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The Chemistry of Thione *S*-Imides

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THE CHEMISTRY OF THIONE *S*-IMIDES

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Tokyo, Japan

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INTRODUCTION

The thione *S*-imides belong to the thiocumulenes with a central tetravalent sulfur atom between two double bonds.[1]

$$X{=}S{=}Y \quad (X,Y = CRR', NR, O, S)$$

The stability of the thiocumulenes largely depends upon the nature of the ligands X,Y; the more electronegative X,Y are, the more the compounds are stabilized thermodynamically. Thus, the qualitative order of stability of thiocumulenes is as follows.

$$SO_2 > RNSO > RNSNR > R_2CSO > R_2CSNR \cong RNSS > R_2CSCR_2 \cong R_2CSS$$

Actually, sulfur dioxide and *N*-sulfinylamines,[2] the most stable thiocumulenes, have been well-known for a long time, but the last three species, the *N*-thiosulfinylamines,[3] the thione ylides,[4] and the thioxothiones (thiosulfines)[5] can only be isolated in few cases. The chemistry of the thione *S*-oxides (sulfines) has been developed over the last two decades.[6]

The thione *S*-imides, which are expected to be moderately stable compounds, have scarcely been investigated, but interest is being shown, especially in their relation to

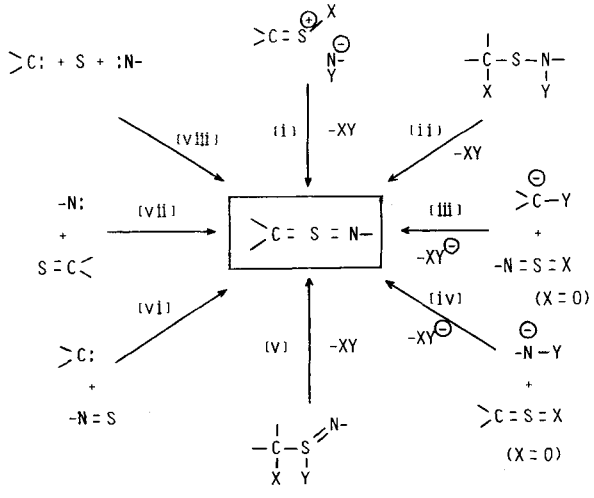
sulfines. This review describes the syntheses, structures, and reactions of thione *S*-imides, all references to thione *S*-imides published before January 1984 being covered.

SYNTHESES

In principle, the following approaches to the synthesis of thione *S*-imides may be considered and pathways [i] to [v] have been realized in the reactions described in the parentheses.

[i] Nucleophilic Substitution on Sulfonium Ions [Reaction of thiones with chloramine salts and related reactions]
[ii] 1,3-Elimination of Substituted Sulfenamides [Base-promoted 1,3-dehydrohalogenation of α-halosulfenamides]
[iii] Conversion of *N*-Sulfinylamines into Thione *S*-Imides [Wittig-type reaction of phosphoranes with *N*-sulfinylamines and alkylidenation of *N*-sulfinylamines (modified Peterson reaction)]
[iv] Conversion of Sulfines into Thione *S*-Imides [Imination of sulfines by *N*-silylamine anions]
[v] 1,2-Elimination of Substituted Sulfilimines [1,2-Elimination of benzamide from *S*-benzoylamino-*S*-benzylsulfilimines]
[vi] Reaction of Thionitroso Compounds with Carbenes
[vii] Reaction of Thiones with Nitrenes
[viii] Combination of Carbenes, Nitrenes and Elemental Sulfur

Scheme I.



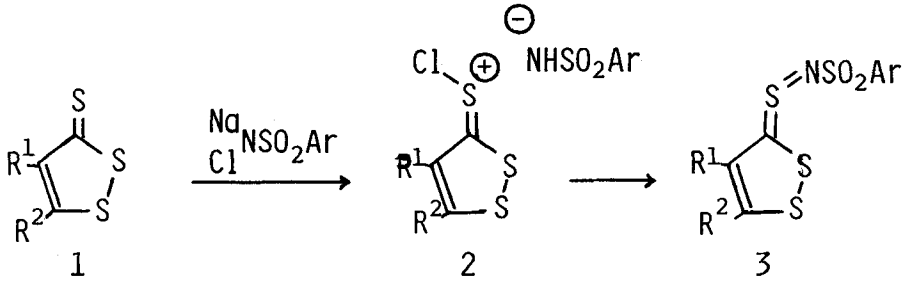
[*i*] *Nucleophilic Substitution on Sulfonium Ions*

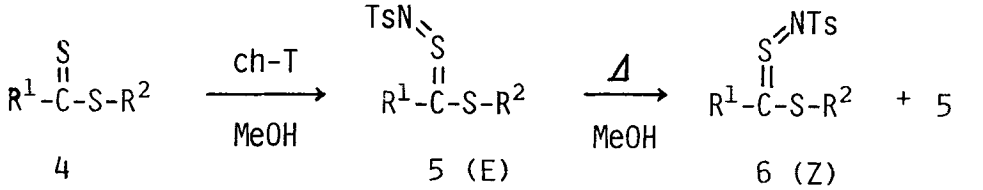
The reactions of thiones with chloramine salts are the most useful method for the preparation of thione *S*-imides. The reaction proceeds *via* initial formation of a chlorosulfonium salt **2** followed by replacement with an amide anion. In 1972

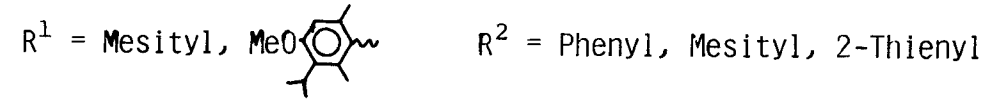
Tamagaki and Oae *et al.*[7] reported the first isolation of stable thione *S*-imides **3** by treating trithiones (**1**) with chloramine salts. By a similar method, Zwanenburg *et al.*[8] synthesized the thione *S*-imides **5**, **6**, **8**, and **9**, and found stereoselective formation of **5** (E) and **8** (E) (*vide infra*). The six-membered heterocyclic thione *S*-imides **11** and **13** and the acyclic α,β-unsaturated thione *S*-imides **15** were prepared by the present authors.[9,10] The compound **15** exists in the thione *S*-imide structure predominantly in EtOH or in the solid state, while in a solvent such as benzene or chloroform **15** easily undergoes a reversible intramolecular 1,5-dipolar cyclization[11] to give **16** (Scheme 1).

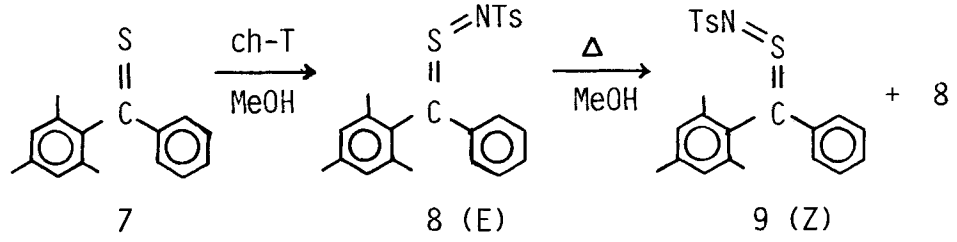
Scheme 1.

(i–1) Reaction of thiones with chloramine salts

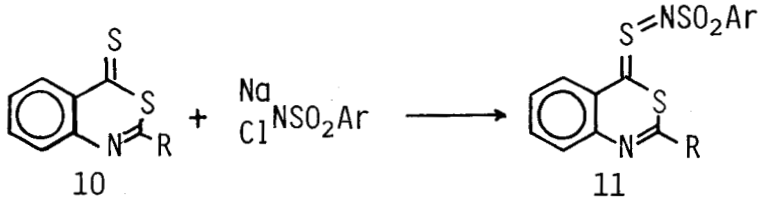




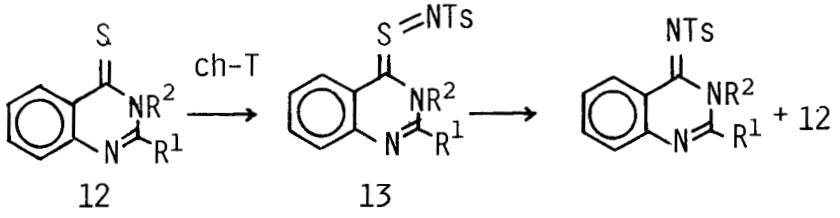




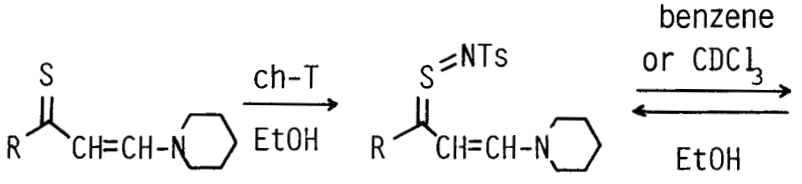
Scheme 1. (continued)



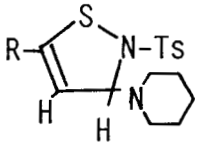
R = Ph, p-Tol, Et Ar = Ph, p-Tol



R^1 = Me, Ph R^2 = Ph, p-Tol



R = Ph, p-BrC_6H_4
p-$MeOC_6H_4$, 2-Thienyl

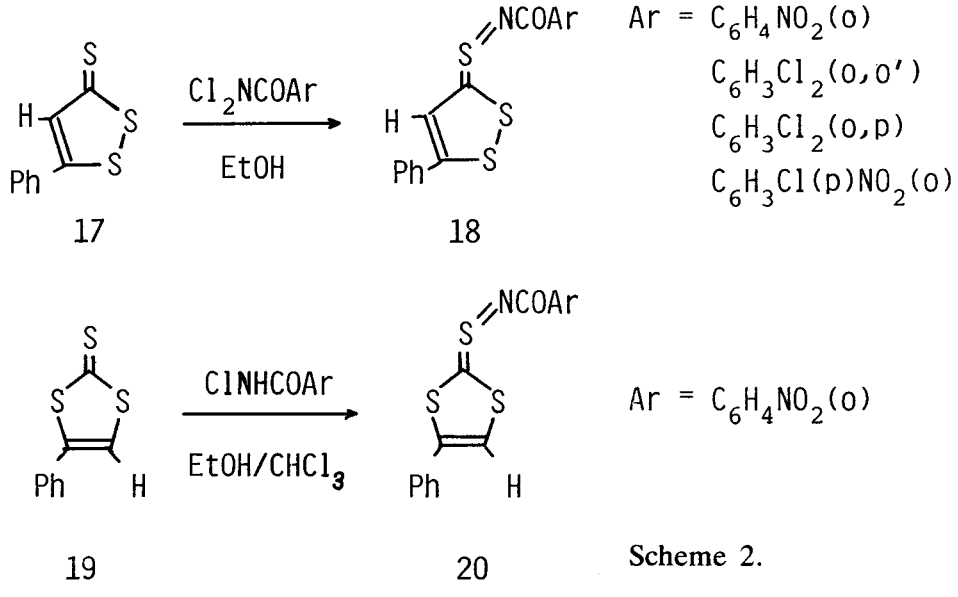


On the other hand, Boberg, Wentrup, *et al.*[12] reported the synthesis of the trithione *S*-imides **18** and **20** with *N,N*-di- or *N*-monochloro substituted benzamides (Scheme 2).

