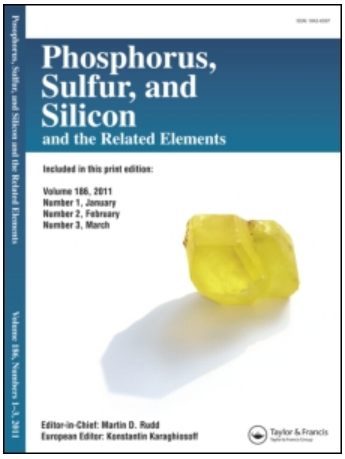

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IMINOSULFURANES FROM BIOLOGICALLY ACTIVE SULFONAMIDES AND RELATED COMPOUNDS

Thomas W. Ku[ab]; Daniel Swern[a]
[a] Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania
[b] Smithkline Corp. Smith, Kline and French Laboratories, Philadelphia, Pa.

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IMINOSULFURANES FROM BIOLOGICALLY ACTIVE SULFONAMIDES AND RELATED COMPOUNDS[1]

THOMAS W. KU[2] and DANIEL SWERN

Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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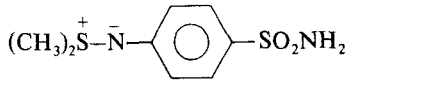
Iminosulfuranes and iminosulfonium salts have been prepared from biologically active sulfonamides and other biologically active and related amino compounds. The new compounds have been characterized by nmr, uv, ir, mass spectra and elemental analysis. Deuterated analogs have also been prepared in selected cases for mass spectral comparison with their nondeuterated counterparts.

Earlier we reported the first generation and low temperature trapping of the highly reactive dimethyl sulfoxide (DMSO)-trifluoroacetic anhydride (TFAA) reagent (**1**) for the preparation in high yields of iminosulfuranes (sulfilimines) (**2**) from aryl amines, aryl amides and aryl sulfonamides (Scheme 1).[3] In that paper the unequivocal preparation of the two possible monoiminosulfuranes [(**3**) and (**4**)] and the diiminosulfuranes (**5a,b**) from sulfanilamide was also described, as well as some exploratory studies on the preparation of an iminosulfurane from sulfadiazine. Prior to our studies no therapeutically active amino species had been used as nucleophiles to prepare iminosulfonium salts and/or iminosulfuranes.

In this paper, we are reporting (a) the preparation of new iminosulfuranes or their trifluoroacetates, or both, from several additional sulfonamides [sulfadiazine (**6**), sulfamerazine (**8**), sulfathiazole (**10**), N^1-acetylsulfanilamide (**12**)], and other biologically



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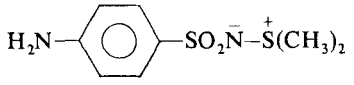

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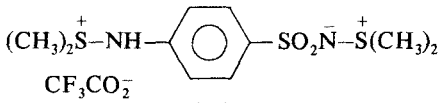
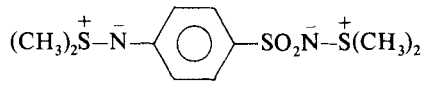
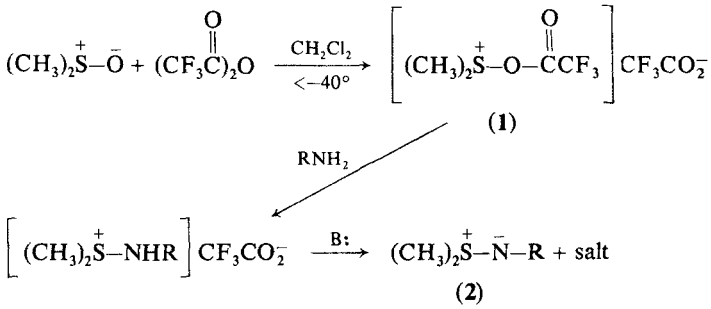


(**5a**)



(**5b**)



(R = aryl, arylcarbonyl, arylsulfonyl)

SCHEME 1

active amino compounds [2-amino-5-nitrothiazole (**14**), 2-amino-pyrimidine (**16**)]; (b) spectral characteristics of the new compounds; and (c) the preparation of some model deuterated and undeuterated iminosulfuranes and iminosulfonium salts for mass spectral fragmentation comparison.

