Reactions of Diaryldialkoxysulfuranes with Primary and Secondary Amines. Preparation and Reactions of *S,S*-Diaryl-*N*-alkylsulfilimines and Oxidation of Secondary Amines to Imines[1]

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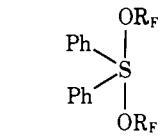
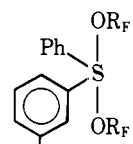
Abstract: The reaction of sulfurane **1**, diphenyldi(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane, with ammonia, with primary amides, primary sulfonamides, anilines, or primary alkylamines provides a general route to *S,S*-diphenylsulfilimines with *N*-H, *N*-acyl, *N*-sulfonyl, *N*-aryl, or *N*-alkyl substituents. The S–N infrared stretching frequencies of the novel *S,S*-diaryl-*N*-alkylsulfilimines are reported. The *S,S*-diphenyl-*N*-alkylsulfilimines undergo rapid alkylation by primary and secondary alkyl halides to form diphenyl(*N,N*-dialkylamino)sulfonium salts. The *S,S*-diaryl-*N*-alkylsulfilimines undergo rapid reactions with hydrogen chloride and water to form diphenyl sulfide, diphenyl sulfoxide, and alkylammonium chlorides. The reaction of benzylamine with 2 equiv of **1** yields benzonitrile in a facile oxidation reaction. Oxidations of several secondary amines with **1** yield imines and diphenyl sulfide. In some cases, the reaction yields stable diaryl(*N,N*-dialkylamino)sulfonium salts, which on pyrolysis give diphenyl sulfide and modest yields of imines. The reactivity patterns observed for the *S,S*-diaryl-*N*-alkylsulfilimines, for the diaryl(*N,N*-dialkylamino)sulfonium salts and in the reactions of **1** with secondary amines are rationalized in terms of the inductive and steric effects of substituents on nitrogen. The oxidation of benzylamine to benzonitrile upon reaction with **1** is discussed in terms of the possible intermediacy of a diaryldialkoxysulfurane imine, a pentacoordinate sulfur(VI) compound.

Although routine procedures have been developed for the preparation of *N*-sulfonyl-,[2] *N*-acyl-,[3] *N*-carbamoyl-,[4] *N*-ethoxycarbonyl-,[5] *N*-aryl-,[6] and free (*N*-H)[7]sulfilimines, no general preparative route to *N*-alkylsulfilimines[8] has been developed. Swern and coworkers report a method which yields *N*-acylsulfilimines but fails to provide *N*-alkyl- and *N*-arylsulfilimines.[9] Shine and Kim[10] report a novel preparation of some *N*-alkylsulfilimines by trapping thianthrene radical cations with amines. We have reported the preparation of *S,S*-diaryl-*N*-alkyl- and *N*-arylsulfilimines by the reaction of sulfurane **1** and secondary amines.[11]



1

$R_F = -C(CF_3)_2Ph$



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We now report in detail a general preparation of *S,S*-diarylsulfilimines with *N*-alkyl, *N*-aryl, *N*-H, *N*-sulfonyl, and *N*-acyl substituents by the reaction of sulfurane **1** with primary alkyl amines, anilines, ammonia, primary sulfonamides, and primary amides. A description of one example of this reaction was reported in the preliminary account of this work.[11] Some of the properties of *S,S*-diaryl-*N*-alkylsulfilimines, which possess a remarkably reactive functional group centered at the sulfur–nitrogen bond, are reported here. We also report the reactions of **1** with some secondary amines forming stable diaryl(*N,N*-dialkylamino)sulfonium salts and a single-step oxidation of secondary amines to imines.

Experimental Section

Sulfurane **1** was prepared according to a published[12a] procedure or according to a simplified standard procedure developed by us.[12b] The use of this procedure to prepare sulfurane **2** is described below. All reactions were carried out in reaction vessels allowing rigorous exclusion of water or under dry nitrogen in an inert atmosphere glove box.

Chloroform-*d*, chloroform, methylene chloride, and carbon tetrachloride were dried by passage through alumina. Reagent grade ether was dried by treatment with and storage over sodium wire.

Elemental analyses for the new compounds reported in this paper are available in Table III in the microfilm edition of this journal.[13] Analyses were within 0.3% of the theoretical values for C, H, N, and S unless indications to the contrary are presented.

Sulfurane 2. To a solution of 2.5 g (10.8 mmol) of *m*-nitrophenyl phenyl sulfide and 6.1 g (21.6 mmol) of KOR_F in 30 ml of stirring CCl_4 was introduced 0.29 ml (0.857 g, 10.8 mmol) of bromine. The heterogeneous mixture was stirred for 3 hr. Filtration and removal of solvent gave, after one recrystallization from ether–pentane, 6.03 g (8.4 mmol, 78%) of sulfurane **2**, mp 102–104°: nmr ($CDCl_3$) δ 8.67 (t, 1 H, $SC_6H_4NO_2$ proton ortho to $-NO_2$ and S), 8.2 (m, 1 H, $SC_6H_4NO_2$ proton ortho to $SPh(OR_F)_2$), 7.8–7.6 (m, 3 H, ortho protons of $-SC_6H_5(OR_F)_2$ and proton of $SC_6H_4NO_2$-*m* meta to $-SPh(OR_F)_2$), 7.4–7.0 (m, 13 H, meta and para protons of $-SC_6H_5$ and $-OC(CF_3)_2C_6H_5$ protons); 94.1-MHz ^{19}F nmr (ether, −50°) 69.6 and 69.7 ppm upfield from $C_6H_5CF_3$ (multiplets of nonequivalent $-CF_3$ groups); mass spectrum (70 eV) *m/e* 717 ($M^{\cdot+}$), 474 ($M^{\cdot+} - OR_F$), 231 ($M^{\cdot+} - 2OR_F$).

General Procedure for the Preparation of Sulfilimines. To a solution of sulfurane **1** or **2** in chloroform, methylene chloride, or ether was added 1 equiv of an alkyl- or aryl-substituted primary amine, a primary amide or sulfonamide, or ammonia in the same solvent or, in the case of volatile amines or ammonia, as a gas. The *N*-alkylsulfilimines (**3**, Y = alkyl) crystallize from ether–pentane with 1 or 2 equiv of R_FOH. Those R_FOH complexes which were isolated are listed in Table II. Extraction of R_FOH with 15% aqueous KOH (replacing ether, if used, with chloroform or methylene chloride for the extraction since KOR_F is appreciably soluble in ether), drying over Na_2SO_4, and removal of solvent provided the crude *N*-alkylsulfilimines, which were purified by recrystallization from ether–pentane. *S,S*-Diphenyl-*N*-methyl- and *N*-isopropylsulfilimines were heated to 100° (10^{-2} Torr) for 30 min to remove water, and *S,S*-diphenylsulfilimine ($Ph_2S{=}NH$) was freed of water by heating to 60° for 2 hr (10^{-2} Torr). The extraction step is unnecessary in the cases of the less basic *N*-acyl-, *N*-sulfonyl-, and *N*-arylsulfilimines, all of which crystallize directly as the sulfilimine. The sulfilimines of Table I were characterized by nmr, ir, and mass spectra and microanalysis. All the compounds in Table I display substantial molecular ions in their 70-eV mass spectra. In every case, the base peak is that of the parent sulfide (*m/e* 186 for Ph_2S or 231 for $PhSC_6H_4NO_2$-*m*). The ^1H nmr spectra of the R_FOH

complexes in Table II are identical with those of the sulfilimines, with superposed absorptions of R_FOH. *N-n*-Butylsulfilimine is an oil which was characterized by high resolution mass spectrometry (calculated for $C_{16}H_{19}NS$, *m/e* 257.1238, found 257.1244) in lieu of elemental analysis.

The ^{19}F nmr spectra of the R_FOH complexes show sharp singlets at 75.8 ± 0.1 ppm upfield from $CFCl_3$. For example, the ^{19}F spectrum of $CH_3N{=}S(C_6H_4NO_2\text{-}m)Ph{\cdot}HOR_F$ in $CDCl_3$ shows a singlet at 75.7 ppm upfield from $CFCl_3$, near the frequency of the singlet of R_FOH (75.3 ppm upfield from $CFCl_3$). In no case could we observe separate peaks for added R_FOH, even at temperatures down to −50°.

Reaction of *S,S*-Diphenyl-*N*-methylsulfilimine (5a) with Benzoyl Chloride. To 1.43 g (6.65 mmol) of **5a** in 25 ml of dry ether was added 2.8 ml (3.39 g, 24.2 mmol) of benzoyl chloride. Immediate precipitation occurred. Filtration and washing with ether gave 1.85 g (0.55 mmol, 83%) of diphenyl(*N*-benzoyl-*N*-methylamino)sulfonium chloride (**8a**): nmr ($CDCl_3$) δ 8.25–7.2 (m, 15 H, $(C_6H_5)_2SN(CH_3)(COC_6H_5)Cl$), 3.45 (s, 3 H, $SNCH_3$-(COC_6H_5)).