Similar to the preparation of thione ylides from thiones **21**, Br_2, and sodiomalonate,[13] some five-membered heterocyclic thione *S*-imides **23** were obtained by treating **21** with sulfonamide and bromine in the presence of Et_3N (Scheme 3).[14]

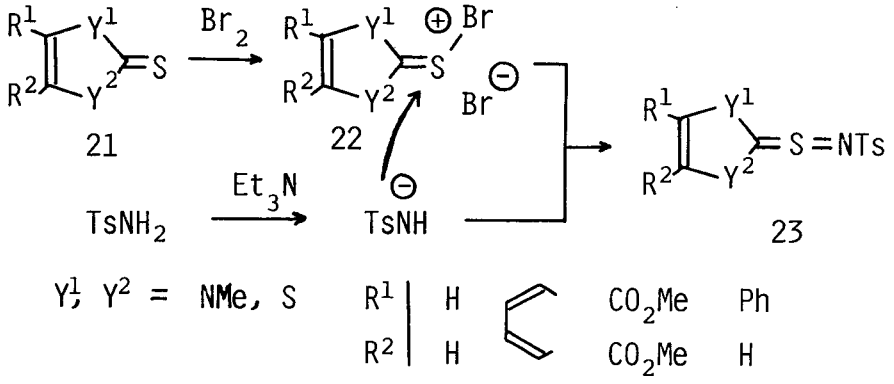
The reactions described in (i–2) and (i–3) also involve an intermediary formation of chloro- or bromosulfonium salts similar to **2** on which nucleophilic substitution by an amide anion can take place.

(i–2) Reaction of thiones with *N*-chloroamides



Scheme 2.

(i–3) Reaction of thiones with bromine and sulfonamide in the presence of triethylamine

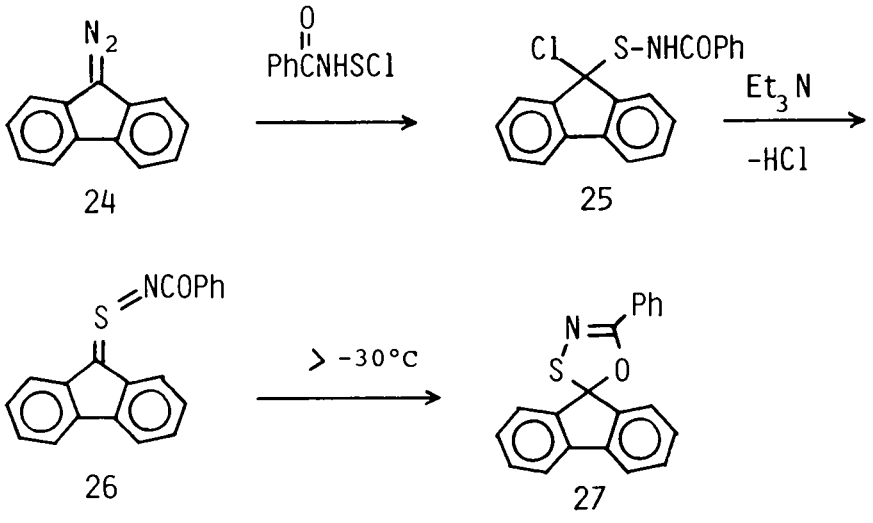


Scheme 3.

[*ii*] *1,3-Elimination of Substituted Sulfenamides*

By dehydrochlorination of *N*-benzoyl-9-chloro-9-fluorenesulfenamide (**25**) with Et_3N, Burgess obtained the thione *S*-imide **26**.[15] However, **26** underwent 1,5-dipolar cyclization above −30 °C in THF solution giving the 1,3,4-oxathiazoline derivative **27** (Scheme 4).

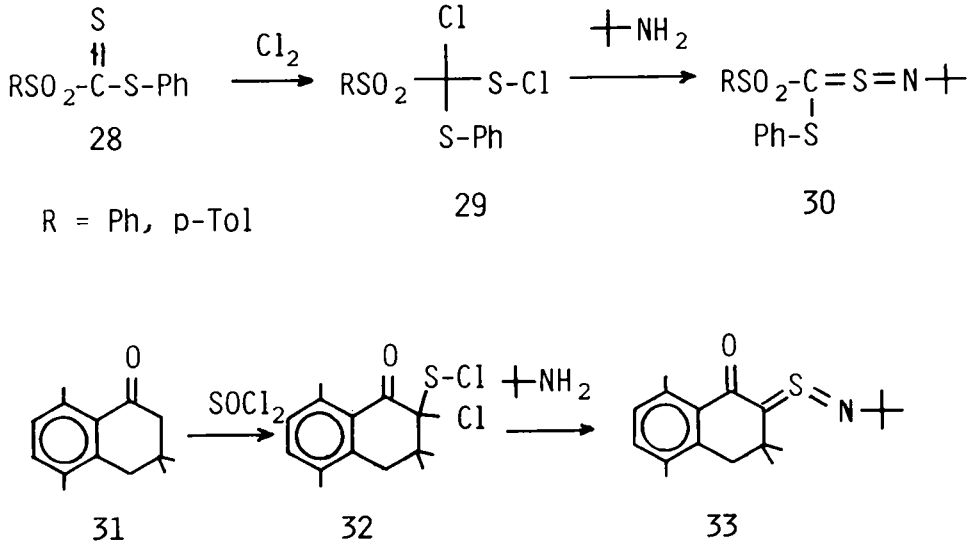
(ii–1) Dehydrochlorination of an *N*-benzoyl-α-chlorosulfenamide with triethylamine



Scheme 4.

In an analogous fashion Senning *et al.*[16] and Crossland[17] synthesized the *N*-*t*-butylthione *S*-imides **30** and **33**, respectively (Scheme 5).

(ii–2) Reaction of an α-chlorosulfenyl chloride with *t*-butylamine

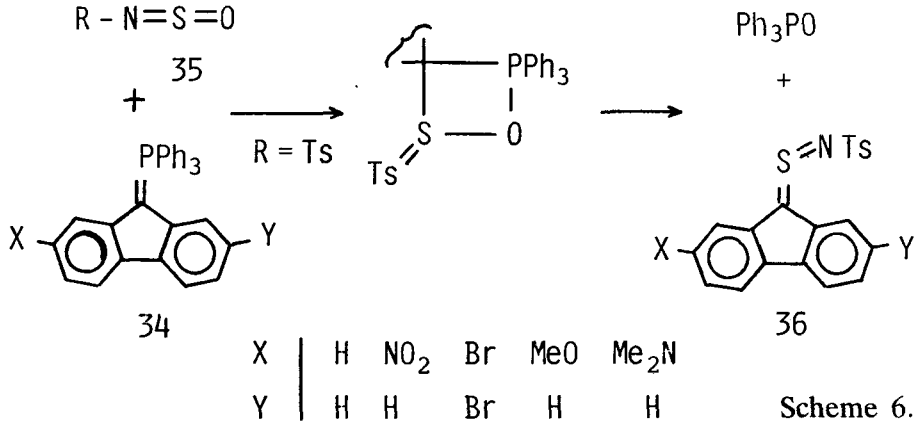


Scheme 5.

[*iii*] *Conversion of N-Sulfinylamines into Thione S-Imides*

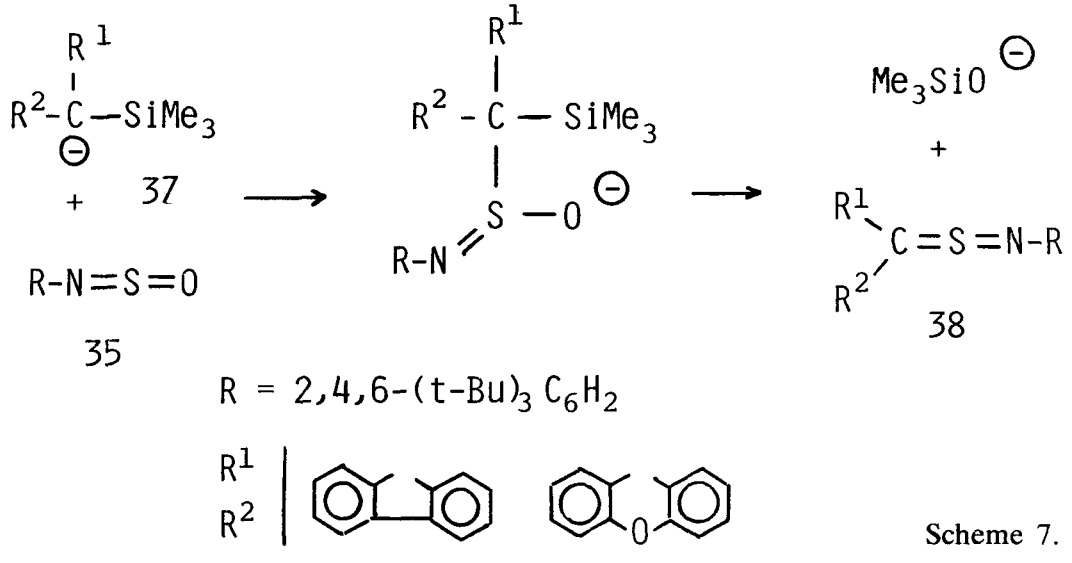
In these reactions *N*-sulfinylamines are converted into thione *S*-imides by replacement of the oxygen in—NSO with an ylide carbon atom or an α-silyl carbanion. The P=O or Si—O bond formation is the driving force of the reactions. The present author obtained relatively stable fluorenethione *S*-imides **36** by utilizing a Wittig-type reaction of the fluorenylidenetriphenylphosphoranes (**34**) with *N*-sulfinyl-*p*-toluenesulfonamide (**35**) (Scheme 6).[18] These imides **36** exhibited considerable reactivity in, *e.g.*, cycloaddition reactions (*vide infra*). The reaction of **34** with **35** (*p*-$NO_2C_6H_4$) formed selectively fluorenethione *S*-oxides.[18]

(iii–1) Wittig-type reactions of phosphoranes with *N*-sulfinyl-*p*-toluenesulfonamide



Scheme 6.