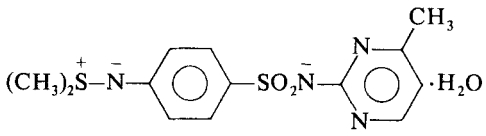
RESULTS AND DISCUSSION

Preparation

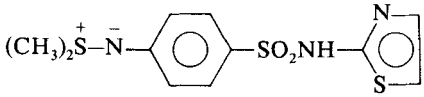
The preparation of *S,S*-dimethyl-N^4-(N^1-2-pyrimidinylsulfanilamido)-iminosulfurane (**7a**) was not a straightforward procedure (Scheme 2). Modelled after the sequence in Scheme 1, the reaction of sulfadiazine (**6**) with the DMSO–TFAA intermediate (**1**) followed by basification with triethylamine (TEA) did not yield the expected iminosulfurane (**7a**) but rather its trifluoroacetate salt (**7b**). Use of aqueous sodium hydroxide instead of TEA for basification yielded the hydrated sodium salt (**7c**) of the ylide. The ylide (**7a**) was finally obtained in good yield by basification of a CH_2Cl_2 slurry of (**7b**) with TEA.

Attempted basification of a water solution of (**7b**) by passing it through an excess of anion-exchange resin (1RA-400, hydroxide form) followed by elution with water yielded no product. The result suggests that the excess hydroxide ions on the polymer matrix not only remove TFA but also abstract the acidic sulfonamido proton; the iminosulfurane ion remains on the column as part of the polymer.

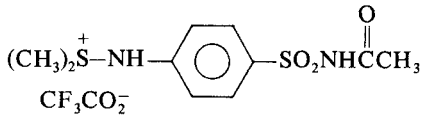
By appropriate minor modification (see Experimental), ylides or salts, or both, were obtained in generally good yields from sulfamerazine [(**8**) → (**9**)], sulfathiazole [(**10**) → (**11**)], N^1-acetylsulfanilamide [(**12**) → (**13a,b**)], 2-amino-5-nitrothiazole [(**14**) → (**15**)], and 2-aminopyrimidine [(**16**) → (**17**)]. The sodium salts (**7c**) and (**9**) derived, respectively, from the aminopyrimidines (**6**) and (**8**) form slightly alkaline aqueous solutions and readily undergo the Sommelet-Hauser rearrangement [(**7c**) → (**7d**), $t_{1/2} \approx$ 24 h)] to form *o*-alkylated products (Eq. 1). The



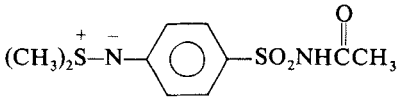
(**9**)



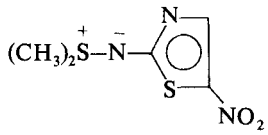
(**11**)



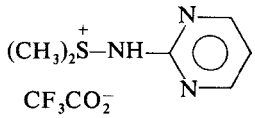
(**13a**)



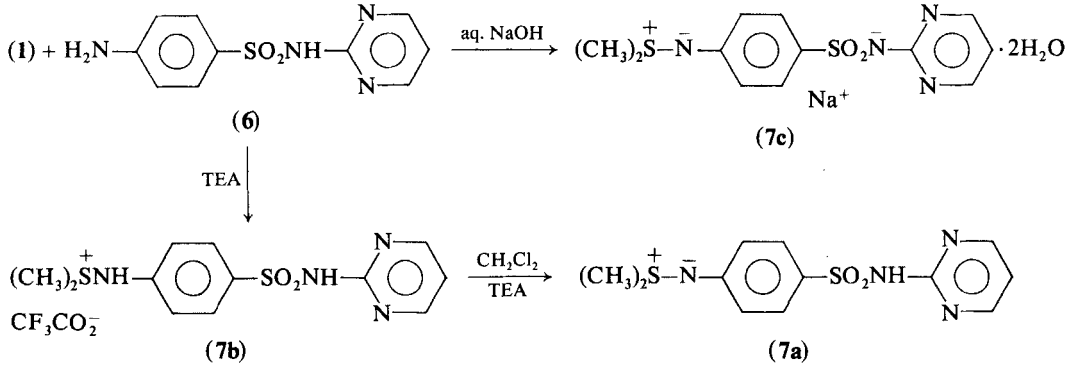
(**13b**)



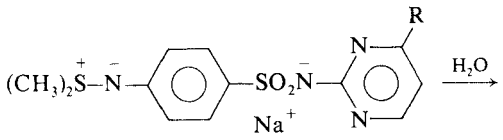
(**15**)



