Synthesis and Cycloaddition Reactions of Fluorenethione S-Benzoylimide

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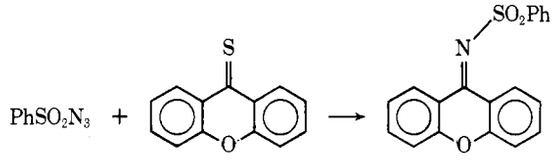
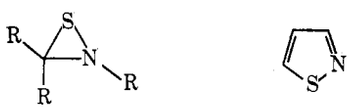
Reaction of *N*-(trimethylsilyl)benzamide with sulfur dichloride afforded benzamide-*N*-sulfenyl chloride, which reacted rapidly with diphenyldiazomethane at −30° to give *N*-benzoylchlorodiphenylmethanesulfenamide. Treatment of the latter with triethylamine at −78° resulted in the formation of 2,2,5-triphenyl-1,3,4-oxathiazole, and no evidence was obtained to support the intermediacy of benzophenthione *S*-benzoylimide in this reaction. Reaction of the above sulfenyl chloride with 9-diazofluorene at −30° gave *N*-benzoyl-9-chlorofluorenesulfenamide, which with triethylamine at −78° resulted in the formation of fluorenethione *S*-benzoylimide which could be isolated as a metastable solid at room temperature; however, in solution at *ca.* −30°, an electrocyclic ring closure to 5′-phenylspiro[fluorene-9,2′-[1′,3′,4′]oxathiazole] resulted. When this thione *S*-imide was treated with *N*-isobutenylpyrrolidine at −78° there was obtained 2′-benzoyl-3′-pyrrolidine-4′,4′-dimethylspiro[fluorene-9,5′-[1′,2′]isothiazolidine] while reaction with *N*-propenylpiperidine afforded 2′-benzoyl-3′-piperidine-4′-methylspiro-[fluorene-9,5′-[1′,2′]isothiazolidine]. The thione *S*-imide was also found to react with the terminal double bond of 1-diethylaminobutadiene to give 2′-benzoyl-3′-(*trans*-*N*-ethenyldiethylamine)spiro[fluorene-9,5′-[1′,2′]isothiazolidine] and an unstable sulfonium ylide, 2-phenyl-4-fluorenylide-5-methyl-6-diethylamino-1,4,3-oxathiazine, was obtained from the reaction with 1-(diethylamino)-1-propyne.

Among the heterocumulenes containing a central tetravalent (d-orbital participation) sulfur atom related to sulfur dioxide shown in Table I, only thione *S*-imides[2] represented an unknown[3] entity. Pedagogically, thione *S*-imides could be derived from the addition of a nitrene to a thione; however, the only reported reaction which might have mechanistically followed this course was the thermal decomposition of benzenesulfonyl azide (**1**) in the presence of xanthione (**2**), which only gave the imine **3**.[4] Electrocyclic

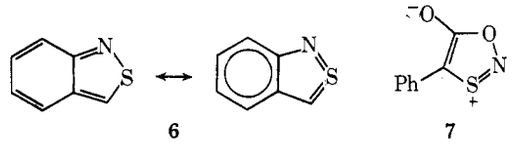


1 **2** **3**

opening of thiaziranes (**4**) would also constitute synthesis of this heterocumulene, although the only reaction in which **4** was possibly an intermediate provided no products which could be rationalized as derived from a thione *S*-imide.[5] In an electronic sense perturbed examples of this grouping appear in isothiazoles (**5**) and more particularly in thioanthranil (**6**) and 4-aryl-1,3,2-oxathiazolium 5-oxides (**7**).

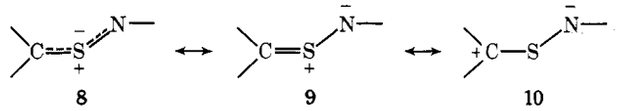


4 **5**



6 **7**

The stability of thione *S*-imides would be expected to be dependent on the relative contributions of the canonical structures **8**–**10** with a substituent unperturbed thione *S*-



8 **9** **10**

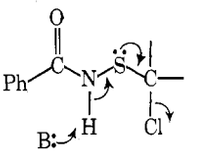
imide charge distribution most closely approximated by structure **9**. We wish to report the details of the synthesis

Table I
Heterocumulenes Containing Tetravalent Sulfur

$R_2C{=}S{=}CR_2$, thione ylides[1]	RN=S=NR, sulfur diimides
$R_2C{=}S{=}NR$, thione *S*-imides	RN=S=O, *N*-sulfinylamines
$R_2C{=}S{=}O$, sulfines	O=S=O, sulfur dioxide

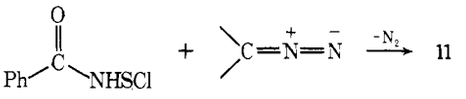
of this new functional group with substitution patterns stabilizing contributor **8**.

An attractive if not challenging synthetic approach to this functional group would focus on a base-promoted 1,3-dehydrohalogenation of a suitably substituted sulfenamide **11** as an ultimate step. A synthetically flexible reaction



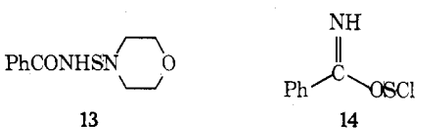
11

envisioned for the production of **11** would involve **12** and a diazo compound, a step for which considerable precedent



12

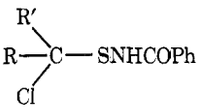
may be found.[6] The reaction of *N*-(trimethylsilyl)benzamide[7] with sulfur dichloride in ether–pentane solution at 0° gave in good yield **12**, mp 105–108° dec, whose 1670-cm^{-1} (C=O) absorption in the infrared and reaction with morpholine to produce[8] **13** substantiates the assigned structure rather than the alternative **14**. Treatment of **12**



13 **14**

with diphenyldiazomethane in THF solution at −30° afforded the rather unstable *N*-benzoylchlorodiphenylmethanesulfenamide (**15a**), mp 114–117 dec, in low yield. Triethylamine reacted rapidly with **15** in THF solution at −78° without visible formation of a colored intermediate to yield 1 equiv of triethylamine hydrochloride and 2,2,5-tri-

phenyl-1,3,4-oxathiazole (**16a**), mp 118–120°, which displayed infrared absorptions at 1605 (C=N) and 1575 cm^{-1}



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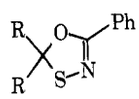

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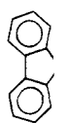
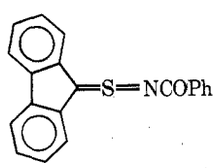
a, R, R′ = Ph

b, R, R′ = 

c, R = H; R′ = CO_2Et

(C=C) along with a mass spectrum which was most informative with fragment ions at *m/e* 182 ($C_{13}H_{10}O^+$) and 103 ($C_7H_5N^+$). Since all attempts to trap an intermediate thione *S*-imide during the dehydrohalogenation of **15a** failed, attention was directed toward stabilization by a fluorenyl substituent. In this case the required chlorosulfenamide **15b,** mp 114–116° dec, was obtained in good yield by an analogous reaction with diazofluorene and when submitted to the action of triethylamine in THF at −78° gave a deep red (λ_{max} 484 nm) solution of 9-fluorenethione *S*-benzoylimide (**17**).

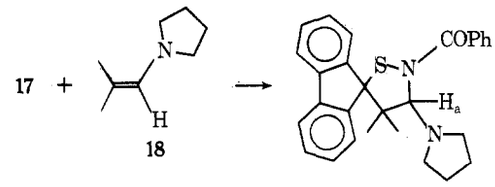


17

Unlike sulfines[9] (R_2CSO), passage of anhydrous HCl into the THF solution of **17** at −78° resulted in the rapid reformation of precursor **15b.** When a solution of **17** was allowed to warm to *ca.* −30° the color was discharged and the electrocyclic closure product, 5-phenylspiro[fluorene-9,2′-[1′,3′,4′]oxathiazole] (**16b**), mp 100–103° dec, was isolated. The latter product had an infrared spectrum similar to that of **16a** with mass spectral ions at *m/e* 196 ($C_{13}H_8S^+$), 180 ($C_{13}H_8O^+$), and 103 ($C_7H_5N^+$). Furthermore, on standing at 30° for 14 days **16b** decomposed to give fluorenone, benzonitrile, and sulfur.[10] Although **17** underwent cyclization at temperatures greater than −30° in solution, it could be isolated as metastable crystals at room temperature which underwent instantaneous transformation to **16b** upon the slightest amount of mechanical deformation.

