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# Preparation and Reactions of Sulfonimidoyl Chlorides

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The first examples of alkanesulfonimidoyl chlorides were prepared by reaction of alkanesulfinyl chlorides with dichloroamines. A new, general route to sulfonimidoyl chlorides based on chlorination of sulfinamides was developed. Base-promoted substitutions of chloride in alkanesulfonimidoyl chlorides were shown to proceed through iminosulfene intermediates which could be trapped in [2 + 2] cycloaddition reactions.

Derivatives of sulfonimidic acid were synthesized for the first time in 1960 by Levchenko and her co-workers.[1] This Russian group has developed methods for the preparation of arenesulfonimidoyl chlorides based on the reaction of arenesulfinyl chlorides with positive *N*-halogen compounds (eq 1). The arenesulfonimidoyl chlorides were found to undergo

$$\mathrm{ArS(O)Cl + RNClX \longrightarrow ArS(O)(NR)Cl + ClX} \qquad (1)$$

X = Cl, Na

the same types of reactions as sulfonyl chlorides, giving the usual derivatives. The reactivity, however, is greatly affected by the substituent R on the imino group.[2] The similarities between sulfonimidoyl chlorides and sulfonyl chlorides led us to consider the possibility of preparing alkanesulfonimidoyl chlorides, and by base-promoted elimination of hydrogen chloride generate iminosulfenes. The latter can be considered as nitrogen analogues of sulfenes which are generated by base-promoted reactions of alkanesulfonyl chlorides.[3-5] The greater possibility of structural variation in sulfonimidoyl chlorides owing to the nitrogen function added interest to this work. During the course of this work, a new method, with increased possibilities of varying the substituent on nitrogen, for the synthesis of sulfonimidoyl chlorides was developed starting from readily available sulfinamides.

**Preparation of Sulfonimidoyl Chlorides.** The first examples of alkanesulfonimidoyl chlorides **1–3** were prepared in like manner to arenesulfonimidoyl chlorides[6] from alkanesulfinyl chlorides and dichloroamines in 57–91% yield. Compound **1** with an *N*-butyl group was found to be quite unstable, decomposing rapidly at room temperature or by the action of moisture. On the other hand, the *N*-*p*-toluenesulfonyl substituted derivatives **2** and **3** were very stable; they react very slowly with water or alcohols in the absence of base and, in fact, can be recrystallized without loss from methanol. This original synthetic method, however, is limited by the lack of availability of sulfinyl chlorides and positive *N*-chloro compounds; no *N*-arylsulfonimidoyl compound, for instance, has been prepared by this route. The simple method we worked out circumvents these limitations. Starting from sulfinamides and oxidizing with chlorine (eq 2) in an organic

$$\mathrm{RS(O)NHR' + Cl_2 \longrightarrow RS(O)(NR')Cl + HCl} \qquad (2)$$

solvent at room or lower temperatures gave sulfonimidoyl chlorides in good yields (Table I). Sulfinamides are available in high yield and with a wide range of structural variations via *N*-sulfinyl compounds and organometallics[7-9] and also by other methods.[10] Other positive chlorine oxidants should also achieve the same reaction; this was demonstrated by oxidizing *N*-methylbenzenesulfinamide to **6** with *N*-chlorobenzotriazole; *tert*-butyl hypochlorite can also be used.[11] After our original communication,[2] Wudl[12] reported a similar oxidation using *N*-chlorobenzotriazole. For most purposes chlorine is an excellent reagent because of ease of handling and neither excess chlorine nor the liberated hydrogen chloride react with the products, in most cases. However, in the case of **8** where an easily chlorinated *N*-phenyl group is present, excess chlorine sometimes caused the reaction mixture to inflame when allowed to warm. At −78 °C no aryl chlorination took place. Compound **4** is comparable in stability and reactivity with **2** and **3**; **5** is stable but rearranges in the presence of base (see below); **6** and **10** are of intermediate stability while **8** and **9** decompose at room temperature within hours. Compounds **11**, **12**, and **13** were not isolated but were directly converted to amides. The most surprising result from this chlorine oxidation of sulfinamides was that unsubstituted benzenesulfinamide gave a monomeric sulfonimidoyl chloride (**7**) which crystallized as the hydrochloride from the reaction mixture; the hydrochloride was unstable at room temperature.

**Preparation of Derivatives.** Amides derived from sulfonimidoyl chlorides are obtained in good yields by standard reactions; simple amides, particularly the dimethylamides, were useful for characterization of the less stable sulfonimidoyl chlorides (Table I). When the hydrochloride of **7** was treated with pyridine, a polymer was formed; but in the re-

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**Table I. Sulfonimidoyl Chlorides**

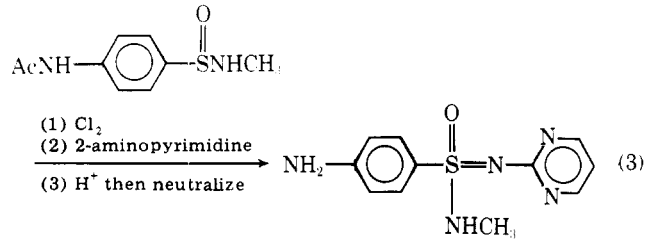
$$RS(=O)(Cl)=NR'$$

| | R | R′ | method of preparation[a] | % yield | mp, °C | amide mp, °C | dimethylamide mp, °C |
|---|---|---|---|---|---|---|---|
| 1 | $CH_3$ | $n$-$C_4H_9$ | A | 91 | oil | 21–23 | |
| 2 | $CH_3$ | $p$-$CH_3C_6H_4SO_2$ | A | 73 | 99–101 | 172–173 | |
| 3 | $CH_3CH_2$ | $p$-$CH_3C_6H_4SO_2$ | A | 57 | 44–45 | | 99–100 |
| 4 | $CH_2Cl$ | $p$-$CH_3C_6H_4SO_2$ | B | 89 | 70–71 | | |
| 5 | $CHCl_2$ | $p$-$CH_3C_6H_4SO_2$ | B | 71 | oil | | |
| 6 | $C_6H_5$ | $CH_3$ | B, C | 89 | oil | | oil |
| 7 | $C_6H_5$ | H | B | 69[b] | | | 73–75 |
| 8 | $C_6H_5CH_2$ | $C_6H_5$ | B | 100 | | 174–175 | 79–80 |
| 9 | $C_6H_5CH_2$ | $p$-$C_6H_4Cl$ | B | 52 | | 143–144 | 93–94 |
| 10 | $C_6H_5CH_2$ | 2,4,6-$C_6H_2Cl_3$ | B | 77 | 76–78 | | 87–88 |
| 11 | $p$-$CH_3CONHC_6H_4$ | $CH_3$ | B | ~50 | c | | 162–164 |
| 12 | $p$-$CH_3CONHC_6H_4$ |  | C | ~50 | c | | |
| 13 | $p$-$CH_3C_6H_4$ | $CONH$-$n$-$C_4H_9$ | C | >80 | c | | |

[a] A, dichloroamine and sulfinyl chloride; B, chlorine oxidation; C, oxidation with $N$-chlorobenzotriazole. [b] Obtained as the hydrochloride. [c] Converted directly to amides.