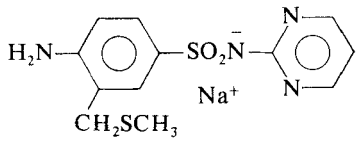
(**17**)



SCHEME 2



(**7c**), R = H; (**9**), R = CH_3



(**7d**), R = H; (**9a**), R = CH_3

rearrangement, similar to that studied in detail by Claus[4] and Gassman,[5] is readily followed by nmr by observing changes with time in the integrated values of the signals associated with the *S*-methyl protons (δ2.7) of the sulfonium group in D_2O, and the appearance of appropriate integrated values for signals (δ1.98, 3.62) consistent with the $-CH_2SCH_3$ group in (**7d**) and (**9a**). TLC is also a very useful tool for monitoring the rearrangement as the R_f values of the sodium salts of the ylides are significantly lower than those of the rearrangement products.

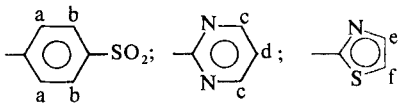
Spectral Characteristics

Nmr (Table I). In an earlier study,[6] we reported the nmr spectra of a series of *S,S*-dimethyl-*N*(*p*-aryl)iminosulfuranes. When the *p*-substituent is an electron-donating group, the S $(CH_3)_2$ proton signal appears as a singlet at δ 2.4–2.5; with electron-withdrawing substituents the signal is shifted downfield to δ 2.7–2.8. The sulfonamido group is a powerful electron-withdrawing group; thus the $\overset{+}{S}(CH_3)_2$ proton signal appears, as expected, as a singlet at δ 2.6–2.9 in the sulfilimines. In the corresponding salts, however, the negative charge on nitrogen is neutralized by a proton and sulfur–nitrogen overlap is not possible, thereby resulting in the development of a full positive charge on sulfur. Consequently, the

TABLE I

Nmr[a] and uv spectral data of iminosulfuranes and salts

Compound $S(CH_3)_2$	NMR, δ							UV		
	H_a	H_b	H_c	H_d	H_e	H_f	CH_3	λ_{max} (nm)	$\varepsilon \times 10^{-3}$	
(**3**)[b]	2.7(s)	6.7(d)	7.5(d)	—	—	—	—	—	203	22.8
									286	23.6
(**4**)[c]	2.65(s)	6.60(d)	7.40(d)	—	—	—	—	—	211	16.3
									265	24.5
(**5a**)[d]	2.70, 3.25 (s,s)	7.25(d)	7.75(d)	—	—	—	—	—	202	28.4
									290	12.0
(**5b**)[b]	2.65, 2.80 (s,s)	6.80(d)	7.50(d)	—	—	—	—	—	204	33.0
									289	22.5
(**7a**)[b]	2.76(s)	6.68(d)	7.62(d)	8.46(d)	6.99(t)	—	—	—	202	33.5
									303	18.0
(**7b**)[b]	3.36(s)	7.26(d)	7.98(d)	8.52(d)	7.08(t)	—	—	—	202	45.5
									303	18.2
(**7c**)[b]	2.68(s)	6.85(d)	7.75(d)	8.25(d)	6.65(t)	—	—	—	285	17.4
(**9**)[c]	2.66(s)	6.50(d)	7.50(d)	7.98(d)	6.30(d)	—	—	2.14(s)	296	21.9
(**11**)[c]	2.80(s)	6.74(d)	7.47(d)	—	—	6.66(d)	7.08(d)	—	293	23.5
(**13a**)[c]	3.34(s)	7.30(d)	7.88(d)	—	—	—	—	1.94(s)	273	9.5
									288	12.2
									302	15.4
(**13b**)[c]	2.72(s)	6.88(d)	7.48(d)	—	—	—	—	1.86(s)	275	18.6
									300	16.7
(**15**)[c]	2.90(s)	—	—	—	—	8.02(s)	—	—	260	7.1
									418	18.0
(**17**)[c]	3.10(s)	—	—	8.59(d)	6.97(t)	—	—	—	273	23.4
									304	3.7

[a] Ring proton code: 

[b] Nmr in DMSO–d_6; uv in 70% ethanol–30% water.
[c] Nmr in DMSO–d_6; uv in 95% ethanol.
[d] Nmr in D_2O; uv in 70% ethanol–30% water.

Proton count by integration, ±5%.

$\overset{+}{S}(CH_3)_2$ protons of the salts undergo considerable deshielding and the signal is shifted significantly downfield to δ 3.1–3.4.