(iii–2) Alkylidenation of *N*-sulfinylamines by α-silyl carbanions (modified Peterson olefination)



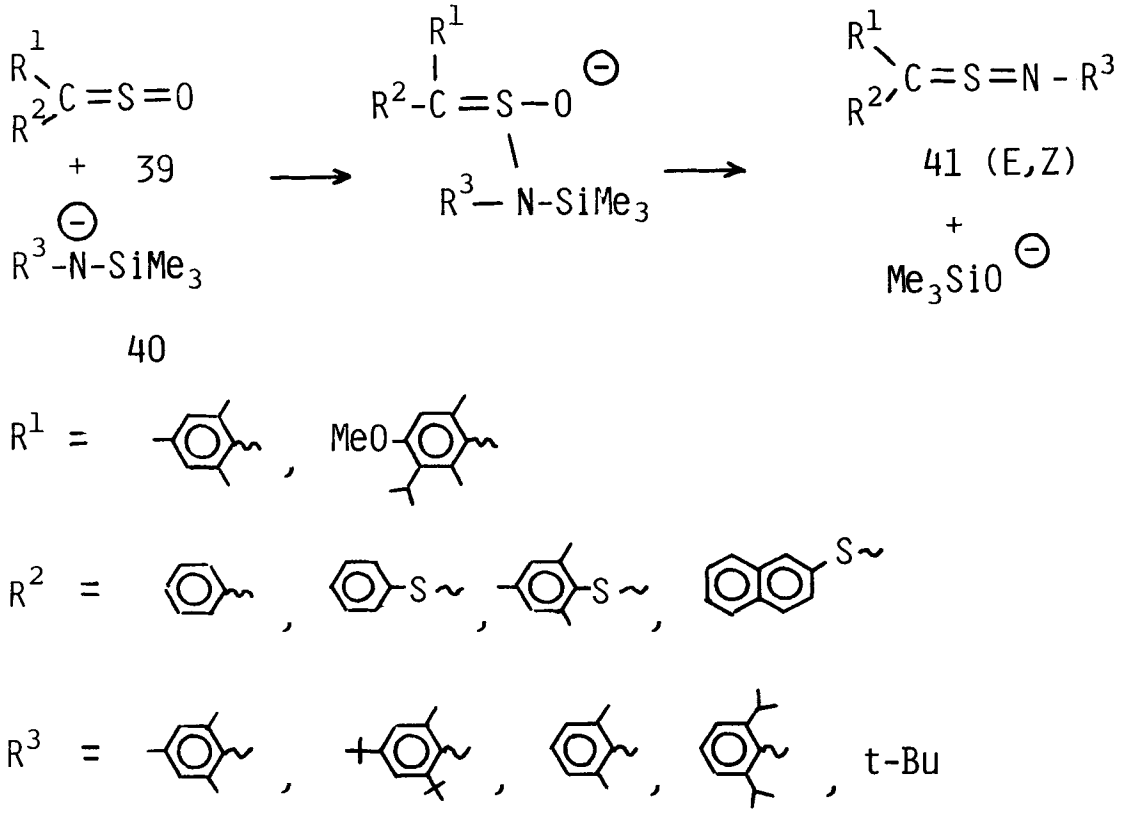
Scheme 7.

Recently, Zwanenburg *et al.*[19] reported the preparation of the thione *S*-imides **38** by alkylidenation of *N*-sulfinylamines (**35**) using α-trimethylsilyl carbanions (**37**), and found that the imides **38** can be stabilized by steric congestion of substituents around the CSN moiety (Scheme 7).

[*iv*] *Conversion of Sulfines into Thione S-Imides*

In a fashion similar to the Peterson olefination,[20] Zwanenburg *et al.*[19] obtained thione *S*-imides with sterically demanding substituents, *i.e.* **41** (E,Z), by imination of the sulfines **39** with trimethylsilylamine anions (**40**) (Scheme 8).

(iv–1) Imination of sulfines by *N*-silylamine anions

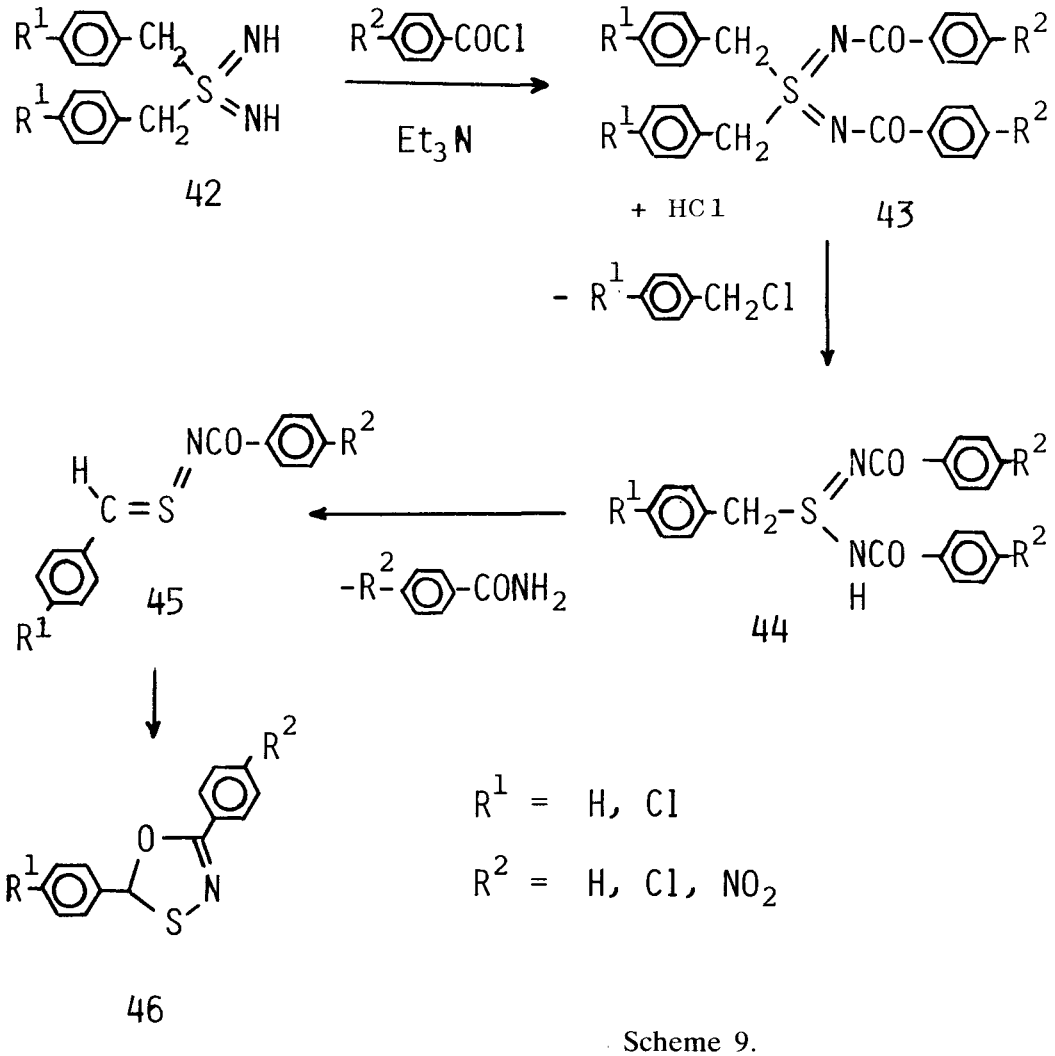


Scheme 8.

[*v*] *1,2-Elimination of Substituted Sulfilimines*

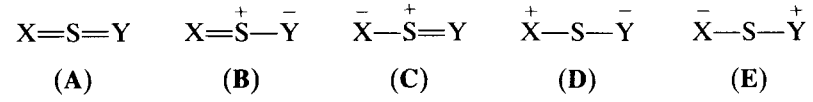
Haake *et al.*[21] reported the formation of the transient thione *S*-imides **45** by treatment of *S*,*S*-dibenzylsulfodiimides (**42**) with excess benzoyl chloride in the presence of Et_3N. Like **26**,[15] the imides **45** cyclized spontaneously to afford the isomeric 1,3,4-oxathiazolines (**46**) (Scheme 9).

(V–1) 1,2-Elimination of benzamide from *S*-benzyl-*S*-benzoylamino-*N*-benzoylsulfilimines



Scheme 9.

Thiocumulenes are isoelectronic with allyl anions and may be represented as a resonance hybrid of the following five canonical structures.