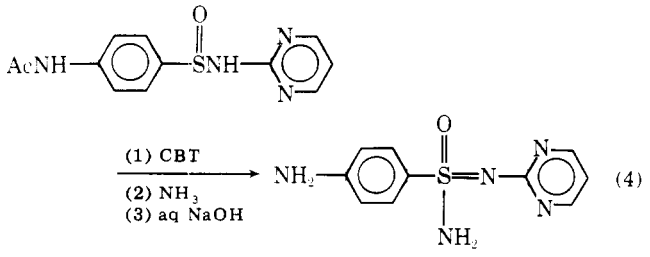
action with dimethylamine a mixture of the desired dimethylamide (30%) and polymer was obtained. Compound **6** upon reaction with ammonia and the hydrochloride of **7** upon reaction with methylamine gave polymeric products.

Using the sulfinamide oxidation technique several analogues of biologically active sulfonamides have been prepared (eq 3, 4, and 5). For compounds in which molecular chlorine



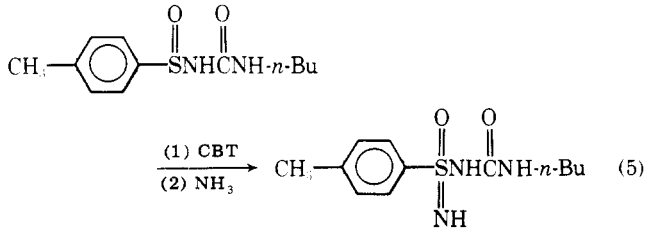

(3)

**14**




(4)

**15**



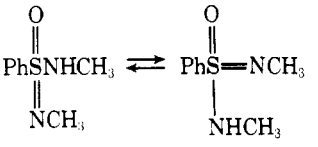

(5)

**16**

CBT = $N$-chlorobenzotriazole

was likely to cause secondary reactions, the milder positive halogen oxidant, $N$-chlorobenzotriazole, was found to be preferable. Compounds **14** and **15**, which are related to the potent sulfanilamide sulfadiazine, did not exhibit sufficient activity to be of interest as antibacterials. Compound **16**, an analogue of the hyperglycemic agent tolbutamide, was found to be inactive in an antidiabetic screen.

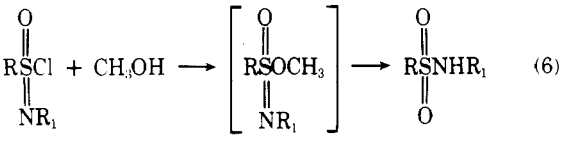
In the monosubstituted sulfonimidamides, tautomeric forms are possible; in the NMR spectra of **17** in carbon tetrachloride and dimethyl sulfoxide, the two $NCH_3$ gave one




**17**

sharp singlet suggesting a rapid exchange of the NH proton. In the corresponding dimethylamide derived from **6** the amide and imine $N$-methyl signals are separated as expected. In **14**, NMR indicates the structure shown.

Solvolyses of the sulfonimidoyl chlorides in methanol produced the corresponding sulfonamide (eq 6). The methyl



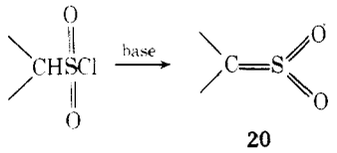

(6)

ester first formed was not isolated because under these reaction conditions, the intermediate ester undergoes substitution very easily with nucleophiles, e.g., chloride ion or methanol present in solution. The reactivity of these sulfonimidates is understandable because the sulfonamide or anion thereof should be superb leaving groups. The factors determining the reactivity of alkyl sulfonimidates have been discussed in a paper by Levchenko.[13] They were able to isolate alkyl $N$-methylarenesulfonimidates and study some of the alkylating properties. Aryl–oxygen cleavage in aryl esters, on the other hand, could be expected to be less favorable and aryl esters therefore stable. The phenyl ester **18** was made from **2** in very good yield via an iminosulfene intermediate (see below). The


**18** **19**

phenyl ester **19** was prepared according to Levchenko[14] by heating **6** with sodium phenoxide in benzene or better, oxidizing with chlorine in ether or with *N*-chlorobenzotriazole in dichloromethane, and adding the solution to sodium phenoxide dissolved in acetone or dimethylformamide (yield 75–85%).

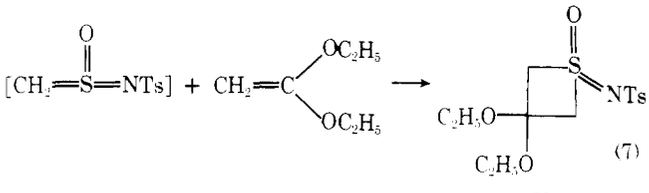
**Generation and Trapping of Iminosulfenes.** There has been considerable interest in the chemistry of the unstable intermediate sulfene **20** generated by a 1,2 elimination of hydrogen chloride from primary and secondary alkanesulfonyl chlorides by means of base (eq 6).[3-5] Sulfenes as short-lived




(6)

**20**

intermediates have been detected by chemical[15,16] and kinetic[17] methods and have been generated under a variety of conditions. In the normally observed reactivity of sulfenes the sulfonyl group exhibits electrophilic character. The isoelectronic nitrogen analogue of sulfene, which we have called iminosulfene, has, due to the nitrogen function, an additional site for structural manipulation. The first indication of the existence of an iminosulfene intermediate was obtained from solvolytic behavior in methanol: **2** and **3** were recrystallized unchanged from this solvent and in order to achieve solvolysis, heating under reflux for several hours was necessary. When triethylamine or pyridine was added, the solvolysis was completed within minutes even at 0 °C; a base-promoted reaction is consistent with an iminosulfene intermediate. To gain conclusive evidence, the same technique of accessing deuterium incorporation as used by King[15] and Truce[16] was employed. When the solvolysis of **2** was run in methanol-*O*-*d* without base present, no deuterium was incorporated on the $\alpha$ carbon. However, when the reaction was run with triethylamine present, the isolated sulfonamide was found by NMR and mass spectral analysis to consist of 80% monodeuterated and 20% undeuterated sulfonamide (Scheme I). The absence of di- and trideuterated products is in line with a sulfene-like intermediate; a simple base-catalyzed exchange should also give some di- and trisubstituted products. Of the more reactive alkanesulfonimidoyl chlorides, **10** was also found to incorporate deuterium almost completely under the same reaction condition as above, but **8** and **9** reacted very sluggishly and gave a mixture of several unidentified products. The iminosulfene generated from **2** was also intercepted (eq 7) by the



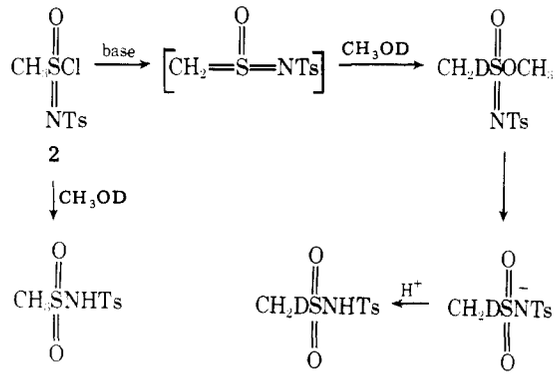

(7)

**21**

electron-rich double bond of 1,1-diethoxyethene to give the cycloaddition product **21**. The yield of isolated product was only 10% when triethylamine was used as base, but increased to 33% employing the stronger base diazobicyclooctane. Similar dependence on base strength in sulfene reactions has been observed by Truce and Norell.[17] The byproduct from this reaction was *N*-(*p*-tolylsulfonyl)chloromethanesulfinamide (**23**), indicating a competition between 1,2 and 1,3 addition. In accordance with this, the bulkier ethanesulfonimidoyl chloride failed to give the cycloaddition product. The ketal **21** was found to be resistant to hydrolysis in concentrated hydrochloric acid under a variety of conditions.