Decomposition of Diphenyl(*N*-benzoyl-*N*-methylamino)sulfonium Chloride (8a). A sample of **8a** (1.4 g, 4.18 mmol) became a liquid after 48 hr at room temperature under nitrogen. Thin-layer chromatography on silica gel (ether) revealed at least three components with R_f values 0.3, 0.5, and 0.6. These values are identical with those of authentic *N*-methylbenzamide, diphenyl sulfoxide, and diphenyl sulfide. Preparative thin-layer chromatography of the liquid on 8 × 8 in. preparative silica gel plates (ether), after Soxhlet extraction of the R_f = 0.3 band with chloroform, gave 0.43 g (81%) of *N*-methylbenzamide, whose nmr and ir spectra were identical with those of authentic material. The Soxhlet extraction ($CHCl_3$) of the band with R_f = 0.6 gave 0.7 g of a mixture of sulfides. The mixture displayed three glpc peaks with retention times on a 5 ft × 0.25 in. 2 SE-30 on Chromosorb W column (AW-DMCS) at 200° which were identical with those of authentic samples[14] of diphenyl sulfide, *p*-chlorophenyl phenyl sulfide, and bis(4-chlorophenyl) sulfide in 28, 60, and 12% yields. Preparative glpc of the sulfide mixture provided samples whose mass spectra displayed molecular ions corresponding to the three sulfides at *m/e* 186, 220, and 254.

Hydrolysis of 8a. A solution of 89 mg (0.25 mmol) of freshly prepared **8a** in $CDCl_3$ was treated with water. The nmr revealed the loss of the methyl peak from the position characteristic of **8a** (δ 3.45) and appearance of the absorption of *N*-methylbenzamide (δ 3.0). The integral of the *N*-methyl peak indicated quantitative formation of *N*-methylbenzamide. Diphenyl sulfoxide and *N*-methylbenzamide were isolated by preparative tlc as in the decomposition of **8a** above. Both products displayed nmr and ir spectra identical with those of authentic materials.

Reaction of *S,S*-Diphenyl-*N*-methylsulfilimine (5a) with *p*-Nitrobenzoyl Chloride. To a slurry of 73.7 mg (0.4 mmol) of *p*-nitrobenzoyl chloride in 1 ml of $CDCl_3$ was added 68.3 mg (0.32 mmol) of sulfilimine **5a**. The solution immediately became homogeneous, and the nmr spectrum displayed, along with a complex aromatic region, a singlet at δ 3.34 (the methyl peak of compound **8b**) and no unreacted sulfilimine. Addition of water to the nmr sample caused the immediate precipitation of *N*-methyl-*p*-nitrobenzamide (39 mg, 0.22 mmol, 68%), mp 205–208°, after crystallization from absolute ethanol, mp 216–217° (lit.[15] 218°). Its infrared spectrum was identical with that of an authentic sample.

Reaction of *S,S*-Diphenyl-*N*-*n*-butylsulfilimine (5c) with Acetyl Chloride. To a solution of 208 mg (1.33 mmol) of **5c** in 50 ml of ether at −40° was added excess acetyl chloride. After standing for 2 hr at *ca.* −20°, the solution was filtered to give 289 mg (0.86 mmol, 65%) of **8c**, a white solid. Attempts to recrystallize the material failed: nmr ($CDCl_3$) δ 8.1–7.5 (m, 10 H, C_6H_5S), 4.0 (t, 2 H, NCH_2), 2.67 (S, 3 H, CH_3CO), 1.8–0.5 (m, 7 H, $NCH_2CH_2CH_2CH_3$). A sample of **8c** underwent no change on storage at room temperature for 7 days. Shaking the sample with water produced no immediate change, but after 72 hr approximately 14% hydrolysis to diphenyl sulfoxide and *N*-*n*-butylacetamide occurred. Treatment of a neat sample of the sulfonium salt **8c** with 15% aqueous KOH gave rapid hydrolysis to a 1:1 mixture of diphenyl sulfoxide and *N*-*n*-butylacetamide, identified by the mixture nmr spectrum of the $CDCl_3$ extract of the hydrolysate and by glpc of the mixture on a 2 ft × 0.25 in. 30% SE-30 on Chromosorb W column at 90 and 200°, which gave peaks with retention times matching those of authentic samples of diphenyl sulfoxide and *N*-*n*-butylacetamide.

Pyrolysis of 5a. Injection of a solution of *S,S*-diphenyl-*N*-methylsulfilimine in $CHCl_3$ onto a glpc column (5 ft × 0.25 in. 20% SE-30 on Chromosorb W) at injector and column temperatures above 175° results in the formation of diphenyl sulfide.

Reactions of *S,S*-Diphenyl-*N*-alkylsulfilimines with HCl. (a) *S,S*-Diphenyl-*N*-methylsulfilimine (5a) (0.110 g, 0.51 mmol) in *ca.* 3 ml of $CHCl_3$ was treated with a stream of hydrogen chloride. Dilution with ether gave 21.5 mg (0.32 mmol, 63%) of methylammonium chloride, identical with an authentic sample (melting point, ir, elemental analysis). The chloroform–ether phase was washed with water, dried over Na_2SO_4, and evaporated, leaving 0.103 g (0.42 mmol, 83%) of crystalline diphenyl sulfoxide which was identical (nmr, ir) with an authentic sample.

(b) *S,S*-Diphenyl-*N*-2-propylsulfilimine (5c) (0.147 g, 0.605 mmol) was treated with hydrogen chloride as in a and yielded 44.2 mg (0.47 mmol, 77%) of 2-propylammonium chloride, identical (mp, ir, elemental analysis) with an authentic sample. Work-up of the chloroform–ether phase as in a gave 118 mg of a mixture of diphenyl sulfoxide and diphenyl sulfide, identified from the mixture nmr spectrum. Chromatography of the mixture on a short silica gel column (pentane) gave diphenyl sulfide (46 mg, 0.25 mmol, 41%), and elution with ether gave diphenyl sulfoxide (28 mg, 0.14 mmol, 23%). Both gave nmr and ir spectra identical with those of authentic material. Chromatography of the isolated diphenyl sulfide on a 5 ft × 0.25 in. 20% SE-30 on Chromosorb W glpc column at 200° revealed an impurity with a retention time identical with that of authentic *p*-chlorophenyl phenyl sulfide present in less than 3% yield.

(c) *S,S*-Diphenyl-*N*-*tert*-butylsulfilimine, (3, Y = *tert*-butyl), 191.7 mg (0.75 mmol), treated with hydrogen chloride as above, gave 53 mg (0.47 mmol, 65%) of *tert*-butylammonium chloride, identical (ir, elemental analysis) with an authentic sample. Work-up of the chloroform–ether base as in a and b gave 113 mg of a mixture of diphenyl sulfide (*ca.* 27%) and diphenyl sulfoxide (*ca.* 73%), identified from the mixture nmr spectrum.

Alkylation of *S,S*-Diphenyl-*N*-alkylsulfilimines. (a) Diphenyl(*N,N*-dimethylamino)sulfonium Iodide (6a). To a slurry of 5.396 g (25.0 mmol) of **5a** in *ca.* 70 ml of ether was added 3.0 ml of iodomethane. The mixture was stirred for 1 hr, filtered, and washed with ether to give 8.0 g (22.5 mmol, 9) of **6a**, mp 129° dec: nmr ($CDCl_3$) δ 7.85 (s, 10 H, C_6H_5), 3.10 (s, 6 H, CH_3).

The rate of methylation was monitored by treatment of a 0.5 *M* solution of **5a** in $CDCl_3$ in the nmr probe with sufficient iodomethane to give 0.5 *M* at zero reaction time. Methylation reached 50% completion in less than 1 min at 41°, as determined by integration of the methyl peaks of the starting sulfilimine, the product, and iodomethane.

