–C bond, or that the S=N–C=O linkage possesses considerable dipolar character ($^{+}$S–N=C–O^{-} contributions), or both. The yield of 1 was not maximized, and the probable acidity of 1 once formed probably complicated its synthesis by consuming base.

Alkylation of nitrogen of aryl methyl sulfoximides with haloacetic esters proceeded well only with bromine

(1) This investigation was supported by the U. S. Public Health Service Research Grant No. GM12640-07 from the Department of Health, Education, and Welfare.

(2) These results appeared as a communication: T. R. Williams and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 7333 (1971).

(3) IUPAC nomenclature is employed for compounds of any complexity [see P. E. Verkade, *Pure Appl. Chem.*, **11**, 1, 155 (1965)].

(4) P. Stoss and G. Satzinger, *Angew. Chem., Int. Ed. Engl.*, **10**, 79 (1971).

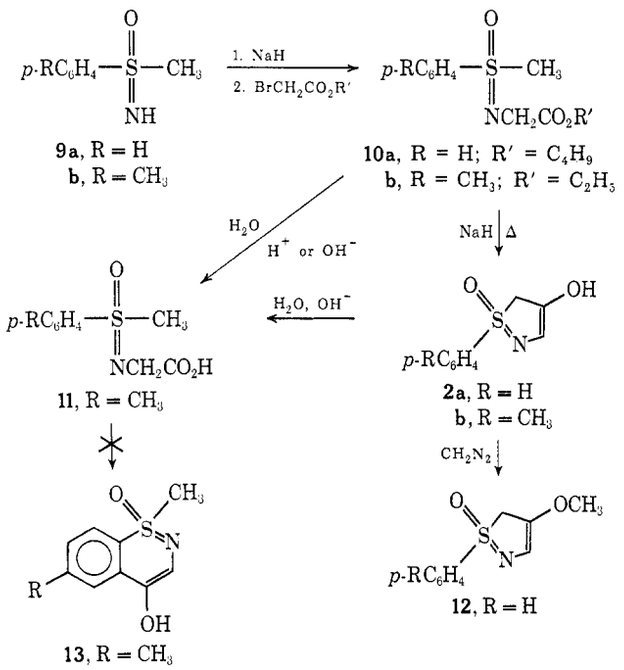
(5) C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *J. Amer. Chem. Soc.*, **93**, 3771 (1971).

(6) K. Nakanishi, "Infrared Absorption Spectroscopy-Practical," Holden-Day, San Francisco, Calif., 1962, p 47.

or iodine as leaving group, and went best in dimethoxyethane at 25° with sodium hydride as base. Use of the thallium salt led to recovered starting material. Treatment of *S*-methyl-*S*-*p*-tolylsulfoximide (**9b**) with ethyl diazoacetate and concentrated sulfuric acid also failed to produce the desired ester, **10a**. Conversions of esters **10** to cycles **2** were plagued by reverse condensations of **2** to give acids **11** under aqueous basic isolation conditions. Enol ether **12** was prepared by treating unpurified **2a** with diazomethane. The similarity in ultraviolet spectra of enol ether **12** and **2b** coupled with the facile diazomethane reaction indicated that **2b** was largely an enol. This structural assignment was supported by nmr and ir spectra of **2b**. Upon melting, **2b** decomposed violently to evolve a gas, possibly ketene. The substance was only slightly soluble in nonpolar spectral solvents, and nmr spectra were obtained only with difficulty.

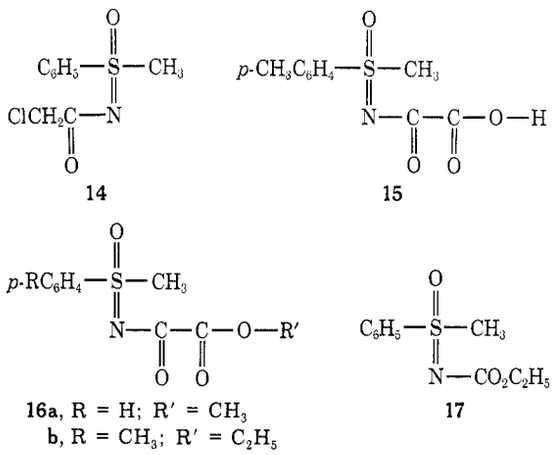
The position of the enol double bond in **2b** and **12** is inferred but not unequivocally demonstrated through nmr spectral comparisons (see Experimental Section). That **2b** exists mainly in the enol form contrasts with cyclopent-3-ene-1-one, which exists to an extent of less than 3% as the enol.[7]

With either aqueous acid or base, ester **10b** produced acid **11**. Attempts to convert **11** to the heterocyclic



system **13** with liquid hydrogen fluoride, polyphosphoric acid (200°), thionyl chloride, or concentrated sulfuric acid (100°) failed. Interestingly, polyphosphoric acid converted **11** to the parent sulfoximide **9b** in 46% yield.

That the benzene ring in *S*-methyl-*S*-phenylsulfoximide is highly deactivated toward electrophilic substitution was shown further as follows. The system when acylated with chloroacetyl chloride in pyridine gave **14**, which with aluminum chloride at 110° failed to give ring-closed product, and only starting material and decomposition products were observed. Treatment of *S*-methyl-*S*-phenylsulfoximide with oxalyl chloride in ether and then with aluminum chloride in dichloromethane also failed to produce a heterocycle. Only **15** (as a hydrate) was ultimately isolated. Ester **16a** readily formed when *S*-methyl-*S*-phenylsulfoximide was heated with excess dimethyl oxalate at 150°. Ester **16b** resulted from mixing *S*-methyl-*S*-*p*-tolylsulfoximide with the half ethyl ester of oxalyl chloride in pyridine. Attempts to ring close **16a** on the *S*-methyl group failed to give product that survived isola-



tion. Although **17** was readily formed from *S*-methyl-*S*-phenylsulfoximide and ethyl chloroformate, its conversion to a cyclic urea *via* its carbamoyl azide failed.[8]

Syntheses of the new heterocycles **3** and **18** were modeled after that of the carbon analog of **18** (thiabenzene oxide).[9] Since optically pure (−)-(*R*)-*S*-methyl-*S*-*p*-toluenesulfoximide was used[10] and no bonds were made or broken to the chiral center, optically pure (−)-(*R*)-**3** was produced. As expected, (−)-**3** gave a much higher optical rotation than the more symmetrical starting material, whose O and NH groups are of similar polarizability. The broad melting point of **3** persisted on repeated recrystallization from many solvents. Molecular models of **3** indicate a puckered disk shape from whose convex face the oxygen protrudes. At 150° the substance starts to undergo a phase change from one solid to a second, and becomes completely liquid at 158°. The substance does not appear (polarizing microscope) to pass through a nematic phase change[11] upon melting. Analog **18** was similarly formed from dimethylsulfoximide.

Although **3** and **18** formally contain six π electrons, the nmr chemical shifts (δ in $CDCl_3$) of their ring protons are unlike those of aromatic model compounds. The proton in the 6 position of **18** resonated at 6.10 and the corresponding proton of **3** was found at 5.90. The analogous proton at C-6 in the carbon analogue of **18** (thiabenzene oxide) was reported[9] at 5.83. The close proximity of the three nmr signals coupled with Hortmann and Harris's full arguments[9] indicate **3** and **18** not to be aromatic. Oae, *et al.*,[12] through pK_a comparisons of aryl-substituted *S*-methyl-*S*-phenylsulfox-

(7) S. Winstein, E. C. Friedlich, R. Baker, and L. Yang-i, *Tetrahedron, Suppl.*, **8**, Part II, 621 (1966).