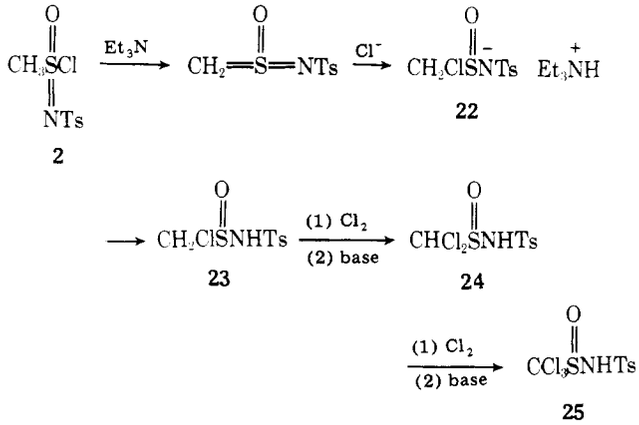
Attempts were made to generate iminosulfene without a trapping agent present in order to obtain a stable solution of

**Scheme I**



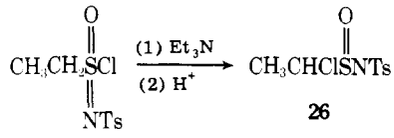

**2**

**Scheme II**




**2** **22** **23** **24** **25**

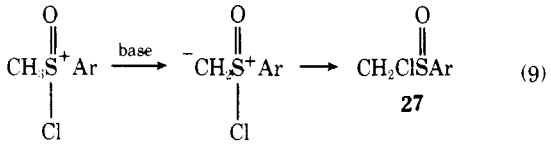
iminosulfene, but without success. Addition of **2** to triethylamine in organic solvents at various temperatures in a nitrogen atmosphere resulted in an instantaneous formation of a precipitate which was found to be the salt of *N*-(*p*-tolylsulfonyl)chloromethanesulfinamide **22** (Scheme II). The sulfinamide **23**, obtained after acidification, was subjected to oxidation with chlorine; after reaction with triethylamine, the dichloromethanesulfinamide **24** was obtained and in a similar way trichloromethanesulfinamide **25** was obtained. With **3** this reaction created a new chiral center and gave rise to two diastereomers (eq 8). The more unstable alkanesulfonimidoyl




(8)

**3** **26**

chlorides **8**, **9**, and **10** were also subjected to reaction with triethylamine in organic solvents, but no conclusive results were obtained because several unidentified products were isolated. Addition of dimethylamine some time after the addition of triethylamine gave no dimethylamides, showing that the initially formed iminosulfenes react with one of the reaction components. That is the normally observed reaction of sulfene generated from alkanesulfonyl chlorides in the absence of trapping agents.[18] The reaction as pictured in Scheme II involving an "abnormal addition" to iminosulfene is the most plausible, especially in the light of the recent findings in sulfene chemistry of King and Beatson,[19] who demonstrated the reverse process, i.e., formation of sulfene from 1-chloroethanesulfinate anion. However, an intramolecular migration of chlorine from the sulfur to the $\alpha$ carbon cannot be excluded. A somewhat similar reaction which has been proposed to be intramolecular is the formation of $\alpha$-chlorosulfoxides[27] by chlorination of sulfoxides in the presence of base (eq 9).[20] This latter reaction is said to be highly stereospecific; in contrast,



(9)

27

our reaction gave a mixture of two diastereomers when the $\alpha$ carbon was a prochiral center.

## Experimental Section

***N*-Butylmethanesulfonimidoyl Chloride (1).** To 3.27 g of methanesulfinyl chloride dissolved in 10 mL of carbon tetrachloride and cooled in an ice bath was added over 15 min 4.26 g of *N,N*-dichlorobutylamine dissolved in 20 mL of carbon tetrachloride. After filtering and evaporation, there remained 5.1 g of **1**, a colorless oil (which decomposed and deposited crystals of butylamine hydrochloride on standing, rapidly at room temperature, slowly at −10 °C): $n^{25}_D$ 1.4905; IR ($CHCl_3$) 1320 and 1150 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 3.62 (s, 3), 3.30 (t, 2), 1.75–0.80 (m, 7).

*N*-Butylmethanesulfonamide, mp 80 °C, was obtained by adding **1** to water or methanol and evaporating.

***N*-Butylmethanesulfonimidamide** was prepared by adding **1** to ammonia in benzene. Dilute hydrochloric acid was added and after extraction with ether and evaporation of solvent, the amide was recrystallized from ether: mp 21–23 °C; IR (neat) 1310 and 1150 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 3.30–2.77 (m, 5), 1.80–0.70 (m, 7).

Anal. Calcd for $C_5H_{14}N_2OS$: C, 39.97; H, 9.39; S, 21.34. Found: C, 39.79; H, 8.89; S, 21.56.

***N*-(*p*-Tolylsulfonyl)methanesulfonimidoyl Chloride (2).** Dichloramine-T (17.6 g, 73.3 mmol) was dissolved in 50 mL of ethanol-free chloroform and filtered. This solution was added over 30 min to 6.56 g (66.6 mmol) of methanesulfinyl chloride in 10 mL of chloroform cooled in an ice bath. After stirring at room temperature for 3 h the solvent was removed and the residue was recrystallized from methanol to yield 13.1 g (73%) of **2** as a white solid: mp 99–101 °C; IR ($CHCl_3$) 1330 and 1155 ($SO_2$), 1280 and 1105 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.85 (m, 2), 7.32 (m, 2), 3.78 (s, 3), 2.43 (s, 3).

Anal. Calcd for $C_8H_{10}ClNO_3S_2$: C, 35.88; H, 3.76; S, 23.95. Found: C, 35.64; H, 3.62; S, 23.73.

***N*-Methylsulfonyl-*p*-toluenesulfonamide,** mp 119–120 °C, was obtained by heating **2** in acetone–water for 3 h or in methanol for 5 h.

***N*-(*p*-Tolylsulfonyl)methanesulfonimidamide** was prepared by heating **2** in concentrated ammonia for 1 h. On cooling the amide crystallized and was recrystallized from ethanol: mp 172–173 °C; IR (Nujol) 1280 and 1150 ($SO_2$), 1250 and 1100 $cm^{-1}$ (N=S=O); NMR ($Me_2SO$-$d_6$) $\delta$ 7.48–7.28 (m, 4), 3.32 (s, 3), 2.42 (s, 3).

Anal. Calcd for $C_8H_{12}N_2O_3S_2$: C, 38.69; H, 4.87; S, 25.82. Found: C, 38.45; H, 4.69; S, 25.55.

***N,N*-Dimethyl-*N'*-(*p*-tolylsulfonyl)methanesulfonimidamide** was obtained from **2** and dimethylamine in benzene. Dilute hydrochloric acid was added and the amide was extracted with ether, the ether was evaporated, and the amide was recrystallized from ethanol: mp 99–100 °C; IR (Nujol) 1310 and 1150 ($SO_2$), 1260 and 1075 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.93–7.20 (m, 4), 3.08 (s, 3), 3.00 (s, 6), 2.43 (s, 3).

Anal. Calcd for $C_{10}H_{16}N_2O_3S_2$: C, 43.46; H, 5.84; S, 23.20. Found: C, 43.61; H, 5.91; S, 22.98.

**Phenyl *N*-(*p*-Tolylsulfonyl)methanesulfonimidate (18).** The chloride **2** (1.34 g, 5 mmol) dissolved in 15 mL of benzene was added to 2.35 g (25 mmol) of phenol and 0.5 mL of pyridine in 15 mL of benzene cooled in an ice bath. The reaction mixture was stirred overnight, poured into 2 M sodium hydroxide, and extracted with ether. After washing and drying the extract, evaporation of the solvent and recrystallization from methanol yielded 1.30 g (80%) of the ester: mp 69–71 °C; IR (Nujol) 1330, 1315, 1275, 1155, and 1080 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.93–7.07 (m, 9), 3.43 (s, 3), 2.40 (s, 3).