Two particularly interesting compounds are (**5a**) (a monoylide-monosalt) and (**5b**) (a diylide), as they each contain a pair of $\overset{+}{S}(CH_3)_2$ groups in different environments. In (**5a**), the proton signals are singlets at δ 2.70 and 3.25, exactly as expected from the discussion in the preceding paragraph. In (**5b**), the proton signals are also singlets and both are in the 2.6–2.8 region with the $\overset{+}{S}(CH_3)_2$ group attached to the sulfonamido group having the (expected) downfield signal.

The chemical shifts of the *o*- and *m*-protons in the aromatic ring of the *p*-substituted iminosulfuranes are also upfield (approximately 0.6 and 0.3 ppm, respectively) of the corresponding protons in their iminosulfonium salts. This result is simply explained by a change in the deshielding effect as the negative charge on nitrogen is neutralized in the conversion of

TABLE II

Mass spectral comparison of selected iminosulfuranes and deuterated analogs[a]

Compound	Molecular ion (M) *m/e* (%)	Base peak	Major peaks (%)
$(CH_3)_2\overset{+}{S}-\overset{-}{N}-C_6H_4-NO_2$ (**18**)[6]	198(98)	183(M–CH_3)	138(M–CH_3–HCS)(9)
$(CD_3)_2\overset{+}{S}-\overset{-}{N}-C_6H_4-NO_2$ (**19**)	204(100)	$M^{+\cdot}$	140(M–CD_3–DCS)(23)
$(CH_3)_2\overset{+}{S}-\overset{-}{N}-C_6H_4-SO_2\overset{-}{N}-\overset{+}{S}(CH_3)_2$ (**5b**)	292(40)	245(M–SCH_3)	232(M–CH_3–DCS)(10)
$(CD_3)_2\overset{+}{S}-\overset{-}{N}-C_6H_4-SO_2\overset{-}{N}-\overset{+}{S}(CD_3)_2$ (**20**)	304(44)	254(M–SCD_3)	238(M–CD_3–DCS)(6)
$(CH_3)_2\overset{+}{S}-\overset{-}{N}-SO_2-C_6H_4-NO_2$ (**21**)	262(100)	$M^{+\cdot}$	198(M–SO_2)(20)
$(CD_3)_2\overset{+}{S}-\overset{-}{N}-SO_2-C_6H_4-NO_2$ (**22**)	268(95)	186(M–SO_2–CD_3)	204(M–SO_2)(33)
$(CH_3)_2\overset{+}{S}-\overset{-}{N}-SO_2-C_6H_4-NH_2$ (**4**)	232(100)	$M^{+\cdot}$	156[M–$NS(CH_3)_2$](50)
$(CD_3)_2\overset{+}{S}-\overset{-}{N}-SO_2-C_6H_4-NH_2$ (**23**)	238(100)	$M^{+\cdot}$	156[M–$NS(CD_3)_2$](61)
$(CH_3)_2\overset{+}{S}-\overset{-}{N}-C_6H_4-SO_2NH_2$ (**3**)	232(37)	185(M–SCH_3)	172(M–CH_3–HCS)(14)
$(CH_3)_2\overset{+}{S}-\overset{-}{N}-C_6H_4-SO_2NH-C_6H_5$ (**11**)	315(—)	269(M–SCH_3)	255(M–CH_3–HCS)(—)
$(CH_3)_2\overset{+}{S}-\overset{-}{N}-C_6H_4-SO_2NHCOCH_3$ (**13b**)	274(19)	227(M–SCH_3)	214(M–CH_3–HCS)(12)

[a] Additional data on fragmentation patterns are given in the Experimental Section.

the ylides to their salts. The deshielding effect is less on the *m*-protons than on the *o*-protons.

Uv (Table 1). Uv spectra of iminosulfuranes and their corresponding salts were compared in three cases [(**5a**) and (**5b**); (**7a**) and (**7b**); (**13a**) and (**13b**)]. There is essentially no difference in absorption maxima between the ylides and their salts but extinction coefficients show significant changes. The magnitudes of ε make uv spectra useful in the analysis of the iminosulfuranes and their salts.