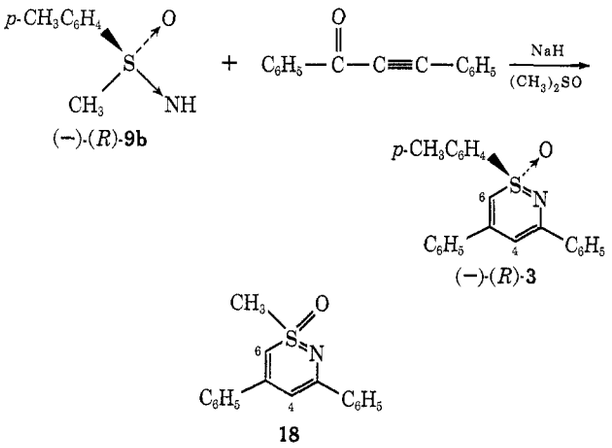
(8) E. S. Levchenko, E. S. Koslov, and A. V. Kirsanov, *J. Gen. Chem. USSR*, **32**, 2548 (1962).

(9) A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **93**, 2471 (1971).

(10) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *ibid.*, **92**, 7369 (1970).

(11) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

(12) S. Oae, K. Tsujihara, and N. Furukawa, *Chem. Ind. (London)*, 1569 (1968).

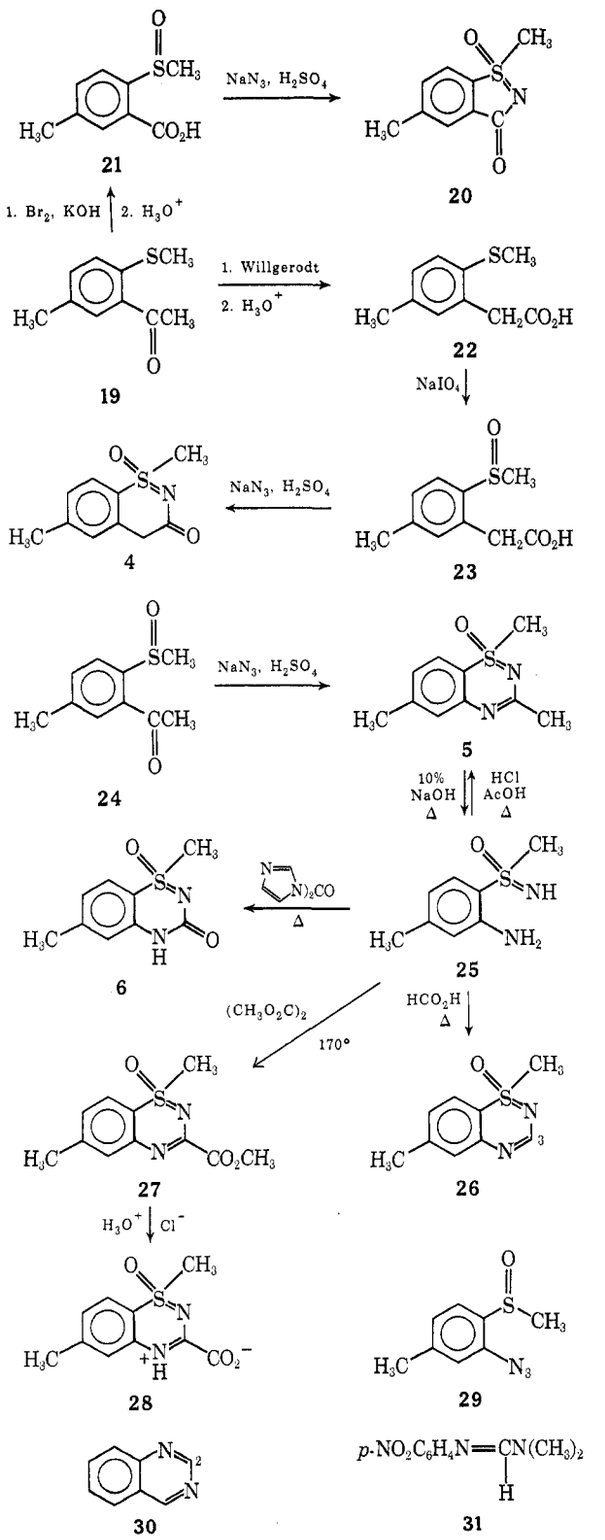


imides, have shown that there is no through conjugation from the sulfoximide nitrogen to the substituted phenyl ring.

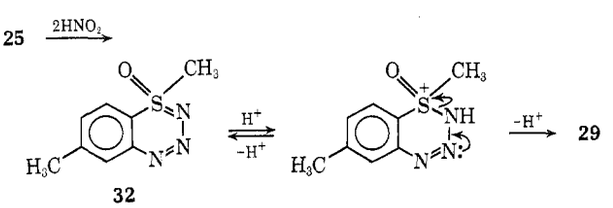
Closures of Rings Linking the Aromatic Ring and Nitrogen of *S*-Aryl-*S*-methylsulfoximides.—Additional new heterocycles utilized 5-methyl-2-methylthioacetophenone[13] (**19**) as starting material. The substance also served in an efficient two-step but multistage synthesis of **20**, which contains the same ring system as the already reported substances,[4] **7**. In our synthesis of the ring system, **19** underwent simultaneous bromoform and sulfide oxidation to give **21** (92%), which with hydrazoic acid–sulfuric acid gave **20** (70%) in a substitution at both carbonyl carbon and at sulfur. In a similar ring closure, the six-membered lactam **4** was prepared (60%) from **23**, the homolog of **21**. That heterocycle **4** exists in the "keto" rather than the potentially aromatic "enol" form is evident from its ir and nmr spectra. The carbonyl of **4** in chloroform absorbs at 1655 cm^{-1}, and thus has less double-bond character than the four-membered lactam, **1**. Lactam **4** with base formed an open-chain salt, which upon acidification regenerated **4**. In one of several attempts to form an enol ether of **4**, the substance was treated with first sodium hydride and then excess methyl iodide. Dimethylation occurred (52%) at the carbon α to the carbonyl group.

Sulfoxide **24** (from **19** and sodium periodate) when treated with sodium azide and sulfuric acid underwent a combined imidation–Schmidt rearrangement–ring closure to give **5** (77%). Attempts to develop a good resolution of **5** gave only partially optically pure material. The open-chain hydrolysis product of **5**, amino sulfoximide **25**, served as starting material for preparation of interesting derivatives. Heterocycle **26** is formally **5** minus a methyl group. The chemical shift (δ) of the proton at C-3 in the nmr spectrum of **26** in $CDCl_3$ occurred at 7.85. The proton at C-2 of the aromatic model compound **30** in CCl_4 was reported[14] at 9.29, whereas the nonaromatic formyl proton in **31** came at 7.61 ($CDCl_3$).[15] Thus heterocycle **26** resembles more the nonaromatic model.