Anal. Calcd for $C_{14}H_{15}NO_4S_2$: C, 51.69; H, 4.62; S, 19.71. Found: C, 51.62; H, 4.72; S, 19.22.

***N*-(*p*-Tolylsulfonyl)ethanesulfonimidoyl Chloride (3)** was prepared in like manner to **2**. Ethanesulfinyl chloride (2.25 g, 20 mmol) yielded after one recrystallization from methanol 3.20 g (57%) of **3**: mp 44–45 °C; IR ($CHCl_3$) 1330 and 1155 ($SO_2$), 1280 and 1105 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.88 (m, 2), 7.32 (m, 2), 3.83 (q, 2), 2.45 (s, 3), 1.60 (t, 3).

Anal. Calcd for $C_9H_{12}ClNO_3S_2$: C, 38.36; H, 4.29; S, 22.76. Found: C, 38.18; H, 4.30; S, 22.76.

***N*-(*p*-Tolylsulfonyl)chloromethanesulfonimidoyl Chloride (4).** To a suspension of 1.07 g (4 mmol) of *N*-(*p*-tolylsulfonyl)chloromethanesulfinamide in 30 mL of benzene was added excess dry chlorine from a tank at a slow rate at room temperature. Stirring was continued until all sulfinamide had dissolved. The solution, yellow from excess chlorine, was evaporated to dryness and the residue was recrystallized from carbon tetrachloride to give 1.06 g (88%) of **4**: mp 70–71 °C; IR ($CHCl_3$) 1340 and 1165 ($SO_2$), 1300 and 1110 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.93 (m, 2), 7.37 (m, 2), 5.20 (s, 2), 2.47 (s, 3).

Anal. Calcd for $C_8H_9Cl_2NO_3S_2$: C, 31.80; H, 3.00; S, 21.22. Found: C, 31.79; H, 3.08; S, 21.07.

***N*-(*p*-Tolylsulfonyl)dichloromethanesulfonimidoyl Chloride (5).** *N*-(*p*-Tolylsulfonyl)dichloromethanesulfinamide (1.2 g) was suspended in 15 mL of benzene. An excess of chlorine was bubbled through the solution until all sulfinamide had dissolved. The solution was evaporated to dryness and the oil was dissolved in a small volume of carbon tetrachloride and filtered to remove insoluble impurities. After evaporating the solvent, 0.95 g (71% yield) of a viscous liquid was obtained. Attempts to purify this chloride by chromatography failed and the crude product was used in the following experiment: IR (neat) 1340 and 1165 ($SO_2$), 1300 and 1110 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 8.00–7.30 (m, 4), 6.91 (s, 1), 2.50 (s, 3).

***N*-(*p*-Tolylsulfonyl)trichloromethanesulfinamide.** Crude **5** (0.40 g) in 10 mL of ether was added to dimethylamine in ether at −78 °C. After warming, the reaction mixture was poured into 2 M hydrochloric acid and was extracted with ether. The extract was washed with water, dried, and taken to dryness. The resulting solid was recrystallized from carbon tetrachloride to give crystals: mp 143–144 °C; IR (Nujol) 1370, 1170, and 1130 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.90–7.27 (m, 4), 6.66 (s, 1), 2.47 (s, 3).

Anal. Calcd for $C_8H_8Cl_3NO_3S_2$: C, 28.54; H, 2.40; S, 19.05. Found: C, 28.61; H, 2.50; S, 19.06.

***N*-Methylbenzenesulfonimidoyl Chloride (6).** To 1.00 g of *N*-methylbenzenesulfinamide dissolved in ether and kept at −78 °C was added dry chlorine to excess. After filtration and removal of solvent, there remained 1.10 g (89% yield) of a colorless oil: IR (neat) 1320 and 1190 $cm^{-1}$. When *N*-chlorobenzotriazole was used instead of chlorine for the oxidation, the solution was used as such (see below) because of difficulties expected in separating the acid chloride from the benzotriazole. When a sample was withdrawn and evaporated to dryness, the infrared spectrum indicated a mixture of **6** and benzotriazole.

**Phenyl *N*-Methylbenzenesulfonimidate (19).** *N*-Methylbenzenesulfinamide (1.55 g, 10 mmol) and 0.8 mL of pyridine in ether cooled in dry ice was oxidized with chlorine. The hydrochloride was filtered off and the solution was evaporated. Benzene was added and the resulting solution was added to a slurry of 1.28 g (11 mmol) of sodium phenoxide in 25 mL of benzene. After heating on a steam bath for 1.5 h and cooling, the sodium chloride was filtered and the solution was evaporated to dryness to give an oil which crystallized. Recrystallization from methanol yield 1.95 g (79%) of **18**, mp 88–89 °C (lit.[6] 88–89 °C).

***N,N'*-Dimethylbenzenesulfonimidamide** was prepared by adding **6** to methylamine. The product, recrystallized from ethanol, had: mp 99–100 °C; IR ($CHCl_3$) 1265 and 1160 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.97 (m, 2), 7.53 (m, 3), 5.20 (s, 1), 2.70 (s, 6).

Anal. Calcd for $C_8H_{12}N_2OS$: C, 52.15; H, 6.56; S, 1740. Found: C, 52.33; H, 6.76; S, 1745.

***N*-Methylbenzenesulfinamide.** Benzenesulfinyl chloride (5.0 g) dissolved in ether was added to methylamine dissolved in ether and cooled in dry ice. The solution was filtered and taken to dryness to yield 4.9 g (100%) of a pale yellow oil. A sample sent for analysis was chromatographed on silica gel with ether and this sample crystallized after several weeks in a refrigerator: mp ~25 °C; IR ($CHCl_3$) 1045 (SO); NMR ($CDCl_3$) $\delta$ 7.57 (m, 5), 5.30 (s, 1), 2.50 (d, 3).

Anal. Calcd for $C_7H_9NOS$: C, 54.17; H, 5.84; S, 20.66. Found: C, 54.11; H, 6.01; S, 20.42.

**Benzenesulfonimidoyl Chloride Hydrochloride.** To 0.30 g of benzenesulfinamide in ether cooled in dry ice was added dry chlorine. The sulfinamide dissolved during the addition and when excess chlorine was added, a solid precipitated. The solvent was evaporated, the residual oil was redissolved in a small volume of dry ether, and the solution was filtered and taken to dryness to give 0.31 g (69%) of a colorless oil which solidified at −15 °C: IR (neat) 2950 (broad NH), 1280 and 1155 $cm^{-1}$ (N=S=O). The hydrochloride decomposed if stored at room temperature. Benzenesulfonamide, mp 152–153 °C, was obtained by treatment of the above hydrochloride with methanol.

***N,N*-Dimethylbenzenesulfonimidamide** was prepared in 30% yield by adding an ether solution of the above hydrochloride to dimethylamine in ether at −78 °C. Amine hydrochloride (2 equiv) was removed and the solvent was evaporated. The remaining oil was

chromatographed on silica gel–ether. After recrystallization from carbon tetrachloride a solid with mp 73–75 °C was obtained (lit.[50] 76–77 °C): IR ($CHCl_3$) 3350 (NH), 1250 and 1130 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.93–7.57 (m, 5), 2.70 (s, 6).