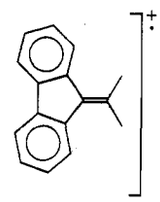
With substantial evidence at hand that the intermediate from the dehydrohalogenation was 9-fluorenethione *S*-benzoylimide, attention was turned to a search for cycloaddition reactions. Initial studies revealed that the cycloadditive reactivity of **17** at 30° for the capture of electrophiles such as phenyldiazomethane or diphenyl ketene, and nucleophiles such as vinyl ethers and ketene acetals, was not sufficient to compete against internal cyclization. However, **17** reacted rapidly with the more nucleophilic alkenes, enamine and ynamines, at −78°.

When **17,** generated *in situ* at −78° in a THF solution, was treated with *N*-isobutenylpyrrolidine (**18**) the solution decolorized immediately and there was obtained 2′-benzoyl-3′-pyrrolidine-4′,4′-dimethylspiro[fluorene-9,5′-[1′,2′]isothiazolidine] (**19**) as the only isolable product. The nmr spectrum of **19** displayed an aromatic multiplet at δ 7.47 (13 H), a singlet for H_a at δ 5.62 (1 H), and nonequivalent methyl singlets at δ 1.66 (3 H) and 0.58 (3 H) as well as pyrrolidine ring multiplets at δ 3.23 (4 H). The infrared



18 19

spectrum contained a tertiary amide C=O absorption at 1635 cm^{-1} and the mass spectrum revealed a molecular ion at *m/e* 440 and fragments at *m/e* 206 and 202 corresponding to **20** and **21** and the major ions resulted from cleavage of the ring system into its chemical precursors (*m/e* 315 and 125).



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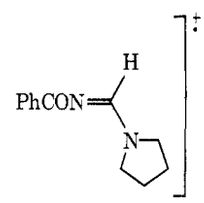

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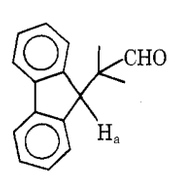
The possibility of **19** having a structure analogous to **37** or **38** may be discounted, since the ultraviolet spectrum of the adduct is not characteristic of fluorenyl sulfonium ylides.[13] A structure analogous to **36** is improbable, since the C=O absorption for acyl iminosulfuranes has been observed at 1600–1540 cm^{-1} in the infrared.[14] Since the C=N linkage may show infrared absorptions in the range 1690–1630 cm^{-1}, spectral data do not adequately distinguish between a five-membered ring adduct and a seven-membered ring structure such as **40;** however, sufficient chemical evidence was also obtained to support an isothiazolidine ring structure. Hydrolysis of **19** in 2 *N* sodium hydroxide afforded 9-isobutyraldehydefluorene (**22**) and benzamide as



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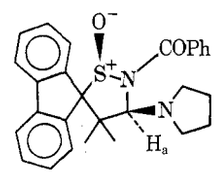
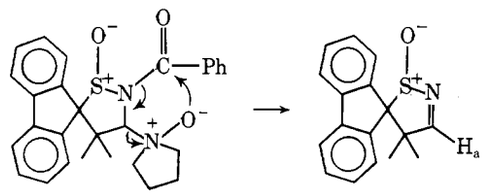


23

the only isolable products and the structure of the former is based on observed nmr singlets for the aldehydic proton at δ 9.78, for H_a at δ 6.83, and for the methyl groups at δ 1.01 while the infrared spectrum displayed an aldehyde C=O absorption at 1725 cm^{-1}. Oxidation of **19** with 1 equiv of *m*-chloroperbenzoic acid provided 2′-benzoyl-3′-pyrrolidine-4′,4′-dimethylspiro[fluorene-9,5′-[1′,2′]isothiazolidine] 1′-oxide (**23**) in moderate yield. The mass spectrum of **23** was consistent with the structure shown and the infrared spectrum contained a C=O absorption at 1665 cm^{-1} and a strong S=O absorption at 1290 cm^{-1}. The nmr spectrum was similar to that of **19** except for a downfield shift of 0.32 ppm for H_a, 0.19 ppm for the lower field methyl, and 0.08 ppm for the higher field methyl. The addition of excess *m*-chloroperbenzoic acid resulted in the formation of 4′,4′-dimethylspiro[fluorene-9,5′-[1′,2′]dihydroisothiazole] 1′-oxide (**24**) in 64% yield. This oxidative elimination may be the result of decomposition of the intermediate *N*-oxide **25,** as shown.

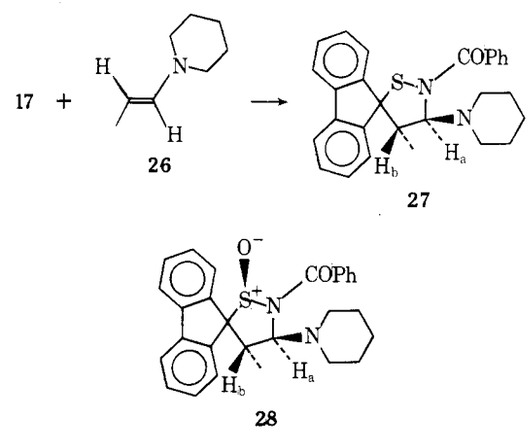
The nmr spectrum of **24** displayed a multiplet at δ 7.46 (9 H) composed of the fluorenyl ring protons and H_a and, in addition, singlets at δ 1.67 (3 H) and 0.96 (3 H) accounted for the nonequivalent methyl groups. The infrared spec-



25 24

trum displayed a C=N stretching absorption at 1595 cm^{-1} and the mass spectrum exhibited a molecular ion at *m/e* 281 with principal fragments at *m/e* 233 ($C_{17}H_{15}N^+$) and 206 ($C_{16}H_{14}^+$). The oxidative elimination to give **31** confirms the structure assigned to **19** and **23,** since the only other possible adduct capable of this elimination mechanism would have a structure analogous to **37.**

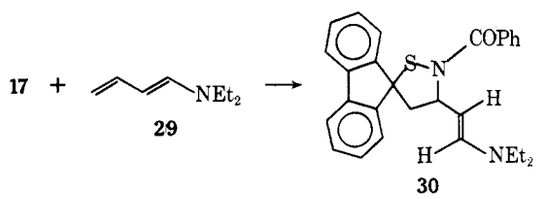
Although the reaction of heterocumulenes with enamines possessing β hydrogens often leads to acyclic adducts, treatment of **17** with *N*-propenylpiperidine (**26**) at −78° resulted in the exclusive formation of 2′-benzoyl-3′-piperidine-4′-methylspiro[fluorene-9,5′-[1′,2′]isothiazolidine] (**27**) in good yield. The nmr spectrum of **27** displayed signals centered at δ 7.46 (m, 13 H), 5.60 (d, 1 H, J = 8 Hz, H_a), 3.17 [m, 5 H, H_b and $(CH_2)_2N$], 1.59 [s, 6 H, $(CH_2)_3$], and 0.56 (d, 3 H, J = 6.5 Hz, CH_3). Although **27** is tentatively assigned as having a trans relationship for H_a and H_b, the possibility cannot be eliminated that it actually possesses cis stereochemistry, since the coupling constant of H_a, H_b is intermediate in the ranges expected for cis or trans isomers of flexible five-membered rings. The infrared spectrum of **27** was similar to that of **19,** having a C=O stretching absorption at 1637 cm^{-1}, and the mass spectrum exhibited a molecular ion at *m/e* 440.