Urea derivative, **6** (82%), gave an ir spectrum that clearly showed that the compound exists in the normal amide and not the imidol form. The substance decomposed with melting at 295–300°, and was stable enough



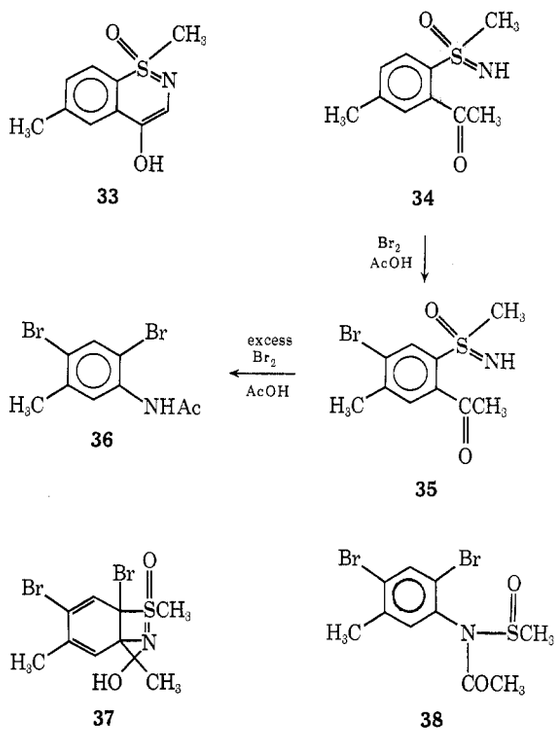
to water at 100° to be recrystallized from that solvent. The new amino acid system, **28**, was sensitive to even cold acid hydrolysis, and was crystallized only as a hydrate. An attempt to form triazine **32** from amino-



(13) K. Auwers and F. Arndt, *Chem. Ber.*, **42**, 537 (1909).
(14) P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **18**, 707 (1965).
(15) J. P. Marsh, Jr., and L. Goodman, *Tetrahedron Lett.*, 683 (1967).

sulfoximide **25** and nitrous acid led to azide **29**. Likely **32** was formed, at least in protonated form, but readily decomposed to azide **29**, as formulated. Attempts to cyclize **29** by both thermal and photolytic loss of nitrogen failed to yield isolable cyclic (four-membered ring) sulfoximide.

Attempts to prepare heterocycle **33** led to the unusual reaction sequence formulated (**34** → **35** → **36**). Although sulfoxide **24** gave sulfoximide **34** as expected, bromination of **34** led to complex substitution–rearrangement reactions, possibly *via* **37** and **38** as intermediates.



Experimental Section

General.—Infrared spectra were obtained with a Beckman IR-5 spectrometer in chloroform or carbon tetrachloride solution, in a Nujol mull, or in a potassium bromide pellet. Nmr spectra were obtained with a Varian T-60, A-60, or A-60D spectrometer in deuteriochloroform, carbon tetrachloride, or deuterium oxide solution. All nmr chemical shifts are given relative to tetramethylsilane as internal standard at 10 τ unless otherwise indicated. Rotations were obtained with a Perkin-Elmer 141 polarimeter in chloroform, acetone, or methanol solution in a 1-dm, jacketed cell, thermostated at 25°. Uv spectra were obtained with a Cary 14 spectrometer in methanol solution. Mass spectra were obtained with an AEI Model MS9 mass spectrometer. Melting points were taken in capillary tubes in a Hoover capillary melting point apparatus and are uncorrected. Solvents designated as "dry" were purified by distillation from lithium aluminum hydride or calcium hybride under dry nitrogen or *in vacuo*. Unless stated otherwise, the term "extraction" describes extracting an aqueous phase with chloroform or dichloromethane, drying the combined organic layers over magnesium sulfate, filtering with vacuum, and removing solvent at aspirator pressure with a heating bath at 50–60°.

Starting Materials.—Methyl *p*-tolyl sulfoxide[16] (~65%) gave bp 116–118° (0.1 mm); methyl phenyl sulfoxide[17] (50%) gave bp 76–79° (0.1 mm); *S,S*-dimethylsulfoximide was prepared as before;[18a] *S*-methyl-*S*-*p*-tolylsulfoximide[18b] (**9b**) was isolated as its hydrochloride salt, mp 173–177° dec. *Anal.* Calcd for $C_{18}H_{12}ClNOS$: C, 46.72; H, 5.84. Found: C, 46.69; H, 5.82. The base itself (70%) gave mp 67–71.5°.[19] Similarly, *S*-methyl-*S*-phenylsulfoximide[20] (**9a**, 85%) gave bp 110–115° (0.1 mm). The (−)-(*R*)-*S*-methyl-*S*-*p*-tolylsulfoximide [(−)-(*R*)-**9b**][10] used gave $[\alpha]^{25}_{546}$ −40.6° (*c* 1.12, acetone). Methyl 2-methylthio-5-methylphenyl ketone[13] (**19**, 59%) gave mp 49–51°.

1-Phenyl-3-oxo-1,2-thiazet-1-ine Oxide (**1**).—To a solution of 1.5 g (9.67 mmol) of **9a** in 50 ml of dry tetrahydrofuran under nitrogen was added 15 ml of a 1.6 *M* solution of butyllithium in hexane (24 mmol), and the resulting yellow solution was stirred at 25° for 1 hr. This solution was added in portions to about 100 g of solid carbon dioxide stirred under nitrogen. The resulting suspension was stirred for 5 min and quenched with 20 ml of 2 *N* hydrochloric acid. The aqueous layer was extracted to give 0.27 g (15%) solid, pure **1** as shown by its ir and nmr spectra. Recrystallization of the substance from ethyl acetate gave mp 204.5–208°. *Anal.* Calcd for $C_8H_7NO_2S$: C, 53.04; H, 3.94. Found: C, 52.92; H, 3.98. Nmr ($CDCl_3$) τ 2.1 (m, 5, ArH), 6.5 (s, 2, CH_2). Mass spectrum *m/e* 181 (p^+).

General Procedure for Alkyl (*S*-Methyl-*S*-arylsulfonimidoyl-*N*) Acetate (**10**).—To a solution of sulfoximide **9** in dry dimethoxyethane under dry nitrogen was added 1.5 equiv of sodium hydride as a 50% mineral oil dispersion. The rate of hydride addition was regulated to keep the reaction mixture from foaming excessively. The resulting suspension was stirred for 3 hr to ensure reaction, and 1.5 equiv of the appropriate alkyl bromoacetate was added at a fast dropwise rate. The resulting mixture was stirred at 25° for 24 hr under nitrogen and quenched with water. After solvent evaporation (*in vacuo*), the residual oil was chromatographed on 50–70 parts of silica gel. Pentane eluted mineral oil and unreacted alkyl bromoacetate. Ether–pentane eluted product **10**, and ether eluted starting material. The product was purified by either rechromatography or vacuum distillation (Kugelrohr).

In this way 23.3 g (0.150 mol) of **9a** was converted with butyl bromoacetate to 17.5 g (50%) of **10a**, bp 150° (0.08 mm). An analytical sample was prepared by preparative vpc. *Anal.* Calcd for $C_{13}H_{19}NO_3S$: C, 57.58; H, 7.12. Found: C, 57.50; H, 7.16. Nmr ($CDCl_3$) τ 2.0–2.8 (m, 5, ArH), 5.8 (t, 2, CH_2-CH_2), 6.3 (q, 2, NCH_2), 6.8 (s, 3, SCH_3), 8.7 (m, 7). Similarly, 5.0 g (29.6 mmol) of **9b** was converted to 4.36 g (58%) of **10b** after rechromatography. An analytical sample was prepared by preparative vpc. *Anal.* Calcd for $C_{12}H_{17}O_3NS$: C, 56.45; H, 6.71. Found: C, 56.40; H, 6.80. Nmr ($CDCl_3$) τ 2.38 (q, 4, ArH), 5.85 (q, 2, J = 7 Hz, CH_2CH_3), 6.33 (q, 2, NCH_2), 6.82 (s, 3, SCH_3), 7.55 (s, 3, $ArCH_3$), 8.78 (t, 3, J = 7 Hz, CH_2CH_3).