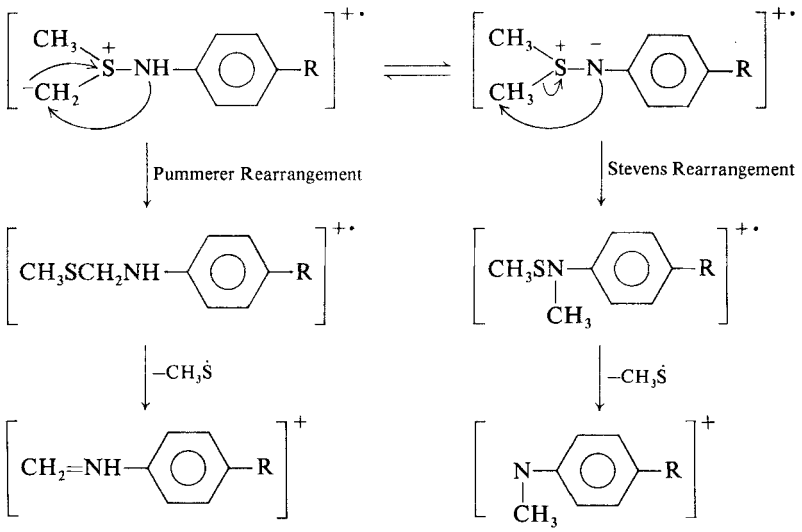
Mass spectra (Table II). There are few reports in the literature that describe systematic examinations of the mass spectral fragmentation patterns of iminosulfuranes; most authors have studied only a few compounds.[4a,8–12] We briefly report here certain salient features of the mass spectral fragmentation patterns of selected iminosulfuranes prepared by us both deuterated and undeuterated in the $\overset{+}{S}(CH_3)_2$ [$\overset{+}{S}(CD_3)_2$] portion of the molecule. The most important features of all the spectra are the similarities in their general fragmentation process.

Mass spectral fragmentation patterns of both members of the pairs of deuterated and undeuterated compounds (**18**) and (**19**); (**5b**) and (**20**); (**21**) and (**22**); and (**4**) and (**23**) are virtually identical; all give intense molecular ion peaks. All mass peaks can be matched and accounted for in each pair of compounds if the isotopic differences are taken into consideration. Examination of the trifluoroacetate salts, however, shows no molecular ion; instead they give mass spectra with base peaks at M–$HOC(=O)CF_3$, and the fragmentation patterns are identical with those of the parent ylides. Loss of methylene (or CD_2) as reported earlier by us in another case,[10] was not observed and is apparently not an important fragmentation pathway.

An important primary process is loss of CH_3 from the molecular ion, as reported earlier by us[9] and others.[12] The M–CH_3 fragment is often indicated by observation of a metastable ion. The M–CH_3 fragment is frequently followed by loss of HCS resulting in the formation of an M-60 fragment via a stepwise or concerted process producing a radical cation assigned to the parent sulfonamide.

The fragment at M-60 can also be explained by the concerted loss of episulfide from the molecular ion. Although loss of episulfide cannot be completely ruled out, sequential loss of CH_3 (CD_3) and HCS (DCS) is an attractive and sufficient explanation at present.

Another interesting fragmentation pathway [(**5b**), (**20**) and (**3**) among others] is the loss of CH_3S (CD_3S) from the molecular ion (Scheme 3). Peaks at *m/e* M-47 can be derived via Pummerer and/or Stevens rearrangements followed by loss of SCH_3. Other characteristic peaks in the low mass region are also observed in all mass spectra at *m/e* 61 (formal loss of $CH_3\overset{+}{S}{=}CH_2$; *m/e* 62 (formal loss of CH_3SCH_3); and *m/e* 76 [formal loss of $(CH_3)_2S{=}N$]. Similar fragmentation patterns have been observed by Claus.[12]



SCHEME 3

The remainder of the fragmentation patterns, after the M-60 peak, invariably have fingerprint patterns derived from the parent therapeutically active sulfonamides; the results confirm those reported earlier by Spiteller and Kaschnitz.[13]

Ir spectra. Data are given in the Experimental Section for the compounds prepared in this study. The SO_2 stretching frequencies are about 20 cm^{-1} lower than in the sulfonamides from which they are derived. Assignments of other absorption bands are difficult to make because of overlapping in the fingerprint region.