26 27 28

Compound **27** was also readily oxidized with *m*-chloroperbenzoic acid to 2′-benzoyl-3′-piperidine-4′-methylspiro-[fluorene-9,5′-[1′,2′]isothiazolidine] 1′-oxide (**28**), albeit in lower yield than the oxidation of **19** to **23.** The infrared spectrum of **28** was similar to that of **23,** containing C=O and S=O stretching absorptions at 1665 and 1295 cm^{-1}, respectively. The nmr spectrum displayed signals at δ 7.60 (m, 13 H, aromatic), 5.78 (d, 1 H, J = 8.5 Hz, H_a), 3.32 [m, 5 H, H_b and $(CH_2)_2N$], 1.55 [s, 6 H, $(CH_2)_3$], and 0.77 (d, 3 H, J = 7 Hz, CH_3). The cis relationship of the oxide function to H_b is tentatively assigned based on the observed nmr downfield shift of H_b and the H_a, H_b coupling constant.

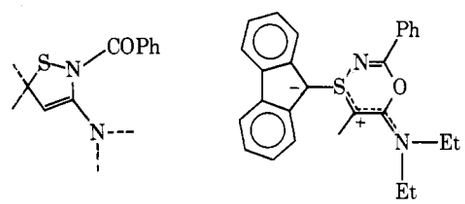
In an attempt to determine if **17** would behave as a dienophile in a manner similar to sulfines,[15] **17** was treated with 2,3-dimethylbutadiene, but no reaction occurred below −30° and only the oxathiazole **16b** was isolated. The thione *S*-imide did react rapidly at −78° with 1-diethylaminobutadiene (**29**); however, no 1,4 cycloadducts were detected. The only product was 2-benzoyl-3′-(*trans*-*N*-ethenyldiethylamino)spiro[fluorene-9,5′-[1′,2′]isothiazolidine] (**30**), which was isolated in 37% yield. Since attempts



29 30

to purify **30** for complete analysis were unsuccessful, the structure assigned is based primarily on its nmr and ir spectrum (see Experimental Section). Furthermore, the ultraviolet absorption spectrum of **30** was very similar to those of adducts **19** and **27.**

Based on the isothiazolidine adducts obtained from the reaction of **17** with enamines, the reaction with ynamines might possibly yield dihydroisothiazoles such as **31.** However, when 1-(diethylamino)-1-propyne was added to a THF solution of **17** at −78°, 2-phenyl-4-fluorenylidine-5-methyl-6-diethylamino-1,4,3-oxathiazine (**32**) was the only adduct isolated. The fluorenyl ylide **32** was a yellow, crys-



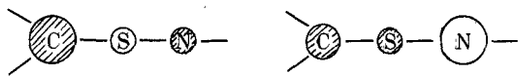
31 32

talline solid which decomposed in solution at room temperature or at the melting point (125–126°). The ultraviolet spectrum was similar to that of 9-dimethylsulfonium fluorenylidine,[16] displaying λ_{max} (ϵ) at 242 (20,500), 253 (25,900), 261 (33,600), 278 (12,500), 327 (9450), 311 (9770), and 375 nm (5800). The nmr spectrum contained aromatic protons centered at δ 7.58 (m, 13 H), a methyl singlet at δ 2.72 (3 H), and nonequivalent *N*-ethyl groups as quartets at δ 3.75 (2 H, J = 7.3 Hz) and 3.60 (2 H, J = 7.3 Hz) and triplets at 1.54 (3 H, J = 7.3 Hz) and 1.06 (3 H, J = 7.3 Hz). The infrared spectrum of **32** was transparent between 1600 and 2900 cm^{-1} and had C=C and C=N absorptions at 1590, 1525, and 1500 cm^{-1} and suggests that the charge-delocalized structure **32** is the best representation of the structure, since no characteristic enamine C=C absorption between 1630 and 1660 cm^{-1} appears. Upon thermal decomposition **32** affords benzonitrile, a trace of difluorenylidine, and a plethora of other products which have not been identified.

A mechanistic rationalization of the formation of such diverse cycloadducts from **17** should depend upon the following considerations. In the family of sulfur 1,3 dipoles ($X{=}S^+{-}Y^-$), those with appropriate stabilizing substituents would be expected to have a lower order of electrophilic reactivity toward alkene cycloaddends than other dipoles where the central atom has a higher electronegativity. The electrophilic center will be sulfur in the case of electron-withdrawing substitution at both termini but a considerable amount of the sulfur positive change would undergo leakage onto carbon if this center were substituted with electron-donating substituents (*cf.* **9** *vs.* **10**). Electron-rich but very asymmetric cycloaddends in nonconcerted charge-controlled[17] addition reactions to such thione *S*-imides should establish initial bond formation to sulfur in the former case and possibly carbon in the latter case. This initial sulfur–cycloaddend union is also enhanced by the large sul-

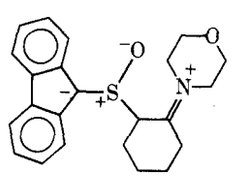
fur (but not as large as carbon, see (Chart I) LUMO coefficient in that frontier orbital (with electron-rich dipolarophiles such LUMO control[18] of the dipole is expected).

Chart I
Estimated Frontier Orbitals of R_2CSNR



LUMO HOMO

The observed formation of **33** from fluorenethione *S*-oxide and *N*-cyclohexenylmorpholine supports this argument, as also observed in the case of sulfines.[19] Therefore it



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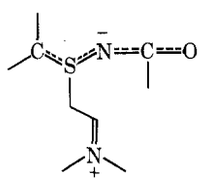

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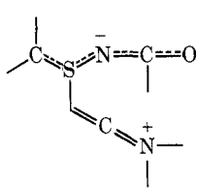
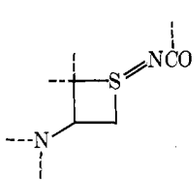


35

may be concluded that nonconcerted cycloaddition reactions of *N*-acyl thione *S*-imides with electron-rich alkenes (NC=C) or alkynes (NC≡C) which proceed *via* the dipolar intermediate, **34** or **35**, would provide ultimate cycloadducts such as **36, 37,** or **38** (or as the dehydro equivalent).



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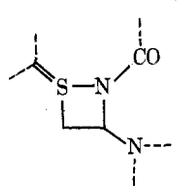

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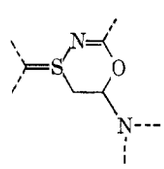

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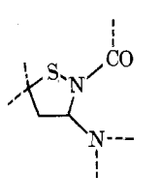
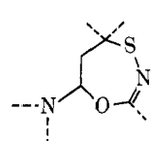


39



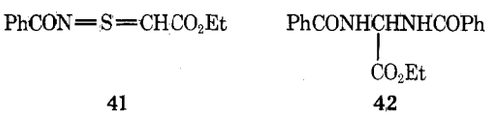
40

For concerted cycloaddition reactions of acyl thione S-imides with electronically asymmetric alkenes the $[_\pi 2 + _\pi 4]$ combinations (**38** and **39**) would be expected. Finally, the formation of adduct **40** requires antarafacial addition in a concerted reaction and is electrostatically unfavorable in the initial step of a charge-controlled nonconcerted reaction.

At first inspection it would appear that these two types of cycloadducts obtained represent the two symmetry allowed [2 + 4] possibilities from a concerted cycloaddition. However, it is difficult to reconcile the remarkably different pathway regioselectivity demonstrated by an enamine *vs.* an ynamine. Orbital control of such concerted cycloadditions requires that the interaction energy (inversely proportional to the LUMO–HOMO cycloaddends energy difference) be minimized and the interacting frontier orbitals have phase-compatible and large coefficients for union. With dipole LUMO control[18] expected in this case a cycloadduct of the type **39** should be preferred and formed from enamines with a smaller interaction energy than from ynamines (the HO orbitals of alkynes are lower in energy than those of the corresponding alkenes). However, the interaction energy is also dependent upon coulombic terms and from such charge-separation considerations (charge control) the concerted formation of cycloadducts such as **38** would be favored. The course followed by the two regioisomeric cycloadditions here may reflect the interplay between orbital and charge control from minor electronic variations in one cycloaddend.

Finally, a nonconcerted cycloaddition mechanism involving the intermediate **34** (for enamines) or **35** (for ynamines) might be involved. The smaller S–C–C angle (owing to a central carbon atom of higher hybridization state) in the case of **34** than that of **35** permits closure of **34** to **19** or **27** while **35** is restricted to the less strained cyclization to **32.** A Stevens rearrangement of **37** involving either a radical[20] or polar intermediate[21] would yield the isolated isothiazolidines.[22] Further expansion of **32** to ring systems such as **40** by such a mechanism is energetically blocked by the increased strength of the C–S ring bond due to the electron-releasing amino substituent.