1-*p*-Tolyl-4-oxo-2,5-dihydroisothiazole Oxide (**2b**).—A solution of 0.774 g (3.21 mmol) of **10b** in 40 ml of dry tetrahydrofuran was added over 2 hr to a vigorously stirred suspension of 0.46 g of sodium hydride (as a 50% mineral oil dispersion) in 100 ml of dry solvent at 25° under nitrogen. The resulting suspension was refluxed under nitrogen for 24 hr, and the reaction was quenched with 5 ml of 2 *N* hydrochloric acid. The solvent was removed *in vacuo*, the residue taken up in chloroform and filtered, the filtrate was evaporated, and the residue was chromatographed on silica gel. Starting material eluted with ether, and the product (0.14 g, 21%) eluted with 5–10% methanol–ether as a white solid, mp 160° dec. Recrystallization of the material from acetone–cyclohexane gave mp 156.5–157.5° dec, when the sample was inserted into the heating bath at 140°. *Anal.* Calcd for $C_{10}H_{11}O_2NS$: C, 57.42; H, 5.26. Found: C, 57.25; H, 5.08. Nmr ($CDCl_3$) τ 2.4 (q, 4, ArH), 5.55 (broad s, 1, CH), 6.0 (m, 3, CH_2 and OH), 7.55 (s, 3, $ArCH_3$). Uv (MeOH) 275 nm (sh) (log ϵ 3.53), 265 (sh) (3.72), 258 (sh) (3.83), 227 (max) (4.18).

1-Phenyl-4-oxo-2,5-dihydroisothiazole Oxide Methyl Ether (**12**).—The above procedure was applied to 1.04 g (3.84 mmol) of **10a**. However, before the product was chromatographed it was treated with a solution of diazomethane in ether until no further reaction appeared to occur. Chromatography of the resulting oil on silica gel (50 g) with 5% methanol–ether eluent gave 0.11 g (13%) of solid, mp 111–115°. Rechromatography of the material through 10 g of alumina with ether eluent, followed by recrystallization from ether, gave mp 113–115.5°. *Anal.* Calcd for $C_{10}H_{11}NO_2S$: C, 57.38; H, 5.30. Found: C, 57.21; H, 5.29. Nmr ($CDCl_3$) τ 2.0–2.8 (m, 5, ArH), 4.3 (s, 1, CH), 5.6

(16) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).
(17) C. C. Price and J. J. Hydock, *J. Amer. Chem. Soc.*, **74**, 1943 (1952).
(18) (a) J. K. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 2081 (1950); (b) *ibid.*, 1572 (1952).
(19) F. Misani, T. W. Fair, and L. Reiner, *J. Amer. Chem. Soc.*, **73**, 459 (1951).
(20) R. Fusco and F. Tenconi, *Chim. Ind.* (*Milan*), **47**, 61 (1965).

(broad s, 2, CH_2), 6.22 (s, 3, OCH_3). Uv (MeOH) 274 nm (sh) (log ϵ 3.20), 266 (sh) (3.34), 259 (sh) (3.39), 225 (max) (4.05).

(*S*-Methyl-*S*-*p*-tolylsulfonimidoyl)acetic Acid (11). A. Basic Hydrolysis.—A suspension of 2.3 g (9.25 mmol) of **10b**, 25 ml of water, 25 ml of methanol, and 25 ml of saturated potassium carbonate solution was stirred at 25° for 20 hr. The resulting solution was brought to pH 3 with hydrochloric acid and extracted. Trituration of the oily residue with ether gave an oil which was crystallized from ethanol–water to give 0.3 g (30%) of *p*-tolyl *p*-toluenethiosulfonate, mp 74–76° (lit.[21] mp 78–79°). The ether-insoluble residue was crystallized from chloroform or methanol to yield 0.6 g (29%) of **11**, mp 99–100°.

B. Acidic Hydrolysis.—A solution of 0.5196 g (2.04 mmol) of **10b** in 15 ml of 2 *N* hydrochloric acid was stirred at 25° for 24 hr. The pH was adjusted to about 3 by solid sodium carbonate addition, and the solution was extracted. The resulting oil was dissolved in chloroform and seeded with the above sample of **11**. The crystals thus obtained weighed 0.396 g (79.4%), mp 98–100°. *Anal.* Calcd for $C_{10}H_{13}O_3NS \cdot H_2O$: C, 48.97; H, 6.17. Found: C, 49.12; H, 6.10. Nmr ($CDCl_3$) τ 2.33 (q, 4, ArH), 5.89 (broad s, 3, OH), 6.42 (broad s, 2, NCH_2), 6.80 (s, 3, SCH_3), 7.55 (s, 3, $ArCH_3$).

***S*-Methyl-*S*-phenyl-*N*-chloroacetylsulfoximide (14).**—To a solution of 1.55 g (10 mmol) of **9a** and 7 ml of dry triethylamine in 40 ml of dry tetrahydrofuran was added *via* syringe 1.59 ml (20 mmol) of chloroacetyl chloride at a slow dropwise rate with stirring and cooling in ice. The resulting brown mixture was allowed to warm to 25° over 30 min and stirred for 1.5 hr. The reaction was quenched with 10 ml of water, the solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane, washed with dilute acid, dried, and chromatographed on 150 g of silica gel. Five 400-ml fractions were taken with 50% ether–pentane eluent, and then 18 100-ml fractions with ether eluent were collected. The product in fractions 8–19 was combined to give 1.82 g (79%) of solid. Recrystallization of this material from dichloromethane–ether gave 1.43 g (62%) of **14**, mp 112–115°. One recrystallization from the same solvent gave mp 113–115°. *Anal.* Calcd for $C_9H_{10}ClNO_2S$: C, 46.64; H, 4.38. Found: C, 46.87; H, 4.50. Nmr ($CDCl_3$) τ 1.8–2.5 (m, 5, ArH), 5.90 (s, 2, CH_2Cl), 6.60 (s, 3, SCH_3).

***S*-Methyl-*S*-*p*-toyl-*N*-hydrogenoxalylsulfoximide (15).**—To a solution of 1.5 g (8.9 mmol) of **9b** in 20 ml of dry pyridine was added a solution of 20 mmol of oxalyl chloride and 19 mmol of ethanol in 30 ml of dry dimethoxyethane. The reaction mixture became quite warm, and a white precipitate formed almost immediately. The resulting mixture was stirred at 25° for 3 hr and then quenched with water. Extraction gave a yellow solution which was washed with dilute acid, dried, and evaporated to give an oil. This oil was chromatographed on 60 g of silica gel, with 50% ether–pentane as eluent, to give 2.0 g (83%) of ester **16b**, pure by tlc, ir, and nmr. Nmr ($CDCl_3$) τ 2.33 (q, 4, ArH), 5.73 (q, 2, J = 7 Hz, CH_2CH_3), 6.59 (s, 3, SCH_3), 7.58 (s, 3, $ArCH_3$), 8.70 (t, 3, J = 7 Hz, CH_2CH_3).