(b) Methylation of *S,S*-Diphenylsulfilimine (5d). To a solution of 31.7 mg (0.144 mmol) of **5d** monohydrate in *ca.* 1.5 ml of $CDCl_3$ was added 22.2 mg (0.157 mmol) of iodomethane. Within 20 min at 25°, 50% of the iodomethane was consumed to form sulfonium iodide **6a** and sulfilimine **5a** in the mole ratio 0.86:1.00, determined by monitoring the methyl peaks of the sulfilimine, sulfonium salt, and iodomethane. Addition of excess iodomethane converted the remaining sulfilimine to **6a.**

(c) Diphenyl(*N*-methyl-*N*-2-propylamino)sulfonium Iodide (6b). To 0.5 g (2.32 mmol) of **5a** was added 6 ml of 2-iodopropane. Crystallization began within a few minutes. After 3 hr, the excess 2-iodopropane was evaporated under a stream of nitrogen to leave 0.89 g (2.3 mmol, 99%) of **6b.** Recrystallization from ethanol–ether gave the analytical sample, mp 124–125° dec: nmr ($CDCl_3$) δ 7.8 (s, 10 H, C_6H_5), 4.2 (septet, 1 H, $CH(CH_3)_2$), 2, 8 (s, 3 H, NCH_3), 1.35 (d, 6 H, $CH(CH_3)_2$).

The rate of alkylation was monitored by integration of the fully resolved nmr peaks of starting sulfilimine and 2-iodopropane and the product sulfonium salt; a solution of 36.8 mg (0.171 mmol) of **5a** and 20 μl. (34 mg, 0.2 mmol) of 2-iodopropane were combined in 1.0 ml of $CDCl_3$. After 20 hr at 25°, 34% conversion to product was achieved.

(d) Diphenyl(*N*-methyl-*N*-benzylamino)sulfonium Iodide (6c). To 1.025 g (3.52 mmol) of **5c** in *ca.* 10 ml of ether was added 1.5 ml of iodomethane. Precipitation began immediately, and after 1 hr filtration gave 1.36 g (3.14 mmol, 89%) of **6c**, mp 127–128° dec:

nmr ($CDCl_3$) δ 7.75 (s, 10 H, $(C_6H_5)_2S$-), 7.35 (m, 5 H, $NCH_2C_6H_5$), 4.72 (s, 2 H, NCH_2PH), 2.82 (s, 3 H, NCH_3).

(e) Diphenyl(di-2-propylamino)sulfonium Iodide (6d). To 1.17 g (4.82 mmol) of **5c** was added 5 ml of 2-iodopropane. Crystallization began after several hours, and after 2 days at 25° removal of excess 2-iodopropane left 2.98 g (4.8 mmol, 99%) of crystalline **6d**: nmr ($CDCl_3$) δ 7.8 (s, 10 H, C_6H_5), 3.95 (septet, 2 H, $CH(CH_3)_2$), 1.34 (d, 12 H, $CH(CH_3)_2$). Recrystallization from ethanol–ether gave the analytical sample, mp 171–172° dec.

(f) *S,S*-Diphenyl-*N*-ethyl-*N*-2-propylaminosulfonium Iodide (6e). To 1.67 g (6.87 mmol) of **5c** was added 5 ml of iodoethane. Crystallization began immediately and continued overnight. After washing with ether there was obtained 2.86 g (5.7 mmol, 83%) of **6e**. Two recrystallizations from ethanol–ether gave the analytical sample, mp 125.5–126° dec: nmr ($CDCl_3$) δ 7.8 (s, 10 H, C_6H_5), 4.0 (septet, 1 H, $CH(CH_3)_2$), 3.5 (q, 2 H, NCH_2CH_3), 1.41 (d, 6 H, $CH(CH_3)_2$), 1.11 (t, 3 H, NCH_2CH_3).

***S,S*-Diphenyl-*N*-methylsulfoximine (12) from 5a.** To 1.15 g (5.35 mmol) of **5a** in 30 ml of pyridine was added 1.8 g of $KMnO_4$ in *ca.* 50 ml of water. Immediate reaction occurred with deposition of MnO_2. The reaction mixture was warmed for 25 min on a steam bath. Excess $KMnO_4$ and MnO_2 were removed by shaking with aqueous $NaHSO_3$, and the product was extracted into chloroform and the solvent removed under vacuum to give 1.4 g of an oil. Thin-layer chromatography on silica gel (ether:pentane, 3:7) indicated the presence of two products and no starting material. The mixture nmr spectrum indicated approximately 26% of sulfoximine, using the total aromatic integral as an internal standard. Preparative thin-layer chromatography of the oil on two 8 × 8 in. silica plates gave two bands, R_f 0.2 and 0.3. Soxhlet extraction of the R_f 0.3 band gave 0.2 g (16%) of **12**, mp 86–88°. Recrystallization from ether–pentane gave mp 88.5–89.5°; nmr ($CDCl_3$) δ 8.2–7.8 (m, 4 H, aromatic protons ortho to S), 7.7–7.3 (m, 6 H, meta and para *S*-phenyl protons), 2.8 (s, 3 H, NCH_3); mass spectrum (70 eV) *m/e* 231 ($M\cdot^+$), 203 (Ph_2SOH^+), 154 ($M\cdot^+ - Ph$), 125 (PhSO), 106 ($PhNCH_3^+$) (base peak), 77 ($C_6H_5^+$). The absence of significant peaks at *m/e* 186 ($Ph_2S\cdot^+$) and 45 ($CH_3NO\cdot^+$) argues against the isomeric *N*-oxide ($Ph_2SN(CH_3)=O$) as an acceptable alternate structure. The other product (R_f 0.3) was not identified.

Hydrogenolysis of *S,S*-Diphenyl-*N*-phenylsulfilimine (3, Y = Ph). To 0.32 g of 5% palladium on carbon catalyst stirring in 40 ml of ethanol was added 0.59 g (2.13 mmol) of **3** (Y = Ph). An equimolar quantity of hydrogen was consumed within 1.5 hr. The catalyst was removed by filtration, and, after acidification of the solution with concentrated HCl, the ethanol was removed by rotary evaporation. Addition of water and extraction with pentane gave, after drying over Na_2SO_4 and removal of solvent, 0.32 g (1.73 mmol, 81%) of diphenyl sulfide, identical with authentic material by nmr, infrared, and retention time on a 5 ft × 0.25 in. 20% SE-30 on Chromosorb W glpc column at 180°. Neutralization of the aqueous phase and extraction with $CHCl_3$ gave a solution of aniline which was isolated as benzanilide (63%), identical by melting point, nmr, and infrared with an authentic sample.

Hydrogenolysis of 5b. A sample of **5b** (0.642 g, 2.2 mmol) was reduced over 0.25 g of 5% palladium on carbon catalyst in 25 ml of ethanol as above to give 0.319 g (1.72 mmol, 79%) of diphenyl sulfide (nmr, ir) and benzylamine, isolated as benzylammonium chloride (0.248 g, 1.73 mmol, 79%) with melting point, nmr, and ir spectra identical with those of authentic material.

Reaction of 6a with Lithium Dimethylamide. A solution of lithium dimethylamide was prepared by adding 8.8 mmol of *n*-butyllithium to 10 ml of dimethylamine at *ca.* −25°. To this solution at *ca.* −25° was added 2.92 g (8.17 mmol) of sulfonium iodide **6a** in *ca.* 8 ml of dimethylformamide. Filtration and removal of the solvent gave an oil, which, after purification by passage through a short silica gel column (pentane), gave diphenyl sulfide (1.06 g, 70%), whose nmr and ir spectra were identical with those of an authentic sample.

Hydrolysis of Diphenyl(dialkylamino)sulfonium Iodide Salts. (a) Sulfonium Iodides 6a, 6b, and 6e. Samples of **6a** (161 mg, 0.45 mmol), **6b** (167 mg, 0.43 mmol), and **6e** (184 mg, 0.46 mmol) were dissolved in 3.5 ml of absolute methanol and 5.0 ml of 15% aqueous KOH. Vials containing these solutions were heated in a water bath at 95°. The solutions were diluted to 100 ml with water and extracted three times with 75-ml portions of CH_2Cl_2, the extracts were dried over Na_2SO_4, and the solvent was removed to give a solid or an oil. The per cent conversion to diphenyl sulfoxide was determined by nmr integration of the aromatic singlet (δ 7.8) of the unreacted sulfonium salt, relative to diphenyl sulfoxide (δ 7.6–7.2) and integration of the aliphatic nmr peaks of the unreacted sulfonium salt using the total integral of the aromatic region as an internal standard. Compound **6a** underwent 100% hydrolysis to diphenyl sulfoxide in less than 10 min, compound **6b** underwent 95% hydrolysis after 1 hr, and compound **6e** underwent 51% hydrolysis after 8 hr.

(b) Sulfonium Iodide 6c, 0.98 g (2.26 mmol), was stirred overnight at 25° with 15% aqueous NaOH. Extraction of the products into $CDCl_3$ provided a solution whose nmr spectrum displayed methylbenzylamine (64%) and *N*-benzylidenemethylamine (36%) yields by nmr integration. Also present were diphenyl sulfide and diphenyl sulfoxide. Chromatography of the chloroform extract of the crude reaction mixture on a 5 ft × 0.25 in. 20% SE-30 on Chromosorb W glpc column displayed peaks with retention times identical with those of authentic samples of diphenyl sulfide, *N*-benzylidenemethylamine, and methylbenzylamine.