To extend this synthetic route to other thione *S*-imides, **12** was treated with ethyl diazoacetate in THF at 30°, which afforded in low yield the unstable sulfenamide, **15c,** mp 111–116° dec. Dehydrohalogenation of **15c** with triethylamine in THF led to the formation of a colored intermediate (probably the thione *S*-imide **41**) with a comparably long life-time even at 30°. However, attempts to isolate **41**



41 **42**

by removal of the solvent led to a complex mixture of products only one of which was obtained crystalline and had spectral and analytical characteristics which suggest structure **42.**

Studies on the synthesis of thione S-imides via the intermediary reaction of **12** with other diazo compounds met only with disappointments. Diazo functions substituted with strong electron-withdrawing groups (such as diazodimethylmalonate and diazoanthrone) failed to react with **12** and the reaction of more nucleophilic 9-diazoxanthone with **12** resulted in the formation of benzonitrile, *N,N'*-thiobisbenzamide, and 9-xanthone azine.

Experimental Section[23]

***N*-(Trimethylsilyl)benzamide.** *N*-(Trimethylsilyl)benzamide was prepared by modification of the procedure of Derkach and Smetankina.[7] Freshly distilled (bp 58–59°) chlorotrimethylsilane (21.7 g, 0.20 mol) was added dropwise over a period of 1 hr under nitrogen to 24.2 g (0.20 mol) of benzamide and 22.3 g (0.22 mol) of triethylamine in 150 ml of anhydrous ether and 75 ml of anhydrous THF. When the addition was complete, stirring was continued for 2 hr and then the precipitated triethylamine hydrochloride was removed by filtration. After the precipitate was washed with two 50-ml portions of anhydrous ether the combined filtrate was concentrated with a rotary evaporator under reduced pressure to a colorless oil. Vigorous stirring of the oil with dry hexane caused the crystallization of 38 g (98%) of *N*-(trimethylsilyl)benzamide, mp 62–65° (lit.[7] mp 63–65°).

Benzamide-*N*-sulfenyl Chloride (12). *N*-(Trimethylsilyl)-benzamide (38 g, 0.196 mol) in 175 ml of anhydrous ether was added dropwise under nitrogen over a 3-hr period to 30.3 g (0.294 mol) of freshly distilled sulfur dichloride in 35 ml of anhydrous ether and 50 ml of pentane maintained at 0°. After about one-third had been added, a yellow precipitate began to separate from the reaction mixture. When the addition was complete, the reac-

tion mixture was stirred at 0° for an additional 6 hr. Pentane (175 ml) was then added and the reaction mixture was cooled to −30° for 1 hr. The precipitate which had separated from the solution was collected by filtration under a nitrogen atmosphere and dried under reduced pressure at 0° to yield 30.9 g (84%) of benzamide-*N*-sulfenyl chloride (**12**) as bright yellow microneedles: mp 105–108° dec; λ_{max} (THF) 209 nm (ϵ 7070), 237 (12,900), and 350 (140); ir ($CHCl_3$) 3200 (NH) and 1670 cm^{-1} (C=O); nmr (DMSO-d_6) δ 11.66 (s, 1 H), 7.97 (m, 2 H), and 7.50 (m, 3 H).

Anal. Calcd for C_7H_6NOSCl: C, 44.80; H, 3.22; N, 7.46; S, 17.09. Found: C, 44.68 H, 3.29; N, 7.52; S, 17.13.

Compound **12** has been kept for 3 months without appreciable deterioration if it was tightly sealed under an inert atmosphere and stored below 0°.

***N,N'*-Thiobenzamidemorpholine (13).** Benzamide-*N*-sulfenyl chloride (3 g, 0.016 mol) in 10 ml of anhydrous THF was added dropwise over a period of 20 min under nitrogen to 2.8 g (0.032 mol) of morpholine in 25 ml of THF maintained at −78°. When the addition was complete, stirring was continued for an additional 1 hr. The precipitated morpholine hydrochloride (1.94 g, 98%) was removed by filtration and the filtrate was concentrated with a rotary evaporator under reduced pressure to a yellow oil. The oil was dissolved in a minimum volume of hot benzene–hexane; and upon cooling, 2.08 g of *N,N'*-thiobenzamidemorpholine (**13**) separated as colorless plates. When the mother liquor was concentrated to half volume and allowed to stand for 12 hr an additional 0.175 g of **13** crystallized to give a total yield of 2.25 g (59%): mp 117–118°; ir ($CHCl_3$) 3410 and 3300 (NH) and 1680 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.12 (s, 1 H), 7.81 and 7.43 (m, 5 H), 3.62 (m, 4 H), and 3.17 (m, 4 H); mass spectrum (70 eV) *m/e* (rel intensity) 238 (33), 121 (73), 105 (100), 86 (44).

Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92; N, 11.76; S, 13.45. Found: C, 55.52; H, 5.98; N, 11.73; S, 13.35.

Compound **13** was also prepared by the dropwise addition of 10 g (0.065 mol) of morpholine-*N*-sulfenyl chloride under nitrogen to 9.3 g (0.065 mol) of the sodium salt of benzamide (prepared by the addition of benzamide to an equimolar amount of sodium hydride in refluxing DME) suspended in 150 ml of DME. When the addition was complete, the solution was filtered and the filtrate was concentrated with a rotary evaporator under reduced pressure to a yellow powder. Recrystallization from benzene–hexane gave 7.1 g (46%) of **13**, mp 117–118°, both pure and when admixed with the above product.

***N,N'*-Thiobenzamideaniline.** Benzamide-*N*-sulfenyl chloride (2 g, 0.011 mol) in 15 ml of anhydrous THF was added dropwise over a period of 45 min under nitrogen to 2.05 g (0.022 mol) of aniline in 15 ml of THF at −78°. When the addition was complete the reaction mixture was stirred for an additional 1 hr, and was then warmed to 30°. The precipitated aniline hydrochloride (1.30 g, 92%) was removed by filtration and the filtrate was concentrated with a rotary evaporator under reduced pressure to a dark residue. The residue was dissolved in ether and decolorized with Norit, and the ether was removed under reduced pressure to give a colorless powder. Two crystallization from benzene–hexane gave 1.43 g (54%) of *N,N'*-thiobenzamideaniline as colorless needles: mp 148–150° dec; ir ($CHCl_3$) 3490 (broad, NH), 1675 (C=O), and 1600 cm^{-1} (C=C); nmr (DMSO-d_6) δ 10.12 (s, 1 H), 8.39 (s, 1 H), 7.93 (m, 2 H), and 7.15 (m, 8 H); mass spectrum (70 eV) *m/e* (rel intensity) 244 (4), 121 (77), 105 (100), 93 (64).

Anal. Calcd for $C_{13}H_{12}N_2OS$: C, 63.90; H, 4.95; N, 11.47; S, 13.13. Found: C, 63.71; H, 5.02; N, 11.38; S, 13.22.

***N*-Benzoylchlorodiphenylmethanesulfenamide (15a).** Diphenyldiazomethane[24] (1.03 g, 0.0053 mol) in 10 ml of anhydrous THF was added dropwise over a period of 30 min under nitrogen to 1.0 g (0.0053 mol) of benzamide-*N*-sulfenyl chloride in 25 ml of THF maintained at −30°. When the evolution of nitrogen had ceased (*ca.* 10 min after the addition was complete) the solvent was removed with a rotary evaporator under reduced pressure. The resulting residue was dissolved in a minimum volume of anhydrous ether and cooled to −30°. After standing overnight, 0.178 g (11%) of *N*-benzoylchlorodiphenylmethanesulfenamide (**15a**) had separated as light yellow needles: mp 114–117° dec; ir ($CHCl_3$) 3410 (NH) and 1675 cm^{-1} (C=O); nmr (acetone-d_6) δ 7.34 (m, 6 H) and 6.83 (m, 10 H).