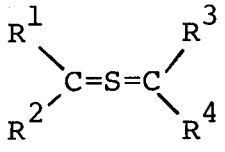
(A) **(B)** **(C)** **(D)** **(E)**

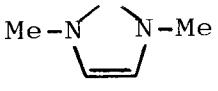
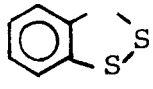
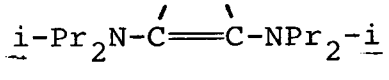
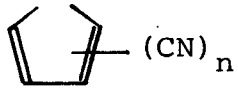
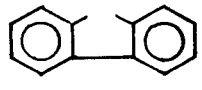
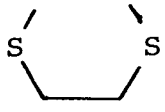
Effective pull-pull (contributor **B** and **C**) and push-pull (contributor **D** and **E**) effects of the ligands X and Y would delocalize the π-electrons in the cumulene moiety and thus cause stabilization of the thiocumulenes. Representative examples can be found in the syntheses of thione ylides in which only ylides with particular ligands have been

isolated as stable compounds.[4,13] Obviously, the ligand X ($R^1R^2C=$) is a strongly electron-releasing group (push) and the ligand Y ($R^3R^4C=$) a strongly electron-withdrawing one (pull).

Regarding the thione *S*-imides isolated, one can also find some prerequisites for the stabilization of these compounds. The thione *S*-imides with a heterocyclic nucleus

Table I. Isolable and Non-isolable Thione Ylides



R^1	R^2	R^3	R^4	
Me_2N	Me_2N	CN	CN	isolable
		COOEt	COOEt	
		Ts	Ts	
				
alkyl	alkyl	alkyl	alkyl	non-isolable
Me_2N	Me_2N			
		CN	CN	

such as 1,2-dithole (**18**), 1,3-dithole (**20**, **23**), 1,3-thiazine (**11**), dihydropyrimidine (**13**), dihydroimidazole (**23**), and dihydrothiazole (**23**) are examples of compounds stabilized by push-pull effect of the ligands. On the other hand, the thione *S*-imides **26** and **36** are typical examples of stabilization by pull-pull effect of the ligands. Evidently, the fluorenylidene nucleus withdraws a π-electron pair from the CSN moiety to form a 6π-electron system in the central five-membered ring. The thione *S*-imides **5**, **6**, **8**, **9**, **30**, **33**, **38**, and **41** are stabilized mainly by steric hindrance of bulky substituents such as *t*-butyl or mesityl groups attached to the nitrogen and/or carbon atom in the CSN moiety.

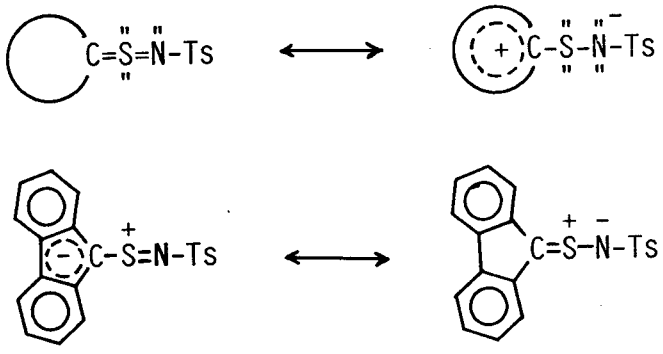
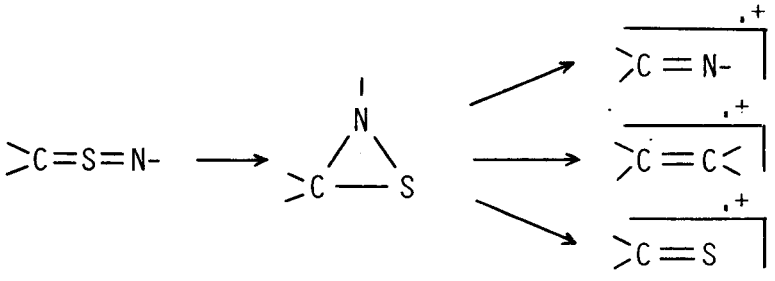


Chart 1.

STRUCTURE AND SPECTRAL PROPERTIES

The thione *S*-imides reported so far possess a characteristic color (usually orange or red) and UV absorptions in the range 380–520 nm. The IR spectra exhibit marked strong absorptions of ν_{CSN} at 920–992 cm^{-1}. In the mass spectra the following fragmentation pattern involving a thiaziridine intermediate is observed (*e.g.*, for **39**).[18]



Scheme 10.

There are three reports of X-ray crystallographic analyses of thione *S*-imides, *i.e.* **6** (Z), **30** and **33**.[22–24]

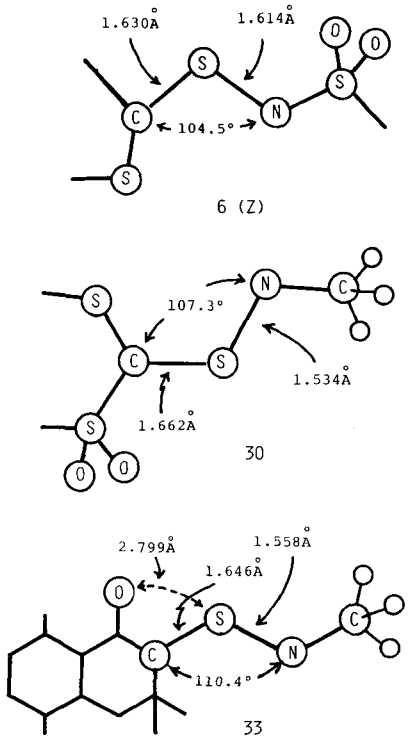
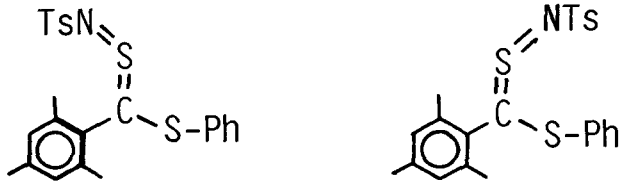


Fig. 1

As a consequence of the bent structure of the CSN moiety geometrical isomerism exists in unsymmetrical thione *S*-imides. Zwanenburg *et al.*[8] were the first to report geometrical isomerism of thione *S*-imides on the basis of ASIS (aromatic solvent induced shifts) experiments.[25]

When the ^{1}H-NMR spectra of **5** and **6** in C_6D_6 are compared with those in $CDCl_3$, the signal of the *ortho*-methyl protons of the mesityl group in **6** (Z) shifts more to higher field than that of **5** (E) owing to an association of solvent benzene with the positive sulfur at the least congested left-hand side.



5 (E) 6 (Z)

Δδ 0.052 ppm Δδ 0.18 ppm

$$\Delta\delta = \delta(CDCl_3) - \delta[CDCl_3 + C_6D_6\ (1{:}1)]$$

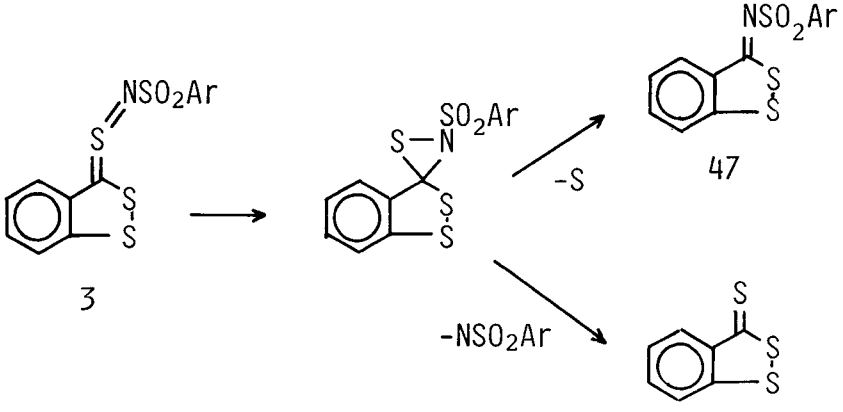
Chart 2.

Based on such configuration assignments for both the thione *S*-imides **5**,**6** and **8**,**9**, the following stereospecific reaction mechanisms are considered:[8] In the reaction of dithiobenzoates (**4**) with chloramine-T, the negatively charged nitrogen atom of the chloramine-T kinetically prefers to attack the thiocarbonyl function from the sterically hindered side rather than from the side of the electron-rich thiolo sulfur atom, thus giving **5** (E), whereas the course of the kinetically controlled process in the reaction of thioketones (**7**) with chloramine-T is determined by steric factors only, leading to the least congested isomer **8** (E). The Z-isomers **6** and **9** are obtained by the thermodynamic equilibration from E-**5** and **8**, respectively, in refluxing methanol (Scheme 1, i-1). The geometrical configurations of some **41** have also been reported.[19]

REACTIONS

[*i*] *Thermolysis*

In the thermolysis of thione *S*-imides an intermediary thiaziridine formation leading to the imines isolated has been suggested. Tamagaki and Oae *et al.*[26] investigated the thermolysis of the 4,5-benzo-1,2-dithiole-3-thione *S*-arenesulfonimides **3** and concluded that the rearrangement takes place through the initial ring closure to a thiaziridine, followed by sulfur extrusion.

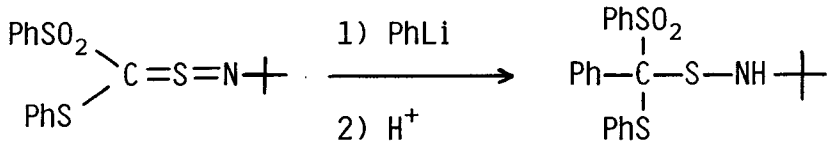


Scheme 11.