Reaction of Benzylamine and 1. Benzylamine (0.39 g, 2.98 mmol) and sulfurane **1** (5.15 g, 7.67 mmol) were combined in 10 ml of $CDCl_3$. Immediate initial formation of **5b** was apparent in the nmr spectrum, and its consumption by excess **1** was complete in 3 hr at 25° (from observations of the disappearance of the benzyl aliphatic ^1H nmr peak). Quantitative glpc of the reaction mixture at 125 or 200° on a 6 ft × 0.25 in. 20% SE-30 on Chromosorb W column established an 89% yield of benzonitrile (based on benzylamine) and an 88% yield of diphenyl sulfide (based on **1**). Benzonitrile was isolated by preparative glpc using the same column and compared by nmr and ir spectroscopy with authentic material.

Reaction of 1 and *S,S*-Diphenylsulfilimine (5d) to Give Diphenyl(*S,S*-diphenylsulfilimino)sulfonium Alkoxide (22). To a solution of 173 mg (0.86 mmol) of anhydrous **5d** in CH_2Cl_2 was added 0.578 g (0.86 mmol) of sulfurane **1** in CH_2Cl_2. Removal of the solvent by heating at 60° (10^{-2} Torr) for 2 hr gave a solid which, after recrystallization from CH_2Cl_2–ether, gave 0.42 g (0.48 mmol, 56%) of $(Ph_2S)_2NOR_F\cdot HOR_F$, mp 102–103°: nmr ($CDCl_3$) δ 8.2–7.8 (m, 4 H, ortho protons of OR_F phenyls), 7.6 (broad s, 20 H, $((C_6H_5)_2S)_2NOR_F\cdot HOR_F$), 7.4–7.1 (m, 6 H, meta and para protons of OR_F phenyls); ^{19}F nmr ($CDCl_3$, −40°) 74.4 ppm upfield from $CFCl_3$ (s, CF_3 of R_FOH and R_FO^-).

Reactions of 1 with Secondary Amines. (a) Dimethylamine. A solution of 2.0 g (2.97 mmol) of sulfurane **1** in 10 ml of CH_2Cl_2 was treated with excess gaseous dimethylamine. The solution was diluted to 100 ml with CH_2Cl_2, washed three times with 15% aqueous NaOH, dried over Na_2SO_4, and filtered. The oil, after removal of the solvent and purification by passage through a short silica gel column (pentane), gave 0.47 g (2.53 mmol, 85%) of diphenyl sulfide.

(b) Benzylmethylamine. To 0.135 g (1.12 mmol) of amine in 1 ml of $CDCl_3$ was added 1.026 g (1.53 mmol) of sulfurane **1** in *ca.* 3 ml of $CDCl_3$. The reaction mixture was warmed to 60° for 30 min. The mixture nmr spectrum revealed a doublet (J = 4 Hz) at δ 3.34 ($PhCH{=}NCH_3$, 55% by integration). The mixture displayed peaks with retention times on a 5 ft × 0.25 in. 2 SE-30 on Chromosorb W column identical with those of authentic samples of *N*-benzylidenemethylamine[16] and diphenyl sulfide. Sufficient imine was collected by glpc for an nmr, which was identical with that of an authentic sample.

(c) Dibenzylamine. To 0.177 g (0.89 mmol) of amine in $CDCl_3$ was added 0.824 g (1.23 mmol) of sulfurane **1** in $CDCl_3$. The rapid appearance of a singlet at δ 4.18 was observed ($Ph_2S{=}N(CH_2Ph)_2$). This absorption disappeared within 1 hr at 25° to give a doublet at δ 4.72 ($PhCH_2N{=}CHPh$, 85% by integration) and simultaneously a multiplet appeared at δ 8.25 ($PhCH_2N{=}CHPh$). Preparative glpc of the reaction mixture on a 5 ft × 0.25 in. 20% SE-30 on Chromosorb W column gave material with glpc retention time, nmr spectrum, and mass spectrum all identical with those of authentic *N*-benzylidenebenzylamine.[17] Diphenyl sulfide, isolated by preparative glpc on the same column, displayed an nmr spectrum identical with authentic material.

(d) Diethylamine. A sample of 1.99 g (2.96 mmol) of sulfurane **1** was treated with 3 ml of diethylamine. The mixture was stirred for 2 hr, and excess amine was removed under vacuum leaving a solid crystalline mass. Recrystallization of this material from CH_2Cl_2–

Table I. Sulfilimines Prepared from Sulfuranes **1** and **2**

Sulfilimines	Mp, °C	Yield, %	ν_{SN},[a] cm^{-1}	^1H nmr
$CH_3N{=}SPh_2$ (**5a**)	79–80	85	1140, 1080	($CDCl_3$) δ 7.45 (s, C_6H_5S), 2.67 (s, NCH_3)
$CH_3N{=}S(C_6H_4NO_2\text{-}m)Ph$	81.3–82.5	65	1130, 1075	($CDCl_3$) δ 8.3–7.4 (m, $SC_6H_4NO_2$-*m*), 7.4 (s, C_6H_5S), 2.67 (s, NCH_3)
$(CH_3)_2CHN{=}SPh_2$ (**5c**)	34–35.5	98	1130, 1120	($CDCl_3$) δ 7.7–7.2 (m, $(C_6H_5)_2S$–), 3.4 (septet, $(CH_3)_2CHN$), 1.15 (d, $NCH(CH_3)_2$)
$(CH_3)_3CN{=}SPh_2$	47–49	82	1030, 990	($CDCl_3$) δ 7.6–7.0 (m, $(C_6H_5)_2S$–), 1.26 (s, $(CH_3)_3CN$–)
$PhCH_2N{=}SPh_2$ (**5b**)	65.5–66.5	93	1090, 1064	($CDCl_3$) δ 7.7–7.0 (m, $(C_6H_5)_2S{=}NCH_2C_6H_5$), 4.1 (s, $PhCH_2N$)
n-$C_4H_9N{=}SPh_2$[b]	Oil	98	1097	($CDCl_3$)[g] δ 7.44 (s, $(C_6H_5)_2S$), 2.84 (t, NCH_2), 1.50 (m, NCH_2CH_2), 1.27 (m, $NCH_2CH_2CH_2$), 0.80 (t, $N(CH_2)_3CH_3$)
$HN{=}SPh_2$[c] (**5d**)	58–60	48	910	($CDCl_3$) δ 7.7–7.2 (m, C_6H_5), 2.8 (s, NH)
$CH_3C_6H_4SO_2N{=}SPh_2$	106–107[d]	83	962 (KBr)[e]	($CDCl_3$) δ 7.8–6.8 (m, $(C_6H_5)_2S{=}NSO_2C_6H_4$-$CH_3$-*p*), 8.3 (s, $O_2SC_6H_4CH_3$-*p*)
$PhCON{=}SPh_2$	123.5–124.2[f]	67	805 (KBr)[e]	($CDCl_3$) δ 8.3 (m, ortho benzoyl protons), 7.88 (m, ortho *S*-phenyl protons), 7.50 (m, remaining aromatic protons)
$PhN{=}SPh_2$	109.5–110.5	51	930	(CCl_4) δ 7.8–7.55 (m, ortho *S*-phenyl protons), 7.53–7.45 (m, meta and para *S*-phenyl protons), 7.45–6.5 (m, *N*-phenyl protons)

[a] Infrared spectra in CCl_4 unless otherwise noted. [b] Isolated as an oil. [c] Reported as the monohydrate in ref 7a. [d] Literature mp 108–110 (ref 2b) and 113°: A. Kucsman, I. Kapovits, and M. Balla, *Tetrahedron*, **18**, 75 (1962). [e] A. Kucsman, I. Kapovits, and F. Ruff, *Acta Chim. Acad. Hung.*, **40**, 75 (1964). [f] Literature mp 124–125°, footnote 6 of ref 7b. [g] 220-MHz ^1H nmr.

ether gave 1.219 g (1.63 mmol, 55%) of $Ph_2SN(CH_2CH_3)_2OR_F{\cdot}HOR_F$: mp 68–70°; nmr ($CDCl_3$) δ 8.2–7.8 (m, 4 H, ortho protons of OR_F phenyls), 7.8–7.4 (m, 10 H, C_6H_5), 3.22 (q, 4 H, CH_2CH_3), 1.02 (t, 6 H, CH_2CH_3); ^{19}F nmr ($CDCl_3$, −40°) 74.3 ppm upfield from $CFCl_3$ (s, CF_3 of R_FOH and R_FO^-).