Compound **15a** rapidly decomposed upon exposure to moisture or if allowed to stand at room temperature. Noticeable decomposition had also occurred after 3 days at −30°. The instability of **15a** precluded elemental analysis.

Treatment of 15a with Triethylamine. Isolation of 2,2,5-Triphenyl-1,3,4-oxathiazole (16a). Triethylamine (0.59 g, 0.0053 mol) was added in one portion to 1.87 g (0.0053 mol) of **15a** under a nitrogen atmosphere at −78°. Although a precipitate of triethylamine hydrochloride formed immediately, no color changes were observed. After warming to 30° the triethylamine hydrochloride was removed by filtration and the filtrate was concentrated with a rotary evaporator under reduced pressure. The resulting residue was crystallized from ether–hexane to give 0.52 g (31%) of 2,2,5-triphenyl-1,3,4-oxathiazole (**16a**) as colorless plates: mp 118–120°; ir ($CHCl_3$) 1605 (C=N) and 1575 cm^{-1} (C=C); nmr ($CDCl_3$) δ 7.98 (m, 2 H) and 7.38 (m, 13 H); mass spectrum (70 eV) *m/e* (rel intensity) 182 (9.2), 103 (100).

Anal. Calcd for $C_{20}H_{15}NOS$: C, 75,68; N, 4.76; N, 4.41; S, 10.10. Found: C, 75.53; H, 4.81; N, 4.45; S, 9.95.

Attempted Trapping of Benzophenthione *S*-Benzoylimide. A THF solution (35 ml) of 1.87 g (0.0053 mol) of **15a** and 0.664 g (0.0053 mol) of *N*-isobutenylpyrrolidine maintained at −78° under a nitrogen atmosphere was treated in one portion with 0.59 g (0.0053 mol) of triethylamine. After warming to 30°, the precipitated triethylamine hydrochloride was removed by filtration, and the filtrate was concentrated with a rotary evaporator under reduced pressure. An infrared spectrum of the resulting residue revealed that the only product present was 2,2,5-triphenyl-1,3,4-oxathiazole (**16a**).

***N*-Benzoyl-9-chloro-9-fluorenesulfenamide (15b).** 9-Diazofluorene[25] (3.06 g, 0.016 mol) in 20 ml of anhydrous THF was added dropwise over a period of 1 hr under nitrogen to 3.0 (0.015 mol) of benzamide-*N*-sulfenyl chloride in 50 ml of THF maintained at −30°. When the addition was complete, stirring was continued until the evolution of nitrogen had ceased (*ca.* 15 min), and then the THF was removed with a rotary evaporator under reduced pressure. The resulting residue was dissolved in anhydrous ether and cooled to −30°. After 4 hr the light yellow crystals that had separated from the solution were collected. Washing the crystals with three 25-ml portions of anhydrous ether gave 4.28 g (76%) of *N*-benzoyl-9-chloro-9-fluorenesulfenamide (**15b**) as colorless needles: mp 114–116° dec; ir (KBr) 3280 (NH) and 1660 cm^{-1} (C=O); nmr (DMSO-d_6) δ 8.10 (s, 1 H) and 7.48 (m, 13 H).

Anal. Calcd for $C_{20}H_{14}NOSCl$: C, 68.27; H, 4.01; N, 3.98; S, 9.11. Found: C, 68.36; H, 4.10; N, 3.94; S, 9.19.

Although **15b** decomposes upon exposure to moisture or if allowed to stand over a 2-day period at 30°, it has been stored for up to 2 months without appreciable decomposition at −30°.

Treatment of 15b with Triethylamine. Isolation of 5-Phenylspiro[fluorene-9,2'-[1',3',4']oxathiazole] (16b). Triethylamine (0.283 g, 0.0028 mol) was added in one portion to 1.0 g (0.0028 mol) of **15b** maintained at −78° under nitrogen. The precipitated triethylamine hydrochloride was removed from the resulting red reaction mixture by rapid filtration at −78°. The colored filtrate was then allowed to warm slowly to 30° and at *ca.* −30° the solution decolorized. The THF was removed with a rotary evaporator under reduced pressure, and the resulting residue was recrystallized from ether–hexane at −30° to give 0.0283 g (46%) of 5'-phenylspiro[fluorene-9,2'-[1',3',4']oxathiazole] (**16b**) as colorless needles, mp 100–103° dec. An analytical sample was prepared by a second recrystallization from ether–hexane: mp 102–103° dec; uv max (dioxane) 213 nm (ϵ 34,000), 230 (50,200), 237 (46,400), 278 (17,800), 287 (shoulder, 16,200), and 306 (shoulder, 9670); ir ($CHCl_3$) 1605 (C=N) and 1575 cm^{-1} (C=C); nmr ($CDCl_3$) δ 7.58 (m, 13 H); mass spectrum (70 eV) *m/e* (rel intensity) 315 (20), 196 (9.2), 180 (100), 135 (32), 103 (19).

Anal. Calcd for $C_{20}H_{13}NOS$: C, 76.16; H, 4.15; N, 4.44; S, 10.17. Found: C, 76.06; H, 4.22; N, 4.38; S, 10.24.

Upon standing at room temperature over a 2-week period **16b** decomposed to give benzonitrile, 9-fluorenone, and sulfur and the former two components were separated by column chromatography over Florisil and identified by comparison with authentic samples.

Isolation of Fluorenethione *S*-Benzoylimide (17). Compound **15b** (0.350 g) was dissolved in 10 ml of anhydrous THF and cooled to −78° under a nitrogen atmosphere. Triethylamine (0.110) was added by syringe and the solution was filtered under nitrogen into a receiving flask which was also at −78°. After an aliquot was removed for uv analysis, 15 ml of dry hexane was added to the red filtrate, causing the precipitation of fluorenethione *S*-benzoylimide (**17**) as red needles. The crystals were collected at −78° under a nitrogen atmosphere and allowed to warm slowly to 30°. Although the crystals appeared to be stable at this temperature, any mechanical deformation resulted in the instantaneous transformation to 5'-phenylspiro[fluorene-9,2'-[1',3',4']oxathiazole] (**16b**).

Reaction of 17 with Anhydrous HCl. An anhydrous THF solution (35 ml) of fluorenethione *S*-benzoylimide (**17**), which had been prepared *in situ* from 3.16 g (0.009 mol) of **15b** and 0.91 g (0.009 mol) of triethylamine at −78°, was treated with a slow stream of anhydrous HCl until the red color of **17** had dissipated. After warming to 30° the precipitated triethylamine hydrochloride was removed by filtration and the filtrate was concentrated with a rotary evaporater under reduced pressure. The resulting residue was recrystallized from anhydrous ether to give 2.6 g (82%) of *N*-benzoyl-9-chloro-9-fluorenesulfenamide (**15b**), mp 114–116° dec on admixture with an authentic sample.

Reaction of 17 with *N*-Isobutenylpyrrolidine. 9-Diazofluorene[24] (5.11 g, 0.027 mol) in 50 ml of anhydrous THF was added dropwise over a period of 1 hr under nitrogen to 5.0 g (0.027 mol) of benzamide-*N*-sulfenyl chloride in 100 ml of THF maintained at −30°. When the addition was complete and the evolution of nitrogen had ceased, the solution was cooled to −78° and 2.96 g (0.029 mol) of triethylamine was added at once. To the resulting red reaction mixture was added 3.66 g (0.029 mol) of *N*-isobutenylpyrrolidine[26] which caused the solution to decolorize immediately. After warming to room temperature the precipitated triethylamine hydrochloride (3.57 g, 96%) was removed by filtration and the filtrate was concentrated with a rotary evaporator to a brown viscous oil. The crude residue was triturated with 800 ml of anhydrous ether and the ethereal solution was decanted from an insoluble brown tar. The volume of the ether was reduced to 300 ml with a rotary evaporator under reduced pressure and the solution was then allowed to stand at −30°. After 24 hr, 6.60 g of 2′-benzoyl-3′-pyrrolidine-4′,4′-dimethylspiro[fluorene-9,5′-[1′,2′]isothiazolidine] (**19**) was collected as colorless plates. When the mother liquor was concentrated to a volume of 100 ml and allowed to stand at −30°, an additional 0.93 g of **19** crystallized to give a total yield of 7.53 g (64%): mp 185–187° dec; λ_{max} ($CHCl_3$) 228 nm (ε 25,300), 265 (15,400), and 310 (2890); ir ($CHCl_3$) 1635 (C=O) and 1600 cm^{-1} (C=C); nmr ($CDCl_3$) δ 7.47 (m, 4 H), 1.66 (s, 3 H) and 0.58 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 440 (1.2), 315 (65), 206 (10), 202 (8.4), 135 (100), 125 (62).