***N*-Phenylbenzenemethanesulfonimidoyl Chloride (8).** Chlorine was bubbled through a suspension of 1.0 g of *N*-phenylbenzenemethanesulfinamide in ether cooled in dry ice until a solution was obtained. On standing a yellow solid precipitated and was collected by filtering at −78 °C or by decanting the solvent. (The low temperature is necessary to prevent chlorination of the *N*-phenyl group.) The crude product (1.15 g, 100%) was obtained and recrystallized by first dissolving the material in ether at room temperature and then adding the same volume of petroleum ether and cooling in dry ice. The acid chloride was found to be very sensitive to moisture and decomposed if stored at room temperature: IR ($CHCl_3$) 1325 and 1220 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.30 (m, 10), 5.00 (s, 2).

***N*-Phenylbenzenemethanesulfonamide,** mp 98–99 °C (lit. 101 °C), IR ($CHCl_3$) 1340 and 1150 $cm^{-1}$ ($SO_2$), was obtained by adding **8** to methanol and recrystallizing the product from ethanol.

***N,N*-Dimethyl-*N'*-phenylbenzenemethanesulfonimidamide** was prepared by adding an ether solution of dimethylamine to **8** dissolved in benzene. The reaction mixture was added to 2 M hydrochloric acid, extracted with ether, washed with water, dried, and evaporated. After recrystallization from ethanol, a white solid, mp 79–80 °C, was obtained: IR ($CHCl_3$) 1290 and 1225 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.40 and 7.13 (m, 10), 4.40 (s, 2), 2.67 (s, 6).

Anal. Calcd for $C_{15}H_{18}N_2OS$: C, 65.66; H, 6.61; S, 11.69. Found: C, 65.39; H, 6.67; S, 11.81.

***N*-Phenylbenzenemethanesulfonimidamide** was prepared from **8** and ammonia in benzene. The precipitate of ammonium chloride was filtered off, and evaporation of the solvent and recrystallization from ethanol afforded a white solid: mp 174–175 °C; IR (Nujol) 1310 and 1220 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.47–7.13 (m, 10), 4.47 (s, 2), 3.77 (s, 2, $NH_2$).

Anal. Calcd for $C_{13}H_{14}N_2OS$: C, 63.39; H, 5.73. Found: C, 63.14; H, 5.71.

***N*-(*p*-Chlorophenyl)benzenemethanesulfonimidoyl Chloride (9).** A similar procedure as in the preparation of **8** was used but after an excess of chlorine had been added at −78 °C the reaction mixture with excess chlorine was allowed to warm to room temperature. Monochlorination of the *N*-phenyl group took place at about 0 °C; occasionally the mixture enflamed, especially if the starting sulfinamide was impure. Compound **9** obtained in 52% yield is less reactive than **8**, but decomposes if stored at room temperature: IR ($CHCl_3$) 1325 and 1220 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.30 (m, 9), 5.00 (s, 2). A safer route to this compound would be to start from *N*-(chlorophenyl)benzenemethanesulfinamide.

***N*-(*p*-Chlorophenyl)phenylmethanesulfonamide** was obtained from **9** and methanol and was recrystallized from ethanol: mp 110–111 °C; IR ($CHCl_3$) 1330 and 1150 $cm^{-1}$ ($SO_2$); NMR ($CDCl_3$) $\delta$ 7.28 (m, 9 + NH), 4.28 (s, 2).

Anal. Calcd for $C_{13}H_{12}ClNO_2S$: C, 55.41; H, 4.29; S, 11.38. Found: C, 55.35; H, 4.27; S, 11.41.

The compound was also prepared from phenylmethanesulfonyl chloride and *p*-chloroaniline; the compounds from the two preparations had identical spectral properties.

***N,N*-Dimethyl-*N'*-(*p*-chlorophenyl)benzenemethanesulfonimidamide,** prepared from **9** and dimethylamide, had: mp 93–94 °C (ethanol); IR ($CHCl_3$) 1300 and 1215 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.43 and 7.10 (m, 9), 4.40 (s, 2), 2.67 (s, 6).

Anal. Calcd for $C_{15}H_{17}ClN_2OS$: C, 58.34; H, 5.55; S, 10.38. Found: C, 58.64; H, 5.67; S, 10.65.

***N*-(*p*-Chlorophenyl)benzenemethanesulfonimidamide,** prepared from **9** and ammonia in benzene, had: mp 143–144 °C (ethanol); IR (Nujol) 1300 and 1210 (N=S=O), 3450–3350 $cm^{-1}$ (NH); NMR ($CDCl_3$) $\delta$ 7.47–6.97 (m, 9), 4.43 (s, 2), 3.87 (s, 2).

Anal. Calcd for $C_{13}H_{13}ClN_2OS$; C, 55.61; H, 4.67; S, 11.42. Found: C, 55.50; H, 4.98; S, 11.38.

***N*-(2,4,6-Trichlorophenyl)benzenemethanesulfonimidoyl Chloride (10).** To 1.65 g of *N*-(2,4,6-trichlorophenyl)benzenemethanesulfinamide suspended in ether at −78 °C was added chlorine to excess. After warming to room temperature the solvent was removed, and the product was recrystallized from ether–petroleum ether to yield 1.40 g (77%) of **10** as white solid: mp 76–78 °C; IR ($CHCl_3$) 1320 and 1230 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.50–7.30 (m, 7), 5.18 (q, 2).

***N,N*-Dimethyl-*N'*-(2,4,6-trichlorophenyl)benzenemethanesulfonimidamide** was obtained from **10** and dimethylamine in ether at −78 °C. Recrystallization once from ether and once from ethanol yielded a white solid: mp 87–88 °C; IR ($CHCl_3$) 1300 and 1220 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.43–7.30 (m, 7), 4.50 (s, 2), 2.83 (s, 6).

Anal. Calcd for $C_{15}H_{15}Cl_3N_2OS$: C, 47.70; H, 4.00; S, 8.49. Found: C, 47.68; H, 4.07; S, 8.64.

***N*-(2,4,6-Trichlorophenyl)benzenemethanesulfonamide** was formed when **10** was heated with ethanol and was recrystallized from ethanol: mp 147–148 °C; IR (Nujol) 1330 and 1160 $cm^{-1}$ ($SO_2$); NMR ($CDCl_3$) $\delta$ 7.47 (m, 7), 6.13 (s, 1), 4.63 (s, 2).

Anal. Calcd for $C_{13}H_{10}Cl_3NO_2S$: C, 44.53; H, 2.88; S, 9.14. Found: C, 44.29; H, 2.93; S, 8.91.

***N*-(2,4,6-Trichlorophenyl)benzenemethanesulfinamide.** A Grignard reagent, prepared in ether from 2.4 g (0.1 g-atom) of magnesium and 12.7 g (100 mmol) of $\alpha$-chlorotoluene, was cooled in an ice bath. To this solution was added 18.0 g (74 mmol) of 2,4,6-trichloro-*N*-sulfinylbenzenamine in ether. When the addition was complete, a saturated ammonium chloride solution was added. A yellow precipitate was obtained which was filtered and washed with ether and yielded 23.5 g of crude product which was recrystallized from benzene to give a yellow solid: mp 125–130 °C dec; IR ($CHCl_3$) 1085 $cm^{-1}$ (SO); NMR ($CDCl_3$) $\delta$ 7.50–7.33 (m, 7), 5.80 (s, 1), 4.27 (s, 2).

The compound decomposed if stored at room temperature, but it was possible to store it unchanged for several weeks in a refrigerator. By oxidation with potassium permanganate the corresponding sulfonamide, mp 147–148 °C, was obtained in low yield and was found to be identical with an authentic sample.