EXPERIMENTAL

Ir spectra were recorded using a Perkin-Elmer Infracord Spectrometer Model 137B or a Pye Unicam SP1000 Spectrophotometer. Uv spectra were obtained using a Perkin-Elmer 202 or a Cary 14 Ultraviolet-Visible Spectrophotometer. ^{1}H-nmr spectra were determined using Varian T-60 or XL-100-15 instruments; tetramethylsilane (TMS) and 2,2-dimethyl-2-silapentane-5-sulfonate, sodium salt (DSS) were used as internal standards in nonpolar and polar solvents, respectively. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV by the thermal electron-impact ionization technique. Melting points were determined using a Thomas-Hoover capillary melting point apparatus; melting points were not corrected. Elemental analyses were performed by Microanalysis, Inc., Wilmington, Delaware, and by the Analytical and Physical Chemistry Department of Smith, Kline and French Laboratories, Philadelphia, Pa.

Thin layer chromatography was performed using Analtech silica gel chromatograms containing fluorescent indicator. Spots were visualized under uv light or developed in a chamber containing iodine crystals. Column chromatography was conducted automatically using a LKB Fraction Collector. Chemicals used directly without further purification were the best available commercial grade and were >97% pure: trifluoroacetic anhydride (Eastman); sulfanilamide, sulfadiazine, sulfamerazine, sulfathiazole, N^1-acetylsulfanilamide (City Chemical); and 2-amino-5-nitrothiazole and 2-aminopyrimidine (Aldrich).

All solvents were the purest commercial grades; they were dried and purified by standard methods. DMSO, used as both reactant and solvent, was distilled under reduced pressure from calcium hydride and the heart cut was stored in a glass bottle over Linde Molecular Sieves, Type 4A in a nitrogen atmosphere. The bottle was sealed with a serum cap and the DMSO was removed by means of a hypodermic syringe. DMSO-d_6 (Merck) was used as received. Triethylamine (TEA) (Aldrich) was fractionally distilled and stored over KOH pellets.

Preparation of iminosulfuranes and iminosulfonium salts. The preparation, isolation and purification of (**3**), (**4**), (**5a**), (**5b**), (**7c**), (**18**), (**21**), (**24**) and (**25**) have already been reported by us.[3,6] *S,S*-Hexadeuterodimethyl analogs of the compounds and those described below were prepared using DMSO-d_6 instead of DMSO in the synthetic sequence [(**19**), (**20**), (**22**), (**23**)].

(a) *S,S-Dimethyl-N⁴-(N¹-2-pyrimidinylsulfonilamido)iminosulfonium trifluoroacetate* (**7b**). To a stirred solution of DMSO (2.3 ml, 0.03 mol) in CH_2Cl_2 (10 ml), TFAA (4.2 ml, 0.03 mol) was added below −45°C. To the resulting white suspension, N^1-2-pyrimidinylsulfanilamide (sulfadiazine) (**6**) (5.0 g, 0.02 mol) dissolved in DMSO (15 ml) was added dropwise while maintaining the reaction temperature at −45°. The reaction mixture was stirred for 1.5 h and TEA (4.1 ml, 0.03 mol) was then added. The reaction mixture was allowed to warm to room temperature and slowly poured into ice and H_2O (400 ml) with stirring. Unreacted (**6**) (2 g) was recovered by filtration and the aqueous filtrate was extracted with CH_2Cl_2 (3 × 80 ml). The aqueous layer was concentrated under vacuum at 45° to a syrup which was dissolved in isopropanol (5 ml). The solution was diluted with ether (100 ml) and chilled to −6°C for 48 h. The white solid trifluoroacetate salt (4.0 g, 67% yield based on (**6**) consumed) was filtered and recrystallized from CH_3CN–CH_3OH, mp 186–187°C. TLC: R_f 0.40, single spot (silica gel GF 250 μ layer plate); developing solvent 25% CH_3OH in $CHCl_3$ (detection by both uv and iodine crystal staining). Nmr and uv: Table I. Ir (Nujol mull), cm^{-1}: 3120 (m), 3050 (m), 1692 (vs), 1600 (s), 1587 (vs), 1502 (vs), 1450 (vs), 1414 (m), 1341 (s), 1244 (w), 1204 (vs), 1170 (vs), 1130 (s), 1095 (s), 1003 (m), 948 (s), 836 (w), 795 (w), 715 (w). Anal. Calcd. for $C_{14}H_{15}F_3N_4O_4S_2$: C, 39.6; H, 3.56; N, 13.2; F, 13.4. Found: C, 39.9; H, 3.73; N, 13.4; F, 13.4.