Anal. Calcd for $C_{28}H_{28}N_2OS$: C, 76.32; H, 6.40; N, 6.36; S, 7.28. Found: C, 76.11; H, 6.59; N, 6.40; S, 7.14.

Hydrolysis of 19. Compound **19** (0.440 g, 0.001 mol) was dissolved in 35 ml of THF and 25 ml of a 2 *N* sodium hydroxide solution. After stirring for 24 hr at 30° the reaction mixture was neutralized with concentrated hydrochloric acid and then extracted with 50 ml of chloroform. The chloroform extract was dried with magnesium sulfate and concentrated with a rotary evaporator under reduced pressure. The resulting residue was dissolved in 25 ml of ether, 10 ml of hexane was added, and the ether was slowly evaporated under reduced pressure until crystallization began. The recrystallizing flask was then allowed to stand at −30°, and after 24 hr, 0.032 g of colorless needles was collected by filtration and subsequently identified as benzamide by mixture melting point with an authentic sample. The filtrate was concentrated with a rotary evaporator under reduced pressure to yield a light yellow oil which upon chromatography on 10 g of florisil using methylene chloride as the eluent afforded a colorless oil which was crystallized from hexane to give colorless needles of 9-isobutyraldehydofluorene (**22**, 0.021 g, 10%): mp 143–146°; ir ($CHCl_3$) 1725 (aldehyde C=O) and 1600 cm^{-1} (C=C); nmr ($CDCl_3$) δ 9.78 (s, 1 H), 7.55 (m, 8 H), 6.83 (s, 1 H), and 1.01 (s, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 236 (2.9), 207 (16), 165 (100); exact mass, 236.118 (calcd. 236.120).

Oxidation of 19 with 1 Equiv of *m*-Chloroperbenzoic Acid. Purified *m*-chloroperbenzoic acid[27] (0.230 g, 0.0013 mol) in 5 ml of methylene chloride was added to 0.605 g (0.0013 mol) of **19** in 10 ml of methylene chloride maintained at 0°. When the addition was complete the reaction mixture was warmed to 30° and stirred for 48 hr. At the end of this period the reaction mixture was cooled to 0° and the precipitated *m*-chlorobenzoic acid was removed by filtration. The filtrate was extracted with 25 ml of a 5% aqueous sodium thiosulfate solution followed by 25 ml of water. The methylene chloride extract was then dried with magnesium sulfate and concentrated with a rotary evaporator under reduced pressure. The resulting residue was dissolved in 35 ml of anhydrous ether, and then 10 ml of hexane was added and the solution was slowly concentrated with a rotary evaporator under reduced pressure. When crystals began to separate from the solution, the flask was removed from the rotary evaporator and allowed to stand at −30°. After 16 hr, 0.320 g (56%) of 2′-benzoyl-3′-pyrrolidine-4′,4′-dimethylspiro-[fluorene-9,5′-[1′,2′]isothiazolidine] 1′-oxide (**23**) was collected as colorless needles: mp 210–213° dec; λ_{max} ($CHCl_3$) 235 nm (ε 28,300), 270 (19,300), and 280 (shoulder, 16,200); ir ($CHCl_3$) 1665 (C=O), 1600 (C=C), and 1290 cm^{-1} (S=O); nmr ($CDCl_3$) δ 7.61 (m, 13 H), 5.94 (s, 1 H), 3.31 (m, 4 H), 1.85 (s, 3 H), 1.80 (m, 4 H), and 0.66 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 456 (2.1), 250 (100), 206 (44), 105 (65).

Anal. Calcd for $C_{28}H_{28}N_2O_2S$: C, 73.65; H, 6.18; N, 6.14; S, 7.02. Found: C, 73.54; H, 6.22; N, 6.08; S, 7.07.

Oxidation of 19 with Excess *m*-Chloroperbenzoic Acid. Purified *m*-chloroperbenzoic acid[27] (0.78 g, 0.0045 mol) in 15 ml of methylene chloride was added dropwise over a period of 10 min to 1.0 g (0.002 mol) of **19** in 15 ml of methylene chloride maintained at 0°. When the addition was complete the reaction mixture was warmed to 30°, and after 24 hr, tlc [silica gel, $CHCl_3$–hexane (4:1 v:v)] indicated the presence of unreacted **19**, compound **23**, and a third unknown component. An additional 0.25 g of *m*-chloroperbenzoic acid was added to the reaction mixture and stirring was continued for 72 hr at 30°. At the end of this period the reaction mixture was cooled to 0° and the precipitated *m*-chlorobenzoic acid was removed by filtration. The filtrate was extracted with 25 ml of a 5% aqueous sodium thiosulfate solution, 25 ml of a 10% aqueous sodium bicarbonate solution, and 25 ml of water. The methylene chloride extract was dried with magnesium sulfate and concentrated with a rotary evaporator under reduced pressure. The resulting residue was recrystallized from methylene chloride–hexane, affording 0.362 g (64%) of 4′,4′-dimethylspiro[fluorene-9,5′-[1′,2′]dihydroisothiazole] 1′-oxide (**24**) as colorless microneedles: mp 168–169°; λ_{max} ($CHCl_3$) 241 nm (ε 12,800), 272 (15,100), and 282 (shoulder, 12,800); ir ($CHCl_3$) 1595 (C=N) and 1295 cm^{-1} (S=O); nmr ($CDCl_3$) δ 7.46 (m, 9 H), 1.67 (s, 3 H), and 0.96 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 381 (2.1), 280 (6.9), 233 (9.3), 206 (100), 191 (92), 165 (83).

Anal. Calcd for $C_{17}H_{15}NOS$: C, 72.56; H, 5.37; N, 4.98; S, 11.40. Found: C, 72.37; H, 5.41; N, 4.90; S, 11.35.

Reaction of 17 with *N*-Propenylpiperidine. 9-Diazofluorene[25] (2.05 g, 0.011 mol) in 15 ml of anhydrous THF was added dropwise over a period of 1 hr under nitrogen to 2.0 g (0.011 mol) of benzamide-*N*-sulfenyl chloride in 35 ml of THF maintained at −30°. When the addition was complete and the evolution of nitrogen had ceased the solution was cooled to −78° and 1.11 g (0.011 mol) of triethylamine was added at once. To the resulting red reaction mixture was added 1.5 g (0.012 mol) of *N*-propenylpiperidine,[28] which caused the solution to decolorize immediately. After warming to 30°, the precipitated triethylamine hydrochloride (1.51 g, 99%) was removed by filtration and the filtrate was concentrated with a rotary evaporater under reduced pressure. After the last traces of solvent had been removed, an nmr of the residue revealed that only the trans isomer of the adduct was present. The residue was dissolved in 200 ml of anhydrous ether, and the solution was clarified by filtering through a Celite pad. The volume of the ether was reduced with a rotary evaporator under reduced pressure to *ca.* 125 ml and the solution was then allowed to stand at −30°. After 24 hr, 3.15 g of 2′-benzoyl-3′-piperidine-4′-methylspiro[fluorene-9,5′-[1′,2′]isothiazolidine] (**27**) was collected as colorless plates. When the mother liquor was concentrated to a volume of *ca.* 50 ml, an additional 0.325 g of **27** was obtained to give a total yield of 3.47 g (71%): mp 159–161° dec; λ_{max} ($CHCl_3$) 242 nm (ε 28,800), 263 (16,600), and 310 (3000); ir ($CHCl_3$) 1637 (C=O) and 1600 cm^{-1} (C=C); nmr ($CDCl_3$) δ 7.46 (m, 13 H), 5.60 (d, 1 H, J = 8 Hz), 3.17 (m, 5 H); mass spectrum (70 eV) *m/e* (rel intensity) 440 (1.3), 287 (46), 192 (35), 165 (30), 105, (100), 84 (38).