**4-Acetamidobenzenesulfinyl Chloride.** 4-Acetamidobenzenesulfinic acid (10 g) was added slowly to 50 mL of thionyl chloride with stirring. The fine white crystals of acid dissolved, and then a heavy yellow precipitate formed. After 30 min, 50 mL of dry ether was added. The yellow precipitate was filtered and washed with ether to yield a finely divided yellow solid (9 g), mp 161–163 °C.

***N*-Methyl-4-acetamidobenzenesulfinamide.** The sulfinyl chloride (9 g) from the above reaction was added to excess methylamine in 50 mL of dry THF at −78 °C. The reaction was allowed to warm to room temperature with stirring. After 1 h, the reaction was taken to dryness in vacuo to yield 13.0 g of white solid which was a mixture of methylamine hydrochloride and sulfinamide. The mixture was never purified but used as such.

***N*-Methyl-4-acetamidobenzenesulfonimidoyl Chloride.** The sulfinamide mixture (5 g) from above was suspended in dry ether at −78 °C. Excess dry chlorine was bubbled through the solution, and it was then stirred at −78 °C for 15 min. The mixture was then taken to dryness in vacuo and used directly in the subsequent reaction. The chloride appeared stable at room temperature.

***N,N,N'*-Trimethyl-4-acetamidobenzenesulfonimidamide.** The sulfonimidoyl chloride from the above reaction was added to an excess of dimethylamine in dichloromethane at −78 °C and then warmed to room temperature. After stirring for about 15 min, the mixture was taken to dryness in vacuo. The resulting solid was suspended in acetone and passed through a 8-cm silica gel column in order to remove the amine hydrochloride. The product was crystallized from acetone–ethyl acetate to yield 2.0 g, mp 162–164 °C.

***N,N,N'*-Trimethyl-4-aminobenzenesulfonimidamide.** The *N*-acetyl compound (2 g) from above was dissolved in 100 mL of 2 M hydrochloric acid and heated on a steam bath for 1 h. The solution was made slightly basic with sodium hydroxide, extracted with methylene chloride, and taken to dryness in vacuo. The resulting solid was crystallized from acetone to yield 1.2 g, mp 161–164 °C.

Anal. Calcd for $C_9H_{15}N_3OS$: C, 50.67; H, 7.08; N, 19.69. Found: C, 50.44; H, 6.86; N, 19.41.

***N*-Methyl-*N'*-2-pyrimidyl-4-acetamidobenzenesulfonimidamide.** To a suspension of 2-aminopyrimidine (5.7 g) in 50 mL of dichloromethane was added, with stirring, *N*-methyl-4-acetamidobenzenesulfonimidoyl chloride (27 mmol) all at once. The solution was stirred for 3 h. A yellow solid was obtained after solvent removal. This solid was stirred in water for 30 min and then filtered to yield a white solid which was crystallized from methanol to yield 2.1 g, mp 263–264 °C.

***N*-Methyl-*N'*-2-pyrimidyl-4-aminobenzenesulfonimidamide.** The above *N*-acetyl compound (2.1 g) was dissolved in 40 mL of 2 M hydrochloric acid and heated on a steam bath for 45 min. The resulting pale green solution was made basic by the addition of sodium hydroxide. The water was then evaporated and the resulting solid was chromatographed on silica gel to yield 300 mg of product, mp 192–193 °C.

Anal. Calcd for $C_{11}H_{13}N_5OS$: C, 50.13: H, 4.97; N, 26.67. Found: C, 50.33; H, 5.07; N, 26.52.

***N*-(2-Pyrimidyl)-4-acetamidobenzenesulfinamide.** 4-Acetamidobenzenesulfinyl chloride (5.9 g, 27 mmol) was suspended in dry THF and 2-aminopyrimidine (5.2 g, 55 mmol) was added at once.

After 1 h, the yellow precipitate was replaced by a white one. The reaction was taken to dryness under reduced pressure, and the resulting white solid was slurried in water; the slurry was made basic by the addition of excess triethylamine. After stirring for 30 min, the mixture was filtered, and the resulting yellow solid was crystallized from methanol to yield 2.5 g of white crystals, mp 181–183 °C.

***N*-(2-Pyrimidyl)-4-acetamidobenzenesulfonimidamide.** The above *N*-pyrimidyl sulfinamide (3.3 g) was suspended in 70 mL of dry THF. *N*-Chlorobenzotriazole (2.6 g) was added at once. The suspended sulfinamide dissolved, and after 30 min a heavy white precipitate formed. This solid was filtered and then immediately added to liquid ammonia at −78 °C. The solution was allowed to warm to room temperature with stirring. The resulting white solid was slurried in water for 30 min, filtered, and dried to yield 1.8 g of a white solid which was not further purified.

***N*-(2-Pyrimidyl)-4-aminobenzenesulfonimidamide (15).** The above *N*-acetyl compound (1.5 g) was dissolved in 20 mL of 2 M sodium hydroxide and heated on a steam bath for 1.5 h. The solution was carefully neutralized to pH 8 with concentrated hydrochloric acid. The free amine precipitated as fine white crystals, 1.1 g, mp 169–170 °C.

Anal. Calcd for $C_{10}H_{11}N_5OS$: C, 48.18; H, 4.45; N, 28.09. Found: C, 48.12; H, 4.60; N, 27.73.

***N*-Butyl-*N'*-(*p*-toluenesulfinyl)urea.** Potassium *tert*-butoxide (6.36 g, 56.8 mmol) was added to *p*-toluenesulfinamide (8.0 g, 516 mmol), mp 119–121 °C, in 100 mL of dry THF to produce an immediate heavy white precipitate. After 1.5 h, butyl isocyanate (60 mmol) was added via syringe. The mixture became clear. After 20 min, the solution was concentrated to a gum under reduced pressure. The gum was dissolved in cold water and neutralized with 20% HCl to produce a heavy white precipitate. The product was filtered and crystallized from benzene to yield 12.4 g of product, mp 139–144 °C.

***N*-Butyl-*N'*-(*p*-toluenesulfonimidoyl)urea (16).** The above urea (7.5 g, 29.5 mmol) was suspended in 100 mL of dry THF. *N*-Chlorobenzotriazole (4.6 g, 30 mmol) was added, and the solution first became clear and then a precipitate formed. After 25 min, the THF suspension was poured into liquid ammonia at −78 °C and allowed to warm to room temperature with stirring. The mixture was taken to dryness under reduced pressure and proportioned between chloroform and aqueous sodium hydrogen carbonate. The chloroform layer was taken to dryness under reduced pressure, and the product crystallized from benzene to yield white crystals, 6.5 g (82%), mp 152–154 °C.

Anal. Calcd for $C_{12}H_{19}N_3O_2S$: C, 53.51; H, 7.11; N, 15.60. Found: C, 53.79; H, 7.10; N, 15.78.

**Reaction of 2 with Triethylamine and Methanol-*O*-*d*.** *N*-(*p*-Tolylsulfonyl)methanesulfonimidoyl chloride (**2**) (0.801 g) was dissolved in 5 mL of benzene and was added over 15 min to 3 mL of methanol-*O*-*d* and 1.5 mL of triethylamine cooled in an ice bath. Stirring was continued for 2 h and then 10 mL of 2 M hydrochloric acid was added and the product was extracted with ether (7 times). The ether layer was dried and evaporated to give 0.782 g of *N*-(*p*-tolylsulfonyl)methanesulfonamide. After recrystallization from benzene–carbon tetrachloride, 0.620 g (83%) was obtained, mp 119–120 °C; the NMR peak at $\delta$ 3.33 appeared as a broad singlet. Integration against the singlet at $\delta$ 2.43 corresponded to a deuterium content of 0.8 atom per molecule. Analyses by mass spectroscopy of the M and M + 1 peaks showed only undeuterated and monodeuterated products averaging 0.80 atom of deuterium per molecule. When **2** was heated with methanol-*O*-*d* without base present, no deuterium was found in the methyl group of the sulfonamide.