(b) *S,S-Dimethyl-N⁴-(N¹-2-pyrimidinylsulfanilamido)iminosulfurane* (**7a**). The trifluoroacetate (**7b**) (200 mg, 0.47 mmol) was suspended in CH_2Cl_2 (2 ml) and TEA (0.5 ml, 3.6 mmol) was added with stirring. After 20 min, petroleum ether was added to the cloud point and the white precipitate was filtered 10 min later, washed with cold CH_2Cl_2 and vacuum dried; yield of (**7a**), 126 mg (86%), mp 153–155°C. TLC: R_f 0.40 single spot. Nmr and uv: Table I. Ir (Nujol mull) cm^{-1}: 3020 (m), 3100 (m), 1585 (vs), 1485 (s), 1450 (s), 1440 (s), 1410 (m), 1340 (m), 1328 (m), 1312 (m), 1280 (w), 1274 (w), 1265 (w), 1150 (vs), 1120 (w), 1089 (m), 998 (w), 938 (s), 921 (m), 899 (m), 834 (w), 812 (w), 800 (w), 680 (m). The mass spectral fragmentation pattern of (**7a**) is somewhat complex and is given in the Ph.D. thesis of T.W.K.[1]

(c) *S,S-Dimethyl-N⁴-(N¹-4-methyl-2-pyrimidinylsulfanilamido)iminosulfurane, sodium salt* (**9**). To the suspension of DMSO (1.45 ml)–TFAA (2.8 ml) prepared at −60°C in CH_2Cl_2 (10 ml), N^1-4-methyl-2-pyrimidinylsulfanilamide (sulfamerazine) (2.64 g, 0.01 mol) (**8**) in DMSO (5 ml) was added. The resulting mixture was stored for 1 h at −60°C followed by the addition of 2*N* NaOH (15 ml, 0.03 mol). The reaction mixture was allowed to warm to room temperature and volatiles were then removed at 35°C using a rotary evaporator. The residue was a thick, light brown syrup that showed one TLC spot which differed from that of (**8**). After 3 weeks storage at −6°C, the syrup crystallized and was triturated with isopropanol–methanol (10 ml, 1:1 v/v) leaving an off-white insoluble solid of crude (**9**) (2.7 g, 70%). It was dissolved in a minimum quantity of water *without heating* and isopropanol was added to the cloud point. The mixture was cooled to 0°C and the precipitate of pure (**9**), mp 228–230°C was obtained by vacuum filtration. TLC: R_f 0.30 single spot. Nmr and uv: Table I. Ir (Nujol mull) cm^{-1}: 1590 (vs), 1500 (s), 1490 (s), 1440 (vs), 1400 (vs), 1300 (vs), 1270 (s), 1240 (s), 1200 (s), 1132 (vs), 1100 (vs), 1065 (m), 990 (m), 900 (m), 870 (s), 820 (m), 805 (m), 765 (m). Anal. Calcd. for $C_{13}H_{15}N_4O_2S_2Na \cdot H_2O$: C, 42.8;

H, 4.70; N, 15.4; S, 17.6; Na, 6.30. Found: C, 42.8; H, 4.64; N, 15.4; S, 17.1; Na, 6.52.

(d) *S,S-Dimethyl-N⁴-(N¹-2-thiazolylsulfanilamido)iminosulfurane* (**11**). Prepared from N¹-2-thiazolylsulfanilamide (sulfathiazole) (**10**) essentially as described for (**9**) except that after the addition of 2*N* NaOH the reaction mixture was poured into isopropanol and chilled in a freezer at −6°C overnight. Crude (**11**) was obtained as a cream-coloured solid by suction filtration. It was washed with isopropanol–CH_2Cl_2 and the residue of pure (**11**) was dried under vacuum [mp 138–139°C (dec); 72% yield]. TLC: R_f 0.30 single spot. Nmr and uv: Table I. Ir (Nujol mull) cm^{-1}: 3230 (vw), 1590 (vs), 1575 (vs), 1490 (s), 1425 (s), 1420 (m), 1398 (s), 1282 (vs), 1272 (vs), 1200 (w), 1188 (w), 1134 (vs), 1088 (vs), 1045 (w), 1000 (w), 985 (m), 930 (vs), 893 (m), 857 (w), 840 (m), 776 (w), 730 (m), 715 (m), 690 (s), 625 (s). Mass Spectral Data:[1] Table II. Anal. Calcd. for $C_{11}H_{13}N_3S_3O_2$: C, 41.9; H, 4.15; N, 13.3; S, 30.5. Found: C, 42.4; H, 4.38; N, 13.2; S, 3.06.