Anal. Calcd for $C_{28}H_{28}N_2OS$: C, 76.32; H, 6.40; N, 6.36; S, 7.28. Found: C, 76.28; H, 6.47; N, 6.33; S, 7.33.

Oxidation of 27 with *m*-Chloroperbenzoic Acid. Purified *m*-chloroperbenzoic acid[27] (0.160 g, 0.0009 mol) in 10 ml of methylene chloride was added dropwise over a period of 20 min to 0.410 g (0.0009 mol) of **27** in 15 ml of methylene chloride maintained at 0°. When the addition was complete, the solution was stirred at 0° for 24 hr. At the end of this period, the reaction mixture was diluted to a volume of 50 ml with methylene chloride and extracted with 50 ml of a 10% aqueous sodium thiosulfate solution, 50 ml of a 10% aqueous sodium bicarbonate solution, and 50 ml of water. The methylene chloride extract was dried with magnesium sulfate and concentrated with a rotary evaporator under reduced pressure. After attempts to crystallize the resulting residue were unsuccessful it was chromatographed on 10 g of Florisil. Eluting with hexane–methylene chloride (2:1 v:v) afforded 0.140 g (34%) of 2′-benzoyl-3′-piperidine-4′-methylspiro[fluorene-9,5′-[1′,2′]isothiazolidine] 1′-oxide (**28**), mp 206–212° dec. An analytical sample was prepared by recrystallization from ether–hexane to give **28** as colorless rods: mp 218–219° dec; λ_{max} ($CHCl_3$) 247 nm (ε 18,000), 274

(12,400), and 284 (shoulder, 10,700); ir ($CHCl_3$) 1665 (C=O), 1600 (C=C), and 1295 cm^{-1} (S=O); nmr ($CDCl_3$) δ 7.60 (m, 13 H), 5.78 (d, 1 H, J = 8.5 Hz), 3.32 (m, 5 H), 1.55 (s, 6 H), and 0.77 (d, 3 H, J = 7 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 456 (1.3), 408 (4.2), 289 (97), 274 (100), 192 (42), 124 (61), 84 (26).

Anal. Calcd for $C_{28}H_{28}N_2O_2S$: C, 73.65; H, 6.18; N, 6.14; S, 7.02. Found: C, 73.51; H, 6.20; N, 6.08; S, 7.14.

Reaction of 17 with 1-Diethylaminobutadiene. 9-Diazofluorene[25] (1.05 g, 0.011 mol) in 15 ml of anhydrous THF was added dropwise over a period of 1 hr under nitrogen to 2.0 g (0.011 mol) of benzamide-*N*-sulfenyl chloride in 35 ml of THF maintained at −30°. When the addition was complete and the evolution of nitrogen had ceased, the solution was cooled to −78° and 1.11 g (0.011 mol) of triethylamine was added at once. To the resulting red reaction mixture was added 1.40 g (0.011 mol) of 1-diethylaminobutadiene,[29] which caused the solution to decolorize immediately. After warming to 30°, the precipitated triethylamine hydrochloride (1.41 g, 92%) was removed by filtration and the filtrate was concentrated with a rotary evaporator under reduced pressure. The resulting dark brown residue was triturated with 250 ml of anhydrous ether. The ethereal solution was decolorized with Norit and then it was concentrated on a rotary evaporator under reduced pressure to a volume of *ca.* 75 ml. After standing at −30° for 16 hr, 1.79 g (36%) of 2′-benzoyl-3′-(*trans*-*N*-ethenyldiethylamino)spiro-[fluorene-9,5′-[1′,2′]isothiazolidine] (**30**) had crystallized from the solution as colorless plates: mp 123–124° dec; λ_{max} ($CHCl_3$) 247 nm (ϵ 18,500), 264 (19,100), and 311 (4410); ir ($CHCl_3$) δ 7.51 (m, 13 H), 6.51 (d, 1 H, J = 13.5 Hz), 5.70 (m, 1 H, J = 8 Hz), 4.42 (d of d, 1 H, $J_{b,d}$ = 13.5, $J_{d,c}$ = 5.5 Hz,) 3.07 (q, 4 H, J = 7.5 Hz), 2.92 (m, 2 H), and 1.11 (t, 6 H, J = 7.5 Hz).

Reaction of 17 with 1-(Diethylamino)-1-propyne. 9-Diazofluorene[25] (2.05 g, 0.011 mol) in 15 ml of anhydrous THF was added dropwise over a period of 1 hr under nitrogen to 2.0 g (0.011 mol) of benzamide-*N*-sulfenyl chloride in 35 ml of THF maintained at −30°. When the addition was complete and the evolution of nitrogen had ceased, the solution was cooled to −78° and 1.11 g (0.011 mol) of triethylamine was added. To the resulting red reaction mixture was added 1.22 g (0.011 mol) of 1-(diethylamino)-1-propyne . Within 5 min the solution had become orange and it was allowed to warm to room temperature. A yellow precipitate was collected by filtration and was found to weigh 0.651 g greater than the theoretical amount of triethylamine hydrochloride. The filtrate was concentrated with a rotary evaporator under reduced pressure to yield a brown oil. Attempts to obtain a crystalline product from the oil were unsuccessful; however, distillation of the oil in a Hickmann still (bath temperature, 50°, 3 mm) afforded a colorless liquid which was identified as benzonitrile by infrared spectral comparison with an authentic sample.

An nmr spectrum of the yellow precipitate indicated the presence of triethylamine hydrochloride and a 1:1 adduct of **17** and 1-(diethylamino)-1-propyne. The precipitate was washed with 100 ml of water and 0.398 g of an insoluble yellow-orange powder, mp 121–124° dec, was collected. The adduct was recrystallized by dissolving the powder in a minimum volume of methylene chloride–hexane followed by slowly concentrating the solution with a rotary evaporator under reduced pressure until crystallization began. In this manner, 0.211 g (4.5%) of 2-phenyl-4-fluorenylide-5-methyl-6-diethylamino-1,4,3-oxathiazine (**32**) was collected as yellow needles: mp 125–126° dec; λ_{max} ($CHCl_3$, 0°) 242 nm (ϵ 20,500), 253 (25,900), 261 (33,600), 278 (shoulder, 12,500), 327 (9450), 311 (9770), and 375 (shoulder, 5800); ir (KBr) 1590, 1525, and 1500 cm^{-1} (C=C and C=N); nmr ($CDCl_3$, −30°) δ 7.58 (m, 13 H), 3.75 (q, 2 H, J = 7.3 Hz), 2.72 (s, 3 H), 1.54 (t, 3 H, J = 7.3 Hz), and 1.06 (t, 3 H, J = 7.3 Hz).

Anal. Calcd for $C_{27}H_{26}N_2OS \cdot CH_2Cl_2$: C, 65.75; H, 5.52; N, 5.48; S, 6.26. Found: C, 65.97; H, 5.28; N, 5.23; S, 6.18.

Although **32** was stable in the crystalline state and in solution below 0°, it rapidly decomposed at the melting point or in solution at room temperature. Upon decomposition **32** gave benzonitrile and a trace of difluorenylidene as the only identifiable products.

Reaction of Benzamide-*N*-sulfenyl Chloride with 9-Diazoxanthene. 9-Diazoxanthene[30] (2.0 g, 0.010 mol) in 20 ml of anhydrous THF was added dropwise over a period of 1 hr under nitrogen to 1.80 g 0.010 mol) of benzamide-*n*-sulfenyl chloride in 35 ml of THF maintained at −78°. Rapid evolution of nitrogen ensued, and as the addition progressed a precipitate formed. When the addition was complete the reaction mixture was filtered to give 0.182 g of an orange powder, mp 282–284°, which was subsequently identified as 9-xanthoneketazine by mixture melting point with an authentic sample. The filtrate was concentrated with a rotary evaporator under reduced pressure to afford a brown residue from which benzonitrile and *N,N*-thiobisbenzamide were obtained as the only isolable products.