A neat sample of 61.2 mg of the above sulfonium salt was heated for 5 min at 155° in a sealed tube. An nmr spectrum of the pyrolysate revealed diphenyl sulfide and *N*-ethylideneethylamine,[18] 54% yield by integration of the doublet at δ 1.9 ($CH_3CH{=}NCH_2CH_3$) using the integral of the total aromatics as an internal standard. A sample of 1.99 g (2.71 mmol) of the sulfonium salt was heated in a sealed tube at 140° oil bath temperature for 5 min. Treatment of the pyrolysate with an excess of a solution of 2,4-dinitrophenylhydrazine in acidic aqueous ethanol, dilution with $CHCl_3$, extraction with water, and removal of solvent gave an oil, which, after treatment with pentane, deposited 120 mg (20%, based on the sulfonium salt) of the 2,4-dinitrophenylhydrazone derivative of acetaldehyde, with an nmr spectrum, ir spectrum, and, after two recrystallizations from CH_2Cl_2–pentane, melting point (148–149°, lit.[19] 147°) consistent with this assignment. The pentane solution was passed through a short silica gel column (pentane) to give 0.348 g (1.87 mmol, 69%) of diphenyl sulfide, identical by nmr and ir with an authentic sample.

(e) **Di(2-propyl)amine.** A sample of 3.53 g (5.25 mmol) of sulfurane **1** was treated with 5 ml of di(2-propyl)amine. An oil appeared after a few minutes. The mixture was stirred overnight. Excess amine was removed under reduced pressure leaving a crystalline mass, which, after recrystallization from CH_2Cl_2–ether, gave 3.02 g (3.89 mmol, 74%) of $Ph_2SNH(CH(CH_3)_2)_2OR_F{\cdot}HOR_F$: mp 110–112°; nmr ($CDCl_3$) δ 8.2–7.8 (m, 4 H, ortho protons of OR_F phenyls), 7.8–7.4 (m, 10 H, $C_6H_5)_2S$–), 7.15–7.05 (m, 6 H, meta and para protons of OR_F phenyls), 3.75 (septet, 2 H, $CH(CH_3)_2$), 1.2 (d, 12 H, $CH(CH_3)_2$); ^{19}F nmr ($CDCl_3$, −40°) 74.4 ppm upfield from $CFCl_3$ (s, CF_3 of rapidly equilibrating R_FOH and R_FO^-).

A sample of 112 mg of the above sulfonium salt was heated in a sealed tube at 175° for 15 min. The nmr spectrum of the pyrolysate displayed singlets at 82.1 (acetone, 10%) and at δ 1.9 and 1.8 (*N*-isopropylideneisopropylamine,[20] 12%). Acetone, presumably resulting from hydrolysis of the imine by tracers of water in the pyrolyzed sample, was detected by glpc on a 20 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P column at 150°. Yields were determined by nmr integration using the total aromatic integral as an internal standard. No starting material was evidenced in the nmr spectrum after 15 min at 175°. A larger sample of the sulfonium salt (1.05 g, 1.36 mmol) was heated in a sealed tube at 175° for 15 min. The pyrolysate was treated with an excess of an acidic aqueous ethanolic solution of 2,4-dinitrophenylhydrazine, diluted with $CHCl_3$, and washed four times with water. Evaporation of the solvent left an oil, whose nmr spectrum ($CDCl_3$) indicated the presence of diphenyl sulfide, R_FOH, and methyl peaks at δ 2.15 and 2.05 assigned to the 2,4-dinitrophenylhydrazone derivative of acetone. The oil was chromatographed on a short silica column (pentane) to give 0.241 g (1.3 mmol, 95%) of diphenyl sulfide and the 2,4-dinitrophenylhydrazone of acetone.[20]

Reaction of 6a and Phenyl Isocyanate. Samples of 0.562 g (4.72 mmol) of phenyl isocyanate and 1.0 g (4.66 mmol) of **6a** were combined in *ca.* 10 ml of chloroform. An exothermic reaction occurred. The crude reaction mixture was chromatographed on four 8 × 8 in. preparative tlc plates (ether) to give four predominant bands at R_f = 0, 0.15, 0.4, and 0.7. Soxhlet extraction (ether) of the band with R_f = 0.4 gave an oil, from which crystallized triphenylsulfilimine (**3**, Y = Ph), 0.13 g (0.47 mmol, 10.2%). The fourth band gave a crude mixture of diphenyl sulfide contaminated with unidentified impurities.

Attempted Reaction of 6a with Acetone. A sample of **6a** (207 mg, 0.96 mmol) was refluxed in 75 ml of acetone for 2 hr. Removal of acetone left crystalline **6a**, with a nmr spectrum identical with that of **6a**.

Results

Table I lists the sulfilimines, their tentatively assigned infrared S=N stretching frequencies, and observed yields for their syntheses, based on the isolated weights of pure sulfilimines. The bands in the infrared spectra of the sulfilimines which are assigned to the S=N stretching frequency are the strongest absorptions in the region 900–1250 cm^{-1} and appear as broad (30–100 cm^{-1}) bands with fine structure. The frequencies listed in Table I for *S,S*-diaryl-*N*-alkylsulfilimines are of the two typically dominant frequencies within the fine structure.

S,S-Diphenylsulfilimine is reported in Table I as the anhydrous free sulfilimine. Previous accounts[7] of the preparation of this compound report the monohydrate. Microanalytical data for this compound, as well as for other compounds in Tables I and II, are reported in the microfilm edition of this paper,[13] as are the infrared spectra of the sulfilimines.

Discussion

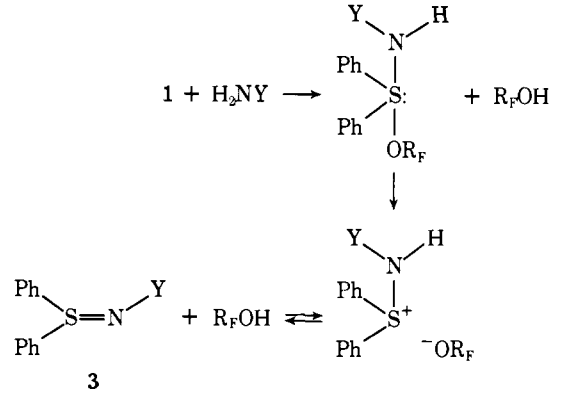
The reactions of sulfurane **1** with compounds containing an N–H bond have been postulated[11] to proceed by a process analogous to the better established[21] sequence of reac-

Table II. R_FOH Complexes of Sulfilimines

R_FOH complex	Mp, °C	Yield, %
$CH_3N{=}SPh_2 \cdot HOR_F$	89–90	95
$CH_3N{=}S(C_6H_4NO_2\text{-}m)Ph \cdot HOR_F$	98.5–99.5	85
$(CH_3)_3CN{=}SPh_2 \cdot 2HOR_F$	75–76	95
$PhCH_2N{=}SPh_2 \cdot HOR_F$	76.5–78.3	85
$CH_2(CH_2)_4CHN{=}SPh_2 \cdot HOR_F$	68–70	81

tions between **1** and compounds containing O–H bonds, such as alcohols. A rapid ligand exchange reaction produces a sulfurane with one nitrogen-centered apical ligand. Ionization of the second alkoxy ligand produces the substituted aminosulfonium alkoxide which, in a subsequent reaction of the nitrogen-centered substituent, provides the observed product. In the reactions leading to the sulfilimines in Table I, the most probable course of the reaction is that of Scheme I.

Scheme I



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The sulfilimine products of Scheme I are formed in high yields for a wide range of structural types (Y = H, alkyl, aryl, acyl, and sulfonyl). The more basic sulfilimines (Y = alkyl) may be isolated either as free sulfilimines or as complexes with R_FOH, perhaps as the protonated sulfilimines in the equilibrium of Scheme I (see a later discussion).