(e) *S,S-Dimethyl-N⁴-(N¹-acetylsulfanilamido)iminosulfonium trifluoroacetate* (**13a**). Prepared from *N*¹-acetylsulfanilamide (**12**) essentially as described for (**7c**): mp 181–182°C; yield, 60%. TLC: R_f 0.15 single spot. Nmr and uv: Table I. Ir (Nujol mull) cm^{-1}: 3425 (vw), 3333 (vw), 1692 (vs), 1592 (vs), 1538 (s), 1408 (m), 1333 (s), 1236 (s), 1200 (vs), 1176 (vs), 1160 (vs), 1124 (vs), 1089 (s), 1055 (m), 1000 (s), 866 (s), 832 (m), 800 (m), 724 (s), 682 (s). Mass Spectral Data:[1] No molecular ion; fragmentation pattern identical with that of (**13b**).

(f) *S,S-Dimethyl-N⁴-(N¹-acetylsulfanilamido)iminosulfurane* (**13b**). Prepared from (**13a**) essentially as described for (**7a**) except that (**13b**) precipitated from the basification reaction mixture without addition of petroleum ether and was filtered off, mp 163–164°C; yield, 77%. TLC: R_f 0.15 single spot. Nmr and uv: Table I. Ir (Nujol mull) cm^{-1}: 3333 (vw), 1698 (vs), 1575 (vs), 1538 (vs), 1408 (m), 1323 (vs), 1285 (m), 1261 (vs), 1222 (s), 1143 (vs), 1112 (m), 1085 (s), 996 (m), 938 (m), 895 (m), 848 (m), 685 (m). Mass Spectral Data:[1] Table II. Anal. Calcd. for $C_{10}H_{14}N_2O_3S_2$: C, 43.8; H, 5.14; N, 10.2; S, 23.4. Found: C, 43.9; H, 5.21; N, 10.1; S, 23.3.

(g) *S,S-Dimethyl-S-(5-nitrothiazolyl)iminosulfurane* (**15**). Prepared from 2-amino-5-nitrothiazole (**14**) essentially as described for (**13b**) except that the bright yellow crude (**15**) was washed with CH_2Cl_2, triturated with isopropanol and then with a minimal quantity of acetone. The insoluble product (92%) consisted of pure (**15**), mp 194–195°C. TLC: R_f 0.35, single spot (1:1 acetone–benzene used for development). Nmr and uv: Table I. Ir (Nujol mull) cm^{-1}: 3400 (vw), 1503 (s), 1480 (vs), 1450 (vs), 1310 (vs), 1228 (vs), 1212 (vs), 1145 (w), 1110 (m), 1046 (w), 992 (m), 968 (w), 922 (w), 841 (m), 760 (w)m 740 (w). Mass Spectral Data:[1] Molecular ion 205 (26). Anal. Calcd. for $C_5H_7N_3O_2S_2$: C, 29.3; H, 3.44; N, 20.5; S, 31.2. Found: C, 29.5; H, 3.75; N, 20.2; S, 31.4.

(h) *S,S-Dimethyl-N-(2-pyrimidinyl)iminosulfonium Trifluoroacetate* (**17**). Prepared from 2-aminopyrimidine (**16**) essentially as described for (**7b**) except that after the addition of TEA, ether was added at room temperature to precipitate crude (**17**). The white precipitate was filtered, washed with ether and dried; yield, 34%. Recrystallization from isopropanol: CH_3OH (3:2 v/v) provided pure (**17**), mp 124–125.5°C. TLC: R_f 0.4, single spot (1:9 CH_3OH–$CHCl_3$ used for development). Nmr and uv: Table I. Ir (Nujol mull) cm^{-1}: 3400 (vw), 1676 (s), 1620 (s), 1546 (w), 1512 (m), 1445 (vs), 1420 (m), 1410 (m), 1347 (s), 1228 (w), 1204 (s), 1164 (s), 1125 (vs), 1100 (w), 1059 (w), 1038 (m), 980 (m), 962 (m), 919 (m), 825 (m), 800 (m), 795 (m), 775 (m), 718 (s). Mass Spectral Data:[1] No molecular ion; base peak, 155 (100, M–$HO\overset{O}{\overset{\|}{C}}CF_3$; 140 (71, 155–$CH_3$; 108 (42), 155–$SCH_3$. Anal. Calcd. for $C_8H_{10}F_3N_3O_2S$: C, 35.7; H, 3.74; N, 15.6; S, 11.9. Found: C, 35.4; N, 3.47; N, 15.7; S, 11.8.

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