After standing in a vial for 1 year exposed to the air this oily ester hydrolyzed to solid acid **15**. Recrystallization of this solid from acetone–cyclohexane gave 1.25 g (58.5% based on **9b**), mp 112.5–115°. *Anal.* Calcd for $C_{10}H_{11}O_4NS \cdot H_2O$: C, 46.33; H, 5.06. Found: C, 46.38; H, 5.11. Nmr (acetone-d_6) τ 2.4 (q, 4, ArH), 4.65 (broad s, 3, OH), 6.83 (s, 3, SCH_3), 7.68 (s, 3, $ArCH_3$).

***S*-Methyl-*S*-phenyl-*N*-carbomethoxycarbonylsulfoximide (16a).**—A mixture of 1.5 g (9.7 mmol of **9a** and 8 g (68 mmol) of dimethyl oxalate was heated at 150° for 5 hr under a slow stream of nitrogen. The excess dimethyl oxalate was sublimed at aspirator pressure, and the residue was chromatographed on 100 g of silica gel with ether eluent. Thirteen 400-ml fractions were taken and the product was contained in fractions 5–13, 1.43 g (60%), as an oil. A sample was purified by molecular distillation. *Anal.* Calcd for $C_{10}H_{11}NO_4S$: C, 49.78; H, 4.60. Found: C, 49.90; H, 4.69. Nmr ($CDCl_3$) τ 2.0–2.8 (m, 5, ArH), 6.1 (s, 3, OCH_3), 6.7 (s, 3, SCH_3).

***S*-Methyl-*S*-phenyl-*N*-carboethoxysulfoximide (17).**—A solution of 4.0 g (25.8 mmol) of **9a** in 40 ml of dry tetrahydrofuran and 10 ml of dry triethylamine was cooled under nitrogen to 0°. With good stirring, 4.12 ml (51.6 mmol) of ethyl chloroformate was added dropwise over 45 min. After the addition was complete, the reaction was allowed to warm up to 25° over 1 hr. The nitrogen was removed and 56 mmol of water was added slowly with stirring. The resulting mixture was poured into 100 ml of water and made strongly acidic with concentrated hydrochloric acid. Extraction at this point gave 4.5 g (77%) of **17** as an oil. Addition of solid sodium carbonate to the water layer followed by extraction gave 0.8 g (20%) of unreacted **9a**. Pure **17** was obtained by molecular distillation. *Anal.* Calcd for $C_{10}H_{13}NO_3S$: C, 52.84; H, 5.78. Found: C, 52.74; H, 5.84. Nmr (CCl_4) τ 2.0–2.4 (m, 5, ArH), 6.01 (q, 2, J = 7 Hz, CH_2CH_3), 6.73 (s, 3, SCH_3), 8.83 (t, 3, J = 7 Hz, CH_2CH_3).

1-Methyl-3,5-diphenyl-1,2-thiazene Oxide (18).—To a solution of 1.306 g (14 mmol) of *S*,*S*-dimethylsulfoximide[18a] in 60 ml of dry dimethyl sulfoxide [freshly distilled from calcium hydride, bp 72° (10 mm)] was added 0.74 g (15.4 mmol) of a mineral oil dispersion of sodium hydride, and the resulting mixture was stirred for 45 min under nitrogen. The mixture was cooled below 25° in ice and a solution of 1.48 g (7.18 mmol) of 1,3-diphenylpropynone in 15 ml of dry dimethyl sulfoxide was added in small portions over 8 min *via* syringe. The resulting dark brown reaction mixture was stirred at 25° for 19.5 hr and poured into 300 ml of ice and water. The mixture was allowed to warm to 25° and was filtered through Celite. The Celite was washed thoroughly with dichloromethane to give a red oil which, when triturated with pentane to remove mineral oil, crystallized to give 0.40 g (20%) of solid, mp 140–144°. Recrystallization of **18** from ethyl acetate–cyclohexane gave mp 142.5–144°. *Anal.* Calcd for $C_{17}H_{15}NOS$: C, 72.56; H, 5.38. Found: C, 72.63; H, 5.57. Nmr ($CDCl_3$) τ 1.9–2.7 (m, 10, ArH), 3.40 (d, 1, J = 0.7 Hz, C_4H), 3.9 (d, 1, J = 0.7 Hz, C_5H), 6.55 (s, 3, SCH_3).

(−)-1-*p*-Tolyl-3,5-diphenyl-1,2-thiazene Oxide [(−)-(*R*)-3].—By the above procedure, 1.24 g (6.0 mmol) of 1,3-diphenylpropynone and 1.12 g (6.6 mmol) of (−)-(*R*)-**9b**,[10] were converted to 1.8 g (84%) of **3** as a yellow solid, mp 150–158°, $[\alpha]^{25}_{546}$ −339° (*c* 1.15, chloroform). The same melting point and rotation were obtained for crystals from methanol, ether, or ethyl acetate solution. *Anal.* Calcd for $C_{23}H_{19}NOS$: C, 77.27; H, 5.37. Found: C, 77.29; H, 5.47. Nmr ($CDCl_3$) τ 1.9–2.8 (m, 14, ArH), 3.3 (broad s, 1, C_4H), 4.1 (broad s, 1, C_5H), 7.6 (s, 3, $ArCH_3$).

Methyl 2-Methylsulfinyl-5-methylphenyl Ketone (24).—The method of Leonard and Johnson[16] was applied to 16.0 g (88.9 mmol) of **19** to give 16.8 g (96.5%) of **24**, mp 88–91°. A sample was recrystallized from ether, mp 89.5–91.5°. *Anal.* Calcd for $C_{10}H_{12}O_2S$: C, 61.21; H, 6.17. Found: C, 61.37; H, 6.19. Nmr ($CDCl_3$) τ 1.50–2.50 (m, 3, ArH), 7.24 (s, 3, SCH_3), 7.35 (s, 3, CCH_3), 7.46 (s, 3, $ArCH_3$).

Methyl 2-Methylsulfonimidoyl-5-methylphenyl Ketone (34).—The method of Whitehead and Bentley[18b] was applied to 3.80 g (19.4 mmol) of **24**. The reaction was allowed to proceed for 3 hr and was then quenched with water. Extraction of the acidic solution gave after crystallization from dichloromethane–ether 2.0 g (49%) of ketone, mp 129–131°. *Anal.* Calcd for $C_{10}H_{13}O_2NS$: C, 56.86; H, 6.20. Found: C, 56.74; H, 6.23. Nmr ($CDCl_3$) τ −0.55 (broad, 1, NH), 1.70 (s, 1, ArH), 2.92, (m, 2, ArH), 7.13 (s, 3, SCH_3), 7.62 (s, 3, CCH_3), 7.82 (s, 3, $ArCH_3$).

Methyl 2-Methylsulfonimidoyl-4-bromo-5-methylphenyl Ketone (35).—Into a flask wrapped in aluminum foil and fitted with a nitrogen inlet was put a solution of 1.5 g (7.11 mmol) of **34** in 10 ml of glacial acetic acid, and the reaction vessel was purged with nitrogen. Bromine (0.43 ml, 7.8 mmol) dissolved in 2 ml of glacial acetic acid was added. The reaction flask was stoppered under a positive pressure of nitrogen and heated in an oil bath at 50–55° for 3 hr. The resulting solution was poured into water, excess bromine was destroyed with sodium thiosulfate solution, the pH was adjusted to 8 by addition of sodium carbonate, and the resulting suspension was extracted to give an oil. Upon trituration with ether, this oil gave 1.89 g (91.8%) of white crystals, mp 184–188°. A sample was crystallized from acetone, mp 186–188°. *Anal.* Calcd for $C_{10}H_{12}BrNO_2S$: C, 41.39; H, 4.17. Found: C, 41.31; H, 4.33. Nmr ($CDCl_3$) τ −0.32 (broad, 1, NH), 1.70 (s, 1, ArH), 2.57 (s, 1, ArH), 7.12 (s, 3, SCH_3), 7.59 (s, 3, CCH_3), 7.82 (s, 3, $ArCH_3$).