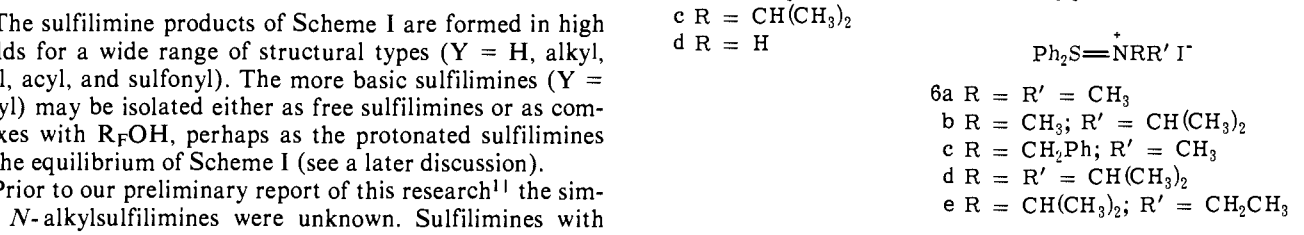
Prior to our preliminary report of this research[11] the simple *N*-alkylsulfilimines were unknown. Sulfilimines with electron-withdrawing substituents on nitrogen were available by several routes.[2-10] The greater stability of such sulfilimines is presumed to reflect the importance of resonance structure **4b** in the resonance hybrid description of sulfilimines.

$$\underset{\textbf{4a}}{R_2S{=}NY} \longleftrightarrow \underset{\textbf{4b}}{R_2\overset{+}{S}{-}\overset{-}{N}Y}$$

The importance of resonance structure **4b** is enhanced by electron-withdrawing Y substituents, and this is reflected in a decrease in the S–N stretching frequency in the infrared spectrum (Table I). Such a decrease in frequency is expected to accompany the decrease in double-bond character as **4b** becomes more important relative to **4a**. The change from *N*-alkyl (1060–1130 cm^{-1}) to *N*-carbamoyl[4] (960–1039 cm^{-1}) to *N*-sulfonyl[22] (940–980 cm^{-1}) to *N*-acyl[3a,d] (800–820 cm^{-1}) produces changes in the S–N stretching frequency which are qualitatively what might be expected on the basis of this rationale. A notable exception, *S,S*-diphenyl-*N*-*tert*-butylsulfilimine, absorbs at lower frequency (990–1030 cm^{-1}) than would be predicted by comparison with the other *N*-alkylsulfilimines. (The *N*-methyl analog absorbs at 1080–1140 cm^{-1}). Steric effects may contribute to this anomaly, perhaps by restricting rotation about the S–N bond to conformations with less than optimum geometry for $p\pi$–$d\pi$ S–N bonding. The infrared peaks assigned to the S–N stretching frequency in Table I show complex structure. This has been attributed[23] to the presence of a multiplicity of conformational isomers resulting from rotation about the S–N bond. Barriers for interconversions of such conformers are low[23] in keeping with the view[24] that the angular requirements for $p\pi$–$d\pi$ bonding are not critical.

The electron-rich nature of the nitrogen atom in *N*-alkylsulfilimines is manifest not only in the basicity of these species but also in a pronounced nucleophilicity at nitrogen. Triphenylsulfilimine fails to react with methyl iodide under conditions which produce rapid reactions of the *N*-alkylsulfilimines with alkyl iodides. The more reactive triethyloxonium tetrafluoroborate is required[25] for the alkylation of *N*-(*p*-toluenesulfonyl)sulfilimines. The *S,S*-diphenyl-*N*-methylsulfilimine of this study is methylated with 0.5 *M* methyl iodide at 25° in minutes and is alkylated with 0.5 *M* isopropyl iodide at 25° in hours. It is convenient for synthetic purposes to use excess alkyl halide in the absence of solvent.

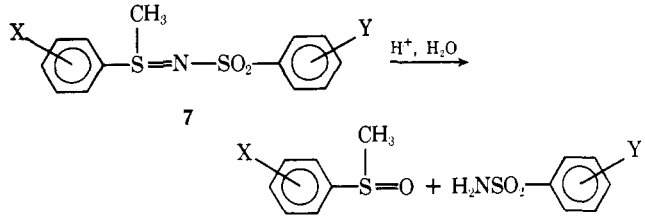
Although certain of the sulfilimines of Table I are, in principal, available by N-alkylation of Oae's[4] N-unsubstituted *S,S*-diphenylsulfilimine, one expects difficulty with the *N*-*tert*-alkylsulfilimines, and we have shown that methylation with 1 equiv of methyl iodide produces a mixture containing not only the *N*-methylsulfilimine but also unmethylated starting material and dimethylated product, *S,S*-diphenyl(dimethylamino)sulfonium iodide. The published methods of Swern[9] and of Shine[10] fail to produce *N*-methylsulfilimines.



The methylation of dimethyl sulfoxide, under conditions of kinetic control of products, occurs at oxygen.[26] In the presence of iodide ion, the resulting methoxysulfonium iodide is quickly converted to the more stable S-methylated product. The methylation of sulfilimines at nitrogen parallels the first step of this reaction, but no evidence was seen for any S-methylated product under any conditions employed.

Diphenyl(dimethylamino)sulfonium iodide (**6a**) is stable in aqueous solution. Treatment of **6a, 6b,** and **6e** with aqueous methanolic potassium hydroxide at 95° gives hydrolysis to diphenyl sulfoxide and the secondary amine. The relative rate order **6a** > **6b** > **6e** is qualitatively that expected from the combined effects of steric hindrance to attack at sulfur and diminishing positive charge at sulfur with increasing electron-releasing character of the substituents at nitrogen. Kapovits, Ruff, and Kucsman,[27] from studies of the hydrolysis of *N*-arylsulfonylsulfilimines **7**, report that electron-withdrawing substituents X and Y enhance the rate of hydrolysis to sulfoxides and sulfonamides.

The nucleophilicity of sulfilimines is further demonstrated by their facile acylation. The rapid acylation of alkylsulfilimines **3** at −20 to −40° yields amidosulfonium salts **8**. As might be expected, these are easily hydrolyzed. At-



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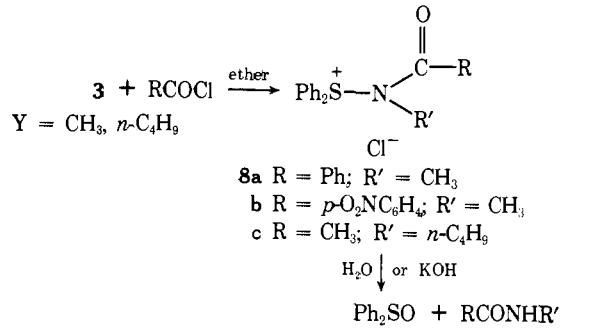
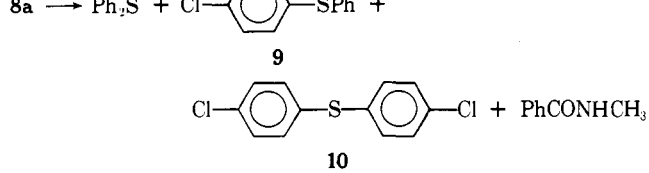
tack is at sulfur, rather than at the carbonyl carbon, to yield sulfoxide and amide in a reaction which is rapid with pure water for **8a** and **8b**. The acetyl analog **8c** reacts slowly with water but rapidly with aqueous base, with nucleophilic attack at sulfur. The lesser reactivity of **8c** may reflect the greater steric bulk of the *N*-alkyl group in this derivative or may perhaps reflect a diminished positive charge at sulfur relative to **8a** and **8b**.



Compound **8a** decomposes within 48 hr at room temperature to form diphenyl sulfide, 4-chlorophenyl phenyl sulfide (**9**), bis(4-chlorophenyl) sulfide (**10**), and *N*-methylbenzamide. Formation of **9** may occur *via* direct nucleophilic attack of chloride on the activated *S*-phenyl ring of **8a**, or an alternative route to **9** and **10** could involve electrophilic chlorination of diphenyl sulfide. The genesis of the chlorinating agent might involve a reaction similar to that depicted by Scheme II, which involves the generation of a catalytic amount of HCl from the facile hydrolysis of **8a**.[28,29] The facile conversion of dichlorosulfurane **11** to **9** and **10** at temperatures above −20° has been reported.[29] Compound **8c** undergoes a similar decomposition in solution to give diphenyl sulfide, **9**, and *N*-*n*-butylacetamide.