A similar cyclization to 3-membered rings followed by their eventual collapse has also been observed in the decomposition of many other thiocumulenes, *i.e.*, sulfines,[6] thione ylides,[4] *N*-thiosulfinylamines,[3] and sulfur-diimides.[27]

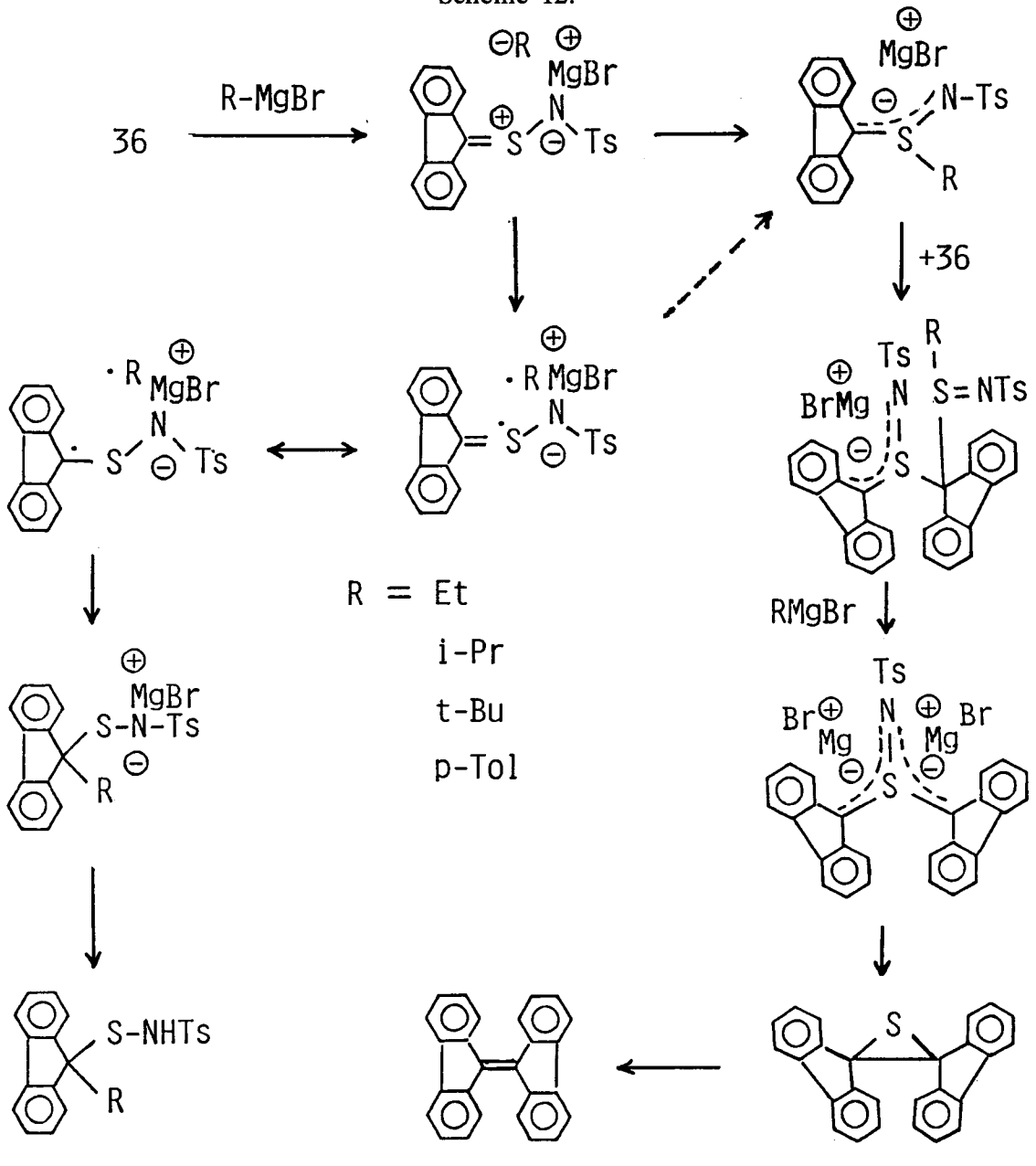
[*ii*] *Reactions with Nucleophiles*

(*ii-1*) *Reactions with carbanions* In nucleophilic reactions of thione *S*-imides with carbanions two reaction modes are observed, *viz.*, a carbophilic and a thiophilic one. Only the sulfenamide **48**, a carbophilic adduct, is obtained in the reaction of **30** with phenyllithium.[16]



30 48

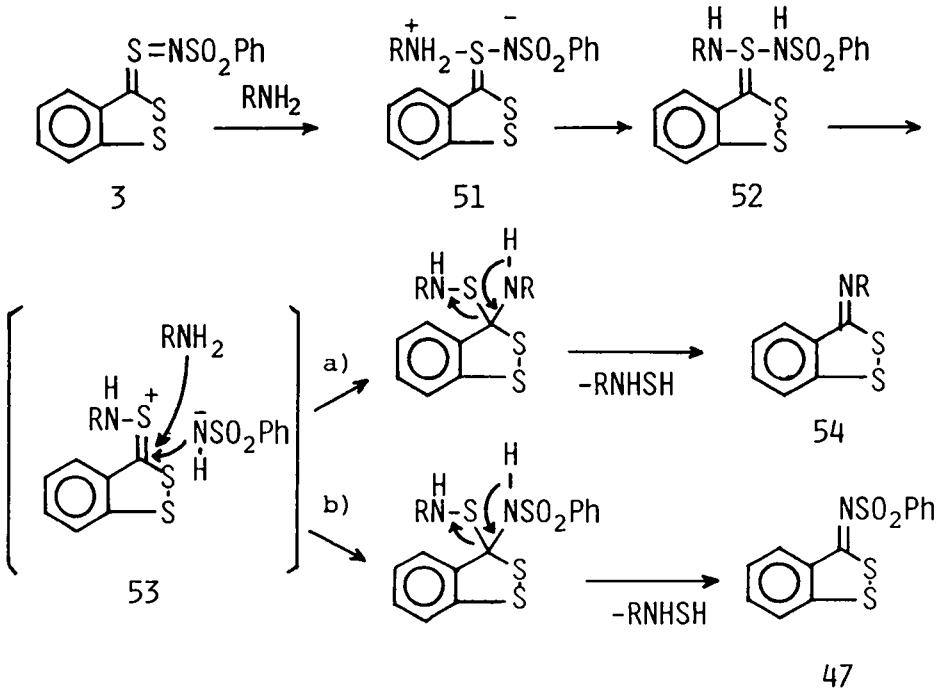
Scheme 12.



49 50 Scheme 13.

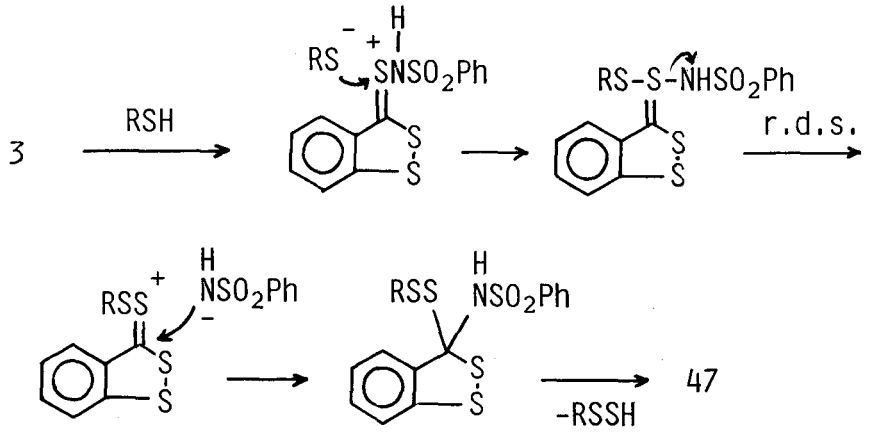
Reaction of **36** with Grignard reagents in diethyl ether gives both the sulfenamide **49** and the 9,9'-bifluorenylidene **50** which are considered to be formed by a carbophilic and a thiophilic reaction, respectively. In contrast, the reaction in THF produces only **50**.[28]

(*ii-2*) *Reaction with amines* Reaction of the thione *S*-imides **3** with amines results in the formation of **47** and **54**.[29] Based on the kinetic studies, the following mechanisms involving addition of the amine to the tetravalent sulfur atom has been proposed. The amine initially attacks the positive sulfur atom of **3** to form the dipolar intermediate **51** followed by a subsequent proton migration. There are two competitive reactions of the ion pair **53** formed by the S—N cleavage of **52**. Path (a) gives the amine-exchanged imine **54** and path (b) eventually gives the imine **47**. In the reactions with secondary and tertiary amines, predominant thione (**1**) formation is observed at the expense of the imine (**54**) formation.



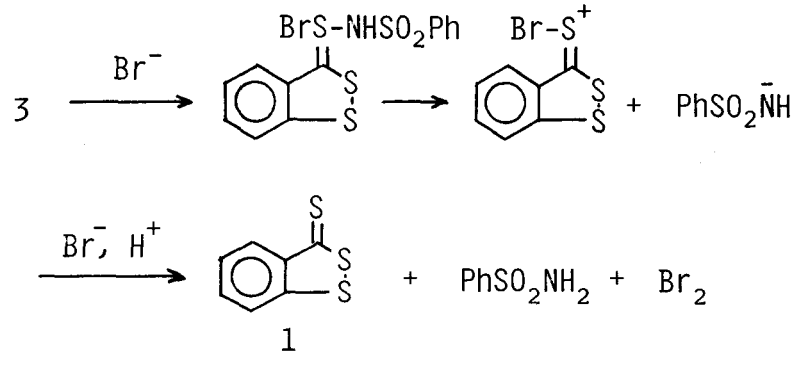
Scheme 14.

(*ii-3*) *Reaction with thiols* Treatment of thione *S*-imide **3** with various inorganic sulfides, organic thiols, and thioacetic or thiobenzoic acid results in an interesting rearrangement:[30] **3** readily reacts catalytically with these thiols to afford mainly the same rearranged product **47** as observed in the amine-catalyzed rearrangement. The reaction mechanisms proposed involve the thiophilic attack of thiols and the subsequent formation of the ion pair in the rate-determining step.



Scheme 15.

(*ii-4*) *Reaction with halides* The thione *S*-imides **3** can be reduced with tetra-*n*-butylammonium bromide or iodide in the presence of trichloroacetic acid to yield a benzotrithione (**1**) and benzenesulfonamide.[31] It is interesting to note that the Br^--reduction itself is the reverse of the formation of the *S*-imide from **1** and a chloramine salt (cf. Scheme 1).