2,4-Dibromo-5-methylacetanilide (36).—A solution of 2.3 g (7.93 mmol) of **35** and 0.48 ml (8.72 mmol) of bromine in 20 ml of glacial acetic acid was heated to 50–55° under nitrogen and protected from light for 48 hr. After the reaction mixture was worked up as described above, 2.2 g of solid was obtained which was chromatographed on 115 g of silica gel with dichloromethane as eluent and 100-ml fractions. Fractions 10–12 contained 0.5 g (20%) of **36**, mp 165–171°. Fractions 47–49 contained 0.95 g (41%) of unreacted starting material. Recrystallization of **36**

(21) L. Field, *J. Amer. Chem. Chem. Soc.*, **74**, 394 (1952).

from ether–benzene gave a pure sample, mp 170–171° (lit.[22] mp 168–168.6°). This compound was also fully characterized by its spectral properties. *Anal.* Calcd for $C_9H_9Br_2NO$: C, 35.18; H, 2.93; Br, 52.12. Found: C, 35.18; H, 3.07; Br, 52.61.

Anilide **36** was hydrolyzed to 2,4-dibromo-5-methylaniline, mp 73.5–75° (lit.[22] mp 74.6–75.5°.

1-(2-Methylthio-5-methyl)phenylthioacetylmorpholide.—A mixture of 5.0 g (27.8 mmol) of **19**, 1.78 g (55.6 mmol) of sublimed sulfur, and 4.85 g (55.6 mmol) of morpholine (distilled from calcium hydride and stored over potassium hydroxide) was refluxed under nitrogen for 18–20 hr. The hot solution was poured into a total of 15 ml of 95% ethanol and cooled to 5° until crystallization was complete. The crystals were filtered, washed, and air dried to give 6.2 g (80%), mp 95–103°. This crude product was usually hydrolyzed without further purification. An analytical sample was prepared by chromatography on 100 parts of silica gel using 25–50% ether–pentane eluent, followed by crystallization from benzene, mp 107.5–109.5°. *Anal.* Calcd for $C_{14}H_{19}NOS_2$: C, 59.77; H, 6.81; S, 22.79. Found: C, 59.86; H, 6.81; S, 22.54. Nmr ($CDCl_3$) τ 2.78 (m, 3, ArH), 5.63 (m, 4, OCH_2), 6.4 (m, 6, $ArCH_2$ and NCH_2), 7.60 (s, 3, SCH_3), 7.70 (s, 3, $ArCH_3$).

2-Methylthio-5-methylphenylacetic Acid (22).—The above morpholide upon basic hydrolysis in ethanolic potassium hydroxide (3 *N*) gave **22** (60%), mp 109–111° (from carbon tetrachloride). Acid hydrolysis in 2:1 concentrated hydrochloric acid–glacial acetic acid gave **22** (55%). *Anal.* Calcd for $C_{10}H_{12}O_2S$: C, 61.21; H, 6.17. Found: C, 61.34; H, 5.95. Nmr ($CDCl_3$) τ −1.55 (s, 1, OH), 2.83 (m, 3, ArH), 6.20 (s, 2, $ArCH_2$), 7.62 (s, 3, SCH_3), 7.72 (s, 3, $ArCH_3$).

2-Methylsulfinyl-5-methylphenylacetic Acid (23).—The method of Leonard and Johnson[16] was applied to 8.0 g (40.8 mmol) of **22** to give 5.8 g (67%) of **23**, mp 151–155° (acetone). *Anal.* Calcd for $C_{10}H_{12}O_3S$: C, 56.60; H, 5.70. Found: C, 56.79; H, 5.72. Nmr ($CDCl_3$) τ −1.50 (s, 1, OH), 2.11 (d, 1, ArH), 2.75 (m, 2, ArH), 6.25 (q, 2, $ArCH_2$), 7.23 (s, 3, SCH_3), 7.66 (s, 3, $ArCH_3$).

4*H*-1,6-Dimethyl-3-oxo-1,2-thiazanapththalene Oxide (4).—The method of Whitehead and Bentley[18b] was applied to 3.5 g (16.5 mmol) of **23** to give 2.07 g (60%) of **4**, mp 180–185° dec, from acetone. *Anal.* Calcd for $C_{10}H_{11}NO_2S$: C, 57.42; H, 5.26. Found: C, 57.64; H, 5.32. Nmr ($CDCl_3$) τ 2.45 (m, 3, ArH), 6.20 (s, 2, $ArCH_2$), 6.63 (s, 3, SCH_3), 7.53 (s, 3, $ArCH_3$).

1,4,4,6-Tetramethyl-3-oxo-1,2-thiazanaphthalene Oxide.—To a solution of 0.519 g (2.48 mmol) of **4** in 35 ml of dry *tert*-butyl alcohol under nitrogen was added in portions 0.179 g (3.72 mmol) of a 50% dispersion of sodium hydride in mineral oil. After 0.5 hr the reaction mixture was a clear, yellow-orange solution. To this solution was added *via* syringe 0.47 ml (7.55 mmol) of methyl iodide, and the mixture was stirred at 25° for 52 hr protected from moisture. Water was added, the solvent was evaporated *in vacuo*, and the resulting yellow-brown oil was chromatographed on silica gel with ether eluent to give 0.305 g (52%) of solid, mp 181–188.5° dec. Recrystallization of the material from dichloromethane–ether gave a pure sample, mp 186–189° dec. *Anal.* Calcd for $C_{12}H_{15}NO_2S$: C, 60.76; H, 6.33. Found: C, 60.97; H, 6.49. Nmr ($CDCl_3$) τ 2.45 (m, 3, ArH), 6.63 (s, 3, SCH_3), 7.53 (s, 3, $ArCH_3$), 8.35 (d, 6, CCH_3).

2-Methylsulfinyl-5-methylbenzoic Acid (21).—A solution was made by adding 1.82 ml (33.3 mmol) of bromine in small portions to 6.21 g (111 mmol) of potassium hydroxide in 50 ml of water. To the resulting yellow was added at 0° a solution of 1.0 g (5.55 mmol) of **19** in 50 ml of dry tetrahydrofuran. The reaction was allowed to proceed at 0° for 1 hr and then at 25° for 15 hr, after which the solvent was removed *in vacuo* and the solution was acidified with concentrated hydrochloric acid. A few crystals of sodium sulfite were added to destroy the excess bromine, and the resulting solid was filtered and air dried to give 1.02 g (92.5%) of white powder, which when crystallized from 95% ethanol gave mp 179.5–180° dec. *Anal.* Calcd for $C_9H_{10}O_3S$: C, 54.54; H, 5.09. Found: C, 54.82; H, 5.06. Nmr (D_2O–sodium carbonate with acetone at τ 7.94) τ 2.53 (m, 3, ArH), 7.25 (s, 3, SCH_3), 7.57 (s, 3, $ArCH_3$).