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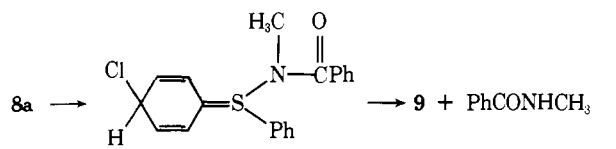
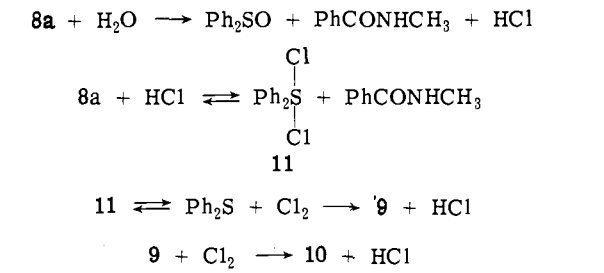
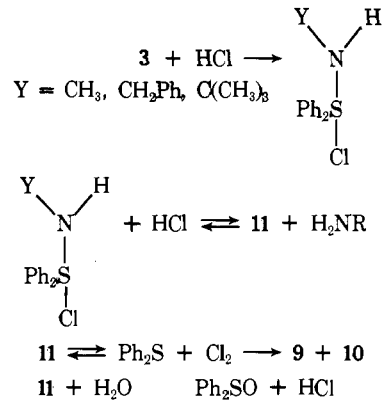


Scheme II

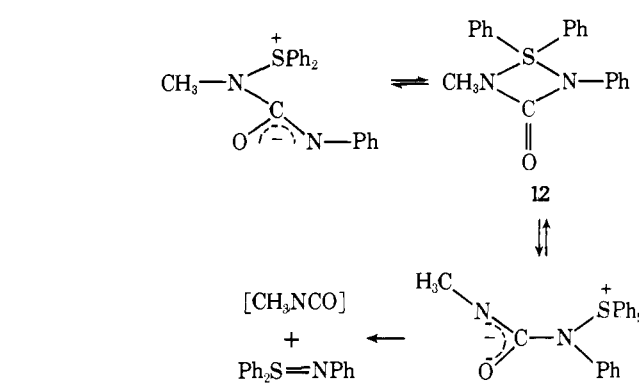


The analogous deamination of *N*-alkylsulfilimines by the action of hydrogen chloride, which was observed by Shine and Kim[10] and also in the present work, may be rationalized to occur by a similar mechanism (Scheme III). This mechanism depicts the formation of a sulfurane (**11**) during the deamination step by the reverse of the sulfilimine-forming sequence of Scheme I.

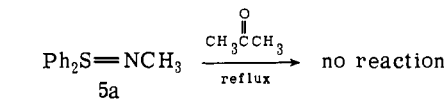
Scheme III



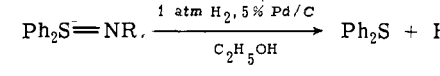
The nucleophilic properties of *N*-alkylsulfilimines are further expressed in the reaction of **5a** with phenyl isocyanate. The isolation of triphenylsulfilimine (**3**, Y = Ph) from this reaction may be rationalized to occur *via* a four-center intermediate **12** reminiscent of the Wittig reaction.



Though *N*-alkylsulfilimines react readily at reactive acid chloride and isocyanate carbonyl carbons, they fail to react with ketones in the pattern of phosphorus–carbon ylides in the Wittig reaction. Sulfilimine **5a** is recovered unchanged after a 2-hr reflux in acetone.



The lability of the S–N bond of sulfilimines is characterized by their hydrogenolysis, pyrolysis, photolysis, and the predominant mode of mass spectral fragmentation to give the parent sulfide and amines or nitrenes. The atmospheric pressure hydrogenolysis of **3** (Y = Ph) and **5b** gave diphenyl sulfide and aniline or benzylamine under the mild conditions known to reduce *S,S*-diphenyl-*N*-*p*-toluenesulfonylsulfilimine (**3**, Y = $O_2SC_6H_4CH_3$-*p*) to diphenyl sulfide



3, R = Ph

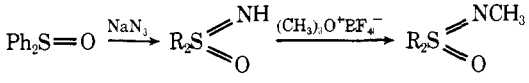
5b, R = CH_2Ph

and *p*-toluenesulfonamide.[30] Photolysis of *S,S*-diphenyl-*N*-methylsulfilimine (**5a**) at 2538 Å or pyrolysis at 175°

$$CH_3N{=}SPh_2 \xrightarrow[\Delta,\ 175^\circ]{h\nu\ (2538\ \text{Å})} Ph_2S + [\ddot{N}CH_3]$$

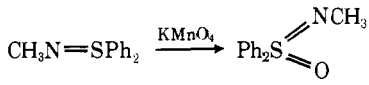
gave diphenyl sulfide. Polymeric material formed in the photolysis of **5a** probably arises from rearrangement products of the short-lived methyl nitrene.[31] By contrast, according to Swern, *et al.*,[32] benzoyl nitrene from the photolysis of *S,S*-dialkyl-*N*-benzoylsulfilimines may be trapped by suitable reagents.

The preparation of *N*-alkylsulfoximines **14** by treatment of a sulfoxide with sodium azide and alkylation of the resulting sulfoximine **13** has been reported.[33] We here report



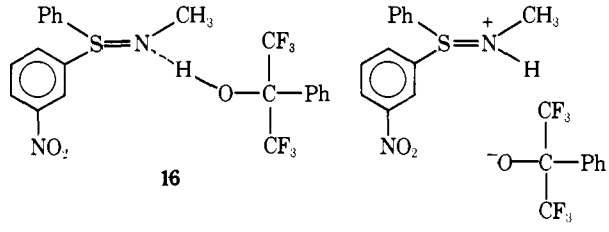
13 **14**

that *N*-alkylsulfoximines may also be formed by direct oxidation of the parent *N*-alkylsulfilimine. Permanganate oxidation of **5a** provided diphenyl-*N*-methylsulfoximine (**15**) in modest (26%) yield.[34]

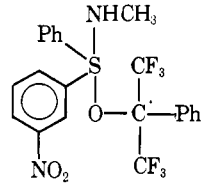


15

The R_FOH complexes of *N*-alkylsulfilimines in solution, reported in Table II, could be represented by structure **16**,

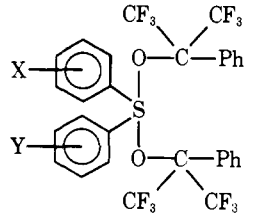


16 **17**



18

17, or **18**. The OR_F groups of numerous tetracovalent sulfuranes (**19**) display singlets in their ^{19}F spectra in ether or



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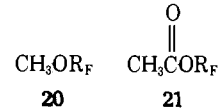
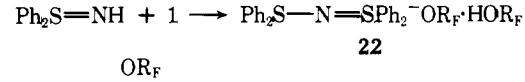


20 **21**

$CDCl_3$ at 70.0 ± 0.5 ppm upfield from $CFCl_3$.[21] When substituents X and Y are different, the geminal CF_3 groups become, in some cases, nonequivalent and appear as quartets (CF_3–CF_3 coupling).[21] Unsymmetrical ethers **20**[12a] and esters **21**[11] show ^{19}F singlets at 70–71 ppm. By contrast, R_FOH displays a singlet in ether or $CDCl_3$ at 75 ppm, and R_FOK displays a singlet at 76.6 ppm in ether. This 5–6 ppm difference in ^{19}F chemical shifts is diagnostic of covalent or ionic bonding in OR_F groups. The R_FOH complex of (*m*-nitrophenyl)phenyl-*N*-methylsulfilimine (**16**) was prepared in order to determine the covalent (*i.e.*, **18**) or ionic (**16** or **17**) nature of the molecule. The ^{19}F spectrum of this complex, unlike the ^{19}F spectrum of its parent sulfurane **2** (which shows a pair of multiplets for nonequivalent, coupled geminal CF_3 groups), shows a sharp singlet at 75.7 ppm in $CDCl_3$, providing strong evidence against structure **18**. When a solution of 1 equiv each of the complex and of R_FOH were cooled to −50°, no change in the ^{19}F spectrum resulted, consistent with a mixture of R_FOH and primarily unprotonated (or hydrogen-bonded) **16**, though a rapid equilibrium between **16** and **17** cannot rigorously be ruled out.

Anhydrous diphenylsulfilimine reacts with **1** to form compound **22**. Examples of other salts containing this cation are known.[35] The structure of **22** is favored over the isomeric structures **23** and **24** from the singlet displayed by its ^{19}F spectrum at 74.4 ppm (near that of R_FOH) in $CDCl_3$ which undergoes no change on reducing the temperature to −40°.



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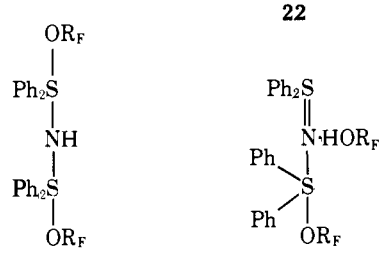
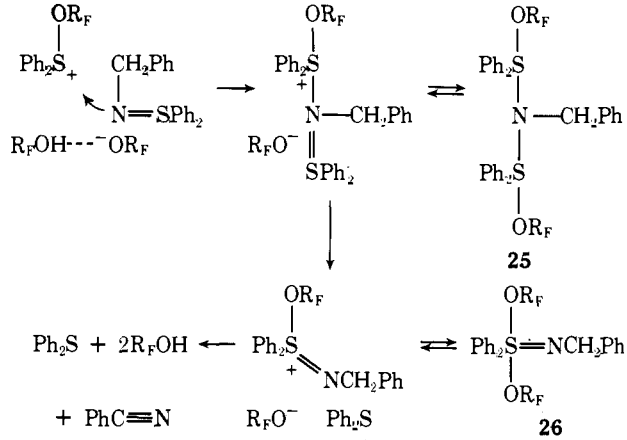
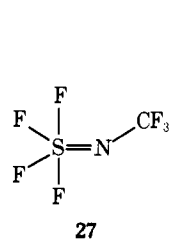