**Reaction of 2 with 1,1-Diethoxyethene.** To a stirred solution of 0.28 g (2.4 mmol) of 1,1-diethoxyethene and 0.26 g (2.3 mmol) of diazabicyclooctane dissolved in 5 mL of benzene and cooled in an ice bath was added over 10 min 0.534 g (2 mmol) of **2** dissolved in 10 mL of benzene. After 15 min 20 mL of 2 M hydrochloric acid was added to the yellow solution and the mixture was extracted with ether. The organic extracts were washed, dried, and evaporated to yield 0.42 g of a yellow solid. This solid was redissolved in 4 mL of chloroform and the insoluble material was removed by filtration. After evaporation and recrystallization three times from ethanol there was obtained 0.23 g (33%) of **21** as a white solid: mp 121–122 °C; IR ($CHCl_3$) 1320 and 1150 $cm^{-1}$ (N=S=O); NMR ($CDCl_3$) $\delta$ 7.80 (m, 2), 7.22 (m, 2), 4.75–4.12 (m, 4), 3.44 and 3.40 (2q, 4), 2.37 (s, 3), 1.20 (t, 6).

Anal. Calcd for $C_{14}H_{21}NO_5S_2$: C, 48.40; H, 6.09; S, 18.46. Found: C, 48.62; H, 5.98; S, 18.33.

When triethylamine was used as base in the above reaction, only 10% yield was obtained; the main product was the chlorosulfinamide **23**.

***N*-(*p*-Tolylsulfonyl)chloromethanesulfinamide (23).** Compound **2** (3.22 g) in benzene was added over 15 min to 6 mL of triethylamine in 15 mL of benzene cooled in an ice bath. After stirring for 15 min, dilute hydrochloric acid was added, and the product was extracted (five times) with ether. Recrystallization from methanol gave 1.61 g of **23** as white crystals: mp 125–127 °C dec; mass spectrum *m/e* 267 (calcd 267); neutralization equiv calcd 268, found 275; IR (KBr) 1370 and 1160 ($SO_2$), 1080 $cm^{-1}$ (SO); NMR ($Me_2SO$-$d_6$) $\delta$ 11.6 (s, 1), 7.85 (m, 2), 7.45 (m, 2), 4.82 (s, 2), 2.42 (s, 3). The material decomposed slowly at room temperature to yield *p*-toluenesulfonamide.

**Oxidation of 23 to *N*-(*p*-tolylsulfonyl)chloromethanesulfonamide.** To 0.268 g of **23** in 20 mL of dilute sodium carbonate solution was added 0.12 g of potassium permanganate dissolved in 10 mL of water. Excess permanganate was destroyed with sodium bisulfite and manganese dioxide was removed by filtration; the water solution was extracted with ether (four times). After washing and drying over magnesium sulfate, evaporation of the solvent yielded 0.20 g of crude product which was recrystallized from benzene–carbon tetrachloride to give a solid: mp 90–91 °C dec; IR ($CHCl_3$) 1380 and 1165 $cm^{-1}$ ($SO_2$); NMR ($Me_2SO$-$d_6$) $\delta$ 12.9 (s, 1), 7.72 (m, 2), 7.28 (m, 2), 4.68 (s, 2), 2.35 (s, 3); $M^+$, *m/e* 283.

Anal. Calcd for $C_8H_{10}ClNO_4S_2$: C, 33.86; H, 3.55; S, 22.60. Found: C, 33.69; H, 3.60; S, 22.47.

***N*-(*p*-Tolylsulfonyl)dichloromethanesulfinamide (24).** To 2 mL of triethylamine in 5 mL of benzene and cooled in an ice bath was added with stirring 1.06 g of **4** dissolved in 5 mL of benzene. After 30 min the solution was poured into 2 M hydrochloric acid and extracted five times with ether; the ether layer was washed with water, dried, and evaporated to yield a yellow oil. This oil was dissolved in a small volume of ether and after standing at room temperature 0.76 g (72%) of a white solid was collected, mp 108–111 °C. Two recrystallizations from benzene–carbon tetrachloride (1:1) gave a solid: mp 113–114 °C; IR (Nujol) 1350 and 1135 ($SO_2$), 1110 $cm^{-1}$ (SO); NMR ($Me_2SO$-$d_6$) $\delta$ 11.6 (s, 1), 7.78 (m, 2), 7.42 (m, 2), 6.95 (s, 1), 2.42 (s, 3).

Anal. Calcd for $C_8H_9Cl_2NO_3S_2$: C, 31.80; H, 3.00; S, 21.22. Found: C, 31.80, H, 3.26; S, 20.99.

***N*-(*p*-Tolylsulfonyl)-1-chloroethanesulfinamide (26).** A similar procedure as used above to prepare **24** from **2** was used. From 2.10 g of sulfonimidoyl chloride **3** was obtained 2.0 g of crude sulfinamide **26**. NMR indicated that the crude material was a mixture of two isomers. Attempts were made to separate the two compounds by thin layer chromatography on silica gel, but trials with a variety of solvents failed to resolve the isomeric sulfinamides. A partial separation, however, was achieved by recrystallization. The crude material was recrystallized three times from chloroform to yield 0.76 g of a white solid, mp 122–124 °C. A sample sent for analyses was recrystallized three times further from a small volume of methanol: mp 126–127 °C; IR ($CHCl_3$) 1370 and 1170 ($SO_2$), 1120 and 1090 $cm^{-1}$ (presumably one peak SO); NMR ($Me_2SO$-$d_6$) $\delta$ 11.5 (s, 1), 7.83 (m, 2), 7.45 (m, 2), 5.13 (q, 1), 2.42 (s, 3), 1.64 (d, 3).

Anal. Calcd for $C_9H_{12}ClNO_3S_2$: C, 38.36; H, 4.29; S, 22.76. Found: C, 38.14; H, 4.23; S, 22.61.

The chloroform filtrate from the first recrystallization was taken to dryness and the residue was recrystallized three times from benzene–carbon tetrachloride to give a white solid, mp 90–92 °C. NMR of this material revealed the presence of about 25% of the higher melting isomer. The spectra of the two isomers were almost identical; only the peaks were somewhat separated. Peaks in $Me_2SO$-$d_6$ corresponding to the lower melting isomer appeared at $\delta$ 7.78 (m, 2), 7.42 (m, 2), 5.07 (q, 1), 2.40 (s, 3), 1.67 (d, 3); IR ($CHCl_3$) 1370 and 1170 ($SO_2$), 1120 and 1090 $cm^{-1}$.

**Oxidation of 26 (Higher Melting Isomer) to 1-Chloro-*N*-(*p*-tolylsulfonyl)ethanesulfonamide.** The higher melting isomer of **26** was oxidized with potassium permanganate to give the sulfonamide: mp 102–103 °C (ethanol); IR (Nujol) 1370 and 1160 $cm^{-1}$ ($SO_2$); NMR ($CDCl_3$) $\delta$ 7.90 (m, 2), 7.37 (m, 2), 6.87 (s, 1), 5.37 (q, 1), 2.47 (s, 3), 1.93 (d, 3).

Anal. Calcd for $C_9H_{12}ClNO_4S_2$: C, 36.30; H, 4.06; S, 21.54. Found: C, 36.04; H, 4.25; S, 21.45.