1,5-Dimethyl-3-oxobenzo[*d*]-1,2-isothiazole Oxide (20).—The method of Whitehead and Bentley[18b] was applied to 0.50 g (2.52 mmol) of **21** to give 0.334 g (68%) of solid, mp 168–174°. Recrystallization of **20** from dichloromethane–ether gave mp 172–173.5°. *Anal.* Calcd for $C_9H_9NO_2S$: C, 55.36; H, 4.66. Found: C, 55.45; H, 4.65. Nmr ($CDCl_3$) τ 1.9–2.4 (m, 3, ArH), 6.45 (s, 3, SCH_3), 7.4 (s, 3, $ArCH_3$).

1,3,6-Trimethylbenzo[*e*]-1,2,4-thiadiazene Oxide (5).—The method of Whitehead and Bentley[18b] was applied to 20 g (0.102 to 20 g (0.102 mol) of **24**, except that the reaction was allowed to proceed for 15 hr. Normal work-up, including extraction of the acidic reaction medium, gave 16.35 g (77%) of crystalline **5**, mp 140–145° (acetone). Recrystallization of **5** from acetone gave mp 143–145°. *Anal.* Calcd for $C_{10}H_{12}N_2OS$: C, 57.68; H, 5.81. Found, C, 57.88; H, 5.97. Nmr ($CDCl_3$) τ 2.32 (d, 1, ArH), 2.8 (d, 2, ArH), 6.58 (s, 3, SCH_3), 7.6 (d, 6, $ArCH_3$ and CCH_3).

2-Methylsulfonimidoyl-5-methylaniline (25).—A solution of 5.00 g (24.0 mmol) of **5** in 25 ml of 10% sodium hydroxide and 25 ml of water was refluxed for 4 hr. The resulting cloudy solution was diluted with an equal volume of water and extracted to give **25** after crystallization from ether–pentane, 4.24 g (96%) of white solid, mp 85–87.5°. *Anal.* Calcd for $C_8H_{12}N_2OS$: C, 52.17; H, 6.52. Found: C, 52.40; H, 6.65. Nmr ($CDCl_3$) τ 2.34 (d, 1, ArH), 3.40 (d, 2, ArH), 5.7 (broad, 3, NH), 6.93 (s, 3, SCH_3), 7.72 (s, 3, $ArCH_3$).

1,6-Dimethylbenzo[*e*]-1,2,4-thiadiazene Oxide (26).—A solution of 1.00 g (5.44 mmol) of **25**, 0.50 g (10.88 mmol) of formic acid, and 0.045 ml of water was heated in an oil bath at 95–100° for 2.5 hr. After cooling to 25°, the acid was neutralized by adding 10% sodium hydroxide solution to pH 7, and the mixture was extracted to give 0.99 g (94%) of solid. Recrystallization of **26** from dichloromethane–ether gave 0.819 g (78%), mp 132–134°. *Anal.* Calcd for $C_9H_{10}N_2OS$: C, 55.67; H, 5.15. Found: C, 55.54; H, 5.24. Nmr ($CDCl_3$) τ 2–2.9 (m, 4, ArH and CH), 6.50 (s, 3, SCH_3), 7.55 (s, 3, $ArCH_3$).

Heterocycle 5 from 25.—The method of Phillips[23] was applied to 0.208 g (1.13 mmol) of **25**, except that the reaction mixture was refluxed for 24 hr. Neutralization with concentrated ammonia and extraction gave 0.210 g (90%) of solid, mp broad to 137°. Recrystallization of **25** from dichloromethane–ether gave 0.131 g (56%) of **5**, mp 140.5–145°, identical in all spectral characteristics with **5** obtained as described earlier.

1,6-Dimethyl-3-carbomethoxybenzo[*e*]-1,2,4-thiadiazene Oxide (27).—A mixture of 0.50 g (2.72 mmol) of **25** and 2.0 g (17 mmol) of dimethyl oxalate was heated under a slow nitrogen stream at 165–170° for 4 hr. The excess dimethyl oxalate was sublimed at aspirator pressure and the residue was crystallized from methanol to give 0.458 g (67%) of white solid, mp 205–215°. Sublimation of **27** followed by crystallization from methanol gave mp 212.5–214.5°. *Anal.* Calcd for $C_{11}H_{12}N_2O_3S$: C, 52.36; H, 4.80. Found: C, 52.64; H, 4.96. Nmr ($CDCl_3$) τ 2.2–2.9 (m, 3, ArH), 6.05 (s, 3, OCH_3), 6.43 (s, 3, SCH_3), 7.55 (s, 3, $ArCH_3$).

1,6-Dimethyl-3-carboxybenzo[*e*]-1,2,4-thiadiazene Oxide (28).—A solution of 0.157 g (0.624 mmol) of **27** in 30 ml of 2 *N* hydrochloric was stirred at 25° for 3.5 hr. Solid potassium hydroxide was added until the pH reached 3–4. The solvent was removed *in vacuo*, and the white solid residue was extracted in a Soxhlet apparatus with chloroform for 24 hr. Removal of solvent and trituration of the residual oil with dichloromethane gave a white solid which was recrystallized from methanol–ether to give 8 mg (5%) crystals, mp 163.5–165° dec. *Anal.* Calcd for $C_{10}H_{10}N_2O_3S \cdot H_2O$: C, 46.88; H, 4.72. Found: C, 46.70; H, 4.90. Ir (KBr) 3300–2800 (broad, NH^+), 1590 (CO_2^-), 1230 cm^{-1} (O=S=N).

2-(Methyl-*N*-carboethoxysulfonimidoyl)-5-methylaniline.—A solution of 0.502 g (2.73 mmol) of **25** and 0.553 g (5.46 mmol) of triethylamine in dry ether was stirred at 25° under nitrogen. Through an addition funnel a solution of ethyl chloroformate (0.296 g, 2.73 mmol) in dry ether was added dropwise. After the addition was complete, the reaction mixture was stirred for 1.5 hr, during which time a white precipitate formed. The reaction was quenched with water, the ether layer was washed with dilute acid, and the organic solution was dried. Evaporation of solvent gave 0.4 g (57%) of an oil which was pure product by tlc, ir, and nmr. The oil was passed through a short column of silica gel with ether eluent, and dried *in vacuo*. *Anal.* Calcd for $C_{11}H_{16}O_3N_2S$: C, 51.56; H, 6.25. Found: C, 51.45; H, 6.43. Nmr ($CDCl_3$) τ 2.4 (d, 1, ArH), 3.35 (m, 2, ArH), 5.05 (broad, 2, NH_2), 5.90 (q, 2, J = 7 Hz, CH_2CH_3), 6.73, (s, 3, SCH_3), 7.75 (s, 3, $ArCH_3$), 8.78 (t, 3, J = 7 Hz, CH_2CH_3).

2-[Methyl-*N*-(1-imidazolylcarbonyl)sulfonimidoyl]-5-methylaniline.—To a solution of 0.5058 g (2.75 mmol) of **25** in 15 ml

(22) R. H. C. Neville and A. Winther, *Chem. Ber.*, **13**, 962 (1880).