***N*-Benzoyl-α-chloro-α-carbomethoxymethansulfenamide (15c).** To ethyl diazoacetate (0.6 g, 0.0053 mol) in 10 ml of dry THF was added dropwise over a period of 20 min at 30° benzamide-*N*-sulfenyl chloride (1.0 g, 0.0053 mol) in 25 ml of dry THF under a nitrogen atmosphere. Evolution of nitrogen began immediately and continued rapidly throughout the addition. Removal of the solvent under reduced pressure and crystallization of the residual oil from ether–hexane at −30° gave 0.115 g of the sulfenamide as colorless needles: mp 111–116 dec; ir ($CHCl_3$) 3410 (NH), 1740 (ester C=O), and 1675 cm^{-1} (amide C=O); nmr ($CDCl_3$) δ 1.25 (t, 3 H, J = 7 Hz), 4.25 (q, 2 H, J = 7 Hz), 5.48 (s, 1 H), 6.30 (broad s, 1 H), and 7.60 (m, 5 H).

Compound **15c** rapidly decomposed upon exposure to moisture or if allowed to stand at room temperature and this instability precluded elemental or mass spectral analysis.

Treatment of 15c with Triethylamine. At −78° a THF solution of *N*-benzoyl-α-chloro-α-carboethoxymethanesulfenamide was prepared from benzamide-*N*-sulfenyl chloride (1.0 g, 0.0053 mol) and ethyl diazoacetate (0.6 g, 0.0053 mol) was described above. To this solution at −78° was added triethylamine (0.6 g, 0.0059 mol) which caused immediate formation of a deep red color. After removal of the precipitated triethylamine hydrochloride (0.6 g, 82%) by filtration the red solution was allowed to warm to 30°, after which time (2 hr) the color faded to a light yellow. After removal of the solvent under reduced pressure the yellow semisolid residue was crystallized from THF–hexane at −30° to afford 0.115 g of a crystalline product: mp 209–210°; ir (KBr) 3300 (NH), 1740 (ester C=O), and 1640 cm^{-1} (amide C=O); nmr (DMSO-d_6) δ 1.20 (t, 3 H, J = 7 Hz), 4.20 (q, 2 H, J = 7 Hz), 6.15 (m, 1 H), 7.60 (m, 7 H); mass spectrum (70 eV) *m/e* (rel intensity) 324 (2), 253 (47), 121 (20), 105 (100).

Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.66; H, 5.35; N, 8.64. Found C, 6.43; H, 5.58; N, 8.40.

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Registry No.—**12,** 39593-81-2; **13,** 51933-55-2; **15a,** 39593-82-3; **15b,** 39593-83-4; **15c,** 51933-56-3; **16a,** 51933-57-4; **16b,** 51933-58-5; **17,** 39593-85-6; **18,** 2403-57-8; **19,** 39593-87-8; **22,** 52022-28-3; **23,** 39593-89-0; **24,** 39593-91-4; **26,** 7182-09-4; **27,** 39593-88-9; **28,** 39593-90-3; **29,** 14958-13-5; **30,** 51933-63-2; **32,** 52022-30-7; **42,** 51933-59-6; *N*-(trimethylsilyl)benzamide, 1011-57-0; morpholine, 110-91-8; morpholine-*N*-sulfenyl chloride, 2958-89-6; sodium salt of benzamide, 39536-32-8; *N,N′*-thiobenzamideaniline, 51933-60-9; aniline, 100-46-9; diphenyldiazomethane, 883-40-9; triethylamine, 121-44-8; 9-diazofluorine, 832-80-4; 1-(diethylamine)-1-propyne, 4231-35-0; 9-diazoxanthene, 51933-61-0; ethyl diazoacetate, 623-73-4.

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New Monohemiaminal Derivatives of Thiobinupharidine and Thionuphlutine B. Role of Circular Dichroism and Mass Spectrometry in Ascertaining the Position of the Hemiaminal Function[1]

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Spectral properties of four monohemiaminals belonging to the thiaspirane class of nuphar alkaloids are compared and employed in the structure elucidation of three of these compounds. The new monohemiaminals are 6′-hydroxythiobinupharidine and 6-hydroxythionuphlutine B, both isolated from *N. luteum*, and 6′-hydroxythionuphlutine B, prepared from 6,6′-dihydroxythionuphlutine B. The nmr showed that the hemiaminal group in each of the three monohemiaminals was located at one of two C-6 positions. Distinction of a C-6 from a C-6′ hemiaminal was made chiefly by (1) deuteride reduction to singly labeled thiaspirane followed by a mass spectral analysis for the extent of *m/e* 178 to 179 shift; and (2) the CD of the monohemiaminals in acid solution. Singly deuterated thiaspiranes which were labeled at C-6 resulted in *m/e* 178 shifting to 179 by more than 90%. In contrast, thiaspiranes singly labeled at C-6′ resulted in only a 10% shift of *m/e* 178 to 179. The CD of all the C-6′ hemiaminals in acid solution showed positive CD bands in the region of 260–280 nm but the CD of 6-hydroxythiobinupharidine and 6-hydroxythionuphlutine B show positive and negative CD bands, respectively, in the 290–310-nm region.

Two bishemiaminal derivatives of the C_{30} thiaspirane type of Nuphar alkaloid have been reported.[2] These are 6,6′-dihydroxythiobinupharidine (**1**)[3] and 6,6′-dihydroxythionuphlutine B (**2**). A monohemiaminal derivative, 6-hydroxythiobinupharidine (**3**), has also been reported.[5,6] Chief among the methods for ascertaining the number of the hemiaminal functions was a borodeuteride reduction followed by a mass spectral analysis for the presence of a d_1- or d_2-labeled C_{30} thiaspirane. The location of the hemiaminal groups was determined by nmr, which readily allowed a distinction between a C-6 hemiaminal on the one hand and a C-4 or C-10 hemiaminal on the other. However, the distinction between two C-6 positions (C-6 and C-6′) in a monohemiaminal was somewhat more complex because of the symmetry characteristics of the thiaspirane skeleton and it was necessary to rely on subtle differences between α- and β-thiohemiaminals[7] and their stereochemistry. Thus in the case of the monohemiaminal, **3**, the nearly complete replacement of the hemiaminal hydroxyl by equatorial deuterium through sodium borodeuteride hydrogenolysis was the result which necessitated the attachment of the hydroxyl at C-6, not C-6′, since the replacement of hydroxyl by deuterium at C-6′ was known to occur in a completely axial fashion.[5]

Application of CD to α-thioimmonium ions, or α-thiohemiaminals in acid solution, led to the establishment of the absolute configuration of thiobinupharidine and thionuphlutine B[8] and simultaneously gave supporting evidence for the position of the hemiaminal function in 6-hydroxythiobinupharidine. However, the CD results alone did not furnish independent evidence for the presence of a C-6 hemiaminal, as opposed to a C-6′ hemiaminal, since the CD properties of β-thiohemiaminals and β-thioimmonium ions were not known. We have now isolated and prepared two new β-thiohemiaminals and isolated a new α-thiohemiaminal belonging to the thiobinupharidine and thionuphlutine B series. We illustrate here how several spectral characteristics of α- and β-thiohemiaminals differ. However, we emphasize how the CD of these compounds and comparative mass spectra of singly labeled thiaspiranes prepared from the monohemiaminals can be utilized in determining the hemiaminal position in samples obtained in 2–5-mg amounts.

6′-Hydroxythiobinupharidine (4). This compound was isolated from *N. luteum*. Its mass spectrum revealed a parent ion peak at *m/e* 510 which corresponded to a monohemiaminal derivative of a C_{30} thiaspirane type of nuphar alkaloid. The ir revealed the presence of a hydroxyl group. The appearance of Bohlmann bands[9] in the ir indicated the presence of a trans-fused quinolizidine. Since the hydroxyl group could be reduced by hydride reducing agents and hemiaminal derivatives of quinolizidines do not show Bohlmann bands,[10] the evidence for the presence of both hydride-reducible hydroxyl and a trans quinolizidine ring system revealed the dual amine–hemiaminal character of this alkaloid. Conversion of the new monohemiaminal to an am-