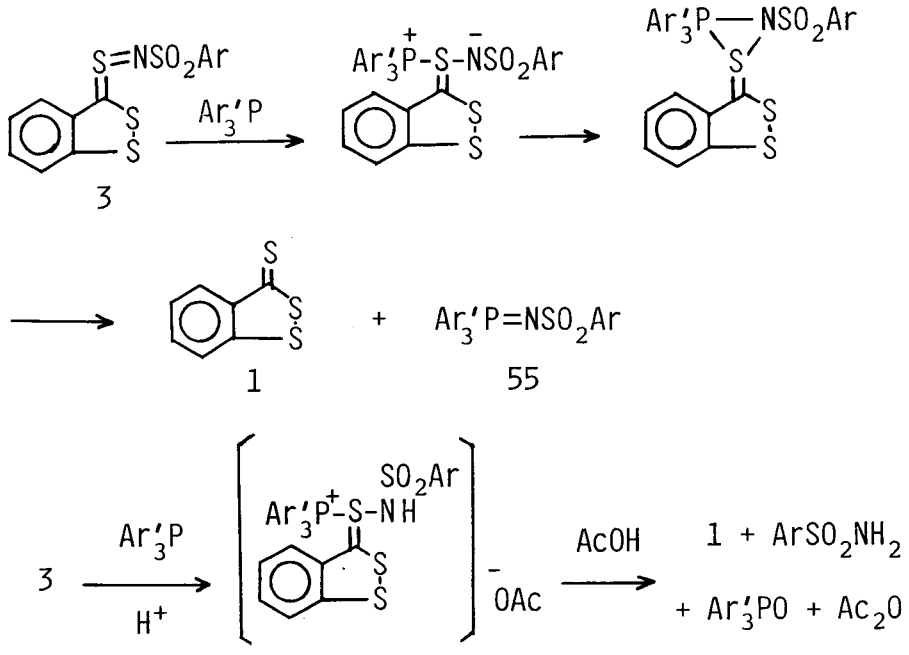


Scheme 16.

(*ii-5*) *Reaction with phosphines* Treatment of **3** with an equimolar amount of a tertiary phosphine also gives the reduced benzotrithione (**1**) and the *N*-arenesulfonyliminophosphorane **55**.[32] Addition of protic solvents such as acetic acid, water, and alcohols to the reaction system changes the mode of the reaction, the thione **1**, phosphine oxide, and sulfonamide being produced. The reduction involves an initial nucleophilic attack of phosphine at the sulfur atom.

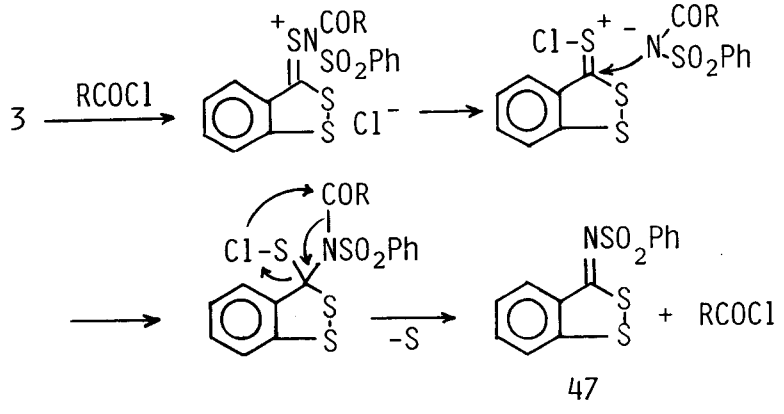
[*iii*] *Reactions with Electrophiles*

The following reactions of thione *S*-imides with three kinds of electrophiles have been reported, *viz.*, (1) acyl halides, (2) carbonium ions, and (3) protic acids. As in the



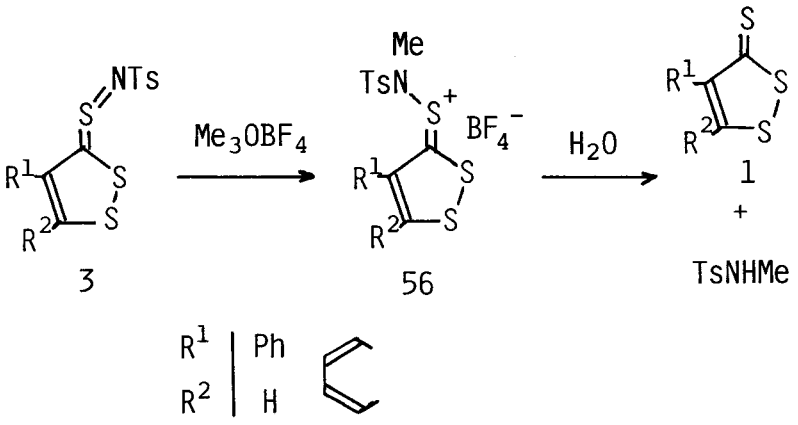
Scheme 17.

reaction with nucleophiles, **3** also forms the imine **47** upon treatment with a variety of acyl halides (Cl_3CCOCl, ArCOCl).[33] Less than half the equimolar amount of acyl halide is sufficient to complete the reaction and other acyl halides such as thionyl chloride or sulfinyl chlorides can also react in a similar manner. The reaction is essentially a rearrangement catalyzed by acyl halides.



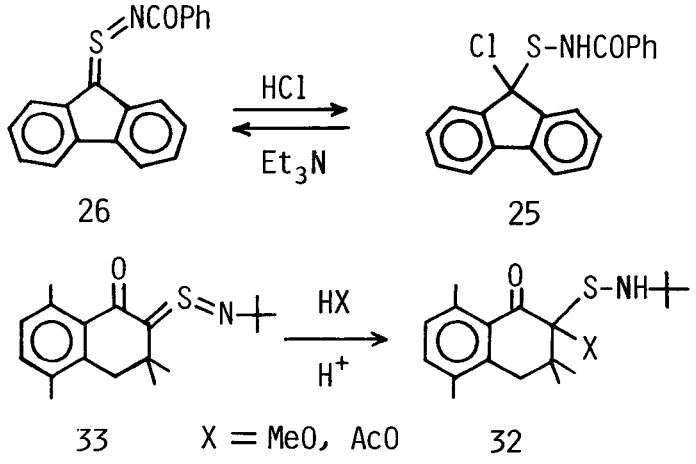
Scheme 18.

Kresze *et al.*[34] reported that 4,5-benzo- 4-phenyl-3*H*-1,2-dithiole-3-thione *S*-imide **3** are alkylated by trimethyloxonium-tetrafluoroborate to give a stable *N*-methylated product **56**. Hydrolysis of **56** affords **1** and *N*-methyltosylamide.



Scheme 19.

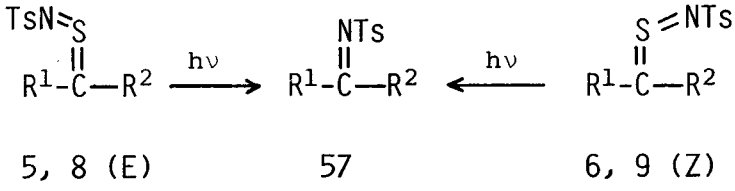
Electrophilic addition of HCl to fluorenethione *S*-benzoylimide **26** leads to the α-chlorosulfenamide **25**. The amide can be reconverted to **26** by the action of Et_3N (cf. Scheme 4).[15] The similar 1,3-addition of MeOH or AcOH to **33** is catalyzed by acids.[17]



Scheme 20.

[*iv*] *Photoreactions*

Extrusion of the sulfur atom under photolytic conditions is observed with the isomeric pairs of thione *S*-tosylimides, **5, 8** (E) and **6, 9** (Z). Irradiation of **5, 8** (E) as well as of **6, 9** (Z) in benzene at 360 nm gives the *N*-tosylimines **57**.[8]

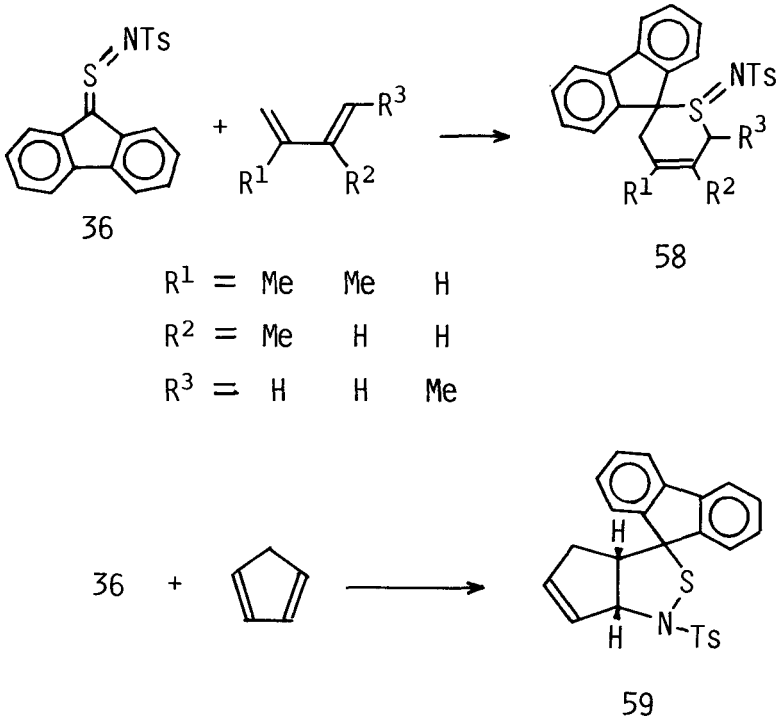


Scheme 21.