23 **24**

The oxidation of benzylamine to benzonitrile by reaction with 2 equiv of sulfurane **1** is postulated to proceed *via* formation of *S,S*-diphenyl-*N*-benzylsulfilimine (**5b**). A ligand exchange reaction of **5b** with an alkoxy ligand of **1** may form **25**, by attack of the sulfilimine at the sulfur of an alkoxysulfonium ion, or by loss of diphenyl sulfide may give **26**, a sulfurane imine. The possible formation of hypervalent sulfur(VI) compound **26** is credible in view of the reported[36] isolation of the analogous tetrafluorosulfurane *N*-trifluoromethylimine (**27**) and the isolation of sulfurane oxide **28** in these laboratories.[37]



25 **26**



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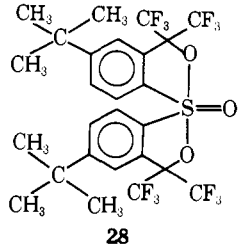

28

Eliminations analogous to Hoffman eliminations of alkylsulfonium salts[38] were seen when aminosulfonium salt **6a** was treated with the strong base lithium dimethylamide or, in the case of **6c**, by treatment with aqueous sodium hydroxide. Bases stronger than iodide (such as R_FO^-) ab-

$$6a + LiN(CH_3)_2HN(CH_3)_2 \longrightarrow Ph_2S + [CH_2{=}NCH_3]$$

$$6c + NaOH(aq) \longrightarrow CH_3NHCH_2Ph + CH_3N{=}CHPh + Ph_2S + Ph_2SO$$

stract a methylene or methine proton activated by an adjacent sulfonium substituent at nitrogen and, losing diphenyl sulfide, form the imine. Generation of a dialkylaminosulfonium salt in the presence of a base (^-OR_F) by treatment of dimethyl-, methylbenzyl-, or dibenzylamine with sulfurane **1** led to rapid formation of diphenyl sulfide and the corresponding imine **30.** Selective abstraction of the more acidic benzylic proton of **29b** occurs giving **30b,** with no de-

$$1 + RCH_2NHCH_2R' \longrightarrow Ph_2S + RCH{=}NCH_2R'$$

29a, R = R′ = H	**30a**, R = R′ = H
b, R = Ph; R′ = H	b, R = Ph; R′ = H
c, R = R′ = Ph	c, R = R′ = Ph

tectable formation of the methylenimine from loss of a methyl proton. Treatment of solutions of **1** with diethyl- or diisopropylamine led to much slower formation (*ca.* 48 hr for half reaction at 25° at 0.5 *M* concentration of **1** and amine) of indefinitely stable diphenyl(dialkylamino)sulfonium salts **31.** The stability of sulfonium salts **31** reflects

$$1 + R_2NH \longrightarrow Ph_2S{=}\overset{+}{N}R_2\,^-OR_F{\cdot}HOR_F$$

R = C_2H_5, i-C_3H_7 **31a**, R = C_2H_5; **b**, R = i-C_3H_7

the decreased acidity of methylene or methine protons adjacent to nitrogen with increasing alkyl substitution. Both **31a** and **31b** decomposed with heating to form diphenyl sulfide, R_FOH, and modest yields of imines.

$$31a \xrightarrow{140^\circ,\,5\ min} Ph_2S + CH_3CH{=}NC_2H_5$$

$$31b \xrightarrow{175^\circ,\,15\ min} Ph_2S + (CH_3)_2C{=}NCH(CH_3)_2 + \text{other products}$$

For secondary amides with methylene protons of moderate acidity, the direct oxidation by treatment with **1** provides imines in significant yields. For amines with significantly lower acidities of methine and methylene protons adjacent to nitrogen, preparation of imines is more difficult. Further work will be directed toward the further development of this oxidative reaction.

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Supplementary Material Available. A table listing microanalytical results for all the compounds described in this paper and copies of the infrared spectra of the sulfilimines will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-583.

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Electrolyte Effects upon the Electrochemical Reduction of Cyclooctatetraene in Dimethyl Sulfoxide

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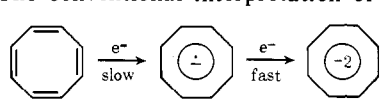
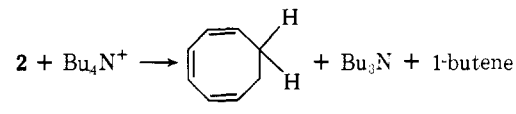
Abstract: The electrochemical reduction of cyclooctatetraene in dimethyl sulfoxide was studied by a variety of techniques, principally dc and phase-sensitive ac polarography, using tetra-*n*-alkylammonium salts as supporting electrolytes, with the alkyl group ranging in size from methyl to heptyl. Cyclooctatetraene (COT) shows two polarographic waves, associated with its stepwise reduction to the corresponding radical anion and dianion, respectively, in the presence of all electrolytes studied. The rate of heterogeneous electron-transfer to COT decreases markedly as the size of the tetraalkylammonium ion increases. The results are discussed, with emphasis upon the role of electrolytes.

A number of studies of the electrochemical reduction of cyclooctatetraene (COT) (**1**) in aprotic solvents have been reported.[1] Two polarographic waves have generally been observed, with the first wave somewhat drawn out (log-plot slope[2] > 59 m*V*), suggesting an element of irreversibility to be associated with this reduction step. This behavior contrasts with that exhibited by aromatic hydrocarbons; the first reduction step of such compounds under aprotic conditions is rapid and reversible using a variety of electrochemical criteria and techniques.[3] The generally accepted interpretation of the electrochemical reversibility of the first reduction step of aromatic hydrocarbons is that the electron-transfer step simply involves injection of an electron into the lowest unoccupied molecular orbital of the hydrocarbon, a process involving no bond breaking and little change in molecular geometry and hence has a very low activation energy.[3] The conventional explanation of the polarographic behavior of COT has on the other hand been that the first electron transfer involves a change in molecular geometry, from the initially tub-shaped COT neutral molecule to a planar or nearly planar radical anion, $COT^{\cdot -}$ (**2**), this geometrical change being associated with an increase in the activation energy for electron transfer and hence the observed irreversibility of the first reduction step.[1] This interpretation also implies that the second reduction step of COT should be reversible or nearly so since a minimum of geometrical change would be involved in converting **2** to the planar dianion **3**, and the data apparently support this corollary.[1a,c] The conventional interpretation of the electro-



1 **2** **3**

chemical behavior of COT has, however, recently been challenged by Thielen and Anderson.[4] They reported the usual two-wave polarogram for **1** in anhydrous acetonitrile containing tetrabutylammonium hexafluorophosphate (TBAHFP) but claimed that the second wave is not observed when tetramethylammonium hexafluorophosphate (TMAHFP) is employed as the supporting electrolyte. They suggested that the second reduction step previously observed for COT and thought to correspond to the reduction of **2** to **3** was actually associated with the reduction of the radical HCOT· (**4**) generated by a Hofmann elimination by **2** upon the tetrapropyl- (TPA) or tetrabutylammonium (TBA) salts previously employed as supporting electrolytes in the reduction of **1**, *e.g.*



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They argued further that when this elimination is prevented through use of tetra*methyl*ammonium (TMA) ion, no second wave for reduction of **2** to **3** could be observed, supported their argument by reference to the calculations of Dewar and coworkers[5] on the relative energies of **1**, **2**, and **3**, and expressed doubts concerning the possibility of reduction of **2** to **3** by alkali metals. We were led to question the conclusions of Thielen and Anderson for a number of reasons, however. First, the evidence from nmr, uv, and ir spectroscopy[6,7] that the product of reaction between 1 mol of **1** and 2 gram-atoms of potassium is indeed the dipotassium salt of **3** seems very strong. Second, an apparent internal inconsistency appeared in the paper; it was claimed that **4** is *easier* to reduce than **1** when formed *via* protonation of **2** by added water but *harder* to reduce than **1** when formed *via* protonation of by tetrabutylammonium ion. Third, it had been reported previously that COT does in fact exhibit two polarographic waves in the presence of tetramethylammonium ion.[8] Finally, it was clear, and in fact has previously been pointed out,[9] that MO calculations, such as those of Dewar,[5] may not be applied to electrochemical measurements in solution, because ion pairing and solvation both act to decrease the energy necessary to add a second electron to hydrocarbon radical anions. Even in a solvent as polar as dimethyl sulfoxide (DMSO), ion pairing of aromatic radical anions and dianions with tetraalkylammonium ions is significant,[10] and indeed it is generally recognized that ion pairing must be considered examining the electrochemical behavior of aromatic and other species in aprotic organic solvents.[11] Because of the considerable im-