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**Registry No.**—**1,** 69726-72-3; **2,** 28614-56-4; **3,** 28614-57-5; **4,** 33872-04-7; **5,** 33872-05-8; **6,** 15934-21-1; **7,** 69726-73-4; **8,** 33872-07-0; **9,** 33872-08-1; **10,** 33872-09-2; **11,** 33872-10-5; **12,** 69726-74-5; **13,** 69726-75-6; **15,** 69726-76-7; **16,** 69726-77-8; **18,** 28614-58-6; **19,** 15934-34-6; **21,** 28614-59-7; **23,** 69726-78-9; **24,** 69726-79-0; **26** isomer 1, 69726-80-3; **26** isomer 2, 69726-81-4; methanesulfinyl chloride,

676-85-7; *N,N*-dichlorobutylamine, 14925-83-8; *N*-butylmethanesulfonamide, 3989-40-0; *N*-butylmethanesulfonimidamide, 69726-82-5; butyl isocyanate, 111-36-4; dichloramine-T, 473-34-7; *N*-methylsulfonyl-*p*-toluenesulfonamide, 14653-91-9; *N*-*p*-tolylsulfonylmethanesulfonimidamide, 69726-83-6; *N,N*-dimethyl-*N'*-(*p*-tolylsulfonyl)methanesulfonimidamide, 69726-84-7; *p*-toluenesulfinamide, 6873-55-8; *N*-(*p*-tolylsulfonyl)chloromethanesulfinamide, 69726-78-9; *N*-(*p*-tolylsulfonyl)dichloromethanesulfinamide, 69726-79-0; *N*-(*p*-tolylsulfonyl)trichloromethanesulfinamide, 69726-85-8; *N,N'*-dimethylbenzenesulfonimidamide, 17247-02-8; *N*-methylbenzenesulfinamide, 69726-27-8; benzenesulfinyl chloride, 4972-29-6; benzenesulfinamide, 16066-31-2; benzenesulfonamide, 98-10-2; *N,N*-dimethylbenzenesulfonimidamide, 69726-86-9; *N*-phenylbenzenemethanesulfinamide, 40723-04-4; *N*-phenylbenzenemethanesulfonamide, 19127-51-6; *N,N*-dimethyl-*N'*-phenylbenzenemethanesulfonimidamide, 69726-31-4; *N*-phenylbenzenemethanesulfonimidamide, 69726-87-0; *N*-(*p*-chlorophenyl)benzenemethanesulfinamide, 69726-88-1; *N*-(*p*-chlorophenyl)phenylmethanesulfonamide, 69726-89-2; phenylmethanesulfonyl chloride, 1939-99-7; *p*-chloroaniline, 106-47-8; *N,N*-dimethyl-*N'*-(*p*-chlorophenyl)benzenemethanesulfonimidamide, 69726-90-5; *N*-(*p*-chlorophenyl)benzenemethanesulfonimidamide, 69726-91-6; *N*-(2,4,6-trichlorophenyl)benzenemethanesulfinamide, 69726-92-7; *N,N*-dimethyl-*N'*-(2,4,6-trichlorophenyl)benzenemethanesulfonimidamide, 69726-93-8; *N*-(2,4,6-trichlorophenyl)benzenemethanesulfonamide, 69726-94-9; α-chlorotoluene, 100-44-7; 2,4,6-trichloro-*N*-sulfinylbenzenamine, 2845-63-8; 4-acetamidobenzenesulfinyl chloride, 69726-95-0; 4-acetamidobenzenesulfinic acid, 710-24-7; *N*-methyl-4-acetamidobenzenesulfinamide, 69726-96-1; *N,N,N'*-trimethyl-4-acetamidobenzenesulfonimidamide, 69726-97-2; *N,N,N'*-trimethyl-4-aminobenzenesulfonimidamide, 69726-98-3; *N*-methyl-*N'*-2-pyrimidyl-4-acetamidobenzenesulfonimidamide, 69726-99-4; *N*-methyl-*N'*-2-pyrimidyl-4-aminobenzenesulfonimidamide, 69727-00-0; *N*-(2-pyrimidyl)-4-acetamidobenzenesulfinamide, 69727-01-1; 2-aminopyrimidine, 109-12-6; *N*-(2-pyrimidyl)-4-acetamidobenzenesulfonimidamide, 69727-02-2; *N*-butyl-*N'*-(*p*-toluenesulfinyl)urea, 13630-85-8; methanol-*O*-*d*, 1455-13-6; *N*-*p*-tolylsulfonylmethanesulfonamide, 14653-91-9; 1,1-diethoxyethene, 2678-54-8; *p*-toluenesulfonamide, 70-55-3; *N*-(*p*-tolylsulfonyl)chloromethanesulfonamide, 69727-03-3; 1-chloro-*N*-(*p*-tolylsulfonyl)ethanesulfonamide, 69727-04-4; *N*-(*p*-tolylsulfonyl)methyl-$d_1$-sulfonamide, 69727-05-5.

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# Nucleophilic Substitution at Sulfur in Sulfonimidoyl Compounds: Synthesis of Sulfoximines


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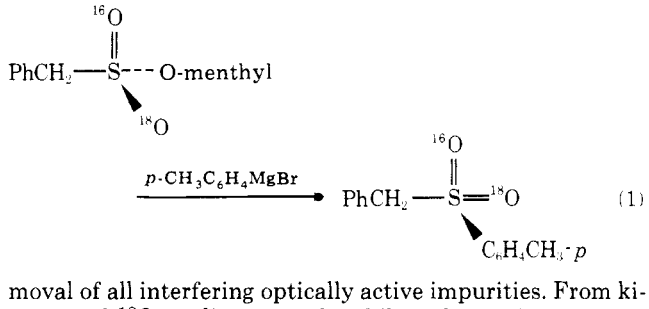
Nucleophilic substitution at tetracoordinate, hexavalent sulfur is shown to occur with inversion at sulfur. Oxidation of (*S*)-*N*-methylbenzenesulfinamide (**1**) with chlorine gave (*R*)-*N*-methylbenzenesulfonimidoyl chloride (**3**) (retention at sulfur). Reaction of **3** with sodium phenoxide gave (*S*)-phenyl *N*-methylbenzenesulfonimidate (**5**) (inversion). Methyllithium and **5** gave (*S*)-*N,S*-dimethyl-*S*-phenylsulfoximine (**4**) (inversion). Reduction of **4** with aluminum amalgam gave **1**. The reactions of alkyllithiums with phenyl benzenesulfonimidate provide sulfoximines that are difficult or impossible to prepare by standard methods.


Nucleophilic substitution at sulfur, a common reaction of organosulfur compounds, has been extensively studied for dicoordinate and tricoordinate sulfur. In the latter case the stereochemical course has been studied in detail.[2,3] On the other hand, the stereochemical course of nucleophilic substitution at tetracoordinate sulfur has been little studied. One reason is obviously the lack of easily obtainable optically active tetracoordinate sulfur compounds for stereochemical studies of substitution. In the singular report by Sabol and Andersen,[4] $^{18}O$-labeled sulfonate with chirality at sulfur due to isotopic label was subjected to treatment with a Grignard reagent to produce an optically active sulfone (eq 1). Their results implied an inversion mechanism, but because of extraordinarily low rotations, the interpretation relied on the complete removal of all interfering optically active impurities. From kinetic and $^{18}O$ studies on nucleophilic substitution at tetracoordinate sulfur in sulfonates and cyclic sulfate esters, a one-step synchronous mechanism is suggested and there is no

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