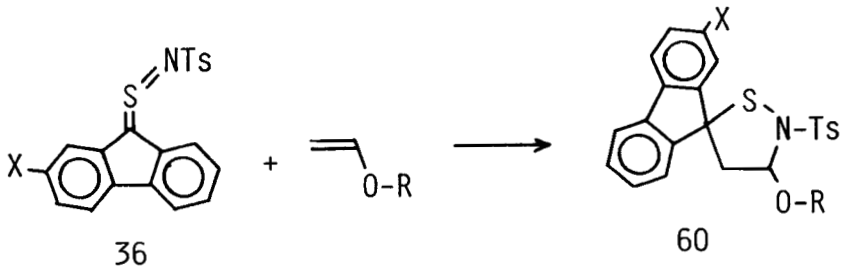
[*v*] *Cycloaddition Reactions and Related Reactions*

Generally, thiocumulenes behave as 1,3-dipoles or dienophiles in cycloaddition reactions with a great variety of multiple bond-containing compounds. *N*-Sulfinylamines (R—N=S=O),[2] sulfur diimides (R—N=S=N—R′)[2] and thione *S*-oxides (RR′C=S=O)[6] react as dienophiles with various dienes, while thione ylides (RR′C=S=CR″R‴)[4] react as 1,3-dipoles with reactive olefins, *i.e.*, TCNE or maleimide and the N=N double bond in azadicarboxylates. 1,3-Dipolar cycloadditions of *N*-thiosulfinylamines (R—N=S=S)[3] with norbornadiene and cyclopentadiene have also been reported. A relationship between such differences in the reactivity of the thiocumulenes X=S=Y and the electronegativity of the ligands (X, Y) have been proposed by Inagaki and Okazaki.[1,3] According to their proposal, thione *S*-imides are 1,3-dipoles. However, the fluorenethione *S*-tosylimide **36** reacts both as a 1,3-dipole and as a dienophile.[35]

(*v-1*) *Reactions with carbon-carbon double bonds* The reaction of the thione *S*-imides **36** with acyclic dienes takes place across the C=S bond of the CSN moiety to give the dihydrothiopyrane derivatives **58** corresponding to a Diels-Alder reaction.[35] On the other hand, **36** reacts as a 1,3-dipole with cyclopentadiene, vinyl ether, norbornadiene, and norbornene to give the 1,2-thiazolidine derivatives **59**, **60**, **61**, and **62**, respectively. Similar to the reaction with vinyl ether, **36** react with 1-(pyrrolidinyl)-2-methyl-1-propene to afford the 1,2-thiazolidines **63** while an ene reaction is observed with *N*-(1-cyclohexenyl) amines.

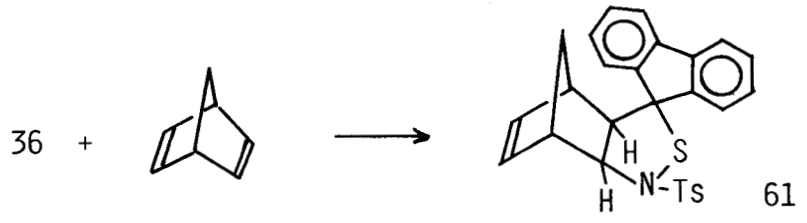


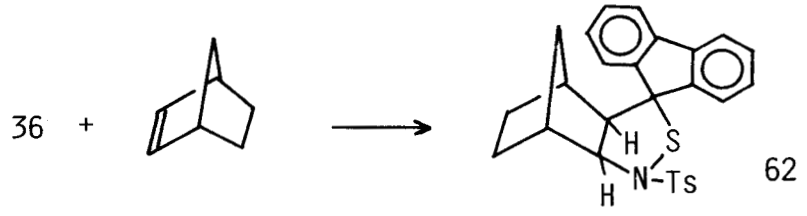
Scheme 22.



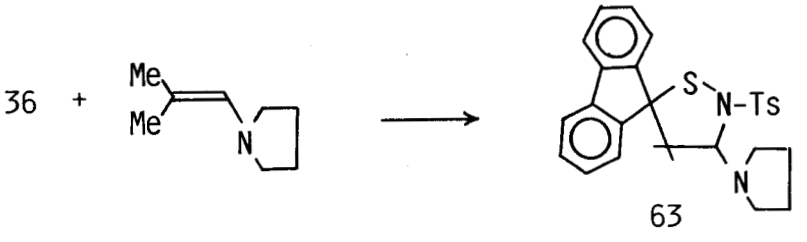
36 60

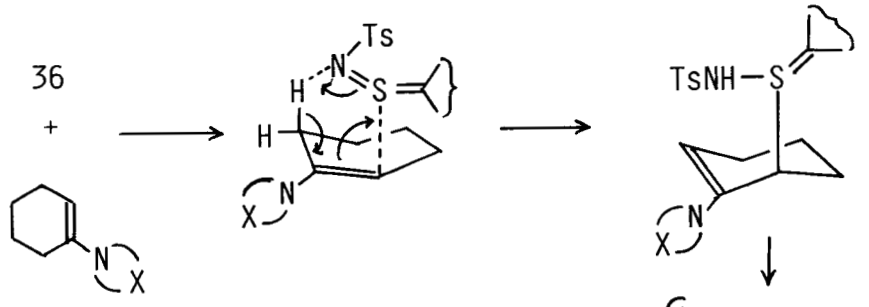
X = H, NO_2 R = Et, n-Bu, i-Bu





Scheme 23.



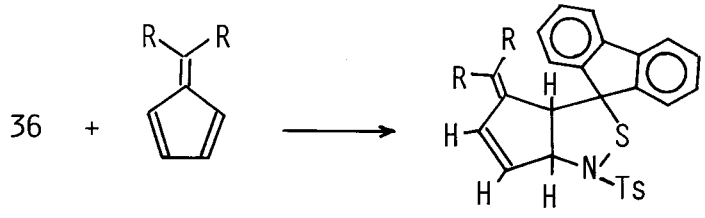


-N X = morpholinyl
piperidinyl

Scheme 24.

The reactions with 1,3-dienes or vinyl ethers proceed regioselectively. Attempts to induce reaction of **36** with normal olefins such as 1-pentene, styrene, cyclohexene, and cyclooctadiene and with electron-poor olefins such as acrylonitrile, ethyl acrylate, and maleic anhydride were unsuccessful.[35]

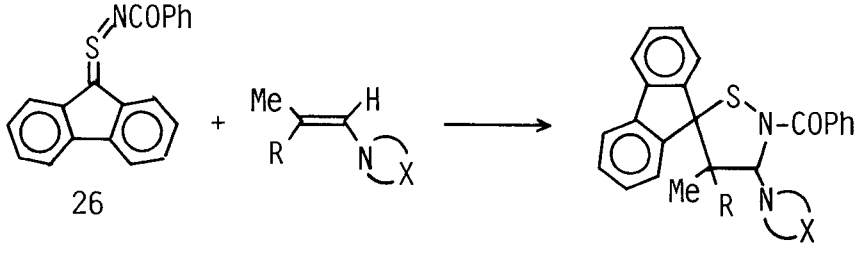
Fulvene is known to be one of the model compounds which undergoes periselective cycloaddition reactions as a $2\pi,4\pi,6\pi$ component.[36] The reactions of **36** with 6,6-dialkyl- or diaryl fulvenes afford only the [3 + 2] cycloadducts **65** as detectable products.[37]



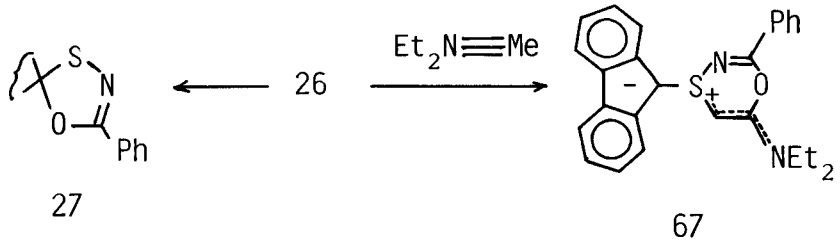
R = Me, Et, Ph 65

Scheme 25

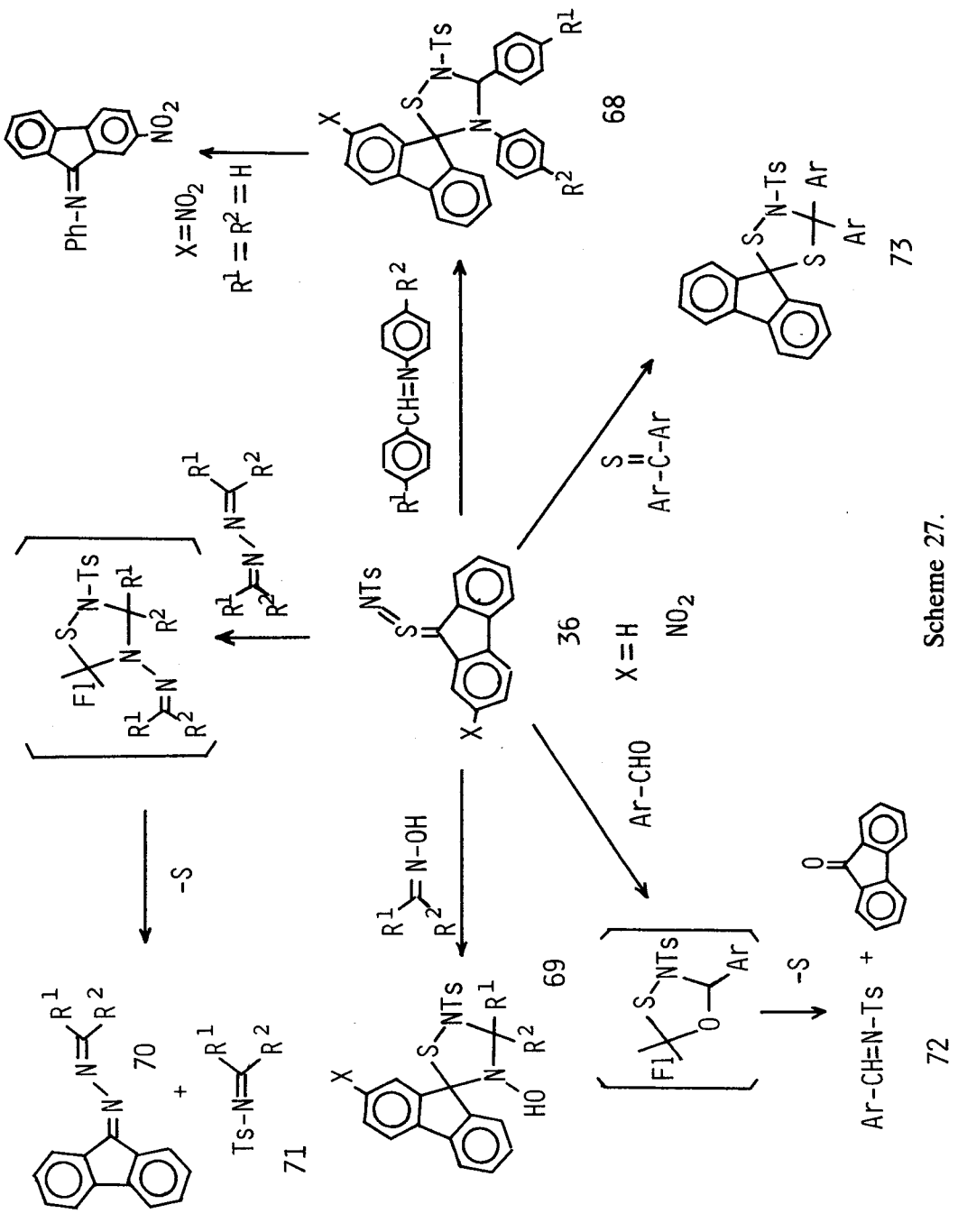
It is more difficult to carry out reactions with **26** because of its instability. The only reactions reported so far are those with enamines and an ynamine giving isothiazolidine and oxathiazine derivatives, respectively.[15] Treatment of **26** with vinyl ether or ketene acetal results in internal cyclization.