(23) M. A. Phillips, *J. Chem. Soc.*, 2393 (1928).

of dry tetrahydrofuran under nitrogen was added a solution of 0.535 g (3.3 mmol) of 1,1'-carbonyldiimidazole in 25 ml of dry tetrahydrofuran, and the resulting clear solution was stirred at 25° for 52 hr protected from moisture. Then 0.48 g (2.96 mmol) of diimidazole reagent was added and the reaction mixture was stirred for another 16 hr at 25°. The solvent was evaporated to give an oil which crystallized, recrystallization of which several times from dichloromethane–ether gave 0.5916 g (77%) of product, mp 159–163°. An analytical sample gave mp 160–163.5°. *Anal.* Calcd for $C_{12}H_{14}N_4O_2S$: C, 51.77; H, 5.08. Found: C, 51.92; H, 5.13. Nmr ($CDCl_3$) τ 1.6–3.4 (m, 6, ArH and ImH), 4.8 (broad s, 2, NH_2), 6.47 (s, 3, SCH_3), 7.67 (s, 3, $ArCH_3$).

1,6-Dimethyl-3-oxobenzo[*e*]-4*H*-1,2,4-thiadiazene Oxide (6).—A solution of 0.21 g (0.756 mmol) of the above imidazole derivative in 15 ml of *p*-dichlorobenzene was heated at 160–175° for 24 hr. The solvent was removed *in vacuo*, and the residue was dissolved in 100 ml of water and cooled. The resulting mixture was filtered, reduced to 30 ml, and cooled further to give 0.13 g (82%) of **6**, mp 295–300° dec. *Anal.* Calcd for $C_9H_{10}N_2O_2S$: C, 51.40; H, 4.80. Found: C, 51.66; H, 4.97. Ir (Nujol) 1650 (C=O), 1220 (O=S=N).

A sample of 2-(methyl-*N*-carboethoxysulfonimidoyl)-5-methylaniline (0.20 g, 0.782 mmol) was heated neat at 170–180° for 24 hr to give a solid residue which, when recrystallized from water, gave about 10 mg (6%) of **6**, mp 295–300° dec.

2-Methylsulfinyl-5-methylphenyl Azide (29).—To a solution of 0.30 g (1.63 mmol) of **25** in 5 ml of 2 N hydrochloric acid was added a 0.2 *M* solution of sodium nitrite (less than 2 equiv) until an excess of nitrous acid was present. The resulting yellow solution was stirred at 25° for 0.5 hr and then extracted to give an oil which solidified into 0.31 g (97%) of a yellow solid. Recrystallization of this solid from ether–pentane gave 0.17 g (53%) of **29**, mp 59–63°. *Anal.* Calcd for $C_8H_9N_3OS$: C, 49.20; H, 4.66. Found: C, 49.40; H, 4.47. Nmr ($CDCl_3$) τ 2.1–3.1 (m, 3, ArH), 7.25 (s, 3, SCH_3), 7.58 (s, 3, $ArCH_3$).

Registry No.—**1**, 34617-79-3; **2b**, 34617-80-6; (−)-(*R*)-**3**, 34617-81-7; **4**, 34617-82-8; **5**, 34617-83-9; **6**, 34662-87-8; **10a**, 36789-40-9; **10b**, 36789-41-0; **11**, 36789-42-1; **12**, 36870-61-8; **14**, 36789-43-2; **15**, 36789-44-3; **16a**, 36789-45-4; **16b**, 36789-46-5; **17**, 36789-47-6; **18**, 34617-85-1; **20**, 34662-88-9; **21**, 34617-86-2; **22**, 34617-93-1; **23**, 34617-94-2; **24**, 34617-87-3; **25**, 34617-88-4; **26**, 34617-90-8; **27**, 34617-89-5; **28**, 34617-91-9; **29**, 34617-92-0; **34**; 36789-27-2; **35**, 36789-28-3; **36**, 36789-29-4; 1-(2-methylthio-5-methyl)phenylthioacetylmorpholide, 36789-30-7; 1,4,4,6-tetramethyl-3-oxo-1,2-thiazanaphthalene oxide, 36789-31-8; 2-(methyl-*N*-carboethoxysulfonimidoyl)-5-methylaniline, 36789-32-9; 2-[methyl-*N*-(1-imidazolylcarbonyl)sulfonimodoyl]-5-methylaniline, 36789-33-0.

Thermal Reactions of Alkyl *N*-Carbomethoxysulfamate Esters

EDWARD M. BURGESS,* HAROLD R. PENTON, JR., AND E. A. TAYLOR

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received September 14, 1972

(Carboxysulfamoyl)triethylammonium hydroxide, inner salt, methyl ester was synthesized and shown to react with a broad spectrum of alcohols resulting in alkyl *N*-carbomethoxysulfamate esters. The scope and synthetic usefulness of the sulfamate ester function as a leaving group in thermolytic dehydration reactions was demonstrated by the facile conversion of tertiary and secondary alcohols to olefins and primary alcohols to urethanes. Stereochemically the reaction was established as a cis-stereospecific elimination by the formation of only protio-*trans*-stilbene from *threo*-2-deuterio-1,2-diphenylethyl-*N*-carbomethoxysulfamate triethylammonium salt and only α-deuterio-*trans*-stilbene from the corresponding erythro compound. The first-order rate constants for the diphenylethanol system were determined spectrophotometrically ($k_{35°} = 2.66 \times 10^{-6}$) and a small β-deuterium isotope effect was observed ($k_H/k_D = 1.05$ for erythro and 1.08 for threo compound). Activation parameters were calculated for the thermolysis with values $E_a = 22.4$ kcal/mol, $\Delta H^{\ddagger} = 21.7$ kcal/mol, $\Delta G^{\ddagger} = 22.8$ kcal/mol, $\Delta S^{\ddagger} = -3.3$ eu. These kinetic and stereochemical results are consistent with an initial rate-limiting formation of an ion pair followed by a fast cis β proton transfer to the departing anion at a rate greater than the interconversion of erythro- and threo ion pairs.

The dehydration of alcohols *via* a first-order thermolytic Ei decomposition of a derived ester has been a valuable method in the portfolio of practiced synthetic organic reactions. When compared to solvolytic elimination, the cis-β hydrogen geometrical constraint and the absence of α-carbon carbonium ion character (and thus skeletal rearrangements) in the transition state of such eliminations provide a predictable and therefore strategically useful step in a directed synthetic sequence. A variant of the Ei mechanism timing exists in which ionization of the α carbon attached group results in an ion pair whose collapse involves transfer of the β hydrogen from the cation to anion. This mechanism is especially important in cases of elimination with good leaving groups in nonpolar media. Such an ion-pair mechanism may show the kinetic order and stereospecificity of an Ei scheme but in many cases carbonium ion rearrangements are observed.

In order to minimize such rearrangements but preserve the stereospecificity of a solution (for operational convenience) Ei reaction in a synthetic step, the reacting system should be of such a design as to reduce the degree of ion-pairing character. To meet this requirement the departing anionic group should have a good incipient proton nucleophilicity in solvents of low polarity. Furthermore, if the developing anion has multiple proton acceptor sites the $\Delta G^{\ddagger}$ will be decreased owing to an increased positive entropy contribution. Finally, the formation of the requisite alcohol derivative should be facile even in the presence of severe steric factors.[1] With such criteria in mind we have examined the thermolytic behavior of alkyl *N*-carbomethoxysulfamate salts, **1**, as intermediates in a potential synthetic method for the conversion of alcohols to alkenes.

The triethylammonium *N*-carbomethoxysulfamates (**1**) employed in this study were generated by the interaction of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt (**2**) with the candidate alcohols

(1) For example, mesylates of alcohols are more readily formed than tosylates, since the former result from an addition to a reactive sulfene generated from the dehydrohalogenation of the precursor methanesulfonyl chloride.