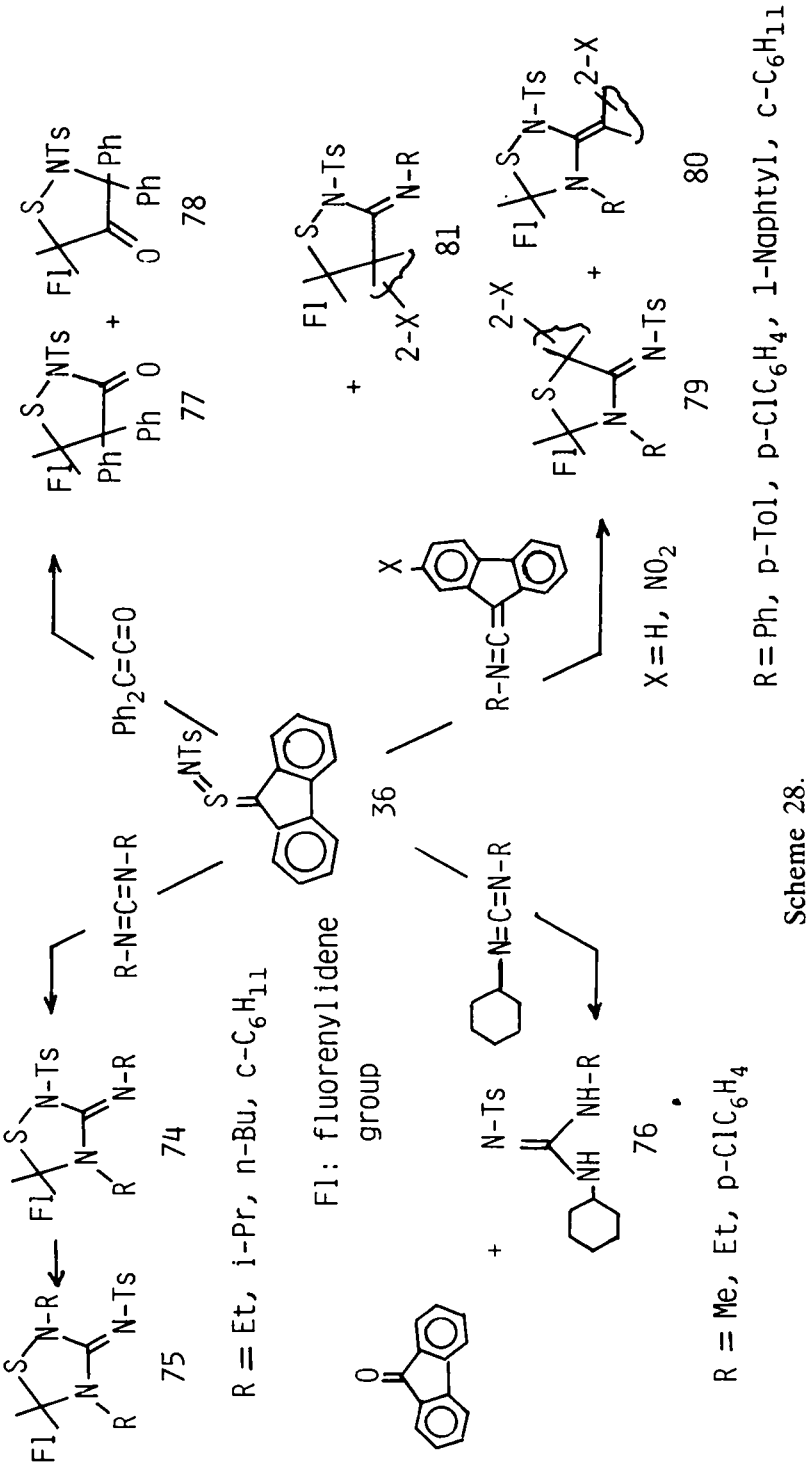
R = H, Me -N X = pyrrolidinyl, piperidinyl



Scheme 26.



Scheme 27.

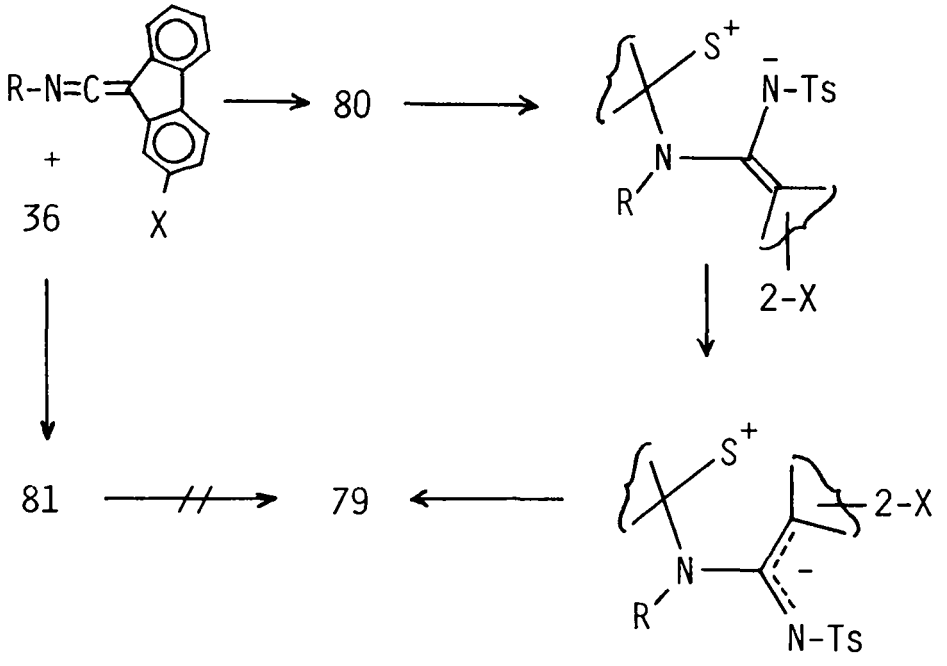


Scheme 28.

(*v-2*) *Reactions with carbon-hetero atom double bonds* In the reactions of **36** with compounds containing C=X bonds (X = NR, O, S), *i.e.*, imines, oximes, azines, aldehydes, and thiones, **36** behaves as a 1,3-dipole.[38] Treatment of **36** with aldimines or oximes gives 1,2,4-thiadiazolidine derivatives (**68**, **69**). The reaction of **36** with *N*-alkylalkanimines or *N*-alkylarylmethanimines leads to complicated decomposition patterns whereas the reaction with ketimines does not proceed under the same reaction conditions.

The reaction of **36** with azines or aromatic aldehydes gives unsymmetrical azines (**70**) and **71** or **72** and fluorenone. These transimidation reactions involve intermediary 1,3-dipolar cycloadducts and subsequent ring fragmentation with extrusion of sulfur. No reaction is observed between **36** and ketones, but diaryl thioketones react with **36** to afford [3 + 2] cycloadducts, the 1,4,2-dithiazolidines (**73**). The adducts **68**, **69**, and **73** are not quite stable and readily dissociate reversibly into their components in appropriate solvents. In these 1,3-dipolar cycloadditions observed, the cumulene carbon of **36** combines regiospecifically with the hetero atom X (O, S, N) of the C=X bond.

(*v-3*) *Reactions with heterocumulenes* The reaction of **36** with symmetrical *N*,*N'*-dialkylcarbodiimides affords 1:1-cycloadducts **75**.[39] The adducts **75** are the rearranged products of the hypothetical primary adducts **74**. Reactions with *N*,*N'*-diarylcarbodiimides do not proceed under the same reaction conditions, while **36** and unsymmetrical carbodiimides afford the guanidines **76** and fluorenone. Intermediary 1,3-dipolar cycloadducts like **74** or **75** may also be formed initially in this case.



Scheme 29.

When **36** is allowed to react with diphenylketene, two regioisomeric [3 + 2] cycloadducts, **77** and **78** are obtained.[39] The reaction of **26** with diphenylketene or phenyldiazomethane is unsuccessful.[15] In the reaction of **36** with ketenimines, 1,3-thiazolidine (**79**) and 1,2,4-thiadiazolidine (**80**) derivatives are obtained.[39] In the reaction with *N-p*-tolylketenimine, a third adduct **81** is obtained. This is the 1,3-cycloadduct of **36** to the C=C bond of the ketenimine. The reaction sequence leading to these cycloadducts (**79–81**) is proposed to proceed as depicted in Scheme 29. It is suggested that **36** predominantly cycloadds to the C=N bond of the ketenimine with kinetic preference over addition to the C=C bond.

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